DEVELOPMENT OF THE SAPRC-07 CHEMICAL MECHANISM AND UPDATED OZONE REACTIVITY SCALES

Report to the California Air Resources Board
Contracts No. 03-318, 06-408, and 07-730

By

William P. L. Carter

Revised January 27, 2010

Center for Environmental Research and Technology
College of Engineering
University of California
Riverside, California 92521

ABSTRACT

A completely updated version of the SAPRC-99 chemical mechanism, designated SAPRC-07, has been developed and is documented in this report. This includes a complete update of the rate constants and reactions based on current data and evaluations, reformulated and less parameterized aromatics mechanisms, a representation of chlorine chemistry, a reformulated method to represent peroxy reactions that is more appropriate for modeling secondary organic aerosol formation, and improved representations for many types of VOCs. This mechanism was evaluated against the result of ~2400 environmental chamber experiments carried out in 11 different environmental chambers, including experiments to test mechanisms for over 120 types of VOCs. The performance of the mechanism in simulating the chamber data was comparable to SAPRC-99, with generally satisfactory results for most types of VOCs but some increases in biases in simulations of some mixture experiments. The mechanism was used to derive an update to the MIR and other ozone reactivity scales for over 1100 types of VOCs. The average changes in relative MIR values was about 10%, with >90% of the VOCs having changes less than 30%, but with larger changes for some types of VOCs, including halogenated compounds. Recommendations are given for future mechanism development research.

The mechanism documentation includes some large tabulations that are being provided only in electronic form. Links to downloading these tabulations are available at http://www.cert.ucr.edu/~carter /SAPRC.

Note: This version of the report and the associated supplementary materials and files superceded those available previously at the above-referenced web site. The changes are summarized in Appendix E to this report.

ACKNOWLEDGEMENTS AND DISCLAIMERS

This work was carried out at the College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California at Riverside (UCR), with funding by the California Air Resources Board (CARB) primarily through contract number 03-318, with additional work carried out through Contracts 06-408 and 07-730. However, the contents of this report reflect only the opinions and conclusions of the author, and not CE-CERT, UCR, or the CARB.

The author wishes to thank Dr. Roger Atkinson of the Air Pollution Research Center at UCR for many helpful discussions concerning available kinetic and mechanistic data and atmospheric chemistry in general, and for partial support during the period of this project. The author also appreciates the patience of the staff of the Research Division of the CARB, particularly Dr. Dongmin Luo, regarding the delays in completing this project and their continuing support. Experiments for this project that were used in this mechanism evaluation were carried out primarily by Ms. Irina Malkina with assistance from Mr. Kurt Bumiller and other members of the CE-CERT Atmospheric Processes Laboratory staff, and their contributions are gratefully acknowledged. Finally, the author wishes to acknowledge the University of California Retirement System, which provided major support to the author during the completion of mechanism development and the preparation of this report.

When discussing materials whose mechanisms were evaluated, this report makes references to "Texanol", which is a trademark of Eastman Chemical Company, and "Exxol" and "Isopar", which are trademarks of ExxonMobil Chemical Company. Mention of trade names and commercial products does not constitute endorsement or recommendation for use.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF TABLES (continued)

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

EXECUTIVE SUMMARY

Background

Airshed models are essential for the development of effective control strategies for reducing photochemical air pollution because they provide the only available scientific basis for making quantitative estimates of changes in air quality resulting from changes in emissions. The chemical mechanism is an important component of the model that represents the processes by which emitted volatile organic compound (VOC) pollutants and oxides of nitrogen (NO_x) react to form secondary pollutants such as ozone (O_3) and other oxidants. If the mechanism is incorrect or incomplete in significant respects, then the model's predictions of secondary pollutant formation may also be incorrect, and its use might result in implementation of inappropriate or even counter-productive air pollution control strategies.

One airshed model application where the accuracy of the chemical mechanism is important is the calculation of reactivity scales that measure relative impacts of different types of VOCs on ozone formation. VOCs differ significantly in their impacts on O_3 formation, and regulations that take this into account are potentially much more cost-effective than those that regulate all VOCs equally. In view of this, several VOC regulations implemented (or being considered) in California take reactivity into account. The current California regulations use the Maximum Incremental Reactivity (MIR) scale calculated using the SAPRC-99 chemical mechanism.

The SAPRC-99 mechanism includes representations of atmospheric reactions of almost 780 types of VOCs for reactivity assessment, and is widely used in other airshed modeling applications for research and regulatory applications. Although this represented the state of the art at the time it was developed, since then there has been continued progress in basic atmospheric chemistry, and new information has become available concerning the reactions and O_3 impacts of many individual VOCs. In addition, the California Air Resources Board (CARB) is obligated to update the reactivity scales used in its regulations approximately every three years so they reflect the current state of the science. Since the mechanism was developed in 1999, updates to the mechanism and the reactivity scale are now due.

Another reason for updating the SAPRC mechanism is to make it more suitable for prediction of secondary particulate matter (PM), which is another air quality issue of concern. SAPRC-99, like most other mechanisms used in current airshed models, incorporates simplifications and approximations that may be appropriate for O_3 modeling, but that restricts its capability to represent how secondary organic aerosol (SOA) formation is affected by chemical conditions. This needs to be addressed.

In view of this, the CARB funded us to provide an update to the SAPRC-99 mechanism used for modeling and VOC reactivity assessment, and to provide some needed improvements and enhancements. This report documents this mechanism, its evaluation against available environmental chamber data, and the updated reactivity scales that were developed.

Accomplishments

The major accomplishment of this project is the development of the SAPRC-07 chemical mechanism and its associated reactivity scales, which are documented in this report. Specific accomplishments are summarized as follows.

Base mechanism updated. All the reactions and rate constants in the mechanism have been reviewed based on results of current evaluations, and updated as needed. Most of the rate constant changes were relatively small, but a few errors were found and corrected and some potentially significant changes occurred. These have been assessed in the evaluations against chamber data.

Aromatics mechanisms reformulated. The mechanisms for the aromatic ring fragmentation reactions were reformulated to be more consistent with estimated explicit mechanisms, and to give predictions that are somewhat more consistent with available data. However, although an improvement over that used in SAPRC-99, the updated mechanism is still simplified in many respects, and is still not completely consistent with all of the available data

Chlorine chemistry added. A representation of chlorine chemistry has been added to the mechanism as an optional capability. In addition to improving the ability of airshed models to simulate air quality in regions impacted by chlorine emissions, the representation of chlorine chemistry has resulted in reduced uncertainties in reactivity estimates for chlorinated VOCs.

Capability for adaptation to SOA predictions improved. The method that the mechanism used to represent the reactions of peroxy radicals was reformulated so that effects of changes in NO_x conditions on organic product formation can be more accurately represented. Because development of SOA mechanisms was beyond the scope of this project, the current mechanism does not fully take advantage of this capability, but it provides a framework upon which improved SOA mechanisms can be developed.

Mechanisms for many types of VOCs added or improved. The number of types of VOCs for which reactivity estimates have been made has been increased by over 20%, and the methods used to estimate mechanisms for a number of compounds were improved. This has involved enhancements of the capabilities of the mechanism estimation and generation system that is used to derive many of the mechanisms, and deriving estimated mechanisms for new classes of VOCs. A few errors found in the SAPRC-99 mechanism for some VOCs were corrected.

Updated mechanism evaluated against chamber experiments. The updated mechanism was comprehensively evaluated by comparing predictions with results of all environmental chamber experiments used for SAPRC-99 evaluation, plus the results of more recent UCR experiments, and experiments in other chambers. The results are summarized below.

Reactivity scales updated. The updated mechanism used to calculate MIR and other reactivity scales for all the ~1100 types of VOCs that are currently represented. Uncertainty classifications were also updated as part of this work. It is recommended that these be used to supercede the reactivity values distributed previously.

The mechanism developed in this project was implemented for the box model calculations used for reactivity scale calculations, and the data files used in this implementation can serve as the basis for implementing in more comprehensive airshed models such as CMAQ or CAMx. The data files are being made available at the project web site at http://www.cert.ucr.edu/~carter/SAPRC.

Results

Evaluation Results. In general, the performance of the updated mechanism in simulating the available environmental chamber data for individual compounds was comparable to SAPRC-99, though there were some differences. Some uncertain parameters for some compounds that were adjusted to fit the data for SAPRC-99 had to be re-adjusted for this mechanism. The updated aromatic mechanism simulated most of the experiments about as well as SAPRC-99, but some discrepancies observed with the previous version were reduced. Model performance was improved in simulating data for some compounds whose mechanisms were not changed, but biases were slightly increased with others. This is attributed to changes in the base mechanism, but the specific causes have not been determined.

One area of potential concern is that the mechanism update caused a slight increase in overall biases in model simulations of experiments with mixtures of VOCs. These changes are small compared to the ±30% variability of the fits overall – which is less than the average biases – but because of the large number of such experiments (>1500 total) it may be statistically significant. The mechanism update also did not solve the problem, noted previously for other mechanisms, of underpredicting O_3 formation and NO oxidation in ambient surrogate - NO_x experiments carried out at relatively low NO_x levels in the new UCR EPA chamber. These biases cannot be attributed to problems with individual VOCs, whose experiments are generally reasonably well simulated.

Preliminary assessment of impacts of updates on predictions of ambient ozone. Results of box model simulations of 1-day urban scenarios used for the reactivity scales indicate that the mechanism update caused changes in maximum ozone concentrations ranging from a ~10% decrease to a ~5% increase, with the predicted O_3 decreasing by about 5% on average. The largest increase appears at the lower ROG/NO_x ratios, but other factors appear to be equally important. However, the scenarios used in the reactivity assessment calculations are highly simplified representations of ambient conditions, and comprehensive models are needed to fully assess the impacts of this update on ambient ozone and control strategy predictions.

Reactivity Scale Update. For most VOCs, the reactivity scale update did significantly affect the reactivity values, with the average change in relative MIR values for the VOCs on the previous scales, being on the order of 10%. However, the MIR value changed by more than 5% for 56% of the VOCs given in the previous tabulation. The MIR change was less than 30% for approximately 93% of these VOCs, but 35 VOCs had changes greater than 35% and 5 VOCs had changes greater than a factor of 2. The latter consisted of halogenated compounds and one compound where a rate constant error was corrected.

Recommendations

Although the accomplishments of this project were significant, there were some objectives of this project that could not be met within the available time and resource, and there are other areas where additional work is recommended. These are summarized below.

Aromatics Mechanisms. Although the aromatics mechanisms developed in this work represent an improvement, problems remain and additional work is needed. Work was begun during this project in developing a more explicit aromatics mechanism, and new environmental chamber data useful for this effort was obtained. Work in this area needs to continue.

Chlorine and Halogen Mechanisms. Uncertainties remain in the mechanisms of halogenated compounds. Estimation methods need to be developed for reactions of halogen-containing radicals, and reactivities of halogenated oxidation products need to be assessed. Reactivity data are available for only a limited number of such compounds, and the available data indicates problems that need to be addressed. Mechanisms for bromine chemistry need to be developed.

Mechanism Generation System. An important component of the current mechanism is the mechanism generation and estimation system that is used to derive the mechanisms for most of the non-aromatic VOCs that are represented. However, because of time constraints we were unable to update most of the estimation methods incorporated in the system, except for the initial VOC rate constants and those related to chlorine chemistry. This needs to be done. The capability of the system needs to be enhanced to more reliably estimate mechanisms for additional classes of VOCs and intermediates, such as halogenated radicals, aromatics, and aromatic products. This will make it valuable for future mechanism improvements and reactivity scale updates. Finally, the system needs to be undergo peer review and be documented in the peer-reviewed literature.

Adaptation to SOA Predictions. Although the capability of the mechanism for improved SOA predictions has been enhanced, the potential of this capability has not been exploited. Recommendations in this regard include adding new species to the mechanism to represent low volatility products, implementing methods in the mechanism generation system to estimate volatility and incorporate them in the mechanisms so derived, and evaluating the predictions against SOA formation measured in chamber experiments.

Mechanism Performance Issues. The reason that the mechanism has biases in simulations of mixture experiments, while simulating single compound experiments reasonably well, needs to be investigated. This is necessary to assess the implications on ambient simulations of the biases in the simulations of the mixture experiments that were found, and for developing methods to reduce these biases. The reason for the relatively poor performance of the mechanisms in simulating the University of North Carolina outdoor chamber database also needs to be investigated. Although existing tools involved in sensitivity, uncertainty, and process analysis may be useful, new analysis methods probably need to be developed. This is an area where original research is needed.

Mechanism Evaluation Database. Although the database of chamber experiments useful for mechanism evaluation is very extensive and comprehensive in some respects, there are gaps and problems that need to be addressed. There are a number of classes of compounds where reactivity chamber data are needed to reduce mechanism uncertainties. Incremental reactivity experiments need to be developed that are more sensitive to reactions of organic oxidation products, which affect predicted reactivities in ambient scenarios much more than in chamber experiments. The current chamber dataset is not adequate for evaluating effects of temperature on mechanism performance. Experiments are needed for testing mechanisms for predictions of SOA formation, particularly under lower pollutant conditions more representative of ambient conditions than are most PM chamber data.

Mechanism Condensation. One of the objectives of this project that was not accomplished was to develop a condensed version of the mechanism to serve as an alternative to CB4/CB05 for modeling applications where computer speed is more important than chemical detail. This still needs to be done.

Reactivity Scenarios. The scenarios used for deriving the reactivity scales developed in this work are poorly documented, oversimplified, and do not represent current ambient conditions. Evaluations carried out by the Reactivity Research Working Group (RRWG) indicate that this methodology could be improved in a number of respects, particularly the scenarios and modeling methods. This update is way overdue, and may result in changes in relative reactivity values that are greater than those resulting from updates to the mechanism.

Next Mechanism Update. The CARB is still committed to updating its regulatory reactivity scale on a periodic basis. This will obviously need to include updated reactivity scenarios, as indicated above. Another problem is that the developer of the SAPRC mechanisms and the MIR scale is now semi-retired, and may be completely retired by the time the next update is needed, and it is unclear who will be carrying out this work in the future. Funding agencies need to show an interest in providing support for this type of mechanism development on a sufficiently consistent basis that it will attract younger researchers into this field. As it is now, support for mechanism development is relatively limited, and not of the type needed for the long-term commitment that this type or research requires.

INTRODUCTION

Airshed models are essential for the development of effective control strategies for reducing photochemical air pollution because they provide the only available scientific basis for making quantitative estimates of changes in air quality resulting from changes in emissions. The chemical mechanism is the portion of the model that represents the processes by which emitted primary pollutants, such as volatile organic compounds (VOCs) and oxides of nitrogen (NO_x), interact in the gas phase to form secondary pollutants such as ozone (O_3) and other oxidants. This is an important component of airshed models because if the mechanism is incorrect or incomplete in significant respects, then the model's predictions of secondary pollutant formation may also be incorrect, and its use might result in implementation of inappropriate or even counter-productive air pollution control strategies.

One airshed model application where the accuracy of the chemical mechanism is particularly important is the assessment or implementation of control strategies to encourage use of VOCs that have lower impacts on ozone or other secondary pollutant formation than VOCs that are currently emitted. Such strategies require a means to quantify the impacts, or "reactivities" of the VOCs with respect to O_3 or other measures of air quality. There are several examples of control strategies where accurate O_3 reactivity estimates are important. In the California Air Resources Board (CARB)'s "Low Emissions Vehicle/Clean Fuels" regulations, "reactivity adjustment factors" are used to place exhaust emissions standards for alternatively-fueled vehicles on an equal ozone impact basis as those for vehicles using conventional gasoline (CARB, 1993). More recently, the CARB implemented reactivity-based regulations for aerosol coatings (CARB, 2000), and is considering expanding such regulations to other types of stationary sources (e.g., CARB, 2006, 2007). In addition, the EPA has used O_3 impacts of VOCs calculated for various environments among the factors they consider when evaluating proposals to exempt various compounds from controls as ozone precursors (Dimitriades, 1999).

The MIR scale initially adopted in the CARB vehicle regulation was calculated using the SAPRC-90 chemical mechanism (Carter, 1990), but it has since been recalculated using an updated version of this mechanism, designated SAPRC-99 (Carter, 2000, 2003a). This mechanism has assigned or estimated mechanisms for over 500 types of VOCs. Although other state-of-the-art mechanisms are available for airshed model applications (e.g., Stockwell et al, 1997; Yarwood et al, 2005, Jenkin et al, 2003; Saunders et al, 2003), the SAPRC mechanisms were used for this purpose because they are the only mechanisms that represent a large number of VOCs that was comprehensively evaluated against environmental chamber data. However, although the SAPRC-99 mechanism represented the state of the art at the time it was developed, since then there has been continued progress in basic atmospheric chemistry, and new information has become available concerning the reactions and O_3 impacts of many individual VOCs. In addition, the CARB is obligated to update the reactivity scales used in its regulations approximately every three years so they reflect the current state of the science. Since the last update was made in 2003 (Carter, 2003a), updates to the scale are now due.

In addition to calculation of reactivity scales for regulatory applications, a condensed version of the SAPRC-99 mechanism (Carter, 2000b) is widely used in comprehensive airshed models for prediction of effects of emissions on secondary pollutant formation in regional and urban atmospheres. Such regional models are required for many research and regulatory applications, so they should represent the current state of the science. In the United States, the two alternative mechanisms most generally used in comprehensive airshed models are the Carbon Bond 4 (CB4) (Gery et al, 1988) and the SAPRC-99 mechanism, and the two mechanisms have been found to give quite different predictions in some cases. The use of CB4 is preferred for many model applications because of it compact nature and because it is more computationally efficient, but SAPRC-99 is preferred in applications where chemical accuracy is a priority because it is more chemically detailed and more comprehensively evaluated against available environmental chamber data. CB4 has recently been updated to "Carbon Bond 05" (CB05) (Yarwood et al, 2005; Sarwar et al, 2008), and this is now being implemented in such models. Therefore, SAPRC-99 needs to be updated so it can continue to be a viable alternative to the Carbon Bond mechanisms for applications where chemical accuracy is a priority.

Another reason for updating the SAPRC mechanism is to make it more suitable for prediction of secondary particulate matter (PM). Fine particulate matter pollution an important issue because of the major health impacts it is believed to cause, and secondary PM is a major contribution to this problem. The formation of secondary PM is even more complex and incompletely understood than the formation of ozone. Models for prediction of secondary PM have appended aerosol models to gas-phase mechanisms such as SAPRC-99 and CB4, but the treatment is necessarily parameterized and approximate because of the condensation approaches incorporated in these mechanisms. These approaches may be appropriate for ozone modeling, but are not necessarily appropriate for prediction of secondary organic aerosol. For example, such mechanism use lumped species to represent oxidation products based on their gas-phase reactivity, but without considerations of volatility, which is the major factor in secondary organic aerosol (SOA) formation. In addition, SAPRC-99, like CB4 and CB05, uses a condensed method to represent the many peroxy + peroxy radical reactions that does not readily permit models to represent how organic product distributions may change under very low NO_x conditions where these reactions are important. Recent data (e.g., Song et al, 2005) indicate that, at least for aromatics, secondary PM formation may be much more dependent on NO_x conditions than represented in current models. The condensation methods used in current mechanisms need to be modified to be more suitably adapted for models for PM prediction

Based on these considerations, the California Air Resources Board funded us to develop and document an updated version of the SAPRC mechanism, and use it to derive updated MIR and other VOC ozone reactivity scales. The specific objectives of the project were as follows:

- Update rate constants and reactions to current state of science.
- Improve mechanisms for aromatics to incorporate new data and improve performance in simulating available chamber data.
- Conduct environmental chamber experiments as appropriate to support this effort.
- Add chlorine chemistry, to support modeling areas impacted by chlorine emissions and also calculating reactivities of chlorinated organics.
- Update and enhance the mechanism generation system used to derive the mechanisms for most of the VOCs (Carter, 2000a). This includes updating the estimation methods and assignments as needed, and also enhancing the capabilities of the system, e.g., to support generating explicit mechanisms for aromatics and chlorine atom reactions;
- Improve capability of the mechanism to be adapted to secondary PM models
- Increase the number of VOC mechanisms to include more compounds present in emissions inventories or otherwise of interest to the CARB.
- Develop new condensed mechanisms from the detailed version (including a highly condensed version as an alternative to CB4).
- Make the mechanism available for implementation in airshed models
- Calculate updated reactivity scales and update associated uncertainty classifications.

The major accomplishments of this project are the development of a completely updated version of SAPRC-99, which is designated SAPRC-07[1], and the update of the associated MIR and other reactivity scales, and their uncertainty classifications. The bulk of this report consists of the documentation of this mechanism and its evaluation, and the reactivity scales. The final section of this report includes a summary of the accomplishments of this project, the objectives that were not fully addressed, recommendations for future research.

---

[1] SAPRC stands for "Statewide Air Pollution Research Center", which is the unit at the University of California at Riverside where the SAPRC mechanisms were initially developed. This unit has since been renamed to "Air Pollution Research Center" (APRC), so strictly speaking this acronym is no longer meaningful. However, this designation for these mechanisms is retained for continuity.

MECHANISM DOCUMENTATION

The major components of the SAPRC mechanisms are the base mechanism used to represent the reactions of the inorganic reactants and the common organic oxidation products and radicals, the representation of the reactions of the individual VOCs, the lumped mechanism used for complex mixtures in airshed models, and the emissions assignments necessary for implementing the mechanism in airshed models. The general structure of this mechanism is essentially the same as that for SAPRC-99 mechanism documented by Carter (2000a), except that in this case chlorine chemistry is added and can be incorporated in the base and lumped mechanisms as an option, and is incorporated in representations and reactivity calculations for halogenated VOCs as needed. Each of these components, and their updates relative to SAPRC-99 are discussed in this section of this report.

Reference is made to the comprehensive documentation of the SAPRC-99 mechanism (Carter, 2000a) for documentation of the features of the mechanism that were retained in this version, so that document must be considered an integral part of the documentation of this mechanism. Appendices to the report include the tabulations or data plots that are too large to include in the main body of the text, and additional information, such as complete listings of the mechanisms of the over 700 types of VOCs that are explicitly represented, is available in electronic form at the SAPRC mechanism website at http://www.cert.ucr.edu/~carter/SAPRC.

Base Mechanism

The base mechanism is the portion of the mechanism that represents the reactions of the inorganic species, the common organic products, and the intermediate radicals leading to these products, including those formed from the initial reactions of the represented VOCs not in the base mechanism. Most of the VOCs that can be separately represented are not in the base mechanism, but can be added to the mechanism, either as explicit reactions for individual VOCs or as lumped model species whose parameters are derived from the mixture of detailed model species they represent, as needed in the model application. However, a few VOCs are represented explicitly and incorporated in the base mechanism, either because they are also common organic oxidation products that are represented explicitly, or are sufficiently important in emissions inventories and have sufficiently different mechanisms than most other VOCs that representation with lumped model species is inappropriate. These include formaldehyde, acetaldehyde, acetone, ethylene, isoprene, and (new to this version) benzene and acetylene. This portion of the mechanism is discussed in this section.

Listing of Standard Base Mechanism and Summary of Changes

The "Standard Base Mechanism" is the portion of the base mechanism excluding the optional additional reactions used to represent chlorine chemistry, and is the portion that is directly comparable to the SAPRC-99 base mechanism. Table A-1 in Appendix A gives the list of model species used in the standard base SAPRC-07 mechanism. These include the inorganic reactants, common reactive organic product species, chemical operators used to represent peroxy radical reactions (discussed below), and explicitly represented primary organics. Except as discussed below, the species used are the same as in the base SAPRC-99, though some model species have been renamed to be more compatible with some airshed model software systems. The changes, and additions, are as follows:

- The set of lumped peroxy radical species and chemical operators was changed because as discussed in the "Project Summary" section, above, a different method was used to represent peroxy radical reactions. SAPRC-99 used three active chemical operators (RO2-R., RO2-N., and

R2O2.) to represent the effects of peroxy radical reactions on NO_x and organic nitrates. The updated mechanism uses two active chemical operators (RO2C and RO2XC) to represent the effects of peroxy radical reactions on NO_x and 34 steady-state operators to represent the effects on formation of organic products (not counting the 3 used in the added chlorine mechanism).

Two additional model species were added to represent the reactions of the higher hydroperoxides that were previously lumped with one generic hydroperoxide species in SAPRC-99. These higher hydroperoxides are expected to have different reactivities and SOA formation potentials than propyl hydroperoxide, which was used as the basis for the single generic hydroperoxide in SAPRC-99.

- Although three active model species are still used to represent the reactions of the unsaturated aromatic ring fragmentation products, the types of compounds they represent have been changed. This is discussed in conjunction with the discussion of the revised aromatic mechanisms, below.
- The reactions of formic acid, acetic acid, and the lumped higher organic acids were added to the mechanism. These species were in SAPRC-99 as inert tracers, but their reactions with OH radicals were added to this mechanism because they may be non-negligible loss processes in some regional modeling applications.
- Acetylene and benzene are now represented explicitly in this mechanism. This is because both compounds are relatively important in emissions inventories, their reactivities are quite different than the other compounds with which they previously were lumped (monoalkylbenzenes and low reactivity alkanes, respectively), and are not well represented by other species used in the lumped mechanism. In addition, explicit simulations of benzene are of interest for toxics modeling, and acetylene can provide a useful tracer for vehicle emissions.

Although the objective of this update was to provide a mechanism with similar or, if appropriate, greater level of detail as SAPRC-99, a few SAPRC-99 model species were judged to be unnecessary and were removed from this version. These are as follows.

- Phenol was removed from the mechanism because it is important only in the oxidation of benzene, and representing it by the lumped cresol species (CRES) did not significantly affect results of simulations of benzene, whose mechanism is very uncertain in any case.
- The SAPRC-99 model species BZNO2-O, used in the mechanism for the reaction of NO_3 with lumped nitrophenols, was removed. It was found that representing it with the phenoxy model species used in the cresol mechanism gave model simulations that were essentially the same, especially considering the large uncertainty in the nitrophenol and cresol mechanisms.
- The SAPRC-99 model species CCO-OOH and RCO-OOH, used to represent various peroxy acids formed in the reactions of acyl peroxy radicals with HO_2, were removed. These are represented by the reactions of the corresponding acid model species. It was judged that separate representation of these species was not necessary, though this could be changed in future versions of the mechanism if desired.

The reactions and rate parameters used in the base mechanism are given in Table A-2 in Appendix A, and Table A-3 gives the absorption cross sections and quantum yields used for the photolysis reactions listed in this table. Footnotes to Table A-2 indicate the source of the rate constants and mechanisms used. As indicated there, most of the updated rate constants are based on results of the IUPAC (2006) and NASA (2006) evaluations, though a number of other sources were also used as the basis for the updates. The major changes to the inorganic and common organic radical and product mechanisms are discussed further below. The changes to the mechanisms for the explicitly represented species are discussed later in conjunction with the mechanisms for the other individual VOCs.

Table 1 shows the changes in rate constants or atmospheric photolysis rates for this version of the base mechanism compared to SAPRC-99, for the cases where the rate constants or photolysis rates were changed by more than 5%. Reactions used to represent unsaturated aromatic ring fragmentation products, or reactions of chemical operators used to represent peroxy radical reactions are not shown because the representations are not comparable on a reaction-by-reaction basis; these are discussed below or later in this report. Specific changes of potential interest are as follows.

- The most important single change to the base mechanism may be the ~19% increase in the rate constant for the OH + NO_2 reaction, based on the results of the recent NASA (2006) evaluation. This affected the mechanism evaluation against the chamber experiments because it required re-deriving some chamber effects parameters and also some uncertain mechanistic parameters derived to fit chamber data. It is also expected to result in somewhat lower O_3 predictions in ambient simulations, though this may be offset somewhat by the changes in the parameters adjusted to fit chamber data.
- The ~7% increase in the NO_2 photolysis rate under atmospheric conditions has no effect on NO_2 photolysis rates used in chamber simulations because all photolysis rates are normalized to measured NO_2 photolysis rates. However, rates of other photolysis reactions in chamber simulations will decrease accordingly.
- There was a relatively large increase in the calculated atmospheric photolysis rates for the α-dicarbonyl aromatic ring fragmentation products. However, this will not result in increases in calculated reactivities of aromatics because of changes that were made to the representation of the other reactive aromatic fragmentation products, discussed later in this report.
- The ~30% increase in the calculated photolysis rates for methacrolein and the model species used to represent C_5 aldehyde products formed from isoprene did not seem to have a significant effect on simulations of isoprene chamber experiments or calculations of the atmospheric reactivity of this important biogenic compound. Despite the relatively large decrease in the peroxy + HO_2 rate constant, this reaction is still calculated to be the major loss process for peroxy radicals competing with reaction with NO under low NO_x conditions.
- The photolysis of PAN was added to the mechanism at the request of Deborah Luecken of the EPA. Although not important in urban simulations, this reaction may be important under low temperature conditions such as occur at higher altitudes.
- New information available concerning the reactions of nitrophenols indicates that the major atmospheric loss processes are photolysis and reactions with OH (see footnotes for these reactions on Table A-2). The speculative reaction of nitrophenols with NO_3 was deleted, though it may still occur to some extent.
- As discussed below, the mechanism for PROD2 is based on mechanism for various C_5-C_9 ketones. The updated mechanism gives better simulations of incremental reactivity environmental chamber experiments for higher ketones if lower photolysis rates for higher ketones are assumed (see discussion of mechanisms of individual VOCs and the evaluation against chamber experiments later in this report). The overall quantum yield for photolyses of C_{7+} ketones are set to a sufficiently low value that photolysis is unimportant. This is reflected in the average overall quantum yield used for PROD2.
- As indicated above, several model species were removed and the base mechanism now explicitly represents the reactions of some additional compounds. These changes should have relatively small effects on most simulations except that atmospheric simulations will now simulate these species explicitly, rather than ignoring their reactions (as with the acids) or lumping them with other compounds. Note that this change does not, by itself, affect reactivity calculations for these compounds because the compound of interest (or the compound used to represent them if the "lumped molecule" approach is used) is always represented explicitly in reactivity calculations.

Table 1. Reactions where the rate constants or photolysis rates changed by more than 5% or that were added or removed in the standard base mechanism relative to SAPRC-99.

Rate constant or photolysis rate [a]			Reaction [b]	Notes [c]
SAPRC-07	SAPRC-99	Change		
7.23e-1	6.69e-1	8%	NO2 + HV = NO + O3P	1
1.64e-12	2.45e-12	-33%	O3P + NO = NO2	
1.03e-11	9.70e-12	6%	O3P + NO2 = NO + O2	
3.24e-12	1.79e-12	81%	O3P + NO2 = NO3	2
2.02e-14	1.87e-14	8%	O3 + NO = NO2 + O2	
1.24e-12	1.53e-12	-19%	NO2 + NO3 = N2O5	
5.69e-2	6.74e-2	-16%	N2O5 = NO2 + NO3	
1.80e-39			N2O5 + H2O + H2O = #2 HNO3 + H2O	3
1.91e+0	1.59e+0	20%	NO3 + HV = NO + O2	
1.99e-10	2.20e-10	-10%	O1D + H2O = #2 OH	
3.28e-11	2.87e-11	14%	O1D + M = O3P + M	
1.14e-1	1.27e-1	-10%	HONO + HV = OH + NO	
-	1.60e-2		HONO + HV = HO2 + NO2	
5.95e-12	6.42e-12	-7%	OH + HONO = H2O + NO2	
1.05e-11	8.81e-12	19%	OH + NO2 = HNO3	1
2.28e-13	2.08e-13	10%	OH + CO = HO2 + CO2	
7.41e-14	6.78e-14	9%	OH + O3 = HO2 + O2	
8.85e-12	8.36e-12	6%	HO2 + NO = OH + NO2	
1.12e-12	1.36e-12	-18%	HO2 + NO2 = HNO4	
1.07e-1	9.61e-2	11%	HNO4 = HO2 + NO2	
5.42e-4	4.69e-4	16%	HNO4 + HV = Products	
4.61e-12	4.98e-12	-7%	HNO4 + OH = H2O + NO2 + O2	
1.69e-15	1.89e-15	-11%	HO2 + O3 = OH + #2 O2	
1.80e-12	1.70e-12	6%	HO2H + OH = HO2 + H2O	
4.65e-12	5.12e-12	-9%	MEO2 + HO2 = COOH + O2	
4.50e-13			MEO2 + HO2 = HCHO + O2 + H2O	
2.16e-13	2.61e-13	-17%	MEO2 + MEO2 = MEOH + HCHO + O2	
1.31e-13	1.08e-13	21%	MEO2 + MEO2 = #2 {HCHO + HO2}	
7.63e-12	1.45e-11	-47%	Peroxy + HO2 = Products	4
9.37e-12	1.04e-11	-10%	MECO3 + NO2 = PAN	
6.27e-4	7.04e-4	-11%	PAN = MECO3 + NO2	
6.12e-5			PAN + HV = Products	1
1.97e-11	2.12e-11	-7%	MECO3 + NO = MEO2 + CO2 + NO2	
2.30e-12	4.00e-12	-43%	MECO3 + NO3 = Products	2,5
1.06e-11	9.53e-12	11%	MECO3 + MEO2 = Products	5
1.56e-11	7.50e-12	108%	MECO3 + Peroxy = Products	2,4,5
5.48e-4	5.90e-4	-7%	PAN2 = RCO3 + NO2	
2.08e-11	2.78e-11	-25%	RCO3 + NO = Products	
7.63e-12	1.45e-11	-47%	BZO + HO2 = CRES	
	3.80e-11		BZNO2-O. + NO2 = inert products	6
	1.49e-11		BZNO2-O. + HO2 = NPHE	6
	1.00e-3		BZNO2-O. = NPHE	6
2.76e-3	2.32e-3	19%	HCHO + HV = #2 HO2 + CO	
8.47e-12	9.19e-12	-8%	HCHO + OH = HO2 + CO + H2O	

Table 1 (continued)

Rate constant or photolysis rate [a] SAPRC-07	 SAPRC-99	 Change	Reaction [b]	Notes [c]
1.49e-11	1.57e-11	-6%	CCHO + OH = MECO3 + H2O	
6.74e-15	3.82e-15	76%	RCHO + NO3 = HNO3 + RCO3	
3.24e-5	4.16e-5	-22%	ACET + HV = Products	
1.69e-4	1.42e-4	19%	MEK + HV = Products	
6.78e-12	1.10e-11	-38%	ROOH + OH = Products	
3.18e-3	1.08e-3	193%	GLY + HV = HCHO + CO	
1.56e-2	1.10e-2	42%	MGLY + HV = HO2 + CO + MECO3	
2.67e-2	1.90e-2	41%	BACL + HV = #2 MECO3	
	2.63e-11		PHEN + OH = products	6
	3.78e-12		PHEN + NO3 = products	6
3.50e-12	-		NPHE + OH = BZO + XN	1
	3.78e-12		NPHE + NO3 = products	1
1.08e-3			NPHE + HV = HONO + #6 XC	1
1.08e-2			NPHE + HV = #6 XC + XN	1
1.20e-11	1.29e-11	-7%	BALD + OH = BZCO3	
2.84e-11	3.35e-11	-15%	MACR + OH = Products	
1.28e-18	1.19e-18	8%	MACR + O3 = Products	
3.54e-15	4.76e-15	-26%	MACR + NO3 = Products	
1.97e-4	1.36e-4	45%	MACR + HV = Products	
1.99e-11	1.87e-11	6%	MVK + OH = Products	
5.36e-18	4.74e-18	13%	MVK + O3 = Products	
7.50e-5	6.97e-5	8%	MVK + HV = Products	
1.97e-4	1.36e-4	45%	IPRD + HV = Products	
4.69e-6	1.90e-5	-75%	PROD2 + HV = Products	1
7.20e-12	7.80e-12	-8%	RNO3 + OH = Products	
4.50e-13			HCOOH + OH = HO2 + CO2	7
7.26e-13			CCOOH + OH =products	7
1.20e-12			RCOOH + OH = products	7
1.64e-11	-		R6OOH + OH = products	7
3.94e-4	-		R6OOH + HV = products	7
1.08e-10	-		RAOOH + OH = products	7
3.94e-4			RAOOH + HV = products	7
7.56e-13			ACETYLEN + OH = products	7
1.16e-20			ACETYLEN + O3 = products	7
1.22e-12			BENZENE + OH = products	7

[a] Rate constants are for $T=300^{o}K$ and are in molecule, cm^3 sec^{-1} units. Photolysis rates are calculated for direct overhead sunlight based on the actinic fluxes used in the reactivity scale calculations (Carter, 1994a,b).

[b] Reactions used to represent unsaturated aromatic ring fragmentation products, and reactions of chemical operators used to represent peroxy radical reactions, are not directly comparable in the two mechanisms. They are discussed separately later in this report.

[c] Notes concerning changes for reaction. See also text and footnotes to Table A-2

1 See text for a discussion of this change.

2 This is a relatively minor process under most conditions of interest, so the change should not have a significant effect on most model predictions.

Table 1 (continued)

3 This reaction is added to represent the expected humidity dependence of this process.

4 "Peroxy" refers to the various model species used to represent various types of peroxy radicals or peroxy radical operators.

5 The same rate constants are used for all the higher acyl peroxy radical model species.

6 This model species was deleted. See text.

7 The reactions of these compounds were added to the base mechanism. See text.

Note that the discussion given above of expected effects of these changes on model simulations is based on expectations that have not, in most cases, been verified by actual model sensitivity calculations. Such sensitivity calculations would be useful to assess the effects of various changes, and help focus on areas where basic research may be useful.

Representation of Peroxy Radical Operators

Because of the large number of peroxy radicals that are involved even in condensed atmospheric chemistry mechanisms, it is generally not practical to represent the many possible peroxy + peroxy reactions explicitly, especially considering that under most conditions, especially conditions favorable for O_3 formation, most of these reactions are relatively unimportant. Even highly explicit mechanisms such as the MCM (Jenkin et al, 2003; Saunders et al, 2003) use an approximate method to represent the many peroxy + peroxy cross reactions involving a chemical operator representing the total peroxy radical concentration. The RADM-2 and RACM mechanisms (Stockwell et al, 1990, 1997) have separate peroxy radical species for each VOC or VOC product model species whose reactions form peroxy radicals, but neglect peroxy + peroxy reactions except for those involving HO_2 and methyl peroxy radicals. Because of the large number of reactions and model species involved even with the more approximate RADM-2 representation, SAPRC-99 represents methyl peroxy radicals explicitly, but uses a limited number of "chemical operators" to represent effects of peroxy radical reactions on NO_x and radicals, and represents the organic products formed when higher peroxy radicals react with other peroxy radicals by those formed when they react with NO_x. The CB4/05 mechanisms use a similar, though somewhat more condensed approach.

Use of these condensed representations of peroxy radical reactions has been shown to have relatively little effects on predictions of O_3 formation and overall gas-phase reactivity because they involve no approximation when the major fate of peroxy radicals is reaction with $NO_,$ as is the case when O_3 formation occurs, and because they give reasonably good representations of how NO to NO_2 conversions, organic nitrate formation, and regeneration of radicals change when NO_x levels are reduced to the point where the competing peroxy + peroxy become non-negligible. However the representations incorporated in SAPRC-99 and CB4/05 do not represent the changes in organic oxidation products that occur when these peroxy + peroxy reactions become non-negligible, since they use the set of products formed in the peroxy + NO reaction as the surrogate for the generally different products formed in the competing reactions. The inability of this representation to represent the formation of hydroperoxides formed in the peroxy + HO_2 reaction is of particular concern, because these are predicted to be the major competing products formed under low NO_x conditions (e.g., see Carter, 2004), and as discussed above are believed to be important precursors to secondary organic aerosol (SOA) formation.

Therefore, the peroxy radical representation used in SAPRC-99 is not satisfactory for use of the mechanism for prediction of SOA formation, and for this reason was changed as part of this update. The peroxy radical operator method implemented in SAPRC-99 is described in the SAPRC-99 documentation (Carter, 2000a). Briefly, it involves the operator RO2-R. to represent the reactions converting NO to NO_2

forming HO_2, RO2-N. to represent reactions with NO forming organic nitrates, and R2O2. to represent extra NO to NO_2 conversions involved in multi-step peroxy radical reactions. Since it uses the set of products formed in the NO reaction to represent the products in the competing peroxy + peroxy reactions, it uses no additional model species for this purpose except for the inclusion of a generic "ROOH" species to represent reactions at the hydroperoxide group formed in the peroxy + HO_2 reaction (with the set of products formed in the NO reaction also being formed in the HO_2 reaction.)

The SAPRC-07 representation is similar in that operators are also used to represent the effects of peroxy radicals on NO_x, with "RO2C" representing NO to NO_2 conversions and "RO2XC" representing NO consumption that occurs in conjunction with nitrate formation, but uses separate chemical operator model species to represent the formation of radicals and oxidation products, and how they depend on which peroxy radical reactions are occurring. Three sets of chemical operators are used for this purpose: "xPROD" species are used to represent the formation of the alkoxy radical products resulting when the peroxy radical react with NO, NO_3, and (in part) RO_2; "yPROD" species are used to represent the formation of hydroperoxides formed when peroxy radicals react with HO_2 or H-shift disproportion products formed when peroxy radicals react with acyl peroxy radicals or (in part) with RO_2; and "zRNO3" species are used to represent the formation of organic nitrates when peroxy radicals react with NO or the alkoxy radical formed (in part) in RO_2 + RO_2 reactions. The products formed in the reactions of these operators are summarized on Table 2. Table A-2 and footnotes to Table A-2 indicate how they are implemented in the model.

Table 2. Products formed in the reactions of the chemical operators used to represent peroxy radical reactions in the SAPRC-07 mechanism.

Reaction		RO2C	RO2XC	xPROD	yROOH	zRNO3
NO		- NO + NO_2 [a]	- NO [a]	PROD		RNO3
NO_3		- NO_3 + NO_2 [a]		PROD		PROD2 + HO2 [b]
HO_2					ROOH	
RO_2·	→ RO·.			PROD		PROD2 + HO2 [b]
	H-Shift				MEK or PROD2 [c]	
$RC(O)O_2$·				PROD		PROD2 + HO2 [b]

[a] "-NO" or "-NO_3" means that the reaction consumes these reactions. If this is not shown, it means that the reaction should not consume any reactant other than the peroxy radical operator. For example, the reaction of RO2C with HO2 would be simulated as "RO2C + HO2 → HO2".

[b] This represents products formed from alkoxy radicals formed in the absence of NO_x that are not represented by xPROD model species because they are not used for the portions of the reactions that form organic nitrates in the presence of NO_x. The present version of the mechanism has only a single zRNO3 species, and uses PROD2 for this purpose. HO_2 is used to represent the radicals formed.

[c] The model species used to represents the H-shift disproportion products depends on the size of molecules being represented by yROOH. For the operators forming the ROOH model species used for 4 or fewer carbons, MEK is used for these processes. For operators forming larger hydroperoxides (R6OOH or RAOOH), PROD2 is used.

Note that in this representation the total yield of RO2C or RO2C + RO2XC may be greater than unity in multi-step processes involving formation of secondary peroxy radicals that cause additional NO to NO_2 conversions or nitrate formation. However, radical conservation requires that the sum of RO2XC and all xPROD operators where PROD is a radical be equal to 1 in VOC + radical (e.g., VOC + OH) reactions, and the sum of all yROOH species must be equal to the total yield of all peroxy radicals formed in the initial reaction.

The main approximation involved in this representation concerns the treatment of the cases of multi-step mechanisms where the peroxy radicals undergo reactions to form other peroxy radicals, which can react with NO or other peroxy radicals, etc. This would result in different (generally intermediate) branching ratios in the competitions of the peroxy radical reactions in terms of the overall products. In this representation it is assumed that the overall branching ratios, e.g., the extent to which hydroperoxides are formed from peroxy + HO_2 reactions, are the same in multi-step as in single step mechanism. Removing this approximation would require a much more complex mechanism, with more operators or model species, than is appropriate given its level of importance. Note that this approximation is incorporated in all mechanisms that use the more approximate peroxy radical representations, such as SAPRC-99 or CB4/05.

Although this representation can otherwise potentially give the same predictions as fully explicit mechanisms, it is not particularly intuitive from a chemical perspective. It involves using separate model species for each type of product that is formed, and its "reactions" do not have a straightforward correspondence to explicit reactions. An alternative method, that is more straightforward to understand in terms of actual chemical processes (and gives the same predictions), is to use separate model species for each group of peroxy radicals formed from the reactions of each of the various VOCs, and represent the competing overall reactions of these lumped groups of peroxy radicals with NO, NO_3, HO_2, RCO_3, and other peroxy radicals. Chemical operators would still be needed to represent NO to NO_2 conversions in multi-step processes and to determine a total RO_2 concentration for calculating peroxy + peroxy rates, but the result would be closer to the actual chemical processes that occur. This is the approach used in the RADM2/RACM mechanisms (Stockwell et al, 1990, 1997), with the problem of representing peroxy + peroxy reactions dealt with by ignoring all but reactions with methyl peroxy; which is not a bad approximation (Carter and Lurmann, 1990).

Although we considered use of the RADM2 approach for this mechanism, we had to abandon it because it was incompatible with the "lumped parameter" approach incorporated in the SAPRC mechanisms for flexible representation of the hundreds of individual VOCs or deriving parameters for lumped model species based on the specific compounds they represent. This representation involves having a numerical parameter represent each of the product or radical model species involved in their overall reactions, including NO to NO_2 conversions and NO consumptions. This is not readily adaptable to the RADM2 peroxy radical representation because the overall products are not associated directly with the reacting VOCs but with their peroxy radicals, and the yield of peroxy radicals from VOCs can vary. On the other hand, it is readily adaptable to the peroxy radical representation incorporated in SAPRC-07, where each overall product is still directly related to each reacting VOC.

Base Chlorine Mechanism

The model species added to the base mechanism to represent the atmospheric reactions of chlorine species are listed on Table A-4 in Appendix A. These include 8 model species to represent active inorganic reactants and radicals, 2 to represent chlorine-containing oxidation products, 3 steady state chemical operators to represent formation of chlorine species in peroxy radical reactions, and 2 chlorine-containing inert tracer species. Table A-5 gives the reactions and rate parameters used in the base chlorine mechanism, and Table A-6 gives the absorption cross sections and quantum yields for the photolysis reactions listed in this table. Footnotes to Table A-5 and indicate the source of the rate constants and mechanisms used. As indicated there, most of the rate constants are based on results of the IUPAC (2006) and NASA (2006) evaluations, though several other sources were also used in some cases.

Except for the updated rate constants and photolysis data, the base inorganic chlorine mechanism is very similar to that developed previously by Carter et al (1996a, 1997b). The major difference is the addition of separate model species to represent the reactions of chlorinated aldehydes and ketones that may be formed in the reactions of chlorinated VOCs. Carter and Malkina (2007) found that the reactivities of the 1,3-dichloropropenes are significantly underpredicted if the standard aldehyde model species are used to represent the reactions of the chloroacetaldehyde predicted to be formed, but satisfactory simulations are obtained if a separate model species is used, using the NASA (2006)-recommended absorption cross sections and quantum yields for this compound. This is because this compound is calculated to photolyze ~15 times faster than acetaldehyde and ~4.5 times faster than the lumped higher aldehyde model species used in the standard base mechanism. This model species (CLCCHO) is also used to represent the reactions of other α-chloroaldehydes, which are assumed to be similarly photoreactive. Because chloroacetone is calculated to photolyze ~7 times faster than MEK and even more for higher ketones, a chloroacetone (CLACET) model species is added to represent the reactions of α-chloroketones. However, β-chloro- aldehydes and ketones and other chlorinated aldehydes are still represented by the generic higher aldehyde or ketone species (RCHO, MEK, or PROD2) in the standard mechanism.

Chlorine atoms react rapidly with most reactive VOCs and any complete chlorine mechanism must include a representation of their reactions, at least for the VOCs present in the chamber experiments with chlorine-containing species, and for the explicit and lumped VOC species used in atmospheric models. The mechanisms for these reactions are discussed in conjunction with the mechanisms for individual VOCs and lumped mechanisms for airshed models, below.

Representation of Organic Products

The set of model species to represent the reactions of the organic oxidation products are given in Table A-1 in Appendix A. Some of these are compounds represented explicitly (e.g. formaldehyde) and some are lumped species whose mechanisms are derived based on that for a compound or group of compounds chosen as representative. In the latter case, the compound or compounds used to derive the mechanisms for the lumped species are given in Table A-1 and in applicable footnotes to Table A-2. Except for the additional species added to represent higher hydroperoxides and the removal of phenol and the organic peroxyacids (now lumped with cresols or organic acids, respectively), this mechanism uses essentially the same set of model species to represent the organic products, and the same set of compounds to derive their mechanisms in the case of lumped species, as does SAPRC-99. Therefore the discussion of these species, and the choice of representative compounds used to derive the mechanisms of the lumped species, given in the SAPRC-99 documentation (Carter, 2000a) are still applicable. However, the rate constants and in some cases the products used for the reactions of these species or representative compounds were updated, and the reactions of these species with chlorine atoms were added and incorporated in the base chlorine mechanism discussed above.

The optional added chlorine mechanism given in Table A-5 includes the reactions of Cl atoms with most of the model species used reactive organic products in the base mechanism. Although reactions of Cl with some organic product species have been omitted[1], the processes represented should be sufficient for most ambient and chamber simulations, where the major sinks for the chlorine atoms or the

---

[1] The reactions of Cl atoms with the following model species have been omitted: HCOOH, CCOOH, RCOOH, COOH, BACL, NPHE, AFG1, AFG2, and AFG3.

product species are other reactions. As indicated above the added chlorine mechanism also includes model species for chlorinated aldehydes and ketones that may be formed from the reactions of chlorinated VOCs. The mechanism also includes the reactions of chlorine atoms with these compounds.

Mechanisms for Individual VOCs

An important distinguishing feature of the current SAPRC mechanisms is their ability to optionally include separate representations of the atmospheric reactions of many hundreds of different types of VOCs. Generally these are not all included in the airshed model at the same time, but selected individual compounds can be represented explicitly for the purpose of calculating reactivity scales or for toxics modeling, or mechanisms for groups of compounds can be used for deriving parameters for lumped model species used for representing complex mixtures such as ambient emissions. The current mechanism has separate explicit representations for 734 types of VOCs, making it the most comprehensive in terms of types of VOCs than any current gas-phase atmospheric mechanism. In addition, for deriving reactivity scales or representations of complex mixtures, 304 additional types of VOCs are represented using the "lumped molecule approach", where their impacts are estimated by assuming they are the same, on a per molecule basis, of an explicitly represented VOC. This yields a total of 1038 types of VOCs that are represented by a "detailed model species" in the mechanism.

A listing of all of the detailed model species in the SAPRC-07 in the mechanism, their molecular weights and general representation method (explicit or lumped molecule) is given in Table B-1 in Appendix B. That table also gives codes for availability of mechanism evaluation data, calculated ozone reactivity values, and reactivity uncertainty classifications. Table B-2 and Table B-4 through Table B-6 give the reactions and rate parameters for all the explicitly represented VOCs, Table B-3 gives the mechanisms for those VOCs where "adjusted product" mechanisms (discussed below) were used in the reactivity calculations, Table B-7 gives the mechanisms for the reactions of chlorine with the VOCs that were used in developing the fixed parameter lumped mechanism discussed in the following section. In addition to giving the OH radical rate constants and references for all VOCs that are explicitly represented in the mechanism, Table B-4 gives codes indicating the general type of mechanism used for each, and gives the structures used for compounds whose mechanisms were derived using the mechanism generation system. Footnotes to Table B-2 and Table B-4 through Table B-7 document the sources of the rate constants used, and Table B-8 gives the absorption cross sections and quantum yields for those that are photoreactive and have different absorption cross sections and quantum yields than those used in the base mechanism. Table B-9 gives the lumped molecule assignments used for the types of VOCs that are represented using this approximation. The derivations of these mechanisms are discussed further in the remainder of this section.

Mechanism Generation and Estimation System

A major tool used in the derivation of the SAPRC-99 mechanisms for individual VOCs was the automated mechanism generation and estimation software system that is described in the SAPRC-99 documentation (Carter, 2000a). Given the structure of the molecule, available information concerning applicable rate constants and branching ratios, and various estimation methods, this system can derive fully explicit mechanisms for the atmospheric reactions of many classes of VOCs in the presence of NO_x, and then use these mechanisms to derive the appropriate representations of the VOCs in terms of the model species in the base mechanism. This was used to derive the SAPRC-99 mechanisms for the acyclic and monocyclic alkanes, acyclic and monocyclic monoalkenes, many classes of oxygenates including alcohols, ethers, glycols, esters, aldehydes, ketones, glycol ethers, carbonates, etc, and the organic nitrates. Although many of the estimated rate constants and rate constant ratios are highly uncertain, this procedure provided a consistent basis for deriving "best estimate" mechanisms for chemical systems which are too complex to be examined in detail in a reasonable amount of time. The system allows for assigning or adjusting rate constants or branching ratios in cases where data are available, or where adjustments are necessary for model simulations to fit chamber data. Therefore, it could be used for deriving fully detailed mechanisms for VOCs that fully incorporate whatever relevant data are available, relying on various estimation methods only when information is not otherwise available. The program also outputs documentation for the generated mechanism, indicating the source of the estimates or assumptions or explicit assignments that were used.

This SAPRC-99 mechanism generation system, with some enhancements and updates as described below, was also used for deriving mechanisms for many of the VOCs in the SAPRC-07 mechanism. Since this system is comprehensively documented by Carter (2000a) and most of the estimation methods were not updated as part of this project, in this section we will restrict our discussion to the changes, updates, and enhancements that were made as part of this project and utilized when deriving the updated mechanisms for the individual VOCs. These are described below

Enhanced Capabilities for VOCs and Reactions

During the period of this project, the capabilities of the mechanism generation system were enhanced to support generating mechanisms for VOCs and radicals that could not previously be processed. These are briefly summarized below. These enhancements, and the associated estimates and branching ratio assignments, will be described in more detail in a future report when the current system is more comprehensively documented.

- Reactions of VOCs with chlorine atoms can now be generated. This is discussed in the following subsection.
- The ability to represent compounds with more than one ring has been added. This required revising the way structures were identified. Because of this, mechanisms for terpenes can now be generated. This is also useful in generating estimated mechanisms for aromatics, discussed below.
- The ability to represent compounds with more than one double bond has been added. This also required revising the way structures were identified. However, estimation methods for reactions of compounds with conjugated or cumulated double bonds were not developed, and automatically generated rate constants and branching ratios for OH and NO_3 reactions of such compounds are not necessarily chemically reasonable, and reactions of O_3 with compounds with more than one double bond are still not supported. Explicit assignments have to be made for such reactions, as was the case with, for example, isoprene and 1,3-butadiene.
- The ability to estimate reactions of unsaturated radicals has been added. The system recognizes allylic resonance and the probability of reaction at various positions of alkyl radicals with allylic resonance is estimated by assuming that the probability of reaction at a particular structure is proportional to $\exp(H_f/RT)$, where H_f is the estimated heat of formation of the structure, R is the gas constant, and T is the temperature. If the heat of formation cannot be estimated, equal probability for reaction at all positions (or the positions with the most conjugated double bonds if there are more than one double bond) is assumed.
- Reactions involving H-atom abstractions are now considered when generating mechanisms for reactions of OH, NO_3, and Cl with alkenes. These previously had to be assumed to be negligible because of lack of support for generating mechanisms for unsaturated radicals. These are still neglected if they are estimated to occur less than 1% of the time, as is generally the case in OH and NO_3 reactions. However, abstraction reactions are generally not negligible in chlorine + alkene reactions, as discussed below.
- The ability to generate mechanisms for amines (compounds with >N-, -NH-, or $-NH_2$ groups) was added. The new amine mechanisms, and their evaluation against chamber data, are documented by Carter (2008a). The available kinetic data indicates that reaction with OH occurs by H-atom

abstraction from the amino group and that the rate of H-atom abstraction from the carbon next to the amino group is significantly enhanced, and group-additivity estimates for rates of reaction at these positions were derived. The data of Aschmann and Atkinson (1998) on N-methyl pyrrolidinone (NMP) indicate that reaction of amines with NO_3 radicals may also occur to a non-negligible extent, and estimates (albeit highly uncertain) of NO_3 reactions for amines in general were derived. Methods for estimating rate constants and mechanisms for reactions of amines with O_3 were also developed. A more complete discussion and documentation of the amine mechanisms are given by Carter (2008a).

- The ability to represent alkynes was added. The mechanisms for OH reactions were assumed to be analogous to that derived for acetylene (Carter et al, 1997c, Carter, 2000a).
- The ability to represent alkylbenzenes and their initial reactions has also been added. However, our ability to estimate these reactions has not evolved to the point where this can be used to generate reliable mechanisms useful for modeling, and this has been used primarily as a research tool in working towards eventually developing more explicit mechanisms for aromatics. This work, which is still underway, was useful in deriving the updated condensed mechanisms for aromatics discussed later in this section.

The enhanced capabilities required group additivity estimates deriving rate constants for additional types of abstraction reactions that were not previously supported, such as abstractions from compounds with double bonds, abstractions from aromatics, and abstraction reactions by NO_3 radicals and Cl atoms. As discussed previously (e.g., see Kwok and Atkinson, 1995 or Carter, 2000a), rate constants for abstraction processes can be estimated using

$$\text{Total Rate Constant} = \sum\nolimits_{\text{Groups}} \text{Group Rate Constant} \times \prod\nolimits_{\text{Substituents on Group}} \text{Correction Factor}$$

where "group" refers to various parts of the molecule for which group additivity assignments are made. Group additivity parameters used for estimating abstraction reactions are given in Table 3. The assignments for abstractions by OH are the same as used previously (Carter, 2000a), with assignments for reactions of aromatics or amines added as indicated by footnotes to the table. The assignments for the NO_3 reactions are primarily from Atkinson (1991). The assignments for abstractions by chlorine atoms are discussed in the following section.

Support for Chlorine Reactions

As indicated above, in order to support the extension of the mechanism to represent chlorine chemistry, the mechanism generation system was enhanced to generate mechanisms for chlorine + VOC reactions. Since the reactions of Cl radicals with VOCs are similar to those of OH. This general procedure can be readily adapted to generate mechanisms for Cl + VOC reactions. This requires (1) making group-additivity estimates for all the possible initial reactions of Cl with VOCs, (2) generating mechanisms for the Cl-containing radicals that can be formed when Cl adds to double bonds, and (3) generating mechanisms for the radicals formed. The general procedures are discussed in detail by Carter (2000a). The specific adaptations to chlorine atom reactions are discussed below.

Chlorine can react with VOCs either by abstracting a hydrogen atom to form HCl and the corresponding alkyl radical, or by adding to a double bond. For abstraction reactions, the rate constants can be estimated using group additivity methods, with the rate constant being determined by the sum of the abstraction rate constant assigned to the group, multiplied by substituent correction factors for each non-hydrogen substituent on the group, summed over all groups with hydrogen atoms (e.g., see Kwok and Atkinson, 1995 or Carter, 2000a). Note that the correction factor for methyl substitution is arbitrarily set at unity, with the factors for the other substituents being determined based on differences in rate constants at groups that are only methyl substituted.

Table 3. Group additivity parameters used for estimating rate constants for abstraction reactions by OH and NO_3 radicals and by Cl atoms.

Table 3a. Abstraction rate constants assigned to groups

Group	OH [a]					NO_3		Cl	
	k(300)	A	B	D	Notes [b]	k(300)	Notes	k(300)	Notes
CH_3	1.39e-13	4.49e-18	2	320	1,2	7.00e-19	9	3.43e-11	13
CH_2	9.41e-13	4.50e-18	2	-253	1,2	1.50e-17	9	6.77e-11	13
CH	1.94e-12	2.12e-18	2	-696	1,2	8.20e-17	9	4.46e-11	13
OH	1.42e-13	2.10e-18	2	85	1,2	0	10	0	10
CHO	1.56e-11	5.55e-12	0	-311	1,3	2.84e-15 [c]	11	6.64e-11	13
HCO(O)	0				1,4	0	10	0	12
OH(O)	5.30e-12	7.82e-17	2	85	5	0	10	0	10
CH_3(Bz) [d]	4.92e-13				6	7.00e-19	12	3.43e-11	12
CH_2(Bz) [d]	1.88e-12				7	1.50e-17	12	6.77e-11	12
CH(Bz) [d]	1.33e-12				8	8.20e-17	12	4.46e-11	12
$CH_3(NH_x)$ [e]	1.67e-11				22	~6.2e-14	24	[f]	
$CH_2(NH_x)$ [e]	1.84e-11				22	~4.4e-14	24	[f]	
$CH(NH_x)$ [e]	2.01e-11				23	~9.9e-14	24	[f]	
NH_2	1.41e-11				22	~5.2e-14	24	[f]	
NH	3.17e-11				22	~5.7e-14	24	[f]	

[a] Temperature dependences for OH rate constants given by $k(T) = A\ B^T \exp(-D/T)$, where T is in ^{o}K.

[b] Notes for derivations of the group rate constants and substituent correction factors are given below (Note [a] with Table 3b).

[c] The temperature dependence of this group rate constant is given by 1.40e-12 x exp(-1860/T).

[d] "Bz" refers to any aromatic carbon.

[e] Applicable for x=0,1,2.

[f] Group rate constants for reactions of chlorine with amines were not derived

Table 3b. Group correction factors for abstraction reactions

Group	Substituent Correction Factor					
	OH		NO_3		Cl	
	Factor	Note [a]	Factor	Note	Factor	Note
CH_3	1	1,2,14	1	17	0	14
CH_x (x<3)	1.23	1,2	1.34	11	0.95	13
CH_x(CO)	3.90	1,2	1.34	17	0.95	17
CH_x(CO-O)	1.23	1,2	1.34	17	0.95	17
CH_x(Cl)	0.36	1,2	1.34	17	0.19	19
CH_x(Br)	0.46	1,2	1.34	17	0.95	17
CH_x(F)	0.61	1,2	1.34	17	0.95	17
OH	3.50	1,2	0	18	1.07	13
CHO	0.75	1,2	0.18	11	0.40	13
CO	0.75	1,2	0.89	11	0.04	13
CO(O)	0.31	15	0	12	0.04	17

Table 3 (continued)

Table 3b. Substituent Correction Factors (continued)

Group	Substituent Correction Factor					
	OH		NO_3		Cl	
	Factor	Note [a]	Factor	Note	Factor	Note
CO(OH)	0.74	1,2	0	12	0.04	17
O	8.40	1,2	0	18	1.07	20
O(CO)	1.60	1,2	0	18	1.07	17
O(HCO)	0.90	1,15	0	18	1.07	17
O(NO2)	0.04	1,2	0	18	1.07	17
O(OH)	16.26	5	1	18	1.07	17
NO2	0.00	1,2	0	12	n/a	
F	0.09	1,2	0	12	0.01	21
Cl	0.38	1,2	0	12	0.01	13
Br	0.28	1,2	0	12	n/a	
I	0.53	1,2	0	12	n/a	
C=C	1.00	1,2	1	17	0.95	13
ONO_2	0.04	1,2	0	12	0.12	
Bz	1	14	1	17	2.03	13
NH_2, NH, N	1	14	1	14	[b]	

[a] Notes for derivations of the group rate constants and group correction factors are as follows:

1 Same as used in SAPRC-99

2 Kwok and Atkinson (1995)

3 Based on IUPAC (1997) recommendations for acetaldehyde and propionaldehyde

4 Reaction at formate group assumed to be negligible based on tabulated formate rate constants.

5 Derived to fit the NASA (2006) recommended rate constant and branching ratio for reaction of OH with methyl hydroperoxide. This results in an unusually large group substituent factor.

6 Average of estimated rate constants per methyl group for the alkylbenzenes for which aromatic aldehyde yields have been derived. Reaction at the methyl group is estimated based on the aromatic aldehyde yield and the total rate constant.

7 Derived from the difference for the total rate constants for ethylbenzene and toluene, assuming the same rate constant for addition to the aromatic ring and the estimated rate constant at the methyl group in ethylbenzene.

8 Derived from the difference for the total rate constants for isopropyl benzene and toluene, and p-cymene and p-xylene, assuming the same rate constant for addition to the aromatic ring and the estimated rate constants for reactions at the methyl groups in isopropyl benzene and p-cymene.

9 From Atkinson (1991). Derived from the correlation between NO_3 and OH radical rate constants.

10 Assumed to be negligible.

11 Derived from the IUPAC (1997) recommended rate constant for acetaldehyde.

12 No explicit assignment made. By default, the system uses the same assignment as for standard CH_3, CH_2, or CH groups.

13 Derived in this work from measured chlorine + VOC rate constants. See text and Table 4

14 Assigned.

15 From Kwok et al (1996).

16 Adjusted to fit OH + ethyl and propyl formate rate constants (Wallington et al, 1988b)

17 No assignment made. This is the default value used by the mechanism generation system, and may not be appropriate.

18 This is the assignment incorporated into the current system. It may not be appropriate. It is not used as the basis for estimating NO_3 rate constants for any detailed model species.

19 Based on chloroacetaldehyde only

20 Estimated to be approximately the same as the factor for OH.

21 Estimated to be approximately the same as the factor for Cl.

22 Derived to give the best fits to the available kinetic data for simple amines and alcohol amines for which kinetic data are available, as indicated in Table 3c. In order to fit the data for tertiary amines, it is necessary to assume that OH reacts with an enhanced rate at groups next to the amino group, and in order to fit the data for amines, such as AMP and t-butyl amine, that do not have abstractable hydrogens next to the amino group it is necessary to assume that reaction also occurs at a significant rate at the NH or NH_2 groups.

23 No data are available for which to derive group-additivity estimates for this type of group. The group rate constant is estimated by linear interpolation from those used for $CH_3(NH_x)$ and $CH_2(NH_x)$.

24 The only kinetic data concerning the reactions of NO_3 radicals with amines is for N-methyl-2-pyrrolidinone (NMP), where a relatively high rate constant of 1.26 x 10^{-13} cm^3 $molec^{-1}$ s^{-1} is measured (Aschmann and Atkinson, 1999). This suggests that this reaction is also rapid for other amines. We assume that this is an H-atom abstraction reaction, forming HNO_3. For lack of other data, use the rate constant for NMP as the basis for estimating the group rate constants for reaction at the -CH_2(N) or CH_3(N) groups. The group rate constants for reactions at other amine groups, including NH and NH_2, are estimated assuming that the ratios of rate constants for reactions at the various groups are the same for the NO_3 reaction as derived for the OH reaction. This is highly uncertain.

[b] Group rate constants for reactions of chlorine with amines were not derived

Table 3c. Experimental and best fit estimated rate constants for the reactions of OH radicals with amines that were used as the basis for deriving structure-reactivity estimates

Compound	OH Rate Constant (10^{-11} cm^3 $molec^{-1}$ s^{-1})						
	Measured value, reference				Avg	Calc	Diff
Methyl amine	1.73	1	2.20	2	1.97	3.08	36%
Dimethyl amine	6.49	1	6.54	3	6.52	6.51	0%
Trimethyl amine	3.58	1	6.09	3	4.84	5.01	4%
Ethyl amine	2.38	1	2.77	3	2.58	3.59	28%
N,N-Dimethylethanolamine (DMAE)	9.00	4	4.70	5	6.85	6.02	-14%
t-Butyl amine	1.18	6			1.18	1.79	34%
2-Amino-2-methyl-1-propanol (AMP)	2.80	5			2.80	2.19	-28%

References for measured rate constants:

1	Carl and Crowley (1998)	4	Anderson and Stephens (1988)
2	Atkinson et al. (1977)	5	Harris and Pitts (1983)
3	Atkinson et al. (1978)	6	Koch et al (1996)

For addition to double bonds, we assume that the rate constant is determined only by the number of non-hydrogen substituents about the double bond, with correction factors used for some non-alkyl substituents such as halogens. Although this doesn't affect the rate constant, for the purpose of estimating mechanisms it is also necessary to assign factors for the fractions that react at each position around the double bond. This has to be estimated because we are aware of no data available concerning this.

The organic + Cl atom rate constants that were used as the basis for deriving group-additivity estimates for the mechanism generation system are given in Table 4, with footnotes indicating the sources of the rate constants used. (Note that the rate constants in Table 4 are restricted to those used for deriving the group-additivity methods, and does not include compounds for which the estimation method was not developed to support. See Table B-7 for the chlorine atom rate constants for all the VOCs in the mechanism.) Group additivity parameters found to give the best fits to the data on Table 4 are shown on Table 3, above, for the abstraction reactions, and on Table 5 for reactions at double bonds. The "Est'n error" column on Table 4 shows the extent to which the estimated rate constant agrees with the measured value, with positive numbers indicating overprediction, and vise-versa. If there is no entry in this column it means that the current estimation method is not applicable to those compounds. The group additivity parameters were determined by minimizing the sum-of-square relative errors in for the compounds listed on Table 4. In most cases the estimated rate constants agree with the measured values to better than 25%. However, cases with prefect agreement usually indicate that a parameter was determined only by the data for a single compound, so perfect agreement is not always evidence for the success of the method.

The Cl abstraction reactions form the same radicals as the corresponding reactions with OH, so the procedures for generating the subsequent reactions of those radicals formed have already been developed and described (Carter, 2000a). Therefore, for VOCs for which only the abstraction reaction is important, which include all saturated VOCs and also simple aldehydes, ketones, and esters, the derived mechanisms for the chlorine reactions are the same as those for the reaction with OH, except for the different branching ratios for the initial reactions because of the differences in the group additivity parameters, discussed above.

Although in principle the system could also derive mechanisms for the reactions of chlorine atoms with alkenes, in practice this proved difficult because at present the system does not contain the necessary thermochemical or kinetic assignments to estimate reaction rates for many of the chlorine-substituted alkoxy radicals predicted to be formed. The only way to deal with this is to make explicit assignments of branching ratios for the Cl-substituted radicals that cannot presently be handled by the system, which can be time consuming for large molecules because of the number of radicals that can be formed. For that reason, assignments were made only to permit the generation of mechanisms for the explicitly represented alkenes (ethylene and isoprene), those chosen as representative of the lumped model species used in airshed models (discussed later in this report), or those present in the chamber experiments relevant to evaluating mechanisms for the chlorine-containing compounds for which chamber data are available.

The alkoxy radical branching ratio assignments used to generate the chlorine + alkene mechanisms that were derived for this project are summarized on Table 6, with footnotes giving a brief indication of the basis of the assignments. In addition, except as indicated on Table 6, it is assumed that α-chloro-alkoxy radicals predominantly decompose to form chlorine atoms, e.g.,

$$ClCH_2O\cdot \rightarrow HCHO + Cl\cdot$$

$$RCH(Cl)O\cdot \rightarrow RCHO + Cl\cdot$$

$$RC(R')(Cl)O\cdot \rightarrow RC(O)R' + Cl\cdot$$

Table 4. Rate constants for reactions with chlorine atoms for organic compounds used to derive parameters for group-additivity estimates.

Compound	Rate Constant Assignment [a] k(298)	A	Ea (deg K)	Note [b]	Est'n Error [c]
Methane	1.03e-13	6.60e-12	1240	1	
Ethane	5.93e-11	8.30e-11	100	1	15%
Propane	1.37e-10	1.20e-10	-40	2	-3%
n-Butane	2.05e-10	2.05e-10	0	1	-5%
n-Pentane	2.80e-10			2	-8%
n-Hexane	3.40e-10			2	-6%
n-Heptane	3.90e-10			2	-3%
n-Octane	4.60e-10			2	-4%
n-Nonane	4.80e-10			2	5%
n-Decane	5.50e-10			2	3%
Isobutane	1.43e-10			2	0%
Neopentane	1.11e-10	1.11e-10	0	2	18%
Iso-Pentane	2.20e-10			2	-7%
2,3-Dimethyl Butane	2.30e-10			2	-6%
2-Methyl Pentane	2.90e-10			2	-8%
3-Methylpentane	2.80e-10			2	-4%
2,2,3-Trimethyl Butane	2.90e-10			2	-29%
2,4-Dimethyl Pentane	2.90e-10			2	-4%
2-Methyl Hexane	3.50e-10			2	-6%
2,2,3,3-Tetramethyl Butane	1.75e-10			2	12%
2,2,4-Trimethyl Pentane	2.60e-10			2	3%
Cyclohexane	3.50e-10			2	6%
Methylcyclohexane	3.90e-10			2	-2%
Propene	2.67e-10			4	-1%
1-Butene	3.39e-10			5	-3%
1-Pentene	4.05e-10			5	-4%
3-Methyl-1-Butene	3.52e-10			6	-4%
3-Methyl-1-Pentene	3.78e-10			6	6%
Isobutene	3.25e-10			6	9%
2-Methyl-1-Butene	3.82e-10			6	10%
cis-2-Butene	3.88e-10			6	-15%
trans-2-Butene	3.55e-10			4	-7%
2-Methyl-2-Butene	3.23e-10			6	7%
Cis 4-Methyl-2-Pentene	4.04e-10			6	0%
Toluene	6.20e-11			7	12%
m-Xylene	1.35e-10			7	3%
o-Xylene	1.40e-10			7	-1%
p-Xylene	1.44e-10			7	-4%
1,3,5-Trimethyl Benzene	2.42e-10			8	-14%
Methanol	5.50e-11	5.50e-11	0	1	-34%
Ethanol	1.00e-10	8.60e-11	-45	1	5%
Isopropyl Alcohol	8.60e-11			1	31%
n-Propyl Alcohol	1.62e-10	2.50e-10	130	1	3%
Acetic Acid	2.65e-14			1	0%
Acetaldehyde	8.00e-11	8.00e-11	0	1	0%
Propionaldehyde	1.23e-10			9	0%
Acetone	2.69e-12	7.70e-11	1000	10	0%
Methyl Ethyl Ketone	3.60e-11			1	2%
Methyl Chloride	4.89e-13	2.17e-11	1130	10	-7%
Dichloromethane	3.49e-13	7.40e-12	910	10	11%

Table 4 (continued)

Compound	Rate Constant Assignment [a] k(298)	A	Ea (deg K)	Note [b]	Est'n Error [c]
Chloroform	1.19e-13	3.30e-12	990	10	-7%
Vinyl Chloride	1.27e-10			11	4%
1,1-Dichloroethene	1.40e-10			11	-19%
Trans-1,2-Dichloroethene	9.58e-11			11	8%
Cis-1,2-Dichloroethene	9.65e-11			11	7%
Trichloroethylene	8.08e-11			11	-18%
Perchloroethylene	4.13e-11			11	9%
3-Chloropropene	1.30e-10			12	0%
Chloroacetaldehyde	1.29e-11			13	0%

[a] Rate constants and A factors in units of cm^3 $molec^{-1}$ s^{-1}. If no A factor or activation energy is given, rate constant is given only for 298K. Otherwise, 298K rate constant is calculated from A factor and activation energy.

[b] Notes:

1 IUPAC (2006) recommendation.

2 Atkinson (1997) recommendation.

3 This reaction is in the pressure falloff region under atmospheric conditions.

4 Average of values tabulated by Wang et al (2002). Value of Wang et al (2002) placed on an absolute basis using the Atkinson (1997)-recommended rate constant for n-heptane.

5 Average of value of Coquet et al (2000), placed on an absolute basis using the Atkinson (1997)-recommended n-hexane rate constant, and the value of Wang et al (2002), placed on an absolute basis using the Atkinson (1997)-recommended rate constant for n-heptane.

6 Value of Wang et al (2002), placed on an absolute basis using the Atkinson (1997)-recommended rate constant for n-heptane.

7 Average of values tabulated by Wang et al (2005).

8 Wang et al (2005).

9 Average of values listed by Le Crane et al (2005)

10 NASA (2006) recommendation.

11 From rate constants relative to n-butane from Atkinson and Aschmann (1987), placed on an absolute basis using the n-butane rate constant recommended by IUPAC (2006).

12 Average of values tabulated by Albaladejo et al (2003).

13 Average of values tabulated by Scollard et al (1993)

[c] (Estimated rate constant - measured rate constant) / measured rate constant.

Table 5. Group additivity rate constants and factors used for estimating rates of addition of Cl atoms to double bonds.

Group	k(add)	Add'n to most substituted end	Note	Group	Substituent Correction	Note
CH2=CH-	2.30e-10	35%	1,2	Alkyl	1	3
CH2=C<	2.89e-10	25%	1,4	-Cl	0.58	1
-CH=CH-	2.63e-10	50%	1,5	2 -Cl's	0.68	1
-CH=C<	2.47e-10	25%	1,4	-CH_2Cl	0.56	1,6
>C=C<	2.47e-10	50%	1,5			

1 Addition rate constant and substituent correction factor derived to minimize sum of squares error in predictions of Cl + alkene rate constants. (Optimization for group additivity parameters for abstraction reaction carried out at the same time.)

2 Assume same terminal bond addition fraction as used for the reaction of OH with propene (Carter, 2000a).

3 All alkyl substituents assumed to have the same factor. Unit factor assigned.

4 No information available concerning relative addition rates at the different positions. Assume addition at terminal position occurs about 25% of the time

5 Assume equal probability of addition, regardless of substituents.

6. Based on rate constant for 3-chloropropene.

These assignments, and therefore the mechanisms derived for the chlorine + alkene reactions that are based on them, are uncertain. However, reactions of alkenes with chlorine atoms are generally not major sinks either for chlorine or alkenes under most conditions, so these assumptions are probably not major sources of uncertainty in terms of overall model predictions.

Updates to Rate Constants and Mechanisms

Because of time and resource limitations, we were not able to update most of the estimation methods incorporated in the SAPRC-99 mechanism generation system used for this project, so most of the various estimation assignments given by Carter (2000a) are still applicable for this version. However, we did update the assignments for the rate constants for the initial reactions of the individual VOCs in those cases where rate constant measurement data are available, and these were used when generating the mechanisms for the applicable VOCs. Table B-2, and Table B-4 through Table B-6 and their footnotes indicate the rate constants used and the sources of those rate constants, where applicable.

Based on results of recent evaluations and also results the evaluation against chamber data, some updates were also made to assigned reactions of excited Criegee radicals involved in the ozone + alkene reactions. The current assignments for Criegee biradical reactions are summarized on Table 7. Note that the amount of radical formation in the decomposition of the primary biradicals, which was adjusted based on simulations of chamber data, is somewhat higher than used in the SAPRC-99 mechanism, but still lower than currently recommended radical yields for these reactions. This inconsistency, which is also seen in evaluations of the MCM, is discussed further by Pinho et al (2006).

Additional updates or modifications were made for mechanisms of some individual VOCs, based primarily on results of model simulations of chamber experiments. For example, the mechanism for the reaction of O^3P with ethene was updated based on the Calvert et al. (2000)

Table 6. Branching ratio assignments for chlorine-substituted alkoxy radicals made to generate mechanisms for the reactions of chlorine with representative alkenes.

Used for	Reaction	Fract.	Notes
Propene	$CH_3CH(O\cdot)CH_2Cl + O_2 \rightarrow CH_3C(O)CH_2Cl + HO_2\cdot$	100%	1
	$CH_3CH(CH_2O\cdot)Cl + O_2 \rightarrow CH_3CH(CHO)Cl + HO_2\cdot$	100%	2
2-Butenes	$CH_3CH(O\cdot)CH(CH_3)Cl + O_2 \rightarrow CH_3C(O)CH(CH_3)Cl + HO_2\cdot$	100%	3
1-Pentene	$CH_3CH_2CH_2CH(O\cdot)CH_2Cl \rightarrow \cdot CH_2CH_2CH_2CH(OH)CH_2Cl$	100%	4
	$CH_3CH_2CH_2CH(CH_2O\cdot)Cl \rightarrow CH_3CH(\cdot)CH_2CH(Cl)CH_2OH$	100%	4
	$CH_3CH(O\cdot)CH_2CH(Cl)CH_2OH \rightarrow CH_3CH(OH)CH_2CH(Cl)CH(\cdot)OH$	100%	4
2-Pentenes	$CH_3CH_2CH(O\cdot)CH(CH_3)Cl \rightarrow CH_3CH_2CHO + CH_3CH(\cdot)Cl$	100%	5
	$CH_3CH_2CH(Cl)CH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_3CH_2CH(\cdot)Cl$	100%	5
Isoprene	$CH_2{=}C(CH_3)CH(\cdot)CH_2Cl + O_2 \rightarrow CH_2{=}C(CH_3)CH(OO\cdot)CH_2Cl$	60%	6
	$\rightarrow CH_3C(CH_2OO\cdot){=}CHCH_2Cl$	41%	
	$CH_2{=}CH\text{-}C(\cdot)(CH_3)CH_2Cl + O_2 \rightarrow CH_2{=}CH\text{-}C(OO\cdot)(CH_3)CH_2Cl$	44%	6
	$\rightarrow CH_3C({=}CH\text{-}CH_2OO\cdot)CH_2Cl$	56%	
	$CH_2{=}C(CH_3)CH(O\cdot)CH_2Cl + O_2 \rightarrow CH_2{=}C(CH_3)C(O)CH_2Cl + HO_2\cdot$	100%	7
	$CH_3C({=}CH\text{-}CH_2O\cdot)CH_2Cl + O_2 \rightarrow CH_3C(CH_2Cl\ ){=}CHCHO + HO_2\cdot$	100%	8
	$CH_3C(CH_2O\cdot){=}CH\text{-}CH_2Cl + O_2 \rightarrow CH_3C(CHO){=}CHCH_2Cl + HO_2\cdot$	50%	9
	$\rightarrow CH_3C(CH_2OH){=}CH\text{-}CH(\cdot)Cl$	50%	
	$CH_2{=}CH\text{-}C(O\cdot)(CH_3)CH_2Cl \rightarrow CH_2{=}CHC(O)CH_3 + .CH_2Cl$	100%	5
	$CH_2{=}C(CHO)CH_2O\cdot + O_2 \rightarrow CH_2{=}C(CHO)CHO + HO_2\cdot$	100%	10
	$CH_2{=}C(CH_3)CH(CH_2O\cdot)Cl + O_2 \rightarrow CH_2{=}C(CH_3)CH(CHO)Cl + HO_2\cdot$	50%	9
	$\rightarrow CH_2{=}C(CH_2\cdot)CH(Cl)CH_2OH$	50%	
	$CH_2{=}C(CH_2O\cdot)CH(Cl)CH_2OH \rightarrow CH_2{=}C(CH_2OH)CH(Cl)CH(\cdot)OH$	50%	9
	$+ O_2 \rightarrow CH_2{=}C(CHO)CH(Cl)CH_2OH + HO_2\cdot$	50%	
	$CH_2{=}CH\text{-}C(CH_3)(CH_2O\cdot)Cl + O_2 \rightarrow CH_2{=}CH\text{-}C(CH_3)(CHO)Cl + HO_2\cdot$	100%	10
α-Pinene	$CH_3C(O\cdot){*}^1CH(Cl)CH_2CH{*}^2CH_2CH{*}^1C{*}^2(CH_3)CH_3 \rightarrow CH_3C(O)CH(Cl)\text{-}CH_2CH{*}^1CH_2CH(\cdot)C{*}^1(CH_3)CH_3$	100%	4,11
	$CH_3C(O)CH(Cl)CH_2CH(O\cdot)CH_2CHO \rightarrow HCOCH_2CHO + CH_3C(O)\text{-}CH(CH_2\cdot)Cl$	100%	5
	$CH_3C(O)CH(CH_2O\cdot)Cl \rightarrow \cdot CH_2C(O)CH(Cl)CH_2OH$	100%	4
	$.OCH_2C(O)CH(Cl)CH_2OH \rightarrow HOCH_2C(O)CH(Cl)CH(\cdot)OH$	100%	4
	$CH_3C{*}^1(Cl)CH(O\cdot)CH_2CH{*}^2CH_2CH{*}^1C{*}^2(CH_3)CH_3 \rightarrow CH_3C(\cdot)(Cl)CH{*}^1\text{-}CH_2CH(CH_2CHO)C{*}^1(CH_3)CH_3$	100%	4,11
2-(Chloromethyl)-3-chlororopene			
	$ClCH_2C(O\cdot)(CH_2Cl)CH_2Cl \rightarrow ClCH_2C(O)CH_2Cl + .CH_2Cl$	100%	12
	$\cdot OCH_2C(Cl)(CH_2Cl)CH_2Cl + O_2 \rightarrow HCOC(Cl)(CH_2Cl)CH_2Cl + HO_2\cdot$	100%	10
1,3-Dichloropropenes			
	$ClCH_2CH(O\cdot)CH(Cl)Cl + O_2 \rightarrow Cl\text{-}CH_2C(O)CH(Cl)Cl + HO_2\cdot$	100%	13

1 Assumed to be favored over decomposition on the basis of estimates for $CH_3C(O\cdot)CH_3$ and the expectation that Cl-substitution makes radicals less stable

2 Assumed to be favored over decomposition on the basis of estimates for $CH_3CH_2CH_2O\cdot$ and the expectation that Cl-substitution makes radicals less stable

3 Assumed to be favored over decomposition on the basis of estimates for the radical where H- replaces Cl- and the expectation that Cl-substitution makes radicals less stable

4. Isomerization is assumed to dominate over competing processes for this radical.

Table 6 (continued)

5 This decomposition is assumed to dominate based on estimates for similar radicals.

6 Branching ratios based on the mechanism of Fan and Zhang (2004)

7 Assumed to be fast on the basis of observation of this compound as a product in the isoprene - chlorine reactions.

8 Although isomerizations might be expected to be more important than O2 reaction, this is assumed to dominate to account for the observed formation of CMBA as a product in the isoprene + chlorine reactions.

9 Reaction with O_2 is assumed to be the dominant product when the radical is in the trans configuration, and isomerization is assumed to be the dominant process when it is in the cis configuration. Equal possibility of cis and trans configuration is assumed.

10 It is expected that the competing decomposition isn't favorable, so the reaction with O_2 is assumed to dominate. However, this is uncertain.

11 The "$*^1$" and "$*^2$" symbols indicate join points for these cyclic radicals.

12 This appears to be the only available reaction.

13 Assumed to be favored over decomposition on the basis of estimates for $CH_3C(O\cdot)CH_3$ and the expectation that Cl-substitution makes radicals less stable

recommendation, but it was still necessary to assume lower fragmentation yields than recommended in order to simulate the chamber data, as was the case for the reactions of O^3P with other alkenes (Carter, 2000a; Pinho et al, 2006). Overall nitrate yields that were derived based on simulations of chamber data had to be readjusted for a number of compounds because changes to the base mechanism apparently caused the values of the nitrate yields that best fit the data to change somewhat. Assignments are made to the mechanism generation system to implement these adjustments where applicable.

Adjusted Product Mechanisms

Although the mechanism generation system derives fully explicit mechanisms, by default it lumps all the reactive products predicted to be formed into the set of organic product model species in the base mechanism, as indicated on Table A-1 in Appendix A. The mechanisms so derived are given in Table B-3 in Appendix B. Because the mechanisms used for the product species are fixed regardless of what VOC is being represented, these are referred to as "fixed product" mechanisms in the subsequent discussion. However, lumping the many types of reactive products into a few model species is an approximation, and some VOCs may form products that are not particularly well represented by any of the generic product model species. This could introduce inaccuracies to calculations of atmospheric reactivity scales. For this reason the mechanism generation system is also capable of deriving mechanisms for the major reactive products of the VOCs that could be used "adjustable product" mechanisms where the more reactive product species are represented by lumped (or explicit) product species whose mechanisms were derived based on the distribution of products they are being used to represent. Note that these adjustable mechanism products are only used on the mechanism for the particular VOC in the reactivity calculations, not for mechanisms of other VOCs in the base mechanism. The derivation and implementation of these adjustable product mechanisms is discussed by Carter et al (2000a). Since the same procedures were used for deriving the adjustable product mechanisms in this work, they are not discussed further here.

Table 7. Assigned mechanisms for Crigiee Biradicals used for deriving mechanisms for reactions of O_3 with alkenes.

Reaction	Fraction	Discussion
H_2COO[excited] →		Branching ratios based on recommendations by Atkinson (1997), modified to be consistent with the OH yield in the IUPAC (2006) recommendations
H_2COO[stab]	37%	
HCO + OH	16%	
$CO_2 + H_2$	12%	
$CO + H_2O$	35%	
CH_3CHOO[excited] →		Atkinson (1997) recommendation.
CH_3CHOO[stab]	15%	
$CH_3\cdot + CO + OH$	54%	
$CH_3\cdot + CO_2 + H$	17%	
$CH_4 + CO_2$	14%	
RCX(X')CXOO[excited] →		(R=Alkyl other than CH3; X, X' = H or alkyl): Available data concerning stabilization and decompositions of RCHOO Criegee biradicals are limited and inconsistent. In order to fit chamber data to fit results of 1-butene and 1-hexene experiments, it is necessary to assume that stabilization occurs ~85% of the time for 4+-carbon Criegee biradicals.
RCX(X')CXOO[stab]	85%	
$RCX(X')\cdot + CO + OH$	9.5%	
$RCX(X')\cdot + CO_2 + H$	3.0%	
$RCHXX' + CO_2$	2.5%	
XCX'H-COO[excited]-R →		(X, X' = H or alkyl; R = alkyl): OH formation after hydroperoxide rearrangement assumed to be dominant process for disubstituted Criegee biradicals based on high OH yields, as discussed by Atkinson (1997). Relative importance of competing rearrangements estimated to be approximately proportional to estimated OH abstracting rate constant from H-donating group. (Unchanged from SAPRC-99)
·CXX'-CO-R + OH	100%	
Rt-COO[excited]-Rt' →		(Rt = tertiary alkyl): Most reasonable decomposition mode is formation of CO2 and radicals. No information about reactions of disubstituted Criegee biradicals that cannot undergo the hydroperoxide rearrangement. Roughly estimate that most is stabilized. The decomposition fraction is a guess. It probably depends on size of the molecule, but this is not taken into account. (Unchanged from SAPRC-99)
Rt-COO[stab]-Rt'	90%	
$Rt\cdot + Rt' + CO_2$	10%	

Adjustable product mechanisms were derived for all VOCs whose reactions and product reactions could be completely generated using the mechanism generation system. To assess the effects of using adjustable product mechanisms on calculated atmospheric incremental reactivities, Figure 1 shows a comparison of incremental reactivities calculated for the "averaged conditions MIR scale" calculated using the two methods for all VOCs for which adjustable product mechanisms could be derived. [Incremental reactivity scales are discussed in the "Updated Reactivity Scales" section, below. Briefly, the Averaged Conditions MIR scale gives a good approximation of the MIR scale used in CARB regulations (CARB 1993, 2000) using a single scenario rather than the average of 39 MIR scenarios.] It can be seen that for most VOCs the adjustable mechanism reactivities are very close to the fixed mechanism values, with the average bias being -1% and the average error being 6%[1]. However, there were a number of compounds with non-negligible differences where use of the adjustable product mechanisms for reactivity calculations is appropriate. The compounds where the magnitude of the change was greater than 20% are listed in Table 8, with the reasons for the differences indicated for the top three compounds.

For the purpose of calculating reactivity scales, we used the adjustable product mechanism if the calculated reactivity difference in the averaged conditions MIR scale was greater than 8%, and the fixed product mechanism otherwise. The use of 8% is somewhat arbitrary, but given the uncertainties in mechanisms in general, and product mechanisms derived using the mechanism generation system in particular, we did not consider the added complexity to be appropriate if the effect of less than approximately this amount. Table B-3 in Appendix B gives the adjustable product mechanisms that were employed in the reactivity scale calculations as determined by this criterion. Note that the primary VOC rate constants and methods for deriving the mechanisms are the same as indicated in Table B-2 for the fixed parameter mechanism, so this documentation is not duplicated on this table. If the mechanism for a

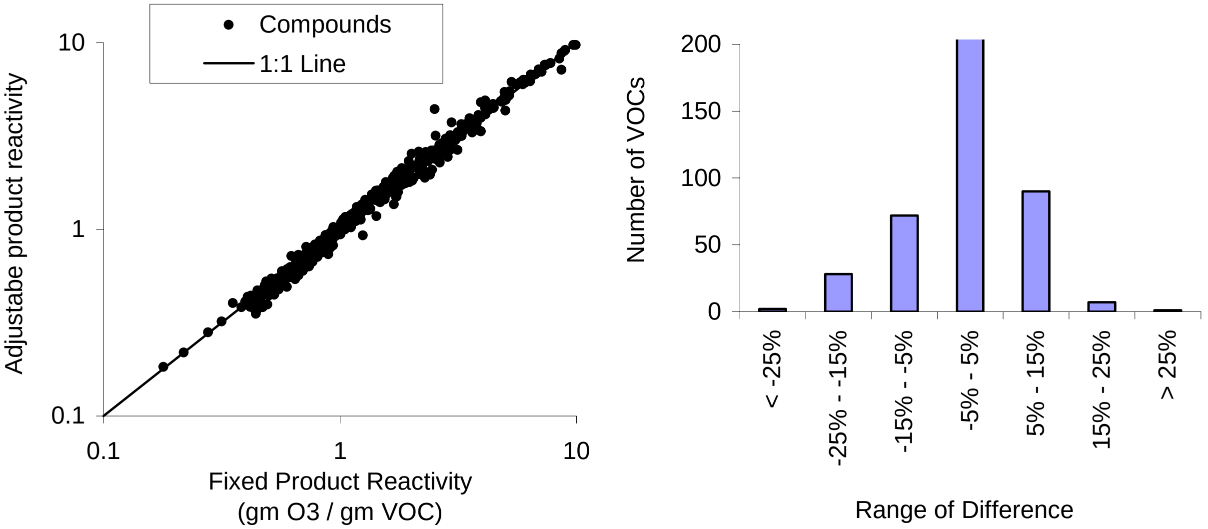


Figure 1. Effect of using the adjustable product mechanisms vs. the standard fixed product mechanisms on incremental reactivities in the "Averaged Conditions" MIR scale for those VOCs for which adjustable product mechanisms could be derived.

---

[1] The average bias is calculated as the average relative difference, while the average error is the average of the absolute magnitude of the relative difference.

Table 8. Compounds whose Averaged Conditions MIR reactivities changed by more than 20% when adjustable product mechanisms were employed.

Compound	Averaged Conditions MIR (gm O3 / gm VOC) Fixed	Adj'd	Diff	Discussion
2,3-Butanediol	2.51	4.41	75%	High yield product reacts to form biacetyl
1,2-Dihydroxy hexane	2.01	2.54	26%	Products react to form methyl glyoxal
Dimethoxy methane	1.25	0.93	-26%	Product represented by PROD2 has a relatively low rate constant for this group
cis-5-Decene	2.96	3.73	26%	
Glycerol	2.53	3.17	25%	
4-Methyl-2-pentanol	2.15	2.61	21%	
cis-4-Octene	3.94	4.79	22%	

VOC is not given in Table B-3, the mechanism used in Table B-2 was used to calculate its reactivity. The reactivity listings on Table B-1 in Appendix B indicate those cases where adjustable products mechanisms were used.

Updated Aromatics Mechanisms

Although significant progress has been made in recent years concerning the atmospheric reactions of aromatics and their reactive products (e.g., Calvert et al, 2002, Barnes, 2006, and references therein), the aromatics continue to represent the major class of compounds for which insufficient information exists for deriving predictive and explicit mechanisms based on mechanistic considerations alone. The most important uncertainties concern the reactions of the aromatic ring fragmentation products, which include highly photoreactive compounds that make significant contributions to overall aromatic reactivity. SAPRC-99 mechanism incorporates a highly simplified and parameterized set of model species to represent these products, whose yields and photolysis rates are adjusted to fit chamber data. In addition, the mechanisms for the reactions of ring-retaining products such as phenols, cresols, and nitrophenols are also highly uncertain, and SAPRC-99 uses simplified and parameterized representations for these reactions as well. Other mechanisms currently used in airshed models (Gery et al, 1988, Yarwood et al, 2005; Stockwell et al, 1990, 1997) also incorporate simplified and parameterized representations of aromatics, and although the MCM incorporates an attempt at a more explicit aromatics representation, its performance in simulating available environmental chamber data is so poor that it is not suitable for airshed modeling (Bloss et al, 2005).

The uncertain parameters in the SAPRC-99 aromatics mechanisms were optimized to give reasonably good simulations of results of aromatics - NO_x and environmental chamber experiments, and the mechanisms so derived also gave generally satisfactory results of incremental reactivity experiments with aromatics (Carter, 2000a), including some experiments carried out after the SAPRC-99 mechanism was developed at lower NO_x concentrations in the new UCR EPA chamber (Carter, 2004). However, Carter (2004) also found that the SAPRC-99 mechanism consistently underpredicts the extent of ozone enhancement caused by adding CO to aromatics - NO_x irradiations, Carter and Malkina (2002) found that the mechanism overpredicts "direct reactivity" in experiments designed to be sensitive to the direct effects of the primary reactions of aromatics on NO to NO_2 conversions. This suggests that there may be compensating errors in the SAPRC-99 aromatics mechanisms. In addition Carter (2004) found that

SAPRC-99 (and also CB4) tends to underpredict ozone formation in at low ROG/NO$_x$ ratios and low NO$_x$ concentrations in Surrogate - NO$_x$ experiments when the surrogate contains aromatics, but this is not seen in surrogates where the aromatics have been removed (unpublished results from this laboratory – also see "Mechanism Evaluation" section, below). Because of these problems, updating and improving the aromatics mechanisms was an important priority for this project.

The approach that was initially attempted to derive updated aromatics mechanisms was to derive fully (or at least nearly) explicit mechanisms for representative aromatic hydrocarbons and their oxidation products, and use these as a basis for deriving more condensed mechanisms that can be used for representing aromatics in general. However, this turned out to be unworkable in practice, at least within the time and resource constraints for this project. Developing fully explicit mechanisms that are entirely consistent with available data as given by Calvert et al (2002) is not possible because the low and inconsistent measured product yields can not account for complete reaction pathways, and mechanisms based on some of the data could not be made to give predictions that were consistent with the available environmental chamber reactivity data. This was found to be the case both for the initial aromatic ring-opening reactions, where yields of the expected unsaturated dicarbonyl ring-opening products were found to be low, and the photolysis reactions of the unsaturated dicarbonyl products, where assuming relatively high yields of non-radical products gave mechanisms that significantly underpredicted aromatic reactivities in chamber experiments. Also, mechanism incorporating new product data for phenols and cresols (Barnes, 2006; Berndt and Boge, 2003, Olariu et al, 2002) gave predictions that were inconsistent with the limited chamber data and therefore could not be used.

The approach that was therefore adopted for this version of the mechanism is to use a simplified but consistent and chemically reasonable model for the initial ring fragmentation reactions that give improved simulations of the direct reactivity data of Carter and Malkina (2002), and derive new mechanisms for the model species used to represent the unknown or uncertain aromatic ring fragmentation products based on estimated mechanisms for representatives of the unsaturated 1,4- and 1,6-dicarbonyls expected to be formed. The only adjustable parameters employed concerned the ratio of photoreactive to un-photoreactive model species representing the unsaturated 1,4-dicarbonyls, which were adjusted to fit the data for the aromatics - NO$_x$ experiments for the individual compounds. This yielded mechanisms that performed as well as SAPRC-99 in simulating aromatics - NO$_x$ and aromatics incremental reactivity experiments, and that performed somewhat better in simulating the direct reactivity results of Carter and Malkina (2002). However, the problem of underpredicting the effects of adding CO to aromatics - NO$_x$ irradiations and underpredicting O$_3$ formation in surrogate - NO$_x$ experiments at low NO$_x$ and low ROG/NO$_x$ conditions remained. Therefore, although the updated mechanisms are probably more chemically reasonable and consistent with somewhat more of the available data than was the case previously, not all of the problems could be resolved.

Reactions of Alkylbenzenes with OH

The major initial atmospheric reaction of aromatics is with OH radicals. Table 9 gives the measured or estimated product yields for the known products for the OH radical reaction that are used as the bases for the aromatics mechanisms developed in this work, with footnotes indicating the sources of these yields. The initial reactions can either be abstraction of H from side groups off the ring, or OH addition to the aromatic ring. The fractions reacted at the various positions, and their subsequent mechanisms, are derived as described below.

Reactions off the Aromatic Ring. The reactions following abstraction from the groups off the ring are exactly analogous to those in the alkane photo-oxidation system, and are assumed to proceed as shown below for toluene

Table 9. Measured or estimated yields of known products for benzene and methylbenzene reactions that were incorporated in the SAPRC-07 aromatics mechanisms

Compound	Yields and Notes [a]					
	Aromatic Aldehyde	Phenol or Cresol	Glyoxal	Methyl Glyoxal	Biacetyl	Nitrate yield [b]
Benzene		57% [1]	29% [2]			*7.7% [3]*
Toluene	6.5% [4]	18% [5]	24% [6]	15% [7]		10.6% [8]
Xylenes						*13.6% [3]*
o-	4.7% [9]	16% [10]	8.4% [11]	24% [11]	19% [12]	
m-	4.1% [13]	16% [14]	10% [15]	38% [16]		
p-	8.8% [17]	16% [18]	29% [19]	11% [20]		
Trimethylbenzenes						*16.2% [3]*
1,2,3-	*4.5% [21]*	*3.1% [22]*	7.2% [23]	18% [23]	45% [24]	
1,2,4-	3.6% [25]	2.2% [26]	7.4% [27]	41% [28]	11% [29]	
1,3,5-	3.0% [30]	4.0% [31]		64% [34]		

[a] Footnotes giving the sources of the assignments are as follows. *Italic* indicates estimated values.

1 Average of values of Berndt and Boge (2006) and Volkamer et al (2002).

2 The yields of Berndt and Boge (2006), which are reasonably consistent with previous studies (Calvert et al, 2002), are used.

3 Estimated based on carbon number and the nitrate yield derived for toluene as discussed in the text and shown on Figure 3.

4 Yields tabulated by Calvert et al (2002) range from 5-12%. Value used is average of data from studies published since 1989, which tend to be reasonably consistent as a group. This is lower than the 8.5% used in SAPRC-99

5 Total of yields for individual isomers from Calvert et al (2002)

6 Data tabulated by Calvert et al (2002) indicate a range of yields, from 4-24%, with Volkamer and co-workers (Volkamer, personal communication) reporting 35%. We tentatively use the value of Smith et al (1998), which is the highest tabulated by Calvert et al (2002) but still lower than the Volkamer value. The methyl glyoxal yield reported by Smith et al (1998) are in good agreement with the value used, which tends to support use of their data. Also, the mechanism estimation system estimates higher yields of glyoxal than methyl glyoxal will be formed from toluene.

7 Data tabulated by Calvert et al (2002) indicate a range of yields, but a number of recent studies are reasonably consistent in indicating yields of ~15%. The average of the data from the studies with the higher yields is used.

8 Derived from the ratio of the benzyl nitrate to the benzaldehyde yield as discussed in the text. Assumed that the same ratio is applicable to the other peroxy radicals in the toluene photo-oxidation system.

9 Most of the recent *o*-tolualdehyde yield data tabulated by Calvert et al (2002) are around 5%, and the value used is the average of those studies. A few studies indicate higher yields, but these are not used in computing the average.

10 The total dimethylphenol yields of Atkinson et al (1991) are used because they were conducted at the lowest NOx levels.

11 The data of Bandow and Washida (1985a) and Tuazon et al (1986) are in good agreement, and the average is used. The low value of Shepson et al (1984) is not used.

12 The low NO_x limit value of Atkinson and Aschmann (1994) is used. It is reasonably consistent with data from other studies at lower NO_x levels tabulated by Calvert et al (2002).

Table 9 (continued)

13 Most of the recent *o*-tolualdehyde yield data tabulated by Calvert et al (2002) are around 5%, and the value used is the average of those studies. A few studies indicate higher yields, but these are not used in computing the average.

14 Average of the total dimethylphenol data reported by Atkinson et al (1991) and Smith et al (1999). However, these two studies are not in particularly good agreement on yields for the individual isomers. The total is consistent with the value used for *o*-xylene.

15 Average of the data tabulated by Calvert et al (2002). There is not particularly agreement among the studies, but there are no obvious outliers.

16 Average of the data tabulated by Calvert et al (2002), excluding the low value of Tuazon and co-workers which is superceded by a more recent measurement from the same group.

17 Average of the various measurements tabulated by Calvert et al (2002). There is not particularly good agreement, but no obvious outliers to exclude from the average.

18 Average of 2,5-dimethylphenol yields of Atkinson et al (1991) and Smith et al (1999). Yields reported by Becker et al (1997) are lower and not used.

19 Average of yields reported by Bandow and Washida (1985a), Tuazon et al (1986) and Smith et al (1999).

20 The data tabulated by Calvert et al (2002) show some variation, but three studies give good agreement and indicate yields of about 10%. The value used is the average from those studies.

21 No data available. Estimated from the average rate constant per methyl group for the other methylbenzenes and the total OH rate constant.

22 No data available. The average of the assigned phenolic product yield for the other trimethylbenzenes is used.

23 The yields determined by Bandow and Washida (1985b) are used for consistency with assignment for biacetyl.

24 Average of Bandow and Washida (1985b) and Atkinson and Aschmann (1994). The slightly lower yield of Tuazon et al (1986) not used but may not be outside of range of uncertainty.

25 Sum of yields of 2,4-, 2,5-, and 3,4-dimethylbenzaldehyde from Smith et al (1999)

26 Sum of 2,4,5-, 2,3,5-, and 2,3,6-trimethylphenol from Smith et al (1999)

27 Average of glyoxal yields of Bandow and Washida (1985b) and Smith et al (1999) and 3-methyl-3-hexene-2,5-dione of Smith et al (1999). The lower value of Tuazon et al (1986) is not used. Yields of glyoxal and 3-methyl-3-hexene-2,5-dione are assumed to be equal.

28 Average of Bandow and Washida (1985b) and Smith et al (1999). The value of Tuazon et al (1986) is not used because of the higher NO_x levels and for consistency with other assignments.

29 Average of Bandow and Washida (1985b) and Atkinson and Aschmann (1994). The lower yield of Tuazon et al (1986) is not used but may not be outside of range of uncertainty.

30 The 3,5-dimethylbenzaldehyde yield from Smith et al (1999) is used.

31 The 2,4,6-trimethylphenol yield from Smith et al (1999) is used.

34 The yield from Bandow and Washida (1985b) is used. The data of Smith et al (1999) appear to be high and the data from Tuazon et al (1986) was not used for consistency with assignments for the other trimethylbenzenes.

[b] Nitrate yield for each peroxy reaction. Total nitrate yield is less because not all pathways involve peroxy reactions.

$$\begin{array}{rll} BzCH_3 + OH \rightarrow H_2O + BzCH_2\cdot & & \\ BzCH_2\cdot + O_2 \rightarrow BzCH_2OO\cdot & & \\ BzCH_2OO\cdot + NO \rightarrow NO_2 + BzCH_2O\cdot & & \text{(Fraction = n7)} \\ \rightarrow BzCH_2ONO_2 & & \text{(Fraction = 1-n7)} \\ BzCH_2O\cdot + O_2 \rightarrow BzCHO + HO_2 & & \end{array}$$

or ethylbenzene

$$\begin{array}{rll} BzCH_2CH_3 + OH \rightarrow H_2O + BzCH(\cdot)CH_3 & & \\ BzCH(\cdot)CH_3 + O_2 \rightarrow BzCH(OO\cdot)CH_3 & & \\ BzCH(OO\cdot)CH_3 + NO \rightarrow NO_2 + BzCH(O\cdot)CH_3 & & \text{(Fraction = n8)} \\ \rightarrow BzCH(ONO_2)CH_3 & & \text{(Fraction = 1-n8)} \\ BzCH(O\cdot)CH_3 + O_2 \rightarrow BzC(O)CH_3 + HO_2 & & \end{array}$$

Here, "Bz" refers to the aromatic ring, and n7 and n8 refer to the nitrate yields assumed for aromatics with 7 or 8 carbons, which are derived as discussed below. In terms of SAPRC-07 model species, these overall processes are represented as

TOLUENE + OH → (1-n7) {RO2C + xBALD} + (n7) zRNO3 + yR6OOH
C2-BENZ + OH → (1-n8) {RO2C + PROD2} + (n8) Zrno3 + yR6OOH

In general, the model species "BALD" is used to represent aromatic aldehydes such as benzaldehyde and tolualdehyde, PROD2 is used to represent aromatic ketones such as methyl phenyl ketone and methyl benzyl ketone, RNO3 is used to represent the organic nitrates formed from peroxy + NO reactions in the aromatic and other systems, and R6OOH is used to represent the hydroperoxides formed in the reactions off the aromatic ring.

Reactions on the Aromatic Ring. The major uncertainty concerning the reactions of aromatics with OH radicals concern the subsequent reactions after OH adds to the aromatic ring. Information and data concerning what is known about these processes is discussed by Calvert et al (2002), and that discussion is not duplicated here. The general model we assume for these reactions, which is probably an oversimplification of what really happens, is shown on Figure 2, using benzene as an example. The processes are assumed to be analogous for the substituted benzenes such as toluene, xylenes, etc., except that the number of reactions and products are much greater because of various possible positions of the substituents on the intermediates and the products.

The products that are known to be formed and whose yields have been quantified include the phenols and cresols, and the α-dicarbonyls (phenol and glyoxal in the case or benzene). The formation of phenols is generally assumed to occur by OH abstraction of the initial OH - aromatic adduct, as shown on Figure 2 as "A". The observed yields of these phenolic products are then used to derive the branching ratio (a)/(1-a) as shown on the figure. The co-product is HO_2, formed without the intermediacy of any peroxy radicals and without any NO to NO_2 conversions.

The processes forming the α-dicarbonyls are more uncertain, but the most chemically reasonably process involves O_2 addition to form a peroxy radical that then internally adds to the double bonds to form an allylic-stabilized bicyclic radical, which subsequently reacts to form the α-dicarbonyl(s) as shown on Figure 2 as the processes leading to product set "B". The predicted co-products are the monounsaturated 1,4-dicarbonyls, such as the 2-butene 1,4-dial predicted for the benzene system. These products are indeed observed (Calvert et al, 2002, and references therein), though the total yields are generally much less than the total α-dicarbonyl yields. This could be due to other, unknown, processes leading to the α-dicarbonyls, or with problems with quantifying the unsaturated 1,4-dicarbonyls, which are highly reactive. In any case, because of lack of available information and chemically reasonable

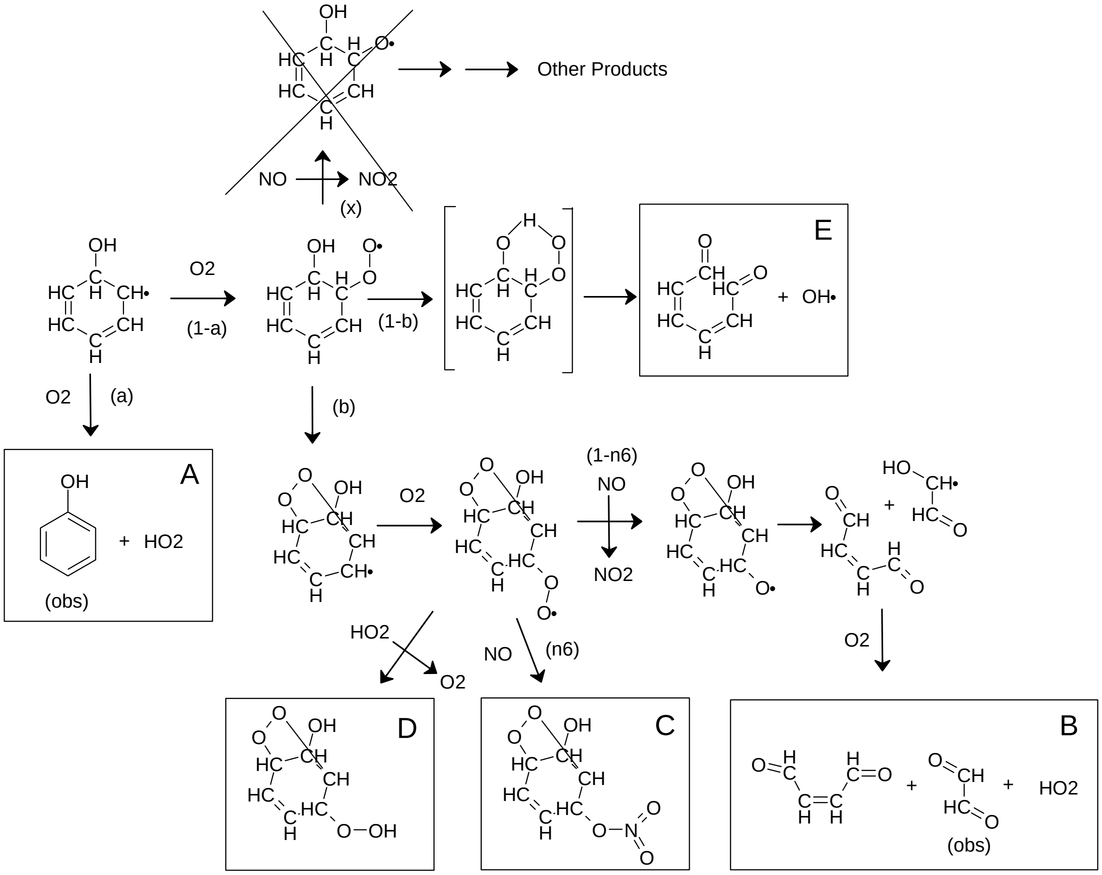


Figure 2. Reactions of the OH - aromatic ring adduct that are assumed in the current mechanism. The example shown is for benzene, but analogous reactions are assumed for the alkylbenzenes.

alternatives to explain the products that are observed, we assume that the processes leading to "B" as indicated on Figure 2 are the only processes in the forming the α-dicarbonyls in the primary OH + aromatic reactions, and that the unsaturated 1,4-dicarbonyls are the corresponding co-products. The yields of the model species used to represent the unsaturated 1,4-dicarbonyls (discussed below) are then set as the total yields of the measured α-dicarbonyl products. The total α-dicarbonyl and phenolic product yields are used to determine the branching ratio indicated as (b)/(1-b) on Figure 2.

Note that this process that are assumed to account for the α-dicarbonyl formation involve the intermediacy of a peroxy radical that converts NO to NO_2 in the processes of forming these products, but that can also react with NO to form an alkyl nitrate ("C" on Figure 2), react with HO_2 to form a highly oxygenated bicyclic hydroperoxide ("D" on Figure 2), or react with other peroxy radicals to form other products (not shown on the figure). The hydroperoxides formed in the HO_2 reaction (e.g., "D") are represented by a separate model species RAOOH because they are expected to have higher PM formation potential than other hydroperoxides, though they could be lumped with R6OOH if SOA predictions are not important. The general procedures used for representing products formed from peroxy reactions in this mechanism have been discussed previously, and these procedures are employed for these α-dicarbonyl and mono-unsaturated 1,4-dicarbonyl products.

The sum of the measured yields of the phenolic and α-dicarbonyl products from the OH addition reactions, the aromatic aldehydes from the abstraction reactions off the aromatic ring, and estimated nitrate yields from the peroxy + NO reactions (discussed below) is not sufficient to account for all the processes involved in the OH reactions of toluene, xylene, and trimethylbenzenes (Calvert et al, 2002), so additional processes must also occur. The results of aromatic - NO_x environmental chamber experiments at various NO_x levels cannot be simulated by mechanisms that assume that yields of the photoreactive aromatic products such as α-dicarbonyls or the monounsaturated 1,4-dicarbonyls are affected by total NO_x levels, and most of the available product data for the α-dicarbonyls from methylbenzenes do not indicate a NO_x -dependence on α-dicarbonyl yields at the NO_x levels relevant to the atmosphere and the chamber experiments used for mechanism evaluation. This rules out mechanisms involving competitions between unimolecular reactions of peroxy radicals and reactions of peroxy radicals with NO, such as between (b) and (x) shown on Figure 2.

An additional consideration concerning potential competing processes is the fact that the direct reactivity experiments of Carter and Malkina (2002) indicate that the SAPRC-99 mechanism has too many NO to NO_2 conversions in the reactions of aromatics with OH. We were unable to come up with chemically reasonable mechanisms for α-dicarbonyl, phenol or cresol, or aromatic aldehyde formation that involved fewer NO to NO_2 conversions, which leaves only the remaining process(es) forming the remaining products. Because of this, and also to avoid introducing competitions between unimolecular and peroxy + NO reactions, we assume that the additional process involves a 6-member ring H-shift of the aromatic - OH - O_2 adduct, giving rise to formation of a di-unsaturated 1,6-dicarbonyl and OH radicals, shown as process (1-b) and "E" on Figure 2. This is a competition between two unimolecular reactions and thus the photoreactive product yields are predicted to be independent of NO_x, and the direct formation of OH radicals in this set of reactions involves two fewer NO to NO_2 conversions than assumed for these unknown processes in the SAPRC-99 mechanism. Therefore, this is used in the current mechanism to represent all the processes that are not otherwise accounted for by the observed formation of aromatic aldehyde, phenolic, and α-dicarbonyl products and the estimated formation of organic nitrates. The model species used to represent these di-unsaturated 1,6-dicarbonyls is discussed below.

Estimation of Nitrate Formation Reactions. The mechanisms involving OH abstractions off the aromatic ring, and also the mechanism involving the formation of the α-dicarbonyls and the monounsaturated 1,4-dicarbonyls all involve the intermediacy of peroxy radicals that can react with NO to form the corresponding nitrate. The only data available concerning nitrate formation from peroxy + NO reactions in alkylbenzene systems concerns the observed formation of benzyl nitrate in the toluene system, for which the average of the yields tabulated by Calvert et al (2002) is ~0.8%. This is attributed to the reaction of benzyl peroxy radicals with NO (shown above), for which the competing process is formation of the alkoxy radical that reacts with O_2 to form benzaldehyde. Based on this and the benzaldehyde yield used in our toluene mechanism (discussed below), we derive an overall nitrate yield for the benzyl peroxy radical to be 10.6%. This can be compared with the 13.5% nitrate yield predicted by the mechanism generation system for 7 carbons for standard secondary alkylperoxy radicals formed in the alkane photooxidation system (Carter, 2000a). Based on this, we assume that nitrate yields for all peroxy radicals in aromatic systems, whether resulting from abstractions by OH off the ring or formation of α-dicarbonyls following OH + aromatic ring additions, are 78.5% those estimated for secondary alkyl peroxy radicals. Figure 3 shows the dependence of the nitrate yields on carbon number that is used when deriving aromatic mechanisms for SAPRC-07. The nitrate yields are assumed to range from ~8% for benzene (n6) to ~21% for aromatics with carbon numbers greater than ~13 (n13+).

Assignments of Branching Ratios and Product Yields. Table 9 gives the measured or estimated yields from the known products from benzene, toluene, the xylenes, and the trimethylbenzenes that are used as the basis for the aromatic mechanisms derived for this work. Footnotes to the table

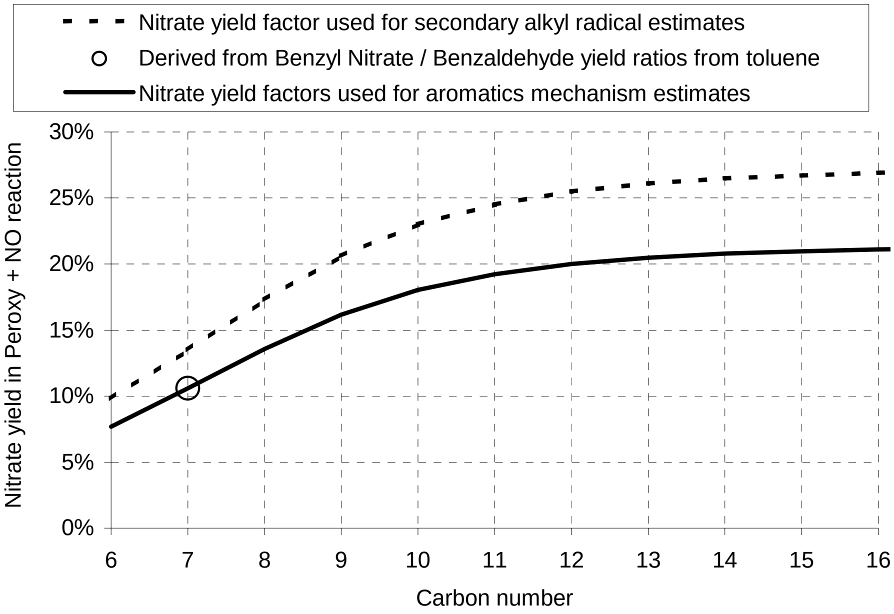


Figure 3. Nitrate yield factors used for estimating aromatic oxidation mechanisms

indicate the basis for the assignments or estimates used. These were used, in conjunction with the nitrate yield estimates derived above, as the basis for deriving the branching ratios for all the reactions in the mechanisms for these aromatics. Note that, as discussed above, the total yields of the model species used for the mono-unsaturated 1,4-dicarbonyls were set to the sum of the glyoxal, methyl glyoxal, and biacetyl yields shown on Table 9, and the yields of the model species representing the di-unsaturated 1,6-dicarbonyls was set at 1 - the sum of the aromatic aldehyde, phenol or cresol, α-dicarbonyl, and estimated nitrate yields.

For the other alkylbenzenes or model species used to represent groups of alkylbenzenes with similar structures and carbon numbers, the mechanisms were derived based on estimates for reactions at various positions on the molecule and other estimates, as follows. The total rate constants for abstraction reactions off the aromatic ring were derived using structure-reactivity estimates, using the OH abstraction rate parameters given on Table 3, above. These total non-ring rate constants are given for the various aromatic model species on Table 10, along with the substituents assumed for the various model species used to represent groups of compounds. The total rates for additions to the aromatic ring were estimated by assuming they were the same as to those derived for the methylbenzene with the most similar structure, as indicated on Table 10. The ring addition reactions for those compounds were derived from the total rate constant and the estimated extent of abstraction off the aromatic ring derived from the aromatic aldehyde and estimated off-ring abstraction rate constant derived from the aromatic aldehyde and estimated nitrate yield as indicated on Table 9. The fractions of ring additions vs. off-ring abstractions were derived from the ratio of the estimated rate constants for the two processes, and are shown on Table 10. Note that for the compounds listed on Table 9 the mechanisms used the values derived based on the measured or estimated product yields shown on that table, not based on the estimated rate constants shown on Table 10. Table 10 shows the differences between the off-ring abstraction fractions derived using these two methods for these compounds.

Table 10. Rate constants and assumptions used to estimate fractions of reaction of on and off the aromatic ring for the reactions of OH with aromatic compounds or groups of compounds for which mechanistic parameters have been derived.

Compound or detailed model species group	Rate Constant [a]			Ring k Based on	Non-Ring Rxn.		Substituents [c]
	Total	Non-Ring	Ring		Expt [b]	Est'd	
Toluene	5.58e-12	4.92e-13	5.18e-12	Toluene	7%	9%	methyl
o-Xylene	1.36e-11	9.85e-13	1.29e-11	o-Xyl.	5%	7%	dimethyl
m-Xylene	2.31e-11	9.85e-13	2.20e-11	m-Xyl.	5%	4%	dimethyl
p-Xylene	1.43e-11	9.85e-13	1.28e-11	p-Xyl.	10%	7%	dimethyl
1,2,3-Trimethyl benzene	3.27e-11	1.48e-12	3.11e-11	124-TMB		5%	trimethyl
1,2,4-Trimethyl benzene	3.25e-11	1.48e-12	3.11e-11	124-TMB	4%	5%	trimethyl
1,3,5-Trimethyl benzene	5.67e-11	1.48e-12	5.47e-11	135-TMB	4%	3%	trimethyl
Ethylbenzene	7.00e-12	2.05e-12	5.18e-12	Toluene		28%	ethyl
n-Propyl benzene	5.80e-12	3.64e-12	5.18e-12	Toluene		41%	1-propyl
o-Ethyl toluene	1.19e-11	2.54e-12	1.29e-11	o-Xyl.		16%	methyl ethyl
m-Ethyl toluene	1.86e-11	2.54e-12	2.20e-11	m-Xyl.		10%	methyl ethyl
p-Ethyl toluene	1.18e-11	2.54e-12	1.28e-11	p-Xyl.		17%	methyl ethyl
Isopropyl benzene	6.30e-12	1.68e-12	5.18e-12	Toluene		24%	2-propyl
1-Methyl-4-isopropylbenzene	1.45e-11	2.17e-12	1.28e-11	p-Xyl.		14%	methyl 2-propyl
t-Butyl benzene	4.50e-12	5.13e-13	5.18e-12	Toluene		9%	t-butyl
C10 monosubstituted benzenes	9.58e-12	4.40e-12	5.18e-12	Toluene		46%	0.33 n-butyl + 0.33 2-methyl-1-propyl + 0.34 1-methyl-1-propyl
C11 monosubstituted benzenes	1.10e-11	5.82e-12	5.18e-12	Toluene		53%	0.33 n-pentyl + 0.33 3-methyl-1-butyl + 0.34 1-methyl-1-butyl
C12 monosubstituted benzenes	1.24e-11	7.25e-12	5.18e-12	Toluene		58%	As above, but with -CH2- added
C13 monosubstituted benzenes	1.38e-11	8.67e-12	5.18e-12	Toluene		63%	
C14 monosubstituted benzenes	1.53e-11	1.01e-11	5.18e-12	Toluene		66%	
C15 monosubstituted benzenes	1.67e-11	1.15e-11	5.18e-12	Toluene		69%	
C16 monosubstituted benzenes	1.81e-11	1.29e-11	5.18e-12	Toluene		71%	
o-C10 disubstituted benzenes	1.64e-11	3.51e-12	1.29e-11	o-Xyl.		21%	0.25 methyl n-propyl + 0.25 methyl isopropyl + 0.5 diethyl
m-C10 disubstituted benzenes	2.55e-11		2.20e-11	m-Xyl.		14%	
p-C10 disubstituted benzenes	1.64e-11		1.28e-11	p-Xyl.		21%	
o-C11 disubstituted benzenes	1.82e-11	5.40e-12	1.29e-11	o-Xyl.		30%	0.34 methyl (2-metyl-1-propyl) + 0.33 ethyl isopropyl + 0.33 ethyl n-propyl
m-C11 disubstituted benzenes	2.74e-11		2.20e-11	m-Xyl.		20%	
p-C11 disubstituted benzenes	1.82e-11		1.28e-11	p-Xyl.		30%	
o-C12 disubstituted benzenes	1.90e-11	6.14e-12	1.29e-11	o-Xyl.		32%	0.25 methyl (3-methyl-1-butyl) + 0.25 ethyl (1-methyl-1-propyl) + 0.25 propyl isopropyl + 0.25 ethyl n-butyl
m-C12 disubstituted benzenes	2.82e-11		2.20e-11	m-Xyl.		22%	
p-C12 disubstituted benzenes	1.90e-11		1.28e-11	p-Xyl.		32%	
o-C13 disubstituted benzenes	2.05e-11	7.63e-12	1.29e-11	o-Xyl.		37%	0.25 ethyl (3-methyl-1-butyl) + 0.25 propyl (1-methyl-1-propyl) + 0.25 (2-methyl-1-propyl) isopropyl + 0.25 ethyl n-pentyl
m-C13 disubstituted benzenes	2.96e-11		2.20e-11	m-Xyl.		26%	
p-C13 disubstituted benzenes	2.05e-11		1.28e-11	p-Xyl.		37%	

Table 10 (continued)

Compound or detailed model species group	Rate Constant [a]			Ring k Based on	Non-Ring Rxn.		Substituents [c]
	Total	Non-Ring	Ring		Expt [b]	Est'd	
o-C14 disubstituted benzenes	2.19e-11	9.05e-12	1.29e-11	o-Xyl.		41%	As above, but with -CH2- added
m-C14 disubstituted benzenes	3.11e-11		2.20e-11	m-Xyl.		29%	
p-C14 disubstituted benzenes	2.19e-11		1.28e-11	p-Xyl.		41%	
o-C15 disubstituted benzenes	2.33e-11	1.05e-11	1.29e-11	o-Xyl.		45%	
m-C15 disubstituted benzenes	3.25e-11		2.20e-11	m-Xyl.		32%	
p-C15 disubstituted benzenes	2.33e-11		1.28e-11	p-Xyl.		45%	
o-C16 disubstituted benzenes	2.48e-11	1.19e-11	1.29e-11	o-Xyl.		48%	
m-C16 disubstituted benzenes	3.39e-11		2.20e-11	m-Xyl.		35%	
p-C16 disubstituted benzenes	2.47e-11		1.28e-11	p-Xyl.		48%	
1,2,3-C10 trisubstituted benzenes	3.41e-11	3.03e-12	3.11e-11	124-TMB		9%	Dimethyl ethyl
1,2,4-C10 trisubstituted benzenes	3.41e-11		3.11e-11	124-TMB		9%	
1,3,5-C10 trisubstituted benzenes	5.77e-11		5.47e-11	135-TMB		5%	
1,2,3-C11 trisubstituted benzenes	3.57e-11	4.60e-12	3.11e-11	124-TMB		13%	0.5 dimethyl propyl + 0.5 methyl diethyl
1,2,4-C11 trisubstituted benzenes	3.57e-11		3.11e-11	124-TMB		13%	
1,3,5-C11 trisubstituted benzenes	5.93e-11		5.47e-11	135-TMB		8%	
1,2,3-C12 trisubstituted benzenes	3.66e-11	5.47e-12	3.11e-11	124-TMB		15%	0.34 dimethyl 2-methyl-1-propyl + 0.33 methyl ethyl isopropyl + 0.33 methyl ethyl n-propyl
1,2,4-C12 trisubstituted benzenes	3.66e-11		3.11e-11	124-TMB		15%	
1,3,5-C12 trisubstituted benzenes	6.01e-11		5.47e-11	135-TMB		9%	
1,2,3-C13 trisubstituted benzenes	3.81e-11	7.00e-12	3.11e-11	124-TMB		18%	0.34 methyl ethyl 2-methyl-1-propyl + 0.33 methyl ethyl n-butyl + 0.33 methyl propyl isobutyl
1,2,4-C13 trisubstituted benzenes	3.81e-11		3.11e-11	124-TMB		18%	
1,3,5-C13 trisubstituted benzenes	6.17e-11		5.47e-11	135-TMB		11%	
1,2,3-C14 trisubstituted benzenes	3.93e-11	8.16e-12	3.11e-11	124-TMB		21%	0.25 methyl ethyl 3-methyl-1-butyl + 0.25 methyl n-propyl n-butyl + 0.25 ethyl isopropyl n-propyl
1,2,4-C14 trisubstituted benzenes	3.93e-11		3.11e-11	124-TMB		21%	
1,3,5-C14 trisubstituted benzenes	6.28e-11		5.47e-11	135-TMB		13%	
1,2,3-C15 trisubstituted benzenes	4.04e-11	9.31e-12	3.11e-11	124-TMB		23%	0.25 methyl ethyl 4-methyl-1-pentyl + 0.25 ethyl n-propyl 1-methyl-1-propyl + methyl propyl 1-methyl-1-butyl + ethyl isopropyl 2-methyl-1-propyl
1,2,4-C15 trisubstituted benzenes	4.04e-11		3.11e-11	124-TMB		23%	
1,3,5-C15 trisubstituted benzenes	6.40e-11		5.47e-11	135-TMB		15%	
1,2,3-C16 trisubstituted benzenes	4.17e-11	1.06e-11	3.11e-11	124-TMB		25%	0.25 ethyl propyl 3-methyl-1-butyl + 0.25 ethyl propyl 1-methyl-1-butyl + methyl propyl 1,3-dimethyl-1-butyl + 0.25 propyl isopropyl 2-methyl-1-propyl
1,2,4-C16 trisubstituted benzenes	4.17e-11		3.11e-11	124-TMB		25%	
1,3,5-C16 trisubstituted benzenes	6.52e-11		5.47e-11	135-TMB		16%	

[a] Rate constant in cm^3 molec^{-1} s^{-1}. "Total" is total rate constant is rate constant used in the mechanism, either experimental or estimated. "Non-Ring" is total rate constant for abstraction at various positions off the aromatic ring, estimated using the group additivity factors shown in Table 4. "Ring" is estimated rate constant for addition to the aromatic ring, derived by assuming the same aromatic ring addition rate constant as the indicated compound.

[b] Derived from the measured yields of the expected non-ring abstraction product, corrected for estimated nitrate formation, relative to the total rate constant. These can be compared with the estimated ratios of non-ring reaction, derived from the estimated ring and non-ring rate constants.

[c] Substituents assumed when estimating rate constants for abstraction reactions off the aromatic ring.

The products formed from the off-ring abstraction reactions are represented by the organic nitrate model species RNO3 and either the aromatic aldehyde model species BALD or the reactive ketone model species PROD2, depending on the substituent. The RNO3 yield was derived from the carbon number as discussed above. If the substituent is a methyl group the reaction was expected to form an aromatic aldehyde and the product was represented by the benzaldehyde model species BALD. Otherwise, the products are assumed to be primarily ketones and are represented by PROD2.

The products used to represent those formed from the reactions following the addition to the aromatic ring were derived based on those derived for the corresponding reactions of ethylbenzene, a xylene, or a trimethylbenzene, depending on the structure of the compound or group of compounds being represented. The ring-reaction products for ethylbenzene were used for the ring reactions products for the monoalkylbenzenes, the ring-reaction products for o-xylene were used for all 1,2-disubstituted benzenes, those for 1,2,3-trimethylbenzene were used for all the 1,2,3-trisubstituted benzenes, and similarly for the other isomers. The ring-reaction products for ethylbenzene were derived from those derived for toluene, taking into account estimated differences in off-ring reactions and nitrate yields, and with the ratio of the photoreactive and non-photoreactive model species used for the mono-unsaturated 1,4-dicarbonyls adjusted to fit the chamber data for ethylbenzene (see discussion of these products, below). The ring reaction products for the xylene and trimethylbenzene isomers were derived from the product data for those compounds as shown on Table 9, ratio of the photoreactive and non-photoreactive model species used for the monounsaturated 1,4-dicarbonyls adjusted to fit the chamber data for those compounds. These are summarized on Table 11.

The mechanistic assignments shown on Table 9, Table 10, Table 11 and Figure 3 were used to derive overall mechanisms for the individual aromatics or groups or aromatics as listed on Table 10. The resulting overall rate constants are given on Table B-4 and the mechanisms are given in Table B-2 in Appendix B. Footnotes to Table B-4 indicate the sources of the rate constants that were used.

Representation of Unsaturated Dicarbonyl Products

As discussed above, the co-products assumed to be formed with the α-dicarbonyls in the ring opening products are the monounsaturated 1,4-dicarbonyls, and the ring opening reactions not involving these products are assumed to be di-unsaturated 1,6-dicarbonyls. For the benzene system, these consist of 2-butene-1,4-dial and 2,4-hexadienedial as shown on Figure 2, while for the methylbenzenes various methyl substituted isomers can be formed, with relative yields depending on the position of OH addition to the double bond, and also where the O_2 adds to the OH - aromatic adduct. Estimated distributions of these products for the various methylbenzene isomers are shown on Table 12. These estimates were derived based on estimated fractions of reaction of OH radicals at various positions of the molecules and estimated branching ratios for O_2 addition at the various positions of the OH + aromatic adducts, adjusted to be consistent with the observed yields of the α-dicarbonyl co-products[1].

This product distribution can serve as the basis for deriving explicit or semi-explicit mechanisms for the OH reactions of these aromatics. However, for airshed and reactivity simulations a more generalized mechanism, with a more limited number of model species, is needed. The model species used to represent these products in this version of the mechanism is indicated on Table 12. The reasoning behind this representation, and the derivations of their mechanisms, are discussed below. Note that this is the same number of model species used to represent uncharacterized ring fragmentation products in SAPRC-99, but in this case the mechanisms are derived based on estimations for actual compounds.

---

[1] These estimates were made as part of the initial effort to derive explicit aromatics mechanisms, which is beyond the scope of the present report.

Table 11. Model species used to represent non-nitrate products from the reactions of OH radicals at aromatic rings for various types of ring structures. Yields are normalized to OH ring addition only, excluding nitrate formation.

Ring structure	A [a]	B [b]						B, C, D	E
	CRES + HO2	xGLY	xMGLY	xBACL	xAFG1+2 [c]	AFG1/2 [d]	xAFG3 [e]	Peroxy Total [f]	AFG3 + OH [e]
Benzene	12%	31%			31%	0.11		31%	31%
Toluene	34%	29%	18%		47%	1.00		29%	29%
Ethylbenzene [g]		(based on toluene)				0.39	(same as toluene)		
o-Xylene	21%	10%	29%	23%	62%	1.00		10%	10%
m-Xylene	25%	12%	46%		58%	2.33		12%	12%
p-Xylene	31%	37%	14%		14%	0.67	37%	37%	37%
1,2,3-Trimethylbenzene	9%	9%	23%	56%	88%	1.00		9%	9%
1,2,4-Trimethylbenzene	24%	9%	50%	14%	55%	0.25	19%	9%	9%
1,3,5-Trimethylbenzene	17%		79%		79%	1.00			

[a] Pathway on Figure 2 that these model species are being used to represent.

[b] Yields depend on nitrate yield in peroxy + NO reactions, and are shown for nitrate yields of zero. Actual yields are (tabulated yields) x (1-nx), where "nx" refers to the nitrate yield for carbon number "x", determined as shown on Figure 3. The prefix "x" is used to indicate that they are formed following reactions of peroxy radicals with NO (see discussion of the base mechanism).

[c] This is the total yield of monounsaturated 1,4 dialdehydes or aldehyde-ketones, represented by xAFG1 + xAFG2.

[d] This is the ratio of the xAFG1 to xAFG2 yield, which is adjusted to aromatic - NO_x chamber data for the indicated compound

[e] AFG3 is the model species used to represent both monounsaturated 1,4-diketones and di-unsaturated 1,6-dicarbonyls.

[f] This is the total level of peroxy radicals in the reaction, and also the total NO to NO_2 conversion + nitrate formation. The yield of RO2C, representing NO to NO_2 conversion, is given by the tabulated value x (1-nx), and the nitrate yield, represented by RO2XC + zRNO3, is given by the tabulated value x (nx), where "nx" is the nitrate yield factor as indicated in Footnote [b]. The tabulated values also give the yields of yRAOOH, which is used to represent the

[g] The yields are based on those derived for toluene, but are slightly different because of differences between the estimated and total rate constants. However, the AFG1/AFG2 yields (AFG1/2) were adjusted separately to fit the chamber experiments for ethylbenzene.

Available data and theories concerning the atmospheric reactions of these unsaturated dicarbonyl ring-opening products are discussed by Calvert et al (2002). These compounds react at significant rates with OH radicals and O_3 and information is available concerning the rate constants for representative compounds. These compounds can also photolyze at significant rates under atmospheric conditions, and absorption cross-section data are also available for representative compounds. The quantum yields are more uncertain but measurements of photolysis consumption rates have been made in the Euphore outdoor chamber that can serve as a basis for estimating overall quantum yields for consumption by photolysis. The extent to which these photolysis reactions form radicals is a very important factor affecting the contribution of these products to the overall reactivity of the aromatic starting material. The limited product and environmental chamber reactivity data indicate that photolysis to form radicals is important for the mono-unsaturated 1,4-dialdehydes and aldehyde-ketones, but that the photolysis of the mono-unsaturated 1,4-diketones and the di-unsaturated 1,6-dicarbonyls is much less

Table 12. Estimated yields for unsaturated dicarbonyl products in the OH reactions of the methylbenzenes for which α-dicarbonyl yield data are available.

Ring fragmentation product compound or type of compound	Methylbenzene Reactant						
	Toluene	Xylenes			Trimethylbenzenes		
		o-	m-	p-	1,2,3-	1,2,4-	1,3,5-
<u>Aldehydes and aldehyde-ketones</u> (Represented by AFG1 and AFG2)							
2-Butene-1,4-dial	0.15	0.19					
2-Methyl-2-butene-1,4-dial	0.12		0.19	0.11		0.11	
2,3-Dimethyl-2-butene-1,4-dial		0.03				0.12	
4-Oxo-2-penteneal	0.11	0.24	0.19		0.45		
2-Methyl-4-oxo-2-penteneal			0.10			0.10	0.64
3-Methyl-4-oxo-2-penteneal		0.05			0.18	0.11	
2,3-Dimethyl-4-oxo-2-penteneal					0.07		
<u>Diketones</u> (Represented by AFG3)							
3-Methyl-3-hexene-2,5-dione				0.29		0.08	
<u>Diunsaturated dicarbonyls</u> (Represented by AFG3)							
Methyl-substituted 1,4-hexadienedials	0.22	0.09	0.09	0.12	0.03	0.05	
6-Oxo-2,4-hepadienedial and methyl substituted isomers	0.09	0.08	0.15	0.15	0.03	0.15	0.16
3,5-Octadiene-2,7-dione and methyl substituted isomers		0.03			0.03	0.03	

efficient, or forms primarily non-radical products. Calvert et al (2002), and references therein, should be consulted for details.

Based on this information, we use two model species, designated AFG1 and AFG2, to represent the highly photoreactive mono-unsaturated dialdehydes and aldehyde-ketones, and a separate model species, AFG3, to represent the less photoreactive unsaturated diketones and di-unsaturated dicarbonyls. Because the overall quantum yields for photolyses of the mono-unsaturated dialdehydes and aldehyde-ketones to form radicals are very important in affecting overall reactivity but are uncertain and may vary from compound to compound, these are treated as adjustable parameters in the mechanism. This is implemented by using two model species for these compounds that have exactly the same mechanisms, except that one (AFG1) photolyzes to form radicals, while the other (AFG2) photolyzes at the same rate but forms non-radical products. The total yields of these model species are set at the total estimated monounsaturated aldehyde yield as indicated on Table 12, while the yield of one relative to the other are adjusted to predict overall reactivities that are consistent with results of environmental chamber experiments with the various aromatics. This is equivalent to adjusting separately the overall quantum yields for formation of radical vs. non-radical products for photoreactive dicarbonyls for each compound without having to use a separate model species for each compound.

As indicated in footnotes to Table A-2 in Appendix A, the mechanisms for AFG1 and AFG2 was derived based on those estimated for the representative dialdehydes and diketones 2-butene 1,4-dial 2-methyl-2-butene-1,4-dial, 4-oxo-2-petenal, and 2-methyl-4-oxo-2-pentenal, and the mechanism for AFG3 was derived based on those estimated for the represented di-unsaturated dicarbonyl products 3-methyl 2,4-hexene-1,6-dial, 6-oxo-2,4-heptadienal, and 3,5-octadien-2,7-dione. The relative contributions of each are based on relative yields of these and similar products from the methylbenzenes, as indicated on Table 12. Use of a separate model species, based on mechanisms for 3-methyl-3-hexene-2,5-dione, to represent the mono-unsaturated diketones was examined in an initial version of this mechanism. However, but it was found that lumping it with the model species used for the di-unsaturated dicarbonyls gave essentially the same reactivity predictions for p-xylene and 1,2,4-trimethylbenzene, the only compounds for which reactivity data are available where these products are predicted to be formed. Therefore, it was determined that use of a separate model species to represent these mono-unsaturated diketones was not necessary.

The mechanisms for the reactions of these model species with OH and O_3 were derived using the enhanced mechanism generation system, using assignments for the specific compounds that are given on Table 13. The reactions of these species with NO_3 and O^3P were assumed to be negligible compared to the other processes and are not included in the mechanism. The mechanism for the photolysis of AFG1 to form radicals is based on the assignments for the initial reactions that are also given on Table 13. Specific mechanisms were not generated for the photolyses of AFG2 to form stable products; the unspecified products formed are assumed to be moderately reactive and are represented by the model species PROD2. The overall mechanisms that were derived for these model species using this method are given with the listing of the base mechanism on Table A-2 in Appendix A.

The absorption cross sections and quantum yields for the photolyses of AFG1 and AFG2 were derived from those for 2-butene-1,4-dial and 4-oxo-2-pentenal, assuming those for 2-methyl-2-butene-1,4-dial and 2-methyl-4-oxo-2-pentenal are the same as those for 2-butene-1,4-dial and 4-oxo-2-pentenal, respectively. The derivations of the absorption cross sections and quantum yields used are indicated on Table 13, and plots of the action spectra (absorption cross sections x overall quantum yields) for these two compounds are shown on Figure 4, where they are compared with that derived for AFG1 and AFG2, which is the weighed average based on ratios of these compounds used to derive the rate constants and mechanisms for the other reactions (see footnotes to Table A-2 in Appendix A). The action spectrum for AFG1,2 most closely resembles that for 4-oxo-2-pentenal because of the higher absorption cross sections and quantum yields and also because of the higher weighting of the aldehyde-ketone products (68%) compared to the dialdehyde products (32%).

Note that although this representation uses the same number of model species as SAPRC-99 to represent the unspecified non-α-dicarbonyl aromatic ring opening products, the meaning and the mechanisms of these species is different. In SAPRC-99 the model species DCB1 is used to represent non-photoreactive product species, DCB2 represents photoreactive products with action spectra like α-dicarbonyls, and DCB3 represents photoreactive products with action spectra like acrolein. The yields of DCB1 for various aromatics were set more or less arbitrarily, while those for DCB2 and DCB3 were adjusted to fit the aromatics - NO_x chamber data, with species with the different action spectra being needed to simulate experiments using differing light sources. In this mechanism, the total yields are set based on other product data or estimates that are independent of the chamber data, and only the AFG1/AFG2 yield ratio is adjusted to fit the chamber data. Note that the action spectra are derived independently of the chamber data, with no adjustments to account for reactivity differences using chambers with different light sources. This resulted in some cases in the SAPRC-07 mechanism not performing as well as SAPRC-99 in simulating blacklight chamber data, but in general model performance was satisfactory, indicating that the un-adjustable action spectra used in the model may be appropriate. This is discussed further in the "Mechanism Evaluation Results" section, below.

Table 13. Mechanism estimation assignments made for representative unsaturated dicarbonyl compounds for the purpose of generating mechanisms for the aromatic fragmentation product model species AFG1-3.

Compound, reaction, and rate parameters		Fraction
2-Butene-1,4-dial		
OH	Rate Constant = 5.29e-11 cm^3 $molec^{-1}$ s^{-1}	
	HCOCH=CHCHO + OH → HCOCH(·)CH(CHO)OH	44%
	HCOCH=CHCHO + OH → H_2O + HCOCH=CHC(O)·	56%
	Rate constant from Bierbach et al (1994). Branching ratios estimated by assuming that abstraction from CHO has a rate constant per CHO group as estimated acrolein.	
O_3	Rate Constant = 1.60e-18 cm^3 $molec^{-1}$ s^{-1}	
	HCOCH=CHCHO + O_3 → HCOCHOO[excited] + HCOCHO	
	Rate constant from Liu et al (1999).	
hν	Photolysis Set = BUTEDIAL, Quantum Yield = 0.723	
	HCOCH=CHCHO + hν → HCOCH=CHC(O)· + H.	50%
	HCOCH=CHCHO + hν → HCO· + HCOCH=CH.	50%
	The absorption coefficients are from Liu et al (1999) (file provided by Ken Sexton, University of North Carolina), normalized as discussed by Calvert et al (2002). The quantum yield is set to give the photolysis rate, relative to NO_2, of 0.18, based on data of Sorensen and Barnes (1998). Only the radical formation pathways (used for AFG1) are shown on this table -- stable compounds formed by AFG2 are represented by PROD2 regardless of the compounds used to derive the mechanisms. The radical-producing processes are uncertain, and the two shown are assumed to be most likely and to be equally important.	
2-Methyl-2-butene-1,4-dial		
OH	Rate Constant = 9.63e-11 cm^3 $molec^{-1}$ s^{-1}	
	CH_3C(CHO)=CHCHO + OH → CH_3C(·)(CHO)CH(CHO)OH	52%
	CH_3C(CHO)=CHCHO + OH → CH_3C(CHO)(OH)CH(·)CHO	17%
	CH_3C(CHO)=CHCHO + OH → H_2O + CH_3C(CHO)=CHC(O)·	31%
	The rate constant and branching ratios derived from estimated rate constants for reactions at various locations. Reaction by abstraction from CHO assumed to have same rate constant per CHO as assumed for acrolein. Addition to the double bond is calculated from OH addition rate constants for 1,4-butanedial x methacrolein / acrolein. The relative rates of addition at the various positions are assumed to be the same as used by the mechanism generation system for alkenes with 3 substituents about the double bond.	
O_3	Rate Constant = 6.66e-18 cm^3 $molec^{-1}$ s^{-1}	
	CH_3C(CHO)=CHCHO + O_3 → CH_3COO[excited]CHO + HCOCHO	70%
	CH_3C(CHO)=CHCHO + O_3 → HCOCHOO[excited] + CH_3C(O)CHO	30%
	The rate constant is estimated from the O_3 rate constants for 1,4-butanedial x methacrolein / acrolein. The branching ratios were derived by the mechanism generation system based on assignments for trisubstituted alkenes.	
hν	Photolysis Set = BUTEDIAL, Quantum Yield = 0.723	
	CH_3C(CHO)=CHCHO + hν → H. + CH_3C(CHO)=CHC(O)·	25%
	CH_3C(CHO)=CHCHO + hν → H. + CH_3CH=C(CHO)C(O)·	25%
	CH_3C(CHO)=CHCHO + hν → HCO· + CH_3C(CHO)=CH.	25%

Table 13 (continued)

	Compound, reaction, and rate parameters	Fraction
	$CH_3C(CHO)=CHCHO + h\nu \rightarrow HCO\cdot + CH_3C(\cdot)=CHCHO$	25%
	The photolysis reaction is assumed to have the same absorption cross-section and overall quantum yield as used for 2-butene-1,4-dial. The radical formation reactions shown above are assumed to have equal probability.	
4-Oxo-2-penteneal		
OH	Rate Constant = 5.67e-11 cm^3 molec^{-1} s^{-1}	
	$CH_3C(O)CH=CHCHO + OH \rightarrow CH_3C(O)CH(OH)CH(\cdot)CHO$	37%
	$CH_3C(O)CH=CHCHO + OH \rightarrow CH_3C(O)CH(\cdot)CH(CHO)OH$	37%
	$CH_3C(O)CH=CHCHO + OH \rightarrow H_2O + CH_3C(O)CH=CHC(O)\cdot$	26%
	Rate constant from Bierbach et al (1994). Branching ratios estimated based on ratio of total rate constant relative to the rate constant for abstraction from CHO based on that derived for acrolein. Equal probability OH addition at the two positions about the bond is assumed.	
O_3	Rate Constant = 4.80e-18 cm^3 molec^{-1} s^{-1}	
	$CH_3C(O)CH=CHCHO + O_3 \rightarrow CH_3C(O)CHOO[excited] + HCOCHO$	50%
	$CH_3C(O)CH=CHCHO + O_3 \rightarrow HCOCHOO[excited] + CH_3C(O)CHO$	50%
	Rate constant from Liu et al (1999). Equal probability of reaction assumed for the two possible routes.	
hν	Photolysis Set = 4OX2PEAL, Quantum yields = 1.	
	$CH_3C(O)CH=CHCHO + h\nu \rightarrow HCOCH=CHC(O)\cdot + CH_3\cdot$	25%
	$CH_3C(O)CH=CHCHO + h\nu \rightarrow H. + CH_3C(O)CH=CHC(O)\cdot$	25%
	$CH_3C(O)CH=CHCHO + h\nu \rightarrow HCOCH=CH. + CH_3C(O)\cdot$	25%
	$CH_3C(O)CH=CHCHO + h\nu \rightarrow HCO\cdot + CH_3C(O)CH=CH.$	25%
	Absorption cross-sections from Calvert et al (2002). A high quantum yield is indicated by the photolysis rate measurements made in the Euphore chamber by Sørensen and Barnes (1998), and a unit quantum yield is assumed. Equal probability of reaction is assumed for the various possible radical formation routes shown above.	
2-Methyl-4-oxo-2-pentenal		
OH	Rate Constant = 8.61e-11 cm^3 molec^{-1} s^{-1}	
	$CH_3C(O)CH=C(CH_3)CHO + OH \rightarrow CH_3C(O)CH(OH)C(\cdot)(CH_3)CHO$	62%
	$CH_3C(O)CH=C(CH_3)CHO + OH \rightarrow CH_3C(O)CH(\cdot)C(CH_3)(CHO)OH$	21%
	Rate constant and branching ratios are derived from estimated rate constants for reactions at various locations. Reaction by abstraction from CHO assumed to have same rate constant as the analogous reaction of acrolein. Addition to double bond calculated from OH addition rate constants for 4-oxo-2-pentenal x methacrolein / acrolein. The reaction shown is assumed to be the major addition process.	
O_3	Rate Constant = 2.00e-17 cm^3 molec^{-1} s^{-1}	
	$CH_3C(O)CH=C(CH_3)CHO + O_3 \rightarrow CH_3C(O)CHOO[excited] + CH_3C(O)CHO$	30%
	$CH_3C(O)CH=C(CH_3)CHO + O_3 \rightarrow CH_3COO[excited]CHO + CH_3C(O)CHO$	70%
	The rate constant estimated from O_3 rate constants for 4-oxo-2-pentenal x methacrolein / acrolein. The branching ratios were derived by the mechanism generation system based on assignments for trisubstituted alkenes.	
hν	Photolysis Set = 4OX2PEAL, Quantum yields = 1.	
	$CH_3C(O)CH=C(CH_3)CHO + h\nu \rightarrow CH_3\cdot + CH_3C(CHO)=CHC(O)\cdot$	25%

Table 13 (continued)

Compound, reaction, and rate parameters	Fraction
$CH_3C(O)CH=C(CH_3)CHO + h\nu \rightarrow H. + CH_3C(O)CH=C(CH_3)C(O)\cdot$	25%
$CH_3C(O)CH=C(CH_3)CHO + h\nu \rightarrow CH_3C(O)\cdot + CH_3C(CHO)=CH.$	25%
$CH_3C(O)CH=C(CH_3)CHO + h\nu \rightarrow HCO\cdot + CH_3C(\cdot)=C(CH_3)CHO$	25%
The photolysis reaction is assumed to have the same absorption cross-section and overall quantum yield as used for 4-oxo-2-pentenal. The radical formation reactions shown above are assumed to have equal probability.	
3-methyl 2,4-hexene-1,6-Dial	
OH Rate Constant = 1.20e-10 cm^3 $molec^{-1}$ s^{-1}	
$CH_3C(=CHCHO)CH=CHCHO + OH \rightarrow H_2O + CH_3C(=CHC(O)\cdot)CH=CHCHO$	12%
$CH_3C(=CHCHO)CH=CHCHO + OH \rightarrow H_2O + CH_3C(=CHCHO)CH=CHC(O)\cdot$	12%
$CH_3C(=CHCHO)CH=CHCHO + OH \rightarrow CH_3C(=CHCHO)CH(\cdot)CH(CHO)OH$	75%
Rate constant and branching ratios estimated from sum of estimated rate constants for reactions at various positions. Rate constant for abstraction from CHO assumed to be same as for analogous reaction of acrolein. Rate constant for addition to double bond estimated from addition rate constant estimated from addition rate constant for 2,4-hexene-1,6-dial x rate constant for isoprene / rate constant for 1,3-butadiene. The addition rate constant for 2,4-hexene-1,6-dial is estimated from the total rate constant of 9.00e-11cm^3 $molec^{-1}$ s^{-1} for that compound and the estimated rate constant for reaction at the CHO groups, based on the rate constant estimated for acrolein. The total rate constant for 2,4-hexene-1-6-dial is representative of values reported by Klotz et al (1995, 1999) for the trans,trans and the cis,trans isomers. The addition reaction shown is assumed to be the major process.	
O_3 Rate Constant = 2.01e-17 cm^3 $molec^{-1}$ s^{-1}	
$CH_3C(=CHCHO)CH=CHCHO + O_3 \rightarrow CH_3C(O)CH=CHCHO +$ $HCOCHOO[excited]$	25%
$CH_3C(=CHCHO)CH=CHCHO + O_3 \rightarrow HCOCHO + CH_3COO[excited]-CH=CHCHO$	25%
$CH_3C(=CHCHO)CH=CHCHO + O_3 \rightarrow HCOCHO +$ $CH_3C(CHOO[excited])=CHCHO$	25%
$CH_3C(=CHCHO)CH=CHCHO + O_3 \rightarrow CH_3C(CHO)=CHCHO +$ $HCOCHOO[excited]$	25%
The rate constant is estimated from rate constants for 2,4-hexene-1,6-dial x isoprene / 1,3-butadiene. The rate constant used for 2,4-hexene-1,6-dial is 1.00e-17 cm^3 $molec^{-1}$ s^{-1}, based on the upper limit rate constant of Klotz et al (1995). Equal probability is assumed for reactions at the various positions, as shown above.	

Table 13 (continued)

Compound, reaction, and rate parameters	Fraction
6-oxo 2,4-heptadienal	
OH Rate Constant = 7.51e-11 cm^3 molec^{-1} s^{-1}	
$CH_3C(O)CH=CH-CH=CHCHO + OH \rightarrow H_2O + CH_3C(O)CH=CH-CH=CHC(O)\cdot$	20%
$CH_3C(O)CH=CH-CH=CHCHO + OH \rightarrow CH_3C(O)CH=CH-CH(\cdot)CH(CHO)OH$	40%
$CH_3C(O)CH=CH-CH=CHCHO + OH \rightarrow CH_3C(O)CH(OH)CH(\cdot)CH=CHCHO$	40%
The rate constant and branching ratios estimated from estimated rate constants for reactions at various positions. Rate constant for abstraction from CHO assumed to be same as for analogous reaction of acrolein. Rate constant for addition to double bond assumed to be the same as the analogous reaction of 1,4-hexadiene-1,6-dial, derived as indicated above for 3-methyl-2-4-hexene-1,6-dial. The addition reactions shown are assumed to be the major processes, and equal probability for each is assumed.	
O_3 Rate Constant = 1.00e-17 cm^3 molec^{-1} s^{-1}	
$CH_3C(O)CH=CH-CH=CHCHO + O_3 \rightarrow CH_3C(O)CHO +$ $HCOCH=CHCHOO$[excited]	25%
$CH_3C(O)CH=CH-CH=CHCHO + O_3 \rightarrow HCOCH=CHCHO +$ $CH_3C(O)CHOO$[excited]	25%
$CH_3C(O)CH=CH-CH=CHCHO + O_3 \rightarrow HCOCHO +$ $CH_3C(O)CH=CHCHOO$[excited]	25%
$CH_3C(O)CH=CH-CH=CHCHO + O_3 \rightarrow CH_3C(O)CH=CHCHO +$ $HCOCHOO$[excited]	25%
The rate constant is assumed to be the same as that assigned for 3,4-hexene-1,6-dial, based on the upper limit data of Klotz et al (1995). Equal probability of reaction at the various positions is assumed.	
3,5-octadien-2,7-dione	
OH Rate Constant = 6.02e-11 cm^3 molec^{-1} s^{-1}	
$CH_3C(O)CH=CH-CH=CHC(O)CH_3 + OH \rightarrow CH_3C(O)CH=CH-CH(\cdot)CH(OH)C(O)CH_3$	100%
The rate constant for addition to the double bond is assumed to be the same as that derived for 2,4-hexadiene-1,6-dial, as indicated above for 3-methyl-2,4-hexene-1,6-dial. The reaction shown is assumed to be the major process.	
O_3 Rate Constant = 1.00e-17 cm^3 molec^{-1} s^{-1}	
$CH_3C(O)CH=CH-CH=CHC(O)CH_3 + O_3 \rightarrow CH_3C(O)CHO +$ $CH_3C(O)CH=CHCHOO$[excited]	50%
$CH_3C(O)CH=CH-CH=CHC(O)CH_3 + O_3 \rightarrow CH_3C(O)CH=CHCHO +$ $CH_3C(O)CHOO$[excited]	50%
The rate constant is assumed to be the same as that assigned for 3,4-hexene-1,6-dial, based on the upper limit data of Klotz et al (1995). Equal probability of reaction at the various positions is assumed.	

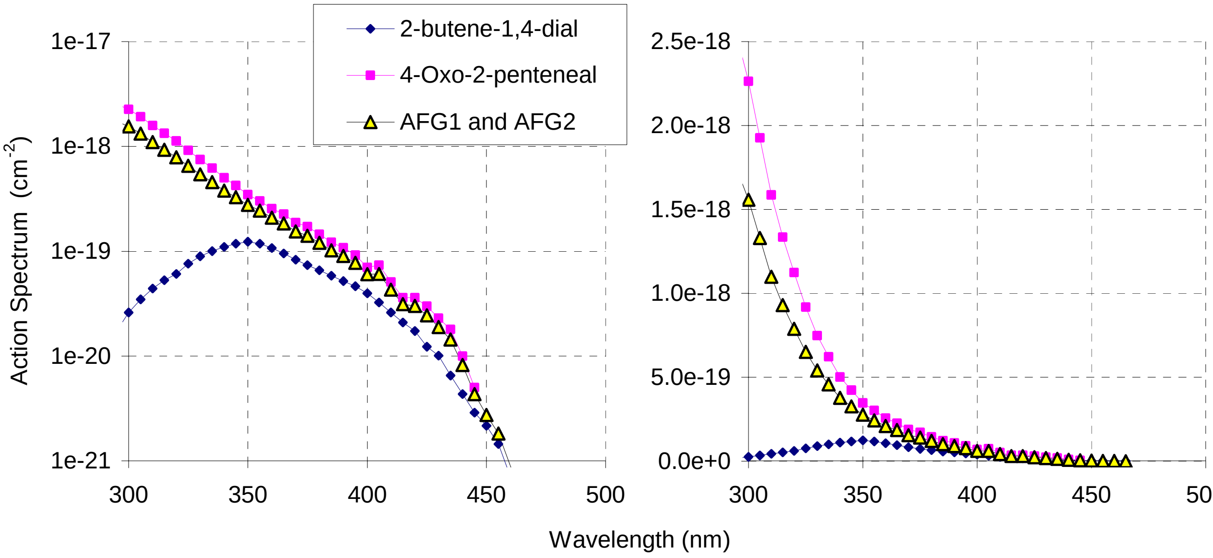


Figure 4. Action spectra for photodecompositions of 2-buene-1,4-dial, 4-oxo-2-penteneal and used for the model species AFG1 and AFG2.

Aromatic Ring Retaining Products

In addition to ring fragmentation, aromatics also react to form products where the aromatic ring is retained, such as phenols, cresols, aromatic aldehydes, and nitrophenols. Mechanisms for these species are included in the base mechanism, and are given in Table A-2 in Appendix A. The general methods used to represent these products are the same as employed in SAPRC-99, though rate constants and some mechanisms were updated. The various types of products that are represented, and changes relative to SAPRC-99, are summarized briefly below. Footnotes to Table A-2 document these reactions in more detail.

<u>Phenols and Cresols</u>. Although SAPRC-99 had a separate model species for phenol, in this mechanism the phenol and cresol model species are lumped together because representing phenol was found not to have a significant affect on model predictions for benzene, the only compound that forms phenol as a primary product in its reactions. The major atmospheric reactions of these compounds are with OH and NO_3 radicals, with the latter generally being the more important sink under most conditions. Because very little was known about the mechanisms of these reactions at the time SAPRC-99 was developed, SAPRC-99 had very simplified and parameterized representations of these mechanisms, adjusted to fit results of a single o-cresol - NO_x environmental chamber experiment. However, recently

Berndt and Boge (2003) and Olairu et al (2003) determined that the major products of the reactions of OH with these compounds were various dihydroxybenzenes, and Olariu et al (2000) obtained rate constants for these compounds indicating that they were very reactive. However, if it was assumed that these were the major products of the OH + cresol reaction then the mechanism could not simulate the results of the o-cresol - NO_x chamber experiment. Because of this it was decided to defer updating the mechanism used for these compounds until more information is available, and the general parameterization used in SAPRC-99 for the reactions of the cresols was retained. The rate constants were updated and the parameters in the mechanism were re-adjusted to fit the data for the current mechanism.

Nitrophenols. As with SAPRC-99, the nitrophenol model species (NPHE) is used to represent the products formed in the NO_3 + cresol reactions. In SAPRC-99 it was assumed that the major reactions of nitrophenols were with OH and NO_3 radicals, as was the case with cresols. However, recent data presented by Barnes (2006) and Bejan et al (2006) indicate that photolysis is a major loss process for nitrophenols, with some of the photolysis resulting in the formation of HONO, but most forming unspecified products. Evidence was not given for significant reaction of nitrophenols with NO_3 radicals, though the possibility that it may occur at least to some extent cannot necessarily be ruled out. Based on this, the current mechanism includes photolysis as a major sink for nitrophenols, and assumes that its reaction with NO_3 radicals is not significant.

Aromatic Aldehydes. Benzaldehyde and similar aromatic aldehydes may be formed when OH abstracts from methyl groups of methylbenzenes, and these continue to be represented using the benzaldehyde (BALD) model species. Its mechanism is the same as used in SAPRC-99, though the rate constants were updated. The mechanism incorporates updated absorption cross sections for its photolysis to unspecified products, but the overall photodecomposition rate was not changed.

Non-Alkylbenzene Aromatics

The alkylbenzenes are not the only types of aromatics for which mechanisms were derived. Mechanism assignments were also made for styrenes, naphthalenes, tetralin, various halo- and nitro-benzenes, phthalates, and other aromatic-containing compounds. The derivation of the mechanisms for these compounds is summarized on Table 14, the rate constants are given in Table B-2 and Table B-4, and the mechanisms are given in Table B-2 in Appendix B. As indicted on Table B-4, some of these are based on the general procedures derived for the alkylbenzenes as discussed above, while others (e.g., styrenes, naphthalenes, tetralin, and the isocyanates) appear to have quite different mechanisms. In those cases mechanisms are derived based on considerations for the individual compounds (as with the styrenes), or parameterized mechanisms, that were adjusted to fit environmental chamber data, were used.

Other non-alkylbenzene aromatics are represented using the lumped molecule method based on mechanisms for aromatics for which mechanism assignments were made. These are discussed in the "Lumped Molecule Representation" section, below.

Reactions with Chlorine

Alkylbenzenes. The low rate constant for the reaction of chlorine atoms with benzene (1.3×10^{-16} cm^3 $molec^{-1}$ s^{-1}, Sokolov et al, 1998), indicates that the only significant reactions of Cl with aromatics are abstractions off the aromatic ring. The rate constants for these reactions have been measured for some of the methylbenzenes (see Table 4) and can be estimated for other alkylbenzenes using the group-additivity parameters given on Table 3. The products formed are expected to be aromatic aldehydes that are represented using the benzaldehyde (BALD) model species if the reaction is on a methyl group, or primarily various aromatic ketones that are represented by the lumped higher ketone model species (PROD2), plus organic nitrates formed in the peroxy + NO reaction or hydroperoxides formed in the peroxy + HO_2 reaction. These result from reactions of the same radicals formed when OH radicals react off the aromatic ring, and the mechanisms can be derived in the same way, except for the different branching ratios for the initial reactions at the various positions, where applicable.

Chlorine + alkylbenzene mechanisms were derived in this manner for all the alkylbenzenes that are used to derive parameters for the lumped model species ARO1 and ARO2, as discussed below. The rate constants and mechanisms so derived are given in Table B-7 in Appendix B.

Table 14. Discussion of mechanisms for the non-alkylbenzene aromatic compounds that for which mechanistic assignments have been derived. The rate constants and additional documentation are given in Table B-4 and the reactions are given in Table B-2 in Appendix B.

Compound	Reacts With (reaction type)
Styrene	OH, O_3, NO_3, O^3P (double bond reaction only)
Mechanism as described by Carter et al (1999b) was used, except for some minor rate constants updates and the overall nitrate yield being increased from 13% to 18% to improve simulations of incremental reactivity data with styrene with the current mechanism. Results of model simulations of the chamber experiments with this compound are summarized on Table 23 in the Mechanism Evaluation Results section.	
β-Methyl styrene	OH, O_3, NO_3, O^3P (double bond addition only)
Assumed to react analogously to the mechanism derived for styrene. The nitrate yield in the OH reaction was increased to correspond to the additional carbon.	
Monochlorobenzene	OH (100% ring addition)
p-Dichlorobenzene	OH (100% ring addition)
Hexafluorobenzene	OH (100% ring addition)
Nitrobenzene	OH (100% ring addition)
The products formed in the reactions of these compounds are represented by those formed from in the reactions of OH with benzene. The appropriate measured rate constants for the compounds were used.	
Benzotrifluoride	OH (100% ring addition)
p-Trifluoromethyl-Cl-benzene	OH (100% ring addition)
The reaction is assumed to proceed only by addition of OH to the aromatic ring. The products formed are represented by those formed in the ring-addition reactions of toluene, as shown on Table 11. The nitrate yields in the reactions of the peroxy radicals are also assumed to be the same as used for toluene.	
Benzyl Alcohol	OH (70% ring addition)
The mechanism and environmental chamber data for this compound are discussed by Carter et al (2005a). The measured concentrations of benzaldehyde in the chamber experiments are consistent with a fraction reacted by abstraction from the $-CH_2OH$ of 30%, which is assumed in the mechanism. This is formed by O_2 reacting with the BzCH(·)OH radical forming benzaldehyde + HO_2 without NO to NO_2 conversions or nitrate formation. The products formed following the addition to the aromatic ring are assumed to be the same as used for ethylbenzene, as shown on Table 11. The nitrate yield factor derived for toluene is used for the peroxy reactions involved in the ring addition mechanism. Results of model simulations of the benzyl nitrate experiments are summarized on Table 23 in the Mechanism Evaluation Results section.	
Methoxybenzene; Anisole	OH (93% ring addition)
m-Nitrotoluene	OH (60% ring addition)
The fraction reacting by addition to the aromatic ring is estimated from the difference between the measured total OH rate constant and the rate constant for abstraction off the ring estimated using group-additivity methods as shown on Table 3. The products formed following ring addition are represented by those formed from ring addition to toluene, as shown on Table 11. The products formed from reaction off the ring are represented by the lumped higher oxygenated product PROD2 in the case of methoxybenzene and by the aromatic aldehyde species BALD in the case of m-nitrotoluene. The nitrate yield factor of toluene was assumed.	

Table 14 (continued)

2-Phenoxyethanol; Ethylene glycol phenyl ether OH (54% ring addition)

The total rate constant was estimated by the sum of the estimated rate constants for addition to the aromatic ring and abstraction reactions off the aromatic ring. The latter was estimated using the group-additivity methods shown in Table 3, and the products formed were derived using the estimates and procedures incorporated in the mechanism generation system. The rate constant and products for the ring addition reaction were assumed to be the same as derived for methoxybenzene, as discussed above.

1,2-Diacetyl benzene OH (100% ring addition)

100% ring addition is assumed – reaction on the methyl group is assumed to be relatively slow. The products formed are represented by those formed in the mechanism for OH ring addition to o-xylene, except that the nitrate yield factor for a C_{10} compound, shown on Figure 3, was used.

Phthalic anhydride OH (100% ring addition)

The rate constant was assumed to be the same as the measured rate constant for 1,2-diacetyl benzene. The products formed are also represented by those formed in the mechanism for OH ring addition to o-xylene, except that the nitrate yield factor for a C_8 compound, shown on Figure 3, was used.

Diethyl phthalate OH (71% ring addition)
Dibutyl phthalate OH (47% ring addition)

The total rate constant was estimated by the sum of the estimated rate constants for addition to the aromatic ring and abstraction reactions off the aromatic ring. The latter was estimated using the group-additivity methods shown in Table 3, and the products formed were derived using the estimates and procedures incorporated in the mechanism generation system. The rate constant and products for the ring addition reaction were assumed to be the same as derived for 1,2-diacetylbenzene, as discussed above, except that the nitrate factors appropriate for the carbon numbers of the particulate compounds, shown on Figure 3, were used.

2-Ethylhexyl benzoate OH (20% ring addition)

The rate constant for reaction at the aromatic ring estimated to be the same as the total rate constant for acetophenone (as tabulated by Atkinson, 1989), assuming that ring addition is the major reaction for that compound. The mechanism for reaction at aromatic ring based on that of toluene. The rate constant and mechanism for reaction at groups off the aromatic ring based on those estimated for 2-ethyl hexyl acetate, since reaction at the acetate group is estimated to be negligible for that compound.

Naphthalene OH (parameterized)
Tetralin OH (parameterized)
2,3-Dimethyl naphthalene OH (parameterized)

The details of the mechanisms for these compounds are still too uncertain to attempt to derive more explicit predictive mechanisms. The highly parameterized representations employed in SAPRC-99 (Carter, 2000a) are retained, though the values of the parameters were re-adjusted to fit the chamber data with the current mechanism. As discussed by Calvert (2002), the mechanisms for the reactions of these compounds are expected to be affected by total NO_2 levels, since competitions apparently exist between reactions with O_2 and NO_2 for some of the intermediate radicals. In order to avoid introducing new model species into the mechanism to represent speculative and uncertain processes, this NO_x dependence is in effect represented in SAPRC-99 and SAPRC-07 by using formation of lumped peroxyacetyl radicals (RCO3) in the parameterized mechanism. Results of adjusted model simulations of the chamber data with these compounds are summarized on Table 23 in the Mechanism Evaluation Results section.

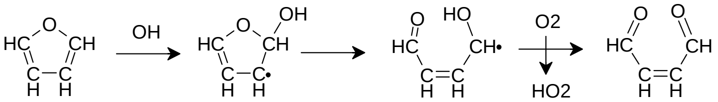
Table 14 (continued)

Methyl naphthalenes OH (parameterized)

Estimated mechanism derived by averaging the parameters for naphthalene and 2,3-dimethylnaphthalene, as was the procedure used when deriving the mechanism for this compound for SAPRC-99.

Furan
2-Methyl furan
3-Methyl furan
2,5-Dimethyl furan

As discussed in the Introduction, chamber experiments were carried out for several furans as part of this project because their initial reactions are expected to form unsaturated 1,4-dicarbonyls in high yield, which as discussed above are believed to be important photoreactive products formed in the oxidations of the aromatic hydrocarbons. The expected mechanism is as follows, using furan as the example:



Model simulations of experiments with these compounds could therefore serve as a means to evaluate mechanisms for the individual unsaturated 1,4-dicarbonyls without the uncertainties involved with handling these highly reactive compounds directly. However, there was insufficient time and resources available to this project to complete the development of explicit mechanisms for aromatics and their ring-opening products, so the evaluation of mechanisms using experiments with these compounds will be completed in future projects. For this version of the mechanism, the unsaturated 1,4-dicarbonyls expected to be formed from these furans were represented using the same approach as used for the aromatic hydrocarbons, i.e., by the AFG1 and AFG2 model species with their relative yields adjusted to fit the chamber data. Results of adjusted model simulations of the chamber data with this compound are summarized on Table 23 in the Mechanism Evaluation Results section.

2,4-Toluene Di-isocyanate (TDI) OH (parameterized)

The details of the mechanism of this compound, which was found by Carter et al (1997d) to be a strong radical inhibitor, are unknown. The parameterized mechanism used by Carter et al (1997d) to fit the chamber data, which is retained in SAPRC-99, is still retained for SAPRC-07, though the parameters were re-adjusted to fit the data with the current base mechanism. Results of adjusted model simulations of the chamber data with this compound are summarized on Table 23 in the Mechanism Evaluation Results section.

Para Toluene Isocyanate (PTI) OH (parameterized)

This was experimentally studied by Carter et al (1999a) as a model compound from which to derive an estimated mechanism for MDI, which has too low a volatility to be studied experimentally. Like TDI, the mechanism for this compound is unknown and Carter et al (1999a) derived a highly parameterized mechanism to fit the chamber data. This was used in SAPRC-99 and is retained in SAPRC-07, but with the parameters re-adjusted to fit the data for the current mechanism. Results of adjusted model simulations of the chamber data with this compound are summarized on Table 23 in the Mechanism Evaluation Results section.

Methylene Diphenylene Diisocyanate (MDI) OH (parameterized)

The mechanism for this compound was derived from the PTI mechanism as discussed by Carter et al (1999a). Based on structural considerations, the rate constant is assumed to be twice that for PTI, but the same set of products is assumed to be formed.

Aromatic Products. Reactions of chlorine atoms with the α-dicarbonyls and the aromatic ring-retaining products are included in the base chlorine mechanism, as shown in Table A-5 in Appendix A. Footnotes to that table document the sources of the rate constants and mechanisms that were used. Although the unsaturated dicarbonyls represented by AFG1-3 undoubtedly react relatively rapidly with chlorine atoms, these reactions are ignored in the base chlorine mechanisms. This is because it is expected that the other reactions would be more important sinks for these products under most atmospheric conditions, and their high reactivity would result in low concentrations that would make them unimportant as sinks for chlorine atoms. This is probably true for the α-dicarbonyls as well, though their chlorine reactions are included.

Mechanisms for Amines

Amines react relatively rapidly with OH radicals, and are also expected to relatively rapidly with NO_3, based on a relatively high rate constant for reaction of NO_3 with 1-methyl-2-pyrrolidinone (Aschmann and Atkinson, 1999). Rate constant data of Tuazon et al (1994) suggests that the reaction with O_3 may also be non-negligible for some amines. Mechanisms for all three of these types of reactions were derived, as discussed by Carter (2008a) and summarized below.

In the case of the OH and NO_3 reactions, the reaction is assumed to proceed by H-atom abstraction from the amino group or from the group next to the amino group, forming HNO_3 and the corresponding carbon- or nitrogen-centered radicals. Group-additivity parameters that can be used to estimate rates of these reactions are given in Table 3, above, and footnotes to that table indicate how these parameters were derived. Table 3c indicates that the group-additivity methods can estimate the rate constants to within ±26% on the average.

The subsequent reactions of the carbon-centered radicals formed in these reactions can be derived using the mechanism generation system as employed for other compounds, except that estimates need to be made for reactions of α-amino alkoxy radicals, e.g., RCH[O·]-NHR'. Although this is uncertain, to simplify the mechanism generation we assume that decompositions forming N-centered radicals, e.g., RCH[O·]-NHR' → RCHO + R'NH·, and estimate the relative rates of reactions for the competing routes based on estimates for other radicals considered to be similar. The applicable radicals and reactions assumed to dominate when generating mechanisms for amines in the current version of the mechanism are indicated on Table 15 These assumptions are uncertain, though alternative assumptions probably do not yield mechanisms with significantly different reactivities.

The subsequent reactions of the nitrogen-centered radicals formed after H-abstraction from NH_2 or NH groups depends on whether there is an abstractable hydrogen in the α-position to the amine. If there is, then it is assumed that the dominant reaction is abstraction of this hydrogen by O_2, forming HO_2 and the corresponding C=N compound, e.g.,

$$RCH_2NH\cdot + O_2 \rightarrow HO_2 + RCH{=}NH$$

This is based on kinetic data obtained by Lindley et al (1979) for reactions of $(CH_3)_2N\cdot$ with O_2, NO, and NO_2, where the reaction with O_2, forming HO_2 + CH_3-N=CH_2, is calculated to dominate under atmospheric conditions.

The subsequent reactions of the C=N products formed in this reaction are unknown and therefore this is an additional source of uncertainty in the mechanism. These are expected to be reasonably reactive compounds. For the current mechanism, they are represented by the generic reactive non-aldehyde oxygenated species PROD2. The appropriateness of this representation is highly uncertain.

Table 15. Assignments made for alkoxy radical intermediates predicted to be formed in the photooxidation mechanisms of the amines.

Radical	Reaction Assumed to Dominate
$\cdot OCH_2-NH_2 + O_2$	$HCO-NH_2 + HO_2\cdot$
$CH_3-NH-CH_2O\cdot + O_2$	$CH_3-NH-CHO + HO_2\cdot$
$.OCH_2CH_2-NH_2$	$HCHO + .CH_2-NH_2$
$CH_3CH(O\cdot)NH_2 + O_2$	$CH_3C(O)NH_2 + HO_2\cdot$
$CH_3-N(CH_3)CH_2O\cdot + O_2$	$CH_3-N(CH_3)CHO + HO_2\cdot$
$NH_2CH(O\cdot)CH_2OH$	$HCO-NH_2 + .CH_2OH$
$CH_3C(O\cdot)(CH_3)NH_2$	$CH_3C(O)NH_2 + CH_3\cdot$
$CH_3C(CH_3)(CH_2O\cdot)NH_2$	$HCHO + CH_3C(\cdot)(CH_3)NH_2$
$CH_3-N(CH_2O\cdot)CH_2CH_2OH$	$CH_3-N(CH_2OH)CH_2CH(\cdot)OH$
$CH_3C(CH_2O\cdot)(NH_2)CH_2OH + O_2$	$CH_3C(CHO)(NH_2)CH_2OH + HO_2\cdot$
$.OCH_2CH_2CH(NH_2)CH_2OH$	$NH_2CH(CH_2CH_2OH)CH(\cdot)OH$
$CH_3-N(CH_3)CH(O\cdot)CH_2OH$	$CH_3-N(CH_3)CHO + .CH_2OH$
$CH_3CH(O\cdot)CH(NH_2)CH_2OH$	$CH_3CHO + NH_2CH(\cdot)CH_2OH$
$CH_3CH_2C(O\cdot)(NH_2)CH_2OH$	$CH_3CH_2C(O)NH_2 + .CH_2OH$
$HOCH_2CH_2-NH-CH(O\cdot)CH_2OH$	$HCO-NH-CH_2CH_2OH + .CH_2OH$
$CH_3CH_2-N(CH_2CH_3)CH_2CH_2O\cdot$	$CH_3CH_2-N(CH_2CH_2OH)CH(\cdot)CH_3$
$CH_3CH_2-N(CH_2CH_3)CH(O\cdot)CH_3$	$CH_3CH_2-N(CH_2CH_2\cdot)CH(CH_3)OH$
$CH_3CH_2-N(CH_2CH_2O\cdot)CH(CH_3)OH$	$CH_3CH(\cdot)N(CH_2CH_2OH)CH(CH_3)OH$
$CH_3CH_2-N(CH_2CH_2OH)CH(O\cdot)CH_3$	$CH_3CH_2-N(CH_2CH(\cdot)OH)CH(CH_3)OH$
$CH_3CH(O\cdot)N(CH_2CH_2OH)CH(CH_3)OH$	$CH_3CH(OH)N(CH_2CH(\cdot)OH)CH(CH_3)OH$
$HOCH_2CH_2-N(CH_2CH_2OH)CH(O\cdot)CH_2OH$	$HCO-N(CH_2CH_2OH)CH_2CH_2OH + .CH_2OH$
$CH_3CH(OH)CH_2-N(CH_2CH(CH_3)OH)CH_2-CH(CH_2O\cdot)OH$	$HCHO + CH_3CH(OH)CH_2-N(CH_2CH(\cdot)OH)CH_2CH(CH_3)OH$
$CH_3CH(OH)CH_2-N(CH_2CH(CH_3)OH)-CH(O\cdot)CH(CH_3)OH$	$CH_3CH(OH)CH_2-N(CHO)CH_2CH(CH_3)OH + CH_3CH(\cdot)OH$

The above type of reaction cannot occur if the nitrogen-centered radical lacks an abstractable hydrogen in the α-position, as is the case in radicals predicted to be formed in the reactions of t-butyl amine and 2-Amino-2-Methyl-1-Propanol (AMP). In this case, the only expected reactions of the nitrogen-centered radical is reaction with NO, NO_2, or HO_2, e.g.,

$$(CH_3)_3CNH\cdot + NO \rightarrow (CH_3)_3CNHNO \quad \text{(a)}$$

$$(CH_3)_3CNH\cdot + NO_2 \rightarrow (CH_3)_3CNHNO_2 \quad \text{(b)}$$

$$(CH_3)_3CNH\cdot + HO_2 \rightarrow O_2 + (CH_3)_3CNH_2 \quad \text{(c)}$$

If NO_x is present, the major reaction is expected to be process (b), forming the nitramine, since the nitrosamine formed in process (a) is expected to undergo rapid photolysis back to NO and the radical, resulting in no net reaction. Since this is a radical inhibiting process, this mechanism predicts that t-butyl amine and AMP would be radical inhibitors, since reaction forming the N-centered radical is estimated to be the major initial reaction. This is consistent with the fact that these compounds are indeed found to be strong ozone and radical inhibitors in environmental chamber experiments (Carter, 2008a)

For implementation in the mechanism, the model species "NRAD" is used to represent the reactions of the N-centered radicals that lack abstractable hydrogens in the α position. This species is representing as reacting with NO_2 to form a nitramine, with a rate constant estimated by assuming that it is the same as for the reaction of NO_2 with the generic higher acyl peroxy radical species RCO3. The nitramine is approximately represented by PROD2 in the current mechanism, though the appropriateness of this representation is also highly uncertain. The reaction with NO, forming the nitrosoamine, is neglected because of the expected rapid photolysis of the nitrosoamine to reverse the reaction. In the absence of NO_x, the NRAD is represented as reacting with HO_2 to re-form the amine, with a rate constant assumed to be the same as used for the reaction of RCO3 with HO_2. Because of the way the mechanism is implemented it is not practical to represent the amine formed in the reaction as the amine itself, so its subsequent reactions are therefore neglected. This is because the two amines represented to form NRAD are inhibitors, so representing them with reactive product model species such as PROD2 is inappropriate.

Methods for estimating rate constants and mechanisms for the reactions of O_3 with amines were also derived. These are discussed in detail by Carter (2008a) and briefly summarized here. Based on the available rate constants of Tuazon et al (1994) and limited information concerning the products given by Tuazon et al (1994) and Murphy et al (2007), Carter (2008a) estimates that the initial reaction of O_3 with amines is at the group next to the amino group, ultimately resulting in abstraction from α C-H bonds, forming OH radicals and the same types of radicals as formed in the OH reaction, e.g.,

$$CH_3NH_2 + O_3 \rightarrow [\text{adduct?}] \rightarrow O_2 + OH + \cdot CH_2NH_2$$

The available kinetic data for the methylamines and DMAE are fit by

$$K(\text{group},O_3) = 10^{-42.97 - \{5.84\ k(\text{group},OH)\}},$$

where k(group) refers to net H-atom abstraction at a group adjacent to the amino group and the rate constants are in $cm^3\ molec^{-1}\ s^{-1}$. This gives estimates for rate constants that agree with those of Tuazon et al (1994) to within a factor of two. This was also used as the basis for estimating relative rates of reaction at different positions secondary or tertiary amines that have non-equivalent substituents. The subsequent reactions of the radicals formed are derived as discussed above for the OH and NO_3 mechanisms.

A significant uncertainty in terms of calculations of the atmospheric ozone impacts of the amines concerns the extent to which they react with gas-phase HNO_3, forming the amine salt. If this reaction is sufficiently fast, and if most of the salt formed partitions to the vapor phase, then the amine would not be available to react in the gas phase and promote ozone formation. Although model simulations of the available environmental chamber experiments with amines are not sensitive to this reaction because the amount of HNO_3 formed in the experiments is small compared to the amount of amine added, the atmospheric incremental reactivity simulations are very sensitive to this because of the amount of amine added is relatively small compared to the amount of HNO_3 predicted to be formed (Carter, 2008a). The importance of this under atmospheric conditions is difficult to estimate because of uncertainties and variabilities concerning sources and sinks for HNO_3 in the atmosphere. As discussed by Carter (2008a) in order to obtain upper limit magnitude estimates for the ozone impacts of the amines we assume that removal of the amines by reaction with HNO_3 is negligible, but this is likely not to be the case in actual atmospheres.

Miscellaneous Assigned Mechanisms

There are several compounds for which mechanisms have been derived where the procedures discussed above could be employed. In those cases, mechanisms were derived based on considerations of the relevant reactions of the particular compounds, or, if the details of the reactions for the particular compound are sufficiently uncertain, parameterized mechanisms were derived and adjusted to fit available environmental. These compounds are listed in Table 16, along with a brief discussion of how

Table 16. Discussion of mechanisms for miscellaneous compounds that were not derived using the procedures discussed previously in this report. The rate constants, reactions, and additional documentation are given in Table B-2, and Table B-4 through Table B-6 in Appendix B.

Compound	Reacts With
N-Methyl-2-Pyrrolidone	OH, NO_3
Mechanism based on that originally developed by Carter et al (1996b), using the kinetic data of Aschmann and Atkinson (1999). The SAPRC-99 mechanism had an incorrect conversion of the original mechanism that did not incorporate all the NO to NO_2 conversions in the OH and NO_3 reactions, and compensated for this by reducing the overall nitrate yield to fit the chamber data. Once this was corrected, the chamber data are best fit using the nitrate yield originally derived by Carter et al (1996b). Note that the (presumably incorrect) SAPRC-99 mechanism fit some of the chamber data somewhat better than the original and the current updated mechanism, but is not as consistent with our current estimation of the chemistry. Results of model simulations of the chamber experiments with this compound are summarized on Table 23 in the Mechanism Evaluation Results section.	
Dimethyl Sulfoxide	OH, NO_3
Environmental chamber experiments and possible mechanisms for DMSO reactions were discussed by Carter et al (2000d). No mechanism that was entirely consistent with the available data was found, but the best fit "Mechanism C", as adopted for the ambient reactivity calculations given by Carter et al (2000d) is retained for this version of the mechanism. Results of model simulations of the chamber experiments with this compound are summarized on Table 23 in the Mechanism Evaluation Results section.	
1,3-Butadiyne	OH, NO_3
It is assumed that the primary reaction is OH or NO_3 adding to terminal position, forming an allylic-stabilized radical. In the case of the OH reaction, the 1,2-unsaturated alpha-hydroxy radical reacts with O_2 to form HO_2 and 1,2-butadien-4-al, and in the case of the NO_3 reaction the analogous compound reacts unimolecularly to form NO_2 and the same aldehyde. The aldehyde is represented by RCHO, on the basis that this is probably not as bad an approximation as MACR. It is assumed that the reaction with O_3 is slow.	
Methyl Bromide	OH
Ethyl Bromide	OH
1,2-Dibromoethane	OH
n-Propyl Bromide	OH
n-Butyl Bromide	OH
The mechanisms for these compounds are approximated by that of the corresponding chloride, but with the appropriate OH rate constant for the compound. This may somewhat overestimate the reactivity of the compounds, and may underestimate inhibition under low NO_x conditions. This can be considered to be useful for upper-limit mechanism estimates, but will need to be refined for "best estimate" reactivity estimates. Results of model simulations of the chamber experiments with n-propyl bromide and n-butyl bromide, summarized on Table 23 in the Mechanism Evaluation Results section, are consistent with this assessment.	
Hexamethyldisiloxane	OH
D4 Cyclosiloxane	OH
Hydroxymethyldisiloxane	OH
Parameterized mechanisms adjusted to fit the incremental reactivity chamber data of Carter et al (1992) that were considered to be suitable for mechanism evaluation are employed. (Several runs had	

Table 16 (continued)

Compound	Reacts With
no assigned initial NO_2 concentrations or non-standard run conditions, and were not used.) No chemically reasonable mechanism was found that was consistent with the data (Carter et al, 1992), so a highly simplified parameterized mechanism, which assumes an adjustable amount of radical loss and the remainder of the reaction forming HO_2 after an NO to NO_2 conversion, and assumes no reactive products formed, was used. Results of model simulations of the chamber experiments with these compounds are summarized on Table 23 in the Mechanism Evaluation Results section.	
D5 Cyclosiloxane	OH
Although reactivity chamber experiments were conducted for this compound (Carter et al, 1992), none of these runs were considered suitable for mechanism evaluation because of uncertainties concerning initial NO_x concentrations. Qualitatively the results were similar to those for D4 cyclosiloxane in that large inhibition was assumed. The amount of inhibition used was assumed to be approximately the same as that derived for D4, since a similar mechanism is expected.	
Acrylonitrile	OH
The data of Hashimoto et al (1984) indicate that the products are formaldehyde and HCO-CN after an NO to NO_2 conversion. HCO-CN is assumed to be relatively unreactive, which is supported by the concentration-time profiles reported by Hashimoto et al (1984). Reactions with NO_3 and O_3 are assumed to be relatively slow, though no data are available concerning these reactions.	
Methyl nitrite	OH, $h\nu$
The reaction with OH is assumed to proceed by abstraction from the methyl group, followed by decomposition to form NO and formaldehyde. The photolysis absorption cross sections are from Calvert and Pitts (1966). The major reaction pathway is photolysis, which is assumed to form methyl radicals and NO with unit quantum yields.	
Chloropicrin	$h\nu$
Carbon disulfide	OH, $h\nu$
Methyl isothiocyanate	OH, $h\nu$
EPTC (S-Ethyl dipropylthiocarbamate)	OH, NO_3
Molinate	OH, NO_3
Pebulate	OH, NO_3
Thiobencarb	OH, NO_3
The mechanisms for these pesticide VOCs as given by Carter and Malkina (2007) are used without modifications other than adaptation to this version of the mechanism. Results of model simulations of the chamber experiments with these compounds are discussed in the Mechanism Evaluation Results section.	
trans 1,3,3,3-Tetrafluoropropene	OH
2,3,3,3-Tetrafluoropropene	OH
The mechanisms derived for these compounds and evaluated against chamber data by Carter (2009a) and Carter (2009b), respectively, were used.	
Ethyl methyl ketone oxime	OH
An estimated mechanism was derived explicitly for this compound. About 24% of the reaction is assumed to occur at the methyl or CH2 groups, with the subsequent reactions estimated using the procedures in the mechanism generation system. The remainder of the reaction is assumed to be addition of OH to the C=N double bond, which is assumed to form primarily $C_2H_2C(CH_3)(OH)N(.)OH$, which is assumed to react with O_2 to form $C_2H_5C(CH_3)(OH)NO + HO_2$.	

Table 16 (continued)

Compound	Reacts With
The rate constant is estimated by the rate constant for OH + isobutene x the average of the ratio of the rate constants for CH_2=NOH / Ethene and CH_3CH=NOH / Propene, with abstractions from the methyl group subtracted off. The CH_2=NOH and CH_3CH=NOH rate constants are from the tabulation of Atkinson (1989). The $C_2H_5C(CH_3)(OH)NO$ is assumed to photolyze rapidly, forming NO + an alpha-hydroxy radical that reacts with O_2 to form MEK and HO_2. The absorption cross-sections and quantum yields are unknown, but photolysis is assumed to be relatively rapid, and estimated to be comparable to that of methyl nitrite.	
Methyl iodide	OH, hν
The mechanism for this compound as given by Carter (2007) was used without modification. This mechanism, and the reactions of the inorganic iodine species formed in both the OH and photolysis reactions, are also included in Table B-2, with is available with the electronic version of this report. Results of model simulations of the chamber experiments with these compounds are discussed by Carter (2007) and summarized in the Mechanism Evaluation Results section.	

the mechanisms were derived. The initial rate constants are given in Table B-4 and their reactions are given in Table B-2 in Appendix B, along with notes giving references for the rate constants and in some cases the mechanisms. The references cited can be consulted for additional information concerning the derivation of the mechanisms for these compounds.

Lumped Molecule Representations

A number of compounds or classes of compounds do not have explicit mechanistic assignments in the SAPRC-99 or SAPRC-07 mechanisms, but instead are represented by the "lumped molecule" approach for the purpose of estimating their reactivities or contributions to mixtures. In this approach, the impacts of a compound or class of compounds are assumed to be the same, on a per-molecule basis, as a compound or group of compounds for which a mechanism has been derived. This is used for compounds whose reactivities or impacts are of interest, but are either not considered to be sufficiently important to have an explicit mechanism derived, or whose mechanism is considered to be not significantly different from that for the compound representing it, or where the mechanistic difference with the representing compound is considered to be small compared to the uncertainty of the mechanism. It is also used for unspeciated mixtures of isomers, where a representative compound or group of compounds is used to estimate the impact of the mixture.

The SAPRC-07 lumped molecule representations are given in Table B-9 in Appendix B. In most cases the same representations are used in SAPRC-07 as implemented in SAPRC-99 (Carter, 2000a). The exceptions are primarily compounds or groups of compounds for which mechanisms have since been assigned, the representation of the higher alkylbenzenes, and the new detailed model species that have been added. The compounds or mixtures that were previously represented using the lumped molecule approach but now have mechanistic assignments are furan and lumped higher alkylbenzene species as discussed above in conjunction with the aromatics mechanisms. The new lumped aromatic model species is used to give a better lumped molecule representation for the higher aromatics that is more appropriate to their carbon numbers than by representing them using methylbenzenes or ethylbenzene, as was the case previously. In addition, a total of 31 new types of compounds that were not represented in SAPRC-99 are now represented in SAPRC-07 using the lumped molecule approach.

The lumped molecule assignments shown on Table B-9 are used to estimate the atmospheric reactivities of these compounds or mixtures, and are also used where applicable to derive the mechanisms for the lumped mechanisms in airshed models based on mixtures containing them, as discussed in the following section.

Lumped Mechanisms for Airshed Models

Airshed model applications require simulations of highly complex mixtures of large numbers of VOCs, and in most cases it is not necessary or practical to represent each of them separately. For such applications, models with lumped model species that represent reactions of a large number of species with similar reaction rates and mechanisms are generally employed. Even for VOC reactivity assessment it is only really necessary to separately represent the VOC whose reactivity is being assessed, with the reactions of most of the other VOCs present in the ambient simulation being represented using appropriate lumped model species. This is the approach used in the SAPRC-99 mechanism, and is retained for SAPRC-07. The lumping approach and recommended set of lumped model species is also unchanged in this version of the mechanism.

Adjustable Parameter Mechanisms

The SAPRC-99 mechanism has the option to vary the lumping approach in terms of the number of model species used and how they are lumped, and also to vary the mixture of compounds used to derive the parameters for the lumped model species, based on the emissions in model scenario or other considerations (Carter, 2000a,b; Adleman et al, 2005). This is referred to as the "adjustable parameter" mechanism for airshed models. This feature is retained in this version of the mechanism, with the procedures and software for adjustable parameter SAPRC-07 being the same as employed for SAPRC-99, as discussed by Carter (2000a) and Adleman et al (2005). The data files implementing the variable parameter version of SAPRC-07 will be made available at the Speciation Database website[1] and the SAPRC mechanism website[2]. The files will have the same format as those currently used to implement SAPRC-99.

Fixed Parameter Mechanism

In practice most model applications have used the "fixed parameter" version of SAPRC-99. This involves use of a fixed set of lumped model species, with the parameters for the adjustable parameter lumped species being derived using a pre-defined mixture. The updates to the fixed parameter mechanism for SAPRC-07 are documented in the remainder of this section.

The lumped model species and general lumping approach used in fixed parameter SAPRC-99 is the retained in SAPRC-99. The list of lumped and explicit model species used for representing various types of emitted VOCs is given in Table 17, and lumped model species added to the base mechanism for the fixed parameter mechanism are included in Table A-1 in Appendix A. These include the lumped model species that are added to the base mechanism whose parameter can be adjusted based on the emissions mixture being represented, the organic product model species already in the base mechanism that are also used to represent various types of primary emitted organics, and the model species for compounds that are explicitly represented. In all cases the lumped or explicit species represent the emitted compound on a mole-for-mole basis; there is no "reactivity weighting" in this version of the mechanism.

---

[1] The Speciation Database website is at http://www.cert.ucr.edu/~carter/emitdb.

[2] The SAPRC mechanism web site is at http://www.cert.ucr.edu/~carter/SAPRC.

Table 17. List of model species used in the lumped mechanism for airshed models for representing the various types of emitted VOCs.

Name	Description	Amount in Base ROG [a]
Lumped model species added to the base mechanism. Parameters can optionally be adjusted based on mixture being represented.		
ALK1	Alkanes and other non-aromatic compounds that react only with OH, and have kOH (OH radical rate constant at 300°K) between 1.36 and 3.41 x 10^{-13} cm^3 molec^{-1} s^{-1}. (Primarily ethane)	17.7
ALK2	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 3.41 x 10^{-13} and 1.70 x 10^{-12} cm^3 molec^{-1} s^{-1}. (Primarily propane)	14.8
ALK3	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 1.70 and 3.41 x 10^{-12} cm^3 molec^{-1} s^{-1}.	27.7
ALK4	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 3.41 and 6.81 x 10^{-12} cm^3 molec^{-1} s^{-1}.	35.5
ALK5	Alkanes and other non-aromatic compounds that react only with OH, and have kOH greater than 6.81 x 10^{-12} cm^3 molec^{-1} s^{-1}.	18.8
ARO1	Aromatics with kOH < 1.36 x 10^{-11} cm^3 molec^{-1} s^{-1}.	12.9
ARO2	Aromatics with kOH > 1.36 x 10^{-11} cm^3 molec^{-1} s^{-1}..	17.2
OLE1	Alkenes (other than ethene) with kOH < 4.77 x 10^{-11} cm^3 molec^{-1} s^{-1}.	11.3
OLE2	Alkenes with kOH > 4.77 x 10^{-11} cm^3 molec^{-1} s^{-1}.	12.5
TERP	Terpenes	0.7
Lumped organic product model species that are already in the base mechanism that are also used to represent certain types of primary emitted VOCs. (Mechanisms are not adjustable)		
RCHO	C3+ saturated aldehydes	2.9
MEK	Ketones and other non-aldehyde oxygenated compounds with kOH between 5 x 10^{-13} and 5 x 10^{-12} cm^3 molec^{-2} sec^{-1}.	1.2
PROD2	Ketones and other non-aldehyde oxygenated compounds with greater than 5 x 10^{-12} cm^3 molec^{-2} sec^{-1}.	
RCOOH	C3+ organic acids	
MGLY	Methyl glyoxal and C3+ α-dicarbonyl aldehydes	
BACL	Biacetyl and other highly photoreactive compounds that are not otherwise represented.	
CRES	Phenols and cresols	
BALD	Aromatic aldehydes	0.2
MACR	Acrolein and methacrolein	
IPRD	Other unsaturated aldehydes	
MVK	Unsaturated ketones	
RNO3	Organic nitrates	

Table 17 (continued)

Name	Description	Amount in Base ROG [a]
<u>Model species for explicitly represented product compounds that can also be emitted</u>		
HCHO	Formaldehyde	8.3
CCHO	Acetaldehyde	5.0
ACET	Acetone	3.2
MEOH	Methanol	
HCOOH	Formic acid	
CCOOH	Acetic acid	
GLY	Glyoxal	
<u>Model species for explicitly represented primary emitted VOCs.</u>		
CH4	Methane	
ETHENE	Ethene	14.1
ISOPRENE	Isoprene	1.4
ACETYLEN	Acetylene	10.2
BENZENE	Benzene (also used for halo- and nitro-benzenes)	3.5

[a] Relative amount in the base ROG mixture used to represent emissions from all sources, in units of ppb model species per ppmC of mixture. This mixture was used to derive the parameters for the adjustable parameter lumped model species as discussed in this section, and was also used in the reactivity assessment calculations discussed in the "Updated Reactivity Scales" section, below.

The mechanisms for the model species already in the base mechanism have been discussed previously, and are given in Table A-2 in Appendix A. The mechanisms for the lumped species added to the base mechanism fixed parameter SAPRC-07 are derived using the same standard mixtures as used to derive their parameters for parameter SAPRC-99. For the model species ALKn, AROn, and OLEn, the mechanisms are derived based on the mixture of alkanes, aromatics, and alkenes in base reactive organic gas (ROG) mixture used to represent anthropogenic emissions from all sources used when calculating the Carter (1994) reactivity scales. This is based on an analysis by Jeffries et al. (1989) of urban ambient air measurements made by Lonneman (1986). For the model species TERP, the mechanisms are derived based on the top 5 terpenes in the North American Biogenic Inventory from the Guenther et al (2000) NARSTO assessment.

The mixtures of compounds used to derive the parameters for the adjustable parameter model species for the fixed parameter mechanism are given in Table 18 and Table 19, and Table A-7 in Appendix A gives the mechanisms that were so derived. The latter includes the reactions that were added to the standard base mechanism and also the reactions of these model species with chlorine atoms that are included when the mechanism is used to represent chlorine chemistry. These are based on the mechanisms for the individual components given in Table B-2 and Table B-7 in Appendix B, with the weighting factors shown in Table 18 and Table 19. Note that because of the difficulties in generating complete mechanisms for the Cl + alkene reactions (discussed above), the terpene + Cl mechanism is based entirely on that derived for α-pinene, and, as indicated in Table B-7 the mechanisms and rate constants for many of the alkenes were assumed to be the same as structurally similar compounds.

Note that the mixtures used to derive the parameters for the model species in the fixed parameter mechanism may be out of date and need to be updated. An update to the base ROG mixture used to derive

Table 18. Compounds and weighting factors used to derive the parameters for the ALK and ARO model species in the fixed parameter mechanism for airshed models

Group and Compound	Mole Fract.	Group and Compound	Mole Fract.	Group and Compound	Mole Fract.
ALK1		ALK5		ARO2	
Ethane	100%	2,4-Dimethyl Hexane	12%	m-Xylene	13%
		n-Decane	11%	p-Xylene	13%
ALK2		3-Methyl Hexane	11%	o-Xylene	11%
Propane	100%	2,3-Dimethyl Pentane	7%	1,2,3-Trimethyl Benzene	9%
		2-Methyl Heptane	6%	1,3,5-Trimethyl Benzene	9%
ALK3		4-Methyl Heptane	6%	1,2,4-C10 trisubstituted benzenes	6%
n-Butane	68%	2,4-Dimethyl Heptane	5%	m-Ethyl Toluene	5%
Isobutane	30%	2,6-Dimethyl Octane	5%	o-Ethyl Toluene	5%
2,2-Dimethyl Butane	2%	Methylcyclohexane	4%	p-Ethyl Toluene	5%
		n-Nonane	4%	1,2,4-Trimethyl Benzene	5%
ALK4		n-Octane	4%	1,2,3-C10 trisubstituted benzenes	4%
Isopentane	43%	Cyclohexane	4%	1,3,5-C10 trisubstituted benzenes	2%
n-Pentane	17%	2-Methyl Nonane	3%	m-C10 disubstituted benzenes	2%
2-Methyl Pentane	10%	2-Methyl Hexane	3%	o-C10 disubstituted benzenes	2%
3-Methylpentane	7%	2-Methyl Octane	3%	p-C10 disubstituted benzenes	2%
2,4-Dimethyl Pentane	5%	4-Methyl Octane	3%	1-methyl-4-isopropylbenzene	2%
Methylcyclopentane	5%	n-Dodecane	2%	m-C11 disubstituted benzenes	0.4%
n-Hexane	4%	4-Methyl Nonane	1.4%	1,3,5-C12 trisubstituted benzenes	0.3%
n-Heptane	3%	Ethylcyclohexane	1.1%	m-C12 disubstituted benzenes	0.2%
2,3-Dimethyl Butane	3%	n-Undecane	1.0%	p-C12 disubstituted benzenes	0.2%
Cyclopentane	2%	3,6-Dimethyl Decane	1.0%	1,2,4-C11 trisubstituted benzenes	0.2%
1,1-dimethylcyclopentane	0.1%	2,6-Dimethyl Nonane	0.5%	1,2,3-C11 trisubstituted benzenes	0.2%
		3-Methyl Undecane	0.5%	1,3,5-C11 trisubstituted benzenes	0.2%
ARO1		5-Methyl Undecane	0.5%	1,2,4-C12 trisubstituted benzenes	0.12%
Toluene	75%	3-Methyl Decane	0.2%	1,2,3-C12 trisubstituted benzenes	0.12%
Ethyl Benzene	10%	4-Methyl Decane	0.2%	o-C11 disubstituted benzenes	0.10%
C11 Monosubstituted Benzenes	5%	1,2-dimethylcyclopentane	0.12%	p-C11 disubstituted benzenes	0.10%
n-Propyl Benzene	4%	Ethyl Cyclopentane	0.12%	o-C12 disubstituted benzenes	0.06%
C10 Monosubstituted Benzenes	3%	n-Tridecane	0.09%		
Isopropyl Benzene (cumene)	2%	3,6-Dimethyl Undecane	0.03%		
t-Butyl Benzene	0.7%	3-Methyl Dodecane	0.02%		
C12 Monosubstituted Benzenes	0.2%	5-Methyl Dodecane	0.02%		

Table 19. Compounds and weighting factors used to derive the parameters for the OLE and TERP model species in the fixed parameter mechanism for airshed models

Group and Compound	Mole Fraction	Group and Compound	Mole Fraction]
OLE1		OLE2	
Propene	29%	cis-2-Pentene	14%
1-Hexene	24%	trans-2-Pentene	14%
1-Butene	12%	trans-2-Butene	11%
1-Pentene	11%	Isobutene	10%
1-Heptene	11%	cis-2-Butene	9%
1-Nonene	5%	2-Methyl-1-Butene	8%
3-Methyl-1-Butene	3%	1,3-Butadiene	6%
1-Octene	2%	2-Methyl-2-Butene	5%
1-Undecene	2%	Cis-2-Hexene	5%
1-Decene	0.9%	Trans-2-Hexene	5%
		Trans-3-Heptene	4%
TERP		Trans-4-Nonene	2%
α-Pinene	38% [a]	Trans-4-Octene	2%
β-Pinene	27%	Trans-5-Undecene	2%
3-Carene	17%	Trans-2-Heptene	2%
Sabinene	10%	Cyclohexene	2%
d-Limonene	9%	Trans-4-Decene	0.7%
		3,4-Diethyl-2-Hexene	0.2%

[a] The TERP + chlorine mechanism is assumed to be the same as that derived for α-pinene.

the ALK, ARO, and OLE parameters is almost certainly called for given changes in anthropogenic emissions since the mid 80's, and advances in analytical methods. However, deriving updated base ROG mixtures is beyond the scope of this project, and the CARB and the EPA were unable to provide recommendations for an updated mixture within the time frame of this project. Therefore, the same mixture is retained in this update for consistency with SAPRC-99. However, the mechanisms for the individual compounds given in Table B-2 in Appendix B could be used as the basis for deriving updated mechanisms for these lumped model species once updated base ROG or terpene compositions become available.

Emissions Assignments

An important part of implementing mechanisms into airshed models involves assigning individual chemical compounds and categories used in speciation profiles to lumped species in the mechanism. The general types of compounds assigned to the various model species in the fixed parameter version of SAPRC-07 are indicated in Table 17, and the assignments of lumped model species to the individual compounds or types of compounds for which mechanistic assignments are made are shown in Table B-11 in Appendix B. For compounds or groups of compounds that are represented using the lumped molecule method as shown on Table B-9, the lumped model assignments are derived from those that are assigned to the explicitly represented compounds that are used to represent them.

Emissions speciation profiles use a variety of types of chemical categories, many of which do not refer to individual compounds or chemical categories used in the SAPRC mechanism. Because of this, we have previously developed an emissions speciation database for the purpose of assigning chemical categories used in emissions profiles to model species in various mechanisms in a consistent manner. The mechanisms currently supported in the database include CB4, CB05, RADM2, as well as SAPRC-99 (Adelman et al, 2005; Carter, 2008b). This speciation database has been updated to support SAPRC-07 and the files needed to process emissions for the fixed-parameter version of SAPRC-07 are available at the speciation database project web site (Carter, 2008b).

Note that emissions assignments are different than lumped molecule representations. Lumped molecule representations involve representing the compound or categories by a detailed model species, of which there are over 700, while emissions assignments involve representing id by one of the ~30 lumped model species used in airshed models. Obviously lumped molecule assignments are less approximate and should be used for purposes of reactivity scale calculations or deriving optimum mechanistic parameters for mixtures, where maximum chemical detail is appropriate. Emissions assignments such shown on Table B-11 and given in the speciation database (Carter, 2008b) should be reserved for applications where using the more limited number of lumped model species is necessary and appropriate.

MECHANISM EVALUATION

The performance of the mechanism in simulating O_3 formation, rates of NO oxidation, and other measures of reactivity was evaluated by conducting model simulations of over 2500 environmental chamber experiments carried out in 11 different environmental chambers at 4 different laboratories[1]. The experiments included 682 single VOC experiments, consisting primarily of VOC - NO_x or VOC - NO_x experiments with added CO or alkane, 591 incremental reactivity experiments, and 973 experiments with mixtures, though approximately 2/3 of the mixture runs were replicate base case reactivity experiments of various types. These include not only the experiments used when evaluating the SAPRC-99 mechanism (Carter, 2000a), but also the more recent experiments carried out at out at our laboratories at CE-CERT through June, 2006, experiments carried out in the Tennessee Valley Authority (TVA) chamber that were used in the low NO_x mechanism evaluation study of Carter (2004), and also earlier University of North Carolina (UNC) chamber experiments used in the SAPRC-90 and RADM-2 mechanism evaluations of Carter and Lurmann (1990, 1991) and in the isoprene mechanism evaluation of Carter and Atkinson (1996).

The chambers whose data were used for mechanism evaluation are summarized on Table 20, the types of experiments are summarized on Table 21, and the individual experiments are listed in Table C-1 in Appendix C. The input files, chamber data, and the computer programs used for the chamber simulations will be made available on the SAPRC mechanism web site[2]. The results of the evaluation are given on Table C-1 and in the numerous figures in Appendix C, and are summarized below.

Note that the largest database of environmental chamber experiments used for mechanism evaluation for this project is from indoor chamber experiments carried out at the University of California at Riverside (UCR). These experiments serve as the primary basis for mechanism evaluation and any adjustments made to mechanisms for individual VOCs are based on simulations of UCR indoor chamber runs. However, simulations of the available experiments from the Tennessee Valley Authority (TVA) chamber a subset of the experiments carried out in the University of North Carolina (UNC) outdoor chamber were also carried out, and results are also shown for information purposes. We believe that the TVA chamber is reasonably well characterized for modeling, and the results of these simulations provide useful supporting information for mechanism evaluation. However, because of time and resource constraints we were unable to obtain and process the most complete and quality-assured set of UNC chamber data. The generally poor performance of the model in simulating the non-isoprene UNC experiments may reflect this. For this reason, the simulations of the UNC chamber experiments are shown for information only, and were not used as the primary basis for mechanism evaluation. A re-evaluation using an improved UNC chamber dataset may be appropriate, but was beyond the scope of this project.

The performance of the mechanism is measured primarily in terms of its ability to simulate O_3 formation and NO oxidation. The effect of the compounds on overall OH radicals in the incremental reactivity experiments is also assessed. Although the model simulations of the experiments also give information on the ability of the mechanism to predict other chemical transformations, such as rates of consumption of reactants other than NO and formation of various products besides O_3 that may have been measured, a comprehensive mechanism evaluation in this regard was beyond the scope of this project.

---

[1] The experiments used to evaluate mechanisms for some of the compounds for which mechanisms and reactivity estimates are given were carried out after the experiment list for this report was finalized in March, 2009. In those cases, citations referencing the reports giving results of the evaluations for those compounds are given in footnotes to Table 23.

[2] The SAPRC mechanism web site is at http://www.cert.ucr .edu/~carter/SAPRC.

Table 20. Summary of environmental chambers whose data were used for mechanism evaluation

ID	Brief description and references for additional information
	Chambers at the Statewide Air Pollution Research Center (SAPRC) or the College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California at Riverside (UCR)
EC	A 5774-liter evacuable chamber constructed of Teflon-coated aluminum with Quartz end windows. Located at SAPRC. Xenon arc solar simulator light source. Most experiments at ~50% RH and around 300°K. Experiments carried out 1975 - 1984. See Carter et al (1995a) for description of chamber and experimental methods and Carter (2000a) for a discussion of the modeling methods used. This chamber is now primarily being used for mechanistic studies.
ITC	One semi-collapsible ~6400-liter reactor constructed of 2 mil FTP Teflon film held in a framework. Blacklight light source. Located at SAPRC. Most experiments at ~50% RH and around 300°K. Experiments carried out 1982 - 1986. See Carter et al (1995a) for description of chamber and experimental methods and Carter (2000a) for a discussion of the modeling methods used. This chamber is now primarily being used for mechanistic studies.
ETC	One semi-collapsible ~3000-liter reactor constructed of 2 mil FTP Teflon film held in a framework. Blacklight light source. Located at SAPRC. Most experiments used dry air and carried out around 300°K. Experiments carried out 1989 - 1993. See Carter et al (1995a) for description of chamber and experimental methods and Carter (2000a) for a discussion of the modeling methods used. This chamber no longer exists.
OTC	Two completely collapsible ~20,000-liter "pillow bag" reactors constructed of 2 mil FTP Teflon located outdoors. Located at the outdoor laboratory at SAPRC. Natural sunlight irradiation. Two irradiations carried out simultaneously, one in Side "A" and the other in Side "B". Experiments used dry air, with temperature varying with ambient conditions. Experiments carried out 1992 - 1993. See Carter et al (1995a,b) for description of chamber and experimental methods and Carter et al (1995b) and Carter (2000a) for a discussion of the modeling methods used. This chamber no longer exists.
DTC	Two semi-collapsible ~5000-liter reactors constructed of 2 mil FTP Teflon film held in a framework. Initially located at the outdoor laboratory building at SAPRC, but subsequently re-constructed at CE-CERT. Two irradiations carried out simultaneously, one in Side "A" and the other in Side "B". Blacklight light source. Most experiments used dry air at around 300°K. Experiments carried out 1993 - 1999. See Carter et al (1995a) for description of chamber and experimental methods and Carter (2000a) for a discussion of the modeling methods used. This chamber no longer exists.
XTC	One semi-collapsible ~5000-liter reactor constructed of 2 mil FTP Teflon film held in a framework. Xenon arc light source. Located the outdoor laboratory building at SAPRC. Experiments used dry air at around 300°K. Experiments carried out in 1993. See Carter et al (1995a) for description of chamber and experimental methods and Carter (2000a) for a discussion of the modeling methods used. This chamber no longer exists.
CTC (≤82)	Semi-collapsible ~5000-liter reactor constructed of 2 mil FTP Teflon film held in a framework. Xenon arc light source. Located at CE-CERT. Experiments used dry air at around 300°K. Experiments carried out in 1994 - 1995. See Carter et al (1995a) for description of chamber and experimental methods and Carter (2000a) for a discussion of the modeling methods used. This configuration is applicable to runs from 11 through 82.

Table 20 (continued)

ID	Brief description and references for additional information
CTC (≥83)	Two semi-collapsible ~2500-liter reactors constructed of 2 mil FTP Teflon film held in a framework. Xenon arc light source. Located at CE-CERT. Experiments used dry air at around 300°K. Experiments carried out in 1995 - 1999. This configuration is applicable to runs 83 and higher. See Carter et al (1995a) for description of chamber and experimental methods and Carter (2000a) for a discussion of the modeling methods used. This chamber no longer exists.
EPA	(Also referred to as the UCR EPA chamber.) Two ~90% collapsible ~100,000-liter reactors constructed of 2 mil FEP Teflon film held on a framework with a moveable top for positive pressure control. Located in a temperature-controlled "clean room" clean room enclosure flushed with purified air. Located at CE-CERT. Can use either an argon arc solar simulator light source or blacklights. Two irradiations carried out simultaneously, one in Side "A" and the other in Side "B". Although the temperature and humidity can be varied, all experiments in this evaluation were carried out with dry air at around 300°K. Experiments carried out from 2003 through present, but latest run in this evaluation was carried out in mid-2006. See Carter (2004) and Carter et al (2005b) for a description of the chamber and experimental methods and Carter (2004) for a discussion of the modeling methods used. Note that mechanism evaluation experiments in this chamber can be carried out under lower NO_x conditions than the other chambers at UCR or the UNC outdoor chamber. This chamber is still in operation.
	Chamber at the Tennessee Valley Authority (TVA).
TVA	One 28,300-liter reactor constructed of 0.13 mm FEP Teflon film on a rigid frame located inside an enclosure flushed with purified air. Special procedures used to clean between experiments to permit experiments at lower concentrations. Light source consisted of blacklights and sunlamps. Experiments carried out at about 15% RH and the temperature varied from ~300-315°K. Experiments carried out in 1993 - 1995. See Simonaitis and Bailey (1995) and Bailey et al (1996) for a description of the chamber and experimental methods and Carter (2004) for a discussion of the modeling methods used. Note that mechanism evaluation experiments in this chamber were carried out under lower NO_x conditions than in the other chambers except for UCR EPA, but the chamber experience high background formaldehyde levels that needed to be taken into account when modeling the experiments (Carter, 2004). This chamber no longer exists.
	Chamber at the University of North Carolina (UNC)
UNC	A very large dual reactor chamber consisting of 5 mil FEP Teflon film held on a rigid A-frame structure located outdoors. Natural sunlight light source. Located in a rural site in North Carolina with filtered but otherwise unpurified air used for experiments that were conducted at ambient temperature. Two irradiations carried out simultaneously, one in side "R" and the other in side "B". Experiments are designated by their run date and side (e.g., JN1279R). Most of the experiments used in this evaluation were carried out between 1978 and 1985, but a few isoprene experiments were carried out in 1992 and 1993. See Jeffries et al (1982, 1985a,b) for descriptions of the chamber and experimental methods and Carter and Lurmann (1990, 1991) for a discussion of the modeling methods used for the earlier experiments and Carter and Atkinson (1996) for the isoprene experiments. Note that this may not be a complete dataset or contain the best quality-assured data from this chamber. This chamber has since been rebuilt and is probably not the primary chamber now used at UNC.

Table 21. Summary of types of experiments used for mechanism evaluation.

Designation	Mixture irradiated or description
Radical Source Characterization	
CO - NO$_x$	CO - NO$_x$
C4 - NO$_x$	n-Butane - NO$_x$
NO$_x$ Offgasing characterization	
CO - Air	CO - Air
HCHO - CO - Air	Formaldehyde - CO - Air
ACETALD - Air	Acetaldehyde - Air
VOC Mechanism Evaluation	
VOC - NO$_x$	VOC - NO$_x$
VOC - CO - NO$_x$	VOC - NO$_x$ with added CO
VOC - C4 - Air	VOC - air with added n-butane
VOC - C4 - NO$_x$	VOC - NO$_x$ with added n-butane
VOC - C2 - NO$_x$	VOC - NO$_x$ with added ethane
VOC - O3	VOC + O$_3$ (also includes control experiment in the other reactor without the VOC)
IR	Incremental reactivity experiment. Type of base case indicated
Standard surrogate - NO$_x$ experiments used in recent UCR experiments for mechanism evaluation	
Surg-8	Standard 8-component "full surrogate" consisting of n-butane, n-octane, ethene, propene, trans-2-butene, toluene, m-xylene and formaldehyde (e.g., Carter et al, 1995c; Carter, 2002)
Surg-7	Standard 8-component "full surrogate", above, but without formaldehyde (e.g. Carter and Malkina, 2005, 2007, Carter et al, 2005a)
Surg-3	Standard mini-surrogate consisting of ethene, n-hexane, and m-xylene (e.g., Carter et al, 1993, 1995c).
Surg-NA	Standard 8-componene "full surrogate" but without aromatics and formaldehyde (unpublished results from this laboratory).
Surg-E	Ethene surrogate consisting of ethene alone (e.g., Carter et al, 1995c).
Surg-x	Miscellaneous 3- or 4-componene surrogates (e.g., Carter et al, 1993, Carter and Malkina, 2002)
Types of surrogate or incremental reactivity base case experiments	
MIR1	Low ROG/NO$_x$, MIR-like conditions. NO$_x$ 300-500 ppb (e.g., Carter et al, 1993, 1995c)
MIR2	Low ROG/NO$_x$, MIR-like conditions, NO$_x$ < 100 ppb (e.g., Carter, 2002; Carter and Malkina, 2005, 2007, Carter et al, 2005a)
LN1	Lower NO$_x$, e.g., MOIR/2. NO$_x$ >100 ppb (e.g., Carter et al, 1993, 1995c)
LN2	Lower NO$_{x,,}$ e.g. MOIR/2 conditions, NO$_x$ < 50 ppb (e.g., Carter, 2002; Carter and Malkina, 2005, 2007, Carter et al, 2005a)
vary	Non-standard ROG/NO$_x$. Conditions varied
Older UCR and UNC and TVA surrogate and mixture - NO$_x$ experiments	
ITCsrg-4	Experiments in the ITC chamber (primarily) using a 4-component surrogate, primarily for the early incremental reactivity study of Carter and Atkinson (1987). Surrogate consisted of propene, n-butane, trans-2-butene, and m-xylene.
ITCsrg-4R	Based on ITCsrg-4, but with propene removed. Used in the study of Carter and Atkinson (1987).

Table 21 (continued)

Designation	Mixture irradiated or description
ECsrg-7	A surrogate mixture of seven hydrocarbons used in several runs in the SAPRC EC (Pitts et al, 1979). Consisted of n-butane, 2,3-dimethyl butane, ethene, propene, trans-2-butene, toluene, m-xylene
MDsrg-8	A surrogate mixture of 8 hydrocarbons used in the "multi-day effects" study of Carter et al (1984). Consisted of n-butane, n-pentane, isooctane, ethene, propene, isobutene, toluene, and m-xylene
TVAsrg-1	A complex surrogate mixture of alkanes, alkenes, and aromatics used in the TVA chamber (Simonaitis and Bailey, 1995; Bailey et al, 1996).
TVAsrg-2	A complex surrogate mixture of alkanes, alkenes, and aromatics used in the TVA chamber (Simonaitis and Bailey, 1995; Bailey et al, 1996).
UNCsrg-3	A simple surrogate of propene, n-butane and an aromatic used in the UNC chamber (Jeffries et al, 1982, 1985a).
SynUrb	A complex "synthetic urban" VOC mixture used in the UNC chamber (Jeffries et al, 1985a)
SynAuto	A synthetic auto exhaust VOC mixture used in the UNC chamber (Jeffries et al, 1985b)
UNCsrg-x	Miscellaneous surrogates used in the UNC chamber (Jeffries et al, 1982, 1985a).
Simple mixtures (incomplete surrogates)	
Mix-A	Mixture of alkanes
Mix-E	Mixture of alkenes
Mix-AE	Mixture of alkanes and alkenes
Mix-AO	Mixtures of alkanes and oxygenates (generally aldehydes)
Mix-EO	Mixture of alkenes and oxygenates
Mix-RO	Mixtures of aromatics and oxygenates (generally aldehydes)
Mix-AR	Mixtures of alkanes and aromatics
Mix-ER	Mixtures of alkenes and aromatics
Light Source Designations used in run listing	
A	Arc light (Xenon or Argon arc) solar simulator
Bl	Blacklights
Bs	Mixture of blacklights and sunlamps
S	Solar light

This would be a major effort because of the considerable amount of variation from experiment to experiment in terms of measurements of other species that were made, and the highly variable and uncertain quality of much of the measurements (e.g., see Carter et al, 1995a for a discussion of the measurement data for the earlier UCR chamber experiments). However, evaluations of model performance in simulating individual oxidation products was often used when developing mechanisms for individual VOCs when relevant data were available, and in general the mechanisms for these compounds retain the product yield predictions so developed when updated for this version.

Methods

The procedures used when evaluating the mechanism against the chamber data were the same as employed in previous evaluations of the SAPRC-90 (Carter and Lurmann, 1990, 1991) and SAPRC-99

(Carter, 2000a, 2004; Carter and Malkina, 2007) mechanisms. Briefly, evaluations of mechanisms using chamber data require an appropriate representation of the conditions of the chamber experiments that affect the simulation results. These include initial reactant concentrations, physical conditions such as temperature and dilution, light intensity and spectrum, and the major wall effects such as the chamber radical source, O_3 decays, NO_x offgasing, etc. These considerations are discussed in detail elsewhere (e.g., Carter et al, 1982; Carter and Lurmann, 1990, 1991; Carter et al, 1995a,b, 1997a; Carter, 2000a and references therein), and that discussion will not be duplicated here.

The parameters in the chamber effects model used when modeling the experiments for this mechanism evaluation are given in Table 22. Except for the parameters used to model the chamber-dependent radical source and NO_x offgasing, which have to be adjusted for each mechanism, the input data used in modeling the chamber experiments were the same as used in previous studies. The reports describing the methods used to derive the input data, and giving the chamber effects characterization parameters employed, are given in footnotes to Table 20. As indicated above, the input data files will be made available at the SAPRC mechanism web site.

The most important and variable chamber background effect is the "chamber radical source" first noted by Carter et al (1982) and background NO_x offgasing. The former causes enhanced NO oxidation and O_3 formation experiments, such as CO - NO_x or alkane - NO_x irradiations with no significant radical sources in the gas-phase mechanism, while the latter causes O_3 formation in experiments where NO_x has not been added. Both of these effects are attributed to offgasing of HONO, which have been observed experimentally in the SAPHIR outdoor chamber in Germany (Brauers et al, 2003, Rohrer et al, 2004) to occur at rates similar to the radial source and NO_x offgasing rates derived for the UCR EPA chamber (Carter et al, 2005b). The magnitudes of the radical source and NO_x offgasing effects are larger in the older chambers (Carter and Lurmann, 1990, 1991; Carter et al, 1995a, 2005b; Carter, 2000a), but they are still generally comparable to each other, consistent with the assumption that both are due to the same process. This is represented in the chamber model by the parameter RN, which is the rate of HONO offgasing relative to the light intensity as measured by the NO_2 photolysis rate.

Since HONO has not been measured directly in any of the chambers used for mechanism evaluation for the conditions relevant to the experiments, the HONO offgasing rate parameter has to be determined by adjusting the parameter so the model calculations can simulate results of the appropriate characterization experiments. The most sensitive experiments are the CO - NO_x and alkane (primarily n-butane) - NO_x experiments used for radical source characterization, and modeling these experiments is the primary method used to derive the RN parameters used when modeling the mechanism evaluation runs. The best fit parameters depend to some extent on the chemical mechanism used, particularly the rate constant for the OH + NO_2 reaction, which is the main radical terminating reaction in the characterization experiments. Since this rate constant changed in SAPRC-07 compared to SAPRC-99, the set of RN parameters used in the mechanism evaluation also changed.

The RN parameters that were used when modeling the chamber experiments for this mechanism evaluation are given on Table 22. They were derived to minimize biases in simulations of the radical source characterization experiments, as indicated on Table 21 and Table C-1 in Appendix C. For this purpose, experiments were grouped into "characterization sets" that were assumed to have similar chamber effects parameters. As discussed by Carter et al (1995a) and Carter (2002), for some chambers the conditions affecting radical sources and NO_x offgasing appeared to change from time to time due to changes in reactors, exposure to reactants, etc., and assignments to characterization sets are used to take this into account. The characterization sets associated with the individual experiments are included with the run listing in Table C-1.

Table 22. Chamber wall effect and background characterization parameters used in the environmental chamber model simulations for mechanism evaluation.

Cham.	Set(s)	Value	Discussion
RN-I (ppb)			Ratio of the rate of wall + hν -> HONO to the NO_2 photolysis rate.
EPA	2	0.0075	Average of values that gave best fits to n-butane - NO_x and CO - NO_x, radical source characterization and CO - air NO_x offgasing characterization experiments carried out in this chamber. Note that for Set 3 the best fit RN-I values depended on the reactor.
	3A	0.0165	
	3B	0.0115	
	4	0.0055	
	5	0.0110	
	6	0.0150	
	7	0.0100	
ITC	All	0.0475	Average of value of RS-I that gave best fits to n-butane - NO_x radical source characterization chamber experiments carried out in this chamber.
ETC	2-3	0.04	Same procedure as above
DTC	1	0.058	Same procedure as above
	3	0.210	
	4	0.300	
	10	0.055	
	11	0.092	
	12	0.310	
	13	0.170	
	14	0.095	
	15	0.063	
	16	0.240	
	17	0.083	
	18	0.074	
XTC	All	0.085	Same procedure as above
CTC	1	0.06	Same procedure as above
	2,3	0.10	
	4-8	0.095	
	9	0.115	
	10	0.08	
OTC		7.2e+9 exp(-9712/T) 0.063 @ 300K	Based on Arrhenius plots of values of RS-I that give fits to n-butane - NO_x chamber experiments carried out in this chamber for the average temperatures of the experiments.
EC	1	0.235	Based on the NO_2 dependence radical source derived by Carter et al (1982), adjusted to reduce biases in simulations of n-butane - NO_x experiments carried out in this chamber using this mechanism. The NO_2-dependent radical source term, RS-S, was reduced by an equal factor.
TVA	All	0.008	Estimated value. Could not be determined by modeling radical source characterization because of the large formaldehyde offgasing. See Carter (2004).
UNC	All	4.0e+14 exp(-12581/T) 0.248 @ 300K	Based on Arrhenius plots of values of RS-I that give fits to the few available alkane - NOx chamber experiments carried out in this chamber for the average temperatures of the experiments. Older experiments modeled by Carter and Lurmann (1990, 1991) were used.
RS-S (unitless)			Ratio of the rate of NO_2 + hν -> 0.5 HONO + 0.5 wall NO_x to the NO_2 photolysis rate.

Table 22 (continued)

Cham.	Set(s)	Value	Discussion
EC	1	0.0017	Based on the NO_2 dependence radical source derived by Carter et al (1982), adjusted downward by 20% to reduce biases in simulations of n-butane - NO_x experiments carried out in this chamber. The NO2-independent radical source term, RN-I, was reduced by an equal factor.
All others		0	Any dependence of apparent radical source on initial NOx levels in Teflon bag chambers was found to be much less than the run-to-run variability.
<u>HONO-I (ppb)</u>			Initial HONO in experiment, assumed to be independent of other reactants unless indicated.
EPA	All	0.05	Value that usually gives best fits to model simulations of results of n-butane - NO_x and CO - NO_x experiments in this chamber.
ITC	All	1.7	Average of initial HONO value that gave best fits to n-butane - NO_x chamber experiments carried out in this chamber. The RN-I parameter was optimized at the same time. The best fit initial HONO values appear to be approximately independent of the initial NO_2.
ITC	All	1.7	Similar procedure as above.
TVA	All	0.5	Similar procedure as above.
DTC	1	0.001 x $[NO_2]$init	Similar procedure as above, except for this chamber the best fit initial HONO appeared to be correlated with the initial NO_2 concentrations.
	3,4	0.004 x $[NO_2]$init	
	10,18	0.008 x $[NO_2]$init	
	11,14	0.006 x $[NO_2]$init	
	12,16	0.005 x $[NO_2]$init	
	13	0.009 x $[NO_2]$init	
	15	0.007 x $[NO_2]$init	
	17	0.003 x $[NO_2]$init	
XTC	All	0.012 x $[NO_2]$init	Similar procedure as above
CTC	All	0.008 x $[NO_2]$init	Similar procedure as above
EC	All	0.07 x $[NO_2]$init	Similar procedure as above
ETC, OTC, UNC		0	For most (though not all) characterization runs in these chambers the data are simulated best if the effect of any initial HONO is small compared to other chamber radical sources, o
<u>E-NO2/K1 (ppb)</u>			Ratio of rate of NO_2 offgasing from the walls to the NO_2 photolysis rate.
EC	1	0.10	Adjusted to fit O_3 formation in acetaldehyde/air run EC-253.
All Teflon Film Chambers		0	The NO_x offgasing caused by representing the radical source by HONO offgasing appears to be sufficient for accounting for NO_x offgasing effects in most cases. RN-I parameters adjusted to fit experiments sensitive to the radical source are consistent with NOx offgasing rates adjusted to fit pure air or aldehyde - air runs, to within the uncertainty and variability.
<u>K(NO2W) (min^{-1})</u>			Rate of unimolecular loss (or hydrolysis) of NO_2 to the walls.
All Teflon Film Chambers		1.6e-4	Based on dark NO_2 decay and HONO formation measured in the ETC by Pitts et al. (1984). Assumed to be the same in all Teflon bag chambers, regardless of volume.
EC	1	2.8e-4	Based on dark NO_2 decay and HONO formation measured in the EC by Pitts et al. (1984).
UNC	All	5.0e-5	Value used by Carter and Lurmann (1990, 1991) was not updated.

Table 22 (continued)

Cham.	Set(s)	Value	Discussion
<u>YHONO</u>			Yield of HONO in the unimolecular reaction (hydrolysis) of NO_2 on the walls.
All Teflon Film Chambers		0.2	Based on dark NO2 decay and HONO formation measured in the ETC by Pitts et al. (1984). Assumed to be the same in all Teflon bag chambers, regardless of volume.
EC	1	0.5	Based on dark NO2 decay and HONO formation measured in the EC by Pitts et al. (1984).
<u>E-ALD/K1 (ppb)</u>			Ratio of rate of formaldehyde offgasing from the walls to the NO_2 photolysis rate.
EPA	All	0.01	Gives best fits to formaldehyde data in most pure air irradiations and other experiments where formaldehyde should not otherwise be present.
TVA		0.045 + other sources (see discussion)	This chamber had significant wall offgasing of formaldehyde and assuming a constant offgasing rate did not give best fits to the data. The additional process required to fit the data, derived by Simonaitis et al (1997) and used by Carter (2004), are as follows: Walls + hν → WALLVOC; rate = NO_2 photolysis rate x 0.135 ppb WALLVOC + OH → HO2 + 0.2 HCHO; k = 2 x 10^4 ppm^{-1} min^{-1}
All other chambers		0	Simulations of characterization experiments do not require assuming formaldehyde offgasing. Formaldehyde measurements not sufficiently sensitive to determine formaldehyde offgasing.
<u>K(O3W) (min^{-1})</u>			Unimolecular loss rate of O_3 to the walls.
EPA	All	1.08e-4	Based on results of O_3 decays carried out in this chamber
ITC, ETC, DTC, XTC		1.5e-4	Based on results of O_3 decay in Teflon bag chambers experiments as discussed by Carter et al (1995a).
CTC	All	8.5e-5	Based on results of O_3 decay experiments in this chamber
OTC	All	1.67e-4	Similar procedure as above
EC	All	1.1e-3	Similar procedure as above
TVA	All	7.0e-4	Similar procedure as above
UNC	All	1.43e-4	Similar procedure as above
<u>k(N26I) (min^{-1})</u>			Rate constant for <u>N2O5 -> 2 Wall-NO_x</u>. This represents the humidity-independent portion of the wall loss of N_2O_5, or the intercept of plots of rates of N_2O_5 loss against humidity.
All Teflon Bag Chambers		2.8e-3	Based on N_2O_5 decay rate measurements made by Tuazon et al (1983) for the ETC. Assumed to be independent of chamber size (Carter et al, 1995a).
EC	1	4.7e-3	Based on N_2O_5 decay rate measurements made by Tuazon et al (1983) for the EC. See also Carter et al (1995a).
<u>k(N26S) (ppm^{-1} min^{-1})</u>			Rate constant for <u>N2O5 + H2O -> 2 Wall-NOx</u>**.** This represents the humidity dependent portion of the wall loss of N_2O_5, or the slope of plots of rates of N_2O_5 loss against humidity. Note that this is in addition to the N_2O_5 hydrolysis reaction in the gas-phase mechanism.
All Teflon Bag Chambers		1.1e-6	Based on N_2O_5 decay rate measurements made by Tuazon et al (1983) for the ETC. Assumed to be independent of chamber size (Carter et al, 1995a).
EC	1	1.8e-6	Based on N_2O_5 decay rate measurements made by Tuazon et al (1983) for the EC. See also Carter et al (1995a).

Table 22 (continued)

Cham.	Set(s)	Value	Discussion
EPA	All	0	Assumed to be negligible compared to the homogeneous process already in the base mechanism
UNC	All	2.0e-8	Value used by Carter and Lurmann (1990, 1991) was not updated.
k(XSHC) (min^{-1})			Rate constant for OH -> HO2. This represents the effects of reaction of OH with reactive VOCs in the background air or offgassed from the chamber walls. This parameter does not significantly affect model simulations of experiments other than pure air runs.
All Teflon Bag Chambers		250	Estimated from modeling several pure air in the ITC (Carter et al, 1996d), and also consistent with simulations of pure air runs in the ETC (Carter et al, 1997a).
EC	1	0	Assumed to be negligible because the EC is generally evacuated overnight between experiments (Carter et al, 1995a).
EPA, TVA		0	Assumed to be negligible because steps are taken to reduce background effects for low concentration experiments.
UNC		750	Value used by Carter and Lurmann (1990, 1991) was not updated.
H2O (ppm)			Default water vapor concentration for runs where no humidity data are available.
EPA	All	3.4e+2	The EPA chamber experiments used for mechanism evaluation to date were not humidified. This is the expected upper limit water concentration.
ITC	All	2.0e+4	This corresponds to ~50% RH at 303K, which is the condition for most experiments in this chamber.
DTC	4	2.0e+4	This corresponds to ~50% RH at 303K, which is the condition for experiments in this characterization set. (The other DTC experiments are not humidified)
EC	1	2.0e+4	This corresponds to ~50% RH at 303K, which is the condition for most experiments in this chamber. Humidity data are available for most EC runs, so the default is usually not used.
TVA, UNC		(no default)	The water concentration is specified in the input files for all experiments.
All Other Chambers or char. sets.		1.0e+3	Experiments in these chambers were carried out using dried purified air. The limited humidity data for such runs indicate that the humidity was less than 5%, probably no more than ~2.5%, and possibly much less than that. The default value corresponds to ~2.5 - 3% RH for the conditions of most experiments.
Dilution rate (min^{-1})			Default rate of dilution in the experiment (used for most experiments if no dilution specified for the experiment)
EPA	All	0	Dilution expected to be small because of the design of the chamber
ITC	All	0	Dilution not well characterized but assumed to be small.
ETC	All	8.0e-5	Based on CO dark decays or other dilution characterization data.
DTC	1 3,4 10-18	5.3e-5 1.8e-4 5.3e-5	Similar procedure as above
XTC	All	2.7e-5	Similar procedure as above
CTC	All	6.7e-5	Similar procedure as above
OTC	All	6.7e-5	Similar procedure as above
EC	All	2.0e-4	Similar procedure as above

Table 22 (continued)

Cham.	Set(s)	Value	Discussion
TVA		(no default)	Dilution specified in input files for each experiment
UNC	All	2.0e-4	Value used by Carter and Lurmann (1990, 1991) was not updated.

Note that, as discussed by Carter (2002) and Carter et al (2005b), the UCR EPA and the TVA chambers have much lower apparent NO_x offgasing rates than the older chambers, because these chambers were designed for conducting experiments at lower pollutant concentrations. Runs in these chambers were generally carried out at lower pollutant levels than in the other chambers, and the concentrations are generally more representative of ambient conditions. However, the TVA chamber had very high background levels of formaldehyde (Carter, 2002), so of these two chambers the UCR EPA chamber has the lowest overall background effects.

Although most of the mechanism evaluation is based on simulations of environmental chamber experiments, we will also present results of simulations of the "direct reactivity" experiments developed by Carter and Malkina (2002). These consist of plug flow experiments where the effect of adding the VOC to HONO - air irradiations is determined. In the absence of added VOCs, the HONO - air plug flow irradiations results in the formation of NO, which is measured. If a VOC is added to the mixture, the OH radicals formed in the photolysis of HONO become peroxy radicals that convert the NO to NO_2, and, if the amount of added VOC is sufficient to consume all the NO, causes O_3 to be formed. The change in NO consumption and O_3 formation, relative to the no-VOC case, for the limit of zero added VOC is the measure of direct reactivity that is used. Model calculations carried out by Carter and Malkina (2002) show that this measurement is sensitive to the rate constant for the reactions of the VOC and the number of NO to NO_2 conversions caused when it reacts, but is not sensitive to indirect reactivity effects such as effects of VOCs on radical or NO_x levels. They showed that the results were generally consistent with the predictions of the SAPRC-99 mechanism except for benzene and toluene, where the direct reactivities were significantly overpredicted.

The methods used to simulate the direct reactivity experiments for this evaluation were the same as described by Carter and Malkina (2002) for SAPRC-99.

Data Presented

The results of the model simulations of the various types of experiments are given primarily in various plots and tables in Appendix C, and a few representative results are presented in conjunction with the discussion below. In most cases, results are given for SAPRC-99 as well as this version of the mechanism, so the changes caused by the mechanism update can be assessed. As indicated above, the performance of the mechanism is measured primarily in terms of its ability to simulate O_3 formation and NO oxidation, though the effect of the compounds on overall OH radicals in the incremental reactivity experiments is also assessed.

The amount of O_3 formed and NO oxidized in the experiments is measured by the quantity $\Delta([O_3]-[NO])$, which is calculated by $[O_3]_t$ - $[NO]_t$ - ($[O_3]_0$ - $[NO]_0$), where $[O_3]_0$, $[NO]_0$, $[O_3]_t$, and $[NO]_t$ are the initial and time=t concentrations of ozone, and NO, respectively. As discussed previously (e.g., Carter and Atkinson, 1987; Carter and Lurmann, 1990, 1991), this gives a measure of the ability of the model to simulate the chemical processes that cause ozone formation that gives a useful measure even where ozone is suppressed by the presence of excess NO. The ability of the mechanism to simulate this quantity in the experiments is measured by its "model error", which is calculated as

$$\Delta([O_3]\text{-}[NO])\text{ model error} = \{\Delta([O_3]\text{-}[NO])_{\text{model}} - \Delta([O_3]\text{-}[NO])_{\text{experimental}}\} / \Delta([O_3]\text{-}[NO])_{\text{experimental}}.$$

These values are calculated for each hour of the experiments, with the experimental values being derived by linear interpolation if no measurement were made exactly on the hour. Table C-1 in Appendix C gives the model errors for the second hour and the sixth hour (or final hour if the experiment was less than 6 hours) for all the experiments, and distributions of these values are shown for various types of experiments as discussed below.

Because of the very large number of VOC - NO_x and mixture - NO_x experiments used in the evaluation, in most cases experimental and calculated concentration time plots are not shown for individual experiments, and only distributions of model errors are presented. The model error results for the different types of experiments are shown in various figures in Table C-1 and in the discussion of the results below. These figures show how the average model errors vary with time during the experiments, which give information on the model performance in terms of simulating rates of NO oxidation and O_3 formation, as well as simulating final O_3 yields. These figures also show distribution plots of model errors for hour 2 and final $\Delta([O_3]\text{-}[NO])$. These show the degree of run-to-run variability of model performance in simulating these quantities. Results for comparable types of experiments are shown together, but because of the large number of types of experiments, a relatively large number of plots is needed.

As indicated in Table 20, a large number of mechanism evaluation experiments consisted of incremental reactivity experiments, and a different method was used to present the results for these experiments. Incremental reactivity experiments consist of simultaneous (or alternating) irradiations of a "base case" reactive organic gas (ROG) - NO_x mixture providing a simplified model of ambient chemical conditions, and irradiations of the same mixture with a test compound or mixture added. In this case the measures of model performance of interest concern the ability of the mechanism to predict the effects of the compound on the experiment. However, it is also important to see how well the model simulates the base case experiment as well, because if it performs poorly it may introduce errors in the simulations of the effects of adding the test compound if the chemical conditions influencing these effects are not correctly simulated.

Because of the relatively limited number of incremental reactivity experiments for any given compound combined with the additional considerations involved in assessing model performance for such experiments, the presentation of the evaluation results for the incremental reactivity experiments in Appendix C give plots for each experiment. These include experimental and calculated time plots of $\Delta([O_3]\text{-}[NO])_{\text{Base}}$, $\Delta([O_3]\text{-}[NO])_{\text{Test}}$, and IR $\Delta([O_3]\text{-}[NO])$, where $\Delta([O_3]\text{-}[NO])_{\text{Base}}$ and $\Delta([O_3]\text{-}[NO])_{\text{Test}}$ are the Δ([O3]-[NO]) in the base case and the added test VOC experiments, respectively, and

$$\text{IR }\Delta([O_3]\text{-}[NO]) = \{\Delta([O_3]\text{-}[NO])_{\text{Test}} - \Delta([O_3]\text{-}[NO])_{\text{Base}}\} / \text{amount of test VOC added}$$

where $\Delta([O_3]\text{-}[NO])_{\text{Base}}$ and $\Delta([O_3]\text{-}[NO])_{\text{Test}}$ are the Δ([O3]-[NO]) in the base case and the added test VOC experiments, respectively. The IR $\Delta([O_3]\text{-}[NO])$ values are given in molar units (e.g., ppm $\Delta([O_3]\text{-}[NO])$ / ppm VOC added) if the test VOC is a single compound, or in mole carbon units if the test VOC is a complex mixture such as a petroleum distillate. Each figure includes plots for experiments with a single compound or group of similar compounds.

Note that in the incremental reactivity experiments carried out in the ETC, the base case experiments were not carried out at the same time as the added test VOC experiments, but were carried out separately. This is because this is a single reactor chamber that does not permit simultaneous injections and irradiations of common reactants. For those experiments, the base case results for a given added test VOC experiment were interpolated or derived using correlations between initial reactant concentrations and other characterization results in the base case experiment. Therefore, in the plots of the $\Delta([O_3]-[NO])$ data, the figures only show the model calculations for the base case experiment, not the experimental data.

The figures with the evaluation results for the incremental reactivity experiments also show plots of the experimental and calculated effects of the VOC on the integrated OH radical levels. This is useful for mechanism evaluation because an important factor affecting a VOC's incremental reactivity is its effect on overall radical levels, which affects O_3 formation caused by the reactions of other VOCs that are present. For radical inhibiting VOCs such as higher alkanes, the reduced O_3 formation caused by the effect of the VOCs on the reactions of the other compounds present counter-acts the direct O_3 formation caused by the compound's own reactions, resulting in a low net incremental reactivity for $\Delta([O_3]-[NO])$. However, for such compounds the effects on integrated OH levels, or IntOH are quite large, indicating that the compound indeed is having a large effect on the chemistry of the system.

The IntOH levels in the experiments are calculated from the rates of consumption of the most reactive VOC in the base case mixture that reacts only with OH radicals (usually m-xylene but sometimes n-octane or 1,3,5-trimethylbenzene) (Carter et al, 1993). The effect of the test VOC on this quantity is measured by

$$\text{IR IntOH} = \{\text{IntOH}_{\text{Test}} - \text{InOH}_{\text{Base}}\} \text{ / amount of test VOC added}$$

where $\text{IntOH}_{\text{Base}}$ and $\text{IntOH}_{\text{Test}}$ are the IntOH values derived from the base case and the added test VOC experiments, respectively. They are given in units of ppt-minute per ppm of test VOC added if the test VOC is a compound, or ppt-minute per ppmC of test VOC if it is a complex mixture.

Results

Results for Chamber Characterization Experiments

The results of the simulations of the radical source and NO_x offgasing characterization experiments are shown on Figure 5 and Figure 6, respectively. These show distribution of model errors for both the SAPRC-99 and SAPRC-07 mechanisms as described above. It can be seen that there is relatively large variation from run to run, indicating the variability of the chamber effects related to radical source and NO_x offgasing. The average biases for the radical source characterization runs are generally small being within ±25%, as would be expected since the radical source parameters were adjusted to minimize the biases. Except for the single CTC experiment, the biases for the NO_x offgasing characterization runs are also not large compared to the variability, despite the fact that, except for the TVA chamber where the large formaldehyde offgasing makes runs insensitive to the chamber radical source, the NO_x offgasing parameters were adjusted based on the radical source characterization runs. This is consistent with the expectation that they are both due to the same effect.

From the perspective of mechanism evaluation it is important to realize that these radical source and NO_x offgasing characterization experiments are, by design, particularly sensitive to these variable chamber effects. The experiments used for mechanisms evaluation, discussed in the following section, are much less sensitive to these effects, and variabilities in radical source or NO_x offgasing should not be important sources of variability in the simulations of these experiments. However, it is important that these chamber effects not be a source of bias in the simulations of the mechanism evaluation runs, so it is important that appropriate values of the parameters representing these effects be used.

Results for Mechanism Evaluation Experiments

The performance of the SAPRC-07 mechanism in simulating NO oxidation and O_3 formation in the mechanism evaluation experiments is given in Table C-1 and in the various figures in Appendix C. The ability of the mechanism to simulate effects of the added test compounds on integrated OH levels in the incremental reactivity experiments is also shown in the figures for those experiments. For comparison purposes, results for SAPRC-99 are also shown on the figures, except for those few compounds that are not represented in SAPRC-99. The results for various types of experiments are summarized below.

Overall Performance in Simulating Entire Dataset

Figure 7 shows the distributions and averages of model errors in the SAPRC-07 and SAPRC-99 simulations of NO oxidized and O_3 formation in the entire set of mechanism evaluation chamber experiments modeled for this project. It can be seen that both mechanisms have essentially no bias in simulating $\Delta([O_3]\text{-}[NO])$ after the first hour of the experiment, though they both tend to slightly overpredict NO oxidation rates in the first hour. The same is true for the SAPRC-99 simulations of the mixture experiments. On the other hand, the updated mechanism has a small positive average bias in simulating the mixture experiments, averaging about 20% for the first hour (only slightly greater than that for SAPRC-99), going down to about 6% by the end of the run. However, this bias is small compared to the overall variability of the fits, which are within ±30% for most experiments for both mechanisms. Therefore, this slight positive bias for the updated mechanism in simulating the mixture runs may not be significant.

The reason for the slight positive bias in the simulations of $\Delta([O3]\text{-}[NO])$ in the mixture runs, if significant, is uncertain. The results for the single compounds or individual mixtures do not clearly indicate a cause in terms of particular compounds or types of compounds. It is considered unlikely that the slightly increased positive bias is due to problems with chamber characterization, since the most important chamber characterization parameters, regarding radical sources and NO_x offgasing, were re-adjusted for this version of the mechanism, and the other parameters were the same as used for SAPRC-99.

Indeed, if anything, Figure 5 and Figure 6 suggest that the parameters used with updated mechanism may be slightly biased towards being too unreactive in this regard. Of the rate constant updates made to the base mechanism, potentially the most important is the increase in the OH + NO_2 reaction, which is a major radical termination process that is important in essentially all experiments. But the increase, by itself, should cause slower NO oxidation and O_3 formation, which is opposite of the direction seen. On the other hand, if parameters in the mechanisms for the individual VOCs are adjusted to compensate for this change, it might cause increased reactivity in simulations of experiments that are more sensitive to these parameters than the OH + NO_2 rate constant. As indicated below, some uncertain mechanistic parameters (primarily nitrate yields in peroxy + NO reactions or yields of photoreactive aromatic products) had to be re-adjusted for the updated mechanism to fit results of reactivity and single VOC - NO_x experiments. This may need to be investigated.

Evaluation Experiments for Individual VOCs

The major mechanism evaluation dataset consisted of the >1200 experiments carried out to evaluate mechanisms of almost 130 individual compounds and mixtures. These compounds or mixtures are listed on Table 23, along with an indication of the number and types of experiments for each, and references to the figure or figures in Appendix C where the results of the evaluation are presented. Table 23 also indicates whether any uncertain parameters were adjusted in the mechanisms as a result of this evaluation, and gives codes and comments concerning the overall quality of the fits, which are described

Radical Source Characterization Runs

Chamber	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
EPA	48	6%	4%	5%	7%
Indoor TC [a]	141	1%	0%	-8%	-3%
EC	7	9%	21%	-19%	-3%
TVA	8	-20%	-5%	-21%	-16%
OTC	6	-6%	-6%	-8%	-8%
UNC	6	-1%	20%	-14%	17%

[a] ITC, ETC, DTC, XTC, and CTC

◆ UCR EPA
■ Indoor TC
▲ EC
× TVA
✱ OTC
● UNC

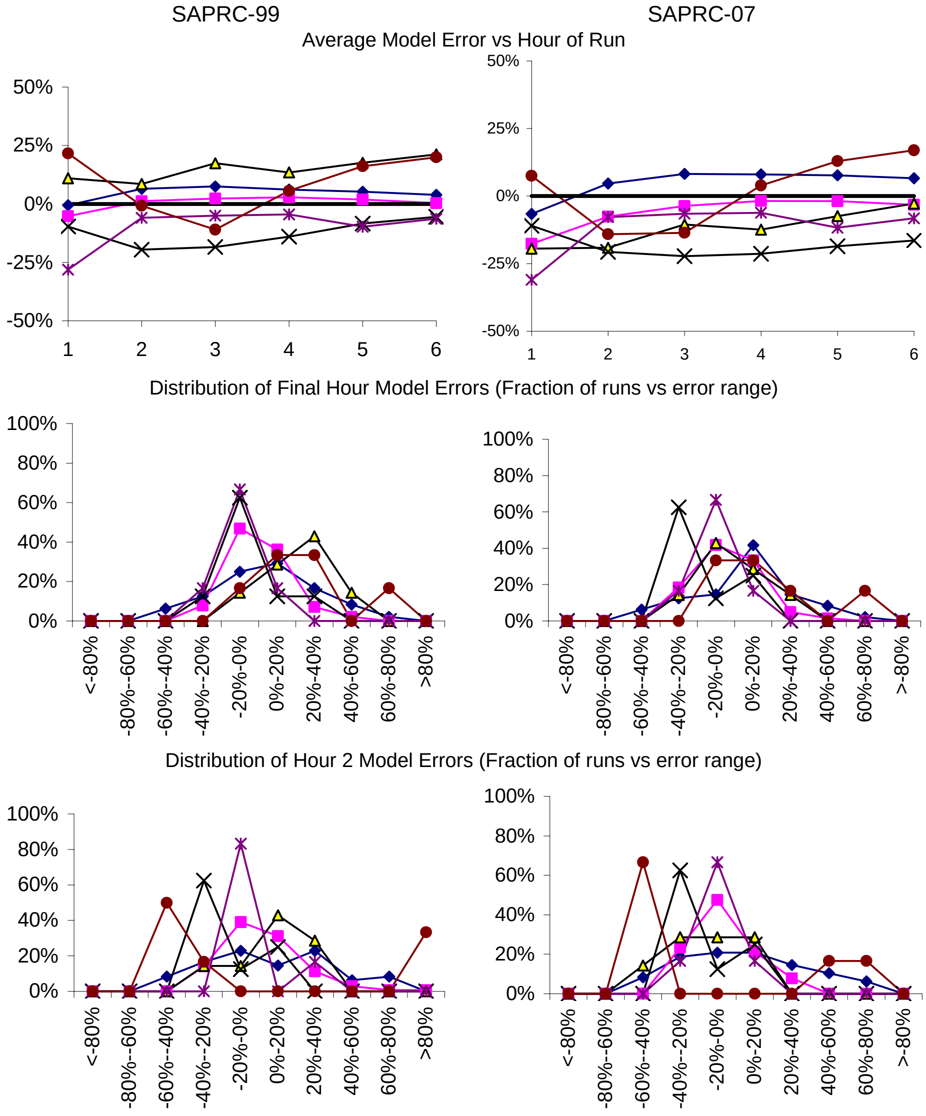


Figure 5. Distribution of Δ([O$_3$]-[NO]) model errors for the radical source characterization experiments.

NOx Offgasing Characterization Runs

Chamber	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
UCR EPA	36	-17%	-5%	-13%	20%
CTC	1	-11%	54%	-19%	36%
ITC	3	-31%	-28%	-33%	-30%
TVA	2	-6%	9%	-10%	10%

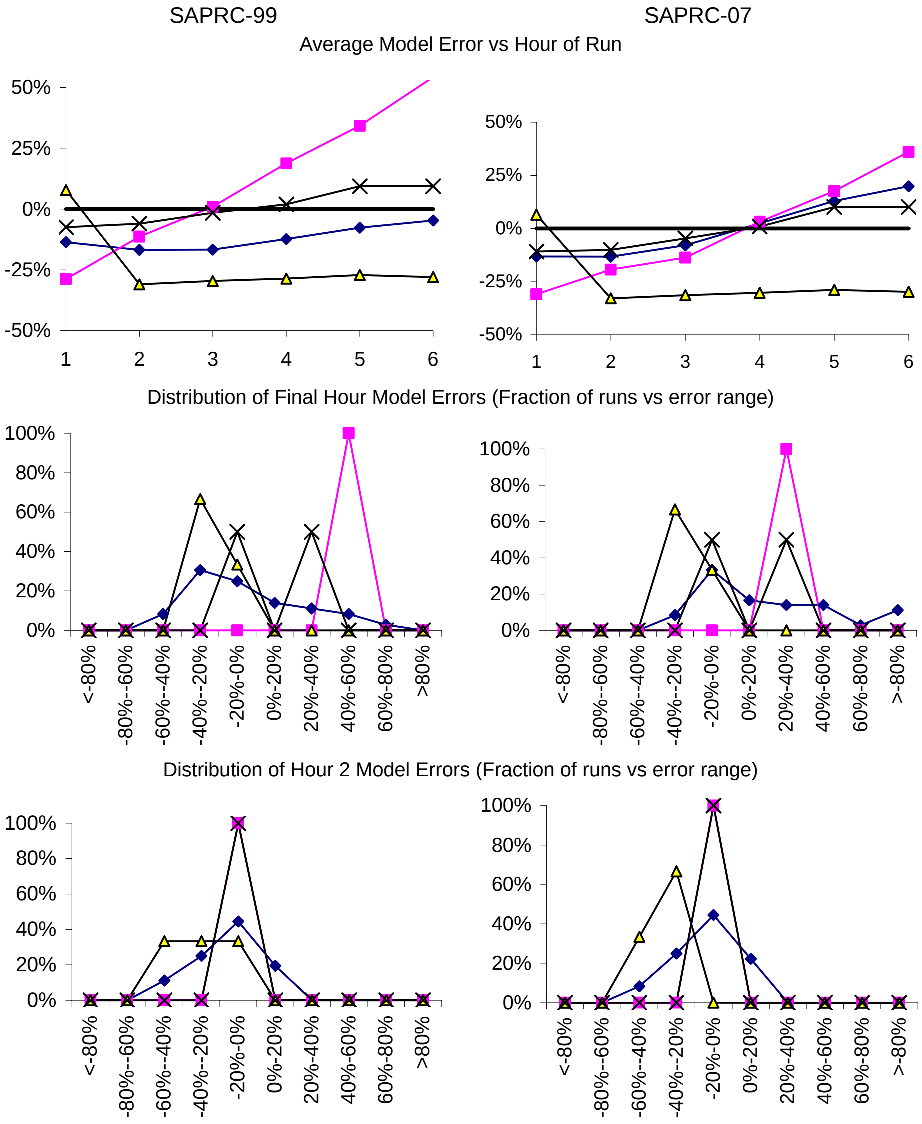


Figure 6. Distribution of O_3 model errors for the NO_x offgasing characterization experiments

All Experiments

Group	Runs	Average Δ([O3]-[NO]) Model Error							
		SAPRC-99				SAPRC-07			
		2-Hr		Final		2-Hr		Final	
		Avg	Sdev	Avg	Sdev	Avg	Sdev	Avg	Sdev
Single VOC	682	3%	34%	2%	19%	0%	34%	0%	26%
Mixtures	1559	4%	32%	2%	20%	10%	40%	5%	23%

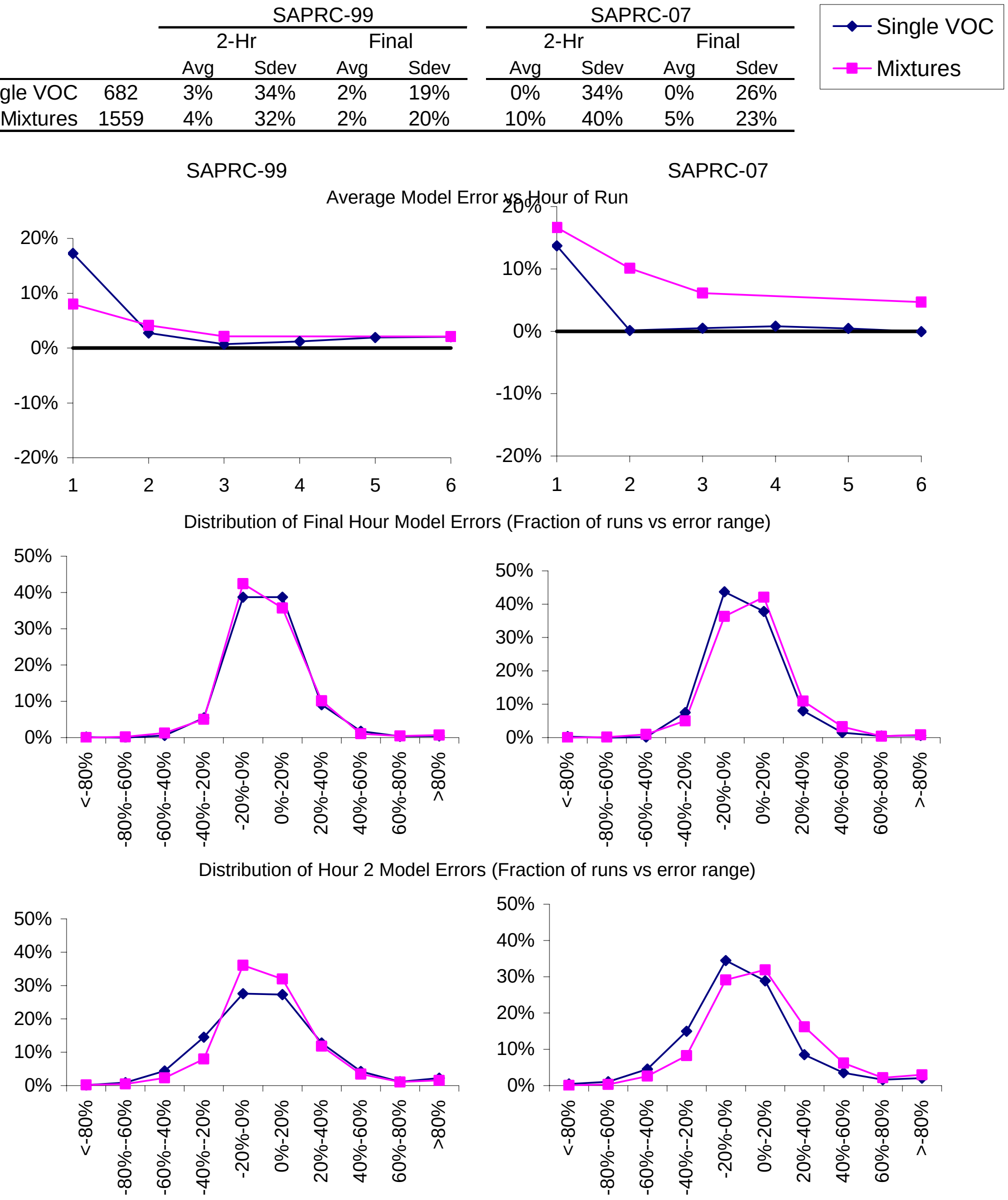


Figure 7. Distributions of Δ([O_3]-[NO]) model errors for all of the single VOC - NO_x and mixture - NO_x experiments used in the mechanism evaluation.

Table 23. Summary of mechanism evaluation results using chamber experiments for individual compounds and mixtures.

Compound or Mixture	No. Runs [a]		Fig. No. [b]		O_3-NO Fits [c]		Adj [d]	Note [e]
	Single	Rct'y	Single	Rct'y	Rate	Max		
Single Compounds (or simple isomeric mixtures)								
Carbon monoxide		13		1	ok	ok		
Ethane		7		2	ok	ok		
Propane		3		2	ok			
N-Butane		10		3	ok	ok		
N-Hexane		3		4	ok	ok		
N-Octane		13		5	ok	ok		
N-Dodecane		9		6	ok	+1		
N-Tetradecane		8		7	ok	+1		
N-Pentadecane		2		8	ok	+1		
N-C16		5		8	ok	+1		
Isobutane		4		9	ok			
2,2,4-Trimethyl pentane		2		9	ok			1
2,6-Dimethyl octane		5		9	ok	ok		
2-Methyl nonane		5		10	ok	+1		
3,4-Diethyl hexane		6		10	ok	+1		
Cyclohexane		6		11	ok	ok		
Hexyl cyclohexane		6		11	ok	ok		
Octyl cyclohexane		7		12	ok	ok		
Ethene	49	4	13	14	ok	ok	Or	
Propene	190	10	15	16	ok	ok	Or	
1-Butene	6		17		ok	ok	Or	
1-Hexene	3		17		-2	-2	Or	
Isobutene	2	3	18	19	ok			
Trans-2-butene	6	9	18	19	ok	ok		
Isoprene	28	10	20	21	ok	ok		
3-carene	4		22		-1	-1		
α-Pinene	6	4	22	23	ok	ok	Or, yN	
β-Pinene	6	2	22	23	ok	note	Or, yN	2
d-Limonene	7	3 [f]	22	23	ok	ok		
Sabinene	3		22		ok	ok		
Cyclohexene		1		24	ok	ok		
Styrene		6		25	ok	ok		
Benzene	9	4	25	27	note	ok	yP	3,4
Toluene	60	6	28	30	note	ok	yP	4,5,6
Ethyl benzene	8	3	29	30	ok	ok	yP	
m-Xylene	66	17	31	34,35	ok	ok	yP	6
o-Xylene	18	2	32	35	ok	ok	yP	7
p-Xylene	14	1	33	35	ok	ok	yP	6
1,2,3-Trimethyl benzene	9	2	36	39	ok	ok	yP	
1,2,4-Trimethyl benzene	11	2	37	39	ok	ok	yP	
1,3,5-Trimethyl benzene	21	1	38	39	note	note	yP	8
Naphthalene	5		40		+1	ok	Prm	
Tetralin	5		40		+1	ok	Prm	

Table 23 (continued)

Compound or Mixture	No. Runs [a]		Fig. No. [b]		O_3-NO Fits [c]		Adj [d]	Note [e]
	Single	Rct'y	Single	Rct'y	Rate	Max		
2,3-Dimethyl naphthalene	4		40		+1	+1	Prm	
Acetylene	4	7	41	42	-1	-1		9
Methanol		3		43	ok			
Ethanol		3		43	ok			
Isopropyl alcohol		10		44	ok	ok		
t-Butyl alcohol		7		45	ok	+1	yN	
1-Octanol		4		46	ok	+1		
2-Octanol		3		46	ok	+1		
3-Octanol		3		46	ok	+1		
Ethylene glycol		5		47	ok	ok		10
Propylene glycol		12		48	ok	ok		10
Dimethyl ether		4		49	ok			
Diethyl ether		6		49	ok	ok	yN	
Methyl t-butyl ether		4		50	ok			
1-Methoxy-2-propanol		6		51	ok	+1		
2-Ethoxyethanol		3		52	ok			
2-(2-Ethoxyethoxy) ethanol		3		52	ok			
2-Butoxyethanol		7		53	ok	ok		
2-(2-Butoxyethoxy)-ethanol		3		54	ok	ok	yN	
Methyl acetate		7		55	ok	ok		
Ethyl acetate		9		56	ok	ok		11
Isopropyl acetate		3		57	ok	ok		
t-Butyl acetate		6		57	ok	+1	yN	
Methyl isobutyrate		7		58	ok	ok		
Methyl pivalate		6		59	ok	ok		
n-Butyl acetate		8		60	ok	+1		
Dimethyl carbonate		6		61	ok	ok	yN	
Methyl isopropyl carbonate		5		61	ok	ok	yN	
Propylene carbonate		7		62	-1	ok	yN	
1-Methoxy-2-propyl acetate		6		63	ok	+1	yN	
Dimethyl succinate		6		64	ok	ok	yN	
Dimethyl glutarate		6		64	ok	ok	yN	
Texanol® isomers		4		65	ok	ok		
Furan	8			66	note	note	yP	12
2-Methyl furan	2		67		ok	ok	yP	
3-Methyl furan	6		67		ok	ok	yP	
2,5-Dimethyl furan	2		67		ok	ok	yP	
Benzyl alcohol	6	3	68	69	ok	ok	yP	
Formaldehyde	33	8	70	71	ok	ok		
Acetaldehyde	18	5	72	73	ok	ok		
Acrolein	3		74		ok	ok		
Methacrolein	12		74		ok	ok		
Benzaldehyde		3		75	ok	ok		
Acetone	7	10	76	77	note	note	QY	13,14
Methyl ethyl ketone	6	5	78	79	ok	ok	QY	13

Table 23 (continued)

Compound or Mixture	No. Runs [a]		Fig. No. [b]		O_3-NO Fits [c]		Adj [d]	Note [e]
	Single	Rct'y	Single	Rct'y	Rate	Max		
2-Pentanone	1	4	78	80	ok	ok	QY	
2-Heptanone	1	3	78	81	note	note	QY	15
4-Methyl-2-pentanone		8		81	ok	ok		
Cyclohexanone		9		82	ok	ok		
Methyl vinyl ketone	6		83		ok	ok		
o-Cresol	1		84		ok	ok	Prm	16
m-Cresol	1	1	84	85	-2	ok?		16,17
p-Cresol	1		84		ok	ok?		16,18
Para toluene isocyanate		6	86		ok	ok	Prm	
2,4-Toluene diisocyanate		7	87		ok	ok	Prm	
2,6-Toluene diisocyanate		2	87		ok	ok	Prm	
N-Methyl-2-pyrrolidone		6	88		ok	ok	yN	
N-Propyl bromide		6	89		-1	+2		19
N-Butyl bromide		6	89		-1	+2		19
Trichloroethylene		8	90		+2	+2		20
trans 1,3,3,3-Tetrafluoropropene		(See notes)			ok	ok	yN	29,30
2,3,3,3-Tetrafluoropropene		(See notes)			ok	ok	yN	29,31
1,3-Dichloropropene mixture	6	3	91	92	ok	ok		21
2-(Chloromethyl)-3-chloropropene		1		93	-1	?		20
Chloropicrin	6	5	94	95	ok	ok		
Chlorine	2	1		96	ok	ok		22
Hexamethyldisiloxane		3		97	ok		Prm	
Hydroxymethyldisiloxane		4		97	ok		Prm	
D4 cyclosiloxane		3		97	ok		Prm	
Carbon disulfide		4		98	ok	ok	Oth	21
Methyl isothiocyanate		4		98	ok	ok	Oth	21
Dimethyl sulfoxide	2	6	99	100	-2	ok	Oth	23
S-ethyl dipropylthiocarbamate (EPTC)		5		101	ok	ok	Oth	21
Ethanolamine		5 [f]		108	ok [g]		Init	27
2-Amino-2-methyl-1-propanol		7 [f]		109	ok [g]		Init	28
Isopropyl amine		1 [f]		108	ok [g]	+2	Init	27
t-Butyl amine		1 [f]		109	ok [g]	+2	Init	28
Methyl Iodide	7	3 [f]	110	111	ok	+1	Oth	26
Complex Mixtures								
Safety-Kleen mineral spirits "A" (type I-b, 91% alkanes)		3		102	ok	+1		24
Safety-Kleen mineral spirits "B" (type II-c)		3		102	ok	+1		24
Safety-Kleen mineral spirits "C" (type II-c)		3		102	ok	+1		24
Safety-Kleen mineral spirits "D" (type II-c)		3		102	ok	+1		24

Table 23 (continued)

Compound or Mixture	No. Runs [a]		Fig. No. [b]		O_3-NO Fits [c]		Adj [d]	Note [e]
	Single	Rct'y	Single	Rct'y	Rate	Max		
Exxon Exxol® D95 Fluid		6		103	ok	ok		24
Exxon Isopar® M Fluid		5		103	ok	ok		24
Oxo-decyl acetate		5		104	ok	ok		24
VMP naphtha		4		105	ok	ok		24
Kerosene		4		105	ok	ok		24
Dearomatized Alkanes, mixed, predominately C10-C12 (ASTM1C)		2		106	ok	ok		24
Synthetic isoparaffinic alkane mixture, predominately C10-C12 (ASTM3C1)		4		106	ok	ok		24,25
Reduced aromatics mineral spirits (ASTM1B)		3		106	ok	ok		24
Regular mineral spirits (ASTM1A)		3		106	ok	ok		24
Aromatic 100		4		107	ok	ok		24

[a] Number of chamber experiments. "Single" refers to single VOC - NOx or VOC + CO or alkane - NOx irradiation; "Rct'y" refers to incremental reactivity experiment.

[b] Figure number in Appendix C where mechanism performance for single VOC or incremental reactivity experiments is shown.

[c] Qualitative indication of ability of mechanism to fit initial rates of O3 formation and NO oxidation ("rate") and final ozone yields ("Max"). The former is more indicative of model performance under relatively high NOx, MIR-like conditions, and the latter is indicative of model performance in simulating O3 impacts under lower NOx conditions. If blank, then data are not available to evaluate this aspect of the mechanism. Codes used are as follows:

ok Model simulates most of the data within the experimental variability, with low or no apparent biases.

±n Model tends to overpredict (+) or underpredict (-) O_3 yield or O_3 formation and NO oxidation rates. ±1 = moderate but apparently consistent biases; ±2 = potentially significant biases

? The data are insufficient to evaluate this aspect of the mechanism.

note See note for a discussion of the model performance.

[d] Indicates if mechanism was adjusted to fit the data in this evaluation. Codes indicate the type of adjustment, as follows:

yN Nitrate yield in peroxy + NO reaction(s) adjusted

yP Yield of photoreactive products(s)adjusted. For aromatics, this is the AFG1/AFG2 ratio.

Or Radical yield in O_3 and O^3P reaction adjusted.

QY Quantum yield for photodecomposition adjusted

Prm Parameterized mechanism used with various parameters adjusted.

Oth Other adjustments were made. See references in notes.

Init Initial reactant concentration injected. See Note [g].

[e] Notes and comments concerning the evaluation results of mechanism adjustment, as follows:

1 The model significantly overpredicts the direct reactivity measured by Carter and Malkina (2002) (see "Iso-Octane" on Figure 15)

2 The model tends to overpredict O_3 in the β-pinene - NO_x experiments but gives reasonably good simulations of the reactivity experiments.

Table 23 (continued)

3 Model overpredicts O_3 formation rate in the arc light benzene - NO_x experiments but tends to underpredict it in the blacklight runs. Model gives reasonably good simulation of most of the incremental reactivity experiments.

4 The model underpredicts the direct reactivities measured by Carter and Malkina (2002), but not as much as SAPRC-99 (see Figure 15).

5 Model overpredicts initial NO oxidation and O_3 formation rates in the toluene - NO_x blacklight experiments but gives good simulations to these experiments in the TVA chamber and in chambers using arc lights. Model gives good simulations of the incremental reactivity results. The model significantly overpredicts the reactivity seen in the toluene - NO_x experiments in the UNC outdoor chamber, but this could be due to chamber characterization problems. The model underpredicts the direct reactivities measured by Carter and Malkina (2002), but not as much as SAPRC-99 (see Figure 15).

6 The model underpredicts the effects of CO addition on O_3 formation, though to a lesser extent than SAPRC-99 (see Figure 8).

7 The model somewhat overpredicts the reactivity seen in the o-xylene - NO_x experiments in the UNC outdoor chamber, but this could be due to chamber characterization problems.

8 The model tends to overpredict O_3 formation in experiments in the EC but gives good simulations to results of more recent experiments using both blacklights and arc lights. The model somewhat overpredicts the direct reactivities measured by Carter and Malkina (2002), but the discrepancy may be within the uncertainty of the measurement.

9 The model consistently underpredicts the reactivities in the acetylene - NO_x experiments, but the underprediction of the incremental reactivity results is relatively small. The SAPRC-99 mechanism, which uses a higher rate constant for OH + acetylene based on an earlier recommendation by Atkinson (1994), simulates the data with much less bias. This rate constant was changed to reflect the recommendation in the NASA (2006) evaluation.

10 Even though the mechanism was not changed, the model performs somewhat better than SAPRC-99 in simulating some experiments.

11 The model somewhat underpredicts the direct reactivity measured by Carter and Malkina (2002) (see Figure 15).

12 The model gives reasonably good simulations of earlier ITC experiments but tends to underpredict maximum O_3 in the new arc light and blacklight experiments carried out for this project.

13 See base mechanism documentation (footnotes to Table A-2) for a discussion of the adjustments made for this compound.

14 The reactivity is somewhat underpredicted in the acetone - NO_x experiments with the arc lights and in the outdoor chamber but is well simulated in the blacklight chamber runs. The incremental reactivity results are reasonably well simulated.

15 The model evaluation results for this compound are highly variable. O_3 formation in the single heptanone - NO_x experiment is significantly underpredicted, but the reactivity in one of the two incremental reactivity experiments is overpredicted, while the other two incremental reactivity experiments are reasonably well simulated. The latter were used as the basis for adjusting the photolysis rate, which was an important uncertain parameter in affecting the results. Note that the photolysis rate adjusted to fit this compound affects the base mechanism because the photolysis rate used for the lumped higher ketone product, PROD2, is based primarily on the photolysis rate derived for this compound.

Table 23 (continued)

16 The parameterized mechanism used for all the cresol isomers was adjusted to fit the data for o-cresol based on the model simulation of a single experiment. The $\Delta([O_3]-[NO])$, cresol and PAN data in that one experiment are simulated reasonably well.

17 The model underpredicts O_3 formation in the m-cresol - NO_x experiment and gives an incorrect prediction of the effect of o-cresol addition on the initial NO oxidation and O_3 formation rate in the reactivity experiment, but simulates the effect on final O_3 reasonably well.

18 The one p-cresol - NO_x experiment is simulated reasonably well.

19 No attempt was made to adjust the approximate mechanisms to fit the chamber data. The performance indicates the performance of the approximation of using chlorine mechanisms to estimate mechanisms for Br-containing species.

20 No attempt was made to adjust this mechanism to improve simulations of the data.

21 See Carter and Malkina (2007) for a discussion of adjustments made to these mechanisms to fit the chamber data.

22 The effects of Cl_2 on n-butane - NO_x irradiations and the effects of multiple Cl_2 additions to a surrogate - NO_x experiment were reasonably well simulated.

23 The initial NO oxidation and O_3 formation rates are significantly underpredicted in the DMSO - NO_x experiments but are only slightly underpredicted in the MIR-type incremental reactivity experiments. Except for one experiment where the model overpredicts DMSO reactivity, the effects of DMSO on final O_3 in the lower NO_x reactivity experiments are reasonably well simulated.

24 The mechanism evaluation with these complex mixtures primarily tests how well the mixtures are represented by the distribution of model species used to represent them. No mechanism adjustments can be made to improve simulations in these cases.

25 The model performance with this version of the mechanism is considerably better than SAPRC-99, which had a consistent bias in underpredicting the O_3 impact (overpredicting the O_3 inhibition) of this mechanism.

26 See Carter (2007) for a discussion to the adjustments made to this mechanism to fit the chamber data. The mechanism tends to underpredict the amount of ozone inhibition caused by the addition of methyl iodide at the end of some of the experiments.

27 See Note [g] and Carter (2008a) for a discussion of the amine experiments. Although the amount of initial amine in the experiments are adjusted to fit the effects of the amine on the initial rates of NO oxidation and O_3 formation in the experiments (see Note [g]), the model does not predict the observed inhibition of ozone at the end of the lower NO_x experiments.

28 See Note [g] and Carter (2008a) for a discussion of the amine experiments. Because these compounds significantly inhibited the rates of O_3 formation, the ability of the mechanism to simulate the effects of the amine on final O_3 yields could not be determined.

29 See the report cited in the other note for the results of the evaluation experiments for these compounds, which were carried out after the list of experiments to be included in this report was finalized.

30 See Carter (2009a) for a discussion of the experiments used to evaluate the mechanism for this compound. Good simulations of MIR and MOIR/2 reactivity experiments were obtained after adjusting the overall nitrate yield.

31 See Carter (2009b) for a discussion of the experiments used to evaluate the mechanism for this compound. Good simulations of MIR and higher ROG/NO_x reactivity experiments were obtained after adjusting the overall nitrate yield.

Table 23 (continued)

[f] These experiments that were not in the original (August, 2007) version of the report.

[g] Amount of injected amine available for reaction is uncertain because initial concentration of the amine in the gas phase could not be measured, and because of expected absorption of amines on the walls and other heterogeneous effects. The fits indicated on the table reflect the fits obtained after adjusting initial amount of amine to fit the initial rates of NO oxidation and O_3 formation in the experiments, and the adjusted initial amine concentrations were always lower than the calculated amount injected. See Carter (2008a). The figures show the fits with the amount of initial amine adjusted to best fit the data.

in footnotes to the table. The figures in Appendix C show the model performance for both SAPRC-99 and SAPRC-07, but Table 23 only summarizes the results for SAPRC-07, though cases where the mechanisms differ significantly are noted.

For the vast majority of the VOCs and mixtures, the performance for SAPRC-07 was similar to that of SAPRC-99, though as indicated on Table 23, mechanism parameters had to be adjusted to obtain the comparable fits. This is expected, since for most VOCs the mechanisms were not significantly changed. Exceptions and other cases worth noting are as follows:

Alkylbenzenes. As discussed above, significant changes were made to the ring-opening mechanisms for the alkylbenzenes and the model species used to represent the non-α-dicarbonyl ring opening products. However, these changes did not result in significant changes in the ability of the model to simulate aromatic - NO_x experiments or incremental reactivity experiments with aromatics, presumably because portions of both mechanisms were optimized to simulate essentially the same database. Like SAPRC-99, the updated mechanism also tended to underpredict the effects of adding CO to aromatics - NO_x irradiations, but to a lesser extent than SAPRC-99. This is shown on Figure 8, which shows results of selected toluene and *m*-xylene - NO_x experiments where CO was added. Likewise, as discussed below, the updated mechanisms also tended to overpredict direct reactivities of benzene and toluene, but again to a lesser extent than SAPRC-99. Therefore, the overall performance of the updated mechanism is an improvement over SAPRC-99 in some at least some respects, but problems in simulating all of the data still remain.

Alkenes. As also indicated above, it was necessary to assume lower radical yields in the reactions of O_3 and O^3P with alkenes than indicated by current laboratory data in order to obtain unbiased simulations of the data. This was the case for SAPRC-99 and is also the case with this updated mechanism. However, the extent to which the yields had to be adjusted to lower values was somewhat less with this version of the mechanism, so at least in this respect the problem may be slightly reduced.

Acetylene. The current NASA (2006) evaluation recommends an OH + acetylene rate constant that is lower than that used in SAPRC-99 by ~17% at ambient temperature and pressure. This caused a negative bias in the model simulations of the acetylene experiments that was not the case for SAPRC-99. However, this bias was not so large that it was considered appropriate to adjust the rate constant, and there were not other uncertain aspects of the mechanism considered to be appropriate to adjust to remove this bias.

Higher Ketones. The photolysis rate used in the base mechanism for the lumped model species used to represent the more reactive ketone products, PROD2, is based on overall quantum yields derived based on model simulations of the experiments with methyl propyl ketone, methyl isobutyl

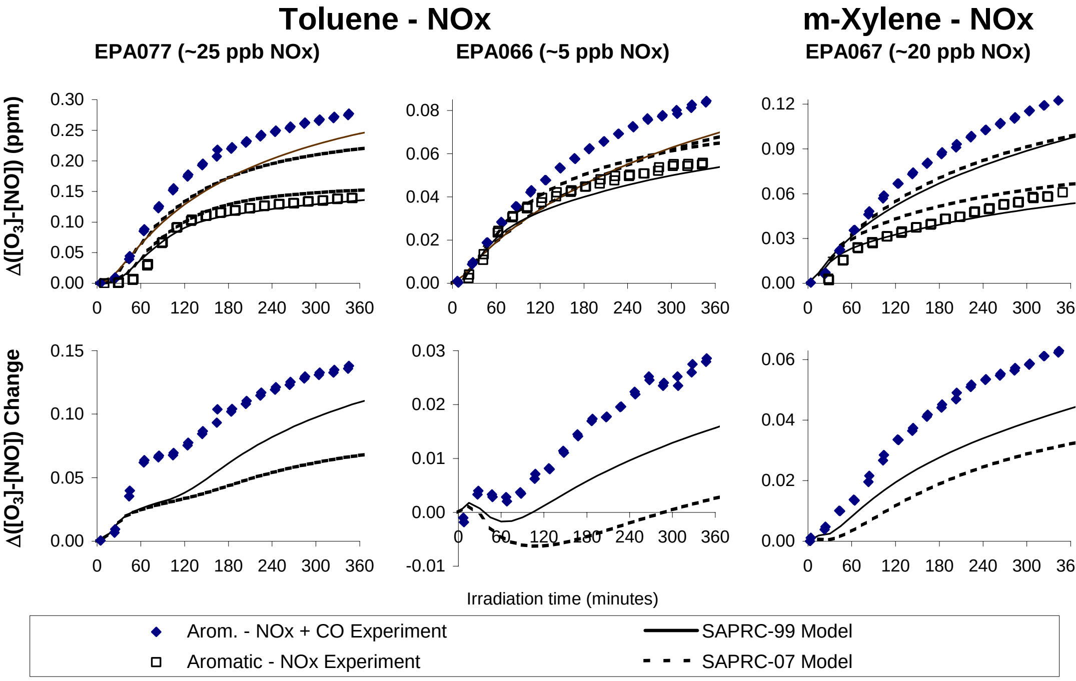


Figure 8. Experimental and calculated effects of CO addition in representative toluene and m-xylene NO_x experiments carried out in the UCR EPA chamber.

ketone and 2-heptanone. The data indicate that the quantum yields decrease with carbon number, but the extent of the decrease with the higher ketones is somewhat greater with the updated mechanism than SAPRC-99. This resulted in a lower overall photolysis rate for the PROD2 model species. However, the very limited and somewhat consistent data for 2-heptanone provides the only information about ketones with greater than 7 carbons, which are used as the basis for the even larger ketones that are important in alkane and other photooxidations. More data are needed to place the estimates for photolysis rates of higher ketones on a firmer basis.

Alkyl Bromides. Since developing mechanisms for bromine species was beyond the scope of this project, the mechanisms for the few bromine-containing compounds that are represented are estimated based on mechanisms derived for the corresponding chlorine-containing compounds. The chamber data for n-propyl and n-butyl bromides, shown on Figure C-89, indicate that this may somewhat underestimate the rate of initial NO oxidation and O_3 formation but significantly overestimate the impact of the compound on final O_3 yields. The implication of this on predicted MIR values for these compounds is uncertain, but it is clear that low NO_x reactivities of these compounds are almost certainly overestimated.

Isoparaffinic Alkane Mixtures. Carter and Malkina (2005) noted that the SAPRC-99 mechanism predicted much more O_3 inhibition in the incremental reactivity experiments with the synthetic isoparaffinic alkane mixture (designated ASTM3C1) than observed experimentally, and concluded that there is a problem either with the characterization of such mixtures or with branched alkane mechanisms in general. However, although neither the composition of the mixture nor the branched alkane mechanisms were changed, the updated mechanism now gives much better simulations of these data, as shown on Figure C-106. This indicates that reactivities of compounds such as these, and presumably others, can be sensitive to changes in the base mechanism that has nothing directly to do with the mechanisms for the compounds themselves.

Amines. The mechanisms for amines were newly derived for this mechanism; SAPRC-99 either has no mechanisms for these compounds or uses highly approximate "placeholder" mechanisms. The amine mechanisms derived for SAPRC-07 are and are discussed above in the "Mechanisms for Individual VOCs" section and in more detail by Carter (2008a). A series of incremental reactivity environmental chamber experiments were carried out with 2-amino-2-methyl-1-propanol (AMP) and ethanolamine and one experiment each was carried out for t-butyl amine and isopropyl amine (Carter, 2008a), and selected results are shown on Figure C-108 and Figure C-109. As discussed by Carter (2008a), because of analytical problems no data were available concerning the amount of amines present in the gas phase at the start of the experiments, and if the amount of initial amine derived from the calculated amounts injected is assumed, then the effects of the amines on the results of the experiments are significantly overpredicted. This is even if it is assumed that the amines react rapidly with HNO_3 formed in the experiments to form the corresponding salt, which is also assumed to be removed from the gas-phase system. Therefore, the amount of amine initially present in the gas phase had to be treated as an adjustable parameter in the model simulations of the experiments, in order to obtain the fits shown on Figure C-108 and Figure C-109. The amount of initial amine that best fit the reactivity data ranged from ~5% to ~60% of the calculated amount of amine injected, with no apparent dependence on reaction conditions or type of experiment (Carter, 2008a). Because of this, the use of these experiments to evaluate amine mechanisms is highly uncertain. Nevertheless, the estimated mechanisms correctly predict that AMP and t-butyl amine significantly inhibit NO oxidation O_3 formation, while they correctly predict that the other two amines have positive effects on initial NO oxidation and O_3 formation rates.

When the amounts of initially present amines are appropriately adjusted to simulate the effects on initial NO oxidation rates, Figure C-109 shows that the data for AMP and t-butyl amine are reasonably well simulated throughout the experiments. On the other hand, as shown on Figure C-108, the chamber data indicated that the two reactive amines studied, aminoethanol and isopropyl amine, tended to inhibit O_3 formation under low NO_x conditions, which was not predicted by the mechanism. The reason for this inhibition is unknown, and this discrepancy could not be resolved by reasonable adjustments to the mechanisms for these compounds and the representations of the reactions of their major products (Carter, 2008a). Therefore, it must be concluded that the mechanisms for the positively reactive amines probably overpredict the reactivities of the compounds under low NO_x conditions, if the uncertainties regarding availability are not considered.

Methyl Iodide. Methyl iodide is another compound that was not represented in SAPRC-99 but whose mechanism has been derived for SAPRC-07. The mechanism for this compound, and its evaluation against chamber data, are described in detail by Carter (2007), and that discussion is not duplicated here. Figure C-110 and Figure C-111 show that the mechanism simulates most of the data of Carter (2007) reasonably well.

Evaluation Experiments for Mixtures

Figure 9 through Figure 13 show distribution plots for the various types of mixture - NO_x experiments in the current evaluation set. For most types of mixtures the model performance is generally satisfactory in terms of overall biases, but there are cases where the updated mechanism does not perform quite as well as SAPRC-99. These are discussed below for the various types of experiments.

Simple mixture experiments. These are runs with mixtures that are not considered to be complete surrogates because they do not contain at least one representative each of alkanes, alkenes, and aromatics. Figure 9 shows distributions of model errors for these runs, grouped by the chamber employed.

It shows that the average biases and distribution of errors are similar for both mechanisms. The mixture experiments in the TVA and UCR EC chamber are reasonably well simulated, while the reactivity experiments in the mixture experiments in the UNC chamber are overpredicted by about the same amount in both mechanisms. Given the good performance for the quite different EC and TVA chambers, the poorer performance in simulating the UNC chamber data is considered to be likely due to characterization rather than mechanism problems.

Miscellaneous Surrogate Experiments. These are experiments with mixtures that contain at least one alkane, alkene and aromatic that are designed to represent, albeit in a simplified fashion, reactive organic gas mixtures that are emitted into ambient atmospheres. The more recent experiments in the UCR EPA chamber are considered separately because they were carried out at generally lower pollutant levels than the earlier chamber experiments, and conditions in that chamber are considered to be somewhat better characterized. Figure 10 shows the distribution of model errors in the earlier surrogate - NO_x experiments carried out in various UCR and the TVA chamber, and Figure 11 shows the results for various surrogate mixtures in the UNC chamber. Because of the large number of the many standard surrogate experiments used as base cases in incremental reactivity studies in the UCR chambers, these are excluded from Figure 10 and are shown separately in Figure 12. Overall the model performance for the updated mechanism is similar to SAPRC-99 for these experiments, though the biases tend to be somewhat more (either positive or negative, depending on the type of experiment) for the miscellaneous mixtures shown on Figure 10. The results with both mechanisms for the UNC or UCR standard surrogate runs, shown on Figure 11 and Figure 12, respectively, are similar for both mechanisms, with the reactivity in the UNC experiments again being consistently overpredicted (though not as much so as for the simple mixture runs shown on Figure 9), and the earlier UCR standard base case surrogate runs being well simulated.

New Surrogate Experiments in UCR EPA Chamber. A large number of surrogate - NO_x experiments have been carried out in the new UCR EPA chamber, most based on a similar 7- or 8-compound mixture designed to represent ambient VOC mixtures (Carter et al, 1995c, Carter and Malkina, 2005)[1]. As discussed by Carter (2004), a large number of such experiments were carried out at a variety of NO_x and ROG levels, including NO_x levels as low as 2 ppb, giving a large and reasonably well characterized database for testing model predictions of how O_3 changes with ROG and NO_x levels. The results indicated a bias in the SAPRC-99 mechanism in underpredicting O_3 formation and NO oxidation at low ROG/NO_x levels, which have not been seen in simulating the earlier surrogate experiments carried out at higher NO_x levels (Carter, 2004; Carter et al, 2005b). Since then, a number of other experiments have been carried out in this chamber to further investigate this, including experiments using the blacklight light source and experiments using a "non-aromatic" surrogate with the aromatic constituents of the 7- or 8- compound surrogate mixture removed. The latter are useful to evaluate whether the bias at low ROG/NO_x is due to problems with the aromatics mechanisms, which are considered to be the most uncertain component of the overall mechanism for mixtures.

The performance of the mechanisms in simulating these experiments is shown in Figure 13 and Figure 14. Figure 13 shows distribution plots of model errors similar to those shown above for other mixtures, and shows that overall the updated mechanism simulates the full surrogate (i.e., the surrogates with the aromatics) approximately as well as SAPRC-99, but that the updated mechanism has a slight positive bias in overpredicting O_3 formation and NO oxidation rates in the non-aromatic surrogate runs. Figure 14 shows plots of model errors against the ROG/NO_x ratio, similar to those shown previously (Carter, 2004; Carter et al, 2005b). This shows that the problem with the model underpredicting O_3.

---

[1] The 7-compound surrogate was the same as the 8-compound surrogate except that formaldehyde was removed because of experimental issues. Carter and Malkina (2005) showed that this removal should not significantly affect experimental or mechanism evaluation results.

Miscellaneous Simple Mixture Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
EC Chamber	25	0%	9%	-14%	5%
TVA chamber	6	-8%	3%	-16%	-6%
UNC Chamber	32	74%	33%	63%	33%

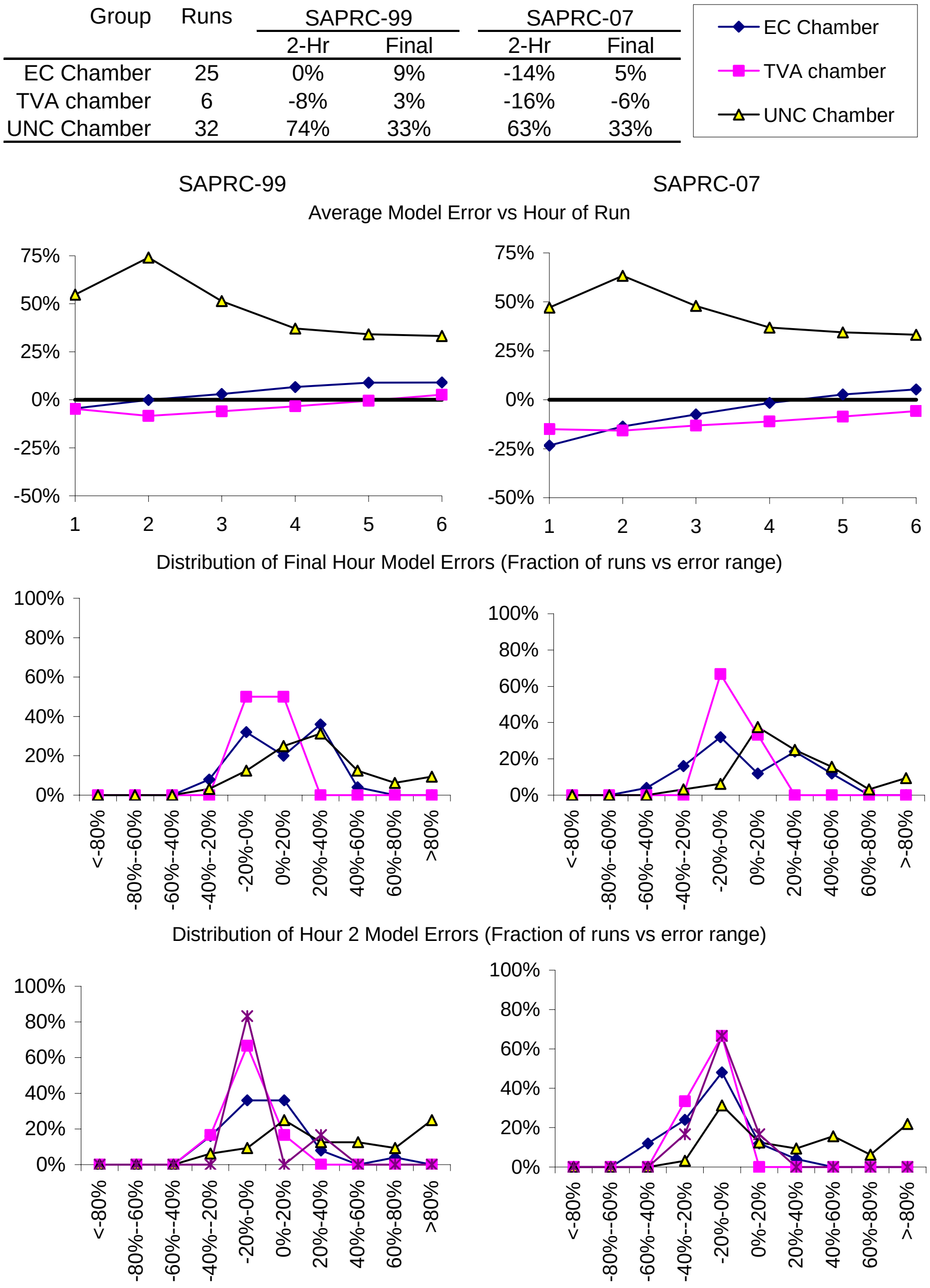
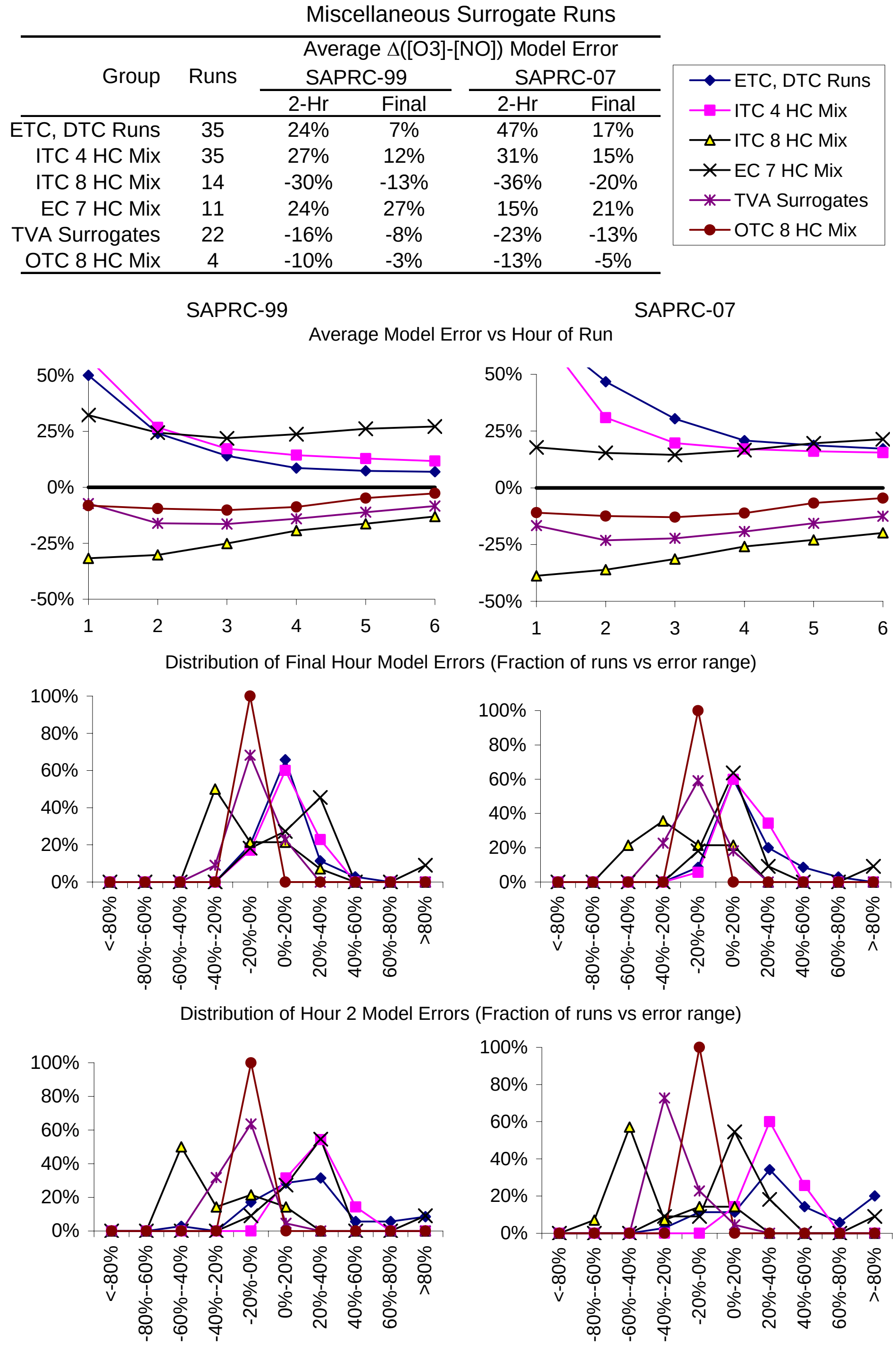


Figure 9. Plots of model errors in simulations of miscellaneous mixture - NO_x experiments carried out in various chambers.



Miscellaneous Surrogate Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
ETC, DTC Runs	35	24%	7%	47%	17%
ITC 4 HC Mix	35	27%	12%	31%	15%
ITC 8 HC Mix	14	-30%	-13%	-36%	-20%
EC 7 HC Mix	11	24%	27%	15%	21%
TVA Surrogates	22	-16%	-8%	-23%	-13%
OTC 8 HC Mix	4	-10%	-3%	-13%	-5%

SAPRC-99 SAPRC-07

Average Model Error vs Hour of Run

Distribution of Final Hour Model Errors (Fraction of runs vs error range)

Distribution of Hour 2 Model Errors (Fraction of runs vs error range)

Figure 10. Plots of model errors in simulations of miscellaneous surrogate - NO_x experiments carried out in various UCR chambers and in the TVA chamber.

UNC Chamber Surrogate Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
Simple Mix	9	18%	21%	7%	25%
SynUrban	11	45%	39%	34%	27%
SynAuto	14	12%	32%	8%	26%

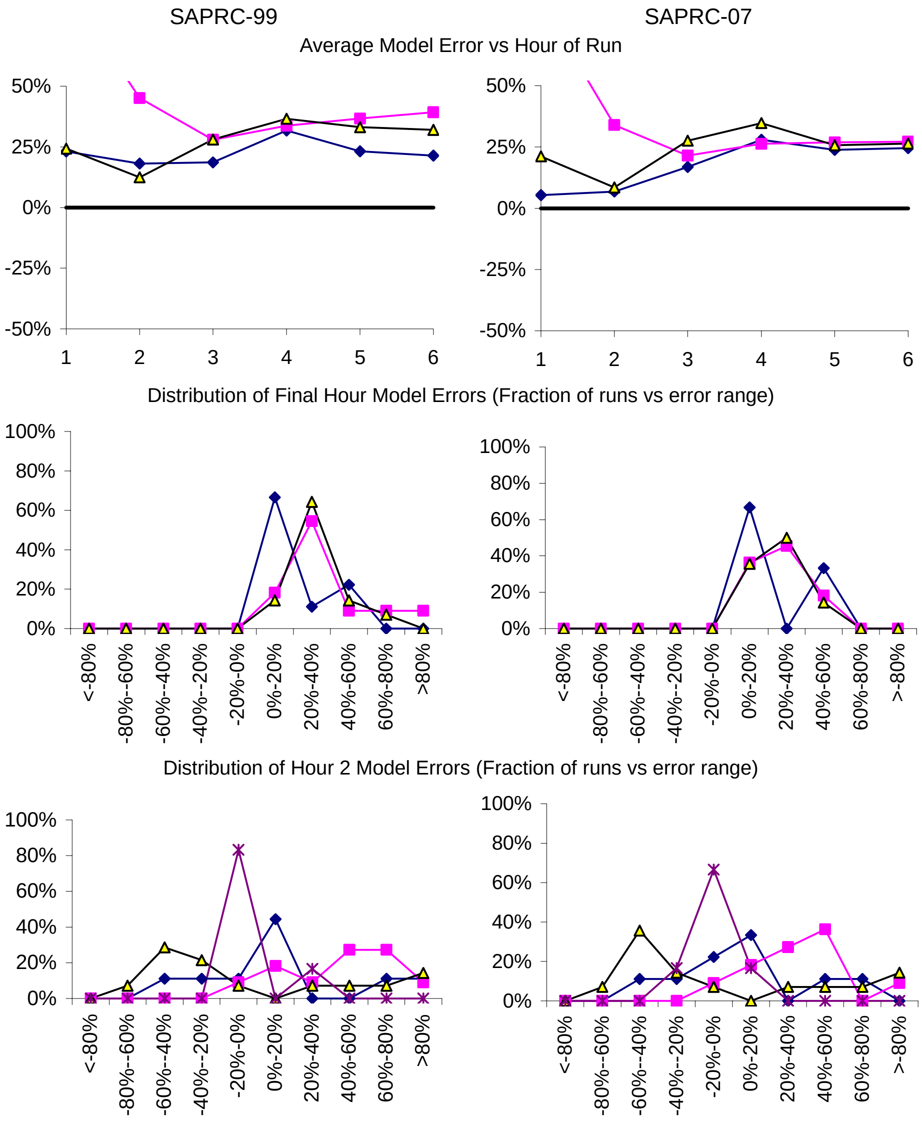


Figure 11. Plots of model errors in simulations of surrogate - NO_x experiments carried out in the UNC chamber.

Earlier Chamber Standard Base Case Surrogate Runs

		Average Δ([O3]-[NO]) Model Error			
Group	Runs	SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
Arc, Surg-3 MIR1	40	21%	7%	6%	-6%
Arc, Surg-8 MIR1	40	2%	5%	0%	4%
Arc, Surg-8 LN1	21	-1%	0%	4%	2%
Black, Surg-3 MIR1	227	13%	3%	22%	7%
Black, Surg-8 MIR1	114	-1%	2%	13%	7%
Black, Surg-8 LN1	96	1%	3%	10%	7%

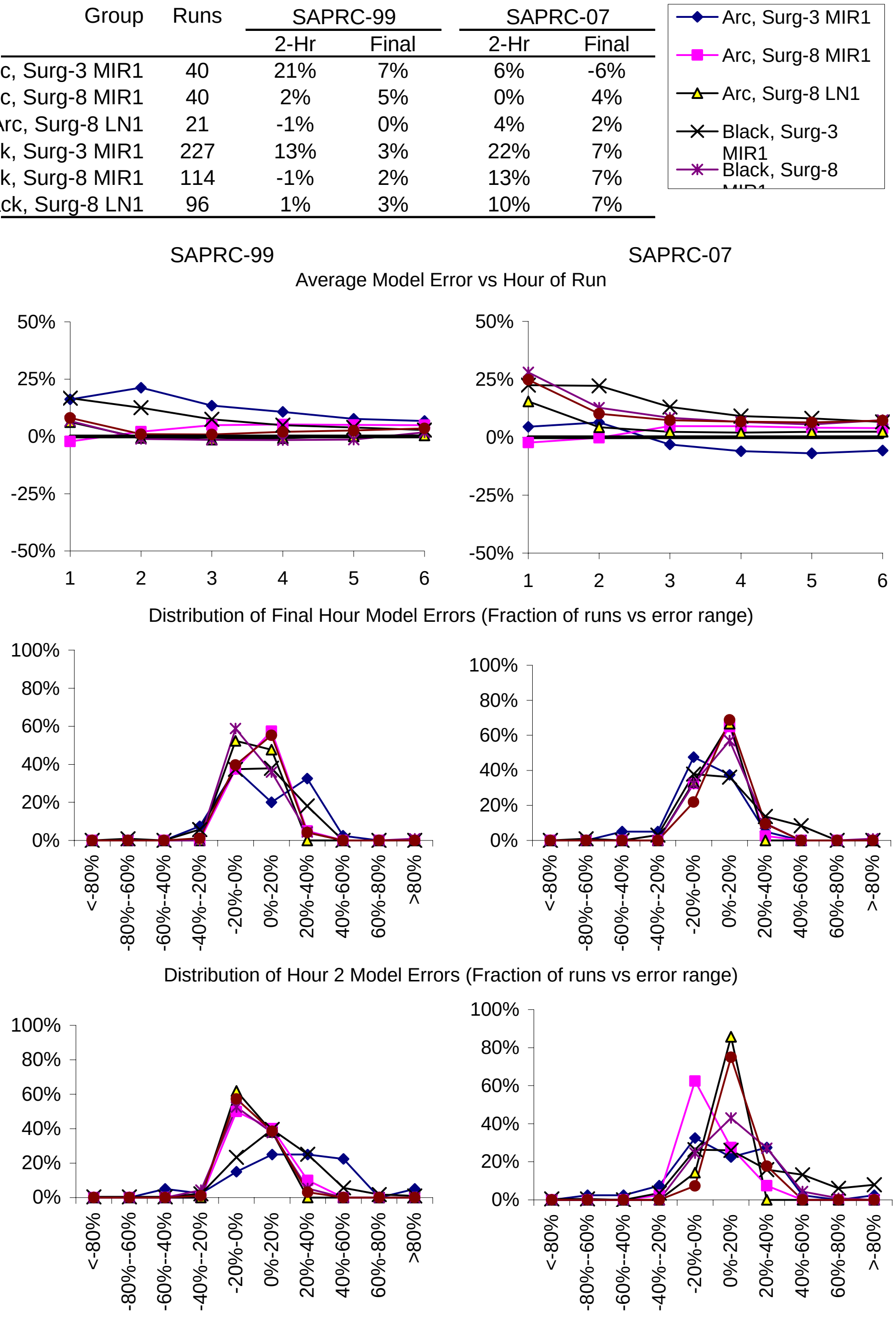


Figure 12. Plots of model errors in simulations of the standard base case surrogate - NO_x irradiations carried out in conjunction with the incremental reactivity experiments in the ETC and DTC (blacklight), and CTC and XTC (arc light) chambers.

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
Full Surg, Arc	111	-10%	-10%	-14%	-14%
Full Surg, Black	75	-19%	-14%	-8%	-11%
Non-Arom Surg, Arc	3	-1%	4%	15%	11%
Non-Arom Surg, Black	23	-3%	-2%	13%	8%

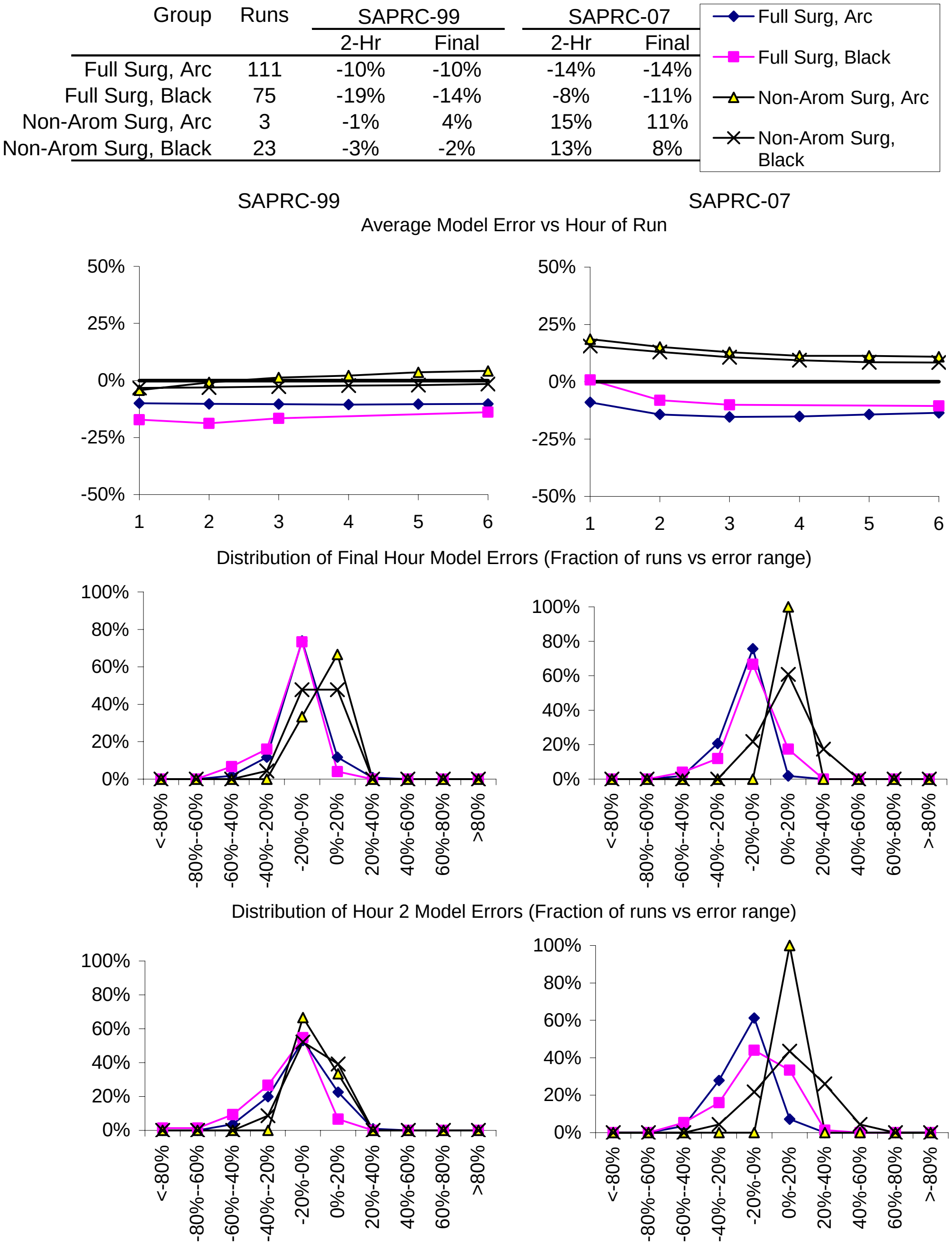


Figure 13. Plots of model errors in simulations of the surrogate - NO_x experiments carried out in the UCR EPA chamber.

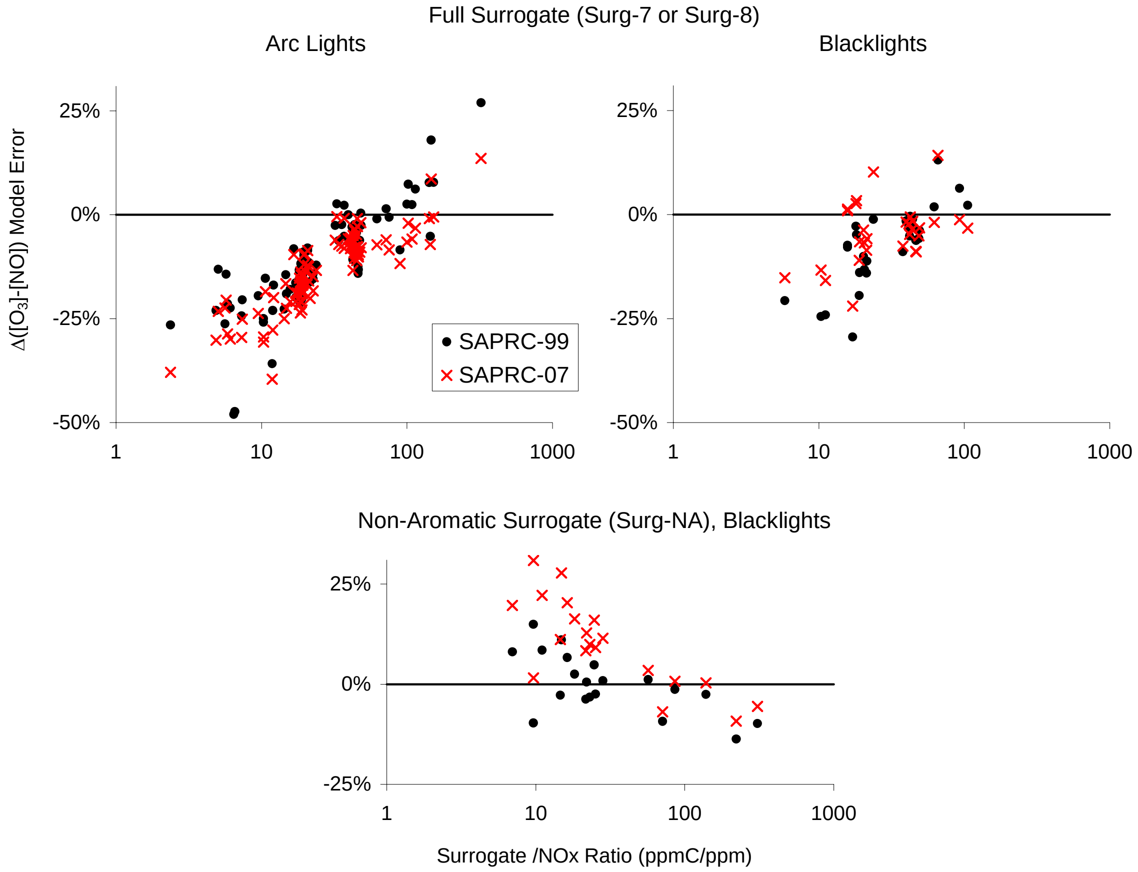


Figure 14. Plots of model errors in simulations of 6-hour $\Delta([O_3]-[NO])$ against initial ROG surrogate $/NO_x$ ratio.

formation and NO oxidation rates at the lower ROG/NO_x ratios has not been eliminated, and that the extent to which the bias is affected by ROG/NO_x ratios is essentially the same. This is observed in the blacklight as well as the arc light chamber experiments.

On the other hand, Figure 14 shows that if the aromatics are removed, the dependence of the bias on ROG/NO_x is in the opposite direction as seen with the full surrogate, with the model tending to overpredict reactivity more at lower ROG/NO_x ratios, and giving better predictions of the data at the higher ROG/NO_x conditions. This is true for both versions of the mechanism, but has been somewhat exacerbated as a result of the mechanism update

Overall, the evaluation with the experiments with mixtures indicate a slight degradation of model performance for the updated mechanism compared to SAPRC-99, though this is not seen for all types of mixtures. Figure 7, above shows a very slight (~5%) bias in the updated mechanism in simulating the mixture experiments when all are lumped together, with the bias being greater (~10%) in simulating initial NO oxidation and O_3 formation rates. However, when examining run types separately, one sees the biases vary with type of experiment, with some types of experiments having greater positive biases and some having greater negative biases, compared to SAPRC-99.

The difference for the UCR EPA full surrogate vs. non-aromatic surrogate at low ROG/NO$_x$ conditions is suggestive, with the experiments with the aromatics having the distinct negative bias while those with aromatics removed having the bias in the opposite direction. But the evaluations of the single compound or incremental reactivity experiments with the individual alkanes, alkenes, and aromatics, shown in figures in Appendix C and summarized on Table 23 above, do not indicate trends in biases with individual compounds that is consistent with this. The cause and significance of this problem is uncertain, and clearly this needs further study. It is important to note, however, the biases are not large compared to overall run-to-run variability and characterization uncertainties in model simulations of environmental chamber experiments.

Mechanism Performance for Direct Reactivity Experiments

Figure 15 shows the model performance in simulating the direct reactivity experiments of Carter and Malkina (2002) for all the compounds for which useful direct reactivity data were obtained. The results for SAPRC-99 are also shown. Except for benzene and toluene the results were very similar for the two mechanisms, with generally good fits being obtained for most compounds except for isooctane (2,2,4-trimethylpentane) and ethyl acetate. This is as expected since the mechanisms for these compounds were not changed significantly. The reasons for the discrepancies for isooctane and ethyl acetate are unknown, and have not been resolved.

Figure 15 shows that the new aromatics mechanisms do perform somewhat better in simulating the direct reactivities for benzene and toluene, though the direct reactivities of these compounds, and to a lesser extent 1,3,5-trimethylbenzene, are still overpredicted. This can be attributed to the updated mechanism assuming direct OH formation, without NO to NO$_2$ conversions, in the ring opening pathways that do not involve α-dicarbonyl formation. However, the results suggest that actual total amount of NO to NO$_2$ conversion may still be less than assumed in this mechanism.

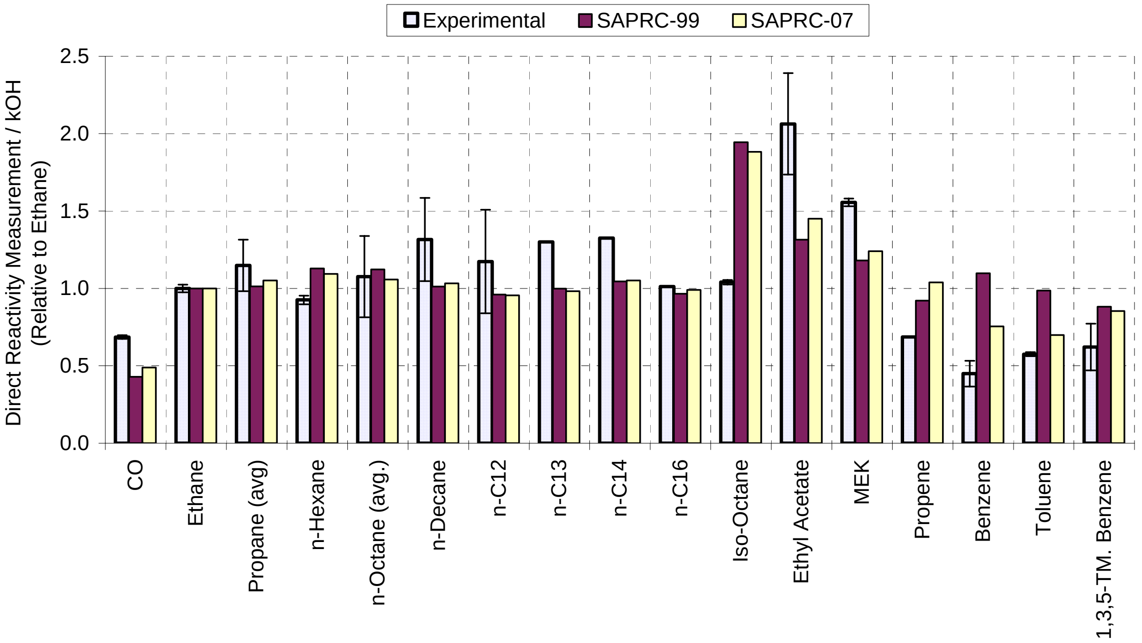


Figure 15. Model performance in simulating the direct reactivity data of Carter and Malkina (2002).

UPDATED REACTIVITY SCALES

One of the major applications of the SAPRC mechanisms is calculation of ozone reactivity scales for VOCs, including the MIR scale that is used or being considered for use in regulatory applications (CARB 1993, 2000, 2006, 2007), and a major reason behind this mechanism update is to update these reactivity scales. The SAPRC-99 mechanism was used to calculate MIR and other reactivity scales for many types of VOCs, with the latest update being that of Carter (2003a). That update includes reactivities for almost 780 types of VOCs, based on explicit or assigned mechanisms for ~560, and lumped molecule or mixture assignments for the rest. The listing included uncertainty codes for the reactivity estimates that may be potentially useful for regulatory applications or determining priorities for research. These scales, and their corresponding uncertainty classifications, have been updated as part of this project.

Methods

The methods, scenarios, and reactivity scales that were used in this reactivity scale update are the same as employed previously for the SAPRC-99 scales (Carter 2000a, 2003), and those references should be consulted for detail. Briefly this is based on the methods and scenarios originally developed by Carter (1994a,b), with slight modifications in the averaging methods as described by Carter (2000a). These are based on 39 single-day "base case" EKMA box model scenarios (EPA, 1984) derived by the EPA for assessing how various ROG and NO_x control strategies would affect ozone nonattainment in various areas of the country (Baugues, 1990). The conditions of these scenarios are summarized on Table 24, and more details concerning the modeling inputs are given by Carter (1994b).

The scenario conditions include specifications of initial concentrations and emissions schedules for NO_x and total anthropogenic VOC emissions and also background O_3, aloft VOCs, and initial and emitted biogenic VOCs (Bauges, 1990; Carter, 1994a,b). The scenarios as originally developed by Bauges (1990) do not specify the composition of the anthropogenic VOCs, and Carter (1994a) used a standard mixture of hydrocarbons derived by Jeffries (Jeffries et al (1989) from analysis of air quality data, with minor modifications as discussed by Carter (1994a,b). This is referred to as the "Base ROG mixture" in the subsequent discussion. This base ROG mixture was not modified for the SAPRC-99 reactivity scale updates (Carter, 2000a, 2003a), and was also used in this update. Note that same base ROG mixture was used as the basis for deriving the "fixed parameter" version of the SAPRC-07 mechanism for airshed models, as discussed above. The composition of this mixture in terms of fixed parameter SAPRC-07 lumped model species in given in Table 17, above.

The base case scenarios with the NO_x inputs as specified by Bauges (1990) were used to derive the updated "base case" reactivity scales, comparable to those given by Carter (1995a, 2000a) for SAPRC-90 or SAPRC-99. Because absolute and even relative impacts of VOCs on O_3 formation are highly dependent on NO_x conditions that are highly variable in the base case scenarios, scenarios with adjusted NO_x inputs were derived to obtain scales that are more representative of standard conditions of conditions of NO_x availability. These are as follows:

- <u>The Maximum Incremental Reactivity (MIR)</u> scale is derived from the scenarios where the NO_x inputs are adjusted to yield highest incremental reactivities (changes in O_3 caused by small VOC additions, divided by the amount of VOC added) of VOCs. Although the NO_x conditions yielding highest incremental reactivities tend to be the same for most VOCs, the sensitivity of O_3 formation to changes in total base ROG inputs was used to determine the NO_x levels corresponding to MIR conditions. This represents relatively high NO_x conditions where, by definition, O_3 is most sensitive to changes in VOC emissions.

Table 24. Scenarios used for reactivity assessment, with updated calculated maximum O_3, Integrated OH, and MIR, MOIR, and EBIR NO_x inputs.

Scenario	Max O_3 (ppb)	Max 8-Hr Avg O_3 (ppb)	ROG / NOx [a]				Max Height (kM)	ROG input [b]	O_3 aloft (ppb)	Int'd OH (ppt-min)
			Base	MIR	MOIR	EBIR				
Averaged Conditions (Used for screening calculations and sensitivity studies)										
Max React (MIR)	179	117		3.70			1.8	15	70	121
Max O_3 (MOIR)	229	161			5.63		1.8	15	70	200
Eq. Benefit (EBIR)	213	166				8.86	1.8	15	70	200
Base Case (Used for MIR, MOIR, and EBIR scales)										
Atlanta, GA	173	127	7.25	3.54	5.37	7.66	2.1	12	63	198
Austin, TX	171	141	9.30	3.36	5.08	8.00	2.1	11	85	180
Baltimore, MD	318	196	5.15	3.90	5.92	10.04	1.2	17	84	171
Baton Rouge, LA	237	168	6.83	4.31	6.36	8.46	1.0	11	62	186
Birmingham, AL	239	198	6.94	2.71	4.09	6.26	1.8	13	81	204
Boston, MA	191	161	6.50	2.69	4.13	6.53	2.6	14	105	250
Charlotte, NC	139	123	7.79	1.80	2.78	3.86	3.0	7	92	207
Chicago, IL	286	230	11.63	4.29	6.39	9.75	1.4	25	40	176
Cincinnati, OH	196	145	6.38	3.29	5.05	9.01	2.8	17	70	208
Cleveland, OH	245	170	6.62	4.24	6.64	10.09	1.7	16	89	180
Dallas, TX	194	128	4.74	3.99	6.10	8.86	2.3	18	75	160
Denver, CO	197	132	6.33	4.88	7.37	11.37	3.4	29	57	140
Detroit, MI	237	168	6.82	3.64	5.55	9.85	1.8	17	68	224
El Paso, TX	178	130	6.59	4.49	6.96	9.70	2.0	12	65	136
Hartford, CT	167	140	8.39	2.74	4.26	7.09	2.3	11	78	213
Houston, TX	303	206	6.08	3.94	5.96	9.36	1.7	25	65	217
Indianapolis, IN	205	141	6.64	3.87	6.22	9.61	1.7	12	52	203
Jacksonville, FL	150	111	7.62	3.44	5.18	7.22	1.5	8	40	202
Kansas City, MO	152	120	7.09	2.95	4.59	8.34	2.2	9	65	221
Lake Charles, LA	289	211	7.42	3.46	5.01	6.91	0.5	7	40	235
Los Angeles, CA	566	401	7.59	5.11	7.75	11.08	0.5	23	100	136
Louisville, KY	204	148	5.53	3.10	4.77	7.17	2.5	14	75	248
Memphis, TN	224	174	6.78	3.21	4.79	7.59	1.8	15	58	240
Miami, FL	129	108	9.63	2.71	4.19	6.09	2.7	9	57	178
Nashville, TN	162	134	8.05	2.46	3.74	5.79	1.6	7	50	224
New York, NY	371	293	8.09	4.59	6.41	9.54	1.5	39	103	161
Philadelphia, PA	237	157	6.18	3.98	6.00	9.44	1.8	19	53	213
Phoenix, AZ	271	189	7.58	4.87	7.61	12.98	3.3	40	60	155
Portland, OR	160	121	6.46	2.90	4.66	6.68	1.6	6	66	223
Richmond, VA	233	162	6.18	3.44	5.25	9.30	1.9	16	64	204
Sacramento, CA	198	136	6.59	3.73	5.75	8.89	1.1	7	60	200
St Louis, MO	311	194	6.08	4.55	6.93	11.51	1.6	26	82	167
Salt Lake City, UT	181	147	8.47	3.36	5.30	8.96	2.2	11	85	182
San Antonio, TX	124	90	3.92	2.85	4.42	6.11	2.3	6	60	173
San Diego, CA	188	142	7.09	4.54	6.86	9.63	0.9	8	90	141
San Francisco, CA	231	124	4.77	5.99	8.86	11.87	0.7	25	70	62
Tampa, FL	219	141	4.36	3.32	4.93	6.71	1.0	8	68	192
Tulsa, OK	221	149	5.31	3.08	5.06	8.57	1.8	15	70	242
Washington, DC	274	198	5.32	3.06	4.59	7.22	1.4	13	99	225

[a] Ratio of initial + emitted anthropogenic reactive organic gas (ROG) input to initial + emitted NO_x. Biogenic VOC input not included.

[b] Initial + emitted anthropogenic VOC input, in units of millimoles m^{-2}.

- The Maximum Ozone Incremental Reactivity (MOIR) scale is derived from the scenarios where NO_x inputs are adjusted to yield highest maximum O_3 concentrations. This represents NO_x conditions that are most favorable to O_3 formation. MOIR NO_x levels are generally about a factor of 1.5 lower than those yielding maximum incremental reactivities.
- The Equal Benefits Incremental Reactivity (EBIR) scale is derived from scenarios where NO_x inputs are adjusted so that the reduction in O_3 caused by reducing base ROG inputs are the same as those caused by changing total NO_x inputs by the same percentage. This represents the lowest NO_x conditions where controls of VOCs are at least as effective as controlling NO_x; since for lower NO_x levels NO_x controls are always more effective for reducing O_3. EBIR NO_x levels are generally about a factor of 1.5 lower than those yielding maximum O_3 concentrations, or 2.3 times lower than MIR levels.

Table 24 gives the NO_x levels that correspond to these various conditions of NO_x availability that were used to derive the MIR, MOIR, or EBIR scales. The incremental reactivities for those scales were averages of the incremental reactivities calculated for the 39 scenarios of the various types.

The fixed parameter version of SAPRC-07 with the base ROG mixture composition given in Table 17 was used to simulate the base cases for the reactivity assessment scenarios used in this work. For the purpose of calculating incremental reactivities of individual compounds, model species were added to explicitly represent the compound, and also to represent the more reactive oxidation products if the "adjustable products" mechanisms were employed. For simulating reactivities of complex mixtures, lumped model species were added as indicated on Table 17, above, with the mechanisms for the adjustable parameter species (ALKn, OLEn, and AROn) being derived based on the particular mixture being assessed.

Note that as discussed by Carter (2008a) the impacts of the reactions of amines with HNO_3 under atmospheric conditions are very uncertain. This is because they are sensitive to atmospheric sources and other sinks of HNO_3, which are highly variable and not determined for the reactivity assessment scenarios. For the purpose of deriving reactivity scales for regulatory applications, it is probably appropriate to use upper limit estimates of the ozone impacts of these compounds under conditions where they will have their highest impacts. For that reason, the atmospheric reactivities calculated for the amines are based on assuming that loss by reaction with HNO_3 is negligible. As discussed by Carter (2008a) if this reaction is important the magnitudes of the O_3 impacts of the amines could be lower by more than an order of magnitude.

The incremental reactivity calculations were carried out by adding the amount of test compound or mixture such that the estimated amount reacted would be 0.05% the mole carbon of the base ROG input. The incremental reactivities were calculated change in final (i.e., maximum) O_3 concentrations in terms of total moles formed, divided by the moles of test compound or mixture added in the calculations. The incremental reactivities are then converted from mole to mass basis by using the molecular weights for O_3 and the test VOCs.

Results

Predicted Ozone Formation in the Scenarios

Before presenting the incremental reactivity results, it may be of interest to show the model predictions of O_3 formation in the various scenarios used for reactivity assessment. The maximum O_3 formed in the base case (unadjusted NO_x) scenarios are tabulated in Table 24, and Figure 16 shows predicted maximum O_3 levels for all scenarios used, plotted against total ROG inputs, which gives a

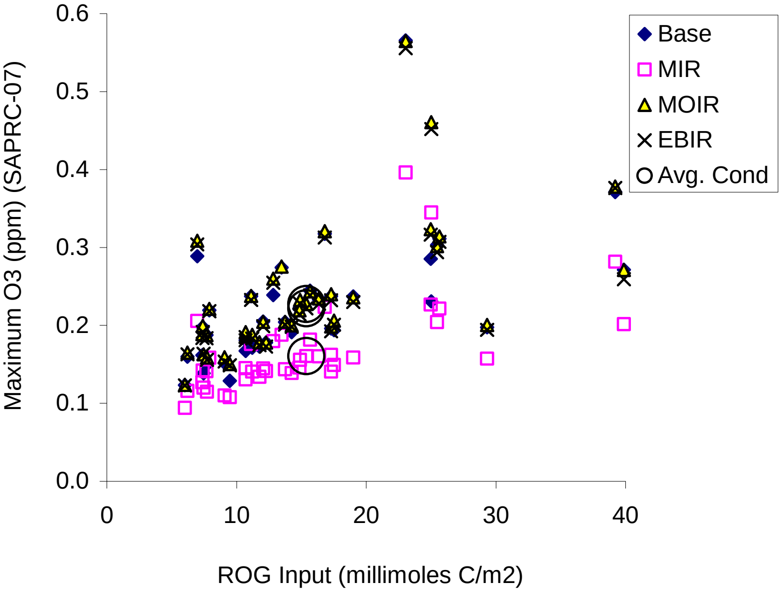


Figure 16. Plots of maximum O_3 concentrations calculated for the various scenarios used for reactivity assessment against the initial ROG levels in the scenarios.

measure of the total amount of pollution in the scenario. As expected the O_3 levels correlate with the total amount of ROG input, though the correlation is not perfect, indicating the importance of other factors such as dilution, etc. As also expected (and by definition) the O_3 levels are highest for the MOIR scenarios, and in all cases are the lowest for the MIR scenarios.

Note that some scenarios have O_3 levels as high as 500 ppb or more, which are much higher than now occurs in urban areas in the United States. This suggests that the scenarios should be updated to reflect present conditions. However, updating the scenarios for reactivity assessment was beyond the scope of this project. Figure 17 shows the changes in O_3 formation in the various scenarios predicted using this updated version of the mechanism, compared to those calculated previously using SAPRC-99. Figure 17a shows the differences when the NO_x levels in the MIR, MOIR, and EBIR scenarios are adjusted separately for each mechanisms to yield the corresponding reactivity characteristics, while Figure 17a shows the differences when the NO_x levels are not adjusted, i.e., when the SAPRC-99 MIR, MOIR or EBIR NO_x levels are used in the SAPRC-07 calculations. (The NO_x levels, and therefore the mechanisms differences, are the same in the base case calculations shown on both plots.) It can be seen that if the NO_x levels are adjusted to yield the same reactivity conditions, the changes in O_3 predictions resulting from the mechanism update varies from scenario to scenario, ranging from a ~10% increase to a ~5% increase, though for most scenarios the update causes a decrease in predicted O_3, by about 5% on average. For a given type of scenario the decrease tends to be correlated with the ROG/NO_x ratio, with the decrease being largest at the lowest ROG/NO_x ratios.

However, the mechanism change caused a ~5 - ~15% decrease in the NO_x levels that yielded MIR, MOIR, or EBIR levels, so the results shown on Figure 17a do not reflect the same NO_x levels. If the NO_x levels are held constant, the changes caused by the update have a much more consistent dependence on ROG/NO_x ratio, and also larger changes for the MIR scenarios and smaller changes for the EBIR scenarios. This is consistent with the fact that O_3 sensitivities to mechanism differences are

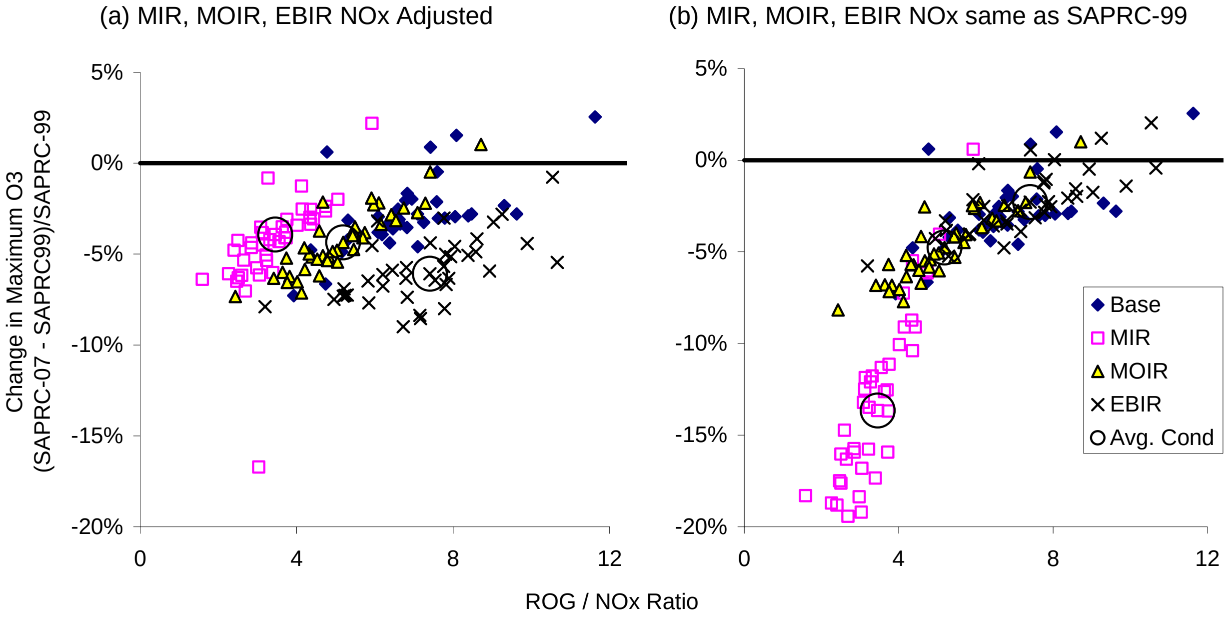


Figure 17. Change in maximum O_3 concentrations in the scenarios used for reactivity assessment, calculated using SAPRC-07 compared to SAPRC-99.

greatest at the lowest ROG/NO_x ratios (e.g., MIR), and simulations become much less sensitive as the higher ROG/NO_x ratios (EBIR). O_3 reductions of up to ~20% are seen for the MIR scenarios with the lowest ROG/NO_x ratios, while the changes for most of the EBIR scenarios are less than 5%.

Updated Ozone Reactivity Scales

Table B-1 in Appendix B gives the results of the MIR, MOIR, EBIR, and average base case reactivity scale calculation for all the VOCs currently represented in this version of the mechanism. This includes a total of 1029 types of VOCs, of which 722 have explicit mechanism assignments and the remainder are represented using the "lumped molecule" approach, and a total of 52 complex mixtures. (The latter include the 32 complex mixtures used in previous reactivity tabulations, using the same compositions as employed previously [Carter, 2000a and references therein, Carter et al, 1997e, 2000a, 2000e; Carter and Malkina, 2005, 2007], plus new or revised unspeciated alkane and aromatic mixture categories. The Unspeciated alkane mixtures assuming equal amounts of normal, branched, and cyclic alkanes[1], and unspeciated aromatic mixtures derived as discussed by Carter and Malkina [2005].) The table indicates whether the VOC is represented explicitly, and if so whether its reactivity was calculated using adjusted product mechanisms, whether the VOC was represented using the lumped molecule method, or whether the reactivities are given for complex mixtures. Molecular weights, carbon numbers, and (where applicable) CAS numbers are also given in the table.

---

[1] This differs from previous tabulations where the unspeciated alkane mixtures had the normal alkanes excluded, on the theory that they could be identified in GC analyses. Therefore, the new unspeciated categories are appropriate mainly for when no analytical data are available. If analytical data are available, the correspond BR-Cnn and CYC-Cnn should be used for the corresponding unspeciated and cyclic alkane constituents, with equal amounts being used if the cyclic vs. branched ratio is unknown.

The incremental reactivities in the MIR scale are of greatest interest because this is the scale that is most often used or proposed for use in regulatory and other applications. Figure 18 shows a plot of the incremental reactivities in the updated scale against those in the latest SAPRC-99 scale provided by Carter (2003a). The 1:1 and ±30% lines are also shown. The average change (excluding the 13 outliers where the change was greater than 50%) in the MIR's was -8%, and the average absolute magnitude of the change (again excluding the outliers) was 11%. The change was less than 30% for approximately 96% of these VOCs. The MIR for the base ROG mixture, which is used as the standard for relative reactivity scales, decreased by about 3%. If this is taken into account, the average change in relative MIR values would be approximately -5%, excluding the outliers.

The compounds whose incremental reactivities in the MIR scale changed by more than 30% are listed in Table 25. The table also indicates the probable reasons for the changes for those with the greatest changes. Excluding 3-methoxy-1-butanol, where the SAPRC-99 mechanism had a factor of 10 error in the OH rate constant, the greatest changes were for halogenated compounds because of the higher estimated photolysis rates for the chloroaldehyde and chloroketone products predicted to be formed, and for amines, for which new mechanisms were derived based on new chamber data by Carter (2008a).

Updated Uncertainty Estimates

The reactivity tabulation in Table B-1 in Appendix B gives updated uncertainty classifications for the various types of VOCs and other information that may be useful in this regard. This includes an indication of the availability of environmental chamber data to evaluate the mechanism for the compound, and the comprehensiveness of the data for this purpose, and also estimates of likely biases in the reactivity estimates, if known. The uncertainty and other codes that are used for this purpose are given and described in footnotes to Table B-1.

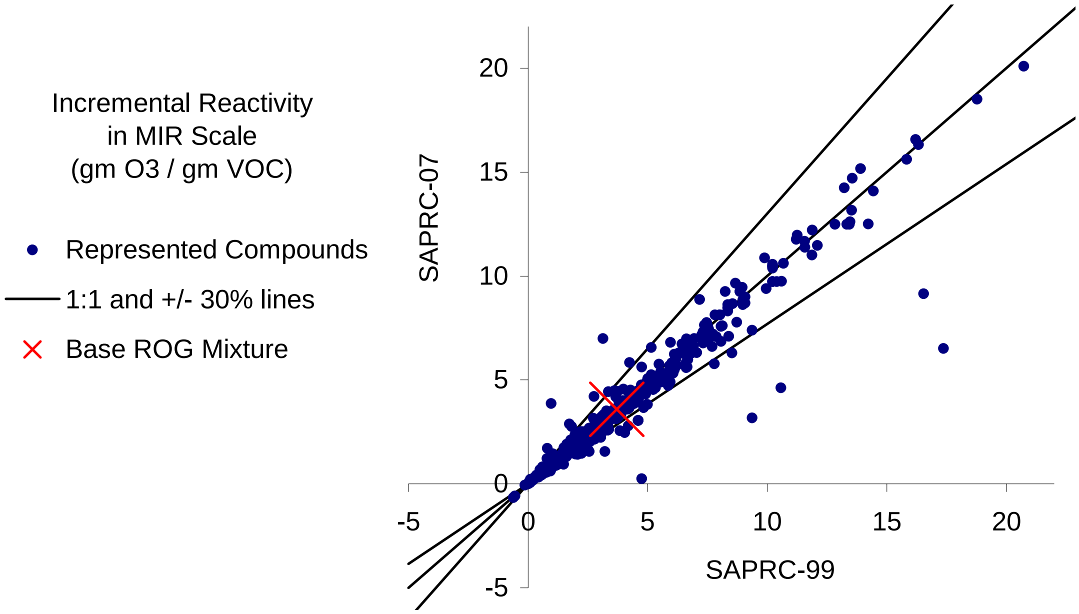


Figure 18. Plots of incremental reactivities in the MIR scale computed using the updated mechanism against those reported previously by Carter (2003a).

Table 25. List of compounds and mixtures whose reactivities in the MIR scale changed by more than 30%.

Compound	MIR (gm O_3 / gm VOC) Old	 New	 Change	Probable Reason [a]
3-Methoxy-1-butanol	0.97	3.87	300%	1
2-(Chloromethyl)-3-chloropropene	3.13	7.00	123%	2
1,2-Dibromoethane	0.046	0.102	119%	3
1,2-Dichloroethane	0.098	0.21	119%	2
trans-1,2-Dichloroethene	0.81	1.70	110%	2
2-Amino-2-methyl-1-propanol	4.75	0.25	-95%	4
Dimethyl amine	9.37	3.17	-66%	4
Mesityl oxide (2-methyl-2-penten-4-one)	17.37	6.51	-63%	5
3,5,5-trimethyl-2-cyclohexenone	10.58	4.63	-56%	5
Propionic acid	0.79	1.22	55%	
Triethanolamine	2.75	4.21	53%	4
2,4-Toluene diisocyanate	-0.133	-0.065	-52%	
Phenol	1.82	2.76	51%	6
1,1,2-Trichloroethane	0.058	0.086	48%	4
Furan	16.54	9.15	-45%	7
2-Methyl-2,4-pentanediol	1.03	1.45	41%	
CARB Hydrocarbon Bin 5	2.56	1.56	-39%	8
Diethanol amine	4.05	2.47	-39%	4
p-Xylene	4.24	5.84	38%	
Dichloromethane	0.066	0.041	-37%	
Chloroform	0.034	0.022	-37%	
Acetic acid	0.50	0.68	37%	
CARB Hydrocarbon Bin 20	1.49	0.95	-37%	8
n-butyl bromide	0.60	0.82	36%	
1,1,1-trichloroethane	0.00	0.00	35%	
CARB Hydrocarbon Bin 3	2.52	1.63	-35%	8
1,2-Propylene glycol diacetate	0.94	0.61	-35%	
CARB Hydrocarbon Bin 4	2.24	1.47	-35%	8
p-diethyl benzene	3.36	4.43	32%	
CARB Hydrocarbon Bin 1	2.08	1.42	-32%	8
1,1-Dichloroethane	0.101	0.069	-31%	

[a] Discussion of probable reasons for MIR change:

1 The OH radical rate constant used in SAPRC-99 was found to be low by a factor of 10.

2 Chlorinated aldehyde and ketone products are now assumed to be much more photoreactive.

3 The approximate method used to represent bromine-containing compounds was changed. SAPRC-99 used a highly approximate "placeholder" mechanism. SAPRC-07 represents them using the mechanism for the corresponding Cl-containing compound.

4 New amine mechanisms developed. Note that amines without hydrogens on groups adjacent to amino groups are now estimated to be inhibitors, though their MIR values are still positive because of their NO_x removal characteristics. Note also that the magnitudes of the amine MIRs could be significantly lower if loss of amines by reaction with HNO_3 is important. See Carter (2008a).

Table 25 (continued)

5 These compounds are now represented by the model species used to represent the lumped C_5 isoprene product IPRD. The estimated mechanisms used in SAPRC-99, derived using the mechanism generation system, are now considered to be too uncertain to use.

6 Phenol is lumped with Cresols in SAPRC-07 but was represented explicitly in SAPRC-99. However, the change in MIR is well within the relatively large uncertainty of the mechanism.

7 Furan is now represented explicitly. Previously it was represented by m-xylene using the lumped molecule method.

8 The "old" value is from Kwok et al (2000), and were derived from correlations between MIR values and boiling points for various types of compounds. The "new" values are calculated using compositions derived from various compounds as discussed by Carter and Malkina (2005). Some of the differences may be due to the change in methodology, though for most bins Carter and Malkina (2005) did not notice large differences between MIRs calculated using SAPRC-99.

It is important to recognize that the uncertainty and bias estimates given on Table B-1 are entirely subjective, and not based on any comprehensive sensitivity and uncertainty analysis. This also does not take into the account that reactivities of some VOCs may be sensitive to environmental conditions or changes in the base mechanism, and may change if the base mechanism or scenarios are updated even if the mechanism for the VOC itself is unchanged. An analysis of such would clearly be useful.

SUMMARY AND RECOMMENDATIONS

This project was successful in accomplishing most of its objectives, particularly the primary objective of developing a complete update to the SAPRC-99 mechanism that represents the current state of the science. However, some of the objectives of this project could not be accomplished or completed in the time frame for this project, and addressing these objectives need to be included among our recommendations for future research. In this section, we summarize the major accomplishments of this project and the results and conclusions that were obtained, followed by a summary of the objectives that could not be fully accomplished and our recommendations for future research.

Summary of Project Accomplishments

The major accomplishment of this project is the development of the SAPRC-07 chemical mechanism and its associated reactivity scales that are documented in this report. Specific accomplishments, results, and conclusions of this project are summarized as follows.

Rate constants updated. All the rate constants in the mechanism have been reviewed based on results of current evaluations, and updated as needed. This includes updates to the absorption cross-sections and quantum yields for the photolysis reactions, where appropriate. The most recent IUPAC (2006) and NASA (2006) evaluations were used as the primary basis for updating the rate constants in the base mechanism and common organic products, the evaluations of Calvert et al (2000, 2002) were used for reactions relevant to alkenes (Calvert et al, 2002) and aromatics (Calvert et al, 2000), and the recent evaluations of Atkinson (1997), Atkinson and Arey (2003) and Calvert et al (2000, 2002) were used for rate constants for individual VOCs. Other sources, including recent work in our laboratory on reactivity studies of specific compounds, were used as appropriate.

Most of the rate constant changes were relatively small, but a few errors were found and corrected and some potentially significant changes occurred. Various uncertainty and sensitivity studies indicate that the rate constant for the OH + NO_2 reaction is particularly important, and based on the results of the recent NASA (2006) evaluation, the rate constant for ground-level conditions increased by ~18%. This could result in somewhat lower O_3 predictions under some conditions (as indicated by results of box model simulations of ambient scenarios, discussed below), and probably contributed to the need to re-adjust uncertain parameters in mechanisms for some individual VOCs to be consistent with chamber data, as indicated below. Photolysis rates for some aromatic and isoprene oxidation products were increased by ~40% or more. The effects on the aromatics mechanism are compensated by other changes in the aromatics mechanisms, but the changes for isoprene may have an impact on airshed simulations, though the model performance in simulating available isoprene chamber data was not affected. However, the effects of the many changes that were made, taken as a whole, have not been fully assessed, other than the limited number of box model simulations carried out in conjunction with updating the reactivity scale.

Aromatics mechanisms reformulated. The mechanisms for the aromatic ring fragmentation reactions were reformulated to be more consistent with estimated explicit mechanisms that were derived as part of this project and to give predictions that are somewhat more consistent with "direct reactivity" results reported by Carter and Malkina (2002). These mechanisms incorporate much of the new information contained in the review of Calvert et al (2000), particularly in the representation of the ring opening products. However, although not as simplified and parameterized as the aromatic representation used in SAPRC-99, the updated mechanisms are still highly simplified in many respects, and are not consistent with all of the available data given by Calvert et al (2000) and others, and some of the inconsistencies with available environmental chamber data still persist.

The approach that was initially employed was to develop explicit versions of the mechanisms for representative aromatic hydrocarbons, and use these to derive more condensed, but chemically reasonable, versions for airshed model calculations. Unfortunately, because of time constraints and other problems, the effort to develop explicit mechanisms that could account for reactivity differences among aromatic isomers could not be completed within the time frame available to this project. However, the explicit mechanisms were developed to the point where they did serve as the basis for the more condensed aromatics mechanism that is described in this report. The aromatic mechanism formulation developed for this project, though simplified in some respects, represents a much closer approximation to the explicit mechanisms than SAPRC-99, and serves a useful basis for future improvements in this area.

As part of this effort, environmental chamber experiments were carried out with several furans, which were studied because these compounds are expected to form the same type of highly photoreactive fragmentation products as formed in the ring opening reactions of the alkylbenzenes, only in higher yields and without the complication of uncertain competing processes. Because the development of the explicit aromatics mechanisms based on these data could not be completed, the results of these experiments could not be incorporated in the final versions of the aromatics mechanisms developed for this work, other than in the mechanisms for the furans themselves. However, these data should be useful in future explicit aromatics mechanism development efforts. This explicit mechanism development effort, and the experiments carried out to support it, will be discussed in more detail in future reports.

Chlorine chemistry added. The representation of chlorine chemistry has been added to the mechanism as an optional capability. The inorganic ClO_x and Cl atom reactions with common organic products have been added as an optional module of the base mechanism, and mechanisms for chlorine atom reactions were derived for all the explicit and lumped VOCs used in the version of the mechanism for ambient simulations and in the mechanisms used to calculate reactivities of individual chlorinated VOCs. The chlorine chemistry mechanisms were based primarily on the recent IUPAC (2006) and NASA (2006) evaluations, various evaluations and studies of VOC + chlorine reactions, results obtained in our previous studies of chloropicrin (Carter et al, 1997a) and dichloropropenes (Carter and Malkina, 2007), and also various estimation methods that were developed as part of this project.

In addition to improving the ability of airshed models to simulate air quality in regions impacted by chlorine emissions, the representation of chlorine chemistry and associated updates has resulted in improved reactivity estimates for a number of VOCs of interest in California, including the pesticides chloropicrin and dichloropropenes (Carter and Malkina, 2007), and reduced uncertainties in reactivity estimates for chlorinated compounds in general.

Mechanism generation system enhanced. The mechanism estimation and generation system is an important component of SAPRC-99 that was used to generate fully explicit mechanisms for most of the non-aromatic VOCs, from which the more condensed mechanisms used in the model were derived. This system was enhanced in a number of respects for this project. Updated rate constants for the primary reactions of the individual VOCs with OH, O_3, NO_3, and O^3P were incorporated in the system. The capability of estimating and generating mechanisms for reactions of VOCs with chlorine atoms was added. The types of compounds and radicals whose reactions could be generated using the system was added to include to include species with more than one ring (e.g., terpenes), species with more than one double bond, alkynes, and (to a limited extent) aromatics and unsaturated aromatic ring opening products. This was used to assist in the derivation of mechanisms for compounds that could not be processed previously, and was also useful in deriving portions of the updated aromatics and aromatic products mechanisms.

Capability for adaptation to SOA predictions improved. Mechanisms for predictions of PM require an appropriate representation of the formation of the low volatility products that contribute to

SOA, and how they depend on reactant conditions such as availability of NO_x. Recent environmental chamber studies (Odum et al, 1996, Hurley et al, 2001, Sato et al, 2004a, Presto et al, 2005, Doherty et al, 2005, Song et al, 2005) indicate that SOA formation can change significantly with VOC/NO_x ratios. This is attributed to competing branching ratios in reactions of peroxy radicals with NO_x, HO_2, and other peroxy radicals. Hydroperoxides formed in the reactions of peroxy radicals with HO_2 appear to be particularly important in this regard. Unfortunately, the SAPRC-90 through SAPRC-99 mechanisms, like CB4 and CB05, uses a chemical operator lumping approach to represent peroxy radical reactions that requires representing hydroperoxide formation in a highly condensed and approximate manner. This is because explicitly representing all the possible peroxy + peroxy reactions that may occur under low NO_x conditions requires an excessive number of reactions to represent processes that are unimportant to ozone formation, and the SAPRC-90/CB4 chemical operator lumping approach results in a large reduction in mechanism size without significantly impacting predictions of O_3 and formation of organic product species that are important when ozone formation occurs. However, this is not as satisfactory an approximation when the model is being used to predict formation of secondary PM.

Appropriately representing hydroperoxide formation under low NO_x conditions, and using separate species to represent low-volatility hydroperoxides, requires that a different method be used to represent peroxy radical reactions. An explicit approach, such as used in the MCM (Jenkin et al, 2003; Saunders et al, 2003), or a semi-explicit approach such as used in RADM-2 (Stockwell et al, 1990) or RACM (Stockwell et al, 1997) mechanisms, would be satisfactory in this respect, but it requires adding a significant number of species and reactions to the mechanism, and is not compatible with the lumped parameter approach used in the SAPRC mechanisms to derived mechanisms for lumped species based on the mixtures of compounds they represent (Carter, 1990, 2000a, 2000b; Adleman et al, 2005). A more computationally efficient approach would be desirable for most comprehensive modeling applications.

The SAPRC-07 mechanism developed for this project addresses these problems by implementing an alternative chemical operator approach for peroxy radicals reactions that involves adding a much smaller number of species and reactions to the mechanism, and is compatible with the SAPRC lumped parameter methods and software that has already been developed. With this method, hydroperoxide formation can be represented more explicitly, with separate lumped species formed from different compounds based on considerations such as reactivity and volatility. It also permits separate representation of organic nitrates formed in peroxy + NO reactions based on reactivity and volatility considerations, which was also difficult under the formulation used in SAPRC-99 and CB4/05.

Because development and evaluating a mechanism for prediction of SOA precursors is a major project that was well beyond the scope of this project, the initial version of SAPRC-07 does not fully take advantage of the enhanced capabilities of this mechanism to represent formation of SOA precursors. It does include a separate model species to represent the low volatility hydroperoxides formed from aromatics, primarily as a means to illustrate this capability, but its ability to predict SOA chamber experiments has not yet been evaluated. However, this version serves as a useful starting point in this regard, and can be used in a much more straightforward way to develop models that more accurately predict how SOA formation varies with conditions of NO_x availability.

Mechanisms for many types of VOCs added or improved. A major feature of the SAPRC mechanisms is the ability to separately represent the many hundreds of types of VOCs for reactivity assessments, toxics modeling or other applications, and for deriving condensed mechanisms tailored for the specific mixtures of compounds that are present. The rate constants and mechanisms for the VOCs represented in SAPRC-99 were updated for this project, and in some cases improvements were made for VOCs previously represented using more approximate methods. The number of types of VOCs with distinct mechanisms was increased by 23% from 585 to approximately 720, and the total number of VOC classes for which reactivity estimates could be derived (whether by explicit representation or using the "lumped molecule" approach[1]) was increased by 22% from 873 to over 1050. Most of the increases in distinct mechanisms are for alkanes, alkenes, and oxygenates found in emissions inventories, whose mechanisms could be readily derived using the mechanism generation system, but also an increased number of mechanisms were derived for more appropriate representation of the higher alkylbenzenes[2]. Improved mechanisms are incorporated for halogenated compounds incorporating chlorine chemistry as discussed above, though most of these need to be experimentally evaluated. A few errors were found in SAPRC-99 mechanism assignments that were corrected, the most significant being a factor of 10 error in the rate constant for 3-methoxy-1-butanol.

Although mechanisms and representations were changed for a large number of the compounds, the number of compounds with significant MIR changes was relatively limited. The MIR changes were less than 25% for 95% of the chemical classes, and only 12 compounds had changes of more than 50%. However, some compounds whose MIRs were not previously listed have regulatory reactivities estimated using only "upper limit" methods (Appendix D in Carter, 2000a), so the addition of new compounds to the reactivity list may in some cases result in significantly different reactivities for regulatory applications.

Updated mechanism evaluated against chamber experiments. The updated mechanism was comprehensively evaluated by comparing predictions with results of all environmental chamber experiments used for SAPRC-99 evaluation, plus the results of more recent UCR experiments, and also the TVA chamber experiments used by Carter (2004), the UNC experiments used in the RADM2, and SAPRC-90 evaluations of Carter and Lurmann (1990, 1991). The results of this evaluation can be summarized as follows:

For some compounds it was found that re-adjustments to some of the uncertain mechanistic parameters had to be made to obtain mechanism performance comparable to SAPRC-99. This is apparently because changes to the base mechanism resulted in changes in parameter values that gave best fits to the data. This included primarily re-adjustments to overall nitrate yields in peroxy + NO reactions for VOCs where these are uncertain, but also the radical yields in some ozone + alkene reactions could be increased to values that are somewhat more consistent with, but still lower than, results of laboratory studies of these reactions (e.g., see Carter, 2000a, Pinho et al, 2006). These adjustments were incorporated in the updated mechanism.

In general, the model performance of the updated mechanism in simulating experiments for individual compounds or types of VOCs was comparable to that for SAPRC-99, with the overall bias for all single compound experiments, taken as a whole, being very low. Although major changes were made to the aromatics mechanism, the model performance in simulating the single aromatic and aromatic reactivity experiments did not change significantly. This can be attributed to the fact that for both SAPRC-99 and SAPRC-07, the yields or (in the case of SAPRC-07) effective quantum yields of photoreactive aromatic ring-fragmentation products were adjusted to optimize fits to the data. However, the updated mechanism did perform somewhat better in simulating direct reactivity data or effects of added CO (Carter and Malkina, 2002; Carter, 2004), though the results were still not completely satisfactory.

---

[1] In the lumped molecule approach, the compound is represented by assuming it has the same impact, on a per-molecule basis, as another compound or mixture of compounds assumed to have similar reactivities.

[2] In SAPRC-99, the higher alkylbenzenes are represented using mechanisms derived for the methylbenzenes. The updated mechanism has separate model species that incorporates the increased rate constants for reaction on the larger alkyl substituents of the aromatic ring, higher estimated nitrate yields, and reactivity differences for o-, m-, p-, and 1,2,3-, 1,2,4-, and 1,3,5-isomers.

The model performance for simulating data for some types of compounds changed even though no changes were made to their mechanisms. Biases that were previously seen in model simulations in propylene and ethylene glycol (Carter et al, 2005a) and synthetic isoparaffinic mixtures (Carter and Malkina, 2005) were significantly reduced. On the other hand, slightly increased positive biases were seen in simulations of effects for some types of compounds, such as the larger n-alkanes, on maximum O_3 yields in lower NO_x conditions. These results indicate that O_3 reactivity predictions, at least for chamber experiments, can be sensitive to changes in the base mechanism even if the mechanism of the VOC is not changed.

One area of potential concern is that the mechanism update caused a slight increase in overall biases in model simulations of experiments with mixtures of VOCs, including those designed to simulate ambient conditions. For all such experiments, the average bias in the simulations of the O_3 formation and NO oxidation rates in the second hour of the experiments increased from 5% to 12%, and the biases in simulations of final O_3 formed and NO oxidized increased from 3% to 6%. However, when examining run types separately, one sees the biases vary with type of experiment, with some types of experiments having greater positive biases and some having greater negative biases, compared to SAPRC-99. These changes are small compared to the ±30% variability of the fits overall, but because of the large number of such experiments (>1500 total) it may be statistically significant.

The mechanism update also did not solve the problem, noted by Carter (2004) and Carter et al (2005b) that SAPRC-99 had a consistent bias in underpredicting rates of O_3 formation and NO oxidation in surrogate - NO_x experiments carried out at relatively low NO_x levels in the new UCR EPA chamber, with the bias decreasing at higher ROG/NO_x ratios. This bias still exists with the updated mechanism, with the dependence of ROG/NO_x ratios being approximately the same. It is interesting to note that the dependence of the bias on ROG/NO_x in experiments in this chamber is in the opposite direction when the aromatics are removed from the surrogate, suggesting that the problem may be related to the aromatics mechanism, both for SAPRC-99 and SAPRC-07.

Mechanism implementation. The mechanism developed in this project was implemented for the box model calculations used for reactivity scale calculations, and the data files used in this implementation can serve as the basis for implementing in more comprehensive airshed models such as CMAQ or CAMx. Although there was insufficient time and resources remaining in this project to adapt the updated mechanism into such a model, the necessary data files and associated implementation documentation are being made available at the project web site at http://www.cert.ucr.edu/~carter/SAPRC. The types of data and files formats provided are similar to those used when distributing SAPRC-99, which has been successfully implemented into various models. However, we will continue to provide guidance to modelers in implementing this mechanism, as needed.

An important part of mechanism implementation is providing assignments of the many chemical categories used in speciation profiles for emissions inventories to the model species used in the mechanism. As part of this project, the emissions speciation database previously developed to provide a comprehensive and consistent speciation approach for the SAPRC-99, RADM2, CB4, and CB05 were updated to include SAPRC-07 as one of the optional mechanisms (Carter, 2008b). At present, only the fixed-parameter version of SAPRC-07 is implemented. Work on updating the system for the variable parameter version is planned, and when completed will be made available at the SAPRC mechanism web site noted above.

Reactivity scales updated. The updated mechanism developed for this project was used to calculate MIR and other reactivity scales for all the ~780 types of VOCs for which reactivities values were provided on the most recent SAPRC-99 update (Carter, 2003a), plus ~285 additional types of VOCs that have been added as part of this update. Uncertainty classifications were also updated as part of this work, and an additional code, indicating the estimated likely bias of the reactivity value (if known) was added. Although as indicated above the number of VOCs for which large changes in MIR values is relatively limited, the MIR values changed by more than 5% for a majority (56%) of the VOCs whose MIRs were tabulated previously. It is recommended that these be used to supercede the reactivity values distributed previously (Carter, 2000a, 2003a).

Preliminary assessment of impacts of updates on predictions of ambient ozone. Although this mechanism has not yet been implemented in comprehensive airshed models, the results of the box model simulations carried out in conjunction with the reactivity scale update provides some indication of how the mechanism update may affect predictions of ambient ozone. These are one-day of 39 simplified EKMA model scenarios designed to represent O_3 formation in 39 areas in the United States in the late '80's (Baugues, 1990), with NO_x levels adjusted to represent various conditions of relative NO_x availability that are relevant to VOC reactivity (Carter, 1994a). The results indicate that the mechanism update causes changes in maximum ozone concentrations ranging from a ~10% decrease to a ~5% increase, with the predicted O_3 decreasing by about 5% on average. For a given type of scenario, the decrease tends to be correlated with the ROG/NO_x ratio, with the decrease being largest at the lowest ROG/NO_x ratios. However, this is not necessarily the case if the NO_x levels are varied with the other scenario conditions held constant, which means that the ROG/NO_x ratio is not the only factor determining how the mechanism update changes predictions of O_3 formation in ambient scenarios.

Overall, this suggests that it is more likely than not that the mechanism updates will cause slight decreases in predicted ambient O_3, though this may not be true for all areas or scenarios. However, the box models used in the reactivity assessment calculations are highly simplified representations of ambient conditions, and comprehensive models are needed to fully assess the impacts of this update on ambient O_3 predictions, and also on predictions of effects of control strategies.

Recommendations

Although the accomplishments of this project were significant, there were some objectives of this project that could not be met within the time and resource constraints available for this project, and there areas where work is needed that were beyond the scope of the project as proposed. These objectives are still important, so the first recommendation resulting from this project is that work be carried out to address these objectives. These and other recommendations are summarized below.

Aromatics Mechanisms. Although the reformulated aromatics mechanisms developed in this work represent an improvement over SAPRC-99 in terms of representation of the actual chemistry expected to be involved, they still contain significant simplifications and approximations, and are not fully consistent with all recent laboratory results. A considerable effort was expended in this project in an attempt to develop explicit or near-explicit mechanisms that could predict reactivity differences in aromatic isomers (such as indicated in the chamber data of Carter et al, 1997a), but because of time constraints this could not be completed, and the preliminary explicit mechanisms were used as a basis for generalized mechanisms for aromatics that is incorporated in the current SAPRC-07. This explicit mechanism development work, and the environmental chamber experiments with furan carried out to support this effort, will be described in more detail in future reports once more progress can be made in this area.

As indicated above, the reformulated aromatics mechanisms gave somewhat improved performance in simulating the direct reactivity results of Carter and Malkina (2002), and also somewhat improved performance in simulating the effects of CO when added to aromatic - NO_x experiments (Carter, 2004). However, the performance, though improved, was still not entirely satisfactory in these regards, since direct reactivity was still somewhat overpredicted, and the effects of CO addition was still underpredicted. In addition, the problem of underpredicting O_3 at low ROG/NO_x ratios and low NO_x levels (as noted by Carter, 2004), which is attributed to problems with the aromatics mechanisms, has not been resolved. Therefore, although progress has been made, work on the aromatics mechanisms is still needed.

Chlorine and Other Halogen Mechanisms. Significant progress was made in improving the representation of chlorine chemistry and chlorine-containing compounds, but more work is needed in this area. Because of limitations in the mechanism generation system's ability to estimate reactions of chlorine-containing alkoxy radicals, the system could not derive complete mechanisms for the reactions of chlorine atoms for the alkenes without having to make explicit assignments for these radicals as required. Because this is a time-consuming process, chlorine mechanisms could only be derived for the most important or representative alkenes, with the mechanisms for the others being approximated based on these results. This is probably not a major problem for most airshed and reactivity calculations, but is a limitation of the present system.

A more significant problem is the fact that mechanism evaluation and reactivity data is available for only a limited number of chlorinated compounds, and the limited data that exist suggest that halogen-containing oxygenated products of these compounds may be considerably more reactive than the model species used to represent the oxygenated products of the unhalogenated compounds (see, for example, Carter and Malkina, 2007). Although the data for chloropicrin and the 1,3-dichloropropenes (Carter and Malkina, 2007) are reasonably well simulated by the current mechanism, the simulations of the experiments with trichloroethylene (Carter et al, 1996a) are not as satisfactory in some respects. Therefore, more data and mechanism development work is needed on individual chlorinated compounds and their oxidation products.

A similar effort is needed for adding bromine chemistry and reducing uncertainties in reactivity estimated for bromine- or iodine-containing compounds, but this was beyond the scope of this project. Such compounds are also present in emissions inventories, and bromine or iodine chemistry may need to be represented in some ambient scenarios. The few bromine-containing compounds representing in the current mechanism are approximately represented using the mechanisms for the corresponding chlorine-containing compounds, but the biases introduced by this representation are highly uncertain, and iodine-containing compounds are not currently represented in this mechanism.[1] Work in this area is needed if these compounds, or non-chlorine halogen chemistry, are determined to be important.

Mechanisms for Amines. Although estimated mechanisms for amines were developed and to some extent evaluated as part of the study of Carter (2008a), significant uncertainties remain concerning their atmospheric ozone impacts. The largest uncertainty concerns the extent to which emitted amines are available for atmospheric reaction, and which is removed from the gas phase due to gas-phase reaction with HNO_3 or to heterogeneous processes. Atmospheric reactivity estimates vary by over an order of magnitude depending on what assumptions are made concerning removal by reaction with HNO_3. The current reactivity values for amines are based on assuming that removal by reaction with HNO_3 is not important, in order to obtain upper limit magnitude ozone impact estimates. But use of these upper limit magnitude estimates may not be appropriate for all regulatory applications. The current mechanisms also do not correctly predict the effects of reactive amines on O_3 formation under low NO_x conditions, even if the amount present is adjusted to optimize model fits to initial rates of NO oxidation and O_3 formation. However, that uncertainty probably does not affect MIR predictions. Therefore, the amines mechanisms given here are much more uncertain than those given for most other VOCs, and more data, with improved

---

[1] Work on methyl iodide is being carried out under separate funding, and a mechanism for this compound and iodine species may be included in a future update.

analytical methods, and better characterization of sources and sinks of HNO_3 and amine salts in the atmosphere, are needed to reduce uncertainties for mechanisms and ozone impact estimates for amines.

Mechanism Generation System. As discussed by Carter (2000a), the mechanism generation system incorporates a large number of estimation methods for alkoxy, peroxy, and other radical reactions that serve as the basis for the full oxidation mechanisms that are derived. These are based on various estimation methods and a large body of data for individual reactions that were available up to the time SAPRC-99 was developed. Although an objective of this project was to update these radical reaction estimation methods based on any new data or theories that may have become available since then, because of time constraints we were unable to carry out these updates as part of this project. Although there is no indication that significant changes or updates to this system are needed, and in general the system has performed reasonably well for the types of compounds it is designed to represent, the predictions of the system is an integral part of the current SAPRC mechanisms, and updating its assignments should be included as part of the next comprehensive mechanism update effort.

As indicated above, the lack of estimation assignments for reactions of halogenated radicals makes generation of most chlorine + alkene reactions difficult, and methods for estimating more of such reactions need to be implemented to permit full incorporation of chlorine chemistry for unsaturated VOCs. Estimation assignments, or heat of formation estimates needed to support the existing estimation methods, are also lacking or unreliable for many types of radicals formed in aromatic systems or other systems with multiple double bonds, limiting the utility of the system for development of explicit mechanisms for aromatics. Although progress was made in this project to adapt this system to be more useful in mechanism development for such compounds, it has not yet evolved to the point where it can used to derive complete or reliable mechanisms for actual implementation in airshed models. Further work in this area, and expanding its capabilities to other types of compounds, would clearly be useful, and ultimately aid mechanism development and reactivity estimates for a wider variety of VOCs than currently possible.

Adaptation to SOA Predictions. As discussed above, the initial version of SAPRC-07 documented in this report does not fully take advantage of the enhanced capabilities of this mechanism to represent formation of low volatility SOA precursors and how they depend on NO_x conditions. Work in this area is clearly the next step in developing improved models for secondary PM formation that can predict how PM formation varies with chemical conditions. Although the chemistry and physics of SOA formation is complex and much long-term research is needed, significant advances can be made in the short term to enhance SAPRC-07, and its associated mechanism generation system, to take better advantage of the capability of this mechanism for SOA predictions. This could include the following.

- Adding new lumped organic product model species to represent compounds of low volatility. This would include new model species for low volatility hydroperoxides (besides those formed from aromatics) and organic nitrates, as well as those formed in the oxidations in the presence of NO_x such as those represented in current PM models
- Implementing methods to estimate product volatility based on structure in the mechanism generation system, and using these to lump the products formed in the fully explicit generated mechanisms into the appropriate low volatility model species. In principle, this would result in generations of mechanisms for predicting SOA as well as O_3 reactivity.
- Evaluating the enhanced mechanisms' predictions of SOA using available environmental chamber data where PM measurement data are available. There is an increasing body of environmental chamber data suitable for this purpose, being generated at our laboratories and elsewhere that can be used for this purpose.

- Conducting environmental chamber experiments with PM measurements suitable for testing predictions of the enhanced mechanism that cannot be evaluated with available data. A priority would be to evaluate the predictive capability of the mechanism generation system in this regard, and to determine which parameterization and volatility lumping approaches are most consistent with the data for the widest variety of compounds.

The current mechanism does include a separate model species to represent the low volatility hydroperoxides formed from aromatics, primarily as a means to illustrate this capability, but its ability to predict SOA chamber experiments has not yet been evaluated. However, this version serves as a useful starting point in this regard, and will therefore allow a much more straightforward approach to develop models that more accurately predict how SOA formation varies with conditions of NO_x availability.

Once adapted and evaluated as indicated above, the enhanced PM mechanism would need to be implemented in actual airshed models and evaluated against ambient data. It could also serve as a basis for deriving SOA reactivity scales for VOCs, should that be of interest in regulatory applications (Seinfeld et al, 1999).

Mechanism Performance Issues. Although the updated mechanism simulates the available environmental chamber database reasonably well, the results of the mechanism evaluation carried out for this project indicated several potential problems that need to be investigated. The fact that the mechanism update caused slightly increased biases in simulations of experiments with various mixtures is an area of concern. The statistical significance of these small biases needs to be assessed, and an analysis of their potential sources needs to be carried out. The tendency of the mechanism to underpredict O_3 at low ROG/NO_x ratios is clearly statistically significant, and has not been resolved with this update. The experiments with the individual compounds do not clearly point to any specific compound or group of compound whose mechanism is causing the problems, and suggest that this is due to some change in the base mechanism. A related issue is the fact that changes to the base mechanism have caused changes in model performance in simulations of experiments with compounds or mixtures whose mechanisms have not changed, with reduced biases for some glycols and isoparaffinic alkane mixtures, and slightly increased biases for some other compounds.

Assessing the mechanism performance issues with mixtures, and the effects of base mechanism changes on evaluation results for individual compounds, will probably require more in-depth analysis of mechanism behavior than previously has been carried out. Application of existing uncertainty and sensitivity analysis and process analysis methods may be useful in this regard, but probably new analysis methods will need to be developed. The objective would be to determine what uncertain portions of the base mechanisms may be introducing biases in the model evaluations, the extent to which these biases may be significant when the mechanism is used in ambient simulations or control strategy assessments, whether adjustments of these uncertain areas to reduce these biases may be justifiable, and if so what adjustments should be made. This is an area where original research is needed.

Mechanism Evaluation Database. Although the updated mechanism includes what we believe are improved estimates for a number of types of VOCs for which no data is available, in many cases the reliability of these estimates needs to be experimentally tested. This is particularly true for amines and those halogenated compounds for which no environmental chamber reactivity data are available. Environmental chamber reactivity studies of representatives of these and other previously unstudied chemical classes are needed to reduce uncertainties in their mechanisms and associated reactivity estimates. The reactivity tabulations include uncertainty codes indicating those compounds for which experimental data are most needed.

Although in general both SAPRC-99 and SAPRC-07 perform reasonably well in simulating results of experiments in the various UCR chambers and also the TVA chamber, the performance is not as satisfactory in simulating the results of some of the older UNC outdoor chamber experiments used in the SAPRC-90 and RADM2 evaluations (Carter and Lurmann, 1990, 1991). This is true in experiments with propene, toluene, o-xylene, and a number of mixture runs. On the other hand, the SAPRC mechanisms perform reasonably well in simulating results of more recent UNC chamber experiments that were used in the evaluation of Carter and Atkinson (1996), suggesting that some of the differences may be reduced if more recent datasets were employed. The difference performance in the case of aromatics may be one source of difference between the SAPRC and Carbon Bond mechanisms, since the latter relied more heavily on the UNC chamber datasets during its development (Gery et al, 1988). This needs to be investigated. An improved evaluation of mechanism performance issues, discussed above, may be useful in this regard. In the meantime, we believe that characterization uncertainties and background problems for the indoor SAPRC and TVA chambers are significantly less than for the earlier UNC chamber experiments, and consequently the indoor chamber data are used as the primary means of mechanism evaluation.

For many types of compounds, the primary dataset for mechanism evaluation consists of incremental reactivity experiments, in which the effect of adding the compound to simplified representative ambient mixtures is assessed. This provides the only useful mechanism evaluation dataset for compounds that are not radical initiators[1], and more closely approximates the environments where the VOC reacts than other types of experiments. However, model sensitivity calculations indicate that results of the currently available types of incremental reactivity experiments are much less sensitive to effects of secondary reactions of reactive organic products than is calculated for the atmosphere. This means that this aspect of the mechanism is not being adequately evaluated with the available dataset. Calculations indicate that experiments with higher overall radical levels, such as experiments with longer reaction times, higher light intensities, or various radical sources, are needed to improve mechanism evaluations in this respect.

The current dataset of environmental chamber experiments is also not adequate for systematically evaluating model predictions of temperature effects on secondary pollutant formation. The UCR-EPA chamber is suitable for carrying out such experiments, and in fact the plan for this project included conducting a limited number of experiments with temperature varied. However, because of problems with the light source, only a limited number of such experiments could be successfully carried out, and the conditions are not yet adequately characterized for mechanism evaluation. Additional work in this area is still needed.

Mechanism Adaptation. Because the mechanism development and evaluation was not completed until well after the project was scheduled for completion, there was insufficient time and resources remaining to implement this mechanism in any comprehensive airshed model. This work remains to be done, and as indicated above we will assist the model implementers in this regard as needed. This report, and the files and additional documentation that are being made available at the SAPRC mechanism web site at http://www.cert.ucr.edu/~carter/SAPRC should provide the information needed.

In addition, there was also insufficient time and resources in this project to prepare a condensed version of the updated mechanism as discussed in the proposal for this project (Carter, 2003b). Although computer capabilities are continuing to increase, for some modeling applications a more condensed, and computationally efficient, mechanism may give adequate predictions, and it may be more important to apply more of the available computer resources to other modules in the model, or to enhance spatial

---

[1] Chamber experiments with compounds without significant internal radical sources are dominated by uncertain and variable chamber effects unless other reactants are present to provide the radical initiation.

resolution. Therefore, a more condensed version of this updated and evaluated mechanism is still needed. Preliminary versions of SAPRC-07 condensed mechanisms have been developed (Carter, 2008c), but these mechanisms have not yet been finalized.

In order to derive a condensed mechanism for representing complex mixtures in airshed model applications, it is necessary to use a standard "base reactive organic gas (ROG)" mixture to represent the mixture of anthropogenic VOCs emitted into ambient atmospheres to derive the parameters for the mechanism's lumped model species. Ideally this mixture should be derived for each scenario being modeled, and procedures and data files exist for doing this for the SAPRC-99 mechanism (Carter, 2000b, Adleman et al, 2005; Carter, 2008b), which will be adapted to the updated mechanism in the future (Carter, 2008b). However, in practice modelers have preferred to continue to use the "fixed parameter" version of the mechanism, where the parameters for the lumped model species are derived using a standard mixture used for this purpose, and incorporated in the mechanism without change. Such a fixed parameter mechanism was developed as part of this work.

The updated fixed parameter mechanism developed in this work employed the same standard base ROG mixture as used for the fixed-parameter version of SAPRC-99 (Carter, 2000b), which is the base ROG mixture used in the original reactivity calculations of Carter (1994a). This mixture was derived by Jeffries (1989) from analysis of air quality data of Lonneman (1986), with minor modifications as discussed by Carter (1994a,b). Since advances have been made in analytical methods and emissions compositions have probably changed since the mid-80's, this mixture is out of date and needs to be updated. However, attempts to obtain a documented updated base ROG mixture from the CARB or EPA have been unsuccessful. Once such a mixture becomes available, the fixed parameter version of the mechanism should be updated accordingly.

Reactivity Scales Update. The updated reactivity scales developed in this work can be considered to represent the state of the science in atmospheric chemistry, though as indicated above there are uncertainties and areas where further research is needed. However, updating the scenarios and reactivity calculation methodology was beyond the scope of this project, so the same scenarios and methodologies were used as employed by Carter (1994a). Evaluations carried out by the Reactivity Research Working Group (RRWG) indicate that this methodology could be improved in a number of respects (NARSTO, 2007), particularly the scenarios and modeling methods. At a minimum the scenarios should be updated to represent the range of conditions currently occurring in urban areas, and the derivation of the scenarios should be better documented. The mechanism developed in this work can then be used for calculating reactivity scales with scenarios and methodology updated as well as the mechanism.

Research Priorities. The priorities for the recommended research discussed above depend on the time frame and the priorities of the funding agencies. In terms of use of the mechanism for modeling, the highest near-term priorities are adaptation of the mechanism for airshed models, implementing the emissions assignments, and developing and adapting the condensed version of the mechanism. This work is presently unfunded, but is needed before this mechanism can be widely used. In terms of the reactivity scales, the highest near-term priority is probably reducing uncertainties concerning availabilities of amines to react in the gas phase, assuming that suitable experimental procedures to assess this can be developed. Improved reactivity estimates for other classes of compounds may become priorities in the near future, but as far as we are aware the amines is the greatest near-term concern for the CARB.

In the medium term the highest priority is probably reducing the uncertainty in the gas-phase predictions of the mechanism in general. Even for applications where PM modeling is a priority, one needs a mechanism that can appropriately simulate gas-phase processes before it can be expected to appropriately simulate formation of secondary PM. In this regard, we recommend that priority be given for research aimed as assessing the existing discrepancies between model predictions and chamber data, discussed above under the heading "Mechanism Performance Issues," and uncertainty and process analyses aimed at relating these performance issues and associated uncertainties to ambient predictions of interest. This would aid in the development of effective research agendas for improving mechanism performance in priority areas, and obtaining the data (either environmental chamber or basic laboratory measurements) most needed to serve this objective.

Regardless of the results of the process or performance analysis, it is clear that the mechanisms for aromatics remain an important uncertainty. However, breakthroughs in fundamental studies, perhaps using improved analytical methods that actually give reliable quantitative product yields, or development of improved theoretical methods that actually have predictive capabilities, are probably needed before additional mechanism update work and chamber studies may be useful. Medium and longer term research priorities should include support for exploratory methods that might achieve the needed breakthroughs, even if there is some risk of failure.

The priority for adaptation of the mechanism for PM modeling depends on the priority to the funding agency for predictive modeling of secondary PM and SOA. The CARB should use an integrated approach for developing improved mechanisms for gas-phase and PM formation processes, and building on the mechanism development effort they supported for ozone modeling, as discussed above under the heading "Adaptation to SOA Predictions" would be consistent with this approach. If the CARB decides instead to use another mechanism as the basis for PM and SOA predictions, then the priority becomes assuring that that mechanism performs sufficiently well in simulating gas-phase processes to reliably predict rates of formation of low-volatility PM precursors from gas-phase processes. At a minimum, that mechanism should also be suitable for ozone modeling.

The work needed to improve the scenarios and methodology for reactivity assessment should be given sufficient priority so that it is complete by the time the next reactivity scale update is due. Otherwise, we will continue to use the poorly documented EKMA scenarios that are already way out-of-date, and this may eventually impact the credibility of the reactivity scales as a whole. Ideally this should be funded on a national level.

REFERENCES

Adelman, Z. J. Vukovich, and W. P. L. Carter (2005): "Integration of the SAPRC Chemical Mechanism in the SMOKE Emissions Processor for the CMAQ/Models-3 Airshed Model," Final report to American Chemistry Council Agreement No. 1846. Available at http://www.cert.ucr.edu/~carter /absts.htm#smokespr

Alvarez, R. A. and B. Moore (1994): "Quantum Yield for Production of CH_3NC in the Photolysis of CH_3NCS," Science, 263, 205-207.

Albaladejo, J., A. Notario, C. A. Cuevas, B. Ballesteros, and E. Martínez (2003): "A Pulsed Laser Photolysis-Resonance Fluorescence Kinetic Study of the Atmospheric Cl Atom-Initiated Oxidation of Propene and a Series of 3-Halopropenes at Room Temperature," J. Atm. Chem, 45, 35-50.

Anderson, L. G., and R. D. Stephens (1988): "Kinetics of the reaction of hydroxyl radicals with 2-(dimethylamino)ethanol from 234-364 K," Int. J. Chem. Kinet., 20, 103-110.

Aschmann, S. M. and R. Atkinson (1998): "Kinetics of the Gas-Phase Reactions of the OH Radical with Selected Glycol Ethers, Glycols, and Alcohols," Int. J. Chem. Kinet, 30, 533-540.

Aschmann, S. M. and R. Atkinson (1999): "Atmospheric chemistry of 1-methyl-2-pyrrolidinone," Atmos. Environ. 33, 591-599.

Atkinson, R. (1989): "Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds," J. Phys. Chem. Ref. Data, Monograph no 1.

Atkinson, R. (1991): "Kinetics and Mechanisms of the Gas-Phase Reactions of the NO_3 Radical with Organic Compounds," J. Phys. Chem. Ref. Data, 20, 459-507.

Atkinson, R. (1994): "Gas-Phase Tropospheric Chemistry of Organic Compounds," J. Phys. Chem. Ref. Data, Monograph No. 2.

Atkinson, R. (1997): "Gas Phase Tropospheric Chemistry of Volatile Organic Compounds: 1. Alkanes and Alkenes," J. Phys. Chem. Ref. Data, 26, 215-290.

Atkinson, R., R. A. Perry, and J. N. Pitts, Jr. (1977): "Rate constants for the reaction of the OH radical with CH_3SH and CH_3NH_2 over the temperature range 299–426 °K," J. Chem. Phys 66, 1578-1581.

Atkinson, R., R. A. Perry, and J. N. Pitts, Jr. (1978): "Rate constants for the reactions of the OH radical with $(CH_3)_2NH$, $(CH_3)_3N$, and $C_2H_5NH_2$ over the temperature range 298–426 °K," J. Chem. Phys 68, 1850-1853.

Atkinson, R., S. M. Aschmann and J. N. Pitts, Jr. (1983): "Kinetics of the Gas-Phase Reactions of OH Radicals with a Series of α,β-Unsaturated Carbonyls at 299±2 K," Int. J. Chem. Kinet. 15, 75.

Atkinson, R. and W. P. L. Carter (1984): "Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds under Atmospheric Conditions," Chem. Rev. 84, 437-470.

Atkinson, R. and S. M. Aschmann (1984): "Rate constants for the reactions of O_3 and OH radicals with a series of alkynes," Int. J. Chem. Kinet. 16, 259-268.

Atkinson, R., S. M. Aschmann, A. M. Winer and J. N. Pitts, Jr. (1985): "Atmospheric Gas Phase Loss Processes for Chlorobenzene, Benzotrifluoride, and 4-Chlorobenzotrifluoride, and Generalization of Predictive Techniques for Atmospheric Lifetimes of Aromatic Compounds," Arch Environ. Contamin. Toxicol. 14, 417.

Atkinson, R. and S. M. Aschmann (1987): "Kinetics of the Gas-Phase Reactions of Cl Atoms with Chloroethenes at 298 ± 2 K and Atmospheric Pressure," Int. J. Chem. Kinet. 19, 1097-1105.

Atkinson, R., S. M. Aschmann, and M. A. Goodman (1987): "Kinetics of the Gas-Phase Reactions of NO_3 Radicals with a Series of Alkynes, Haloalkenes, and α,β-Unsaturated Aldehydes," Int. J. Chem. Kinet. 19, 299-307.

Atkinson, R, S. M. Aschmann, E. C. Tuazon, J. Arey and B. Zielinska (1989): Int. J. Chem. Kinet. 21, 593.

Atkinson, R., S. M. Aschmann, and J. Arey (1991): "Formation of ring-retaining products from the OH radical-initiated reactions of o-, m-, and p-xylene," Int. J. Chem. Kinet., 23, 77-97.

Atkinson, R. and S. M. Aschmann (1994): "Products of the gas-phase reactions of aromatic hydrocarbons: effect of NO_2 concentration," Int. J. Chem. Kinet., 26, 929-944.

Atkinson, R., and W. P. L. Carter (1995): "Measurement of OH Radical Reaction Rate Constants for Purasolv ELS and Purasolv ML and Calculation of Ozone Formation Potentials," Final Report to Purac America, Inc., June.

Atkinson, R. and J. Arey (2003): "Atmospheric Degradation of Volatile Organic Compounds," Chem. Rev. 103, 4605-4638

Bailey, E. M., C. H. Copeland and R. Simonaitis (1996): "Smog Chamber Studies at Low VOC and NO_x Concentrations," Report on Interagency Agreement DW64936024 to EPA/NREL, Research Triangle Park, NC.

Bandow, H. N. and N. Washida (1985a): "Ring-cleavage reactions of aromatic hydrocarbons studied by FT-IR spectroscopy. II. Photooxidation of o-, m- and p-xylenes in the NO_x -air system," Bull. Chem. Soc. Jpn., 58, 2541-2548.

Bandow, H. N. and N. Washida (1985b): "Ring-cleavage reactions of aromatic hydrocarbons studied by FT-IR spectroscopy. III. Photooxidation of 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzenes in the NO_x -air system," Bull. Chem. Soc. Jpn., 58, 2549-2555.

Bandow, H., N. Washida, and H. Akimoto (1985): "Ring-cleavage reactions of aromatic hydrocarbons studied by FT-IR spectroscopy. I. Photooxidation of toluene and benzene in the NO_x -air system," Bull. Chem. Soc. Jpn., 58, 2531-2540.

Barnes, I. (2006): "Mechanisms of the Photoxidation of Aromatic Hydrocarbons: Chemistry of Ring-Retaining Products," Presented at the International Conference on Atmospheric Chemical Mechanisms, Davis CA, December 6-8. See http://www.cert.ucr.edu/~carter/Mechanism_Conference.

Barnes, I., V. Bastian, K. H. Becker, and D. Martin (1989), "Fourier Transform IR Studies of the Reaction of Dimethyl Sulfoxide with OH, NO_3, and Cl Radicals," in "Biogenic Sulfur in the Environment," E. S. Saltzman and W. J. Cooper, Editors, ACS Symposium Series 393, American Chemical Society, Washington, DC.

Baugues, K. (1990): "Preliminary Planning Information for Updating the Ozone Regulatory Impact Analysis Version of EKMA," Draft Document, Source Receptor Analysis Branch, Technical Support Division, U. S. Environmental Protection Agency, Research Triangle Park, NC, January.

Becker, K. H., V. Bastian, and Th. Klein (1988): "The Reactions of OH Radicals with Toluene Diisocyanate, Toluenediamine and Methylenedianiline Under Simulated Atmospheric Conditions," J. Photochem. Photobiol A., 45 195-205.

Becker, K. H., et. al., (1997): "OH initiated oxidation of VOC under variable NO_x conditions," in "Chemical Processes in Atmospheric Oxidation," edited by G. Le Bras, pp. 79-90, Springer-Verlag, Berlin, Germany.

Becker, K. H., and F. Graedler (1999): "Photochemie ausgewahlter Dicarbonylverbindungen unter atmospharischen Bedingungen, Bericht Nr. 49, Physikalische Chemie (Fachbereich 9), Bergische Universitat, GH-Wuppertal, December.

Bejan, Y. Abd el Aal, I. Barnes, T. Benter, B. Bohn, P. Wiesen and J. Kleffmann (2006): "The photolysis of ortho-nitrophenols: a new gas-phase source of HONO, " Physical Chemistry Chemical Physics 8, 2028–2035.

Berndt, T. and O. Böge (2003): "Gas-phase reaction of OH radicals with phenol," Phys. Chem. Chem. Phys. 5, 342-350.

Berndt, T. and O. Böge (2006): "Formation of phenol and carbonyls from the atmospheric reaction of OH radicals with benzene," Phys. Chem. Chem. Phys 8, 1205-1214.

Bennett, P. J. and J. A. Kerr (1989): "Kinetics of the Reactions of Hydroxyl Radicals with Aliphatic Esters Studied Under Simulated Atmospheric Conditions," J. Atmos. Chem. 8, 87.

Bethel, H. L., R. Atkinson, and J. Arey (2001): "Kinetics and Products of the Reactions of Selected Diols with the OH Radical," Int. J. Chem. Kinet. 33, 310-316.

Bierbach A., Barnes I., and Becker K.H. (1992): Atmos. Environ. 26A, 813.

Bierbach A., Barnes I., Becker K.H. and Wiesen E. (1994) Atmospheric chemistry of unsaturated carbonyls: Butenedial, 4-oxo-2-pentenal, 3-hexene-2,5-dione, maleic anhydride, 3H-furan-2-one, and 5-methyl-3H-furan-2-one. Environ. Sci. Technol., 28, 715-729.

Blitz, M. A., D. E. Heard, M. J. Pilling, S. R. Arnold and M. P. Chipperfield (2004): "Pressure and temperature-dependent quantum yields for the photodissociation of acetone between 279 and 327.5 nm," Geophys. Res. Lett., 31, L06111.

Bloss, C., V. Wagner, A. Bonzanini, M. E. Jenkin, K. Wirtz, M. Martin-Reviejo, and M. J. Pilling (2005): "Evaluation of detailed aromatic mechanisms (MCMv3 and MCMv3.1) against environmental chamber data, Atmos Chem Phys, 5, 623-639.

Brauers, T., B. Bohn, F.-J. Johnen, F. Rohrer, S. Rodriguez Bares, R. Tillmann, and A. Wahner (2003): "The Atmosphere Simulation Chamber SAPHIR: a Tool for the Investigation of Photochemistry," Presented at the EGS - AGU - EUG Joint Assembly, Nice, France, April 11, 2003. See also http://www.fz-juelich.de/icg/icg-ii/saphir/home.

Bridier, I., F. Caralp, H. Loirat, R. Leschux, B. Veyret, K. H. Becker, A. Reimer, and F. Zabel (1991): "Kinetic and Theoretical Studies of the Reactions $CH_3C(O)O_2 + NO_2 + M = CH_3C(O)O_2NO_2 + M$ between 248 and 393 K and between 30 and 760 Torr," J. Phys. Chem., 95, 3594-3600

Calvert, J. G., R. Atkinson, J. A. Kerr, S. Madronich, G. K. Moortgat, T. J. Wallington and G. Yarwood (2000): "The Mechanisms of Atmospheric Oxidation of Alkenes," Oxford University Press, New York.

Calvert, J. G., and J. N. Pitts, Jr. (1966): "Photochemistry," John Wiley and Sons, New York.

Calvert, J. G., R. Atkinson, K. H. Becker, R. M. Kamens, J. H. Seinfeld, T. J. Wallington and G. Yarwood (2002): "The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons," Oxford University Press, New York.

CARB (1993): "Proposed Regulations for Low-Emission Vehicles and Clean Fuels -- Staff Report and Technical Support Document," California Air Resources Board, Sacramento, CA, August 13, 1990. See also Appendix VIII of "California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light Duty Trucks and Medium Duty Vehicles," as last amended September 22, 1993. Incorporated by reference in Section 1960.

CARB (2000): "Initial Statement of Reasons for the Proposed Amendments to the Regulation for Reducing Volatile Organic Compound Emissions from Aerosol Coating Products and Proposed Tables of Maximum Incremental Reactivity (MIR) Values, and Proposed Amendments to Method 310, 'Determination of Volatile Organic Compounds in Consumer Products'," California Air Resources Board, Sacramento, CA, May 5.

CARB (2006): "Air Resources Board Reactivity Programs." Web page at http://www.arb.ca.gov/research/reactivity/reactivity.htm. Last updated April, 2006

CARB (2007): "Architectural Coatings Program - Reactivity." Web page at http://www.arb.ca.gov/coatings/arch/reactivity/reactivity.htm. Last updated January, 2007.

Carl, S. A. and J. N. Crowley (1998): "Sequential two (blue) photon absorption by NO_2 in the presence of H_2 as a source of OH in pulsed photolysis kinetic studies: rate constants for reactions of OH with CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, and $C_2H_5NH_2$ at 295 K," J. Phys. Chem. A, 102, 8131-8141.

Carter, W. P. L. (1990): "A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds," Atmos. Environ., 24A, 481-518.

Carter, W. P. L. (1994a): "Development of Ozone Reactivity Scales for Volatile Organic Compounds," J. Air & Waste Manage. Assoc., 44, 881-899.

Carter, W. P. L. (1994b): "Calculation of Reactivity Scales Using an Updated Carbon Bond IV Mechanism," Report Prepared for Systems Applications International Under Funding from the Auto/Oil Air Quality Improvement Research Program, April 12.

Carter, W. P. L. (1996): "Condensed Atmospheric Photooxidation Mechanisms for Isoprene," Atmos. Environ., 30, 4275-4290.

Carter, W. P. L. (2000a): "Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment," Report to the California Air Resources Board, Contracts 92-329 and 95-308, May 8. Available at http://cert.ucr.edu/~carter/absts.htm#saprc99 and http://www.cert.ucr.edu/~carter/reactdat.htm.

Carter, W. P. L. (2000b): "Implementation of the SAPRC-99 Chemical Mechanism into the Models-3 Framework," Report to the United States Environmental Protection Agency, January 29. Available at http://www.cert.ucr.edu/~carter/absts.htm#s99mod3.

Carter, W. P. L. (2003a): "The SAPRC-99 Chemical Mechanism and Updated VOC Reactivity Scales, Updated and Corrected Data as of February 5, 2003," Available at http://www.cert.ucr.edu /~carter/reactdat.htm.

Carter, W. P. L. (2003b): "Updated Chemical Mechanism for Airshed Model Applications," Research Proposal to the California Air Resources Board, October.

Carter, W. P. L. (2004): Evaluation of a Gas-Phase Atmospheric Reaction Mechanism for Low NO_x Conditions," Final Report to California Air Resources Board Contract No. 01-305, May 5. Available at http://www.cert.ucr.edu/~carter/absts.htm#lnoxrpt.

Carter, W. P. L. (2007): "Investigation of the Atmospheric Ozone Impacts of Methyl Iodide," Final Report to Arysta LifeScience Corporation, Contract UCR-07041867, July 31. Available at http://www.cert.ucr.edu/~carter/absts.htm#ch3irep.

Carter, W. P. L. (2008a). "Reactivity Estimates for Selected Consumer Product Compounds," Final Report to the California Air Resources Board Contract 06-408, February 19. Available at http://www.cert.ucr.edu/~carter/absts.htm#aminrep.

Carter, W. P. L. (2008b): "Current Project Information Page: Development of an Improved Chemical Speciation Database for Processing Emissions of Volatile Organic Compounds for Air Quality Models," Web page available at http://www.cert.ucr.edu/~carter/emitdb/, updated May 27.

Carter, W. P. L. (2008c): "Development of a Condensed SAPRC-07 Chemical Mechanism," Draft Final Report to the California Air Resources Board, May 27. Once this report is finalized, it will be made available at http://www.cert.ucr.edu/~carter/SAPRC.

Carter, W. P. L. (2009a): "Investigation of the Atmospheric Ozone Impacts of Trans 1,3,3,3-Tetrafluoropropene," Final Report to Honeywell International Inc. Contract UCR-09010016, February 9. Available at http://www.cert.ucr.edu/~carter/absts.htm #ZEErept.

Carter, W. P. L. (2009b): "Investigation of the Atmospheric Ozone Impacts of 2,3,3,3-Tetrafluoropropene," Final Report to Honeywell International Inc. Contract UCR-09010016, June 2. Available at http://www.cert.ucr.edu/~carter/absts.htm #YFrept.

Carter, W. P. L. (2009c): "Updated Maximum Incremental Reactivity Scale and Hydrocarbon Bin Reactivities For Regulatory Applications," Report to the California Air Resources Board, June 22. Available at http://www.cert.ucr.edu/~carter/SAPRC.

Carter, W. P. L., R. Atkinson, A. M. Winer, and J. N. Pitts, Jr. (1982): "Experimental Investigation of Chamber-Dependent Radical Sources," Int. J. Chem. Kinet., 14, 1071.

Carter, W. P. L., Dodd, M. C., Long, W. D. and Atkinson, R. (1984): Outdoor Chamber Study to Test Multi-Day Effects. Volume I: Results and Discussion. Final report, EPA-600/3-84-115.

Carter, W. P. L. and R. Atkinson (1987): "An Experimental Study of Incremental Hydrocarbon Reactivity," Environ. Sci. Technol., 21, 670-679

Carter, W. P. L., and F. W. Lurmann (1990): "Evaluation of the RADM Gas-Phase Chemical Mechanism," Final Report, EPA-600/3-90-001.

Carter, W. P. L. and F. W. Lurmann (1991): "Evaluation of a Detailed Gas-Phase Atmospheric Reaction Mechanism using Environmental Chamber Data," Atm. Environ. 25A, 2771-2806.

Carter, W. P. L., J. A. Pierce, and I. L. Malkina (1992): "Investigation of the Ozone Formation Potential of Selected Volatile Silicone Compounds," Final report to Dow-Corning Corporation, November.

Carter, W. P. L., J. A. Pierce, I. L. Malkina, D. Luo and W. D. Long (1993): "Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds," Report to Coordinating Research Council, Project No. ME-9, California Air Resources Board Contract No. A032-0692; South Coast Air Quality Management District Contract No. C91323, United States Environmental Protection Agency Cooperative Agreement No. CR-814396-01-0, University Corporation for Atmospheric Research Contract No. 59166, and Dow Corning Corporation. April 1. Available at http://www.cert.ucr.edu/~carter/absts.htm#rct1rept

Carter, W. P. L., D. Luo, I. L. Malkina, and D. Fitz (1995a): "The University of California, Riverside Environmental Chamber Data Base for Evaluating Oxidant Mechanism. Indoor Chamber Experiments through 1993," Report submitted to the U. S. Environmental Protection Agency, EPA/AREAL, Research Triangle Park, NC, March 20.

Carter, W. P. L., D. Luo, I. L. Malkina, and J. A. Pierce (1995b): "Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying Chamber and Light Source," Final report to National Renewable Energy Laboratory, Contract XZ-2-12075, Coordinating Research Council, Inc., Project M-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323, March 26.

Carter, W. P. L., D. Luo, I. L. Malkina, and J. A. Pierce (1995c): "Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying ROG Surrogate and NO_x," Final report to Coordinating Research Council, Inc., Project ME-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323. March 24.

Carter, W. P. L. and R. Atkinson (1996): "Development and Evaluation of a Detailed Mechanism for the Atmospheric Reactions of Isoprene and NO_x," Int. J. Chem. Kinet., 28, 497-530.

Carter, W. P. L., D. Luo, and I. L. Malkina (1996a): "Investigation of the Atmospheric Ozone Formation Potential of Trichloroethylene," Report to the Halogenated Solvents Industry Alliance, August. Available at http://www.cert.ucr.edu/~carter/absts.htm#tcerpt.

Carter, W. P. L., D. Luo, and I. L. Malkina (1996b): "Investigation of the Atmospheric Ozone Formation Potential of t-Butyl Alcohol, N-Methyl Pyrrolidinone and Propylene Carbonate," Report to ARCO Chemical Corporation, July 8.

Carter, W. P. L., D. Luo, and I. L. Malkina (1997a): "Environmental Chamber Studies for Development of an Updated Photochemical Mechanism for VOC Reactivity Assessment," final report to California Air Resources Board Contract 92-345, Coordinating Research Council Project M-9, and National Renewable Energy Laboratory Contract ZF-2-12252-07. November 26. Available at

Carter, W. P. L., D. Luo and I. L. Malkina (1997b): "Investigation of that Atmospheric Reactions of Chloropicrin," Atmos. Environ. 31, 1425-1439; See also Report to the Chloropicrin Manufacturers Task Group, May 19. Report available at http://www.cert.ucr.edu/~carter/absts.htm#clpicrin.

Carter, W. P. L., D. Luo, and I. L. Malkina (1997c): "Investigation of the Atmospheric Ozone Formation Potential of Acetylene," Report to Carbide Graphite Corp., April 1. Available at http://www.cert.ucr.edu/~carter/absts.htm#acetylr

Carter, W. P. L., D. Luo, I. L. Malkina, S. M. Aschmann and R. Atkinson (1997c): "Investigation of the Atmospheric Ozone Formation Potentials of Selected Dibasic Esters," Report to the Dibasic Esters Group, SOCMA, August 29.

Carter, W. P. L., D. Luo, and I. L. Malkina (1997d): "Investigation of the Atmospheric Ozone Formation Potential of Toluene Diisocyanate," Report to Society of the Plastics Industry, December.

Carter, W. P. L., D. Luo, and I. L. Malkina (1997e): "Investigation of the Atmospheric Ozone Formation Potentials of Selected Mineral Spirits Mixtures," Report to Safety-Kleen Corporation, July 25. Available at http://www.cert.ucr.edu/~carter/absts.htm#msrept.

Carter, W. P. L., D. Luo, and I. L. Malkina (1999a): "Investigation of the Atmospheric Ozone Formation Potential of Para Toluene Isocyanate and Methylene Diphenylene Diisocyanate," Report to the Chemical Manufacturers Association Diisocyanates Panel, March. 8. Available at http://www.cert.ucr.edu/~carter/absts.htm#mdirpt

Carter, W. P. L., D. Luo, and I. L. Malkina (1999b): ‘Investigation of the Atmospheric Impacts and Ozone Formation Potential of Styrene," Report to the Styrene Information and Research Center. March 10. Available at http://www.cert.ucr.edu/~carter/absts.htm#styrept.

Carter, W. P. L. and E. C. Tuazon (2000): “Atmospheric Chemistry of Bromine Containing Compounds,” Report to the Brominated Solvents Consortium, September 27. Available at http://www.cert.ucr.edu/~carter/absts.htm#brreport.

Carter, W. P. L., D. Luo, and I. L. Malkina (2000a): "Investigation of the Atmospheric Ozone Formation Potentials of Selected Branched Alkanes and Mineral Spirits Samples," Report to Safety-Kleen Corporation, July 11. Available at http://www.cert.ucr.edu/~carter/absts.htm#msrpt2.

Carter. W. P. L., D. Luo and I. L. Malkina (2000b): "Investigation of Atmospheric Reactivities of Selected Consumer Product VOCs," Report to California Air Resources Board, May 30. Available at http://www.cert.ucr.edu/~carter/absts.htm#cpreport.

Carter, W. P. L., D. Luo, and I. L. Malkina (2000c): "Investigation of the Atmospheric Ozone Formation Potentials of Selected Carbonates," Report to ExxonMobil Chemical Company, November 17. Available at http://www.cert.ucr.edu/~carter/absts.htm#carbonat.

Carter, W. P. L., D. Luo, and I. L. Malkina (2000d): "Investigation of the Atmospheric Ozone Formation Potential of Dimethyl Sulfoxide," Report to Gaylord Chemical Corporation, August 21. Available at http://www.cert.ucr.edu/~carter/absts.htm#dmsorpt.

Carter, W. P. L., D. Luo, and I. L. Malkina (2000e): "Investigation of the Ozone Formation Potentials of Exxsol® D95, Isopar-M®, and the Exxate® Fluids," Report to ExxonMobil Chemical Company, October 31. Available at http://www.cert.ucr.edu/~carter/absts.htm#exxprods.

Carter, W. P. L. and I. L. Malkina (2002): "Development and Application of Improved Methods for Measurement of Ozone Formation Potentials of Volatile Organic Compounds," Final report to California Air Resources Board Contract 97-314, May 22. Available at http://www.cert.ucr.edu/~carter/absts.htm#rmethrpt.

Carter, W. P. L. and I. L. Malkina (2005): "Evaluation of Atmospheric Impacts of Selected Coatings VOC Emissions," Final report to the California Air Resources Board Contract No. 00-333, March 21. Available at http://www.cert.ucr.edu/~carter/absts.htm#coatrpt.

Carter, W. P. L., I. L. Malkina, D. R. Cocker III, and C. Song (2005a): "Environmental Chamber Studies of VOC Species in Architectural Coatings and Mobile Source Emissions," Final Report to the South Coast Air Quality Management District Contract No. 03468, July 5. Available at http://www.cert.ucr.edu/~carter/absts.htm#scaqcham.

Carter, W. P. L., D. R. Cocker III, D. R. Fitz, I. L. Malkina, K. Bumiller, C. G. Sauer, J. T. Pisano, C. Bufalino, and C. Song (2005b): "A New Environmental Chamber for Evaluation of Gas-Phase Chemical Mechanisms and Secondary Aerosol Formation", Atmos. Environ. 39 7768-7788.

Carter, W. P. L. and I. L. Malkina (2007): "Investigation of the Atmospheric Impacts of Selected Pesticides," Final Report to the California Air Resources Board Contract 04-334, January 10. Available at http://www.cert.ucr.edu/~carter/absts.htm#pestrep.

Chen, Y. and L. Zhu (2001). "The Wavelength Dependence of the Photodissociation of Propionaldehyde in the 280-330 nm Region," J.Phys.Chem.A 105, 9689-9696.

Carter, W. P. L., W. S. Goliff, R. Atkinson, J. Arey, and S. M. Aschmann (2010): "Investigation of Atmospheric Ozone Impacts of 3-Methoxy-3-Methyl-1-Butanol," Final report to Kuraray, Ltd. Will be made available at http://www.cert.ucr.edu/~carter/absts.htm #MMBrept when completed. (Estimated completion February, 2010.)

Christensen, L. K., J. Sehested, O. J. Nielsen, M. Bilde, T. J. Wallington, A. Guschin, L. T. Molina, and M. J. Molina (1998): "Atmospheric Chemistry of HFE-7200 ($C_4F_9OC_2H_5$): Reaction with OH Radicals and Fate of $C_4F_9OCH_2CH_2O(\cdot)$ and $C_4F_9OCHO(\cdot)CH_3$ Radicals,"J. Phys. Chem. A, 1998, 102, 4839-4845

Coquet, S. and P. A. Ariya (2000): "Kinetics of the Gas-Phase Reactions of Cl Atom with Selected C2–C5 Unsaturated Hydrocarbons at 283 <T< 323 K," Int. J. Chem. Kinet. 32, 478-484.

Cuevas, C. A., A. Notariob, E. Martıneza, and J. Albaladejo (2006): "Temperature-dependence study of the gas-phase reactions of atmospheric Cl atoms with a series of aliphatic aldehydes," Atmos. Env. 40, 3845–3854.

Dagaut, P., R. Liu, T. J. Wallington, and M. J. Kurylo (1989): "Kinetic Measurements of the Gas-Phase Reactions of OH Radicals with Hydroxy Ethers, Hydroxy Ketones, and Keto Ethers," J. Phys. Chem, 93, 7838-7840.

Docherty, K. S., W. Wu, Y. B. Lim, and P. J. Ziemann (2005): "Contributions of Organic Peroxides to Secondary Aerosol Formed from Reactions of Monoterpenes with O3," Environmental Science and Technology, 39(11), 4049-4059.

Donaghy, T., I. Shanahan, M. Hande and S. Fitzpatrick (1993): Int. J. Chem. Kinet. 25, 273.

EPA (1984): "Guideline for Using the Carbon Bond Mechanism in City-Specific EKMA," EPA-450/4-84-005, February.

Falbe-Hansen, H., S. Sørensen, N. R. Jensen, T. Pedersen, and J. Hjorth (2000): "Atmospheric Gas-Phase Reactions of Dimethylsulfoxide and dimethylsulfone with OH and NO_3 radicals, Cl atoms and ozone," Atmos. Environ. 35, 1543-1551.

Fan, J. and R. Zhang (2004): "Atmospheric Oxidation Mechanism of Isoprene," Environ. Chem.. 2004, 1, 140-149.

Fantechi, G, N. R. Jensen, J. Hjorth- and J. Peeters (1998): "Mechanistic Studies of the Atmospheric Oxidation Of Methyl Butenol by OH Radicals, Ozone And NO3 Radicals," Atmos. Environ. 32, 3547-3556.

Gardner, E. P., P. D. Sperry, and J. G. Calvert, (1987): "Photodecomposition of acrolein in oxygen-nitrogen mixtures," J. Phys. Chem, 91, 1922-1930.

Gery, M. W., G. Z. Whitten, and J. P. Killus (1988): "Development and Testing of the CBM-IV for Urban and Regional Modeling," EPA-600/ 3-88-012, January.

Golden, D. M., J. R. Barker and L. L. Lohr (2003): "Master Equation Models for the Pressure- and Temperature-Dependent Reactions $OH + NO_2 \rightarrow HONO_2$ and $OH + NO_2 \rightarrow HOONO$," J. Phys. Chem. A, 107, 11057-11071.

Grosjean, E and D. Grosjean (1994): "Rate constants for the gas-phase reactions of Ozone with unsaturated Aliphatic Alcohols," Int. J. Chem. Kinet. 26, 1185-1191.

Guenther, A., C. Geron, T.Pierce, B. Lamb, P. Harley, and R.Fall (2000): "Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America" Atmospheric Environment, 34, 2205-2230.

Harris, G. W. and J. N. Pitts, Jr. (1983): "Rates of Reaction of OH with N,N-Dimethylaminoethanol and 2-Amino-2-Methyl-1-Propanol in the Gas Phase at 300+/-2K, Environ. Sci. & Technol., 17, 50-51

Harris, G. W., T. E. Kleindienst, and J. N. Pitts, Jr. (1981): "Rate constants for the reaction of OH radicals with CH3CN, C2H5CN and CH2=CH-CN in the temperataure range 298-425K," Chem. Phys. Lett, 80, 479-483.

Hartmann, D., A. Gedra, D. Rhasa, and R. Zellner (1986): Proceedings, 4th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants, 1986; D. Riedel Publishing Co., Dordrecht, Holland, 1987, p. 225.

Hashimoto, S, H. Bandow, and X.-Y. Tang (1984): "Products and Mechanism for the OH Radical Initiated Oxidation of Acrylonitrile, Methacrylonitrile, and Allylcyanide in the Presence of NO," Int J. Chem. Kinet 16, 1385-1399.

Heicklen, J., J. Desai, A. Bahta, C. Harper, and R. Simonaitis (1986), J. Photochem. 34, 117

Hurley, M. D., O. Sokolov, T. J. Wallington, H. Takekawa, M. Karasawa, B. Klotz, I. Barnes, and K. H. Becker (2001): "Organic aerosol formation during the atmospheric degradation of toluene," Environ Sci Technol, 35(7), 1358-1366.

Hufford, D. L., D. S. Tarbell, and T. R. Koszalka (1952): "Maleic and fumaric dialdehydes, Δ^4-tetrahydrophthaldehyde and related compounds," J. Am. Chem. Soc. 74, 3014-3018.

IUPAC (1997): "Evaluated Kinetic, Photochemical and Heterogeneous Data for Atmospheric Chemistry: Supplement V and VI, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry," Phys. Chem. Ref. Data, 26-, 521-1011 (Supplement V) and 1329-1499 (Supplement VI).

IUPAC (2006): "Evaluated Kinetic and Photochemical Data". IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. Web Version. Available at http://www.iupac-kinetic.ch.cam.ac.uk. Latest data sheets dated June, 2006.

Jeffries, H. E., R. M. Kamens, K. G. Sexton, and A. A. Gerhardt (1982): "Outdoor Smog Chamber Experiments to Test Photochemical Models", EPA-600/3-82-016a, April.

Jeffries, H. E., Sexton, K. G., Kamens, R. M. and Holleman, M. S. (1985a): "Outdoor Smog Chamber Experiments to Test Photochemical Models: Phase II," Final Report, EPA-600/3-85-029.

Jeffries, H. E., Sexton, K. G., Morris, T. P., Jackson, H., Goodman, R. G., Kamens, R. M. and Holleman, M. S. (1985b): "Outdoor Smog Chamber Experiments Using Automobile Exhaust," Final Report, EPA-600/3-85-032.

Jeffries, H. E., K. G. Sexton, J. R. Arnold, and T. L. Kale (1989): "Validation Testing of New Mechanisms with Outdoor Chamber Data. Volume 2: Analysis of VOC Data for the CB4 and CAL Photochemical Mechanisms," Final Report, EPA-600/3-89-010b.

Jenkin, M. E., S. M. Saunders, and M. J. Pilling (1997): "The tropospheric degradation of volatile organic compounds: A protocol for mechanism development," Atmos Environ, 31(1), 81-104.

Jenkin, M. E., S. M. Saunders, V. Wagner, and M. J. Pilling (2003): "Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds," Atmos Chem Phys, 3, 181-193.

Kirchner, F., F. Zabel and K. H. Becker (1992): "Kinetic Behavior of Benzoylperoxy Radicals in the Presence of NO and NO2," Chem. Phys. Lett. 191, 169-174.

Klotz, B. G., A. Bierbach, I. Barnes, and K. H. Becker (1995): "Kinetic and Mechanistic Study of the Atmospheric Chemistry of Muconaldehydes," Environ. Sci. Technol. 29, 2322-2332.

Klotz, B. G., I. Barnes and K. H. Becker (1999): "Kinetic study of the gas-phase photolysis and OH radical reactions of E,Z- and E,E-2,4-hexadienedial," Int. H. Chem. Kinet., 31, 689-697.

Klotz, B., F. Graedler, S. Sørensen, I. Barnes, and K.-H. Becker (2000): "A Kinetic Study of the Atmospheric Photolysis of α-Dicarbonyls," Int. J. Chem. Kinet., 33, 9-20.

Koch, R., H-U. Krüger, M. Elend, W-U. Palm, and C. Zetzsch., (1996): "Rate constants for the gas-phase reaction of OH with amines: tert-Butyl amine, 2,2,2-Trifluoroethyl amine, and 1,4-Diazabicyclo[2.2.2] octane," Int. J. Chem. Kinet., 28, 807-815.

Kwok, E. S. C., R. Atkinson, and J. Arey (1992): "Gas-Phase Atmospheric Chemistry of Selected Thiocarbamates," Environ. Sci. Technol. 26, 1798-1807.

Kwok, E. S. C., and R. Atkinson (1995): "Estimation of Hydroxyl Radical Reaction Rate Constants for Gas-Phase Organic Compounds Using a Structure-Reactivity Relationship: An Update," Atmos. Environ 29, 1685-1695.

Kwok, E. S. C., S. Aschmann, and R. Atkinson (1996): "Rate Constants for the Gas-Phase Reactions of the OH Radical with Selected Carbamates and Lactates," Environ. Sci. Technol 30, 329-334.

Kwok, E. S. C., C. Takemoto and A. Chew (2000): "Methods for Estimating Maximum Incremental Reactivity (MIR) of Hydrocarbon Solvents and their Classification," Appendix C to "Initial Statement of Reasons for the Proposed Amendments to the Regulation for Reducing Volatile Organic Compound Emissions from Aerosol Coating Products and Proposed Tables of Maximum Incremental Reactivity (MIR) Values, and Proposed Amendments to Method 310, 'Determination of Volatile Organic Compounds in Consumer Products'," California Air Resources Board, Sacramento, CA, May 5.

Langford, A. O, and C. B. Moore (1984): "Collision complex formation in the reactions of formyl radicals with nitric oxide and oxygen," J. Chem. Phys. 80, 4211.

Le Crane, J.P., E. Villenave, M. D. Hurley, T. J. Wallington, and J. C. Ball (2005): "Atmospheric Chemistry of Propionaldehyde: Kinetics and Mechanisms of Reactions with OH Radicals and Cl Atoms, UV Spectrum, and Self-Reaction Kinetics of $CH_3CH_2C(O)O_2$ Radicals at 298 K, J. Phys. Chem. A 2005, 109, 11837-11850.

Lindley, C. R. C., J. G. Calvert and J. H. Shaw (1979): "Rate studies of the reactions of the $(CH_3)_3N$ radical with O_2 , NO, and NO_2," Chem. Phys. Lett., 67, 57-62.

Liu, R., R. E. Huie, M. J. Kurylo, O. J. Nielsen (1990): "The gas phase reactions of hydroxyl radicals with a series of nitroalkanes over the temperature range 240-400 K," Chem. Phys. Lett. 167, 519-523

Liu, X, H. E. Jeffries, and K. G. Sexton (1999): "Atmospheric Photochemical Degradation of 1,4-Unsaturated Dicarbonyls," Environ. Sci. Technol. 33, 4212-4220.

Lonneman, W. A. (1986): "Comparison of 0600-0900 AM Hydrocarbon Compositions Obtained from 29 Cities," Proceedings APCA/U.S. EPA Symposium on Measuremtns of Toxic Air Pollutants, Raleigh, NC.

Magnotta, F. and H. S. Johnston (1980): "Photo-Dissociation Quantum Yields for the NO_3 Free-Radical," Geophys. Res. Lett. 7, (10) 769-772.

Murphy, S. M., A. Sorooshian, J. H. Kroll, N. L. Ng, P. Chhabra, C. Tong, J. D. Surratt, E. Knipping, R. C. Flagan, and J. H. Seinfeld (2007): " Secondary aerosol formation from atmospheric reactions of aliphatic amines," Atmos. Chem. Phys. 7, 2313-2337.

NARSTO (2007): "Narsto Activities: VOC Reactivity," NARSTO web page, http://www.narsto.org/section.src?SID=10. Accessed May, 2007.

NASA (1994): "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 11," JPL Publication 94-26, Jet Propulsion Laboratory, Pasadena, California, December.

NASA (1997): "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 12," JPL Publication 97-4, Jet Propulsion Laboratory, Pasadena, California, January.

NASA (2003): "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 14." JPL Publication 02-24, February 1. Available at http://jpldataeval.jpl.nasa.gov.

NASA (2006): "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 15," JPL Publication 06-2, Jet Propulsion Laboratory, Pasadena, California, July.

Nielsen, O.J., M.S. Javadi, M.P. Sulbaek Andersen, M.D. Hurley, T.J. Wallington, and R. Singh (2007): "Atmospheric chemistry of $CF_3CF=CH_2$: Kinetics and mechanisms of gas-phase reactions with Cl atoms, OH radicals, and O3," Chem. Phys. Lett. 439, 18-22

Odum, J. R., T. Hoffmann, F. Bowman, D. Collins, R. C. Flagan, and J. H. Seinfeld (1996): "Gas/particle partitioning and secondary organic aerosol yields," Environ Sci Technol, 30(8), 2580-2585.

Olariu, R. I., B. Klotz, I. Barnes, K.H. Becker, and B. Klotz (2000): "Rate Coefficients for the Gas-Phase Reaction of OH Radicals with Selected Dihydroxybenzenes and Benzoquinonesl," Int. J. Chem. Kinet. 32, 696-702.

Olariu, R. I., B. Klotz, I. Barnes, K.H. Becker, and R. Mocanu (2002): "FT-IR study of the ring-retaining products from the reaction of OH radicals with phenol, o-, m-, and p-cresol," Atmos. Environ. 36, 3685-3697.

Olariu, R. I., I. Bejan, I. Barnes, B. Klotz, K.H. Becker, and K. Wirtz (2004): "Rate Coefficients for the Gas-Phase Reaction of NO_3 Radicals with Selected Dihydroxybenzenes," Int. J. Chem. Kinet. 36, 577-583.

Orlando, J. J. and G. S. Tyndall (2003): "Gas phase UV absorption spectra for peracetic acid, and for acetic acid monomers and dimers," J. Photochem. Photobiol A, 157, 161-166.

Plum, C. N., Sanhuesa, E., Atkinson, R., Carter W. P. L. and Pitts, J. N., Jr. (1983): "OH Radical Rate Constants and Photolysis Rates of alpha-Dicarbonyls," Environ. Sci. Technol. 17, 479-484.

Porter, E., G. Locke, J. Platz, J. Treacy, H. Sidebottom, W. Mellouki, S. Teton, and G. LeBras. (1995): "Kinetics and Mechanisms for the OH Radical Initiated Oxidation of Oxygenated Organic Compounds," Workshop on Chemical Mechanisms Describing Oxidation Processes in the Troposphere, Valencia, Spain, April 25-28.

Pinho, P. G., C. A. Pio, W. P. L. Carter, and M. E. Jenkin (2006): "Evaluation of alkene degradation in the detailed tropospheric chemistry mechanism, MCM v3, using environmental chamber data," J Atmos Chem 55, 55–79 (2006)

Pitts, J. N., Jr., D. Grosjean, K. Van Cauwenberghe, J. P. Smid, and D. R. Fitz (1978): "Photooidation of Aliphatic Amines Under Simulated Atmospheric Conditions: Formation of Nitrosamines, Nitramines, Amides, and Photochemical Oxidant," Environ. Sci. Technol., 12, 946-958.

Pitts, J. N., Jr., K. Darnall, W. P. L. Carter, A. M. Winer, and R. Atkinson (1979): "Mechanisms of Photochemical Reactions in Urban Air," EPA-600/ 3-79-110, November.

Pitts, J. N., Jr., E. Sanhueza, R. Atkinson, W. P. L. Carter, A. M. Winer, G. W. Harris, and C. N. Plum (1984): "An Investigation of the Dark Formation of Nitrous Acid in Environmental Chambers," Int. J. Chem. Kinet., 16, 919-939.

Roberts, J. M. and S. B. Bertman (1992): "The Thermal Decomposition of PeroxyAcetic Nitric Anhydride (PAN) and Peroxymethacrylic Nitric Anhydride (MPAN)," Int J. Chem. Kinet. 24, 297.

Rohrer, F., Bohn, B., Brauers, T., Brüning, D., Johnen, F. -J., Wahner, A. and Kleffmann, J. (2004). "Characterisation of the photolytic HONO-source in the atmosphere simulation chamber SAPHIR," Atmos. Chem. and Physics Disc., 4, 7881-7915

Rudich, Y., Talukdar, R. K., Burkholder, J. B. and Ravishankara, A. R. (1995): "Reaction of Methylbutenol with hydroxyl radical mechanism and atmospheric implications," J. Phys. Chem. 99, 12,188–12,194

Sarwar, G., D. Luecken, G. Yarwood, G.Z. Whitten and W. P. L. Carter (2008): "Impact of an Updated Carbon Bond Mechanism on Predictions from the Community Multiscale Air Quality (CMAQ) Modeling System: Preliminary Assessment," J. of Appl. Met. and Climat., 47, 3-14

Saunders, S. M., M. E. Jenkin, R. G. Derwent, and M. J. Pilling (2003): "Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds," Atmos Chem Phys, 3, 161-180.

Sato, K., B. Klotz, S. Hatakeyama, T. Imamura, Y. Washizu, Y. Matsumi, and N. Washida (2004a): "Secondary organic aerosol formation during the photo-oxidation of toluene: Dependence on initial hydrocarbon concentration," B Chem Soc Jpn, 77(4), 667-671.

Sato, K., B. Klotz, T. Taketsugu, and T. Takayanagi (2004b): "Kinetic measurements for the reactions of ozone with crotonaldehyde and its methyl derivatives and calculations of transition-state theory," Phys. Chem. Chem. Phys. 6 , 3969 - 3976.

Scollard, D. J., J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. LeBras, H. MacLeod, and S. Teton (1993): "Rate constants for the reactions of hydroxyl radicals and chlorine atoms with halogenated aldehydes," J. Phys. Chem. 97, 4683 - 4688.

Seinfeld, J. H., P. Pai, and D. Allen (1999): "Aerosol Forming Potential of Atmospheric Organic Compounds," Prepared by the Reactivity Research Working Group Science Team, May 5, Available at http://www.narsto.org/section.src?SID=10.

Shepson, P. B., E. O. Edney and W. W. Corse (1984): "Ring fragmentation reactions in the photooxidations of toluene and o-xylene," J. Phys. Chem, 88, 4122-4126.

Sidebottom, H. W., G. LeBras, K. H. Becker, J. Wegner, E. Porter, S. O'Donnell, J. Morarity, E. Collins, A. Mellouki, S. Le Calve, I. Barnes, C. Sauer, K. Wirtz, M. Martin-Revejo, L. Theuner and J. Bea (1997): "Kinetics and Mechanisms for the Reaction of Hydroxyl Radicals with $CH_3OCH_2OCH_3$ and Related Compounds," Final Report to Lambiotte & Cie, S.A., September.

Simonaitis, R. and E. M. Bailey (1995): "Smog Chamber Studies at Low VOC and NO_x Concentrations: Phase I," Report on Interagency Agreement DW64936024 to EPA/NREL, Research Triangle Park, NC.

Simonaitis, R., J. Meagher, and E. M. Bailey (1997): "Evaluation of the condensed Carbon Bond Mechanism against smog chamber data at low VOC and NOx Concentrations," Atm. Environ. 31, 27-43

Smith, D. F, T. E. Kleindienst, E. E. Hudgens, C. D. McIver and J. J. Bufalini (1992): "Kinetics and Mechanism of the Atmospheric Oxidation of Ethyl Tertiary Butyl Ether," Int. J. Chem. Kinet. 24, 199-215.

Smith, D. F, C. D. McIver, and T. E. Kleindienst (1998): "Primary product distribution from the reaction of hydroxyl radicals with toluene at ppb NO_x mixing ratios," J. Atmos. Chem., 30, 209-228.

Smith, D. F., T. E. Kleindienst, and C. M. McIver (1999): "Primary product distributions from the reaction of OH with m-, p-xylene, 1,2,4- and 1,3,5-trimethylbenzene," J. Atmos. Chem., 34, 339-364.

Sokolov, O.; Hurley, M. D.; Wallington, T. J.; Kaiser, E. W.; Platz, J.; Nielsen. O. J.; Berho, F.; Rayez, M.-T.; Lesclaux, R. (1998): "Kinetics and mechanism of the gas-phase reaction of Cl atoms with benzene," J. Phys. Chem. A, 102, 10671-10681.

Søndergaard, R., O.J. Nielsen, M.D. Hurley, T.J. Wallington, and R. Singh (2007): "Atmospheric chemistry of trans-$CF_3CH=CHF$: Kinetics of the gas-phase reactions with Cl atoms, OH radicals, and O_3," Chem. Phys. Lett. 443, 199-204

Sørensen, S. and I. Barnes (1998): "Photolysis of unsaturated 1,4-dicarbonyls, in EUPHORE Report 1997, edited by I. Barnes and J. Wenger, pp 149-164, University of Wuppertal, Wuppertal Germany.

Song, C., K. S. Na, and D. R. Cocker (2005): "Impact of the hydrocarbon to NOx ratio on secondary organic aerosol formation," Environ Sci Technol, 39(9), 3143-3149.

Stemmler, K. D. J. Kinnison and J. A. Kerr (1996): "Room Temperature Coefficients for the Reactions of OH Radicals with Some Monoethylene Glycol Monoalkyl Ethers," J. Phys. Chem, 100, 2114.

Stockwell, W. R., P. Middleton, J. S. Chang, and X. Tang (1990): "The Second Generation Regional Acid Deposition Model Chemical Mechanism for Regional Air Quality Modeling," J. Geophys. Res. 95, 16343-16376.

Stockwell, W.R., F. Kirchner, M. Kuhn, and S. Seefeld (1997): "A new mechanism for regional atmospheric chemistry modeling," J. Geophys. Res., 102, 25847-25880.

Tuazon, E. C., R. Atkinson, C. N. Plum, A. M. Winer, and J. N. Pitts, Jr. (1983): "The Reaction of Gas-Phase N_2O_5 with Water Vapor," Geophys. Res. Lett. 10, 953-956.

Tuazon, E. C., R. Atkinson, A. M. Winer and J. N. Pitts, Jr. (1984): "A study of the atmospheric reactions of 1,3-dichloropropene and other selected organochlorine compounds," Arch. Environ. Contam. Toxicol. 13, 691-700.

Tuazon E.C., R. Atkinson R. and W. P. L. Carter W.P.L. (1985): "Atmospheric Chemistry of cis- and trans-3-Hexene-2,5-dione,". Environ. Sci. Technol., 19, 265-269.

Tuazon, E. C., H. MacLeod, R. Atknson, and W. P. L. Carter (1986): "α-Dicarbonyl yields from the NO_x -air photooxidations of a series of aromatic hydrocarbons in air," Environ. Sci. Technol. 20, 33-387..

Tuazon, E. C., R. Atkinson, S. M. Aschmann, M. A. Goodman and A. M. Winer (1988): "Atmospheric reactions of chloroethenes with the OH radical," Int. J. Chem. Kinet. 20, 241-265.

Tuazon, E. C., R. Atkinson, S. M. Aschmann, and J. Arey (1994): "Kinetics and Products of the Gas-Phase Reactions of O_3 with Amines," Res. Chem. Intermed., 20, 303-320.

Tyndall, G. S., J. J. Orlando, C. S. Kegley-Owen, T. J. Wallington, and M. D. Hurley (1999): "Reactions of Chlorine Atoms with Methanol and Acetaldehyde," Int. J. Chem. Kinetics, 31, 776-784.

Volkamer, R., B. Klotz, I. Barnes, T. Imamura, K. Wirtz, N. Washid, K. H. Becker, and U. Platt (2002): "OH-initiated oxidation of benzene. Part I. Phenol formation under atmospheric conditions," Phys. Chem. Chem. Phys, 4, 1598-1610.

Volkamer, R., P. Spietz, J. Burrows, and U. Platt (2005): "High-resolution absorption cross sections of glyoxal in the UV-vis and IR spectral ranges," J. Photochem. Photobiol. A, 172 35-46.

Wahner, A., Mentel, T. F. and Sohn, M (1998): "Gas-phase reaction of N_2O_5 with water vapor: Importance of heterogeneous hydrolysis of N_2O_5 and surface desorption of HNO_3 in a large Teflon chamber," Geophys. Res. Lett. 25, 2169-2172.

Wallington, T. J., R. Liu, P. Dagaut, and M. J. Kurylo (1988a): "The Gas-Phase Reactions of Hydroxyl Radicals with a Series of Aliphatic Ethers over the Temperature Range 240-440 K," Int. J. Chem. Kinet. 20, 41.

Wallington, T. J., P. Dagaut, R. Liu, and M. J. Kurylo (1988b): "The Gas Phase Reactions of Hydroxyl Radicals with a Series of Esters Over the Temperature Range 240-440 K," Int. J. Chem. Kinet. 20, 177.

Wallington, T. J., P. Dagaut and M. J. Kurylo (1988c): "Correlation between Gas-Phase and Solution-Phase Reactivities of Hydroxyl Radicals toward Saturated Organic Compounds," J. Phys. Chem. 92, 5024.

Wallington, T., J., W. O. Siegl, R. Liu, Z. Zhang, R. E. Huie, and M. J. Kurylo (1990): "The Atmospheric Reactivity of α-Methyltetrahydrofuran," Env. Sci. Technol. 24, 1568-1599.

Wallington, T. J., W. F. Schneider, J. Sehested, M. Bilde, J. Platz, O. J. Nielsen, L. K. Christensen, M. J. Molina, L. T. Molina, and P. W. Wooldridge (1997): "Atmospheric Chemistry of HFE-7100 ($C_4F_9OCH_3$): Reaction with OH Radicals, UV Spectra and Kinetic Data for $C_4F_9OCH_2\cdot$ and $C_4F_9OCH_2O_2\cdot$ Radicals, and the Atmospheric Fate of $C_4F_9OCH_2O\cdot$ Radicals," J. Phys. Chem. A 1997, 101, 8264-8274.

Wallington, T. J., Y. Ninomiya, M. Mashino, M. Kawasaki, V. L. Orkin, R. E. Huie, M. J. Kurylo, W. P. L. Carter, D. Luo, and I. L. Malkina (2001): " Atmospheric Oxidation Mechanism for Methyl Pivalate, $CH_3CC(O)OCH_3$," J. Phys. Chem A. 105: 7225-7235.

Wang, W., M. J. Ezell, A. A. Ezell, G. Soskin and B. J. Finlayson-Pitts (2002): "Kinetics of Reactions of Chlorine Atoms with a Series of Alkenes at 1 Atm and 298K: Structure and Reactivity," Phys. Chem. Chem. Phys. 4, 5813-5820.

Wang, L., J. Arey, and R. Atkinson (2005): "Reactions of Chlorine Atoms with a Series of Aromatic Hydrocarbons," Environ. Sci. Technol. 39, 5302-5310.

Wang, L., J. Arey, and R. Atkinson (2006): "Kinetics and Products of Photolysis and Reaction with OH Radicals of a Series of Aromatic Carbonyl Compounds," Environ. Sci. Technol, in press.

Wirtz, K. (1999): "Determination of Photolysis Frequencies and Quantum Yields for Small Carbonyl Compounds using the EUPHORE Chamber," Presented at the Combined US/German Environmental Chamber Workshop, Riverside, California.

Wyatt, S. E., J. S. Baxley and J. R. Wells (1999), "The Hydroxyl Radical Reaction Rate Constant and Products of Methyl Isobutyrate," Submitted to Environ. Sci. Technol.

Yarwood, G., S. Rao, M. Yocke, and G. Whitten (2005): "Updates to the carbon bond chemical mechanism: CB05. Final report to the U.S. EPA, RT-0400675. Available at www.camx.com.

Zhu, L., D. Kellis, and C.-F. Ding (1996): "Photolysis of glyoxal at 193, 248, 308 and 351 nm," Chem. Phys. Lett. 257, 487-491.

Zhang, J., S. Hatakeyama and H. Akimoto (1983): "Rate constants of the reaction of ozone with trans-1,2-dichloroethene and vinyl chloride in air," Int. J. Chem. Kinet. 15, 665-668.

APPENDIX A. GENERAL MECHANISM LISTING TABLES

This appendix contains the tables giving a complete listing of the base SAPRC-07 mechanism, including the version with added chlorine chemistry, and also a listing of the fixed parameter version of the lumped mechanism for airshed models. These tables are also available in electronic form in an Excel as discussed in Appendix D. Note that Table A-3 is only available in electronic form. This is because of its size and the fact that the absorption cross-section and quantum yield are generally more useful in electronic form.

Table A-1. List of model species used in the standard base SAPRC-07 mechanism. The lumped model species added for the fixed parameter lumped mechanism for airshed models are also listed.

Name	Description
<u>Constant Species.</u>	
O2	Oxygen
M	Air
H2O	Water
H2	Hydrogen Molecules
HV	Light
<u>Active Inorganic Species.</u>	
O3	Ozone
NO	Nitric Oxide
NO2	Nitrogen Dioxide
NO3	Nitrate Radical
N2O5	Nitrogen Pentoxide
HONO	Nitrous Acid
HNO3	Nitric Acid
HNO4	Peroxynitric Acid
HO2H	Hydrogen Peroxide
CO	Carbon Monoxide
SO2	Sulfur Dioxide
<u>Active Radical Species and Operators.</u>	
OH	Hydroxyl Radicals
HO2	Hydroperoxide Radicals
MEO2	Methyl Peroxy Radicals
RO2C	Peroxy Radical Operator representing NO to NO_2 and NO_3 to NO_2 conversions, and the effects of peroxy radical reactions on acyl peroxy and other peroxy radicals.
RO2XC	Peroxy Radical Operator representing NO consumption (used in conjunction with organic nitrate formation), and the effects of peroxy radical reactions on NO_3, acyl peroxy radicals, and other peroxy radicals.
MECO3	Acetyl Peroxy Radicals
RCO3	Peroxy Propionyl and higher peroxy acyl Radicals
BZCO3	Peroxyacyl radical formed from Aromatic Aldehydes
MACO3	Peroxyacyl radicals formed from methacrolein and other acroleins.

Table 1 (continued)

Name	Description
Steady State Radical Species	
O3P	Ground State Oxygen Atoms
O1D	Excited Oxygen Atoms
TBUO	t-Butoxy Radicals
BZO	Phenoxy Radicals
PAN and PAN Analogues	
PAN	Peroxy Acetyl Nitrate
PAN2	PPN and other higher alkyl PAN analogues
PBZN	PAN analogues formed from Aromatic Aldehydes
MAPAN	PAN analogue formed from Methacrolein
Explicit and Lumped Molecule Reactive Organic Product Species	
HCHO	Formaldehyde
CCHO	Acetaldehyde
RCHO	Lumped C3+ Aldehydes. Mechanism based on propionaldehyde
ACET	Acetone
MEK	Ketones and other non-aldehyde oxygenated products that react with OH radicals faster than 5×10^{-13} but slower than 5×10^{-12} cm^3 $molec^{-2}$ sec^{-1}. Mechanism based on methyl ethyl ketone.
MEOH	Methanol
HCOOH	Formic Acid
CCOOH	Acetic Acid. Also used for peroxyacetic acid.
RCOOH	Higher organic acids and peroxy acids. Mechanism based on propionic acid.
COOH	Methyl Hydroperoxide
ROOH	Lumped organic hydroperoxides with 2-4 carbons. Mechanism based n-propyl hydroperoxide.
R6OOH	Lumped organic hydroperoxides with 5 or more carbons (other than those formed following OH addition to aromatic rings, which are represented separately). Mechanism based on 3-hexyl hydroperoxide.
RAOOH	Organic hydroperoxides formed following OH addition to aromatic rings, which is represented separately because of their probable role in SOA formation. Mechanism based on two isomers expected to be formed in the m-xylene system.
GLY	Glyoxal
MGLY	Methyl Glyoxal
BACL	Biacetyl
CRES	Phenols and Cresols. Mechanism based on o-cresol.
NPHE	Nitrophenols
BALD	Aromatic aldehydes. Mechanism based on benzaldehyde
MACR	Methacrolein
MVK	Methyl Vinyl Ketone
IPRD	Lumped isoprene product species. Mechanism based on that of Carter and Atkinson (1996).
Aromatic unsaturated ring fragmentation products (see discussion of aromatic mechanisms)	
AFG1	Lumped photoreactive monounsaturated dicarbonyl aromatic fragmentation products that photolyze to form radicals.
AFG2	Lumped photoreactive monounsaturated dicarbonyl aromatic fragmentation products that photolyze to form non-radical products

Table 1 (continued)

Name	Description
AFG3	Lumped diunsaturatred dicarbonyl aromatic fragmentation product.
Lumped Parameter Products	
PROD2	Ketones and other non-aldehyde oxygenated products that react with OH radicals faster than 5 x 10^{-12} cm^3 $molec^{-2}$ sec^{-1}. Mechanism based on $CH_3C(O)CH_2CH_2CH_2OH$, $CH_3C(O)CH_2CH(CH_3)CH_2OH$, $CH_3CH_2C(O)CH_2CH_2CH(CH_3)OH$, $CH_3CH_2C(O)CH_2CH_2CH(OH)CH_2CH_3$, and $CH_3CH_2CH_2CH(OH)CH_2$-$CH_2C(O)CH_2CH_3$ (PROD2-1 through 5), each weighed equally.
RNO3	Lumped Organic Nitrates. Mechanism based on $CH_3CH_2CH(CH_3)ONO_2$, $CH_3CH(OH)CH_2CH_2CH_2ONO_2$, $CH_3CH_2CH(CH_3)CH(CH_3)ONO_2$, $CH_3CH_2CH_2CH_2CH_2CH(ONO_2)CH_2OH$, $CH_3CH_2C(CH_3)(ONO_2)CH_2CH(CH_3)CH_3$, and $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH(ONO_2)CH_2CH_3$ (RNO3-1 through 6), each weighed equally.
Steady state operators used to represent radical or product formation in peroxy radical reactions.	
xHO2	Formation of HO_2 from alkoxy radicals formed in peroxy radical reactions with NO and NO_3 (100% yields) and RO_2 (50% yields)
xOH	As above, but for OH
xNO2	As above, but for NO_2
xMEO2	As above, but for MEO2
xMECO3	As above, but for MECO3
xRCO3	As above, but for RCO3
xMACO3	As above, but for MACO3
xTBUO	As above, but for TBUO
xCO	As above, but for CO
xHCHO	As above, but for HCHO
xCCHO	As above, but for CCHO
xRCHO	As above, but for RCHO
xACET	As above, but for ACET
xMEK	As above, but for MEK
xPROD2	As above, but for PROD2
xGLY	As above, but for GLY
xMGLY	As above, but for MGLY
xBACL	As above, but for BACL
xBALD	As above, but for BALD
xAFG1	As above, but for AFG1
xAFG2	As above, but for AFG2
xAFG3	As above, but for AFG3
xMACR	As above, but for MACR
xMVK	As above, but for MVK
xIPRD	As above, but for IPRD
xRNO3	As above, but for RNO3
zRNO3	Formation of RNO3 in the RO_2 + NO, reaction, or formation of corresponding non-nitrate products (represented by PROD2) formed from alkoxy radicals formed in RO_2 + NO_3 and (in 50% yields) RO_2 + RO_2 reactions.
yROOH	Formation of ROOH following RO_2 + HO_2 reactions, or formation of H-shift disproportionation products (represented by MEK) in the RO_2 + RCO_3 and (in 50% yields) RO_2 + RO_2 reactions.
yR6OOH	As above, but with the RO_2 + HO_2 product represented by R6OOH and the H-shift products are represented by PROD2.

Table 1 (continued)

Name	Description
yRAOOH	As above, but with the RO_2 + HO_2 product represented by R6OOH
Non-Reacting Species	
CO2	Carbon Dioxide
SULF	Sulfates (SO_3 or H_2SO_4)
XC	Lost Carbon or carbon in unreactive products
XN	Lost Nitrogen or nitrogen in unreactive products
Primary Organics Represented explicitly	
CH4	Methane
ETHENE	Ethene
ISOPRENE	Isoprene
ACETYLEN	Acetylene
BENZENE	Benzene
Lumped model species added to the base mechanism to represent various types of emitted species in the lumped mechanism for airshed models (not part of the base mechanism)	
ALK1	Alkanes and other non-aromatic compounds that react only with OH, and have kOH (OH radical rate constant) between 2 and 5 x 10^2 ppm^{-1} min^{-1}. (Primarily ethane)
ALK2	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 5 x 10^2 and 2.5 x 10^3 ppm^{-1} min^{-1}. (Primarily propane)
ALK3	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 2.5 x 10^3 and 5 x 10^3 ppm^{-1} min^{-1}.
ALK4	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 5 x 10^3 and 1 x 10^4 ppm^{-1} min^{-1}.
ALK5	Alkanes and other non-aromatic compounds that react only with OH, and have kOH greater than 1 x 10^4 ppm-1 min-1.
ARO1	Aromatics with kOH < 2x10^4 ppm^{-1} min^{-1}.
ARO2	Aromatics with kOH > 2x10^4 ppm^{-1} min^{-1}.
OLE1	Alkenes (other than ethene) with kOH < 7x10^4 ppm^{-1} min^{-1}.
OLE2	Alkenes with kOH > 7x10^4 ppm^{-1} min^{-1}.
TERP	Terpenes

Table A-2. Listing of reactions and rate parameters in the base SAPRC-07 mechanism.

Label	Reaction and Products [a]	Rate Parameters [b]				Refs & Notes [c]
		k(300)	A	Ea	B	
Inorganic Reactions						
1	NO2 + HV = NO + O3P	Phot Set= NO2-06				2,4
2	O3P + O2 + M = O3 + M	5.68E-34	5.68E-34	0.00	-2.60	3,5
3	O3P + O3 = #2 O2	8.34E-15	8.00E-12	4.09		1,2,3
4	O3P + NO = NO2	1.64E-12	Falloff, F=0.60, N=1.00			2
		0:	9.00E-32	0.00	-1.50	
		inf:	3.00E-11	0.00	0.00	
5	O3P + NO2 = NO + O2	1.03E-11	5.50E-12	-0.37		3
6	O3P + NO2 = NO3	3.24E-12	Falloff, F=0.60, N=1.00			2
		0:	2.50E-31	0.00	-1.80	
		inf:	2.20E-11	0.00	-0.70	
7	O3 + NO = NO2 + O2	2.02E-14	3.00E-12	2.98		2
8	O3 + NO2 = O2 + NO3	3.72E-17	1.40E-13	4.91		1,3
9	NO + NO3 = #2 NO2	2.60E-11	1.80E-11	-0.22		1,3
10	NO + NO + O2 = #2 NO2	1.93E-38	3.30E-39	-1.05		1,3
11	NO2 + NO3 = N2O5	1.24E-12	Falloff, F=0.35, N=1.33			3
		0:	3.60E-30	0.00	-4.10	
		inf:	1.90E-12	0.00	0.20	
12	N2O5 = NO2 + NO3	5.69E-02	Falloff, F=0.35, N=1.33			3
		0:	1.30E-03	21.86	-3.50	
		inf:	9.70E+14	22.02	0.10	
13	N2O5 + H2O = #2 HNO3	2.50E-22				3,6
14	N2O5 + H2O + H2O = #2 HNO3 + H2O	1.80E-39				3,6
	N2O5 + HV = NO3 + NO + O3P		(Slow)			1
	N2O5 + HV = NO3 + NO2		(Slow)			1
15	NO2 + NO3 = NO + NO2 + O2	6.75E-16	4.50E-14	2.50		1,3
16	NO3 + HV = NO + O2	Phot Set= NO3NO-06				2
17	NO3 + HV = NO2 + O3P	Phot Set= NO3NO2-6				2
18	O3 + HV = O1D + O2	Phot Set= O3O1D-06				2,3,7
19	O3 + HV = O3P + O2	Phot Set= O3O3P-06				2,7
20	O1D + H2O = #2 OH	1.99E-10	1.63E-10	-0.12		2
21	O1D + M = O3P + M	3.28E-11	2.38E-11	-0.19		2,5
22	OH + NO = HONO	7.31E-12	Falloff, F=0.60, N=1.00			2
		0:	7.00E-31	0.00	-2.60	
		inf:	3.60E-11	0.00	-0.10	
23	HONO + HV = OH + NO	Phot Set= HONO-06				8
24	OH + HONO = H2O + NO2	5.95E-12	2.50E-12	-0.52		3
25	OH + NO2 = HNO3	1.05E-11	Falloff, F=0.60, N=1.00			2,9
		0:	1.80E-30	0.00	-3.00	
		inf:	2.80E-11	0.00	0.00	
26	OH + NO3 = HO2 + NO2	2.00E-11				1,3
27	OH + HNO3 = H2O + NO3	1.51E-13	k =k0+k3M/(1+k3M/k2)			2
		k0:	2.40E-14	-0.91	0.00	

Table A-2 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Refs & Notes [c]
		k(300)	A	Ea	B	
		k2:	2.70E-17	-4.37	0.00	
		k3:	6.50E-34	-2.65	0.00	
28	HNO3 + HV = OH + NO2	Phot Set= HNO3				1,2,3,10
29	OH + CO = HO2 + CO2	2.28E-13	k = k1 + k2 [M]			3
		k1:	1.44E-13	0.00	0.00	
		k2:	3.43E-33	0.00	0.00	
30	OH + O3 = HO2 + O2	7.41E-14	1.70E-12	1.87		2,3
31	HO2 + NO = OH + NO2	8.85E-12	3.60E-12	-0.54		3
32	HO2 + NO2 = HNO4	1.12E-12	Falloff, F=0.60, N=1.00			2
		0:	2.00E-31	0.00	-3.40	
		inf:	2.90E-12	0.00	-1.10	
33	HNO4 = HO2 + NO2	1.07E-01	Falloff, F=0.60, N=1.00			11
		0:	3.72E-05	21.16	-2.40	
		inf:	5.42E+15	22.20	-2.30	
34	HNO4 + HV = #.61 {HO2 + NO2} + #.39 {OH + NO3}	Phot Set= HNO4-06				12
35	HNO4 + OH = H2O + NO2 + O2	4.61E-12	1.30E-12	-0.76		2
36	HO2 + O3 = OH + #2 O2	2.05E-15	2.03E-16	-1.38	4.57	3
37	HO2 + HO2 = HO2H + O2	2.84E-12	k = k1 + k2 [M]			3
		k1:	2.20E-13	-1.19	0.00	
		k2:	1.90E-33	-1.95	0.00	
38	HO2 + HO2 + H2O = HO2H + O2 + H2O	6.09E-30	k = k1 + k2 [M]			3
		k1:	3.08E-34	-5.56	0.00	
		k2:	2.66E-54	-6.32	0.00	
39	NO3 + HO2 = #.8 {OH + NO2 + O2} + #.2 {HNO3 + O2}	4.00E-12				1,3,13
40	NO3 + NO3 = #2 NO2 + O2	2.41E-16	8.50E-13	4.87		1,2
41	HO2H + HV = #2 OH	Phot Set= H2O2				1,10
42	HO2H + OH = HO2 + H2O	1.80E-12	1.80E-12	0.00		2
43	OH + HO2 = H2O + O2	1.10E-10	4.80E-11	-0.50		1
44	OH + SO2 = HO2 + SULF	9.49E-13	Falloff, F=0.60, N=1.00			2
		0:	3.30E-31	0.00	-4.30	
		inf:	1.60E-12	0.00	0.00	
45	OH + H2 = HO2 + H2O	7.02E-15	7.70E-12	4.17		1,3
<u>Methyl peroxy and methoxy reactions</u>						
BR01	MEO2 + NO = NO2 + HCHO + HO2	7.64E-12	2.30E-12	-0.72		3,14
BR02	MEO2 + HO2 = COOH + O2	4.65E-12	3.46E-13	-1.55	0.36	3,15
BR03	MEO2 + HO2 = HCHO + O2 + H2O	4.50E-13	3.34E-14	-1.55	-3.53	3,15
BR04	MEO2 + NO3 = HCHO + HO2 + NO2	1.30E-12				1,3,14
BR05	MEO2 + MEO2 = MEOH + HCHO + O2	2.16E-13	6.39E-14	-0.73	-1.80	3,16
BR06	MEO2 + MEO2 = #2 {HCHO + HO2}	1.31E-13	7.40E-13	1.03		3
<u>Active Peroxy Radical Operators</u>						
BR07	RO2C + NO = NO2	9.23E-12	2.60E-12	-0.76		3,18,17
BR08	RO2C + HO2 =	7.63E-12	3.80E-13	-1.79		3,18,17

Table A-2 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Refs & Notes [c]
		k(300)	A	Ea	B	
BR09	RO2C + NO3 = NO2	2.30E-12				3,18,17
BR10	RO2C + MEO2 = #.5 HO2 + #.75 HCHO + #.25 MEOH	2.00E-13				1,17,19
BR11	RO2C + RO2C =	3.50E-14				1,17
BR12	RO2XC + NO = XN	Same k as rxn BR07				3,17,18
BR13	RO2XC + HO2 =	Same k as rxn BR08				3,17,18
BR14	RO2XC + NO3 = NO2	Same k as rxn BR09				1,17
BR15	RO2XC + MEO2 = #.5 HO2 + #.75 HCHO + #.25 MEOH	Same k as rxn BR10				3,17,18
BR16	RO2XC + RO2C =	Same k as rxn BR11				1,17
BR17	RO2XC + RO2XC =	Same k as rxn BR11				1,17
<u>Reactions of Acyl Peroxy Radicals, PAN, and PAN analogues</u>						
BR18	MECO3 + NO2 = PAN	9.37E-12	Falloff, F=0.30, N=1.41			20
		0:	2.70E-28	0.00	-7.10	
		inf:	1.21E-11	0.00	-0.90	
BR19	PAN = MECO3 + NO2	6.27E-04	Falloff, F=0.30, N=1.41			20
		0:	4.90E-03	24.05	0.00	
		inf:	4.00E+16	27.03	0.00	
BR20	PAN + HV = #.6 {MECO3 + NO2} + #.4 {MEO2 + CO2 + NO3}	Phot Set= PAN				3
BR21	MECO3 + NO = MEO2 + CO2 + NO2	1.97E-11	7.50E-12	-0.58		3
BR22	MECO3 + HO2 = CCOOH + #.7 O2 + #.3 O3	1.36E-11	5.20E-13	-1.95		3,21
BR23	MECO3 + NO3 = MEO2 + CO2 + NO2 + O2	Same k as rxn BR09				22
BR24	MECO3 + MEO2 = #.1 {CCOOH + HCHO + O2} + #.9 {HCHO + HO2 + MEO2 + CO2}	1.06E-11	2.00E-12	-0.99		3
BR25	MECO3 + RO2C = MEO2 + CO2	1.56E-11	4.40E-13	-2.13		3,18,23
BR26	MECO3 + RO2XC = MEO2 + CO2	Same k as rxn BR25				3,18,23
BR27	MECO3 + MECO3 = #2 {MEO2 + CO2} + O2	1.54E-11	2.90E-12	-0.99		1,3
BR28	RCO3 + NO2 = PAN2	1.21E-11	1.21E-11	0.00	-1.07	24
BR29	PAN2 = RCO3 + NO2	5.48E-04	8.30E+16	27.70		3,25
BR30	PAN2 + HV = #.6 {RCO3 + NO2} + #.4 {RO2C + xHO2 + yROOH + xCCHO + CO2 + NO3}	Phot Set= PAN				26
BR31	RCO3 + NO = NO2 + RO2C + xHO2 + yROOH + xCCHO + CO2	2.08E-11	6.70E-12	-0.68		3,27
BR32	RCO3 + HO2 = RCOOH + #.75 O2 + #.25 O3	Same k as rxn BR22				1,28
BR33	RCO3 + NO3 = NO2 + RO2C + xHO2 + yROOH + xCCHO + CO2 + O2	Same k as rxn BR09				1,28
BR34	RCO3 + MEO2 = HCHO + HO2 + RO2C + xHO2 + xCCHO + yROOH + CO2	Same k as rxn BR24				1,28
BR35	RCO3 + RO2C = RO2C + xHO2 + xCCHO + yROOH + CO2	Same k as rxn BR25				1,28

Table A-2 (continued)

Label	Reaction and Products [a]	Rate Parameters [b] k(300)	 A	 Ea	 B	Refs & Notes [c]
BR36	RCO3 + RO2XC = RO2C + xHO2 + xCCHO + yROOH + CO2	Same k as rxn BR25				1,28
BR37	RCO3 + MECO3 = #2 CO2 + MEO2 + RO2C + xHO2 + yROOH + xCCHO + O2	Same k as rxn BR27				1,28
BR38	RCO3 + RCO3 = #2 {RO2C + xHO2 + xCCHO + yROOH + CO2}	Same k as rxn BR27				1,28
BR39	BZCO3 + NO2 = PBZN	1.37E-11				1,29
BR40	PBZN = BZCO3 + NO2	4.27E-04	7.90E+16	27.82		1,29
BR41	PBZN + HV = #.6 {BZCO3 + NO2} + #.4 {CO2 + BZO + RO2C + NO3}	Phot Set= PAN				26
BR42	BZCO3 + NO = NO2 + CO2 + BZO + RO2C	Same k as rxn BR31				1,28
BR43	BZCO3 + HO2 = RCOOH + #.75 O2 + #.25 O3 + #4 XC	Same k as rxn BR22				1,28
BR44	BZCO3 + NO3 = NO2 + CO2 + BZO + RO2C + O2	Same k as rxn BR09				1,28
BR45	BZCO3 + MEO2 = HCHO + HO2 + RO2C + BZO + CO2	Same k as rxn BR24				1,28
BR46	BZCO3 + RO2C = RO2C + BZO + CO2	Same k as rxn BR25				1,28
BR47	BZCO3 + RO2XC = RO2C + BZO + CO2	Same k as rxn BR25				1,28
BR48	BZCO3 + MECO3 = #2 CO2 + MEO2 + BZO + RO2C	Same k as rxn BR27				1,28
BR49	BZCO3 + RCO3 = #2 CO2 + RO2C + xHO2 + yROOH + xCCHO + BZO + RO2C	Same k as rxn BR27				1,28
BR50	BZCO3 + BZCO3 = #2 {BZO + RO2C + CO2}	Same k as rxn BR27				1,28
BR51	MACO3 + NO2 = MAPAN	Same k as rxn BR28				1,28
BR52	MAPAN = MACO3 + NO2	4.79E-04	1.60E+16	26.80		1,30
BR53	MAPAN + HV = #.6 {MACO3 + NO2} + #.4 {CO2 + HCHO + MECO3 + NO3}	Phot Set= PAN				26
BR54	MACO3 + NO = NO2 + CO2 + HCHO + MECO3	Same k as rxn BR31				1,28
BR55	MACO3 + HO2 = RCOOH + #.75 O2 + #.25 O3 + XC	Same k as rxn BR22				1,28
BR56	MACO3 + NO3 = NO2 + CO2 + HCHO + MECO3 + O2	Same k as rxn BR09				1,28
BR57	MACO3 + MEO2 = #2 HCHO + HO2 + CO2 + MECO3	Same k as rxn BR24				1,28
BR58	MACO3 + RO2C = CO2 + HCHO + MECO3	Same k as rxn BR25				1,28
BR59	MACO3 + RO2XC = CO2 + HCHO + MECO3	Same k as rxn BR25				1,28
BR60	MACO3 + MECO3 = #2 CO2 + MEO2 + HCHO + MECO3 + O2	Same k as rxn BR27				1,28
BR61	MACO3 + RCO3 = HCHO + MECO3 + RO2C + xHO2 + yROOH + xCCHO + #2 CO2	Same k as rxn BR27				1,28

Table A-2 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Refs & Notes [c]
		k(300)	A	Ea	B	
BR62	MACO3 + BZCO3 = HCHO + MECO3 + BZO + RO2C + #2 CO2	Same k as rxn BR27				1,28
BR63	MACO3 + MACO3 = #2 {HCHO + MECO3 + CO2}	Same k as rxn BR27				1,28
Other Organic Radical Species						
BR64	TBUO + NO2 = RNO3 + #-2 XC	2.40E-11				1
BR65	TBUO = ACET + MEO2	1.18E+03	7.50E+14	16.20		1
BR66	BZO + NO2 = NPHE	3.79E-11	2.30E-11	-0.30		1
BR67	BZO + HO2 = CRES + #-1 XC	Same k as rxn BR08				1
BR68	BZO = CRES + RO2C + xHO2 + #-1 XC	1.00E-03				1,31
Steady-State Peroxy Radical operators (for formation of inorganic and radical products)						
RO01	xHO2 = HO2	k is variable parameter: RO2RO				32
RO02	xHO2 =	k is variable parameter: RO2XRO				32
RO03	xOH = OH	k is variable parameter: RO2RO				32
RO04	xOH =	k is variable parameter: RO2XRO				32
RO05	xNO2 = NO2	k is variable parameter: RO2RO				32
RO06	xNO2 = XN	k is variable parameter: RO2XRO				32
RO07	xMEO2 = MEO2	k is variable parameter: RO2RO				32
RO08	xMEO2 = XC	k is variable parameter: RO2XRO				32
RO09	xMECO3 = MECO3	k is variable parameter: RO2RO				32
RO10	xMECO3 = #2 XC	k is variable parameter: RO2XRO				32
RO11	xRCO3 = RCO3	k is variable parameter: RO2RO				32
RO12	xRCO3 = #3 XC	k is variable parameter: RO2XRO				32
RO13	xMACO3 = MACO3	k is variable parameter: RO2RO				32
RO14	xMACO3 = #4 XC	k is variable parameter: RO2XRO				32
RO15	xTBUO = TBUO	k is variable parameter: RO2RO				32
RO16	xTBUO = #4 XC	k is variable parameter: RO2XRO				32
RO17	xCO = CO	k is variable parameter: RO2RO				32
RO18	xCO = XC	k is variable parameter: RO2XRO				32
Explicit and Lumped Molecule Organic Products						
BP01	HCHO + HV = #2 HO2 + CO	Phot Set= HCHOR-06				3
BP02	HCHO + HV = H2 + CO	Phot Set= HCHOM-06				3
BP03	HCHO + OH = HO2 + CO + H2O	8.47E-12	5.40E-12	-0.27		3
BP04	HCHO + HO2 = HOCOO	Assumed to be negligible				34
BP07	HCHO + NO3 = HNO3 + HO2 + CO	6.06E-16	2.00E-12	4.83		1,33
BP08	CCHO + OH = MECO3 + H2O	1.49E-11	4.40E-12	-0.73		3
BP09	CCHO + HV = CO + HO2 + MEO2	Phot Set= CCHO_R				1,3
BP10	CCHO + NO3 = HNO3 + MECO3	2.84E-15	1.40E-12	3.70		1,3
BP11	RCHO + OH = #.965 RCO3 + #.035 {RO2C + xHO2 + xCO + xCCHO + yROOH}	1.97E-11	5.10E-12	-0.80		36,35
BP12	RCHO + HV = RO2C + xHO2 + yROOH + xCCHO + CO + HO2	Phot Set= C2CHO				1,37
BP13	RCHO + NO3 = HNO3 + RCO3	6.74E-15	1.40E-12	3.18		38

Table A-2 (continued)

Label	Reaction and Products [a]	Rate Parameters [b] k(300)	A	Ea	B	Refs & Notes [c]
BP14	ACET + OH = RO2C + xMECO3 + xHCHO + yROOH	1.91E-13	4.56E-14	-0.85	3.65	39
BP15	ACET + HV = #.62 MECO3 + #1.38 MEO2 + #.38 CO	Phot Set= ACET-06, qy= 0.5				40
BP16	MEK + OH = #.967 RO2C + #.039 {RO2XC + zRNO3} + #.376 xHO2 + #.51 xMECO3 + #.074 xRCO3 + #.088 xHCHO + #.504 xCCHO + #.376 xRCHO + yROOH + #.3 XC	1.20E-12	1.30E-12	0.05	2.00	1,3,36
BP17	MEK + HV = MECO3 + RO2C + xHO2 + xCCHO + yROOH	Phot Set= MEK-06, qy= 0.175				41
BP18	MEOH + OH = HCHO + HO2	9.02E-13	2.85E-12	0.69		3
BP19	HCOOH + OH = HO2 + CO2	4.50E-13				3,42
BP20	CCOOH + OH = #.509 MEO2 + #.491 RO2C + #.509 CO2 + #.491 xHO2 + #.491 xMGLY + #.491 yROOH + #-0.491 XC	7.26E-13	4.20E-14	-1.70		3,36
BP21	RCOOH + OH = RO2C + xHO2 + #.143 CO2 + #.142 xCCHO + #.4 xRCHO + #.457 xBACL + yROOH + #-0.455 XC	1.20E-12				3,36
BP22	COOH + OH = H2O + #.3 {HCHO + OH} + #.7 MEO2	7.40E-12	3.80E-12	-0.40		2,43
BP23	COOH + HV = HCHO + HO2 + OH	Phot Set= COOH				1,3
BP24	ROOH + OH = #.744 OH + #.251 RO2C + #.004 RO2XC + #.004 zRNO3 + #.744 RCHO + #.239 xHO2 + #.012 xOH + #.012 xHCHO + #.012 xCCHO + #.205 xRCHO + #.034 xPROD2 + #.256 yROOH + #-0.115 XC	2.50E-11				36,45,44
BP25	ROOH + HV = RCHO + HO2 + OH	Phot Set= COOH				1,45
BP26	R6OOH + OH = #.84 OH + #.222 RO2C + #.029 RO2XC + #.029 zRNO3 + #.84 PROD2 + #.09 xHO2 + #.041 xOH + #.02 xCCHO + #.075 xRCHO + #.084 xPROD2 + #.16 yROOH + #.02 XC	5.60E-11				36,44,46
BP27	R6OOH + HV = OH + #.142 HO2 + #.782 RO2C + #.077 RO2XC + #.077 zRNO3 + #.085 RCHO + #.142 PROD2 + #.782 xHO2 + #.026 xCCHO + #.058 xRCHO + #.698 xPROD2 + #.858 yR6OOH + #.017 XC	Phot Set= COOH				46
BP28	RAOOH + OH = #.139 OH + #.148 HO2 + #.589 RO2C + #.124 RO2XC + #.124 zRNO3 + #.074 PROD2 + #.147 MGLY + #.139 IPRD + #.565 xHO2 + #.024 xOH + #.448 xRCHO + #.026 xGLY + #.030 xMEK + #.252 xMGLY + #.073 xAFG1 + #.073 xAFG2 + #.713 yR6OOH + #2.674 XC	1.41E-10				47

Table A-2 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Refs & Notes [c]
		k(300)	A	Ea	B	
BP29	RAOOH + HV = OH + HO2 + #.5 {GLY + MGLY + AFG1 + AFG2} + #.5 XC	Phot Set= COOH				47
BP30	GLY + HV = #2 {CO + HO2}	Phot Set= GLY-07R				48
BP31	GLY + HV = HCHO + CO	Phot Set= GLY-07M				48
BP32	GLY + OH = #.63 HO2 + #1.26 CO + #.37 RCO3 + #-.37 XC	1.10E-11				1,3,49
BP33	GLY + NO3 = HNO3 + #.63 HO2 + #1.26 CO + #.37 RCO3 + #-.37 XC	1.02E-15	2.80E-12	4.72		1,50
BP34	MGLY + HV = HO2 + CO + MECO3	Phot Set= MGLY-06				3,51
BP35	MGLY + OH = CO + MECO3	1.50E-11				1,3
BP36	MGLY + NO3 = HNO3 + CO + MECO3	2.53E-15	1.40E-12	3.77		1,50
BP37	BACL + HV = #2 MECO3	Phot Set= BACL-07				52
BP38	CRES + OH = #.2 BZO + #.8 {RO2C + xHO2 + yR6OOH} + #.25 xMGLY + #5.05 XC	4.03E-11	1.70E-12	-1.89		53,54
BP39	CRES + NO3 = HNO3 + BZO + XC	1.40E-11				1,53
BP40	NPHE + OH = BZO + XN	3.50E-12				55
BP41	NPHE + HV = HONO + #6 XC	Phot Set= NO2-06, qy= 1.5e-3				56
BP42	NPHE + HV = #6 XC + XN	Phot Set= NO2-06, qy= 1.5e-2				57
BP43	BALD + OH = BZCO3	1.20E-11				59,58
BP44	BALD + HV = #7 XC	Phot Set= BALD-06, qy= 0.06				60
BP45	BALD + NO3 = HNO3 + BZCO3	2.73E-15	1.34E-12	3.70		1,61
Lumped Unsaturated Aromatic Ring-Opening Products						
BP46	AFG1 + OH = #.217 MACO3 + #.723 RO2C + #.060 {RO2XC + zRNO3} + #.521 xHO2 + #.201 xMECO3 + #.334 xCO + #.407 xRCHO + #.129 xMEK + #.107 xGLY + #.267 xMGLY + #.783 yR6OOH + #.284 XC	7.40E-11				62
BP47	AFG1 + O3 = #.826 OH + #.522 HO2 + #.652 RO2C + #.522 CO + #.174 CO2 + #.432 GLY + #.568 MGLY + #.652 xRCO3 + #.652 xHCHO + #.652 yR6OOH + #-.872 XC	9.66E-18				62
BP48	AFG1 + HV = #1.023 HO2 + #.173 MEO2 + #.305 MECO3 + #.500 MACO3 + #.695 CO + #.195 GLY + #.305 MGLY + #.217 XC	Phot Set= AFG1				62,63
BP49	AFG2 + OH = #.217 MACO3 + #.723 RO2C + #.060 {RO2XC + zRNO3} + #.521 xHO2 + #.201 xMECO3 + #.334 xCO + #.407 xRCHO + #.129 xMEK + #.107 xGLY + #.267 xMGLY + #.783 yR6OOH + #.284 XC	7.40E-11				62
BP50	AFG2 + O3 = #.826 OH + #.522 HO2 + #.652 RO2C + #.522 CO + #.174 CO2 + #.432 GLY + #.568 MGLY + #.652 xRCO3 + #.652 xHCHO + #.652 yR6OOH + #-.872 XC	9.66E-18				62

Table A-2 (continued)

Label	Reaction and Products [a]	Rate Parameters [b] k(300)	A	Ea	B	Refs & Notes [c]
BP51	AFG2 + HV = PROD2 + #-1 XC	Phot Set= AFG1				62,63
BP52	AFG3 + OH = #.206 MACO3 + #.733 RO2C + #.117 {RO2XC + zRNO3} + #.561 xHO2 + #.117 xMECO3 + #.114 xCO + #.274 xGLY + #.153 xMGLY + #.019 xBACL + #.195 xAFG1 + #.195 xAFG2 + #.231 xIPRD + #.794 yR6OOH + #.938 XC	9.35E-11				64
BP53	AFG3 + O3 = #.471 OH + #.554 HO2 + #.013 MECO3 + #.258 RO2C + #.007 {RO2XC + zRNO3} + #.580 CO + #.190 CO2 + #.366 GLY + #.184 MGLY + #.350 AFG1 + #.350 AFG2 + #.139 AFG3 + #.003 MACR + #.004 MVK + #.003 IPRD + #.095 xHO2 + #.163 xRCO3 + #.163 xHCHO + #.095 xMGLY + #.264 yR6OOH + #-.575 XC	1.43E-17				64
Isoprene Products						
BP54	MACR + OH = #.5 MACO3 + #.5 {RO2C + xHO2} + #.416 xCO + #.084 xHCHO + #.416 xMEK + #.084 xMGLY + #.5 yROOH + #-0.416 XC	2.84E-11	8.00E-12	-0.76		3,65
BP55	MACR + O3 = #.208 OH + #.108 HO2 + #.1 RO2C + #.45 CO + #.117 CO2 + #.1 HCHO + #.9 MGLY + #.333 HCOOH + #.1 xRCO3 + #.1 xHCHO + #.1 yROOH + #-0.1 XC	1.28E-18	1.40E-15	4.17		3,65
BP56	MACR + NO3 = #.5 {MACO3 + RO2C + HNO3 + xHO2 + xCO} + #.5 yROOH + #1.5 XC + #.5 XN	3.54E-15	1.50E-12	3.61		65,66
BP57	MACR + O3P = RCHO + XC	6.34E-12				1,65
BP58	MACR + HV = #.33 OH + #.67 HO2 + #.34 MECO3 + #.33 MACO3 + #.33 RO2C + #.67 CO + #.34 HCHO + #.33 xMECO3 + #.33 xHCHO + #.33 yROOH	Phot Set= MACR-06				3,65,67
BP59	MVK + OH = #.975 RO2C + #.025 {RO2XC + zRNO3} + #.3 xHO2 + #.675 xMECO3 + #.3 xHCHO + #.675 xRCHO + #.3 xMGLY + yROOH + #-0.725 XC	1.99E-11	2.60E-12	-1.21		3,65
BP60	MVK + O3 = #.164 OH + #.064 HO2 + #.05 {RO2C + xHO2} + #.475 CO + #.124 CO2 + #.05 HCHO + #.95 MGLY + #.351 HCOOH + #.05 xRCO3 + #.05 xHCHO + #.05 yROOH + #-0.05 XC	5.36E-18	8.50E-16	3.02		3,65
BP61	MVK + NO3 = #4 XC + XN		(Slow)			1,65
BP62	MVK + O3P = #.45 RCHO + #.55 MEK + #.45 XC	4.32E-12				1,65

Table A-2 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Refs & Notes [c]
		k(300)	A	Ea	B	
BP63	MVK + HV = #.4 MEO2 + #.6 CO + #.6 PROD2 + #.4 MACO3 + #-2.2 XC	Phot Set= MVK-06				3,68
BP64	IPRD + OH = #.289 MACO3 + #.67 {RO2C + xHO2} + #.041 {RO2XC + zRNO3} + #.336 xCO + #.055 xHCHO + #.129 xCCHO + #.013 xRCHO + #.15 xMEK + #.332 xPROD2 + #.15 xGLY + #.174 xMGLY + #-0.504 XC + #.711 yR6OOH	6.19E-11				1,65
BP65	IPRD + O3 = #.285 OH + #.4 HO2 + #.048 {RO2C + xRCO3} + #.498 CO + #.14 CO2 + #.124 HCHO + #.21 MEK + #.023 GLY + #.742 MGLY + #.1 HCOOH + #.372 RCOOH + #.047 xCCHO + #.001 xHCHO + #.048 yR6OOH + #-.329 XC	4.18E-18				1,65
BP66	IPRD + NO3 = #.15 {MACO3 + HNO3} + #.799 {RO2C + xHO2} + #.051 {RO2XC + zRNO3} + #.572 xCO + #.227 xHCHO + #.218 xRCHO + #.008 xMGLY + #.572 xRNO3 + #.85 yR6OOH + #.278 XN + #-.815 XC	1.00E-13				1,65
BP67	IPRD + HV = #1.233 HO2 + #.467 MECO3 + #.3 RCO3 + #1.233 CO + #.3 HCHO + #.467 CCHO + #.233 MEK + #-.233 XC	Phot Set= MACR-06				65,69
Lumped Parameter Organic Products						
BP68	PROD2 + OH = #.472 HO2 + #.379 xHO2 + #.029 xMECO3 + #.049 xRCO3 + #.473 RO2C + #.071 RO2XC + #.071 zRNO3 + #.002 HCHO + #.211 xHCHO + #.001 CCHO + #.083 xCCHO + #.143 RCHO + #.402 xRCHO + #.115 xMEK + #.329 PROD2 + #.007 xPROD2 + #.528 yR6OOH + #.877 XC	1.55E-11				70
BP69	PROD2 + HV = #.913 xHO2 + #.4 MECO3 + #.6 RCO3 + #1.59 RO2C + #.087 RO2XC + #.087 zRNO3 + #.303 xHCHO + #.163 xCCHO + #.78 xRCHO + yR6OOH + #-.091 XC	Phot Set= MEK-06, qy= 4.86e-3				70,71
BP70	RNO3 + OH = #.189 HO2 + #.305 xHO2 + #.019 NO2 + #.313 xNO2 + #.976 RO2C + #.175 RO2XC + #.175 zRNO3 + #.011 xHCHO + #.429 xCCHO + #.001 RCHO + #.036 xRCHO + #.004 xACET + #.01 MEK + #.17 xMEK + #.008 PROD2 + #.031 xPROD2 + #.189 RNO3 + #.305 xRNO3 + #.157 yROOH + #.636 yR6OOH + #.174 XN + #.04 XC	7.20E-12				72

Table A-2 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Refs & Notes [c]
		k(300)	A	Ea	B	
BP71	RNO3 + HV = #.344 HO2 + #.554 xHO2 + NO2 + #.721 RO2C + #.102 RO2XC + #.102 zRNO3 + #.074 HCHO + #.061 xHCHO + #.214 CCHO + #.23 xCCHO + #.074 RCHO + #.063 xRCHO + #.008 xACET + #.124 MEK + #.083 xMEK + #.19 PROD2 + #.261 xPROD2 + #.066 yROOH + #.591 yR6OOH + #.396 XC	Phot Set= IC3ONO2				72,73
Steady-State Peroxy Radical operators (for formation of organic product species)						
PO01	xHCHO = HCHO	k is variable parameter: RO2RO				32
PO02	xHCHO = XC	k is variable parameter: RO2XRO				32
PO03	xCCHO = CCHO	k is variable parameter: RO2RO				32
PO04	xCCHO = #2 XC	k is variable parameter: RO2XRO				32
PO05	xRCHO = RCHO	k is variable parameter: RO2RO				32
PO06	xRCHO = #3 XC	k is variable parameter: RO2XRO				32
PO07	xACET = ACET	k is variable parameter: RO2RO				32
PO08	xACET = #3 XC	k is variable parameter: RO2XRO				32
PO09	xMEK = MEK	k is variable parameter: RO2RO				32
PO10	xMEK = #4 XC	k is variable parameter: RO2XRO				32
PO11	xPROD2 = PROD2	k is variable parameter: RO2RO				32
PO12	xPROD2 = #6 XC	k is variable parameter: RO2XRO				32
PO13	xGLY = GLY	k is variable parameter: RO2RO				32
PO14	xGLY = #2 XC	k is variable parameter: RO2XRO				32
PO15	xMGLY = MGLY	k is variable parameter: RO2RO				32
PO16	xMGLY = #3 XC	k is variable parameter: RO2XRO				32
PO17	xBACL = BACL	k is variable parameter: RO2RO				32
PO18	xBACL = #4 XC	k is variable parameter: RO2XRO				32
PO19	xBALD = BALD	k is variable parameter: RO2RO				32
PO20	xBALD = #7 XC	k is variable parameter: RO2XRO				32
PO21	xAFG1 = AFG1	k is variable parameter: RO2RO				32
PO22	xAFG1 = #5 XC	k is variable parameter: RO2XRO				32
PO23	xAFG2 = AFG2	k is variable parameter: RO2RO				32
PO24	xAFG2 = #5 XC	k is variable parameter: RO2XRO				32
PO25	xAFG3 = AFG3	k is variable parameter: RO2RO				32
PO26	xAFG3 = #7 XC	k is variable parameter: RO2XRO				32
PO27	xMACR = MACR	k is variable parameter: RO2RO				32
PO28	xMACR = #4 XC	k is variable parameter: RO2XRO				32
PO29	xMVK = MVK	k is variable parameter: RO2RO				32
PO30	xMVK = #4 XC	k is variable parameter: RO2XRO				32
PO31	xIPRD = IPRD	k is variable parameter: RO2RO				32
PO32	xIPRD = #5 XC	k is variable parameter: RO2XRO				32
PO33	xRNO3 = RNO3	k is variable parameter: RO2RO				32
PO34	xRNO3 = #6 XC + XN	k is variable parameter: RO2XRO				32
PO35	zRNO3 = RNO3 + #-1 XN	k is variable parameter: RO2NO				74
PO36	zRNO3 = PROD2 + HO2	k is variable parameter: RO22NN				74

Table A-2 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Refs & Notes [c]
		k(300)	A	Ea	B	
PO37	zRNO3 = #6 XC	k is variable parameter: RO2XRO				74
PO38	yROOH = ROOH + #-3 XC	k is variable parameter: RO2HO2				75
PO39	yROOH = MEK + #-4 XC	k is variable parameter: RO2RO2M				75
PO40	yROOH =	k is variable parameter: RO2RO				75
PO41	yR6OOH = R6OOH + #-6 XC	k is variable parameter: RO2HO2				75
PO42	yR6OOH = PROD2 + #-6 XC	k is variable parameter: RO2RO2M				75
PO43	yR6OOH =	k is variable parameter: RO2RO				75
PO44	yRAOOH = RAOOH + #-8 XC	k is variable parameter: RO2HO2				75
PO45	yRAOOH = PROD2 + #-6 XC	k is variable parameter: RO2RO2M				75
PO46	yRAOOH =	k is variable parameter: RO2RO				75
Explicitly Represented Primary Organics						
BE01	CH4 + OH = H2O + MEO2	6.62E-15	1.85E-12	3.36		1,59
BE02	ETHENE + OH = RO2C + xHO2 + #1.61 xHCHO + #.195 xCCHO + yROOH	8.15E-12	Falloff, F=0.60, N=1.00			2,76
		0:	1.00E-28	0.00	-4.50	
		inf:	8.80E-12	0.00	-0.85	
BE03	ETHENE + O3 = #.16 OH + #.16 HO2 + #.51 CO + #.12 CO2 + HCHO + #.37 HCOOH	1.68E-18	9.14E-15	5.13		59,77
BE04	ETHENE + NO3 = RO2C + xHO2 + xRCHO + yROOH + #-1 XC + XN	2.24E-16	3.30E-12	5.72	2.00	3,76
BE05	ETHENE + O3P = #.8 HO2 + #.51 MEO2 + #.29 RO2C + #.51 CO + #.1 CCHO + #.29 xHO2 + #.278 xCO + #.278 xHCHO + #.012 xGLY + #.29 yROOH + #.2 XC	7.43E-13	1.07E-11	1.59		59,78
BE06	ISOPRENE + OH = #.986 RO2C + #.093 {RO2XC + zRNO3} + #.907 xHO2 + #.624 xHCHO + #.23 xMACR + #.32 xMVK + #.357 xIPRD + yR6OOH + #-0.167 XC	9.96E-11	2.54E-11	-0.81		1,65,79
BE07	ISOPRENE + O3 = #.266 OH + #.066 HO2 + #.192 RO2C + #.008 {RO2XC + zRNO3} + #.275 CO + #.122 CO2 + #.4 HCHO + #.1 PROD2 + #.39 MACR + #.16 MVK + #.15 IPRD + #.204 HCOOH + #.192 {xMACO3 + xHCHO} + #.2 yR6OOH + #-0.559 XC	1.34E-17	7.86E-15	3.80		1,65
BE08	ISOPRENE + NO3 = #.936 RO2C + #.064 {RO2XC + zRNO3} + #.749 xHO2 + #.187 xNO2 + #.936 xIPRD + yR6OOH + #-0.064 XC + #.813 XN	6.81E-13	3.03E-12	0.89		1,65
BE09	ISOPRENE + O3P = #.25 MEO2 + #.24 RO2C + #.01 {RO2XC + zRNO3} + #.75 PROD2 + #.24 xMACO3 + #.24 xHCHO + #.25 yR6OOH + #-1.01 XC	3.50E-11				65,79
BE10	ACETYLEN + OH = #.7 OH + #.3 HO2 + #.3 CO + #.7 GLY + #.3 HCOOH	7.56E-13	Falloff, F=0.60, N=1.00			2,80,81

Table A-2 (continued)

Label	Reaction and Products [a]	Rate Parameters [b] k(300)	A	Ea	B	Refs & Notes [c]
BE11	ACETYLEN + O3 = #.5 OH + #1.5 HO2 + #1.5 CO + #.5 CO2	1.16E-20	1.00E-14	8.15		2,81,82
BE12	BENZENE + OH = #.116 OH + #.29 {RO2C + xHO2} + #.024 {RO2XC + zRNO3} + #.57 {HO2 + CRES} + #.116 AFG3 + #.290 xGLY + #.029 xAFG1 + #.261 xAFG2 + #.314 yRAOOH + #-.976 XC	1.22E-12	2.33E-12	0.38		83

[a] Format of reaction listing: "=" separates reactants from products; "#*number*" indicates stoichiometric coefficient, "#*coefficient* {*product list*}" means that the stoichiometric coefficient is applied to all the products listed.

[b] Except as indicated, the rate constants are given by $k(T) = A \cdot (T/300)^B \cdot e^{-Ea/RT}$, where the units of k and A are cm^3 $molec^{-1}$ s^{-1}, Ea are kcal mol^{-1}, T is ^oK, and R=0.0019872 kcal mol^{-1} deg^{-1}. The following special rate constant expressions are used:

Phot Set = *name*: The absorption cross sections and (if applicable) quantum yields for the photolysis reaction are given in Table A-3, where "*name*" indicates the photolysis set used. If a "qy=*number*" notation is given, the number given is the overall quantum yield, which is assumed to be wavelength independent.

Falloff: The rate constant as a function of temperature and pressure is calculated using $k(T,M) = \{k0(T)\cdot[M]/[1 + k0(T)\cdot[M]/kinf(T)]\}\cdot F^Z$, where $Z = \{1 + [\log10\{k0(T)\cdot[M])/kinf(T)\}/N]^2\}^{-1}$, [M] is the total pressure in molecules cm^{-3}, F and N are as indicated on the table, and the temperature dependences of k0 and kinf are as indicated on the table.

k = k0+k3M(1+k3M/k2): The rate constant as a function of temperature and pressure is calculated using $k(T,M) = k0(T) + k3(T)\cdot[M]\cdot(1 + k3(T)\cdot[M]/k2(T))$, where [M] is the total bath gas (air) concentration in molecules cm-3, and the temperature dependences for k0, k2 and k3 are as indicated on the table.

k = k1 + k2 [M]: The rate constant as a function of temperature and pressure is calculated using $k(T,M) = k1(T) + k2(T)\cdot[M]$, where [M] is the total bath gas (air) concentration in molecules cm-3, and the temperature dependences for k1, and k2 are as indicated on the table.

Same K as Rxn xx: Uses the same rate constant as the reaction in the base mechanism with the same label.

[c] Footnotes documenting sources of rate constants and mechanisms are as follows.

1 Same as used or assumed in the SAPRC-99 mechanism (Carter, 2000a).

2 Rate constant or absorption coefficients and quantum yields based on NASA (2006) recommendation. Mechanism is also as recommended unless indicated by other footnotes.

3 Rate constant or absorption coefficients and quantum yields based on IUPAC (2006) recommendation. Mechanism is also as recommended unless indicated by other footnotes.

4 Absorption cross-sections and quantum yields as recommended for 294-298K. This gives an 8% higher NO_2 photolysis rate for direct overhead sunlight than the action spectrum used in SAPRC-99. Note that the net effect is to decrease rate constants for all other photolysis reactions by the same amount in environmental chamber simulations.

5 Separate recommendations are made for reactions with O_2 and N_2. Rate parameters used are derived to fit those calculated for a mixture of 20.95% O2 and 69.05% N_2 over the temperature range of 250 - 350^o K.

Table A-2 (continued)

6 See also Wahner et al (1998).

7 Absorption cross-sections recommended by NASA (2006) used, which are generally consistent with the IUPAC (2006) recommendations. The quantum yields for O^1D formation are from the IUPAC (2006) recommendation; the NASA (2006) recommendations are consistent with these at the <306 and 329-340 nm range, but the parameterization for deriving quantum yields between these ranges did not give reasonable values. The quantum yield for O1D production is assumed to be zero in the high wavelength ration (wavelength > 390 nm. The O^3P quantum yields in the low wavelength regions are derived from the O^1D quantum yields assuming unit total quantum yield for both processes. The O^3P quantum yields are assumed to be unity in the high wavelength region.

8 NASA (2006) absorption cross-sections used, which give much greater resolution than those recommended by IUPAC (2006). IUPAC data sheet recommends assuming unit quantum yield for NO + OH formation throughout the relevant wavelength range. The absorption cross sections are essentially the same as used in SAPRC-99, but SAPRC-99 has some formation of NO2 + H as well.

9 Rate expression from Golden et al (2003) and NASA (2006) for the reaction forming HNO_3, using the NASA parameterization. The reaction forming HOONO is ignored, based on the assumption that it either decomposes or photolyzes back to the reactants. This expression is only slightly different than that given in the NASA (2003) recommendation, but gives a rate constant that is ~18% larger than that used in SAPRC-99 for ambient conditions.

10 Absorption cross sections used in SAPRC-99 are essentially the same as the NASA (2006) and IUPAC (2006) recommendations, so are not changed. Unit quantum yields are assumed.

11 Parameters derived to predict rate constants calculated from the temperature dependence expressions for the rate constants from the reverse reaction and the equilibrium constant as recommended by NASA (2006).

12 Absorption cross-sections from NASA (2006), and are essentially the same as used in SAPRC-99. Unit quantum yield assumed, as is also the case for SAPRC-99.

13 Measurements of the branching ratios vary, so the mechanism is uncertain. The SAPRC-99 assignment is based on assuming the branching ratio is approximately in the middle of the range given in various evaluations, which is 0.6 - 1.0 for the OH-forming channel.

14 Methoxy radicals formed in the reaction assumed to react primarily with O2, forming HO2 + formaldehyde.

15 Recommendations are given for the total rate constant and the temperature dependence of the two competing processes. The kinetic parameters are derived so the calculated rate constants for the reactions agree with those derived from the recommended total rate constant and rate constant ratio over the temperature range of 270 - 330 K.

16 Recommendations are given for total rate constant and the competing process only. The kinetic parameters for this process were adjusted to minimize the sum of squares difference in rate constants between the rate constants calculated using the difference between the recommended rate constants and the calculated value, over the temperature range 270 - 330 K.

17 The species RO2C and RO2XC are used to represent the effects of peroxy radical reactions on NO, NO_2, NO_3, HO_2, acyl peroxy radicals, and other peroxy radicals. RO2C is used to represent effects peroxy radicals that react with NO to form NO_2 (and the corresponding alkoxy radical, whose ultimate products re represented by separate xPROD species discussed below), while RO2XC represents effects of peroxy radicals that react with NO but do not form NO (i.e., to form organic nitrates that are represented by a separate zRNO3 species discussed below). Separate xPROD, yROOH, and zRNO3 species are used to represent the other radical

and product species formed in peroxy radical reactions, which vary depending on the reactant and radicals formed. See separate footnotes given in conjunction with the reactions of these species, and the discussion in the text concerning the general method used to represent peroxy radical reactions.

18 Rate constants used for generic peroxy radicals are based on recommendations for ethyl peroxy. See SAPRC-99 mechanism documentation (Carter, 2000) for a discussion of these peroxy radical operators.

19 Peroxy + peroxy reactions are assumed to proceed 1/2 the time forming two alkoxy radicals + O2, and the other half of the time by H-shift disproportionation reactions.

20 Rate expression from Bridier et al (1991), based on both NASA (2006) and IUPAC (2006) recommendations. Note that although this was intended to be the source of the rate constant used in the SAPRC-99 mechanism (Carter, 2000a), it was incorrectly implemented using N=1 rather than N=1.61, as used by Bridier et al (1991). This amounts to about an 11% difference in the rate constants calculated for 298K and 1 atm. total pressure, but does not affect the equilibrium constant.

21 The branching ratio is based on an average of the values cited by IUPAC (2006). A third channel forming OH + O2 + CH3CO2 is assumed not to be important, though the data do not completely rule this out (IUPAC, 2005). Peroxyacetic acid (the co-product with O2) is represented by acetic acid to avoid the necessity of adding a new species in the mechanism for this reaction.

22 No recommendations available for this rate constant. Use the same rate constant as used for generic peroxy + NO_3 reactions.

23 No recommendations available concerning the branching ratio. We assume that the major route is alkoxy radical formation, analogous to the route recommended to occur 90% of the time in the case of the reaction of acetyl peroxy with methyl peroxy.

24 Estimated assuming that the ratio of the rate constant ratio for the reaction with NO_2 relative to reaction with NO is the same as for acetyl peroxy radicals at the high pressure limit. Temperature dependence parameters derived to fit rate constants calculated using k(RCO3+NO) x kinf(CCO3+NO_2)/k(CCO3+NO) over the temperature range 270-330 K.

25 The high pressure limit for the recommended PPN decomposition rate expression is used. This is to be consistent with the assumption that the formation reaction is at the high pressure limit, and also because this model species is used to represent higher PAN analogues in addition to PPN. The recommended rate expression for PPN gives a 1 atm rate constant that is about 90% the high pressure limit.

26 Photolyses of higher PAN analogues are assumed to occur with same action spectrum and analogous mechanism as the photolysis of PAN.

27 Rate constants used for generic acyl peroxy radicals and generic higher PAN analogues based on those for R=C_2H_5. See SAPRC-99 documentation (Carter, 2000).

28 Reaction is assumed to be analogous to that for MECO3. Where applicable, the peroxy acid is represented by the corresponding acid to avoid adding a separate species to the mechanism to represent these products. Reaction with peroxy radicals is assumed to proceed primarily via alkoxy radical formation, the major (90%) pathway for the MECO3 + MEO2 reaction.

29 Rate constant expression based on the data of Kirchner et al (1992).

30 Rate parameters from Roberts and Bertman (1992), as used by Carter and Atkinson (1996).

31 This is added to avoid problems in the (generally unlikely) conditions where phenoxy radicals are formed when concentrations of both NO_2 and HO_2 are low. The rate constant used is that used in the SAPRC-99 mechanism, which is arbitrary and is such that this process becomes

Table A-2 (continued)

significant only if [NO_2] < ~3x10-6 ppm and [HO_2] < $1x10^{-5}$ ppm. The likely process is reaction with some VOC forming phenol and radicals, with the latter represented by RO2R.

32 The xPROD chemical operator species are used to represent the formation of radicals and products from alkoxy radicals formed in the reactions of peroxy radicals with NO, NO_3, acyl peroxy radicals, and, in ~50% yields, with other peroxy radicals. These products are not formed when peroxy radicals react with HO_2, and, in ~50% yields, with other peroxy radicals, since those reactions are assumed not to form alkoxy radicals, but instead form hydroperoxides or H-shift disproportion products that are represented by separate yROOH chemical operator species, discussed in a separate footnote. The reactions of peroxy radicals with other peroxy radicals are assumed to form alkoxy radicals 50% of the time, so the products from alkoxy radical reactions are represented as being formed in 50% yields in these reactions. The consumption and products formed from these species can be represented in several ways. The most straightforward method is to include a reaction for each of the types of peroxy radical reactions, as follows:

xPROD + NO $\rightarrow$ NO + PROD
xPROD + HO2 $\rightarrow$ HO2
xPROD + NO3 $\rightarrow$ NO3 + PROD
xPROD + MECO3 $\rightarrow$ MECO3 + PROD (& similar reactions for RCO3, BZCO3, and MACO3)
xPROD + MEO2 $\rightarrow$ MEO2 + 1/2 PROD
xPROD + RO2C $\rightarrow$ RO2C + 1/2 PROD (& a similar reaction for RO2XC)

where "PROD" represents the product species for the operator (e.g., HO2 for xHO2). The rate constants for these reactions should be the same as the rate constant for the corresponding reactions of RO2C or RO2XC. This is a somewhat cumbersome method because it requires 9 reactions for each of the many xPROD species. An alternative method, implemented in this table, uses the coefficient "RO2RO" to determine the rate of formation of the product species and "RO2XRO" to represent processes where the product is not formed. These are calculated as follows, where the k(RO2+..)'s refer to the rate constants for the reactions of RO2C or RO2XC with the indicated reactant.

RO2RO = k(RO2+NO)[NO] + k(RO2+NO3)[NO3] + k(RO2+MECO3){[MECO3]+[RCO3]+ [BZCO3]+[MACO3]) + 0.5 k(RO2+MEO2)[MEO2] + 0.5 k(RO2+RO2) {[RO2C]+[RO2XC])

RO2XRO = k(RO2+HO2)[HO2] + 0.5 k(RO2+MEO2)[MEO2] + 0.5 k(RO2+RO2){[RO2C]+ [RO2XC])

The steady state approximation <u>must</u> be used for these operators when this representation is used, and the operators must not be allowed to be diluted or transported.

33 The 298K rate constant is as estimated by IUPAC (2006). The temperature dependence used in the SAPRC-99 mechanism is consistent with this, so is retained here.

34 This reaction is not believed to be important under atmospheric conditions or in the conditions of the chamber experiments used for mechanism evaluation. The adduct is believed to rapidly rearrange to $HOCH_2OO\cdot$, which can react with NO to ultimately form NO_2 and formic acid, or decompose back to formaldehyde + HO_2, resulting in no net reaction. Based on the rate constants for the $HOCH_2OO\cdot$ decomposition recommended by IUPAC (2006) and the expected peroxy + NO rate constant, the reaction with NO is expected to be negligible unless NO is so high that HO_2 levels are suppressed, so the decomposition, resulting in no net reaction, is expected to dominate. Sensitivity calculations with versions of the mechanism incorporating this reaction confirmed the negligible impact of this process.

35 Mechanism of propionaldehde used for RCHO. IUPAC (2006) recommendation used for total

rate constant. No useful recommendation given for mechanism.

36 Mechanism based on estimated relative rates of reactions at various positions and estimated rate constants or rate constant ratios for reactions of the various radicals formed, derived using current SAPRC mechanism generation system. For this reaction the generated mechanism should be essentially the same as the version developed with the SAPRC-99 mechanism (Carter, 2000a).

37 The absorption cross sections recommended by IUPAC (2006) are the same as used in the SAPRC-99 mechanism. There is a discrepancy in the quantum yields at higher wavelengths from recent measurements from Chen and Ziu (2001), which indicate no falloff at the higher wavelengths, and earlier measurements from Heicklen et al (1986) that indicated a falloff in quantum yields and was the basis of previous recommendation and the propionaldehyde photolysis rates used in the SAPRC-99 mechanism (Carter, 2000a). IUPAC (2006) and NASA (2006) make no recommendations in this regard. We assume that the earlier values are more representative of atmospheric conditions because they were based on measurements made in air while the more recent measurements were in N_2, and the possibility that the falloff could be due to quenching by O_2, and because the photolysis rates obtained are more consistent with those measured in the Euphore chamber (Wirtz et al, 1999). Therefore, the earlier quantum yields, as used in the SAPRC-99 mechanism, are retained.

38 298K rate constant is that recommended by IUPAC (2006) for propionaldehyde. Temperature dependence estimated by assuming this reaction has same A factor as reaction of NO_3 with acetaldehyde.

39 Temperature-dependent parameters derived to give best fits to the IUPAC (2006)-recommended temperature dependence expression for the temperature range 270-330 K. These parameters give a good estimate of the recommended rate constant at ~300^o K, but underestimate the recommended rate constants by about 2% at both ends of this temperature range.

40 Absorption cross sections are for T=298^{o}K. Quantum yields are calculated for 1 atm and T=298^{o}K using the complex expression recommended by IUPAC (2006) and NASA (2006). Separate recommendations are given for temperature, pressure, and wavelength-dependent quantum yields for formation of CO and formation of CH_3CO, and the calculated fraction of the CO formation process relative to total fragmentation to radicals ranges from 35% to 52% for zenith angle of 0 to 80, respectively. The ratios for the indoor light sources used in the chamber experiments used for evaluating the mechanism are in this range. Rather than have two separate photolysis processes in the mechanism, a wavelength-independent ratio of 48% is assumed, which represents the weighed average of these values. However, using the quantum yields derived in this way gives photolysis rates that are about 1.6 times higher than used in SAPRC-99 and significantly overpredicts reactivity in acetone incremental reactivity experiments. In order to remove this bias, it is necessary to reduce the photolysis rates by about a factor of 2, i.e., assume the quantum yields are 1/2 the values derived using the recommended method. This inconsistency between the laboratory data and the chamber experiments need to be evaluated. However, the quantum yields that give the better fits to the chamber data are used because they are a better approximation of atmospheric conditions.

41 Absorption cross-sections from IUPAC (2006) recommendation, but are essentially the same as used in SAPRC-99. The IUPAC (2006)-recommended overall quantum yield is 0.24 (with no recommendation given for wavelength dependence of quantum yields), but this results in a bias towards overpredicting reactivity in MEK incremental reactivity experiments. The data are better fit using an overall quantum yield of 0.175, which is slightly higher than the 0.15 value used in the SAPRC-99 mechanism, based on simulations of the same experiments.

Table A-2 (continued)

42 The reaction would involve the eventual formation of HO_2 + CO_2 regardless of which hydrogen were abstracted in the initial reaction.

43 Branching ratio used for formation of $\cdot CH_2OOH$ vs. $CH_3OO\cdot$ is as recommended by NASA (2006). $\cdot CH_2OOH$ is assumed to rapidly decompose to formaldehyde + OH.

44 Mechanism generation system updated to predict the NASA (2006) recommended rate constant and branching ratio for the reaction of OH with methyl hydroperoxide. The generated mechanism for n-propyl hydroperoxide incorporates the substituent effects for the -OOH group derived from this rate constant and branching ratio.

45 Mechanism for ROOH based on estimated reactions for n-propyl hydroperoxide. Photolysis and rate of reaction of OH at OOH assumed to occur at same rate as for methyl hydroperoxide.

46 Mechanism for R6OOH based on estimated reactions for 3-hexyl hydroperoxide. Photolysis and rate of reaction of OH at OOH assumed to occur at same rate as for methyl hydroperoxide.

47 Mechanism for RAOOH is based on estimated reactions of two isomers expected to be formed in the m-xylene system. Mechanism derived using the mechanism generation system based on estimated reactions at various positions, and assumptions for the major process for some alkoxy radical reactions that could not be estimated using the current system. Photolysis and rates of reaction of OH at OOH assumed to occur at the same rate as for methyl hydroperoxide.

48 Absorption cross sections used are those given by Volkamer et al (2005), which supercede the values of Plum et al (1983) used in previous recommendations. For wavelengths up to 350 nm, the quantum yields for radical production are based on those of Zhu et al (1996), which are consistent with the data of Langford and Moore (1984). The quantum yields for formaldehyde + H_2 production are derived based on assuming a total quantum yield of 1 in this wavelength region. For the higher wavelength region, the decline in quantum yields as a function of wavelength are derived to give photolysis rates, relative to those for NO_2, that are consistent with the data of Klotz et al (2000) based on assuming solar spectral distributions with zenith angles between 0 and 40 degrees, and that are also consistent with the formaldehyde yields, relative to total photolysis, of 13%, as given by Plum et al (1983). In both cases, the quantum yield is assumed to decline exponentially as a function of wavelength below 350 nm, with the decay rate adjusted to give the photolysis rate consistent with the data referenced above.

49 Mechanism based on branching ratios for subsequent reactions of the radicals formed as given by IUPAC (2006) for 1 atm air at 298^oK.

50 No data available for the kinetics of this reaction. Rate parameters used in SAPRC-99 used. See Carter (2000) for method used to estimate rate constant. HCO(CO)OO. and RCO(CO)OO are represented by the lumped higher acyl peroxy species RCO3.

51 Recommended cross sections are essentially the same as used in SAPRC-99. Quantum yields calculated using the temperature- and wavelength-dependence expression recommended by IUPAC (2006) for 760 torr N_2 give an overall photolysis rate, relative to NO_2, for ambient photolysis which are lower than those reported by Klotz et al (2003) for the Euphore outdoor chamber. However, if the quantum yields are calculated for a pressure of 472 torr, the calculated photolysis rate relative to NO_2 for ambient conditions agree with the data of Klotz et al (2003). Therefore, this adjustment is adopted for the quantum yields used for this mechanism.

52 The evaluations give no recommendations for the photolysis of biacetyl. The absorption cross sections used are those from Plum et al (1983), as used in the SAPRC-99 mechanism.

Quantum yields calculated using the IUPAC (2006)-recommended expression for the pressure and wavelength-dependence quantum yields for methyl glyoxal, but with the effective pressure adjusted so the photolysis rate, relative to that for NO_2, under ambient conditions is consistent with that measured by Klotz et al (2000) in the Euphore outdoor chamber.

53 Rate constant expression as recommended by Calvert et al (2002) for o-cresol.

54 "CRES" is used to represent phenol and cresols. (Phenol was represented separately in SAPRC-99 but is lumped with cresols in this mechanism because the lumping had no significant effect on model simulations and the mechanisms of both are highly uncertain and approximate.) Available data (Berndt and Boge, 2003 and Olariu et al 2002) indicate that dihydroxy phenol or cresol formation occurs ~60-80% of the time, and kinetic data cited by Berndt and Boge (2003) suggest that in the case of phenol under atmospheric conditions OH addition occurs ~75-80% of the time, with phenoxy formation occurring the remainder of the time. This suggests that dihydroxybenzene formation (with HO_2 as the co-product) is the major fate of the OH addition reaction. However, this mechanism cannot simulate results of the cresol - NO_x air chamber experiments. In order to simulate the reactivity in those experiments, it is necessary to assume additional NO to NO_2 conversions occur, and it is also necessary to some photoreactive product, such as methyl glyoxal, is also formed. In view of the inconsistency between chamber and laboratory data concerning this reaction, we retain the parameterization used in the SAPRC-99 mechanism (Carter, 2000), which was found to perform the best in simulating the chamber data, after some minor adjustments to optimize fits to the data with the current mechanism. This is consistent with the laboratory data in assuming ~20% phenoxy radical formation, but does not appear to be consistent with other laboratory data in assuming an additional NO to NO_2 conversion is occurring. The photoreactive product(s) are represented by methyl glyoxal, which gives reasonable simulations of the observed PAN yields in the cresol experiments (Carter, 2000).

55 Rate constant is in the range cited by Barnes (2006) for various nitrocresols. Reaction is assumed to occur via abstraction of H from OH, analogous to pathway in the phenol and cresol + OH reactions that occur with similar rates.

56 Photolysis rate forming HONO, relative to the photolysis rate of NO_2, based on the data of Bejan et al (2006) for 2-nitrophenol and various methyl substituted 2-nitrophenols. The co-products are unknown, and are assumed to go mainly into the particle phase and its gas-phase reactivity is assumed not to be significant. Loss by other photolysis processes might be significant, but are ignored.

57 Nitrophenols were found to have lifetimes relative to photolysis in the Euphore chamber of 1-2 hours (Barnes, private communication, 2007). A photolysis rate relative to NO_2 of 0.015 corresponds approximately to this range. The products formed are unknown, but based on the data of Bejan et al (2006) it is apparent that NO_2 formation is not important and that HONO formation represents only about 10% of this process. We assume that the products are unreactive.

58 As with SAPRC-99, is assumed that all the reaction is at the -CHO group, and that addition to the ring is negligible.

59 Rate constant is as recommended or tabulated by Atkinson and Arey (2003).

60 Absorption cross-sections recommended by Calvert et al (2002). Overall quantum yield based on that of SAPRC-99 mechanism, which was adjusted to approximately fit the rate of consumption of benzaldehyde measured in chamber experiments. However, the new absorption cross sections result in a ~17% decrease in the solar photolysis rate for benzaldehyde, so the overall quantum yield is adjusted upward by the same factor to yield the same overall photodecomposition rate. The mechanism is the same as in SAPRC-99, which is

based on the fact that the products are unknown but are apparently unreactive, and not benzene.

61 The 298^{o}K rate constant recommended by Atkinson (1994). Temperature dependence estimated by assuming the reaction has the same A factor as the reaction of NO_3 with acetaldehyde. This gives the same 298^{o}K rate constant but a slightly different temperature dependence than used in SAPRC-99.

62 AFG1 and AFG2 are used to represent the photoreactive monounsaturated dialdehyde or aldehyde-ketone aromatic ring fragmentation products. Their mechanistic parameters are based on those for 2-butene 1,4-dial (10%), 2-methyl-2-butene-1,4-dial (21%), 4-oxo-2-petenal (37%), and 2-methyl-4-oxo-2-pentenal (32%). The action spectrum for the photolysis reactions of both species is also based on weighted averages of action spectra assigned to those species. The weighting factors used for each are based on the relative yields monounsaturated dialdehydes or aldehyde-ketones estimated for toluene and the di- and tri-methylbenzene isomers, each weighed equally, with 2,3-dimethyl-2-butene-1,4-dial represented by 2-methyl-2-butene-1,4-dial, and 3-methyl-4-oxo-2-penetnal and 2,3-dimethyl-4-oxo-2-pentenal represented by 2-methyl-4-oxo-2-pentenal. AFG1 is used to represent those compounds (or portions of the mechanisms) that photolyze to form radicals, while AFG2 is used to represent those which photolyze to form non-radical products, and each have the same OH and O_3 mechanism and overall action spectrum.

63 The mechanisms for the radical formation photolysis for AFG1 is based on that derived for the radical formation photolysis of the species used to derive the mechanistic parameters for the OH and O_3 reactions. The stable species formed in the photolysis of AFG2 are represented by PROD2.

64 AFG3 is used to represent the diunsaturated dicarbonyl products and also the monounsaturated diketone aromatic ring fragmentation products, which are assumed to have relatively low photoreactivity. There mechanisms are based on those derived for the diunsaturated dicarbonyl products 3-methyl 2,4-hexene-1,6-dial (54%), 6-oxo-2,4-heptadienal (66%), and 3,5-octadien-2,7-dione (6%). The weighting factors used are based on estimated diunsaturated dicarbonyls for toluene and the di- and tri-methylbenzene isomers, each weighed equally, with 2,4-hexene-1,6-dial representing all dialdehydes, 3,5-octadien-2,7-dione representing aldehyde-ketones, and 3,5-octadien-2,7-dione representing the diketones. Although this model species is also used to represent the monounsaturated diketone products, which are also assumed to be relatively unphotoreactive, they are formed by only a few isomers and their parameters are not used to derive those used for AFG3. (Representing them explicitly does not yield significantly improved simulations of p-xylene, and 1,2,4-trimethylbenzene, the only compounds with chamber data where such products are predicted to be formed.)

65 Except as indicated in other footnotes, the mechanism is as given by Carter (1996), based on the detailed mechanism of Carter and Atkinson (1996). (The rate constant and mechanism is unchanged from SAPRC-99 if footnote "1" is also given).

66 IUPAC (2006) recommendation of rate constant at 298^{o}K used. Temperature dependence is estimated using the estimated A factor given used in the SAPRC-99 mechanism, based on the estimate of Carter and Atkinson (1996).

67 Absorption cross sections recommended by IUPAC (2006) used. No recommendations given for quantum yield. The quantum yields were derived using the pressure and wavelength-dependent expression given by IUPAC (2006) for MVK, with the total pressure adjusted so that the radical forming photolysis rates for the chamber experiments are the same as those derived by Carter and Atkinson (1996) to fit the chamber experiments with methacrolein.

Table A-2 (continued)

68 Absorption cross sections recommended by IUPAC (2006) used. IUPAC (2006) also gives recommendations for quantum yields for total photodecomposition as a function of wavelength and pressure, and recommend assuming 60% forms propene + CO and the remainder involves radical formation. However, this recommendation gives photolysis rates for radical formation that are significantly higher than those found to fit chamber data for MVK (Carter and Atkinson, 1996). Using an effective pressure of 5 atmospheres gives radical formation photolysis that is consistent with modeling the chamber data, and is used in this mechanism. This is not inconsistent with the IUPAC (2006) recommendations because they stated that their recommended quantum yields should be considered to be upper limits. It is assumed that the radical formation process involves formation of $CH_3 + CH_2{=}CHCO\cdot$, as was assumed in the SAPRC-99 mechanism.

69 Consistent with the assumption in the SAPRC-99 mechanism, all species represented by ISOPROD are assumed to have the same action spectrum for photolysis as used for acrolein. As indicated in the footnotes for the methacrolein photolysis reaction, some modifications were made to the methacrolein action spectrum but the photolysis rates for conditions of chamber experiments are essentially the same as used in SAPRC-99. The other aspects of this reaction are not changed.

70 PROD2 is used to represent the more reactive non-aldehyde organic products formed in the photooxidations of various VOCs. As with SAPRC-99, its mechanism is based on those derived for representative product compounds that are represented by PROD2, which were chosen to be $CH_3C(O)CH_2CH_2CH_2OH$, $CH_3C(O)CH_2CH(CH_3)CH_2OH$, $CH_3CH_2C(O)CH_2\text{-}CH_2CH(CH_3)OH$, $CH_3CH_2C(O)CH_2CH_2CH(OH)CH_2CH_3$, and $CH_3CH_2CH_2CH(OH)CH_2\text{-}CH_2C(O)CH_2CH_3$ (Carter, 2000a). The rate constants and mechanisms for these compounds (designated PROD2-1 through 5, respectively) were derived using the mechanism generation system, and are given in Table B-4 in Appendix B. The mechanisms for PROD2 were derived by weighing those for each of these representative compounds equally.

71 Absorption cross-sections for methyl ethyl ketone used for general ketone photolysis, with quantum yields declining monotonically with carbon number (see discussion of general ketone photolysis elsewhere in this report). Overall quantum yields and mechanisms averages for the compounds used to derive the mechanism for PROD2.

72 As with SAPRC-99, the mechanism for the lumped organic nitrate product species is based on those derived for 6 compounds chosen to be representative of thee compounds, specifically $CH_3CH_2CH(CH_3)ONO_2$, $CH_3CH(OH)CH_2CH_2CH_2ONO_2$, $CH_3CH_2CH(CH_3)CH(CH_3)ONO_2$, $CH_3CH_2CH_2CH_2CH_2CH(ONO_2)CH_2OH$, $CH_3CH_2C(CH_3)(ONO_2)CH_2CH(CH_3)CH_3$, and $CH_3\text{-}CH_2CH_2CH_2CH_2CH_2CH_2CH(ONO_2)CH_2CH_3$ (RNO3-1 through 6) (Carter, 2000a). The rate constants and mechanisms for these compounds were derived using the current mechanism generation system, which should be similar to those predicted using the SAPRC-99 mechanism generation system documented by Carter (2000a). The mechanisms for RNO3 were derived by weighing those for each of these representative compounds equally.

73 Absorption cross section for isopropyl nitrate as given by IUPAC (2006) used, assuming unit quantum yields. This is the same as used for RNO3 in SAPRC-99.

74 The zRNO3 chemical operator species is used to represent the formation organic nitrates formed when peroxy radicals react with NO, or formation of radicals and products from alkoxy radicals formed in the reactions of peroxy radicals with NO_3, acyl peroxy radicals, and (in ~50% yields) with other peroxy radicals. These products are not formed when peroxy radicals react with HO_2 and (in the other ~50% of the time) with other peroxy radicals, since those reactions are assumed not form organic nitrates or alkoxy radicals, but instead form hydroperoxides or H-shift disproportion products that are represented by separate yROOH

chemical operator species, discussed in a separate footnote. At present the mechanism has only one zRNO3 operator to correspond to the single lumped organic nitrate model species, but other such operators can be added if it is desired to have separate organic nitrate model species, such as, for example, those to represent semi-volatile organic nitrates that may contribute to SOA. In the case of zRNO3, the products resulting if alkoxy radicals are formed in the RCO3 or RO2 reactions would depend on reactant and individual radicals, and are approximated by PROD2 and HO2 (as might occur following the reaction of a peroxy radical with O_2 to form HO_2 and a ketone species). As with the xPROD species, the consumption and products formed from these species can be represented in several ways, with the most straightforward method being to include a reaction for each of the types of peroxy radical reactions, as follows:

zRNO3 + NO → NO + RNO3
zRNO3 + HO2 → HO2
zRNO3 + NO3 → NO3 + PROD2 + HO2
zRNO3 + MECO3 → MECO3 + PROD2 + HO2 (& similar reactions for RCO3, BZCO3, and MACO3)
zRNO3 + MEO2 → MEO2 + 1/2 {PROD2 + HO2}
zRNO3 + RO2C → RO2C + 1/2 {PROD2 + HO2} (& a similar reaction for RO2XC)

The rate constants for these reactions should be the same as the rate constant for the corresponding reactions of RO2C or RO2XC. As with xPROD, an alternative method, requiring fewer reactions, is implemented in this table. In this case, the coefficient "RO2NO" is used to determine the rate of formation of organic nitrates, "RO22NN" is used to determine the rate of formation of the alkoxy radical products, and "RO2XRO" is used to represent processes where these products are is not formed, and is the same as used for xPROD. These are calculated as follows, where the k(RO2+..)'s refer to the rate constants for the reactions of RO2C or RO2XC with the indicated reactant.

RO2NO = k(RO2+NO)[NO]

RO22NN = k(RO2+NO3)[NO3] + k(RO2+MECO3){[MECO3]+[RCO3]+[BZCO3]+[MACO3]) + 0.5 k(RO2+MEO2)[MEO2] + 0.5 k(RO2+RO2){[RO2C]+[RO2XC])

RO2XRO = k(RO2+HO2)[HO2] + 0.5 k(RO2+MEO2)[MEO2] + 0.5 k(RO2+RO2){[RO2C]+[RO2XC]) (same as used for xPROD)

The steady state approximation must be used for these operators when this representation is used, and the operators must not be allowed to be diluted or transported.

75 The yROOH chemical operator species is used to represent the formation of organic hydroperoxides formed with peroxy radicals react with HO_2, or of H-shift disproportionation products formed when peroxy radicals react (in 50% yields) with other peroxy radicals. Note that the products formed when peroxy radicals react to form alkoxy radicals or organic nitrates (in the NO reaction) are represented using separate xPROD or zRNO3 species, and together these three types of operators represent all the products and radicals formed. Separate such yROOH species are used to represent formation of hydroperoxides or H-shift disproportion products in different molecular weight ranges or volatilities, and more can be added as needed for appropriate predictions of SOA formation. The hydroperoxide formed in the HO2 reaction is represented by either ROOH, R6OOH, or RAOOH, and the H-shift disproportion products are represented by either MEK (for yROOH) or PROD2 (for the others). As with the xPROD and zRNO3 species, the consumption and products formed from these species can be represented in several ways, with the most straightforward method being to include a reaction for each of the types of peroxy radical reactions, as follows for yROOH (the reactions for the

other two are analogous).

yROOH + NO → NO
yROOH + HO2 → HO2 + ROOH
yROOH + NO3 → NO3
yROOH + MECO3 → MECO3 (& similar reactions for RCO3, BZCO3, and MACO3)
yROOH + MEO2 → MEO2 + 1/2 MEK
yROOH + RO2C → RO2C + 1/2 MEK (& a similar reaction for RO2XC)

The rate constants for these reactions should be the same as the rate constant for the corresponding reactions of RO2C or RO2XC. As with the other operators, an alternative method, requiring fewer reactions, is implemented in this table. In this case, the coefficient "RO2HO2" is used to determine the rate of formation of organic hydroperoxides, "RO2RO2M" to determine the rate of formation of H-shift disproportion products, and "RO2RO" is used to represent processes where these products are is not formed. Note that the latter is the same as the coefficient that is used to represent the formation products from the xPROD species. These are calculated as follows, where the k(RO2+..)'s refer to the rate constants for the reactions of RO2C or RO2XC with the indicated reactant.

RO2HO2 = k(RO2+HO2)[HO2]

RO2RO2M = 0.5 k(RO2+RO2){[RO2C]+ [RO2XC])

RO2RO = k(RO2+NO)[NO] + k(RO2+NO3)[NO3] + k(RO2+MECO3){[MECO3]+[RCO3]+ [BZCO3]+[MACO3]) + 0.5 k(RO2+MEO2) [MEO2] + 0.5 k(RO2+RO2) {[RO2C]+[RO2XC])

The steady state approximation must be used for these operators when this representation is used, and the operators must not be allowed to be diluted or transported.

76 The mechanism is the same as used in SAPRC-99, but the rate constant was updated based on a more recent evaluation.

77 Criegee biradical stabilization yield as recommended by Atkinson (1997) and IUPAC (2006). OH yield of 16% used based on recommendation of IUPAC (2006), which is higher than the 12% yield recommended by Atkinson (1997). The yields of the other decomposition pathways based on Atkinson (1997) recommendations except they were reduced by 8% to account for the higher OH yield of the IUPAC (2006) recommendation.

78 Radical fragmentation distribution as recommended by Calvert et al, (2000), ignoring H_2 + ketene route. Although Calvert et al. (2000) recommends assuming 95% fragmentation, it is necessary to assume ~20% stabilization to remove biases in model simulations of ethene. This is consistent with the need to assume more-than-recommended stabilization in the analogous reaction of propene to remove biases in model simulations of propene experiments. However, this is somewhat lower than the ~50% stabilization used in the SAPRC-99 mechanism to remove biases in simulations of the ethene experiments.

79 Rate constant expression as recommended by Calvert et al (2000)

80 Acetylene is added as an explicitly represented compound in the current base mechanism because of its relatively large emissions and the fact that it is not well represented by other lumped species in the mechanism.

81 The mechanism is derived as discussed by Carter et al (1997c), based in part on the data of Hatakeyama et al (1986) and in part of adjustments to fit chamber data, except that in order to fit chamber data with the current mechanism it is necessary to assume that all of the initial reaction with OH results in the formation of HOCH=CH. radicals.

82 The mechanism is based on assuming the initially formed adduct rearranges to form excited

HCOCHOO Crigiee biradicals. The subsequent reaction of this excited biradical is unknown, but it is assumed that decomposition is dominant, forming CO + HCO + OH half the time and $HCO_2\cdot$ + HCO the other half.

83 Benzene is added as an explicitly represented compound in the current base mechanism because of its non-negligible emissions and the fact that it is not well represented by the other lumped aromatic species in the mechanism. The rate constant expression is as recommended by Atkinson and Arey (2003). The mechanism employs the general mechanism formulation used for aromatics in this version of the mechanism. The yield of phenol (represented by CRES) is the average of values of Berndt and Boge (2006) and Volkamer et al (2002). This is significantly higher than the values used in the SAPRC-99 mechanism (Carter, 2000a). The glyoxal yield is as determined by Berndt and Boge (2006), which is reasonably consistent with previous studies. AFG1 and AFG2 represent the co-product(s) formed with the alpha-dicarbonyls, which react with the same mechanism except that AFG1 is highly photoreactive and AFG2 is not, and with their relative yields adjusted to fit ozone reactivity results in the benzene - NO_x chamber experiments. AFG3 is used to represent ring fragmentation products not involving alpha-dicarbonyl formation, which is assumed to involve formation of OH without NO to NO_2 conversions. The yields of OH, HO_2, and RO2R are derived as used for general aromatics mechanisms, and are equal to the yields of AFG3, phenol, and total alpha-dicarbonyls, respectively.

Table A-3. Absorption cross-sections and quantum yields for the all photolysis reactions in the base mechanism. (Available in electronic form only)

Because of the size of this table, it is only available in as supplementary material in electronic form. See Appendix D.

Table A-4. List of model species used in the base chlorine SAPRC-07 mechanism.

Name	Description
Active Inorganic Species.	
CL2	Chlorine molecules
CLNO	ClNO
CLONO	ClONO
CLNO2	ClNO2
CLONO2	ClONO2
HOCL	HOCl
HCL	Hydrochloric acid
Active Radical Species and Operators.	
CL	Chlorine atoms
CLO	ClO. Radicals
Steady state operators used to represent radical or product formation in peroxy radical reactions.	
xCL	Formation of Cl radicals from alkoxy radicals formed in peroxy radical reactions with NO and NO_3 (100% yields) and RO_2 (50% yields)
xCLCCHO	As above, but for CLCCHO
xCLACET	As above, but for CLACET
Active Organic Product Species	
CLCCHO	Chloroacetaldehyde (and other alpha-chloro aldehydes that are assumed to be similarly photoreactive)
CLACET	Chloroacetone (and other alpha-chloro ketones that are assumed to be similarly photoreactive)
Low Reactivity Compounds Represented as Unreactive	
CLCHO	Formyl Chloride

Table A-5. Listing of reactions and rate parameters added to represent the reactions of chlorine species in the SAPRC-07 mechanism.

Label	Reaction and Products [a]	Rate Parameters [b]				Refs & Notes [c]
		k(298)	A	Ea	B	
Base Chlorine Mechanism						
CI01	CL2 + HV = #2 CL	Phot Set= CL2				1
	CL + O2 + M = CLO2. + M	(Ignored)				3
	CLO2. + M = CL + O2 + M	(Ignored)				3
CI02	CL + NO + M = CLNO + M	7.60e-32	7.60e-32	0.00	-1.80	2
CI03	CLNO + HV = CL + NO	Phot Set= CLNO-06				1
CI04	CL + NO2 = CLONO	1.60e-11	Falloff, F=0.60, N=1.00			2
		0:	1.30e-30	0.00	-2.00	
		inf:	1.00e-10	0.00	-1.00	
CI05	CL + NO2 = CLNO2	3.52e-12	Falloff, F=0.60, N=1.00			2
		0:	1.80e-31	0.00	-2.00	
		inf:	1.00e-10	0.00	-1.00	
CI06	CLONO + HV = CL + NO2	Phot Set= CLONO				1
CI07	CLNO2 + HV = CL + NO2	Phot Set= CLNO2				1
CI08	CL + HO2 = HCL + O2	3.44e-11	3.44e-11	0.00	-0.56	1,4
CI09	CL + HO2 = CLO + OH	9.41e-12	9.41e-12	0.00	2.10	4
CI10	CL + O3 = CLO + O2	1.22e-11	2.80e-11	0.50		1
CI11	CL + NO3 = CLO + NO2	2.40e-11				1
CI12	CLO + NO = CL + NO2	1.66e-11	6.20e-12	-0.59		1
CI13	CLO + NO2 = CLONO2	2.29e-12	Falloff, F=0.60, N=1.00			2
		0:	1.80e-31	0.00	-3.40	
		inf:	1.50e-11	0.00	-1.90	
CI14	CLONO2 + HV = CLO + NO2	Phot Set= CLONO2-1				1
CI15	CLONO2 + HV = CL + NO3	Phot Set= CLONO2-2				1
CI16	CLONO2 = CLO + NO2	4.12e-4	Falloff, F=0.60, N=1.00			5
		0:	4.48e-5	24.90	-1.00	
		inf:	3.71e+15	24.90	3.50	
CI17	CL + CLONO2 = CL2 + NO3	1.01e-11	6.20e-12	-0.29		1
CI18	CLO + HO2 = HOCL + O2	6.83e-12	2.20e-12	-0.68		1
CI19	HOCL + HV = OH + CL	Phot Set= HOCL-06				1
CI20	CLO + CLO = #.29 CL2 + #1.42 CL + O2	1.82e-14	1.25e-11	3.89		6
CI21	OH + HCL = H2O + CL	7.90e-13	1.70e-12	0.46		1
CI22	CL + H2 = HCL + HO2	1.77e-14	3.90e-11	4.59		1
Chlorine reactions with common organic products						
CP01	HCHO + CL = HCL + HO2 + CO	7.33e-11	8.10e-11	0.06		1
CP02	CCHO + CL = HCL + MECO3	8.00e-11	8.00e-11			1
CP03	MEOH + CL = HCL + HCHO + HO2	5.50e-11	5.50e-11	0.00		1

Table A-5 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Refs & Notes [c]
		k(298)	A	Ea	B	
CP04	RCHO + CL = HCL + #.9 RCO3 + #.1 {RO2C + xCCHO + xCO + xHO2 + yROOH}	1.23e-10				7
CP05	ACET + CL = HCL + RO2C + xHCHO + xMECO3 + yROOH	2.75e-12	7.70e-11	1.99		2
CP06	MEK + CL = HCL + #.975 RO2C + #.039 RO2XC + #.039 zRNO3 + #.84 xHO2 + #.085 xMECO3 + #.036 xRCO3 + #.065 xHCHO + #.07 xCCHO + #.84 xRCHO + yROOH + #.763 XC	3.60e-11				1,8
CP07	RNO3 + CL = HCL + #.038 NO2 + #.055 HO2 + #1.282 RO2C + #.202 RO2XC + #.202 zRNO3 + #.009 RCHO + #.018 MEK + #.012 PROD2 + #.055 RNO3 + #.159 xNO2 + #.547 xHO2 + #.045 xHCHO + #.300 xCCHO + #.020 xRCHO + #.003 xACET + #.041 xMEK + #.046 xPROD2 + #.547 xRNO3 + #.908 yR6OOH + #.201 XN + #-.149 XC	1.92e-10				8,9
CP08	PROD2 + CL = HCL + #.314 HO2 + #.680 RO2C + #.116 RO2XC + #.116 zRNO3 + #.198 RCHO + #.116 PROD2 + #.541 xHO2 + #.007 xMECO3 + #.022 xRCO3 + #.237 xHCHO + #.109 xCCHO + #.591 xRCHO + #.051 xMEK + #.040 xPROD2 + #.686 yR6OOH + #1.262 XC	2.00e-10				8,9
CP09	GLY + CL = HCL + #.63 HO2 + #1.26 CO + #.37 RCO3 + #-.37 XC	7.33e-11	8.10e-11	0.06		10
CP10	MGLY + CL = HCL + CO + MECO3	8.00e-11				10
CP11	CRES + CL = HCL + xHO2 + xBALD + yR6OOH	6.20e-11				11
CP12	BALD + CL = HCL + BZCO3	8.00e-11				12
CP13	ROOH + CL = HCL + #.414 OH + #.588 RO2C + #.414 RCHO + #.104 xOH + #.482 xHO2 + #.106 xHCHO + #.104 xCCHO + #.197 xRCHO + #.285 xMEK + #.586 yROOH + #-0.287 XC	1.66e-10				8
CP14	R6OOH + CL = HCL + #.145 OH + #1.078 RO2C + #.117 {RO2XC + zRNO3} + #.145 PROD2 + #.502 xOH + #.237 xHO2 + #.186 xCCHO + #.676 xRCHO + #.28 xPROD2 + #.855 yR6OOH + #.348 XC	3.00e-10				8

Table A-5 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Refs & Notes [c]
		k(298)	A	Ea	B	
CP15	RAOOH + CL = #.404 HCL + #.139 OH + #.148 HO2 + #.589 RO2C + #.124 RO2XC + #.124 zRNO3 + #.074 PROD2 + #.147 MGLY + #.139 IPRD + #.565 xHO2 + #.024 xOH + #.448 xRCHO + #.026 xGLY + #.030 xMEK + #.252 xMGLY + #.073 xAFG1 + #.073 xAFG2 + #.713 yR6OOH + #2.674 XC	4.29e-10				13
CP16	MACR + CL = #.25 HCL + #.165 MACO3 + #.802 RO2C + #.033 RO2XC + #.033 zRNO3 + #.802 xHO2 + #.541 xCO + #.082 xIPRD + #.18 xCLCCHO + #.541 xCLACET + #.835 yROOH + #.208 XC	3.85e-10				8
CP17	MVK + CL = #1.283 RO2C + #.053 {RO2XC + zRNO3} + #.322 xHO2 + #.625 xMECO3 + #.947 xCLCCHO + yROOH + #.538 XC	2.32e-10				8
CP18	IPRD + CL = #.401 HCL + #.084 HO2 + #.154 MACO3 + #.73 RO2C + #.051 RO2XC + #.051 zRNO3 + #.042 AFG1 + #.042 AFG2 + #.712 xHO2 + #.498 xCO + #.195 xHCHO + #.017 xMGLY + #.009 xAFG1 + #.009 xAFG2 + #.115 xIPRD + #.14 xCLCCHO + #.42 xCLACET + #.762 yR6OOH + #.709 XC	4.12e-10				8,14
<u>Reactions of Chlorinated Organic Product Species</u>						
CP19	CLCCHO + HV = HO2 + CO + RO2C + xCL + xHCHO + yROOH	Phot Set= CLCCHO				15
CP20	CLCCHO + OH = RCO3 + #-1 XC	3.10e-12				16
CP21	CLCCHO + CL = HCL + RCO3 + #-1 XC	1.29e-11				16
CP22	CLACET + HV = MECO3 + RO2C + xCL + xHCHO + yROOH	Phot Set= CLACET, qy= 0.50				17
<u>Steady-State Peroxy Radical operators (for formation of chlorine radical and product species)</u>						
CP23	xCL = CL	k is variable parameter: RO2RO				18
CP24	xCL =	k is variable parameter: RO2XRO				18
CP25	xCLCCHO = CLCCHO	k is variable parameter: RO2RO				18
CP26	xCLCCHO = #2 XC	k is variable parameter: RO2XRO				18
CP27	xCLACET = CLACET	k is variable parameter: RO2RO				18
CP28	xCLACET = #3 XC	k is variable parameter: RO2XRO				18
<u>Chlorine Reactions with Explicitly Represented Primary Organics</u>						
CE01	CH4 + CL = HCL + MEO2	1.02e-13	7.30e-12	2.54		1
CE02	ETHENE + CL = #2 RO2C + xHO2 + xHCHO + CLCHO	1.04e-10	Falloff, F=0.60, N=1.00			2

Table A-5 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Refs & Notes [c]
		k(298)	A	Ea	B	
CE03	ISOPRENE + CL = #.15 HCL + #1.168 RO2C + #.085 RO2XC + #.085 zRNO3 + #.738 xHO2 + #.177 xCL + #.275 xHCHO + #.177 xMVK + #.671 xIPRD + #.067 xCLCCHO + yR6OOH + #.018 XC	4.80e-10				19
CE04	ACETYLEN + CL = HO2 + CO + XC	4.97e-11	Falloff, F=0.60, N=1.00			2,20
		0:	5.20e-30	0.00	-2.40	
		inf:	2.20e-10	0.00	0.00	

[a] Format of reaction listing: "=" separates reactants from products; "#*number*" indicates stoichiometric coefficient, "#*coefficient* {*product lis* }" means that the stoichiometric coefficient is applied to all the products listed.

[b] Except as indicated, the rate constants are given by $k(T) = A \cdot (T/300)^B \cdot e^{-Ea/RT}$, where the units of k and A are cm^3 $molec^{-1}$ s^{-1}, Ea are kcal mol^{-1}, T is ^oK, and R=0.0019872 kcal mol^{-1} deg^{-1}. The following special rate constant expressions are used:

Phot Set = *name*: The absorption cross sections and (if applicable) quantum yields for the photolysis reaction are given in Table A-6, where "*name*" indicates the photolysis set used. If a "qy=*number*" notation is given, the number given is the overall quantum yield, which is assumed to be wavelength independent.

Falloff: The rate constant as a function of temperature and pressure is calculated using $k(T,M) = \{k0(T)\cdot[M]/[1 + k0(T)\cdot[M]/kinf(T)]\}\cdot F^Z$, where $Z = \{1 + [\log10\{k0(T)\cdot[M])/kinf(T)\}/N]^2\}^{-1}$, [M] is the total pressure in molecules cm^{-3}, F and N are as indicated on the table, and the temperature dependences of k0 and kinf are as indicated on the table.

Same K as Rxn xx: Uses the same rate constant as the reaction in the base mechanism with the same label (see Table A-2)

[c] Footnotes documenting sources of rate constants and mechanisms are as follows.

1 Rate constant or absorption coefficients and quantum yields based on IUPAC (2006) recommendation. Mechanism is also as recommended unless indicated by other footnotes.

2 Rate constant or absorption coefficients and quantum yields based on NASA (2006) recommendation. Mechanism is also as recommended unless indicated by other footnotes.

3 Reaction is rapidly reversed and can be ignored.

4 IUPAC (2006) gives a recommendation for the total CL + HO_2 rate constant and for the temperature dependence of the rate constant ratio. Temperature-dependent parameters derived to give best fits to the recommended temperature dependence expression for the temperature range 270-330^{o}K.

5 No information could be found concerning the kinetics of this reaction. The temperature- and pressure-dependence expression for the rate constant was estimated from that for the reverse reaction and the equilibrium constant obtained from the thermochemical data given by NASA (2006) for 298^{o}K. The falloff parameters were derived by fitting the falloff expression to the rate constant derived from the rate constant calculated for the reverse reaction and the equilibrium constant as a function of temperature and pressure.

Table A-5 (continued)

6 This reaction is not important under most atmospheric conditions, but may be non-negligible under certain situations near Cl_2 emissions sources. The reaction can form either $Cl_2 + O_2$, Cl + ClOO, or Cl + OClO. To avoid introducing new species into the mechanism for this relatively unimportant reaction, OClO is represented by Cl. ClOO is also represented by Cl because it is expected to rapidly decompose to Cl. The rate expression for the total reaction is derived by fitting an Arrhenius expression to the sum of the temperature-dependent rate constants recommended by IUPAC (2006). The relative product yields are the IUPAC (2006) recommended values for 298K; the temperature dependence of the relative product yields is ignored.

7 The rate constant used for the reaction of Cl with propionaldehyde is the average of values listed by Le Crane et al (2005), who also obtained data indicating that abstraction from -CHO occurs ~88% of the time. The rest of the reaction is assumed to occur at the CH_2 group, resulting in ultimate formation of the corresponding alkoxy radical, which is estimated to decompose primarily to acetaldehyde and HCO (Carter, 2000a).

8 Mechanism estimated using the current mechanism generation system, with rates of initial reactions determined by estimated rates of Cl reactions at various positions. In most cases the reactions of the radicals formed are the same as derived for the SAPRC-99 mechanism generation system documented by Carter (2000a). The total rate constant also estimated, unless another footnote indicates otherwise.

9 Mechanism derived using the mechanism generation system based on the mixture of organic nitrate or higher ketone product compounds used to derive the other mechanistic parameters for the RNO3 or PROD2 model species.

10 Same rate constant as used for formaldehyde (for glyoxal) or acetaldehyde (for methyl glyoxal). Same mechanism as for OH reaction, except HCl formed.

11 Assumed to have same rate constant as used for toluene, which is average of values tabulated by Wang et al (2005). Mechanism based on assuming reaction only involves abstraction from CH_3.

12 Same rate constant as used for acetaldehyde. Reaction is assumed to proceed only by abstraction from -CHO.

13 Mechanism could not be generated completely. The mechanism estimation system was used to estimate the total rate constant and the HCL yield. The set of products formed in the OH reaction are used to approximate the reminder of the products radicals formed.

14 Mechanism derived for $HCOC(CH_3)=CHCH_2OH$, which is taken as representative of the compounds represented by this model species. 0.5 AFG1 + 0.5 AFG2 are used to represent the CH3-C(CHO)=CH-CHO product predicted to be formed.

15 This is used to represent alpha-chloro aldehydes, which need to be represented separately because of their significantly higher photolysis rates (see Carter and Malkina, 2007). Absorption cross-sections from NASA (2006), and are given in Table 5. Unit quantum yields assumed. See Carter and Malkina (2007) for a discussion of the mechanism.

16 Rate constants from Scollard et al (1993). Represented as forming same products as corresponding reaction of propionaldehyde.

17 Absorption cross-sections from NASA (2006) evaluation. Overall quantum yield of 0.5 assumed, based on quantum yields measured at 308 and 351 nm (NASA, 2006).

18 See footnotes in Table A-2 for a discussion of these xPROD operators.

Table A-5 (continued)

19 Rate constant is Atkinson (1997) recommendation. Mechanism derived using the mechanism generation system, with assignments for the formation and reactions of the initially formed radicals based on the mechanism of Fan and Zhang (2004). Note that if it is desired to represent CMBO and CMBA explicitly, the "IPRD" yield should be reduced to 0.272 and the CMBO and CMBA should be added with yields of 0.221 and 0.178, respectively. Their subsequent reactions can be approximated by the mechanism of IPRD.

20 Mechanism based on assuming that reaction involves formation of ClCH=CH· radicals, which react with O_2 to form HCO and ClCHO. The latter is assumed to be relatively unreactive and is not represented.

Table A-6. Absorption cross-sections and quantum yields for the all photolysis reactions added for the chlorine chemistry mechanism.

a) Phot set CL2: Chlorine absorption cross-sections.

wl	abs	wl	abs	wl	abs	wl	abs	wl	abs	wl	abs
280	2.60e-20	320	2.37e-19	360	1.32e-19	400	1.80e-20	440	5.40e-21	480	-
290	6.20e-20	330	2.55e-19	370	8.40e-20	410	1.30e-20	450	3.80e-21		
300	1.19e-19	340	2.35e-19	380	5.00e-20	420	9.60e-21	460	2.60e-21		
310	1.85e-19	350	1.88e-19	390	2.90e-20	430	7.30e-21	470	1.60e-21		

Wavelengths in nm and absorption cross-sections in cm^{-2}. IUPAC (2006) recommendation for absorption-cross sections. Unit quantum yield assumed.

b) Phot Set CLNO-06: ClNO absorption cross-sections.

wl	abs	wl	abs	wl	abs	wl	abs	wl	abs	wl	abs
280	1.06e-19	304	1.05e-19	328	1.46e-19	355	1.36e-19	415	3.38e-20	475	2.61e-20
282	1.02e-19	306	1.08e-19	330	1.47e-19	360	1.29e-19	420	2.89e-20	480	2.53e-20
284	9.99e-20	308	1.11e-19	332	1.49e-19	365	1.20e-19	425	2.45e-20	485	2.33e-20
286	9.84e-20	310	1.15e-19	334	1.51e-19	370	1.10e-19	430	2.21e-20	490	2.07e-20
288	9.71e-20	312	1.19e-19	336	1.53e-19	375	9.95e-20	435	2.20e-20	495	1.78e-20
290	9.64e-20	314	1.22e-19	338	1.53e-19	380	8.86e-20	440	2.20e-20	500	1.50e-20
292	9.63e-20	316	1.25e-19	340	1.52e-19	385	7.82e-20	445	2.07e-20	527	-
294	9.69e-20	318	1.30e-19	342	1.53e-19	390	6.86e-20	450	1.87e-20		
296	9.71e-20	320	1.34e-19	344	1.51e-19	395	5.97e-20	455	1.79e-20		
298	9.89e-20	322	1.36e-19	346	1.51e-19	400	5.13e-20	460	1.95e-20		
300	1.00e-19	324	1.40e-19	348	1.49e-19	405	4.40e-20	465	2.25e-20		
302	1.03e-19	326	1.43e-19	350	1.45e-19	410	3.83e-20	470	2.50e-20		

Wavelengths in nm and absorption cross-sections in cm^{-2}. IUPAC (2006) recommendation. Unit quantum yields assumed. Wavelength where absorption goes to zero estimated by extrapolation.

c) Phot set CLONO: ClONO absorption cross-sections.

wl	abs	wl	abs	wl	abs	wl	abs	wl	abs	wl	abs
280	1.32e-18	305	1.14e-18	330	5.87e-19	355	2.29e-19	380	4.10e-20	405	-
285	1.44e-18	310	1.05e-18	335	5.77e-19	360	1.61e-19	385	3.30e-20		
290	1.44e-18	315	9.81e-19	340	4.37e-19	365	1.13e-19	390	2.20e-20		
295	1.42e-18	320	8.03e-19	345	3.57e-19	370	9.00e-20	395	1.50e-20		
300	1.29e-18	325	7.54e-19	350	2.69e-19	375	6.90e-20	400	6.00e-21		

Wavelengths in nm and absorption cross-sections in cm^{-2}. IUPAC (2006) recommendation for absorption cross-sections. Unit quantum yield assumed.

Table A-6 (continued)

d) Phot set CLNO2: ClNO2 absorption cross-sections

wl	abs	wl	abs	wl	abs	wl	abs
280	2.20e-19	310	1.21e-19	340	3.54e-20	370	6.90e-21
290	1.73e-19	320	8.87e-20	350	2.04e-20	380	-
300	1.49e-19	330	5.84e-20	360	1.15e-20		

Wavelengths in nm and absorption cross-sections in cm^{-2}. IUPAC (2006) recommendation. Unit quantum yields assumed.

e) Phot Set CLONO2-1: ClONO2 + hv = CLO + NO2

wl	abs	qy	wl	abs	qy	wl	abs	qy	wl	abs	qy
280	1.19e-19	0.400	305	2.24e-20	0.400	330	4.66e-21	0.243	355	2.08e-21	0.064
285	8.80e-20	0.400	310	1.60e-20	0.386	335	3.67e-21	0.207	360	2.00e-21	0.029
290	6.41e-20	0.400	315	1.14e-20	0.350	340	3.02e-21	0.171	365	1.80e-21	0.000
295	4.38e-20	0.400	320	8.31e-21	0.314	345	2.58e-21	0.136			
300	3.13e-20	0.400	325	6.13e-21	0.279	350	2.29e-21	0.100			

Wavelengths in nm and absorption cross-sections in cm^{-2}. Absorption cross-sections and quantum yields recommended by IUPAC (2006).

f) Phot Set CLONO2-2: ClONO2 + hv = Cl + NO3

wl	abs	qy	wl	abs	qy	wl	abs	qy	wl	abs	qy
280	1.19e-19	0.600	320	8.31e-21	0.686	360	2.00e-21	0.971	400	6.40e-22	1.000
285	8.80e-20	0.600	325	6.13e-21	0.721	365	1.80e-21	1.000	405	5.40e-22	1.000
290	6.41e-20	0.600	330	4.66e-21	0.757	370	1.59e-21	1.000	410	4.40e-22	1.000
295	4.38e-20	0.600	335	3.67e-21	0.793	375	1.41e-21	1.000	415	3.60e-22	1.000
300	3.13e-20	0.600	340	3.02e-21	0.829	380	1.21e-21	1.000	420	3.20e-22	1.000
305	2.24e-20	0.600	345	2.58e-21	0.864	385	1.37e-21	1.000	425	2.30e-22	1.000
310	1.60e-20	0.614	350	2.29e-21	0.900	390	9.10e-22	1.000	430	1.90e-22	1.000
315	1.14e-20	0.650	355	2.08e-21	0.936	395	7.60e-22	1.000	435	-	1.000

Wavelengths in nm and absorption cross-sections in cm^{-2}. Absorption cross-sections and quantum yields recommended by IUPAC (2006).

g) Phot set HOCL-06: HOCl absorption cross-sections.

wl	abs	wl	abs	wl	abs	wl	abs	wl	abs	wl	abs
280	4.64e-20	304	6.12e-20	328	3.79e-20	352	1.33e-20	376	7.86e-21	400	2.88e-21
282	4.62e-20	306	6.12e-20	330	3.50e-20	354	1.24e-20	378	7.48e-21	402	2.54e-21
284	4.68e-20	308	6.07e-20	332	3.21e-20	356	1.17e-20	380	7.08e-21	404	2.22e-21
286	4.79e-20	310	5.97e-20	334	2.94e-20	358	1.11e-20	382	6.67e-21	406	1.94e-21
288	4.95e-20	312	5.84e-20	336	2.68e-20	360	1.06e-20	384	6.24e-21	408	1.68e-21
290	5.13e-20	314	5.66e-20	338	2.44e-20	362	1.02e-20	386	5.80e-21	410	1.44e-21
292	5.33e-20	316	5.45e-20	340	2.22e-20	364	9.85e-21	388	5.35e-21	412	1.24e-21
294	5.52e-20	318	5.21e-20	342	2.03e-20	366	9.51e-21	390	4.91e-21	414	1.05e-21
296	5.71e-20	320	4.95e-20	344	1.84e-20	368	9.19e-21	392	4.47e-21	416	8.90e-22
298	5.86e-20	322	4.67e-20	346	1.69e-20	370	8.88e-21	394	4.05e-21	418	7.50e-22
300	5.99e-20	324	4.38e-20	348	1.55e-20	372	8.55e-21	396	3.64e-21	420	6.30e-22

Table A-6 (continued)

302	6.08e-20	326	4.09e-20	350	1.43e-20	374	8.22e-21	398	3.25e-21	422	-

Wavelengths in nm and absorption cross-sections in cm^{-2}. IUPAC (2006) recommendation for absorption cross-sections. Unit quantum yields assumed.

h) Phot set CLCCHO: Chloroacetaldehyde absorption cross-sections.

wl	abs	wl	abs	wl	abs	wl	abs	wl	abs	wl	abs
280	3.99e-20	293	5.14e-20	306	5.48e-20	319	3.78e-20	332	1.68e-20	345	1.59e-21
281	4.23e-20	294	5.48e-20	307	5.34e-20	320	3.84e-20	333	1.42e-20	346	1.36e-21
282	4.09e-20	295	5.47e-20	308	5.44e-20	321	3.43e-20	334	1.36e-20	347	9.77e-22
283	4.15e-20	296	5.64e-20	309	5.37e-20	322	3.26e-20	335	1.06e-20	348	7.91e-22
284	4.31e-20	297	5.56e-20	310	5.03e-20	323	2.49e-20	336	7.47e-21	349	6.23e-22
285	4.55e-20	298	5.75e-20	311	4.61e-20	324	2.11e-20	337	6.22e-21	350	5.45e-22
286	4.64e-20	299	5.63e-20	312	3.92e-20	325	1.92e-20	338	5.02e-21	351	5.58e-22
287	4.80e-20	300	5.57e-20	313	3.71e-20	326	1.87e-20	339	4.11e-21	352	6.03e-22
288	4.99e-20	301	5.10e-20	314	3.73e-20	327	1.87e-20	340	3.40e-21	353	6.33e-22
289	5.03e-20	302	4.92e-20	315	3.96e-20	328	1.70e-20	341	2.81e-21	354	5.65e-22
290	5.20e-20	303	5.01e-20	316	3.85e-20	329	1.92e-20	342	2.47e-21	355	3.77e-22
291	4.95e-20	304	5.30e-20	317	4.16e-20	330	1.64e-20	343	2.13e-21	356	2.39e-22
292	4.94e-20	305	5.27e-20	318	3.84e-20	331	1.52e-20	344	1.90e-21	357	1.23e-22
										358	-

Wavelengths in nm and absorption cross-sections in cm^{-2}. Absorption cross-sections from NASA (2006) evaluation. Unit quantum yields assumed.

g) Phot set CLACET: Chloroacetone absorption cross-sections.

wl	abs	wl	abs	wl	abs	wl	abs	wl	abs	wl	abs
280	9.03e-20	294	1.01e-19	308	7.34e-20	322	3.04e-20	336	5.06e-21	350	4.58e-22
281	9.23e-20	295	1.00e-19	309	7.06e-20	323	2.80e-20	337	4.27e-21	351	4.11e-22
282	9.41e-20	296	9.89e-20	310	6.77e-20	324	2.58e-20	338	3.61e-21	352	3.28e-22
283	9.56e-20	297	9.77e-20	311	6.50e-20	325	2.37e-20	339	3.02e-21	353	3.19e-22
284	9.69e-20	298	9.66e-20	312	6.22e-20	326	2.16e-20	340	2.52e-21	354	2.20e-22
285	9.80e-20	299	9.54e-20	313	5.93e-20	327	1.95e-20	341	2.12e-21	355	1.93e-22
286	9.89e-20	300	9.41e-20	314	5.61e-20	328	1.73e-20	342	1.76e-21	356	1.38e-22
287	9.98e-20	301	9.25e-20	315	5.28e-20	329	1.52e-20	343	1.45e-21	357	1.34e-22
288	1.00e-19	302	9.04e-20	316	4.92e-20	330	1.33e-20	344	1.20e-21	358	9.17e-23
289	1.01e-19	303	8.80e-20	317	4.57e-20	331	1.14e-20	345	1.03e-21	359	1.55e-22
290	1.02e-19	304	8.53e-20	318	4.22e-20	332	9.79e-21	346	8.87e-22	360	1.28e-22
291	1.02e-19	305	8.24e-20	319	3.89e-20	333	8.32e-21	347	7.57e-22	365	-
292	1.02e-19	306	7.94e-20	320	3.58e-20	334	7.07e-21	348	6.42e-22		
293	1.02e-19	307	7.63e-20	321	3.30e-20	335	5.98e-21	349	5.47e-22		

Wavelengths in nm and absorption cross-sections in cm^{-2}. NASA (2006) recommendation for absorption cross-sections. Unit quantum yields assumed.

Table A-7. Listing of reactions and rate parameters used for the lumped model species in the fixed parameter version of the lumped SAPRC-07 mechanism.

Label	Reaction and Products [a]	Rate Parameters [b]			
		k(300)	A	Ea	B
Reactions Added to the Standard Base Mechanism					
BL01	ALK1 + OH = xHO2 + RO2C + xCCHO + yROOH	2.54E-13	1.34E-12	0.992	2.0
BL02	ALK2 + OH = #.965 xHO2 + #.965 RO2C + #.035 RO2XC + #.035 zRNO3 + #.261 xRCHO + #.704 xACET + yROOH + #-.105 XC	1.11E-12	1.49E-12	0.173	2.0
BL03	ALK3 + OH = #.695 xHO2 + #.236 xTBUO + #1.253 RO2C + #.07 RO2XC + #.07 zRNO3 + #.026 xHCHO + #.445 xCCHO + #.122 xRCHO + #.024 xACET + #.332 xMEK + #.983 yROOH + #.017 yR6OOH + #-.046 XC	2.31E-12	1.51E-12	-0.251	
BL04	ALK4 + OH = #.83 xHO2 + #.01 xMEO2 + #.011 xMECO3 + #1.763 RO2C + #.149 RO2XC + #.149 zRNO3 + #.002 xCO + #.029 xHCHO + #.438 xCCHO + #.236 xRCHO + #.426 xACET + #.106 xMEK + #.146 xPROD2 + yR6OOH + #-.119 XC	4.34E-12	3.75E-12	-0.088	
BL05	ALK5 + OH = #.647 xHO2 + #1.605 RO2C + #.353 RO2XC + #.353 zRNO3 + #.04 xHCHO + #.106 xCCHO + #.209 xRCHO + #.071 xACET + #.086 xMEK + #.407 xPROD2 + yR6OOH + #2.004 XC	9.40E-12	2.70E-12	-0.744	
BL06	OLE1 + OH = #.904 xHO2 + #.001 xMEO2 + #1.138 RO2C + #.095 RO2XC + #.095 zRNO3 + #.7 xHCHO + #.301 xCCHO + #.47 xRCHO + #.005 xACET + #.026 xMACR + #.008 xMVK + #.006 xIPRD + #.119 xPROD2 + #.413 yROOH + #.587 yR6OOH + #.822 XC	3.29E-11	6.18E-12	-0.996	
BL07	OLE1 + O3 = #.116 HO2 + #.04 xHO2 + #.193 OH + #.104 MEO2 + #.063 RO2C + #.004 RO2XC + #.004 zRNO3 + #.368 CO + #.125 CO2 + #.5 HCHO + #.147 CCHO + #.007 xCCHO + #.353 RCHO + #.031 xRCHO + #.002 xACET + #.006 MEK + #.185 HCOOH + #.022 CCOOH + #.112 RCOOH + #.189 PROD2 + #.007 yROOH + #.037 yR6OOH + #.69 XC	1.09E-17	3.15E-15	3.379	
BL08	OLE1 + NO3 = #.824 xHO2 + #1.312 RO2C + #.176 RO2XC + #.176 zRNO3 + #.009 xCCHO + #.002 xRCHO + #.024 xACET + #.546 xRNO3 + #.413 yROOH + #.587 yR6OOH + #.454 XN + #.572 XC	1.44E-14	4.73E-13	2.081	
BL09	OLE1 + O3P = #.45 RCHO + #.437 MEK + #.113 PROD2 + #1.224 XC	5.02E-12	1.49E-11	0.648	

Table A-7 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]			
		k(300)	A	Ea	B
BL10	OLE2 + OH = #.914 xHO2 + #.966 RO2C + #.086 RO2XC + #.086 zRNO3 + #.209 xHCHO + #.788 xCCHO + #.481 xRCHO + #.136 xACET + #.076 xMEK + #.027 xMACR + #.002 xMVK + #.037 xIPRD + #.022 xPROD2 + #.357 yROOH + #.643 yR6OOH + #.111 XC	6.42E-11	1.26E-11	-0.969	
BL11	OLE2 + O3 = #.093 HO2 + #.039 xHO2 + #.423 OH + #.29 MEO2 + #.147 xMECO3 + #.008 xRCO3 + #.2 RO2C + #.003 RO2XC + #.003 zRNO3 + #.297 CO + #.162 CO2 + #.152 HCHO + #.108 xHCHO + #.428 CCHO + #.067 xCCHO + #.315 RCHO + #.018 xRCHO + #.048 ACET + #.031 MEK + #.001 xMEK + #.033 HCOOH + #.061 CCOOH + #.222 RCOOH + #.028 MACR + #.021 MVK + #.042 PROD2 + #.069 yROOH + #.128 yR6OOH + #.125 XC	1.24E-16	8.14E-15	2.494	
BL12	OLE2 + NO3 = #.423 xHO2 + #.409 xNO2 + #.033 xMEO2 + #1.185 RO2C + #.136 RO2XC + #.136 zRNO3 + #.074 xHCHO + #.546 xCCHO + #.154 xRCHO + #.11 xACET + #.002 xMEK + #.026 xMVK + #.007 xIPRD + #.322 xRNO3 + #.357 yROOH + #.643 yR6OOH + #.269 XN + #.114 XC	7.85E-13	2.20E-13	-0.759	
BL13	OLE2 + O3P = #.014 HO2 + #.007 xHO2 + #.007 xMACO3 + #.013 RO2C + #.001 RO2XC + #.001 zRNO3 + #.006 xCO + #.074 RCHO + #.709 MEK + #.006 xMACR + #.202 PROD2 + #.014 yROOH + #.666 XC	2.07E-11	1.43E-11	-0.220	
BL14	ARO1 + OH = #.166 HO2 + #.482 xHO2 + #.284 OH + #.482 RO2C + #.068 RO2XC + #.068 zRNO3 + #.218 xGLY + #.138 xMGLY + #.166 CRES + #.049 xBALD + #.164 xAFG1 + #.193 xAFG2 + #.284 AFG3 + #.077 xPROD2 + #.403 yRAOOH + #.147 yR6OOH + #.002 XC	6.15E-12			
BL15	ARO2 + OH = #.108 HO2 + #.58 xHO2 + #.202 OH + #.58 RO2C + #.11 RO2XC + #.11 zRNO3 + #.116 xGLY + #.286 xMGLY + #.104 xBACL + #.108 CRES + #.039 xBALD + #.217 xAFG1 + #.21 xAFG2 + #.202 AFG3 + #.08 xAFG3 + #.035 xPROD2 + #.089 yR6OOH + #.601 yRAOOH + #1.486 XC	2.57E-11			

Table A-7 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]			
		k(300)	A	Ea	B
BL16	TERP + OH = #.759 xHO2 + #.042 xRCO3 + #1.147 RO2C + #.2 RO2XC + #.2 zRNO3 + #.001 xCO + #.264 xHCHO + #.533 xRCHO + #.036 xACET + #.005 xMEK + #.009 xMGLY + #.014 xBACL + #.002 xMVK + #.001 xIPRD + #.255 xPROD2 + yR6OOH + #5.056 XC	7.98E-11	1.87E-11	-0.864	
BL17	TERP + O3 = #.052 HO2 + #.067 xHO2 + #.585 OH + #.126 xMECO3 + #.149 xRCO3 + #.875 RO2C + #.203 RO2XC + #.203 zRNO3 + #.166 CO + #.019 xCO + #.045 CO2 + #.079 HCHO + #.15 xHCHO + #.22 xRCHO + #.165 xACET + #.004 MEK + #.107 HCOOH + #.043 RCOOH + #.001 xGLY + #.002 xMGLY + #.055 xBACL + #.001 xMACR + #.001 xIPRD + #.409 PROD2 + #.545 yR6OOH + #3.526 XC	6.99E-17	9.57E-16	1.560	
BL18	TERP + NO3 = #.162 xHO2 + #.421 xNO2 + #.019 xRCO3 + #1.509 RO2C + #.397 RO2XC + #.397 zRNO3 + #.01 xCO + #.017 xHCHO + #.001 xCCHO + #.509 xRCHO + #.175 xACET + #.001 xMGLY + #.003 xMACR + #.001 xMVK + #.002 xIPRD + #.163 xRNO3 + yR6OOH + #.416 XN + #4.473 XC	6.53E-12	1.28E-12	-0.974	
BL19	TERP + O3P = #.147 RCHO + #.853 PROD2 + #4.441 XC	3.71E-11			
<u>Reactions Added to the Base Mechanism with Chlorine Chemistry</u>					
BC01	ALK1 + CL = xHO2 + RO2C + HCL + xCCHO + yROOH	5.95E-11	8.30E-11	0.199	
BC02	ALK2 + CL = #.97 xHO2 + #.97 RO2C + #.03 RO2XC + #.03 zRNO3 + HCL + #.482 xRCHO + #.488 xACET + yROOH + #-.09 XC	1.37E-10	1.20E-10	-0.079	
BC03	ALK3 + CL = #.835 xHO2 + #.094 xTBUO + #1.361 RO2C + #.07 RO2XC + #.07 zRNO3 + HCL + #.078 xHCHO + #.34 xCCHO + #.343 xRCHO + #.075 xACET + #.253 xMEK + #.983 yROOH + #.017 yR6OOH + #.18 XC	1.86E-10			
BC04	ALK4 + CL = #.827 xHO2 + #.003 xMEO2 + #.004 xMECO3 + #1.737 RO2C + #.165 RO2XC + #.165 zRNO3 + HCL + #.003 xCO + #.034 xHCHO + #.287 xCCHO + #.412 xRCHO + #.247 xACET + #.076 xMEK + #.13 xPROD2 + yR6OOH + #.327 XC	2.63E-10			

Table A-7 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]			
		k(300)	A	Ea	B
BC05	ALK5 + CL = #.647 xHO2 + #1.541 RO2C + #.352 RO2XC + #.352 zRNO3 + HCL + #.022 xHCHO + #.08 xCCHO + #.258 xRCHO + #.044 xACET + #.041 xMEK + #.378 xPROD2 + yR6OOH + #2.368 XC	4.21E-10			
BC06	OLE1 + CL = #.902 xHO2 + #1.42 RO2C + #.098 RO2XC + #.098 zRNO3 + #.308 HCL + #.025 xHCHO + #.146 xCCHO + #.051 xRCHO + #.188 xMACR + #.014 xMVK + #.027 xIPRD + #.225 xCLCCHO + #.396 xCLACET + #.413 yROOH + #.587 yR6OOH + #1.361 XC	3.55E-10			
BC07	OLE2 + CL = #.447 xHO2 + #.448 xCL + #.001 xMEO2 + #1.514 RO2C + #.104 RO2XC + #.104 zRNO3 + #.263 HCL + #.228 xHCHO + #.361 xCCHO + #.3 xRCHO + #.081 xACET + #.04 xMEK + #.049 xMACR + #.055 xMVK + #.179 xIPRD + #.012 xCLCCHO + #.18 xCLACET + #.357 yROOH + #.643 yR6OOH + #.247 XC	3.83E-10			
BC08	ARO1 + CL = #.88 xHO2 + #.88 RO2C + #.12 RO2XC + #.12 zRNO3 + #.671 xBALD + #.21 xPROD2 + #.323 XC	1.00E-10			
BC09	ARO2 + CL = #.842 xHO2 + #.842 RO2C + #.158 RO2XC + #.158 zRNO3 + #.618 xBALD + #.224 xPROD2 + #2.382 XC	2.18E-10			
BC10	TERP + CL = #.252 xHO2 + #.068 xCL + #.034 xMECO3 + #.05 xRCO3 + #.016 xMACO3 + #2.258 RO2C + #.582 RO2XC + #.582 zRNO3 + #.548 HCL + #.035 xCO + #.158 xHCHO + #.185 xRCHO + #.274 xACET + #.007 xGLY + #.003 xBACL + #.003 xMVK + #.158 xIPRD + #.006 xAFG1 + #.006 xAFG2 + #.001 xAFG3 + #.109 xCLCCHO + yR6OOH + #3.543 XC	5.46E-10			

[a] Format of reaction listing: "=" separates reactants from products; "#*number*" indicates stoichiometric coefficient, "#*coefficient* {*product list*}" means that the stoichiometric coefficient is applied to all the products listed.

[b] The rate constants are given by $k(T) = A \cdot e^{-Ea/RT}$, where the units of k and A are cm^3 $molec^{-1}$ s^{-1}, Ea are kcal mol^{-1}, T is ^{o}K, and R=0.0019872 kcal mol^{-1} deg^{-1}.

APPENDIX B. MECHANISM AND REACTIVITY LISTINGS FOR INDIVIDUAL VOCS

This Appendix contains the tables documenting the mechanisms and giving the calculated atmospheric reactivity values and associated codes for the individual VOCs for which mechanistic assignments have been made. These tables are also available in electronic form in an Excel file, as discussed in Appendix D. Because of their size, Table B-2 , Table B-3, Table B-10, and Table B-11 are only available in this electronic format.

Table B-1. Listing of detailed model species, their representation in the model, and calculated atmospheric reactivity values in various reactivity scales

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
Alkanes											
methane	74-82-8	16.04	Exp	1		0	6	.0144	.0085	.0060	.0073±.0016
ethane	74-84-0	30.07	Exp	1	3	0	1	0.28	0.196	0.142	0.167±0.045
propane	74-98-6	44.10	Exp	1	3	0	1	0.49	0.34	0.25	0.29±0.07
cyclopropane	75-19-4	42.08	Exp	1		0	6	0.087	0.061	0.043	0.051±0.015
n-butane	106-97-8	58.12	Exp	1	2	0	1	1.15	0.76	0.52	0.64±0.17
isobutane	75-28-5	58.12	Exp	1	3	0	2	1.23	0.73	0.50	0.62±0.14
cyclobutane	287-23-0	56.11	Exp	1		0	6	1.20	0.80	0.54	0.66±0.22
n-pentane	109-66-0	72.15	Exp	1		0	6	1.31	0.88	0.56	0.70±0.21
branched C5 alkanes		72.15	LM			0	8	1.45	0.93	0.65	0.79±0.20
neopentane	463-82-1	72.15	Exp	1		0	6	0.67	0.39	0.26	0.33±0.08
isopentane	78-78-4	72.15	Exp	1		0	6	1.45	0.93	0.65	0.79±0.20
cyclopentane	287-92-3	70.13	AdjP	1		0	6	2.39	1.41	0.89	1.15±0.35
n-hexane	110-54-3	86.18	Exp	1	3	0	2	1.24	0.84	0.50	0.65±0.22
branched C6 alkanes		86.18	LM			0	8	1.31	0.83	0.55	0.68±0.18
2,2-dimethyl butane	75-83-2	86.18	Exp	1		0	6	1.17	0.71	0.46	0.58±0.16
2,3-dimethyl butane	79-29-8	86.18	Exp	1		0	6	0.97	0.65	0.44	0.54±0.13
2-methyl pentane	107-83-5	86.18	Exp	1		0	6	1.50	0.92	0.57	0.74±0.23
3-methyl pentane	96-14-0	86.18	Exp	1		0	6	1.80	1.11	0.73	0.92±0.26
C6 cycloalkanes		84.16	LM			0	8	1.25	0.82	0.47	0.63±0.22
cyclohexane	110-82-7	84.16	AdjP	1	2	0	2	1.25	0.82	0.47	0.63±0.22
isopropyl cyclopropane	3638-35-5	84.16	Exp	1		0	6	1.22	0.80	0.54	0.66±0.18
methyl cyclopentane	96-37-7	84.16	AdjP			0	7	2.19	1.23	0.73	0.98±0.33
Unspeciated C6 Alkanes		85.51	Mix			0	8	1.27	0.83	0.50	0.65±0.21
n-heptane	142-82-5	100.20	Exp	1		0	6	1.07	0.73	0.39	0.54±0.21
2,2,3-trimethyl butane	464-06-2	100.20	Exp	1		0	6	1.11	0.66	0.42	0.54±0.14
2,2-dimethyl pentane	590-35-2	100.20	Exp	1		0	6	1.12	0.68	0.41	0.54±0.17
2,3-dimethyl pentane	565-59-3	100.20	Exp			0	7	1.34	0.83	0.52	0.67±0.19
2,4-dimethyl pentane	108-08-7	100.20	Exp	1		0	6	1.55	0.90	0.55	0.72±0.22
2-methyl hexane	591-76-4	100.20	AdjP			0	7	1.19	0.76	0.42	0.58±0.21
3,3-dimethyl pentane	562-49-2	100.20	Exp			0	7	1.20	0.76	0.49	0.62±0.18
3-methyl hexane	589-34-4	100.20	Exp			0	7	1.61	0.96	0.57	0.76±0.26
3-ethyl pentane	617-78-7	100.20	Exp			0	7	1.90	1.11	0.69	0.90±0.27
branched C7 alkanes		100.20	LM			0	8	1.48	0.88	0.52	0.69±0.22
1,1-dimethyl cyclopentane	1638-26-2	98.19	AdjP			0	7	1.08	0.66	0.35	0.49±0.19
1,2-dimethyl cyclopentane	2452-99-5	98.19	AdjP			0	7	1.99	1.10	0.61	0.85±0.31
C7 cycloalkanes		98.19	LM			0	7	1.70	1.00	0.53	0.75±0.29
1,3-dimethyl cyclopentane	2453-00-1	98.19	AdjP			0	7	1.94	1.06	0.58	0.82±0.30
cycloheptane	291-64-5	98.19	AdjP	1		0	6	1.96	1.11	0.61	0.85±0.32
ethyl cyclopentane	1640-89-7	98.19	AdjP			0	7	2.01	1.13	0.63	0.87±0.33
methyl cyclohexane	108-87-2	98.19	AdjP	1		0	6	1.70	1.00	0.53	0.75±0.29
Unspeciated C7 Alkanes		99.53	Mix			0	8	1.41	0.87	0.48	0.66±0.24
n-octane	111-65-9	114.23	Exp	1	1	0	2	0.90	0.61	0.29	0.43±0.19
branched C8 alkanes		114.23	LM			0	8	1.45	0.86	0.46	0.64±0.24
2,2,3,3-tetramethyl butane	594-82-1	114.23	Exp	1		0	6	0.33	0.20	0.113	0.154±0.052
2,2,4-trimethyl pentane	540-84-1	114.23	Exp	1	3	0	2	1.26	0.71	0.44	0.57±0.17

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
2,2-dimethyl hexane	590-73-8	114.23	Exp	1		0	6	1.02	0.61	0.33	0.46±0.17
2,3,4-trimethyl pentane	565-75-3	114.23	Exp	1		0	6	1.03	0.65	0.39	0.51±0.16
2,3-dimethyl hexane	584-94-1	114.23	Exp			0	7	1.19	0.75	0.42	0.57±0.20
2,4-dimethyl hexane	589-43-5	114.23	Exp			0	7	1.73	0.98	0.54	0.75±0.27
2,5-dimethyl hexane	592-13-2	114.23	Exp			0	7	1.46	0.86	0.47	0.65±0.24
2-methyl heptane	592-27-8	114.23	Exp			0	7	1.07	0.69	0.35	0.50±0.21
3-methyl heptane	589-81-1	114.23	Exp			0	7	1.24	0.78	0.41	0.58±0.23
4-methyl heptane	589-53-7	114.23	Exp			0	7	1.25	0.76	0.40	0.57±0.23
2,3,3-trimethyl pentane	560-21-4	114.23	Exp			0	7	1.02	0.65	0.41	0.52±0.15
3,3-dimethyl hexane	563-16-6	114.23	Exp			0	7	1.24	0.75	0.43	0.58±0.20
2,2,3-trimethyl pentane	564-02-3	114.23	Exp			0	7	1.22	0.71	0.42	0.56±0.17
3,4-dimethyl hexane	583-48-2	114.23	Exp			0	7	1.51	0.91	0.54	0.71±0.23
3-ethyl 2-methyl pentane	609-26-7	114.23	Exp			0	7	1.33	0.79	0.46	0.62±0.21
C8 bicycloalkanes		110.20	LM			0	8	1.51	0.89	0.48	0.67±0.26
1,1,2-trimethyl cyclopentane	4259-00-1	112.21	Exp			0	7	1.12	0.65	0.33	0.48±0.20
1,1,3-trimethyl cyclopentane	4516-69-2	112.21	Exp			0	7	1.01	0.60	0.29	0.43±0.19
1,1-dimethyl cyclohexane	590-66-9	112.21	Exp			0	7	1.22	0.73	0.37	0.53±0.22
1,2,3-trimethyl cyclopentane		112.21	Exp			0	7	1.63	0.93	0.49	0.70±0.27
1,2,4-trimethyl cyclopentane		112.21	Exp			0	7	1.53	0.85	0.43	0.63±0.26
1-methyl-3-ethyl cyclopentane		112.21	AdjP			0	7	1.64	0.92	0.47	0.68±0.29
1,2-dimethyl cyclohexane	583-57-3	112.21	AdjP			0	7	1.41	0.87	0.43	0.63±0.28
1,4-dimethyl cyclohexane	589-90-2	112.21	AdjP			0	7	1.62	0.91	0.45	0.67±0.29
C8 cycloalkanes		112.21	LM			0	8	1.47	0.87	0.45	0.65±0.26
1,3-dimethyl cyclohexane	591-21-9	112.21	AdjP			0	7	1.52	0.86	0.41	0.62±0.28
cyclooctane	292-64-8	112.21	AdjP	1		0	6	1.46	0.84	0.41	0.61±0.28
ethyl cyclohexane	1678-91-7	112.21	Exp			0	7	1.47	0.87	0.45	0.65±0.26
propyl cyclopentane	2040-96-2	112.21	AdjP			0	7	1.69	0.94	0.48	0.70±0.30
Unspeciated C8 Alkanes		113.56	Mix			0	8	1.27	0.78	0.40	0.57±0.23
n-nonane	111-84-2	128.26	Exp	1		0,+	6 b	0.78	0.53	0.23	0.36±0.18
branched C9 alkanes		128.26	LM			0	8 b	1.14	0.69	0.33	0.49±0.22
2,2,5-trimethyl hexane	3522-94-9	128.26	Exp			0	7 b	1.13	0.65	0.36	0.50±0.18
2,3,5-trimethyl hexane	1069-53-0	128.26	AdjP	1		0	6 b	1.22	0.73	0.39	0.55±0.20
2,4-dimethyl heptane	2213-23-2	128.26	Exp			0	7 b	1.38	0.79	0.39	0.58±0.25
2-methyl octane	3221-61-2	128.26	Exp	1		0,+	6 b	0.83	0.55	0.24	0.38±0.19
3,3-diethyl pentane	1067-20-5	128.26	Exp	1		0,+	6 b	1.21	0.74	0.44	0.58±0.20
3,5-dimethyl heptane	926-82-9	128.26	Exp			0	7 b	1.56	0.92	0.48	0.69±0.28
4-ethyl heptane	2216-32-2	128.26	Exp			0	7 b	1.22	0.74	0.37	0.54±0.23
4-methyl octane	2216-34-4	128.26	Exp	1		0,+	6 b	0.95	0.62	0.29	0.43±0.20
2,4,4-trimethyl hexane	16747-30-1	128.26	Exp			0	7 b	1.34	0.76	0.42	0.58±0.21
3,3-dimethyl heptane	4032-86-4	128.26	Exp			0	7 b	1.13	0.69	0.37	0.52±0.20
4,4-dimethyl heptane	1068-19-5	128.26	Exp			0	7 b	1.27	0.73	0.39	0.55±0.22
2,2-dimethyl heptane	1071-26-7	128.26	Exp			0	7 b	1.00	0.59	0.30	0.44±0.18
2,2,4-trimethyl hexane	16747-26-5	128.26	Exp			0	7 b	1.26	0.71	0.36	0.53±0.21
2,6-dimethyl heptane	1072-05-5	128.26	Exp			0	7 b	1.04	0.63	0.31	0.46±0.20
2,3-dimethyl heptane	3074-71-3	128.26	Exp			0	7 b	1.09	0.69	0.35	0.50±0.21
2,5-dimethyl heptane	2216-30-0	128.26	Exp			0	7 b	1.35	0.82	0.43	0.61±0.24
3-methyl octane	2216-33-3	128.26	Exp			0	7 b	0.99	0.63	0.30	0.45±0.20
3,4-dimethyl heptane	922-28-1	128.26	Exp			0	7 b	1.24	0.76	0.41	0.57±0.22
3-ethyl heptane	15869-80-4	128.26	Exp			0	7 b	1.10	0.68	0.33	0.49±0.22

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
cis-hydrindane; bicyclo[4.3.0]nonane	496-10-6	124.22	AdjP			0	7 b	1.31	0.76	0.32	0.52±0.28
C9 bicycloalkanes		124.22	LM			0	8 b	1.39	0.80	0.39	0.58±0.26
1,2,3-trimethyl cyclohexane	1678-97-3	126.24	AdjP			0	7 b	1.22	0.75	0.33	0.52±0.26
1,3,5-trimethyl cyclohexane	1839-63-0	126.24	Exp			0	7 b	1.15	0.66	0.28	0.46±0.24
1,1,3-trimethyl cyclohexane	3073-66-3	126.24	Exp	1		0	6 b	1.19	0.68	0.31	0.48±0.23
1-ethyl-4-methyl cyclohexane	3728-56-1	126.24	AdjP			0	7 b	1.44	0.82	0.38	0.59±0.28
propyl cyclohexane	1678-92-8	126.24	Exp			0	7 b	1.29	0.76	0.38	0.55±0.24
C9 cycloalkanes		126.24	LM			0	8 b	1.36	0.79	0.38	0.57±0.26
Unspeciated C9 Alkanes		127.59	Mix			0	8	1.09	0.67	0.31	0.47±0.22
n-decane	124-18-5	142.28	Exp	1		0,+	6 b	0.68	0.47	0.184	0.30±0.17
branched C10 alkanes		142.28	LM			0	8 b	0.94	0.58	0.26	0.40±0.20
2,4,6-trimethyl heptane	2613-61-8	142.28	Exp			0	7 b	1.28	0.72	0.34	0.52±0.23
2,4-dimethyl octane	4032-94-4	142.28	Exp			0	7 b	1.03	0.62	0.28	0.44±0.21
2,6-dimethyl octane	2051-30-1	142.28	Exp	1	2	0,+	2 b	1.08	0.64	0.31	0.46±0.21
2-methyl nonane	871-83-0	142.28	Exp	1	2	0,+	2 b	0.73	0.49	0.195	0.32±0.18
3,4-diethyl hexane	19398-77-7	142.28	Exp	1	2	0,+	2 b	0.89	0.55	0.28	0.40±0.17
3-methyl nonane	5911-04-6	142.28	Exp			0	7 b	0.75	0.50	0.20	0.33±0.18
4-methyl nonane	17301-94-9	142.28	Exp			0	7 b	0.86	0.55	0.24	0.38±0.19
4-propyl heptane	3178-29-8	142.28	Exp			0	7 b	1.02	0.62	0.29	0.44±0.21
2,4,4-trimethyl heptane		142.28	Exp			0	7 b	1.31	0.72	0.37	0.54±0.22
2,5,5-trimethyl heptane		142.28	Exp			0	7 b	1.25	0.72	0.38	0.54±0.21
3,3-dimethyl octane	4110-44-5	142.28	Exp			0	7 b	1.09	0.65	0.33	0.48±0.20
4,4-dimethyl octane	15869-95-1	142.28	Exp			0	7 b	1.14	0.67	0.33	0.49±0.21
2,2-dimethyl octane	15869-87-1	142.28	Exp			0	7 b	0.83	0.50	0.23	0.35±0.16
2,2,4-trimethyl heptane	14720-74-2	142.28	Exp			0	7 b	1.16	0.64	0.31	0.47±0.20
2,2,5-trimethyl heptane		142.28	Exp			0	7 b	1.26	0.72	0.39	0.55±0.20
2,3,6-trimethyl heptane	4032-93-3	142.28	AdjP			0	7 b	0.90	0.58	0.27	0.40±0.19
2,3-dimethyl octane	7146-60-3	142.28	Exp			0	7 b	0.86	0.56	0.26	0.39±0.19
2,5-dimethyl octane		142.28	Exp			0	7 b	1.03	0.63	0.29	0.44±0.22
2-methyl-3-ethyl heptane	14676-29-0	142.28	Exp			0	7 b	0.99	0.62	0.30	0.44±0.20
4-ethyl octane	15869-86-0	142.28	AdjP			0	7 b	0.79	0.53	0.20	0.34±0.21
C10 bicycloalkanes		138.25	LM			0	8 b	1.09	0.65	0.30	0.46±0.22
isobutyl cyclohexane; (2-methylpropyl) cyclohexane	1678-98-4	140.27	LM			0	8 b	0.99	0.61	0.28	0.43±0.21
sec-butyl cyclohexane	7058-01-7	140.27	LM			0	8 b	0.99	0.61	0.28	0.43±0.21
C10 cycloalkanes		140.27	LM			0	8 b	1.07	0.65	0.30	0.46±0.22
1,3-diethyl cyclohexane	1678-99-5	140.27	AdjP			0	7 b	1.26	0.74	0.34	0.52±0.25
1,4-diethyl cyclohexane	1679-00-1	140.27	Exp			0	7 b	1.23	0.71	0.33	0.50±0.24
1-methyl-3-isopropyl cyclohexane	16580-24-8	140.27	Exp			0	7 b	1.00	0.62	0.29	0.43±0.21
butyl cyclohexane	1678-93-9	140.27	Exp	1		0	6 b	0.99	0.61	0.28	0.43±0.21
unspeciated C10 alkanes		141.61	Mix			0	8	0.90	0.56	0.25	0.39±0.20
n-undecane	1120-21-4	156.31	Exp	1		0,+	6 b	0.61	0.42	0.157	0.27±0.16
branched C11 alkanes		156.31	LM			0	8 b	0.73	0.47	0.188	0.31±0.18
2,3,4,6-tetramethyl heptane	61868-54-0	156.31	Exp			0	7 b	1.11	0.67	0.33	0.48±0.21
2,6-dimethyl nonane	17302-28-2	156.31	Exp			0	7 b	0.79	0.50	0.21	0.33±0.18
3,5-diethyl heptane	61869-02-1	156.31	Exp			0	7 b	1.11	0.66	0.30	0.46±0.23
3-methyl decane	13151-34-3	156.31	Exp			0	7 b	0.65	0.44	0.163	0.28±0.17

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
4-methyl decane	2847-72-5	156.31	Exp			0	7 b	0.68	0.45	0.174	0.29±0.17
C11 bicycloalkanes		152.28	LM			0	8 b	0.91	0.56	0.24	0.38±0.21
C11 cycloalkanes		154.29	LM			0	8 b	0.90	0.56	0.23	0.38±0.21
1,3-diethyl-5-methyl cyclohexane	164259-42-1	154.29	Exp			0	7 b	1.04	0.61	0.26	0.42±0.22
1-ethyl-2-propyl cyclohexane	62238-33-9	154.29	AdjP			0	7 b	0.81	0.53	0.21	0.35±0.21
pentyl cyclohexane	4292-92-6	154.29	Exp			0	7 b	0.84	0.53	0.23	0.36±0.19
unspeciated C11 alkanes		155.64	Mix			0	8	0.74	0.48	0.193	0.32±0.18
n-dodecane	112-40-3	170.33	Exp	1	2	0,+	3 b	0.55	0.38	0.139	0.24±0.15
branched C12 alkanes		170.33	LM			0	8 b	0.63	0.43	0.141	0.26±0.18
2,3,5,7-tetramethyl octane	62199-32-0	170.33	Exp			0	7 b	0.91	0.55	0.23	0.38±0.20
2,6-diethyl octane	62183-94-2	170.33	Exp			0	7 b	0.97	0.59	0.27	0.42±0.20
3,6-dimethyl decane	17312-53-7	170.33	AdjP			0	7 b	0.70	0.47	0.156	0.29±0.19
3-methyl undecane	1002-43-3	170.33	Exp			0	7 b	0.59	0.40	0.145	0.25±0.16
5-methyl undecane	1632-70-8	170.33	AdjP			0	7 b	0.55	0.39	0.105	0.22±0.18
C12 tricycloalkanes		164.29	LM			0	8 b	0.82	0.51	0.196	0.33±0.20
C12 bicycloalkanes		166.30	LM			0	8 b	0.81	0.50	0.194	0.33±0.20
C12 cycloalkanes		168.32	LM			0	8 b	0.80	0.49	0.192	0.32±0.19
1,3,5-triethyl cyclohexane	164259-43-2	168.32	Exp			0	7 b	1.02	0.59	0.27	0.42±0.21
1-methyl-4-pentyl cyclohexane	75736-67-3	168.32	Exp			0	7 b	0.72	0.46	0.177	0.30±0.18
hexyl cyclohexane	4292-75-5	168.32	AdjP	1	2	0	2 b	0.65	0.43	0.133	0.26±0.19
unspeciated C12 alkanes		169.66	Mix			0	8	0.66	0.44	0.157	0.28±0.18
n-tridecane	629-50-5	184.36	Exp	1		0,+	6 b	0.53	0.37	0.133	0.23±0.15
branched C13 alkanes		184.36	LM			0	8 b	0.60	0.40	0.140	0.25±0.16
2,3,6-trimethyl 4-isopropyl heptane		184.36	Exp			0	7 b	0.93	0.55	0.25	0.39±0.19
2,4,6,8-tetramethyl nonane	14638-54-1	184.36	AdjP			0	7 b	0.76	0.47	0.170	0.30±0.19
3,6-dimethyl undecane	17301-28-9	184.36	Exp			0	7 b	0.69	0.44	0.175	0.29±0.17
3,7-diethyl nonane		184.36	Exp			0	7 b	0.89	0.52	0.23	0.37±0.19
3-methyl dodecane	17312-57-1	184.36	Exp			0	7 b	0.54	0.37	0.134	0.24±0.15
5-methyl dodecane	17453-93-9	184.36	AdjP			0	7 b	0.47	0.34	0.079	0.188±0.168
C13 tricycloalkanes		178.31	LM			0	8 b	0.71	0.46	0.173	0.30±0.18
C13 bicycloalkanes		180.33	LM			0	8 b	0.70	0.45	0.171	0.29±0.18
C13 cycloalkanes		182.35	LM			0	8 b	0.70	0.45	0.170	0.29±0.18
1,3-diethyl-5-propyl cyclohexane		182.35	Exp			0	7 b	0.96	0.56	0.25	0.39±0.20
1-methyl-2-hexyl cyclohexane	92031-93-1	182.35	Exp			0	7 b	0.58	0.40	0.144	0.25±0.17
heptyl cyclohexane	5617-41-4	182.35	AdjP			0	7 b	0.55	0.38	0.113	0.23±0.18
unspeciated C13 alkanes		183.69	Mix			0	8	0.61	0.40	0.148	0.26±0.16
n-tetradecane	629-59-4	198.39	Exp	1	2	0,+	3 b	0.51	0.36	0.133	0.23±0.14
branched C14 alkanes		198.39	LM			0	8 b	0.55	0.37	0.130	0.23±0.15
2,4,5,6,8-pentamethyl nonane		198.39	Exp			0	7 b	0.95	0.59	0.26	0.41±0.21
2-methyl 3,5-diisopropyl heptane		198.39	AdjP			0	7 b	0.56	0.37	0.123	0.23±0.16
3,7-dimethyl dodecane	82144-67-0	198.39	Exp			0	7 b	0.62	0.40	0.158	0.26±0.16
3,8-diethyl decane	6224-52-8	198.39	AdjP			0	7 b	0.60	0.40	0.136	0.25±0.17
3-methyl tridecane	6418-41-3	198.39	Exp			0	7 b	0.51	0.35	0.126	0.22±0.14
6-methyl tridecane	13287-21-3	198.39	AdjP			0	7 b	0.46	0.33	0.079	0.183±0.162
C14 tricycloalkanes		192.34	LM			0	8 b	0.66	0.42	0.161	0.27±0.17

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
C14 bicycloalkanes		194.36	LM			0	8 b	0.66	0.42	0.159	0.27±0.17
C14 cycloalkanes		196.37	LM			0	8 b	0.65	0.41	0.157	0.27±0.17
1,3-dipropyl-5-ethyl cyclohexane		196.37	Exp			0	7 b	0.91	0.53	0.24	0.37±0.19
trans-1-methyl-4-heptyl cyclohexane	205324-73-8	196.37	Exp			0	7 b	0.53	0.36	0.125	0.22±0.16
octyl cyclohexane	1795-15-9	196.37	AdjP		2	0	7 b	0.51	0.36	0.106	0.21±0.17
unspeciated C14 alkanes		197.72	Mix			0	8	0.57	0.38	0.140	0.24±0.16
n-pentadecane	629-62-9	212.41	Exp	1	4	0,+	3 b	0.50	0.34	0.133	0.22±0.14
branched C15 alkanes		212.41	LM			0	8 b	0.50	0.34	0.119	0.21±0.15
2,6,8-trimethyl 4-isopropyl nonane		212.41	Exp			0	7 b	0.63	0.40	0.154	0.26±0.16
3,7-dimethyl tridecane		212.41	Exp			0	7 b	0.55	0.37	0.140	0.24±0.15
3,9-diethyl undecane	13286-72-1	212.41	Exp			0	7 b	0.51	0.35	0.128	0.22±0.14
3-methyl tetradecane	18435-22-8	212.41	Exp			0	7 b	0.48	0.33	0.122	0.21±0.14
6-methyl tetradecane	26730-16-5	212.41	AdjP			0	7 b	0.42	0.31	0.072	0.169±0.153
C15 tricycloalkanes		206.37	LM			0	8 b	0.63	0.40	0.154	0.26±0.16
C15 bicycloalkanes		208.38	LM			0	8 b	0.62	0.40	0.152	0.26±0.16
C15 cycloalkanes		210.40	LM			0	8 b	0.61	0.39	0.151	0.26±0.16
1,3,5-tripropyl cyclohexane		210.40	Exp			0	7 b	0.87	0.50	0.23	0.36±0.18
1-methyl-2-octyl cyclohexane		210.40	AdjP			0	7 b	0.50	0.35	0.127	0.22±0.15
nonyl cyclohexane	2883-02-5	210.40	AdjP			0	7 b	0.47	0.33	0.093	0.193±0.157
1,3-diethyl-5-pentyl cyclohexane		210.40	Exp			0	7 b	0.66	0.41	0.159	0.27±0.16
unspeciated C15 alkanes		211.74	Mix			0	8	0.54	0.36	0.134	0.23±0.15
n-C16	544-76-3	226.44	AdjP	1	3	0,+	3 b	0.45	0.32	0.104	0.194±0.144
branched C16 alkanes		226.44	LM			0	8 b	0.47	0.33	0.120	0.21±0.13
2,7-dimethyl 3,5-diisopropyl heptane		226.44	AdjP			0	7 b	0.52	0.35	0.114	0.22±0.16
3-methyl pentadecane	2882-96-4	226.44	Exp			0	7 b	0.46	0.32	0.118	0.20±0.13
4,8-dimethyl tetradecane	175032-36-7	226.44	Exp			0	7 b	0.49	0.33	0.124	0.21±0.14
7-methyl pentadecane	6165-40-8	226.44	Exp			0	7 b	0.45	0.32	0.117	0.20±0.13
C16 tricycloalkanes		220.39	LM			0	8 b	0.59	0.37	0.144	0.24±0.15
C16 bicycloalkanes		222.41	LM			0	8 b	0.58	0.37	0.143	0.24±0.15
C16 cycloalkanes		224.43	LM			0	8 b	0.55	0.36	0.135	0.23±0.15
1,3-propyl-5-butyl cyclohexane		224.43	Exp			0	7 b	0.75	0.45	0.20	0.31±0.16
1-methyl-4-nonyl cyclohexane	39762-40-8	224.43	Exp			0	7 b	0.46	0.32	0.115	0.20±0.14
decyl cyclohexane	1795-16-0	224.43	AdjP			0	7 b	0.43	0.31	0.087	0.180±0.149
unspeciated C16 alkanes		225.77	Mix			0	8	0.49	0.34	0.120	0.21±0.14
n-C17	629-78-7	240.47	LM			0,+	7 b	0.42	0.30	0.098	0.183±0.136
branched C17 alkanes		240.47	LM			0	8 b	0.44	0.31	0.113	0.194±0.126
C17 tricycloalkanes		234.42	LM			0	8 b	0.55	0.35	0.135	0.23±0.14
C17 bicycloalkanes		236.44	LM			0	8 b	0.55	0.35	0.134	0.23±0.14
C17 cycloalkanes		238.45	LM			0	8 b	0.52	0.34	0.127	0.22±0.14
unspeciated C17 alkanes		239.80	Mix			0	8	0.46	0.32	0.113	0.198±0.134
n-C18	593-45-3	254.49	LM			0,+	7 b	0.40	0.29	0.093	0.173±0.129
branched C18 alkanes		254.49	LM			0	8 b	0.42	0.29	0.107	0.184±0.119
C18 tricycloalkanes		248.45	LM			0	8 b	0.52	0.33	0.128	0.22±0.14
C18 bicycloalkanes		250.46	LM			0	8 b	0.52	0.33	0.127	0.21±0.13

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
C18 cycloalkanes		252.48	LM			0	8 b	0.49	0.32	0.120	0.21±0.13
unspeciated C18 alkanes		253.82	Mix			0	8	0.44	0.30	0.107	0.187±0.127
n-C19	629-92-5	268.52	LM			0,+	7 b	0.38	0.27	0.088	0.164±0.122
branched C19 alkanes		268.52	LM			0	8 b	0.40	0.27	0.102	0.174±0.113
C19 tricycloalkanes		262.47	LM			0	8 b	0.49	0.31	0.121	0.20±0.13
C19 bicycloalkanes		264.49	LM			0	8 b	0.49	0.31	0.120	0.20±0.13
C19 cycloalkanes		266.51	LM			0	8 b	0.46	0.30	0.113	0.194±0.126
n-C20	112-95-8	282.55	LM			0,+	7 b	0.36	0.26	0.084	0.156±0.116
branched C20 alkanes		282.55	LM			0	8 b	0.38	0.26	0.097	0.165±0.108
C20 tricycloalkanes		276.50	LM			0	8 b	0.47	0.30	0.115	0.194±0.121
C20 bicycloalkanes		278.52	LM			0	8 b	0.46	0.30	0.114	0.193±0.121
C20 cycloalkanes		280.53	LM			0	8 b	0.44	0.29	0.108	0.185±0.119
n-C21	629-94-7	296.57	LM			0,+	7 b	0.34	0.25	0.080	0.148±0.110
branched C21 alkanes		296.57	LM			0	8 b	0.36	0.25	0.092	0.158±0.103
C21 tricycloalkanes		290.53	LM			0	8 b	0.44	0.28	0.109	0.185±0.116
C21 bicycloalkanes		292.54	LM			0	8 b	0.44	0.28	0.108	0.184±0.115
C21 cycloalkanes		294.56	LM			0	8 b	0.42	0.27	0.103	0.176±0.114
n-C22	629-97-0	310.60	LM			0,+	7 b	0.33	0.23	0.076	0.142±0.105
branched C22 alkanes		310.60	LM			0	8 b	0.34	0.24	0.088	0.151±0.098
C22 tricycloalkanes		304.55	LM			0	8 b	0.42	0.27	0.104	0.177±0.110
C22 bicycloalkanes		306.57	LM			0	8 b	0.42	0.27	0.103	0.175±0.110
C22 cycloalkanes		308.58	LM			0	8 b	0.40	0.26	0.098	0.168±0.108
			Alkenes								
ethene	74-85-1	28.05	Exp	1	1	0	3 d	9.00	3.64	2.21	3.11±1.08
propene	115-07-1	42.08	Exp	1	1	0	3 d	11.66	4.44	2.73	3.85±1.38
1,2-propadiene (allene)	463-49-0	40.06	Exp	1		0	11	8.45	3.99	2.53	3.36±1.01
1-butene	106-98-9	56.11	Exp	1	3	0	3 d	9.73	3.82	2.37	3.30±1.13
C4 terminal alkenes		56.11	LM			0	7	9.73	3.82	2.37	3.30±1.13
isobutene	115-11-7	56.11	Exp	1	3	0	3	6.29	2.16	1.18	1.83±0.83
cis-2-butene	590-18-1	56.11	Exp	1		0	6	14.24	5.08	3.08	4.45±1.78
trans-2-butene	624-64-6	56.11	Exp	1	1	0	3	15.16	5.30	3.16	4.63±1.93
C4 internal alkenes		56.11	LM			0	7	14.70	5.19	3.12	4.54±1.85
1,2-butadiene	590-19-2	54.09	Exp	1		0	11	9.35	4.02	2.53	3.43±1.08
1,3-butadiene	106-99-0	54.09	Exp	1		0	6	12.61	4.71	2.88	4.07±1.46
C4 alkenes		56.11	LM			0	8	12.22	4.51	2.74	3.92±1.48
1-pentene	109-67-1	70.13	Exp	1		0	6 d	7.21	2.88	1.78	2.47±0.84
3-methyl-1-butene	563-45-1	70.13	Exp	1		0	6 d	6.99	2.81	1.74	2.41±0.81
C5 terminal alkenes		70.13	LM			0	7	7.21	2.88	1.78	2.47±0.84
2-methyl-1-butene	563-46-2	70.13	Exp	1		0	8	6.40	2.30	1.31	1.96±0.81
2-methyl-2-butene	513-35-9	70.13	Exp	1		0	6	14.08	4.57	2.57	3.99±1.96
cis-2-pentene	627-20-3	70.13	Exp	1		0	6	10.38	3.94	2.45	3.44±1.22
trans-2-pentene	646-04-8	70.13	Exp	1		0	6	10.56	3.97	2.45	3.46±1.25
2-pentenes		70.13	LM			0	7	10.47	3.95	2.45	3.45±1.24
C5 internal alkenes		70.13	LM			0	7	10.47	3.95	2.45	3.45±1.24
cyclopentene	142-29-0	68.12	Exp	1		0	8	6.77	2.53	1.55	2.20±0.80
trans-1,3-pentadiene	2004-70-8	68.12	Exp			0	8	12.50	4.76	2.95	4.12±1.43
cis-1,3-pentadiene	1574-41-0	68.12	LM			0	8	12.50	4.76	2.95	4.12±1.43
1,4-pentadiene	591-93-5	68.12	Exp	1		0	8	9.24	3.73	2.40	3.25±1.03

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
1,2-pentadiene	591-95-7	68.12	Exp	1		0	11	7.86	3.23	2.00	2.76±0.90
3-methyl-1,2-butadiene	598-25-4	68.12	Exp	1		0	11	10.29	3.98	2.44	3.43±1.18
isoprene (2-methyl-1,3-butadiene)	78-79-5	68.12	Exp	1	2	0	1	10.61	3.92	2.35	3.37±1.25
cyclopentadiene	542-92-7	66.10	LM			0	8	6.98	2.61	1.59	2.27±0.82
C5 alkenes		70.13	LM			0	8	8.84	3.42	2.11	2.96±1.04
1-hexene	592-41-6	84.16	Exp	1	4	0	4 d	5.49	2.33	1.45	1.98±0.65
3,3-dimethyl-1-butene	558-37-2	84.16	Exp	1		0	8 d	5.82	2.42	1.51	2.07±0.67
3-methyl-1-pentene	760-20-3	84.16	Exp			0	8	6.14	2.52	1.56	2.15±0.72
4-methyl-1-pentene	691-37-2	84.16	Exp			0	8	5.68	2.30	1.40	1.96±0.67
C6 terminal alkenes		84.16	LM			0	8	5.49	2.33	1.45	1.98±0.65
2,3-dimethyl-1-butene	563-78-0	84.16	Exp			0	8	4.75	1.75	0.99	1.48±0.60
2-ethyl-1-butene	760-21-4	84.16	Exp			0	8	5.07	1.85	1.05	1.57±0.64
2-methyl-1-pentene	763-29-1	84.16	Exp	1		0	8	5.26	1.90	1.07	1.61±0.67
2,3-dimethyl-2-butene	563-79-1	84.16	Exp	1		0	8	12.49	3.78	1.96	3.28±1.91
2-methyl-2-pentene	625-27-4	84.16	Exp	1		0	8	11.00	3.75	2.15	3.25±1.46
cis 4-methyl-2-pentene		84.16	LM			0	8	8.12	3.11	1.92	2.70±0.97
cis-2-hexene	7688-21-3	84.16	Exp			0	8	8.31	3.20	1.98	2.78±0.98
cis-3-hexene	7642-09-3	84.16	Exp			0	8	7.61	3.07	1.94	2.66±0.88
cis-3-methyl-2-pentene	922-62-3	84.16	Exp			0	8	12.49	4.22	2.42	3.67±1.69
trans-3-methyl-2-pentene	616-12-6	84.16	Exp			0	8	13.17	4.42	2.52	3.84±1.78
trans-4-methyl-2-pentene	674-76-0	84.16	Exp	1		0	8	8.12	3.11	1.92	2.70±0.97
trans-2-hexene	4050-45-7	84.16	Exp			0	8	8.62	3.24	1.99	2.82±1.03
trans-3-hexene	13269-52-8	84.16	Exp			0	8	7.57	3.04	1.92	2.63±0.88
2-hexenes	592-43-8	84.16	LM			0	8	8.47	3.22	1.99	2.80±1.00
C6 internal alkenes		84.16	LM			0	8	8.47	3.22	1.99	2.80±1.00
3-methyl cyclopentene	1120-62-3	82.14	Exp			0	8	5.10	2.05	1.29	1.77±0.60
1-methyl cyclopentene	693-89-0	82.14	AdjP			0	8	12.49	4.32	2.49	3.74±1.63
cyclohexene	110-83-8	82.14	Exp	1	4	0	4	5.00	2.04	1.29	1.76±0.59
trans,trans-2,4-hexadiene	5194-51-4	82.14	LM			0	8	8.83	3.32	2.04	2.89±1.06
trans-1,3-hexadiene	20237-34-7	82.14	LM			0	8	10.37	3.95	2.45	3.42±1.19
trans-1,4-hexadiene	7319-00-8	82.14	Exp	1		0	8	8.64	3.33	2.06	2.88±1.01
C6 cyclic olefins or di-olefins		82.14	LM			0	8	8.68	3.30	2.04	2.87±1.03
C6 alkenes		84.16	LM			0	8	6.98	2.77	1.72	2.39±0.82
1-methyl cyclohexene	591-49-1	96.17	Exp	1		0	8	6.61	2.44	1.41	2.08±0.86
4-methyl cyclohexene	591-47-9	96.17	Exp			0	8	4.18	1.71	1.07	1.47±0.50
C7 cyclic olefins or di-olefins		96.17	LM			0	8	7.29	2.83	1.74	2.44±0.88
1-heptene	592-76-7	98.19	AdjP	1		0	8 d	4.43	1.91	1.14	1.59±0.54
3,4-dimethyl-1-pentene	7385-78-6	98.19	Exp			0	8	4.84	2.00	1.21	1.69±0.57
3-methyl-1-hexene	3404-61-3	98.19	Exp			0	8	4.41	1.92	1.15	1.60±0.54
2,4-dimethyl-1-pentene	2213-32-3	98.19	AdjP			0	8	6.01	2.39	1.42	2.02±0.72
2,3-dimethyl-1-pentene	3404-72-6	98.19	Exp			0	8	5.15	2.12	1.24	1.77±0.64
3,3-dimethyl-1-pentene	3404-73-7	98.19	Exp			0	8	4.91	2.17	1.39	1.85±0.56
2-methyl-1-hexene	6094-02-6	98.19	Exp			0	8	5.10	2.11	1.22	1.75±0.64
2,3,3-trimethyl-1-butene	594-56-9	98.19	Exp			0	8	4.49	1.78	1.06	1.51±0.54
4,4-dimethyl-cis-2-pentene	762-63-0	98.19	Exp			0	8	6.64	2.54	1.53	2.19±0.81
2,4-dimethyl-2-pentene	625-65-0	98.19	Exp			0	8	9.29	3.15	1.79	2.73±1.25
2-methyl-2-hexene	2738-19-4	98.19	Exp			0	8	9.47	3.21	1.81	2.77±1.28
3-ethyl-2-pentene	816-79-5	98.19	Exp			0	8	9.75	3.43	1.99	2.97±1.31

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
3-methyl-trans-3-hexene	3899-36-3	98.19	Exp			0	8	9.72	3.45	2.01	2.98±1.26
cis-2-heptene	6443-92-1	98.19	Exp			0	8	7.16	2.78	1.70	2.40±0.86
2-methyl-trans-3-hexene	692-24-0	98.19	Exp			0	8	6.25	2.55	1.60	2.20±0.73
3-methyl-cis-3-hexene	4914-89-0	98.19	Exp			0	8	9.72	3.45	2.01	2.98±1.26
3,4-dimethyl-cis-2-pentene	4914-91-4	98.19	Exp			0	8	9.15	3.10	1.72	2.66±1.28
2,3-dimethyl-2-pentene	10574-37-5	98.19	Exp	1		0	8	9.74	3.11	1.65	2.67±1.43
cis-3-heptene	7642-10-6	98.19	Exp			0	8	6.33	2.58	1.62	2.22±0.74
trans-4,4-dimethyl-2-pentene	690-08-4	98.19	Exp	1		0	8	6.64	2.54	1.54	2.19±0.81
trans-2-heptene	14686-13-6	98.19	Exp	1		0	8	7.14	2.77	1.70	2.39±0.86
trans-3-heptene	14686-14-7	98.19	Exp			0	8	6.32	2.57	1.62	2.22±0.74
cis-3-methyl-2-hexene	10574-36-4	98.19	Exp			0	8	10.07	3.46	1.975	2.99±1.36
trans-4-methyl-2-hexene		98.19	Exp			0	8	7.18	2.78	1.71	2.40±0.86
trans-3-methyl-2-hexene		98.19	Exp			0	8	10.07	3.46	1.98	2.99±1.36
2-heptenes		98.19	LM			0	8	6.32	2.58	1.62	2.22±0.74
C7 terminal alkenes		98.19	LM			0	8	4.43	1.91	1.14	1.59±0.54
C7 internal alkenes		98.19	LM			0	8	6.32	2.57	1.62	2.22±0.74
C7 alkenes		98.19	LM			0	8	5.37	2.24	1.38	1.91±0.64
1,2-dimethyl cyclohexene	1674-10-8	110.20	Exp			0	8	5.63	2.09	1.11	1.73±0.78
C8 cyclic olefins or di-olefins		110.20	LM			0	8	4.89	2.02	1.21	1.70±0.61
1-octene	111-66-0	112.21	Exp			0	8	3.25	1.42	0.82	1.16±0.42
2,4,4-trimethyl-1-pentene	107-39-1	112.21	Exp			0	8	3.34	1.23	0.66	1.02±0.43
3-methyl-2-isopropyl-1-butene	111823-35-9	112.21	AdjP			0	8	3.31	1.40	0.78	1.14±0.43
trans-2-octene	13389-42-9	112.21	Exp			0	8	6.00	2.33	1.42	2.00±0.73
2-methyl-2-heptene	627-97-4	112.21	Exp			0	8	8.33	2.86	1.60	2.45±1.13
cis-4-octene	7642-15-1	112.21	AdjP			0	8	4.73	1.97	1.18	1.65±0.59
trans-2,2-dimethyl 3-hexene	690-93-7	112.21	Exp			0	8	5.00	2.11	1.32	1.80±0.60
trans-2,5-dimethyl 3-hexene	692-70-6	112.21	AdjP			0	8	4.82	2.04	1.29	1.75±0.57
trans-3-octene	14919-01-8	112.21	AdjP			0	8	5.34	2.22	1.37	1.89±0.65
trans-4-octene	14850-23-8	112.21	AdjP	1		0	8	4.81	1.98	1.18	1.67±0.59
2,4,4-trimethyl-2-pentene	107-40-4	112.21	Exp			0	8	6.29	2.23	1.24	1.89±0.84
2,3-dimethyl-2-hexene		112.21	Exp			0	8	8.53	2.74	1.44	2.35±1.25
3-octenes		112.21	LM			0	8	5.34	2.22	1.37	1.89±0.65
C8 terminal alkenes		112.21	LM			0	8	3.25	1.42	0.82	1.16±0.42
C8 internal alkenes		112.21	LM			0	8	4.81	1.98	1.18	1.67±0.59
C8 alkenes		112.21	LM			0	8	4.03	1.70	1.00	1.41±0.51
1-nonene	124-11-8	126.24	Exp			0	8	2.60	1.16	0.65	0.94±0.35
C9 terminal alkenes		126.24	LM			0	8	2.60	1.16	0.65	0.94±0.35
4,4-dimethyl-1-pentene	762-62-9	126.24	Exp			0	8	3.13	1.34	0.77	1.10±0.40
4-nonene	2198-23-4	126.24	LM			0	8	4.54	1.90	1.15	1.60±0.56
3-nonenes		126.24	LM			0	8	4.54	1.90	1.15	1.60±0.56
C9 internal alkenes		126.24	LM			0	8	4.54	1.90	1.15	1.60±0.56
trans-4-nonene	10405-85-3	126.24	AdjP			0	8	4.54	1.90	1.15	1.60±0.56
C9 cyclic olefins or di-olefins		124.22	LM			0	8	4.62	1.93	1.17	1.63±0.57
C9 alkenes		126.24	LM			0	8	3.57	1.53	0.90	1.27±0.45
1-decene	872-05-9	140.27	Exp			0	8	2.17	0.98	0.54	0.78±0.30
C10 terminal alkenes		140.27	LM			0	8	2.17	0.98	0.54	0.78±0.30
3,4-diethyl-2-hexene	59643-70-8	140.27	Exp			0	8	3.38	1.50	0.85	1.22±0.46
cis-5-decene	7433-78-5	140.27	AdjP			0	8	3.66	1.57	0.91	1.29±0.48
trans-4-decene	19398-89-1	140.27	AdjP			0	8	3.87	1.64	0.98	1.37±0.49

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
C10 3-alkenes		140.27	LM			0	8	3.87	1.64	0.98	1.37±0.49
C10 internal alkenes		140.27	LM			0	8	3.87	1.64	0.98	1.37±0.49
C10 cyclic olefins or di-olefins		138.25	LM			0	8	3.93	1.67	0.99	1.39±0.50
3-carene	13466-78-9	136.23	Exp	1	3	0	4	3.24	1.28	0.75	1.08±0.40
alpha-pinene	80-56-8	136.23	Exp	1	2	0	4	4.51	1.65	0.89	1.38±0.60
beta-pinene	127-91-3	136.23	Exp	1	2	0	4	3.52	1.44	0.79	1.17±0.46
d-limonene	5989-27-5	136.23	Exp	1	2	0	4	4.55	1.70	0.96	1.44±0.60
sabinene	3387-41-5	136.23	Exp	1	3	0	4	4.19	1.70	0.97	1.41±0.53
Terpinolene	586-62-9	136.23	Exp			0	8	6.36	2.22	1.18	1.88±0.93
Camphene	79-92-5	136.23	LM			0	8	4.51	1.65	0.89	1.38±0.60
terpene (monoterpenes)		136.23	LM			0	8	4.04	1.55	0.86	1.29±0.52
C10 alkenes		140.27	LM			0	8	3.31	1.42	0.83	1.17±0.43
1-undecene	821-95-4	154.29	Exp			0	8	1.87	0.86	0.46	0.67±0.27
C11 terminal alkenes		154.29	LM			0	8	1.87	0.86	0.46	0.67±0.27
trans-5-undecene	764-97-6	154.29	AdjP			0	8	3.60	1.54	0.92	1.28±0.46
C11 3-alkenes		154.29	LM			0	8	3.60	1.54	0.92	1.28±0.46
C11 internal alkenes		154.29	LM			0	8	3.60	1.54	0.92	1.28±0.46
C11 cyclic olefins or di-olefins		152.28	LM			0	8	3.65	1.56	0.93	1.30±0.47
C11 alkenes		154.29	LM			0	8	2.73	1.20	0.69	0.98±0.36
C12 terminal alkenes		168.32	LM			0	8	1.64	0.76	0.41	0.60±0.24
1-dodecene	112-41-4	168.32	Exp			0	8	1.64	0.76	0.41	0.60±0.24
C12 2-alkenes		168.32	LM			0	8	3.14	1.36	0.79	1.12±0.41
C12 3-alkenes		168.32	LM			0	8	3.14	1.36	0.79	1.12±0.41
C12 internal alkenes		168.32	LM			0	8	3.14	1.36	0.79	1.12±0.41
trans-5-dodecene	7206-16-8	168.32	AdjP			0	8	3.14	1.36	0.79	1.12±0.41
C12 cyclic olefins or di-olefins		166.30	LM			0	8	3.18	1.37	0.80	1.13±0.42
C12 alkenes		168.32	LM			0	8	2.39	1.06	0.60	0.86±0.32
1-tridecene	2437-56-1	182.35	Exp			0	8	1.48	0.69	0.37	0.54±0.22
C13 terminal alkenes		182.35	LM			0	8	1.48	0.69	0.37	0.54±0.22
trans-5-tridecene	23051-84-5	182.35	Exp			0	8	2.59	1.13	0.67	0.93±0.35
C13 3-alkenes		182.35	LM			0	8	2.59	1.13	0.67	0.93±0.35
C13 internal alkenes		182.35	LM			0	8	2.59	1.13	0.67	0.93±0.35
C13 cyclic olefins or di-olefins		180.33	LM			0	8	2.62	1.14	0.67	0.94±0.35
C13 alkenes		182.35	LM			0	8	2.03	0.91	0.52	0.74±0.28
1-tetradecene	1120-36-1	196.37	Exp			0	8	1.34	0.63	0.33	0.49±0.20
C14 terminal alkenes		196.37	LM			0	8	1.34	0.63	0.33	0.49±0.20
trans-5-tetradecene	41446-66-6	196.37	Exp			0	8	2.35	1.03	0.61	0.85±0.32
C14 3-alkenes		196.37	LM			0	8	2.35	1.03	0.61	0.85±0.32
C14 internal alkenes		196.37	LM			0	8	2.35	1.03	0.61	0.85±0.32
C14 cyclic olefins or di-olefins		194.36	LM			0	8	2.38	1.04	0.61	0.86±0.33
C14 alkenes		196.37	LM			0	8	1.85	0.83	0.47	0.67±0.26
1-pentadecene	13360-61-7	210.40	LM			0	8	1.25	0.59	0.31	0.46±0.19
C15 terminal alkenes		210.40	LM			0	8	1.25	0.59	0.31	0.46±0.19
trans-5-pentadecene	74392-33-9	210.40	Exp			0	8	2.16	0.95	0.56	0.78±0.30
C15 3-alkenes		210.40	LM			0	8	2.16	0.95	0.56	0.78±0.30
C15 internal alkenes		210.40	LM			0	8	2.16	0.95	0.56	0.78±0.30
C15 cyclic olefins or di-olefins		208.38	LM			0	8	2.19	0.96	0.56	0.79±0.30
C15 alkenes		210.40	LM			0	8	1.71	0.77	0.43	0.62±0.24

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
					Aromatic Hydrocarbons						
benzene	71-43-2	78.11	Exp	1	2	0?	4	0.72	0.101	-0.159	-.008±0.185
toluene	108-88-3	92.14	Exp	1	2	0	4	4.00	1.36	0.52	1.02±0.60
ethyl benzene	100-41-4	106.17	Exp	1	3	0	4	3.04	1.15	0.50	0.88±0.44
m-xylene	108-38-3	106.17	Exp	1	1	0	4	9.75	3.09	1.48	2.53±1.30
o-xylene	95-47-6	106.17	Exp	1	2	0	4	7.64	2.51	1.16	2.02±1.04
p-xylene	106-42-3	106.17	Exp	1	3	0	4	5.84	1.93	0.82	1.51±0.82
C8 disubstituted benzenes	1330-20-7	106.17	LM			0	8	7.76	2.51	1.15	2.02±1.05
isomers of ethylbenzene		106.17	LM			0	8	6.57	2.17	0.99	1.73±0.90
styrene	100-42-5	104.15	Exp	1	2	0	2	1.73	0.21	-0.48	-.107±0.500
Unspeciated C8 Aromatics		106.17	Mix			0	8	7.64	2.49	1.15	2.01±1.03
C9 monosubstituted benzenes		120.19	LM			0	8	2.03	0.82	0.36	0.62±0.30
n-propyl benzene	103-65-1	120.19	Exp	1		0	8	2.03	0.82	0.36	0.62±0.30
isopropyl benzene (cumene)	98-82-8	120.19	Exp	1		0	8	2.52	0.94	0.39	0.71±0.37
C9 disubstituted benzenes		120.19	LM			0	8	5.81	1.95	0.89	1.55±0.79
m-ethyl toluene	620-14-4	120.19	Exp	1		0	8	7.39	2.40	1.13	1.95±0.99
o-ethyl toluene	611-14-3	120.19	Exp	1		0	8	5.59	1.90	0.87	1.51±0.76
p-ethyl toluene	622-96-8	120.19	Exp	1		0	8	4.44	1.54	0.67	1.20±0.62
C9 trisubstituted benzenes	25551-13-7	120.19	LM			0	8	10.87	3.59	1.94	3.04±1.38
1,2,3-trimethyl benzene	526-73-8	120.19	Exp	1	2	0	4	11.97	3.93	2.12	3.33±1.52
1,2,4-trimethyl benzene	95-63-6	120.19	Exp	1	2	0	4	8.87	3.05	1.65	2.56±1.12
1,3,5-trimethyl benzene	108-67-8	120.19	Exp	1	2	0	4	11.76	3.80	2.05	3.24±1.51
isomers of propyl benzene		120.19	LM			0	8	6.23	2.12	1.06	1.74±0.82
indene	95-13-6	116.16	LM			0	10	1.55	0.191	-0.43	-.095±0.448
indane	496-11-7	118.18	LM			0	10	3.32	1.18	0.47	0.89±0.48
allylbenzene	300-57-2	118.18	LM			0	8	1.53	0.188	-0.43	-.094±0.441
α-methyl styrene	98-83-9	118.18	LM			0	8	1.53	0.188	-0.43	-.094±0.441
C9 styrenes		118.18	LM			0	8	1.53	0.188	-0.43	-.094±0.441
β-methyl styrene	637-50-3	118.18	Exp	1		0	8	1.01	0.155	-0.32	-.074±0.300
Unspeciated C9 Aromatics		120.09	Mix			0	8	7.99	2.68	1.38	2.23±1.03
C10 monosubstituted benzenes		134.22	Exp			0	8	2.36	0.94	0.42	0.72±0.34
n-butyl benzene	104-51-8	134.22	LM			0	8	2.36	0.94	0.42	0.72±0.34
sec-butyl benzene	135-98-8	134.22	LM			0	8	2.36	0.94	0.42	0.72±0.34
tert-butyl benzene	98-06-6	134.22	Exp	1		0	8	1.95	0.70	0.27	0.52±0.30
o-cymene; 1-methyl-2-(1-methylethyl) benzene	527-84-4	134.22	LM			0	8	5.49	1.87	0.89	1.51±0.74
1-methyl-2-n-propyl benzene	1074-17-5	134.22	LM			0	8	5.49	1.87	0.89	1.51±0.74
m-cymene; 1-methyl-3-(1-methylethyl) benzene	535-77-3	134.22	LM			0	8	7.10	2.30	1.12	1.89±0.94
1-methyl-3-n-propyl benzene	1074-43-7	134.22	LM			0	8	7.10	2.30	1.12	1.89±0.94
1-methyl-4-n-propyl benzene	1074-55-1	134.22	LM			0	8	4.43	1.54	0.71	1.22±0.61
C10 disubstituted benzenes		134.22	LM			0	8	5.68	1.91	0.91	1.54±0.76
m-C10 disubstituted benzenes		134.22	Exp			0	8	7.10	2.30	1.12	1.89±0.94
o-C10 disubstituted benzenes		134.22	Exp			0	8	5.49	1.87	0.89	1.51±0.74
p-C10 disubstituted benzenes		134.22	Exp			0	8	4.43	1.54	0.71	1.22±0.61
m-diethyl benzene	141-93-5	134.22	LM			0	8	7.10	2.30	1.12	1.89±0.94
o-diethyl benzene	135-01-3	134.22	LM			0	8	5.49	1.87	0.89	1.51±0.74
1-methyl-4-isopropyl benzene (p-cymene)	99-87-6	134.22	Exp	1		0	8	4.44	1.52	0.67	1.19±0.61

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
p-diethyl benzene	105-05-5	134.22	LM			0	8	4.43	1.54	0.71	1.22±0.61
1,2,3-C10 trisubstituted benzenes		134.22	Exp			0	8	10.15	3.37	1.81	2.85±1.29
1,2,4-C10 trisubstituted benzenes		134.22	Exp			0	8	7.55	2.62	1.41	2.19±0.96
1,3,5-C10 trisubstituted benzenes		134.22	Exp			0	8	10.08	3.28	1.77	2.79±1.29
1,2,3,4-tetramethyl benzene	488-23-3	134.22	LM			0	8	9.26	3.09	1.67	2.61±1.18
1,2,4,5-tetramethyl benzene	95-93-2	134.22	LM			0	8	9.26	3.09	1.67	2.61±1.18
1,2-dimethyl-3-ethyl benzene	933-98-2	134.22	LM			0	8	10.15	3.37	1.81	2.85±1.29
1,2-dimethyl-4-ethyl benzene	934-80-5	134.22	LM			0	8	7.55	2.62	1.41	2.19±0.96
1,3-dimethyl-2-ethyl benzene	2870-04-4	134.22	LM			0	8	10.15	3.37	1.81	2.85±1.29
1,3-dimethyl-4-ethyl benzene	874-41-9	134.22	LM			0	8	7.55	2.62	1.41	2.19±0.96
1,3-dimethyl-5-ethyl benzene	934-74-7	134.22	LM			0	8	10.08	3.28	1.77	2.79±1.29
1,4-dimethyl-2-ethyl benzene	1758-88-9	134.22	LM			0	8	7.55	2.62	1.41	2.19±0.96
1,2,3,5-tetramethyl benzene	527-53-7	134.22	LM			0	8	9.26	3.09	1.67	2.61±1.18
C10 trisubstituted benzenes		134.22	LM			0	8	9.26	3.09	1.67	2.61±1.18
C10 tetrasubstituted benzenes		134.22	LM			0	8	9.26	3.09	1.67	2.61±1.18
butylbenzenes		134.22	LM			0	8	5.76	1.98	1.00	1.62±0.75
methyl indanes		132.20	LM			0	10	2.97	1.05	0.42	0.80±0.43
tetralin (1,2,3,4-tetrahydronaphthalene)	119-64-2	132.20	Exp	1	4	+	5	2.97	1.05	0.42	0.80±0.43
naphthalene	91-20-3	128.17	Exp	1	4	+	5	3.34	1.14	0.49	0.90±0.46
C10 styrenes		132.20	LM			0	8	1.37	0.168	-0.38	-.084±0.394
Unspeciated C10 Aromatics		133.91	Mix			0	8	7.07	2.37	1.22	1.97±0.92
n-pentyl benzene	538-68-1	148.24	LM			0	8	2.12	0.86	0.40	0.66±0.30
C11 monosubstituted benzenes		148.24	Exp			0	8	2.12	0.86	0.40	0.66±0.30
m-C11 disubstituted benzenes		148.24	Exp			0	8	6.15	2.02	0.99	1.66±0.82
o-C11 disubstituted benzenes		148.24	Exp			0	8	4.73	1.64	0.79	1.32±0.63
p-C11 disubstituted benzenes		148.24	Exp			0	8	3.88	1.38	0.64	1.09±0.53
1-butyl-2-methyl benzene		148.24	LM			0	8	4.73	1.64	0.79	1.32±0.63
1-ethyl-2-n-propyl benzene		148.24	LM			0	8	4.73	1.64	0.79	1.32±0.63
o-tert-butyl toluene; 1-(1,1-dimethylethyl)-2-methyl benzene	1074-92-6	148.24	LM			0	8	4.73	1.64	0.79	1.32±0.63
1-methyl-3-n-butyl benzene	1595-04-6	148.24	LM			0	8	6.15	2.02	0.99	1.66±0.82
p-isobutyl toluene; 1-methyl-4-(2-methylpropyl) benzene	5161-04-6	148.24	LM			0	8	3.88	1.38	0.64	1.09±0.53
C11 disubstituted benzenes		148.24	LM			0	8	4.92	1.68	0.81	1.36±0.66
1,2,3-C11 trisubstituted benzenes		148.24	Exp			0	8	8.88	2.96	1.60	2.50±1.13
1,2,4-C11 trisubstituted benzenes		148.24	Exp			0	8	6.62	2.31	1.25	1.94±0.84
1,3,5-C11 trisubstituted benzenes		148.24	Exp			0	8	8.90	2.91	1.57	2.47±1.14
pentamethyl benzene	700-12-9	148.24	LM			0	8	8.13	2.73	1.47	2.30±1.03
1-methyl-3,5-diethyl benzene	2050-24-0	148.24	LM			0	8	8.90	2.91	1.57	2.47±1.14
C11 trisubstituted benzenes		148.24	LM			0	8	8.13	2.73	1.47	2.30±1.03
C11 tetrasubstituted benzenes		148.24	LM			0	8	8.13	2.73	1.47	2.30±1.03

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
C11 pentasubstituted benzenes		148.24	LM			0	8	8.13	2.73	1.47	2.30±1.03
pentyl benzenes		148.24	LM			0	8	4.90	1.71	0.87	1.40±0.64
C11 tetralins or indanes		146.23	LM			+	10	2.69	0.95	0.38	0.72±0.39
methyl naphthalenes	1321-94-4	142.20	Exp			+	10	3.06	1.02	0.42	0.79±0.43
1-methyl naphthalene	90-12-0	142.20	LM			+	10	3.06	1.02	0.42	0.79±0.43
2-methyl naphthalene	91-57-6	142.20	LM			+	10	3.06	1.02	0.42	0.79±0.43
Unspeciated C11 Aromatics		147.72	Mix			0	8	6.95	2.34	1.23	1.96±0.89
C12 monosubstituted benzenes		162.27	Exp			0	8	1.90	0.79	0.37	0.61±0.27
m-C12 disubstituted benzenes		162.27	Exp			0	8	5.49	1.81	0.89	1.49±0.73
o-C12 disubstituted benzenes		162.27	Exp			0	8	4.23	1.48	0.71	1.19±0.57
p-C12 disubstituted benzenes		162.27	Exp			0	8	3.49	1.25	0.59	0.99±0.47
1,3-di-n-propyl benzene		162.27	LM			0	8	4.23	1.48	0.71	1.19±0.57
1,4 di-isopropyl benzene		162.27	LM			0	8	3.49	1.25	0.59	0.99±0.47
3-isopropyl cumene; 1,3-di-isopropyl benzene	99-62-7	162.27	LM			0	8	5.49	1.81	0.89	1.49±0.73
C12 disubstituted benzenes		162.27	LM			0	8	4.40	1.51	0.73	1.22±0.59
1,2,3-C12 trisubstituted benzenes		162.27	Exp			0	8	7.95	2.66	1.44	2.25±1.01
1,2,4-C12 trisubstituted benzenes		162.27	Exp			0	8	5.94	2.08	1.13	1.74±0.75
1,3,5-C12 trisubstituted benzenes		162.27	Exp			0	8	8.02	2.62	1.42	2.23±1.03
1-(1,1-dimethylethyl)-3,5-dimethylbenzene	98-19-1	162.27	LM			0	8	8.02	2.62	1.42	2.23±1.03
C12 trisubstituted benzenes		162.27	LM			0	8	7.30	2.46	1.33	2.07±0.93
C12 tetrasubstituted benzenes		162.27	LM			0	8	7.30	2.46	1.33	2.07±0.93
C12 pentasubstituted benzenes		162.27	LM			0	8	7.30	2.46	1.33	2.07±0.93
C12 hexasubstituted benzenes		162.27	LM			0	8	7.30	2.46	1.33	2.07±0.93
hexyl benzenes		162.27	LM			0	8	4.39	1.55	0.79	1.27±0.57
C12 tetralins or indanes		160.26	LM			0	10	2.45	0.87	0.34	0.66±0.35
1-ethyl naphthalene	1127-76-0	156.22	LM			+	10	2.78	0.93	0.38	0.72±0.39
C12 naphthalenes		156.22	LM			+	10	3.89	1.28	0.59	1.03±0.52
C12 monosubstituted naphthalene		156.22	LM			+	10	2.78	0.93	0.38	0.72±0.39
C12 disubstituted naphthalenes		156.22	LM			+	10	4.99	1.62	0.80	1.34±0.66
2,3-dimethyl naphthalene	581-40-8	156.22	Exp	1	4	+	5	4.99	1.62	0.80	1.34±0.66
dimethyl naphthalenes		156.22	LM			+	10	4.99	1.62	0.80	1.34±0.66
Unspeciated C12 Aromatics		159.90	Mix			0	8	6.02	2.02	1.06	1.69±0.77
C13 monosubstituted benzenes		176.30	Exp			0	8	1.74	0.74	0.35	0.57±0.25
m-C13 disubstituted benzenes		176.30	Exp			0	8	4.93	1.64	0.81	1.35±0.65
o-C13 disubstituted benzenes		176.30	Exp			0	8	3.78	1.34	0.65	1.08±0.50
p-C13 disubstituted benzenes		176.30	Exp			0	8	3.13	1.14	0.54	0.90±0.42
C13 disubstituted benzenes		176.30	LM			0	8	3.95	1.37	0.67	1.11±0.52
1,2,3-C13 trisubstituted benzenes		176.30	Exp			0	8	7.13	2.40	1.30	2.02±0.91
1,2,4-C13 trisubstituted benzenes		176.30	Exp			0	8	5.35	1.88	1.02	1.58±0.67
1,3,5-C13 trisubstituted benzenes		176.30	Exp			0	8	7.24	2.38	1.29	2.02±0.93

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
C13 trisubstituted benzenes		176.30	LM			0	8	6.57	2.22	1.20	1.87±0.84
C13 tetralins or indanes		174.28	LM			0	10	2.25	0.80	0.32	0.61±0.33
C13 naphthalenes		170.25	LM			0	10	3.57	1.17	0.54	0.95±0.48
C13 monosubstituted naphthalene		170.25	LM			0	10	2.55	0.85	0.35	0.66±0.36
C13 disubstituted naphthalenes		170.25	LM			0	10	4.58	1.49	0.74	1.23±0.60
C13 trisubstituted naphthalenes		170.25	LM			0	10	4.58	1.49	0.74	1.23±0.60
Unspeciated C13 Aromatics		175.85	Mix			0	8	4.81	1.61	0.82	1.34±0.62
C14 monosubstituted benzenes		190.32	Exp			0	8	1.60	0.69	0.33	0.53±0.23
m-C14 disubstituted benzenes		190.32	Exp			0	8	4.45	1.49	0.74	1.23±0.59
o-C14 disubstituted benzenes		190.32	Exp			0	8	3.40	1.22	0.60	0.98±0.45
p-C14 disubstituted benzenes		190.32	Exp			0	8	2.84	1.04	0.50	0.83±0.38
C14 disubstituted benzenes		190.32	LM			0	8	3.56	1.25	0.61	1.01±0.47
1,2,3-C14 trisubstituted benzenes		190.32	Exp			0	8	6.49	2.19	1.19	1.85±0.82
1,2,4-C14 trisubstituted benzenes		190.32	Exp			0	8	4.89	1.73	0.94	1.45±0.62
1,3,5-C14 trisubstituted benzenes		190.32	Exp			0	8	6.63	2.18	1.18	1.86±0.85
C14 trisubstituted benzenes		190.32	LM			0	8	6.00	2.03	1.10	1.72±0.76
C14 tetralins or indanes		188.31	LM			0	10	2.09	0.74	0.29	0.56±0.30
C14 naphthalenes		184.28	LM			0	10	3.30	1.08	0.50	0.88±0.44
Unspeciated C14 Aromatics		189.87	Mix			0	8	3.80	1.27	0.62	1.04±0.50
C15 monosubstituted benzenes		204.35	Exp			0	8	1.48	0.64	0.32	0.50±0.21
C15 disubstituted benzenes		204.35	LM			0	8	3.25	1.15	0.57	0.93±0.43
m-C15 disubstituted benzenes		204.35	Exp			0	8	4.04	1.37	0.68	1.12±0.53
o-C15 disubstituted benzenes		204.35	Exp			0	8	3.09	1.12	0.56	0.90±0.41
p-C15 disubstituted benzenes		204.35	Exp			0	8	2.59	0.96	0.47	0.77±0.35
C15 trisubstituted benzenes		204.35	LM			0	8	5.50	1.87	1.02	1.58±0.70
1,2,3-C15 trisubstituted benzenes		204.35	Exp			0	8	5.94	2.01	1.09	1.70±0.75
1,2,4-C15 trisubstituted benzenes		204.35	Exp			0	8	4.47	1.59	0.87	1.33±0.56
1,3,5-C15 trisubstituted benzenes		204.35	Exp			0	8	6.10	2.01	1.09	1.71±0.78
C15 tetralins or indanes		202.34	LM			0	10	1.94	0.69	0.27	0.52±0.28
C15 naphthalenes		198.30	LM			0	10	3.06	1.01	0.47	0.81±0.41
Unspeciated C15 Aromatics		203.90	Mix			0	8	3.20	1.06	0.50	0.86±0.42
C16 monosubstituted benzenes		218.38	Exp			0	8	1.38	0.61	0.30	0.47±0.20
m-C16 disubstituted benzenes		218.38	Exp			0	8	3.71	1.26	0.63	1.04±0.49
o-C16 disubstituted benzenes		218.38	Exp			0	8	2.83	1.03	0.52	0.83±0.37
p-C16 disubstituted benzenes		218.38	Exp			0	8	2.38	0.89	0.44	0.71±0.32
C16 disubstituted benzenes		218.38	LM			0	8	2.97	1.06	0.53	0.86±0.39
1,2,3-C16 trisubstituted benzenes		218.38	Exp			0	8	5.46	1.86	1.01	1.57±0.69
1,2,4-C16 trisubstituted benzenes		218.38	Exp			0	8	4.13	1.47	0.80	1.23±0.52
1,3,5-C16 trisubstituted benzenes		218.38	Exp			0	8	5.63	1.86	1.01	1.58±0.72

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
C16 trisubstituted benzenes		218.38	LM			0	8	5.07	1.73	0.94	1.46±0.64
C16 tetralins or indanes		216.36	LM			0	10	1.82	0.64	0.26	0.49±0.26
C16 naphthalenes		212.33	LM			0	10	2.86	0.94	0.43	0.76±0.38
Unspeciated C16 Aromatics		217.93	Mix			0	8	2.79	0.92	0.42	0.74±0.37
C17 monosubstituted benzenes		232.40	LM			0	8	1.30	0.57	0.29	0.44±0.18
C17 disubstituted benzenes		232.40	LM			0	8	2.79	1.00	0.50	0.81±0.37
C17 trisubstituted benzenes		232.40	LM			0	8	4.77	1.63	0.89	1.37±0.60
C17 tetralins or indanes		230.39	LM			0	10	1.70	0.60	0.24	0.46±0.25
C17 naphthalenes		226.36	LM			0	10	2.68	0.88	0.41	0.71±0.36
C18 monosubstituted benzenes		246.43	LM			0	8	1.23	0.54	0.27	0.42±0.17
C18 disubstituted benzenes		246.43	LM			0	8	2.63	0.94	0.47	0.76±0.35
C18 trisubstituted benzenes		246.43	LM			0	8	4.49	1.53	0.83	1.29±0.57
C18 tetralins or indanes		244.41	LM			0	10	1.61	0.57	0.23	0.43±0.23
C18 naphthalenes		240.38	LM			0	10	2.53	0.83	0.38	0.67±0.34
C19 monosubstituted benzenes		260.46	LM			0	8	1.16	0.51	0.25	0.40±0.16
C19 disubstituted benzenes		260.46	LM			0	8	2.49	0.89	0.44	0.72±0.33
C19 trisubstituted benzenes		260.46	LM			0	8	4.25	1.45	0.79	1.22±0.54
C19 tetralins or indanes		258.44	LM			0	10	1.52	0.54	0.21	0.41±0.22
C19 naphthalenes		254.41	LM			0	10	2.39	0.78	0.36	0.63±0.32
C20 monosubstituted benzenes		274.48	LM			0	8	1.10	0.48	0.24	0.37±0.16
C20 disubstituted benzenes		274.48	LM			0	8	2.36	0.84	0.42	0.68±0.31
C20 trisubstituted benzenes		274.48	LM			0	8	4.04	1.38	0.75	1.16±0.51
C20 tetralins or indanes		272.47	LM			0	10	1.44	0.51	0.20	0.39±0.21
C20 naphthalenes		268.44	LM			0	10	2.26	0.74	0.34	0.60±0.30
C21 monosubstituted benzenes		288.51	LM			0	8	1.05	0.46	0.23	0.36±0.15
C21 disubstituted benzenes		288.51	LM			0	8	2.25	0.80	0.40	0.65±0.30
C21 trisubstituted benzenes		288.51	LM			0	8	3.84	1.31	0.71	1.11±0.49
C21 tetralins or indanes		286.49	LM			0	10	1.37	0.49	0.193	0.37±0.20
C21 naphthalenes		282.46	LM			0	10	2.15	0.71	0.33	0.57±0.29
C22 monosubstituted benzenes		302.54	LM			0	8	1.00	0.44	0.22	0.34±0.14
C22 disubstituted benzenes		302.54	LM			0	8	2.14	0.77	0.38	0.62±0.28
C22 trisubstituted benzenes		302.54	LM			0	8	3.66	1.25	0.68	1.05±0.46
C22 tetralins or indanes		300.52	LM			0	10	1.31	0.46	0.184	0.35±0.19
C22 naphthalenes		296.49	LM			0	10	2.05	0.67	0.31	0.54±0.27
Oxygenated Organics											
carbon monoxide	630-08-0	28.01	Exp	1	2	0	1	0.056	0.039	0.029	0.034±0.007
formaldehyde	50-00-0	30.03	Exp	1	1	0	1 b	9.46	2.68	1.27	2.27±1.40
methanol	67-56-1	32.04	Exp	1	3	0	2	0.67	0.31	0.190	0.26±0.08
formic acid	64-18-6	46.03	Exp	1		0	6	0.066	0.046	0.034	0.040±0.008
ethylene oxide	75-21-8	44.05	Exp	1		0	6	0.039	0.034	0.028	0.030±0.006
acetaldehyde	75-07-0	44.05	Exp	1	2	0	1	6.54	2.49	1.61	2.20±0.72
ethanol	64-17-5	46.07	Exp	1	3	0	2	1.53	0.87	0.59	0.74±0.22
dimethyl ether	115-10-6	46.07	Exp	1	3	0	2	0.81	0.56	0.44	0.50±0.08
glyoxal	107-22-2	58.04	Exp	1		0	6	12.50	3.68	1.84	3.15±1.82
methyl formate	107-31-3	60.05	Exp	1		0	6	0.057	0.046	0.037	0.041±0.007
acetic acid	64-19-7	60.05	Exp	1		0	6	0.68	0.33	0.21	0.27±0.09
glycolaldehyde	141-46-8	60.05	Exp			0	7	5.10	1.88	1.20	1.66±0.57
ethylene glycol	107-21-1	62.07	Exp	1	2	0	2	3.13	1.51	1.02	1.30±0.37

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
glycolic acid	79-14-1	76.05	AdjP			0	8	2.38	0.89	0.47	0.72±0.33
peroxyacetic acid	79-21-0	76.05	LM			0	8	0.54	0.26	0.162	0.22±0.07
acrolein	107-02-8	56.06	Exp	1	3	0	2	7.45	2.66	1.62	2.31±0.85
trimethylene oxide	503-30-0	58.08	Exp	1		0	6	4.56	2.51	1.82	2.20±0.59
propylene oxide	75-56-9	58.08	Exp	1		0	6	0.29	0.22	0.169	0.192±0.037
propionaldehyde	123-38-6	58.08	Exp	1		0	6	7.08	2.73	1.75	2.39±0.80
acetone	67-64-1	58.08	Exp	1	1	0	2	0.36	0.147	0.089	0.124±0.041
isopropyl alcohol	67-63-0	60.10	Exp	1	2	0	2	0.61	0.36	0.25	0.31±0.07
n-propyl alcohol	71-23-8	60.10	Exp	1		0	6	2.50	1.28	0.83	1.07±0.36
acrylic acid	79-10-7	72.06	AdjP			0	8	11.38	3.84	2.18	3.31±1.45
methyl glyoxal	78-98-8	72.06	Exp	1		0	6	16.56	4.93	2.64	4.28±2.25
1,3-dioxolane	646-06-0	74.08	Exp			0	7	4.96	2.23	1.61	2.00±0.51
ethyl formate	109-94-4	74.08	Exp	1		0	6	0.48	0.29	0.21	0.25±0.07
methyl acetate	79-20-9	74.08	Exp	1	2	0	2	0.072	0.059	0.046	0.052±0.010
propionic acid	79-09-4	74.08	Exp			0	7	1.22	0.58	0.35	0.48±0.17
hydroxy acetone	116-09-6	74.08	Exp	1		0	8	3.23	1.16	0.64	0.97±0.41
propylene glycol	57-55-6	76.09	AdjP	1	2	0	2	2.58	1.17	0.76	1.01±0.30
dimethoxy methane	109-87-5	76.09	AdjP	1		0	6	0.94	0.66	0.51	0.59±0.10
2-methoxy ethanol	109-86-4	76.09	Exp	1		0	6	2.93	1.29	0.84	1.11±0.33
dimethyl carbonate	616-38-6	90.08	Exp	1	2	0	2	0.059	0.048	0.038	0.042±0.008
dihydroxy acetone	96-26-4	90.08	Exp			0	8	3.99	1.44	0.80	1.21±0.50
glycerol	56-81-5	92.09	AdjP			0	7	3.15	1.37	0.84	1.15±0.39
furan	110-00-9	68.07	Exp	1	3	-	4	9.15	3.51	2.06	2.98±1.12
crotonaldehyde	4170-30-3	70.09	Exp	1		0	8	9.39	3.26	1.94	2.84±1.11
methacrolein	78-85-3	70.09	Exp	1	2	0	2	6.01	2.15	1.33	1.88±0.68
cyclobutanone	1191-95-3	70.09	Exp	1		0	8	0.62	0.37	0.25	0.31±0.09
methylvinyl ketone	78-94-4	70.09	Exp	1	3	0	2	9.65	3.63	2.23	3.15±1.13
tetrahydrofuran	109-99-9	72.11	Exp	1		0	6	4.31	2.19	1.47	1.87±0.53
1,2-epoxy butane	106-88-7	72.11	Exp	1		0	6	0.91	0.66	0.49	0.57±0.13
2-methyl propanal	78-84-2	72.11	Exp	1		0	7	5.25	2.08	1.38	1.84±0.58
butanal	123-72-8	72.11	Exp	1		0	7	5.97	2.31	1.48	2.02±0.67
C4 aldehydes		72.11	LM			0	7	5.97	2.31	1.48	2.02±0.67
methyl ethyl ketone	78-93-3	72.11	Exp	1	2	0	2	1.48	0.63	0.39	0.53±0.18
isobutyl alcohol	78-83-1	74.12	Exp	1		0	6	2.51	1.19	0.75	1.00±0.32
n-butyl alcohol	71-36-3	74.12	Exp	1		0	6	2.88	1.43	0.92	1.20±0.39
sec-butyl alcohol	78-92-2	74.12	Exp	1		0	6	1.36	0.76	0.51	0.64±0.17
tert-butyl alcohol	75-65-0	74.12	Exp	1	2	+	2	0.41	0.23	0.144	0.187±0.050
diethyl ether	60-29-7	74.12	Exp	1	2	0	2	3.76	1.75	1.13	1.49±0.42
gamma-butyrolactone	96-48-0	86.09	Exp			0	7	0.96	0.61	0.41	0.51±0.14
methacrylic acid	79-41-4	86.09	Exp			0	8	18.50	5.87	3.34	5.12±2.37
methyl acrylate	96-33-3	86.09	Exp			0	8	11.48	3.74	2.09	3.22±1.47
vinyl acetate	108-05-4	86.09	Exp			0	8	3.20	1.18	0.70	1.02±0.39
hydroxyl-methacrolein	40364-84-9	86.09	Exp			0	8	6.24	2.33	1.41	2.01±0.71
biacetyl	431-03-8	86.09	Exp	1		0	6	20.09	6.09	3.43	5.35±2.63
1,4-dioxane	123-91-1	88.11	Exp			0	7	2.62	1.32	0.92	1.14±0.29
ethyl acetate	141-78-6	88.11	Exp	1	2	0	3	0.63	0.37	0.25	0.31±0.08
methyl propionate	554-12-1	88.11	Exp	1		0	6	0.66	0.33	0.21	0.27±0.09
n-propyl formate	110-74-7	88.11	Exp	1		0	6	0.78	0.48	0.33	0.40±0.14
isopropyl formate	625-55-8	88.11	Exp			0	7	0.37	0.26	0.189	0.22±0.05

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
isobutyric acid	79-31-2	88.11	Exp			0	7	1.20	0.61	0.39	0.51±0.15
butanoic acid	107-92-6	88.11	AdjP			0	7	1.82	0.90	0.56	0.75±0.23
methoxy-acetone	5878-19-3	88.11	Exp	1		0	8	2.03	0.97	0.66	0.84±0.22
1,3-butanediol	107-88-0	90.12	Exp	1		0	6	3.36	1.63	1.06	1.38±0.42
1,2-butandiol	584-03-2	90.12	AdjP	1		0	6	2.52	1.13	0.73	0.97±0.29
1,4-butanediol	110-63-4	90.12	Exp			0	7	2.72	1.29	0.82	1.08±0.36
2,3-butanediol		90.12	AdjP	1		0	6	4.38	1.85	1.07	1.53±0.60
1-methoxy-2-propanol	107-98-2	90.12	AdjP	1	2	0	2	2.44	1.24	0.86	1.08±0.28
2-ethoxy-ethanol	110-80-5	90.12	Exp	1	3	0	2	3.71	1.64	1.03	1.39±0.43
2-methoxy-1-propanol	1589-47-5	90.12	Exp			0	7	3.01	1.19	0.73	1.02±0.35
3-methoxy-1-propanol	1320-67-8	90.12	Exp			0	7	3.84	1.63	1.03	1.40±0.44
propylene carbonate	108-32-7	102.09	Exp	1	2	+	2	0.28	0.196	0.146	0.170±0.037
methyl lactate	547-64-8	104.10	Exp	1		0	6	2.67	1.05	0.58	0.86±0.36
diethylene glycol	111-46-6	106.12	AdjP			0	7	3.35	1.44	0.90	1.23±0.39
malic acid	6915-15-7	134.09	AdjP			0	8	6.94	2.36	1.29	2.00±0.89
2-methyl furan	534-22-5	82.10	Exp	1	3	0	4	8.30	3.12	1.84	2.66±1.01
3-methyl furan	930-27-8	82.10	Exp	1	3	0	4	6.90	2.75	1.66	2.34±0.82
cyclopentanone	120-92-3	84.12	Exp	1		0	8	1.15	0.70	0.46	0.58±0.18
C5 cyclic ketones		84.12	LM			0	8	1.15	0.70	0.46	0.58±0.18
cyclopentanol	96-41-3	86.13	Exp	1		0	6	1.72	0.90	0.59	0.76±0.22
alpha-methyl tetrahydrofuran	96-47-9	86.13	Exp	1		0	6	3.97	1.94	1.28	1.65±0.48
tetrahydropyran	142-68-7	86.13	Exp	1		0	6	3.22	1.73	1.14	1.45±0.41
2-methyl-3-butene-2-ol	115-18-4	86.13	Exp	1		0	8	4.91	2.01	1.29	1.74±0.55
2,2-dimethylpropanal (pivaldehyde)	630-19-3	86.13	Exp	1		0	8	4.89	1.88	1.23	1.66±0.54
3-methylbutanal (isovaleraldehyde)	590-86-3	86.13	Exp	1		0	8	4.97	1.91	1.23	1.68±0.55
pentanal (valeraldehyde)	110-62-3	86.13	Exp	1		0	8	5.08	1.99	1.29	1.75±0.56
C5 aldehydes		86.13	LM			0	8	5.08	1.99	1.29	1.75±0.56
2-pentanone	107-87-9	86.13	Exp	1	2	0	2	2.81	1.38	0.89	1.16±0.34
3-pentanone	96-22-0	86.13	Exp	1		0	6	1.24	0.63	0.40	0.52±0.18
C5 ketones		86.13	LM			0	7	2.81	1.38	0.89	1.16±0.34
methyl isopropyl ketone	563-80-4	86.13	Exp	1		0	6	1.65	0.82	0.53	0.69±0.20
2-pentanol	6032-29-7	88.15	Exp	1		0	6	1.61	0.86	0.57	0.73±0.20
3-pentanol	584-02-1	88.15	Exp	1		0	6	1.63	0.85	0.57	0.72±0.21
pentyl alcohol	71-41-0	88.15	Exp	1		0	6	2.83	1.38	0.88	1.16±0.37
isoamyl alcohol (3-methyl-1-butanol)	123-51-3	88.15	Exp	1		0	6	3.16	1.44	0.92	1.23±0.38
2-methyl-1-butanol	137-32-6	88.15	Exp			0	7	2.40	1.17	0.75	0.98±0.30
ethyl isopropyl ether	625-54-7	88.15	Exp			0	7	3.74	1.62	1.04	1.39±0.42
methyl n-butyl ether	628-28-4	88.15	Exp	1		0	6	3.15	1.64	1.09	1.39±0.40
methyl t-butyl ether	1634-04-4	88.15	Exp	1	3	0	2	0.73	0.46	0.31	0.38±0.09
ethyl acrylate	140-88-5	100.12	Exp			0	8	7.77	2.81	1.64	2.41±0.94
methyl methacrylate	80-62-6	100.12	Exp			0	8	15.61	4.95	2.80	4.31±2.00
glutaraldehyde	111-30-8	100.12	Exp			0	8	4.31	1.70	1.14	1.51±0.46
lumped C5+ unsaturated carbonyl species		100.12	Exp			0	8	6.38	2.30	1.36	1.98±0.75
2,4-pentanedione	123-54-6	100.12	Exp			0	8	1.01	0.39	0.22	0.32±0.12

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
tetrahydro-2-furanmethanol (tetrahydrofurfuryl alcohol)	97-99-4	102.13	Exp			0	7	3.31	1.42	0.89	1.21±0.38
ethyl propionate	105-37-3	102.13	Exp	1		0	6	0.77	0.45	0.30	0.37±0.11
isopropyl acetate	108-21-4	102.13	Exp	1	2	0	2	1.07	0.59	0.40	0.50±0.12
methyl butyrate	623-42-7	102.13	Exp	1		0	6	1.09	0.57	0.36	0.47±0.14
methyl isobutyrate	547-63-7	102.13	Exp	1	2	0	2	0.61	0.36	0.23	0.30±0.09
n-butyl formate	592-84-7	102.13	Exp	1		0	6	0.83	0.52	0.35	0.44±0.14
propyl acetate	109-60-4	102.13	Exp	1		0	6	0.78	0.49	0.34	0.41±0.12
3-methyl butanoic acid	503-74-2	102.13	AdjP			0	7	4.23	1.66	0.96	1.39±0.53
2,2-dimethoxy-propane	77-76-9	104.15	Exp			0	7	0.48	0.31	0.21	0.26±0.06
1-ethoxy-2-propanol	1569-02-4	104.15	Exp			0	7	3.09	1.52	0.97	1.27±0.37
2-propoxy-ethanol	2807-30-9	104.15	AdjP			0	7	3.30	1.53	0.99	1.30±0.38
3-ethoxy-1-propanol	111-35-3	104.15	Exp	1		0	6	4.09	1.76	1.10	1.50±0.47
3-methoxy-1-butanol	2517-43-3	104.15	Exp	1		0	6	3.87	1.54	0.95	1.32±0.45
2-methoxyethyl acetate	110-49-6	118.13	Exp			0	7	1.15	0.68	0.48	0.58±0.13
ethyl lactate	97-64-3	118.13	Exp	1		0	6	2.48	1.05	0.61	0.87±0.33
methyl isopropyl carbonate	51729-83-0	118.13	Exp	1	2	0	2	0.62	0.35	0.24	0.30±0.07
2-(2-methoxyethoxy) ethanol	111-77-3	120.15	AdjP			0	7	2.66	1.29	0.87	1.11±0.30
pentaerythritol	115-77-5	136.15	AdjP			0	7	2.17	1.01	0.65	0.86±0.28
phenol	108-95-2	94.11	LM			0	8	2.76	0.173	-0.85	-0.22±0.76
2-ethyl furan	3208-16-0	96.13	LM			0	8	7.09	2.67	1.57	2.27±0.86
2,5-dimethyl furan	625-86-5	96.13	Exp	1	3	0	4	7.88	2.89	1.69	2.47±0.96
cyclohexanone	108-94-1	98.14	Exp	1	2	0	2	1.35	0.79	0.48	0.63±0.22
C6 cyclic ketones		98.14	LM			0	7	1.35	0.79	0.48	0.63±0.22
mesityl oxide (2-methyl-2-penten-4-one)	141-79-7	98.14	LM			0	8	6.51	2.34	1.39	2.02±0.77
cyclohexanol	108-93-0	100.16	AdjP	1		0	6	1.95	1.07	0.68	0.88±0.27
hexanal	66-25-1	100.16	Exp	1		0	8	4.35	1.71	1.10	1.49±0.48
C6 aldehydes		100.16	LM			0	8	4.35	1.71	1.10	1.49±0.48
4-methyl-2-pentanone	108-10-1	100.16	Exp	1	2	0	3	3.88	1.68	1.08	1.44±0.43
methyl n-butyl ketone	591-78-6	100.16	Exp	1		0	8	3.14	1.54	0.99	1.30±0.39
methyl tert-butyl ketone	75-97-8	100.16	Exp	1		0	8	0.65	0.34	0.21	0.28±0.08
C6 ketones		100.16	LM			0	8	3.14	1.54	0.99	1.30±0.39
1-hexanol	111-27-3	102.17	AdjP	1		0	6	2.69	1.35	0.86	1.13±0.36
2-hexanol	626-93-7	102.17	AdjP	1		0	6	2.08	1.21	0.78	1.00±0.30
4-methyl-2-pentanol (methyl isobutyl carbinol)	108-11-2	102.17	AdjP			0	7	2.64	1.39	0.90	1.16±0.33
di-n-propyl ether	111-43-3	102.17	Exp	1		0	6	3.08	1.60	1.08	1.36±0.36
ethyl n-butyl ether	628-81-9	102.17	Exp	1		0	6	3.48	1.66	1.07	1.40±0.41
ethyl tert-butyl ether	637-92-3	102.17	Exp	1		0	6	2.01	0.99	0.63	0.83±0.23
methyl tert-amyl ether (TAME)	994-05-8	102.17	Exp	1		0	6	1.69	0.94	0.61	0.78±0.21
diisopropyl ether	108-20-3	102.17	Exp			0	7	3.52	1.45	0.89	1.23±0.41
ethyl methacrylate	97-63-2	114.14	Exp			0	8	12.47	4.02	2.27	3.49±1.59
ethyl butyrate	105-54-4	116.16	Exp	1		0	6	1.17	0.64	0.41	0.53±0.15
isobutyl acetate	110-19-0	116.16	Exp			0	7	0.62	0.43	0.30	0.36±0.08
methyl pivalate	598-98-1	116.16	Exp	1	2	0	2	0.35	0.22	0.133	0.172±0.054
n-butyl acetate	123-86-4	116.16	Exp	1	2	0,+	2	0.83	0.54	0.35	0.43±0.13
n-propyl propionate	106-36-5	116.16	Exp	1		0	6	0.84	0.52	0.33	0.42±0.14
sec-butyl acetate	105-46-4	116.16	Exp	1		0	6	1.32	0.79	0.54	0.67±0.17

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
tert-butyl acetate	540-88-5	116.16	Exp	1	3	0	2	0.180	0.102	0.062	0.082±0.024
diacetone alcohol	123-42-2	116.16	Exp			0	8	0.60	0.32	0.20	0.26±0.09
methyl pentanoate; methyl valerate	624-24-8	116.16	Exp			0	7	1.05	0.59	0.37	0.48±0.15
1,2-dihydroxyhexane	6920-22-5	118.17	AdjP			0	7	2.55	1.21	0.76	1.01±0.33
2-methyl-2,4-pentanediol	107-41-5	118.17	Exp	1		0	6	1.45	0.69	0.45	0.59±0.17
ethylene glycol diethyl ether; 1,2-diethoxyethane	629-14-1	118.17	Exp			0	7	2.95	1.44	0.93	1.21±0.35
acetal (1,1-diethoxyethane)	105-57-7	118.17	Exp			0	7	3.58	1.53	0.99	1.32±0.40
1-propoxy-2-propanol (propylene glycol n-propyl ether)	1569-01-3	118.17	AdjP			0	7	2.68	1.36	0.92	1.16±0.31
2-butoxy-ethanol	111-76-2	118.17	Exp	1	2	0	2	2.90	1.30	0.79	1.08±0.35
3 methoxy-3 methyl-butanol	56539-66-3	118.17	Exp	1	2	0	2	2.88	1.32	0.84	1.12±0.34
n-propoxy-propanol	30136-13-1	118.17	Exp			0	7	3.77	1.69	1.07	1.43±0.44
hydroxypropyl acrylate	2918-23-2	130.14	Exp			0	8	4.90	1.94	1.18	1.65±0.57
1-methoxy-2-propyl acetate	108-65-6	132.16	Exp	1	2	0,+	2	1.70	0.86	0.58	0.73±0.19
2-ethoxyethyl acetate	111-15-9	132.16	Exp			0	7	1.84	0.92	0.60	0.77±0.21
2-methyoxy-1-propyl acetate	70657-70-4	132.16	Exp			0	7	1.12	0.60	0.42	0.52±0.12
methoxypropanol acetate	84540-57-8	132.16	Exp			0	7	1.86	0.98	0.64	0.82±0.24
2-(2-ethoxyethoxy) ethanol	111-90-0	134.17	Exp	1	3	0	2	3.26	1.50	0.94	1.26±0.39
dipropylene glycol isomer (1-[2-hydroxypropyl]-2-propanol)	110-98-5	134.17	AdjP			0	7	2.31	1.18	0.79	1.00±0.28
dimethyl succinate	106-65-0	146.14	Exp	1	2	0	2	0.23	0.142	0.089	0.114±0.033
ethylene glycol diacetate	111-55-7	146.14	Exp			0	7	0.66	0.40	0.27	0.33±0.12
adipic acid (hexanedioic acid)	124-04-9	146.14	AdjP			0	8	3.08	1.46	0.93	1.23±0.40
triethylene glycol	112-27-6	150.17	Exp			0	7	3.25	1.51	0.94	1.26±0.40
benzaldehyde	100-52-7	106.12	Exp	1	3	0	2	-0.67	-0.69	-1.05	-0.90±0.29
C7 alkyl phenols	1319-77-3	108.14	LM			0	5	2.40	0.150	-0.74	-.187±0.661
m-cresol	108-39-4	108.14	LM		4	-,0	5	2.40	0.150	-0.74	-.187±0.661
p-cresol	106-44-5	108.14	LM		4	0?	5	2.40	0.150	-0.74	-.187±0.661
o-cresol	95-48-7	108.14	Exp	1	4	?	5	2.40	0.150	-0.74	-.187±0.661
benzyl alcohol	100-51-6	108.14	Exp	1	2	0	4	5.11	1.73	0.82	1.40±0.69
methoxybenzene; anisole	100-66-3	108.14	Exp	1		0	8	6.66	2.19	1.00	1.76±0.91
C7 cyclic ketones		112.17	LM			0	8	1.18	0.69	0.42	0.55±0.19
heptanal	111-71-7	114.19	Exp	1		0	8	3.69	1.45	0.92	1.26±0.41
C7 aldehydes		114.19	LM			0	8	3.69	1.45	0.92	1.26±0.41
2-methyl-hexanal	925-54-2	114.19	Exp			0	8	3.54	1.43	0.91	1.24±0.40
2-heptanone	110-43-0	114.19	Exp	1	3	?	4	2.36	1.23	0.75	1.00±0.33
2-methyl-3-hexanone	7379-12-6	114.19	Exp			0	8	1.53	0.83	0.52	0.68±0.23
di-isopropyl ketone	565-80-0	114.19	Exp	1		0	8	1.31	0.72	0.45	0.58±0.21
C7 ketones		114.19	LM			0	8	2.36	1.23	0.75	1.00±0.33
5-methyl-2-hexanone	110-12-3	114.19	AdjP	1		0	8	2.41	1.26	0.82	1.05±0.32
3-methyl-2-hexanone	2550-21-2	114.19	Exp			0	8	2.55	1.32	0.83	1.09±0.34
1-heptanol	111-70-6	116.20	Exp	1		0	6	1.84	0.97	0.59	0.79±0.26
dimethylpentanol (2,3-dimethyl-1-pentanol)	10143-23-4	116.20	Exp			0	7	2.23	1.09	0.67	0.90±0.29
4,4-diethyl-3-oxahexane	919-94-8	116.20	Exp			0	7	1.95	0.97	0.60	0.80±0.24
n-butyl acrylate	141-32-2	128.17	Exp			0	8	5.02	1.90	1.09	1.60±0.61

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
isobutyl acrylate	106-63-8	128.17	AdjP			0	8	4.72	1.80	1.02	1.51±0.59
butyl propionate	590-01-2	130.18	Exp			0	7	0.84	0.52	0.32	0.42±0.14
amyl acetate (n-pentyl acetate)	628-63-7	130.18	AdjP			0	7	0.84	0.55	0.32	0.42±0.14
n-propyl butyrate	105-66-8	130.18	Exp	1		0	6	1.05	0.61	0.38	0.49±0.16
isoamyl acetate (3-methyl-butyl acetate)	123-92-2	130.18	Exp			0	7	1.09	0.65	0.40	0.52±0.17
2-methyl-1-butyl acetate	624-41-9	130.18	Exp			0	7	1.08	0.67	0.43	0.55±0.15
methyl hexanoate	106-70-7	130.18	Exp			0	7	1.02	0.60	0.35	0.47±0.16
1-tert-butoxy-2-propanol	57018-52-7	132.20	AdjP			0	7	1.61	0.85	0.54	0.70±0.21
2-tert-butoxy-1-propanol	94023-15-1	132.20	Exp			0	7	1.81	0.72	0.41	0.60±0.22
n-butoxy-2-propanol (propylene glycol n-butyl ether)	5131-66-8	132.20	Exp			0	7	2.72	1.33	0.85	1.12±0.34
ethyl 3-ethoxy propionate	763-69-9	146.18	AdjP			0	7	3.58	1.45	0.85	1.21±0.43
diisopropyl carbonate	6482-34-4	146.18	Exp			0	7	0.98	0.51	0.32	0.42±0.12
2-(2-propoxyethoxy) ethanol	6881-94-3	148.20	Exp			0	7	2.85	1.37	0.86	1.14±0.35
dipropylene glycol methyl ether: 1-methoxy-2-(2-hydroxypropoxy)-propane		148.20	AdjP			0	7	1.98	0.99	0.66	0.84±0.23
dipropylene glycol methyl ether: 2-(2-methoxypropoxy)-1-propanol	13588-28-8	148.20	AdjP			0	7	2.58	1.16	0.73	0.98±0.30
1,2-propylene glycol diacetate	623-84-7	160.17	Exp			0	7	0.61	0.38	0.26	0.32±0.08
dimethyl glutarate	1119-40-0	160.17	AdjP	1	2	0	2	0.42	0.25	0.124	0.182±0.073
2-[2-(2-methoxyethoxy) ethoxy] ethanol	112-35-6	164.20	Exp			0	7	2.58	1.27	0.80	1.06±0.32
tolualdehyde		120.15	LM			0	7	-0.59	-0.61	-0.93	-0.79±0.26
4-vinyl phenol	2628-17-3	120.15	LM			0	11	1.50	0.185	-0.42	-.092±0.434
2,4-dimethyl phenol	105-67-9	122.16	LM			0	8	2.12	0.133	-0.66	-.166±0.585
2,5-dimethyl phenol		122.16	LM			0	8	2.12	0.133	-0.66	-.166±0.585
3,4-dimethyl phenol	95-65-8	122.16	LM			0	8	2.12	0.133	-0.66	-.166±0.585
2,3-dimethyl phenol	526-75-0	122.16	LM			0	8	2.12	0.133	-0.66	-.166±0.585
2,6-dimethyl phenol	576-26-1	122.16	LM			0	8	2.12	0.133	-0.66	-.166±0.585
C8 alkyl phenols		122.16	LM			0	8	2.12	0.133	-0.66	-.166±0.585
β-phenethyl alcohol (2-phenyl ethyl alcohol)	98-85-1	122.16	LM			-	11	4.53	1.53	0.73	1.24±0.61
C8 cyclic ketones		126.20	LM			0	8	1.05	0.61	0.37	0.49±0.17
2-butyl tetrahydrofuran	1004-29-1	128.21	Exp			0	7	2.13	1.06	0.62	0.85±0.31
octanal	124-13-0	128.21	Exp			0	8	3.16	1.24	0.77	1.07±0.36
C8 aldehydes		128.21	LM			0	8	3.16	1.24	0.77	1.07±0.36
2-octanone	111-13-7	128.21	Exp	1		0	8	1.40	0.80	0.44	0.61±0.23
C8 ketones		128.21	LM			0	8	1.40	0.80	0.44	0.61±0.23
1-octanol	111-87-5	130.23	Exp	1	2	+	2	1.43	0.79	0.45	0.62±0.22
2-ethyl-1-hexanol	104-76-7	130.23	Exp			0	7	2.00	0.99	0.58	0.80±0.27
2-octanol	4128-31-8	130.23	Exp	1	2	+	2	1.97	1.04	0.63	0.84±0.28
3-octanol	20296-29-1	130.23	Exp	1	2	+	2	2.28	1.16	0.72	0.95±0.31
4-octanol	589-62-8	130.23	AdjP	1		0	6	2.23	1.18	0.71	0.95±0.32
5-methyl-1-heptanol	7212-53-5	130.23	AdjP			0	7	1.79	0.91	0.52	0.72±0.26
di-isobutyl ether	628-55-7	130.23	Exp	1		0	6	1.20	0.67	0.41	0.54±0.17
di-n-butyl ether	142-96-1	130.23	Exp	1		0	6	2.84	1.40	0.88	1.16±0.37

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
2-phenoxyethanol; ethylene glycol phenyl ether	122-99-6	138.16	Exp			0	8	4.49	1.62	0.84	1.33±0.58
butyl methacrylate	97-88-1	142.20	Exp			0	8	8.70	2.85	1.58	2.45±1.12
isobutyl methacrylate	97-86-9	142.20	Exp			0	8	8.62	2.81	1.55	2.41±1.11
hexyl acetates		144.21	LM			0	7	0.80	0.51	0.28	0.38±0.14
2,3-dimethylbutyl acetate		144.21	Exp			0	7	0.75	0.48	0.28	0.37±0.12
2-methylpentyl acetate		144.21	Exp			0	7	0.98	0.59	0.33	0.45±0.17
3-methylpentyl acetate		144.21	AdjP			0	7	1.07	0.64	0.38	0.50±0.17
4-methylpentyl acetate		144.21	Exp			0	7	0.82	0.50	0.28	0.38±0.14
isobutyl isobutyrate	97-85-8	144.21	Exp			0	7	0.60	0.39	0.23	0.30±0.10
n-butyl butyrate	109-21-7	144.21	Exp	1		0	6	1.08	0.62	0.36	0.49±0.17
n-hexyl acetate	142-92-7	144.21	AdjP			0	7	0.69	0.47	0.24	0.34±0.14
methyl amyl acetate (4-methyl-2-pentanol acetate)	108-84-9	144.21	Exp			0	7	1.35	0.72	0.40	0.56±0.19
n-pentyl propionate	624-54-4	144.21	AdjP			0	7	0.71	0.46	0.24	0.34±0.13
2-ethyl hexanoic acid	149-57-5	144.21	Exp			0	7	3.32	1.42	0.79	1.15±0.43
methyl heptanoate	106-73-0	144.21	Exp			0	7	0.82	0.51	0.27	0.38±0.15
2-ethyl-1,3-hexanediol	94-96-2	146.23	AdjP			0	7	2.05	1.03	0.64	0.85±0.28
2-n-hexyloxyethanol	112-25-4	146.23	AdjP			0	7	2.09	1.05	0.63	0.85±0.28
2,2,4-trimethyl-1,3-pentanediol	144-19-4	146.23	Exp			0	7	1.54	0.81	0.51	0.67±0.21
phthalic anhydride	85-44-9	148.12	Exp			0	8	2.58	0.92	0.40	0.71±0.37
methylparaben (4-Hydroxybenzoic acid, methyl ester)	99-76-3	152.15	LM			0	11	1.71	0.107	-0.53	-.133±0.470
2-butoxyethyl acetate	112-07-2	160.21	Exp			0	7	1.62	0.85	0.53	0.70±0.21
2-methoxy-1-(2-methoxy-1-methylethoxy)-propane; dipropylene glycol dimethyl ether	89399-28-0	162.23	AdjP			0	7	2.02	0.98	0.64	0.83±0.23
2-(2-butoxyethoxy)-ethanol	112-34-5	162.23	Exp		2	0	7	2.39	1.15	0.69	0.94±0.32
dipropylene glycol ethyl ether	15764-24-6	162.23	Exp			0	7	2.72	1.24	0.75	1.03±0.34
dimethyl adipate	627-93-0	174.19	AdjP	1		0	6	1.80	0.84	0.48	0.68±0.25
2-(2-ethoxyethoxy) ethyl acetate	112-15-2	176.21	AdjP			0	7	1.48	0.78	0.50	0.64±0.18
2-[2-(2-ethoxyethoxy) ethoxy] ethanol	112-50-5	178.23	Exp			0	7	2.46	1.21	0.75	1.00±0.32
tetraethylene glycol	112-60-7	194.23	Exp			0	7	2.51	1.20	0.75	1.00±0.32
cinnamic aldehyde	104-55-2	132.16	LM			0	10	4.84	1.74	1.03	1.50±0.57
Cinnamic alcohol	104-54-1	134.18	LM			-1	10	0.89	0.136	-0.28	-.065±0.265
2,3,5-trimethyl phenol	697-82-5	136.19	LM			0	8	1.90	0.119	-0.59	-.149±0.525
2,3,6-trimethyl phenol	2416-94-6	136.19	LM			0	8	1.90	0.119	-0.59	-.149±0.525
C9 alkyl phenols		136.19	LM			0	8	1.90	0.119	-0.59	-.149±0.525
isophorone (3,5,5-trimethyl-2-cyclohexenone)	78-59-1	138.21	LM			0	8	4.63	1.66	0.99	1.44±0.54
C9 cyclic ketones		140.22	LM			0	8	0.94	0.55	0.33	0.44±0.15
2-propyl cyclohexanone	94-65-5	140.22	AdjP			0	8	1.54	0.85	0.46	0.65±0.27
4-propyl cyclohexanone	40649-36-3	140.22	Exp			0	8	1.85	0.97	0.56	0.77±0.29
1-nonene-4-one	61168-10-3	140.22	Exp			0	8	3.14	1.28	0.74	1.06±0.39
trimethyl cyclohexanol	1321-60-4	142.24	AdjP			0	7	1.86	1.01	0.56	0.78±0.29

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
2-nonanone	821-55-6	142.24	Exp	1		0	8	1.08	0.64	0.32	0.47±0.20
di-isobutyl ketone (2,6-dimethyl-4-heptanone)	108-83-8	142.24	Exp	1		0	8	2.68	1.20	0.72	0.99±0.33
C9 ketones		142.24	LM			0	8	1.08	0.64	0.32	0.47±0.20
dimethyl heptanol (2,6-dimethyl-2-heptanol)	13254-34-7	144.25	Exp			0	7	0.94	0.53	0.28	0.40±0.16
2,6-dimethyl-4-heptanol	108-82-7	144.25	AdjP			0	7	2.09	1.06	0.62	0.85±0.30
1-phenoxy-2-propanol	770-35-4	152.19	LM			0	8	1.60	0.65	0.28	0.49±0.24
2,4-dimethylpentyl acetate		158.24	Exp			0	7	0.92	0.53	0.26	0.39±0.16
2-methylhexyl acetate		158.24	AdjP			0	7	0.69	0.45	0.21	0.31±0.15
3-ethylpentyl acetate		158.24	Exp			0	7	1.10	0.65	0.36	0.50±0.19
3-methylhexyl acetate		158.24	Exp			0	7	0.89	0.55	0.28	0.40±0.17
4-methylhexyl acetate		158.24	Exp			0	7	0.82	0.50	0.26	0.37±0.15
5-methylhexyl acetate		158.24	AdjP			0	7	0.59	0.39	0.167	0.27±0.14
isoamyl isobutyrate	2050-01-3	158.24	Exp			0	7	0.82	0.48	0.26	0.36±0.14
n-heptyl acetate	112-06-1	158.24	Exp			0	7	0.65	0.44	0.20	0.30±0.14
methyl octanoate	111-11-5	158.24	Exp			0	7	0.69	0.44	0.20	0.31±0.14
1-(butoxyethoxy)-2-propanol	124-16-3	176.25	AdjP			0	7	1.93	1.00	0.63	0.83±0.25
dipropylene glycol n-propyl ether isomer #1		176.25	AdjP			0	7	2.00	1.01	0.64	0.84±0.25
dipropylene glycol methyl ether acetate isomer #1		190.24	AdjP			0	7	1.38	0.72	0.45	0.59±0.17
dipropylene glycol methyl ether acetate isomer #2		190.24	AdjP			0	7	1.52	0.77	0.48	0.63±0.19
dipropylene glycol methyl ether acetate isomers	88917-22-0	190.24	LM			0	7	1.45	0.74	0.46	0.61±0.18
2-[2-(2-propoxyethoxy) ethoxy] ethanol	23305-64-8	192.25	Exp			0	7	2.17	1.08	0.66	0.88±0.29
tripropylene glycol	24800-44-0	192.25	Exp			0	7	2.18	1.10	0.68	0.90±0.29
2,5,8,11-tetraoxatridecan-13-ol	23783-42-8	208.25	Exp			0	7	1.97	1.00	0.62	0.82±0.27
glyceryl triacetate	102-76-1	218.20	Exp			0	7	0.55	0.34	0.20	0.27±0.09
anethol (p-propenyl-anisole)	104-46-1	148.20	LM			0	11	0.80	0.123	-0.25	-.059±0.239
C10 alkyl phenols		150.22	LM			0	8	1.73	0.108	-0.53	-.135±0.476
camphor	76-22-2	152.23	Exp			0	8	0.49	0.31	0.129	0.21±0.12
α-terpineol	98-55-5	154.25	Exp			0	8	4.63	1.63	0.89	1.38±0.64
citronellol (3,7-dimethy-6-octen-1-ol)	106-22-9	154.25	Exp			0	8	5.79	1.99	1.09	1.70±0.79
hydroxycitronella	107-75-5	154.25	Exp			0	8	2.61	1.03	0.64	0.89±0.30
C10 cyclic ketones		154.25	LM			0	8	0.86	0.50	0.30	0.40±0.14
menthol	89-78-1	156.27	Exp			0	7	1.43	0.76	0.44	0.60±0.22
linalool	78-70-6	156.27	Exp			0	8	5.43	1.91	1.07	1.63±0.75
2-decanone	693-54-9	156.27	AdjP	1		0	8	0.90	0.55	0.25	0.38±0.19
C10 ketones		156.27	LM			0	8	0.90	0.55	0.25	0.38±0.19
8-methyl-1-nonanol (isodecyl alcohol)	25339-17-7	158.28	Exp			0	7	1.06	0.58	0.30	0.44±0.18
1-decanol	112-30-1	158.28	Exp			0	7	1.06	0.59	0.31	0.45±0.18
3,7-dimethyl-1-octanol	106-21-8	158.28	Exp			0	7	1.20	0.63	0.34	0.49±0.19
di-n-pentyl ether	693-65-2	158.28	AdjP	1		0	6	2.15	1.16	0.71	0.94±0.31
1,2-diacetyl benzene	704-00-7	162.19	Exp	1		0	8	2.25	0.79	0.33	0.60±0.33

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
2,4-dimethylhexyl acetate		172.26	AdjP			0	7	0.76	0.47	0.21	0.33±0.16
2-ethyl-hexyl acetate	103-09-3	172.26	AdjP			0	7	0.66	0.43	0.175	0.28±0.15
3,4-dimethyl-hexyl acetate		172.26	AdjP			0	7	0.87	0.55	0.28	0.40±0.17
3,5-dimethyl-hexyl acetate		172.26	Exp			0	7	0.99	0.58	0.28	0.41±0.18
3-ethyl-hexyl acetate		172.26	Exp			0	7	0.91	0.55	0.28	0.40±0.17
3-methyl-heptyl acetate		172.26	Exp			0	7	0.67	0.44	0.194	0.30±0.15
4,5-dimethyl-hexyl acetate		172.26	AdjP			0	7	0.68	0.43	0.20	0.30±0.14
4-methyl-heptyl acetate		172.26	Exp			0	7	0.66	0.42	0.187	0.29±0.14
5-methyl-heptyl acetate		172.26	AdjP			0	7	0.61	0.41	0.163	0.27±0.15
n-octyl acetate	112-14-1	172.26	Exp			0	7	0.57	0.39	0.163	0.26±0.14
geraniol	106-24-1	172.26	Exp			0	8	5.12	1.84	1.04	1.58±0.71
methyl nonanoate	1731-84-6	172.26	Exp			0	7	0.59	0.39	0.161	0.26±0.14
2-(2-ethylhexyloxy) ethanol	1559-35-9	174.28	AdjP			0	7	1.55	0.83	0.44	0.63±0.25
propylparaben	94-13-3	180.20	LM			0	11	1.44	0.090	-0.45	-.112±0.397
2-(2-hexyloxyethoxy) ethanol	112-59-4	190.28	AdjP			0	7	1.84	0.97	0.57	0.77±0.26
glycol ether DPnB (dipropylene glycol n-butyl ether) (1-[2-butoxy-1-methylethoxy]-2-propanol)	29911-28-2	190.28	AdjP			0	7	1.83	0.93	0.57	0.76±0.24
2-(2-butoxyethoxy) ethyl acetate	124-17-4	204.26	Exp			0	7	1.38	0.73	0.44	0.59±0.20
2-[2-(2-butoxyethoxy) ethoxy] ethanol	143-22-6	206.28	Exp			0	7	1.96	0.98	0.60	0.80±0.27
tripropylene glycol monomethyl ether	25498-49-1	206.28	Exp			0	7	1.92	0.96	0.59	0.78±0.26
C11 alkyl phenols		164.24	LM			0	8	1.58	0.099	-0.49	-.123±0.435
2-ethyl-hexyl acrylate	103-11-7	184.28	Exp			0	8	2.52	0.99	0.50	0.79±0.33
2,3,5-trimethyl-hexyl acetate		186.29	AdjP			0	7	0.85	0.51	0.24	0.37±0.16
2,3-dimethyl-heptyl acetate		186.29	Exp			0	7	0.71	0.46	0.21	0.32±0.15
2,4-dimethyl-heptyl acetate		186.29	AdjP			0	7	0.68	0.42	0.164	0.28±0.16
2,5-dimethyl-heptyl acetate		186.29	Exp			0	7	0.78	0.49	0.23	0.35±0.16
2-methyloctyl acetate		186.29	AdjP			0	7	0.52	0.35	0.118	0.22±0.15
3,5-dimethyl-heptyl acetate		186.29	AdjP			0	7	0.81	0.50	0.21	0.34±0.18
3,6-dimethyl-heptyl acetate		186.29	Exp			0	7	0.78	0.48	0.21	0.33±0.17
3-ethyl-heptyl acetate		186.29	Exp			0	7	0.63	0.41	0.172	0.28±0.15
4,5-dimethyl-heptyl acetate		186.29	AdjP			0	7	0.69	0.44	0.196	0.30±0.15
4,6-dimethyl-heptyl acetate		186.29	Exp			0	7	0.78	0.47	0.21	0.33±0.16
4-methyloctyl acetate		186.29	Exp			0	7	0.61	0.40	0.167	0.27±0.14
5-methyloctyl acetate		186.29	AdjP			0	7	0.56	0.38	0.134	0.24±0.15
n-nonyl acetate	143-13-5	186.29	Exp			0	7	0.52	0.36	0.139	0.23±0.13
methyl decanoate	110-42-9	186.29	Exp			0	7	0.53	0.35	0.136	0.23±0.13
C12 alkyl phenols		178.27	LM			0	8	1.46	0.091	-0.45	-.114±0.401
2,6,8-trimethyl-4-nonanone (isobutyl heptyl ketone)	123-18-2	184.32	Exp			0	8	1.66	0.81	0.44	0.63±0.24
trimethylnonanolthreoerythro (2,6,8-trimethyl-4-nonanol)	123-17-1	186.33	AdjP			0	7	1.33	0.70	0.36	0.53±0.22
3,6-dimethyl-octyl acetate		200.32	Exp			0	7	0.79	0.48	0.22	0.34±0.17
3-isopropyl-heptyl acetate		200.32	AdjP			0	7	0.54	0.37	0.134	0.23±0.15
4,6-dimethyl-octyl acetate		200.32	Exp			0	7	0.76	0.46	0.20	0.32±0.16

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
methyl undecanoate	1731-86-8	200.32	Exp			0	7	0.50	0.33	0.123	0.21±0.13
1-hydroxy-2,2,4-trimethylpentyl-3-isobutyrate	18491-15-1	216.32	Exp			0	7	0.89	0.43	0.23	0.34±0.13
3-hydroxy-2,2,4-trimethylpentyl-1-isobutyrate	77-68-9	216.32	AdjP			0	7	0.77	0.43	0.22	0.32±0.13
2,2,4-trimethyl-1,3-pentanediol monoisobutyrate and isomers (texanol®)	25265-77-4	216.32	LM	1	2	0	2	0.81	0.43	0.23	0.33±0.13
substituted C7 ester (C12)		216.32	LM			0	7	0.81	0.43	0.23	0.33±0.13
substituted C9 ester (C12)		216.32	LM			0	7	0.81	0.43	0.23	0.33±0.13
diethylene glycol mono(2-ethylhexyl) ether	1559-36-0	218.33	Exp			0	7	1.56	0.82	0.47	0.64±0.24
diethyl phthalate	84-66-2	222.24	Exp			0	8	1.62	0.60	0.26	0.46±0.23
dimethyl sebacate	106-79-6	230.30	Exp			0	7	0.43	0.28	0.102	0.178±0.106
diisopropyl adipate	6938-94-9	230.30	Exp			0	7	1.28	0.55	0.25	0.41±0.19
3,6,9,12-tetraoxa-hexadecan-1-ol	1559-34-8	250.33	AdjP			0	7	1.72	0.88	0.53	0.71±0.24
triethyl citrate	77-93-0	276.28	Exp			0	8	0.70	0.33	0.171	0.25±0.10
3,5,7-trimethyl-octyl acetate		214.34	AdjP			0	7	0.66	0.41	0.157	0.27±0.16
3-ethyl-6-methyl-octyl acetate		214.34	AdjP			0	7	0.63	0.41	0.158	0.27±0.16
4,7-dimethyl-nonyl acetate		214.34	AdjP			0	7	0.50	0.34	0.109	0.21±0.14
methyl dodecanoate (methyl laurate)	111-82-0	214.34	Exp			0	7	0.47	0.31	0.114	0.199±0.124
tripropylene glycol n-butyl ether	55934-93-5	248.36	Exp			0	7	1.64	0.80	0.47	0.64±0.23
amyl cinnamal	122-40-7	202.29	LM			0	10	3.16	1.14	0.68	0.98±0.37
isobornyl methacrylate	7534-94-3	222.32	LM			+	10	5.51	1.80	0.99	1.54±0.71
2,3,5,7-tetramethyl-octyl acetate		228.37	Exp			0	7	0.62	0.39	0.161	0.26±0.15
3,5,7-trimethyl-nonyl acetate		228.37	AdjP			0	7	0.62	0.38	0.149	0.25±0.15
3,6,8-trimethyl-nonyl acetate		228.37	AdjP			0	7	0.59	0.37	0.130	0.24±0.15
methyl tridecanoate	1731-88-0	228.37	Exp			0	7	0.45	0.30	0.109	0.190±0.119
hexyl cinnamal	101-86-0	216.32	LM			0	10	2.96	1.06	0.63	0.92±0.35
2,6-di-tert-butyl-p-cresol	128-37-0	220.35	LM			0	10	1.18	0.074	-0.36	-.092±0.324
2-ethyl-hexyl benzoate	5444-75-7	234.33	Exp			0	10	0.98	0.46	0.20	0.33±0.16
2,4,6,8-tetramethyl-nonyl acetate		242.40	AdjP			0	7	0.51	0.32	0.107	0.20±0.14
3-ethyl-6,7-dimethyl-nonyl acetate		242.40	AdjP			0	7	0.61	0.40	0.156	0.26±0.15
4,7,9-trimethyl-decyl acetate		242.40	AdjP			0	7	0.42	0.28	0.072	0.160±0.134
methyl myristate (methyl tetradecanoate)	124-10-7	242.40	Exp			0	7	0.43	0.29	0.106	0.184±0.115
methyl cis-9-pentadecenoate		254.41	Exp			0	8	1.80	0.79	0.46	0.65±0.25
methyl pentadecanoate	7132-64-1	256.42	Exp			0	7	0.47	0.30	0.125	0.20±0.12
2,3,5,6,8-pentamethyl-nonyl acetate		256.42	Exp			0	7	0.65	0.42	0.183	0.29±0.15
3,5,7,9-tetramethyl-decyl acetate		256.42	AdjP			0	7	0.48	0.31	0.098	0.190±0.143
5-ethyl-3,6,8-trimethyl-nonyl acetate		256.42	AdjP			0	7	0.77	0.46	0.20	0.32±0.16

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
dibutyl phthalate	84-74-2	278.34	Exp			0	8	1.25	0.49	0.23	0.38±0.18
2,2,4-trimethyl-1,3-pentanediol diisobutyrate	6846-50-0	286.41	Exp			0	7	0.38	0.24	0.092	0.157±0.091
methyl cis-9-hexadecenoate (methyl palmitoleate)	1120-25-8	268.43	LM			0	8	1.70	0.75	0.44	0.62±0.23
methyl hexadecanoate (methyl palmitate)	112-39-0	270.45	LM			0	7	0.44	0.29	0.118	0.192±0.111
Methyl cis-9-heptadecenoate		282.46	LM			0	8	1.62	0.71	0.42	0.58±0.22
methyl heptadecanoate (methyl margarate)	1731-92-6	284.48	LM			0	7	0.42	0.27	0.113	0.182±0.105
methyl linolenate (methyl cis,cis,cis-9,12,15-octadecatrienoate)	301-00-8	292.46	Exp			0	8	2.32	0.95	0.57	0.80±0.29
methyl linoelate (methyl cis,cis-9,12-octadecadienoate)	112-63-0	294.47	Exp			0	8	1.84	0.78	0.47	0.65±0.24
methyl cis-9-octadecenoate (methyl oleate)	112-62-9	296.49	LM			0	8	1.54	0.68	0.40	0.56±0.21
methyl octadecanoate (methyl stearate)	112-61-8	298.50	LM			0	7	0.40	0.26	0.107	0.174±0.100
		Other Organic Compounds									
methylamine	74-89-5	31.06	Exp	1		+	13 a,n	7.70	4.24	2.72	3.51±1.06
methyl chloride	74-87-3	50.49	Exp	1		0	10	0.038	0.022	.0140	.0179±.0050
methyl nitrite	624-91-9	61.04	Exp	1		0	6	10.84	4.41	3.89	4.49±1.13
nitromethane	75-52-5	61.04	Exp	1		0	8	0.068	0.042	0.031	0.037±0.007
carbon disulfide	75-15-0	76.14	Exp	1	2	0	2	0.25	0.161	0.121	0.141±0.025
dichloromethane	75-09-2	84.93	Exp	1		0	10	0.041	0.029	0.021	0.024±0.006
methyl bromide	74-83-9	94.94	Exp	1		0	10	.0187	.0106	.0068	.0088±.0024
chloroform	67-66-3	119.38	Exp	1		0	10	0.022	.0152	.0107	.0127±.0033
methyl iodide	74-88-4	141.94	Exp			0	3	-0.56	-2.10	-2.76	-2.30±0.67
carbon tetrachloride	56-23-5	153.82	LM			0	1	0	0	0	0
chloropicrin (trichloro-nitro-methane)	76-06-2	164.38	Exp	1	2	0	1	1.85	1.04	1.13	1.13±0.20
methylene bromide	74-95-3	173.83	LM			0	1	0	0	0	0
acetylene	74-86-2	26.04	Exp	1	2	-	3	0.95	0.37	0.189	0.30±0.14
dimethyl amine	124-40-3	45.08	Exp	1		+	13 a,n	3.17	2.07	1.47	1.74±0.59
ethyl amine	75-04-7	45.08	Exp	1		+	13 a,n	5.78	3.10	1.99	2.58±0.78
ethanolamine	141-43-5	61.08	Exp		3a	+	12 a,n	6.81	3.05	1.88	2.56±0.82
vinyl chloride	75-01-4	62.50	Exp	1		0	10	2.83	1.48	0.99	1.26±0.34
ethyl chloride	75-00-3	64.51	Exp	1		0	10	0.29	0.182	0.122	0.151±0.044
1,1-difluoroethane; HFC-152a	75-37-6	66.05	Exp	1		+	6	.0175	.0123	.0089	.0105±.0028
methyl isothiocyanate	556-61-6	73.12	Exp	1	2	0	2	0.32	0.21	0.180	0.195±0.027
nitroethane	79-24-3	75.07	Exp	1		0	7	0.063	0.044	0.032	0.038±0.010
dimethyl sulfoxide (DMSO)	67-68-5	78.13	Exp	1	2	-2,0	4	6.68	2.37	1.46	2.08±0.81
chloroacetaldehyde	107-20-0	78.50	Exp	1		0	7	12.30	3.52	1.74	3.00±1.71
1,1-dichloroethene	75-35-4	96.94	Exp			0	10	1.79	0.96	0.65	0.82±0.22
trans-1,2-dichloroethene	156-60-5	96.94	Exp	1		0	10	1.70	0.76	0.45	0.62±0.22
cis-1,2-dichloroethene		96.94	LM			0	10	1.70	0.76	0.45	0.62±0.22
1,1-dichloroethane	75-34-3	98.96	Exp	1		0	10	0.069	0.047	0.033	0.040±0.010
1,2-dichloroethane	107-06-2	98.96	Exp	1		0	10	0.21	0.103	0.061	0.083±0.028

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
1,1,1,2-tetrafluoroethane; HFC-134a	811-97-2	102.03	Exp	1		0	6	.0007	.0007	.0006	.0007±.0001
ethyl bromide	74-96-4	108.97	Exp	1		0	20	0.129	0.082	0.055	0.068±0.020
trichloroethylene	79-01-6	131.39	Exp	1	2x	+2	20	0.64	0.35	0.23	0.29±0.08
1,1,1-trichloroethane	71-55-6	133.40	Exp	1		0	10	.0049	.0031	.0021	.0026±.0006
1,1,2-trichloroethane	79-00-5	133.40	Exp	1		0	10	0.086	0.045	0.028	0.037±0.011
perchloroethylene	127-18-4	165.83	Exp	1		0	10	0.031	0.022	.0149	.0179±.0051
1,2-dibromoethane	106-93-4	187.86	Exp	1		0	20	0.102	0.049	0.029	0.040±0.013
methyl acetylene	74-99-7	40.06	Exp	1		-	7	6.72	2.45	1.37	2.06±0.86
acrylonitrile	107-13-1	53.06	Exp	1		0	10	2.24	1.08	0.72	0.93±0.25
trimethyl amine	75-50-3	59.11	Exp	1		+	13 a,n	6.32	3.05	1.95	2.57±0.79
isopropyl amine	75-31-0	59.11	Exp		4a	+	12 a,n	7.23	3.32	2.09	2.80±0.86
1-amino-2-propanol	78-96-6	75.11	Exp			+	13 a,n	5.42	2.64	1.71	2.23±0.66
3-chloropropene		76.52	Exp			0	10	12.22	3.84	2.05	3.28±1.60
1-nitropropane	108-03-2	89.09	Exp			0	8	0.22	0.158	0.116	0.135±0.029
2-nitropropane	79-46-9	89.09	Exp	1		0	6	0.110	0.071	0.049	0.059±0.019
chloroacetone	78-95-5	92.52	Exp	1		0	7	9.41	2.64	1.30	2.24±1.29
trans-1,3-dichloropropene	10061-02-6	110.97	Exp	1	2m	0	3	5.03	1.78	1.00	1.50±0.63
cis-1,3-dichloropropene	10061-01-5	110.97	Exp	1	2m	0	3	3.70	1.41	0.81	1.18±0.46
1,3-dichloropropene mixture		110.97	LM	1	2	0	2	4.29	1.57	0.90	1.32±0.53
1,2-dichloropropane	78-87-5	112.99	Exp			0	10	0.29	0.143	0.087	0.117±0.038
trans-1,3,3,3-tetrafluoropropene	1645-83-6	114.04	Exp	1	2	0	1	0.098	0.076	0.055	0.065±0.013
2,3,3,3-tetrafluoropropene	754-12-1	114.04	Exp	1	2	0	1	0.28	0.155	0.107	0.133±0.031
n-propyl bromide	106-94-5	122.99	Exp	1	2x	-,+2	20 n	0.42	0.23	0.147	0.190±0.061
1,1,1,3,3-pentafluoropropane	460-73-1	134.05	Exp	1		0	6	.0008	.0006	.0004	.0005±.0001
3,3-dichloro-1,1,1,2,2-pentafluoropropane;HCFC-225ca	422-56-0	202.94	Exp	1		0	6	.0029	.0020	.0014	.0017±.0005
1,3-dichloro-1,1,2,2,3-pentafluoropropane;HCFC-225cb	507-55-1	202.94	Exp	1		0	6	.0011	.0007	.0005	.0006±.0002
1,3-butadiyne	460-12-8	50.06	Exp			0	11	5.76	2.64	1.73	2.26±0.73
1-buten-3-yne (vinyl acetylene)	689-97-4	52.07	LM			0	11	10.48	4.12	2.55	3.55±1.22
2-butyne	503-17-3	54.09	Exp	1		0	10	16.32	5.40	3.07	4.67±2.05
ethyl acetylene	107-00-6	54.09	Exp	1		-	7	6.11	2.23	1.25	1.87±0.78
tert-butyl amine	75-64-9	73.14	Exp	1	4a	-	12 a	-0.39	-0.83	-1.86	-1.41±0.68
morpholine	110-91-8	87.12	Exp			+	13 a,n	1.98	1.21	0.84	1.01±0.35
ethyl methyl ketone oxime (methyl ethyl ketoxime)	96-29-7	87.12	Exp			0	10	1.58	1.32	1.47	1.42±0.33
dimethylaminoethanol	108-01-0	89.14	Exp	1		+	13 a,n	5.62	2.32	1.46	1.99±0.65
2-amino-1-butanol	96-20-8	89.14	Exp			+	13 a,n	4.98	2.18	1.34	1.83±0.60
2-amino-2-methyl-1-propanol	124-68-5	89.14	Exp		3a	-	12 a	0.25	-0.19	-1.03	-0.66±0.54
1-chlorobutane	109-69-3	92.57	Exp			0	10	1.10	0.63	0.40	0.52±0.15
diethanol-amine	111-42-2	105.14	Exp			+	13 a,n	2.47	1.17	0.76	0.99±0.32
2-(chloro-methyl)-3-chloro-propene	1871-57-4	125.00	Exp	1	4	-	20	7.00	2.31	1.28	1.96±0.87
n-butyl bromide	109-65-9	137.02	Exp	1	2x	-,+2	20 n	0.82	0.47	0.30	0.38±0.11
1,1,1,3,3-pentafluorobutane; HFC-365mfc	406-58-6	148.07	Exp	1		0	6	.0006	.0005	.0003	.0004±.0001

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
2-amino-2-ethyl-1,3-propanediol	115-70-8	119.16	Exp			-	13 a	0.78	0.163	-0.44	-.161±0.380
n-methyl-2-pyrrolidone	872-50-4	99.13	Exp	1	2	0	2	2.41	1.24	0.74	1.00±0.34
methyl-nonafluoro-butyl ether	163702-07-6	234.06	Exp			0	8	0.055	0.044	0.032	0.037±0.008
methyl-nonafluoro-isobutyl ether	163702-08-7	234.06	LM			0	8	0.055	0.044	0.032	0.037±0.008
methoxy-perfluoro-n-butane	163702-07-6	250.06	Exp	1		0	6	.0006	.0005	.0003	.0004±.0001
methoxy-perfluoro-isobutene	163702-08-7	250.06	LM	1		0	6	.0006	.0005	.0003	.0004±.0001
1,1,1,2,2,3,4,5,5,5-decafluoropentane; HFC-43-10mee	138495-42-8	252.05	Exp	1		0	6	.0002	.0001	.0001	.0001±.0000
triethyl amine	121-44-8	101.19	Exp			+	13 a,n	3.84	1.72	1.05	1.43±0.48
triethylene diamine	280-57-9	112.17	LM			+	13 a,n	3.46	1.55	0.95	1.29±0.44
monochlorobenzene	108-90-7	112.56	Exp	1		0	8	0.32	0.043	-0.074	-.006±0.084
nitrobenzene	98-95-3	123.11	Exp	1		0	8	0.056	.0070	-0.014	-.002±0.015
p-dichlorobenzene	106-46-7	147.00	Exp			0	10	0.178	0.024	-0.042	-.004±0.047
o-dichlorobenzene	95-50-1	147.00	LM			0	8	0.178	0.024	-0.042	-.004±0.047
triethanolamine	102-71-6	149.19	Exp			+	13 a,n	4.21	1.62	0.93	1.36±0.54
hexamethyl-disiloxane	107-46-0	162.38	Exp	1	3	0	5	-0.025	0.026	0.036	0.028±0.018
hydroxymethyl-disiloxane		164.35	Exp	1	3	0	5	-0.133	-0.011	0.021	-.001±0.036
hexafluoro-benzene	392-56-3	186.05	Exp	1		0	8	0.047	.0057	-0.012	-.002±0.013
ethoxy-perfluoro-n-butane	163702-05-4	264.09	Exp	1		0	6	.0082	.0049	.0032	.0040±.0011
ethoxy-perfluoro-isobutane	163702-06-5	264.09	Exp	1		0	6	.0098	.0059	.0038	.0049±.0013
ethyl nonafluorobutyl ether	163702-05-4	264.09	Exp			+	8	0.21	0.132	0.088	0.109±0.026
ethyl nonafluoroisobutyl ether	163702-06-5	264.09	LM			+	8	0.21	0.132	0.088	0.109±0.026
perfluoro-n-hexane	355-42-0	338.04	LM			0	1	0	0	0	0
2-chlorotoluene	95-49-8	126.58	LM			1	8	2.92	0.99	0.38	0.75±0.44
m-nitrotoluene	99-08-1	137.14	Exp	1		0	8	0.50	0.164	0.028	0.103±0.092
benzotrifluoride	98-08-8	146.11	Exp	1		0	8	0.29	0.108	0.040	0.079±0.047
p-trifluoromethyl-chlorobenzene	98-56-6	180.55	Exp	1		0	8	0.126	0.046	.0173	0.034±0.020
p-toluene isocyanate	622-58-2	133.15	Exp	1	2	0	5	1.06	-0.085	-0.53	-0.25±0.34
3-(chloromethyl)-heptane	123-04-6	148.67	LM			0	10	0.95	0.60	0.32	0.44±0.17
cyclosiloxane D4 (octamethylcyclotetrasiloxane)	556-67-2	296.62	Exp	1	3	0	5	-0.058	-0.011	.0029	-.006±0.014
2,4-toluene diisocyanate	584-84-9	174.16	Exp	1	2	0	5	-0.065	-0.52	-0.81	-0.64±0.23
2,6-toluene diisocyanate	91-08-7	174.16	LM		4	0	5	-0.065	-0.52	-0.81	-0.64±0.23
toluene diisocyanate (mixed isomers)	26471-62-5	174.16	LM			0	5	-0.065	-0.52	-0.81	-0.64±0.23
molinate (S-ethyl hexahydro-1H-azepine-1-carbothioate)	2212-67-1	187.30	Exp			0	7	1.51	0.74	0.46	0.62±0.20
EPTC (S-ethyl dipropylthiocarbamate)	759-94-4	189.32	Exp	1	2	0	2	1.67	0.87	0.54	0.71±0.23
triisopropanolamine	122-20-3	191.27	Exp			+	13 a,n	2.70	1.18	0.70	0.98±0.35
pebulate (S-propyl butylethylthiocarbamate)	1114-71-2	203.34	Exp			0	7	1.67	0.84	0.50	0.68±0.23
cyclosiloxane D5 (decamethylcyclopentasiloxane)	541-02-6	370.77	Exp	1	4	0	5	-0.069	-0.013	.0030	-.008±0.017
thiobencarb (S-[4-chlorobenzyl] N,N-diethylthiolcarbamate)	28249-77-6	257.78	Exp			0	8	0.68	0.29	0.110	0.20±0.11

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
methylene diphenylene diisocyanate	101-68-8	250.25	Exp			0	8	0.89	0.021	-0.30	-.100±0.240
lauryl pyrrolidone	2687-96-9	253.42	LM			0	11	0.94	0.48	0.29	0.39±0.13
<u>CARB Hydrocarbon Bins</u>											
CARB Hydrocarbon Bin 1		14.25	Mix			0	7 c	1.42	0.90	0.55	0.72±0.22
CARB Hydrocarbon Bin 2		14.37	Mix			0	7 c	1.31	0.85	0.53	0.68±0.20
CARB Hydrocarbon Bin 3		14.03	Mix			0	7 c	1.63	1.01	0.60	0.80±0.26
CARB Hydrocarbon Bin 4		14.19	Mix			0	7 c	1.47	0.90	0.53	0.71±0.23
CARB Hydrocarbon Bin 5		14.06	Mix			0	7 c	1.56	0.88	0.50	0.69±0.23
CARB Hydrocarbon Bin 6		14.18	Mix			0	7 c	1.17	0.72	0.35	0.52±0.23
CARB Hydrocarbon Bin 7		14.26	Mix			0	7 c	1.03	0.66	0.32	0.47±0.21
CARB Hydrocarbon Bin 8		14.03	Mix			0	7 c	1.44	0.84	0.43	0.62±0.26
CARB Hydrocarbon Bin 9		14.13	Mix			0	7 c	1.44	0.79	0.39	0.58±0.25
CARB Hydrocarbon Bin 10		14.04	Mix			0	7 c	1.98	0.94	0.45	0.70±0.30
CARB Hydrocarbon Bin 11		14.14	Mix			0	8 c	0.70	0.46	0.174	0.30±0.18
CARB Hydrocarbon Bin 12		14.20	Mix			0	8 c	0.62	0.42	0.150	0.26±0.17
CARB Hydrocarbon Bin 13		14.03	Mix			0	8 c	0.86	0.53	0.22	0.36±0.20
CARB Hydrocarbon Bin 14		14.10	Mix			0	8 c	0.99	0.54	0.22	0.37±0.19
CARB Hydrocarbon Bin 15		14.02	Mix			0	8 c	1.57	0.72	0.32	0.52±0.24
CARB Hydrocarbon Bin 16		14.11	Mix			0	8 c	0.52	0.35	0.131	0.22±0.15
CARB Hydrocarbon Bin 17		14.16	Mix			0	8 c	0.48	0.33	0.122	0.21±0.14
CARB Hydrocarbon Bin 18		14.03	Mix			0	8 c	0.60	0.39	0.148	0.25±0.16
CARB Hydrocarbon Bin 19		14.09	Mix			0	8 c	0.66	0.39	0.150	0.26±0.15
CARB Hydrocarbon Bin 20		14.03	Mix			0	10 c	0.95	0.46	0.190	0.33±0.17
CARB Hydrocarbon Bin 21		13.27	Mix			0	8 c	7.64	2.49	1.16	2.01±1.03
CARB Hydrocarbon Bin 22		13.36	Mix			0	8 c	7.60	2.55	1.31	2.12±0.98
CARB Hydrocarbon Bin 23		13.41	Mix			0	10 c	6.85	2.31	1.21	1.93±0.88
CARB Hydrocarbon Bin 24		13.47	Mix			0	11 c	3.82	1.27	0.63	1.04±0.50
<u>Other Complex Mixtures</u>											
Base ROG Mixture		14.44	Mix			0	7	3.60	1.44	0.81	1.19±0.45
final LEV – RFA		14.03	Mix			0	7	3.54	1.41	0.76	1.15±0.45
TLEV Exhaust -- RFA		14.04	Mix			0	7	3.98	1.55	0.84	1.27±0.51
TLEV exhaust – phase 2		14.12	Mix			0	7	3.89	1.53	0.84	1.26±0.49
Final LEV -- Phase 2		14.22	Mix			0	7	3.45	1.39	0.76	1.13±0.44
TLEV Exhaust -- LPG		14.86	Mix			0	7	2.04	0.89	0.55	0.75±0.24
TLEV Exhaust -- CNG		15.22	Mix			0	7	0.73	0.35	0.22	0.29±0.08
TLEV Exhaust -- E-85		20.74	Mix			0	7	2.55	1.19	0.76	1.01±0.30
TLEV Exhaust -- M-85		27.45	Mix			0	7	1.56	0.59	0.33	0.49±0.20
composite mineral spirit (naphthas or lactol spirits) (CARB Profile ID 802)		14.06	Mix			0	7	1.92	0.87	0.41	0.66±0.29
Safety-Kleen Mineral Spirits "A" (Type I-B, 91% Alkanes)		14.08	Mix		2	0,+	7	1.25	0.65	0.29	0.46±0.22
Safety-Kleen Mineral Spirits "B" (Type II-C)		14.10	Mix		2	0,+	7	0.70	0.45	0.171	0.29±0.18
Safety-Kleen Mineral Spirits "C" (Type II-C)		14.11	Mix		2	0,+	7	0.71	0.46	0.173	0.30±0.18
Exxon Exxol® D95 Fluid		14.11	Mix		2	0	7	0.60	0.40	0.146	0.25±0.16

Table B-1 (continued)

Description	CAS	MWt	Codes [a]					Reactivity (gm O3 / gm VOC)			
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
Safety-Kleen Mineral Spirits "D" (Type II-C)		14.12	Mix		2	0,+	7	0.71	0.46	0.173	0.30±0.18
Exxon Isopar® M Fluid		14.15	Mix		2	0	8	0.57	0.38	0.136	0.24±0.16
thinning solvent/mineral spirits (Cal Poly SLO 1996)		14.40	Mix			0	7	1.93	0.91	0.46	0.69±0.28
Aromatic 100®		13.36	Mix		2	0	7	7.38	2.47	1.25	2.04±0.96
Kerosene		13.94	Mix		2	0	7	1.62	0.73	0.33	0.54±0.24
Regular mineral spirits		13.97	Mix		2	0	7	1.89	0.84	0.39	0.63±0.28
Reduced Aromatics Mineral Spirits		14.05	Mix		2	0	7	1.19	0.64	0.28	0.45±0.22
Dearomatized Alkanes, mixed, predominately C10-C12		14.09	Mix		2	0	7	0.87	0.54	0.23	0.37±0.20
VMP Naphtha		14.16	Mix		2	0	7	1.23	0.74	0.36	0.53±0.23
Synthetic isoparaffinic alkane mixture, predominately C10-C12		14.20	Mix		2	0	8	0.75	0.49	0.195	0.32±0.18
Oxo-Tridecyl Acetate		16.19	Mix			0	7	0.55	0.35	0.123	0.22±0.14
Oxo-Dodecyl Acetate		16.30	Mix			0	7	0.59	0.37	0.139	0.24±0.15
Oxo-Decyl Acetate		16.71	Mix		2	0	7	0.70	0.44	0.187	0.30±0.16
Oxo-Nonyl Acetate		16.89	Mix			0	7	0.72	0.45	0.193	0.31±0.16
Oxo-Octyl Acetate		17.23	Mix			0	7	0.81	0.50	0.24	0.36±0.16
Oxo-Heptyl Acetate		17.58	Mix			0	7	0.83	0.51	0.26	0.37±0.16
Oxo-Hexyl Acetate		18.02	Mix			0	7	0.86	0.54	0.30	0.41±0.15
turpentine	8006-64-2	13.62	Mix			0	7	4.28	1.60	0.87	1.33±0.56
soy methyl esters; alkyl C16-C18 methyl esters		15.57	Mix			0	8	1.58	0.69	0.40	0.57±0.22

[a] Codes used in this tabulation are as follows:

"Rep" … Codes for method used to represent the VOC in the mechanism

Exp	An explicit mechanism assignment has been made for this compound or model species. See Table B-2 for the mechanism.
AdjP	An explicit mechanism assignment has been made for this compound and the adjusted product version of the mechanism has been used when calculating its atmospheric reactivity values. The adjusted product mechanism is given in Table B-3.
LM	This compound is represented using the "Lumped Molecule" method. See Table B-9.
Mix	This is represented by a complex mixture of detailed model species. The compositions of these mixtures are given in Table B-10.

"k a" … Codes indicating of measurement data for the reaction rate constants

1	The OH radical rate constant has been measured. See Table B-2 or Table B-4 for the rate constant and reference citation. If the compound is consumed primarily by photolysis, this code means that absorption cross-section and quantum yield are available. In this case, see Table B-6 for the photolysis set, overall quantum yields (if applicable) and documentation, and Table A-3 or Table B-8 for the absorption cross sections and (if applicable) wavelength-dependent quantum yields.
blank	The OH radical rate constant or (if primarily photoreactive) the photolysis rate parameters had to be estimated. See Table B-2 or Table B-4 for the estimated OH rate constant and documentation on how the estimate was made, and Table B-6 for the method used to estimate the photolysis rate.

Table B-1 (continued)

"Expt" … Environmental Chamber Data Availability Codes (if blank, no suitable evaluation data are available).

1	Extensive evaluation data for a variety of conditions.
2	Sufficient data available. At least 2 and often 3 types of evaluation experiments to test data under different conditions.
3	Limited evaluation data; usually representing one set of conditions, or some inconsistencies in evaluation results.
3a	Evaluation data exist for 2 or more sets of conditions, but uncertainties exist concerning amount of compound available to react in the gas phase. See Carter (2008).
4	Data from only a single experiment is available, results from different experiments gave inconsistent results, or problems exist with the data.
4a	Data from only a single experiment is available, and uncertainties exist concerning the amount of compound available for reaction in the gas phase. See Carter (2008).
m	This compound was studied in a mixture with the other isomer. Since the reactivities of the two isomers are different, the uncertainty classification has been increased over that of the mixture that was studied.
x	No attempt was made to improve the mechanism performance to fit the available data.

"Bias" … Probable reactivity prediction bias codes (if blank, this compound has not been rated)

	Chamber data available	No chamber data available
0	No apparent bias	Direction of bias is unknown
+	Some indication of positive bias	Positive bias considered to be more likely than not
-	Some indication of negative bias	Negative bias is considered to be more likely than not
±2	Bias found to be relatively large	Bias may be relatively large
x,x	If two codes given, first indicates observed or probable bias for predictions of rates of NO oxidation and O_3 formation, which is important in affecting MIR reactivity, and the second indicates observed or probable bias for low NO_x conditions. E.g. "0,+" if chamber data available indicates that the model simulated rates of NO oxidation and O_3 formation but overpredicted final O_3 yields in NO_x-limited experiments.	
?	There is some inconsistency in the data concerning this bias indication (or lack thereof), or the bias is unknown but may be large.	
a	The reactivity predictions and representation in the mechanism is based on the assumption that this compound is completely available for reaction in the gas phase. This is likely not to be the case for this compound. Thus the reactivity estimate may be high for compounds that have positive O3 impacts and low for compounds that are calculated to be inhibitors.	

"Unc" … Uncertainty codes (if blank, this compound has not been rated)

The following codes are used when experimental data are available to evaluate the reactivity predictions of the mechanism and the mechanism was (or would have been) adjusted to fit the data as appropriate to improve the fits.

1	The mechanism appears to be reasonably well established or at least its predictions appear to be are reasonably well evaluated. This does not rule out possible changes in reactivity values if the base mechanism, scenario conditions, or reactivity metrics are changed. Also used for compounds known or expected to be inert or to have upper limit reactivities much less than methane.
2	The mechanism has been evaluated at least to some extent, rate constant data are available for its major reactions, and is not considered to have large uncertainties. If a likely bias is indicated it is probably not large.

Table B-1 (continued)

3	The mechanism has been evaluated at least to some extent and rate constant data are available for its major reactions, but the mechanism has some uncertainties or apparent inconsistencies with available laboratory data, or there are some uncertainties in the evaluation data. If a likely bias is indicated it is probably not large.
4	The mechanism has been evaluated at least to some extent and rate constant data are available for its major reactions, but the mechanism has some uncertainties, apparent inconsistencies with available laboratory data exist that may be significant, or the available evaluation database is limited or has problems. If a likely bias of ±1 is indicated it is probably not large.
5	A highly parameterized mechanism has been adjusted to simulate chamber data. The appropriateness of the parameterization, and its ability to extrapolate to ambient conditions, is uncertain.

The following codes are used for compounds for which no experimental data exist to evaluate reactivity predictions of the mechanism, or where such data, if any, were not taken into account when developing the mechanism.

6	The mechanism has not been evaluated but at least the important reaction rate(s) have been measured and the methods used to estimate the mechanism have been found to generally perform reasonably well for compounds where evaluation data are available, or the mechanisms are not expected to be highly complex. If a likely bias is indicated it is based on evaluation results for similar compounds.
7	The mechanism has not been evaluated and the reaction rates had to be estimated, but the methods used to estimate the rate constant(s) and mechanism have been found to generally perform reasonably well for compounds where evaluation data are available. If a likely bias is indicated it is based on evaluation results for similar compounds. This code is also used for mixture or lumped molecule or mixture representations that are considered to be reasonably appropriate.
8	The estimated mechanism and/or relevant rate constant(s) or photolysis rates have some uncertainties, but mechanisms based on similar assumptions have been found to perform satisfactorily for related compounds, or the mechanisms are not expected to be highly complex. The applicability of these assumptions to this compound, or the extrapolation of mechanisms for smaller compounds to one of this size, has some uncertainty. This code is also used for mixture or lumped molecule representations whose appropriateness has some uncertainty.

The uncertainty codes below mean that use of the reactivity values in regulatory applications is problematical.

10	The estimated mechanism is sufficiently uncertain that it needs to be evaluated. This code is also used for mixture or lumped molecule representations whose appropriateness is considered to be highly uncertain. However, the representation employed is the current best estimate, and the direction of the bias is unknown.
11	The estimated mechanism is extremely uncertain that it needs to be evaluated. This code is also used for mixture or lumped molecule representations whose appropriateness is questionable, but no better alternative exists, and the bias of using the representation is unknown. However, the representation employed is the current best estimate, and the direction of the bias is unknown.

Table B-1 (continued)

12	An estimated mechanism for the gas-phase reactions for this compound has been developed and has been evaluated at least qualitatively against available chamber data, but its estimated atmospheric ozone impact is highly uncertain because the amount of emitted compound available for reaction in the gas-phase is unknown. One important issue is that this compound may be removed by gas-phase reaction with HNO_3, whose presence depends on ambient conditions and may not be appropriately represented in the scenarios used for reactivity assessment. For such compounds two reactivity values are given, and "upper limit magnitude" reactivity value based on assuming that all the emitted VOC is available for gas-phase reaction and that reaction with HNO_3 is negligible (as may be applicable if the HNO_3 formed in gas-phase reactions is removed from the gas phase by other means) and one also assuming that all the emitted VOC is available for gas-phase reaction except that the reaction with gas-phase HNO_3 is fast and there is no other sink for HNO_3 formed in the gas-phase reactions.
13	Same as code 12 except that no chamber data are available to test the estimated gas-phase mechanism.
20	The representation or estimated mechanism used is considered to be biased, and the direction of the likely bias is indicted by the bias code. Best estimate mechanisms have not been developed.

Additional codes used where applicable

s	Portions of the mechanism are unknown or highly uncertain and simplified or parameterized representation has been adjusted at lest in part to fit available data for this or relate compounds. This is used primarily for alkylbenzenes.
d	Portions of this mechanism appear to be inconsistent with available laboratory data. This is used primarily for the 1-alkenes, where radical yields in O_3 reactions have to be reduced to simulate chamber data.
u	The mechanism is unknown and a parameterized mechanism adjusted to fit the data for this or related compounds employed.
m	This uncertainty code is only applicable for mixtures whose composition has been analyzed using state-of-the-science methods. Rating of effects of compositional uncertainties is beyond the scope of the project (but see discussion in Carter and Malkina (2005) for hydrocarbon mixtures).
b	The reactivity predictions may be more sensitive than usual to changes in the base mechanism or scenario conditions.
n	Chamber data for this or related compounds suggest that the mechanism may overpredict ozone under conditions where NO_x is limited. This should affect MIR values but will lead to too high reactivities in lower NO_x scenarios.
a	This compound may react with HNO_3 to form a non-volatile salt, which may reduce the availability for this compound to react in the gas phase. The importance of this process under atmospheric conditions is uncertain because (a) the salt may revolatilize to the gas-phase species and the equilibrium constant is unknown, (b) the sources and other sinks for HNO_3 may vary significantly from scenario to scenario and have not been established for the reactivity assessment scenarios, and (c) if ammonia or other amines are present they may compete for the HNO_3 and reduce the importance of this process for this amine, and the importance of these processes have not been established for the reactivity scenarios. In order to derive an upper limit ozone impact estimate, the reactivities of these compounds have been calculated assuming that removal by reaction with HNO_3 is uncertain. If this process is important, the magnitude of the actual ozone impact may be an order of magnitude or more low. Therefore, the tabulated reactivity values are upper limits for positively reactive compounds, and lower limits for ozone inhibitors.
c	CARB hydrocarbon bins are defined as described by Kwok et al (2000), but their reactivities are calculated based on their estimated compositions, which are derived as discussed by Carter (2009c). The uncertainties involved with this derivation are also discussed by Carter (2009c).

Table B-1 (continued)

+	This may appropriately be considered to be an upper limit estimate in the ozone impact of this compound.
--	This may appropriately be considered to be an upper limit estimate in the amount of ozone inhibition caused by this compound. The upper limit reactivity is zero.

Table B-2. Listing of mechanisms for all VOCs for which mechanism assignments have been derived. (Available in electronic form only)

Because of the size of this table, it is only available in as supplementary material in electronic form. See Appendix D.

(The room temperature rate constant and photolysis parameter assignments and their reference citations that are incorporated in this table are also given in Table B-4 through Table B-6)

Table B-3. Listing of adjusted product mechanisms for all VOCs for which such mechanisms have been derived. (Available in electronic form only)

Because of the size of this table, it is only available in as supplementary material in electronic form. See Appendix D.

Table B-4. Listing of compounds for which mechanisms have been derived. 1. OH radical rate constants at 300^{o}K, mechanism types, and structures used for compounds with generated mechanisms.

Compound	kOH [a]		Mec [b]	Structure [c]
	k(300)	Ref		
Methane	6.62E-15	1	1	
Ethane	2.54E-13	1	2	CH_3CH_3
Propane	1.11E-12	1	2	$CH_3CH_2CH_3$
Cyclopropane	8.34E-14	1	2	$CH_2*CH_2CH_2*$
n-Butane	2.38E-12	1	2	$CH_3CH_2CH_2CH_3$
Isobutane	2.14E-12	1	2	$CH_3CH(CH_3)CH_3$
Cyclobutane	2.05E-12	1	2	$CH_2*CH_2CH_2CH_2*$
n-Pentane	3.84E-12	1	2	$CH_3CH_2CH_2CH_2CH_3$
Neopentane	8.38E-13	1	2	$CH_3C(CH_3)(CH_3)CH_3$
Iso-Pentane	3.60E-12	1	2	$CH_3CH_2CH(CH_3)CH_3$
Cyclopentane	5.02E-12	1	2,A	$CH_2*CH_2CH_2CH_2CH_2*$
n-Hexane	5.25E-12	1	2	$CH_3CH_2CH_2CH_2CH_2CH_3$
2,2-Dimethyl Butane	2.27E-12	1	2	$CH_3CH_2C(CH_3)(CH_3)CH_3$
2,3-Dimethyl Butane	5.79E-12	1	2	$CH_3CH(CH_3)CH(CH_3)CH_3$
2-Methyl Pentane	5.20E-12	1	2	$CH_3CH_2CH_2CH(CH_3)CH_3$
3-Methylpentane	5.20E-12	1	2	$CH_3CH_2CH(CH_3)CH_2CH_3$
Cyclohexane	7.02E-12	1	2,A	$CH_2*CH_2CH_2CH_2CH_2CH_2*$
Isopropyl Cyclopropane	2.61E-12	1	2	$CH_3CH(CH_3)CH*CH_2CH_2*$
Methylcyclopentane	5.68E-12	e1	2,A	$CH_3CH*CH_2CH_2CH_2CH_2*$
n-Heptane	6.81E-12	1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
2,2,3-Trimethyl Butane	3.82E-12	1	2	$CH_3CH(CH_3)C(CH_3)(CH_3)CH_3$
2,2-Dimethyl Pentane	3.40E-12	2	2	$CH_3CH_2CH_2C(CH_3)(CH_3)CH_3$
2,3-Dimethyl Pentane	7.15E-12	e1	2	$CH_3CH_2CH(CH_3)CH(CH_3)CH_3$
2,4-Dimethyl Pentane	4.77E-12	1	2	$CH_3CH(CH_3)CH_2CH(CH_3)CH_3$
2-Methyl Hexane	6.89E-12	e1	2,A	$CH_3CH_2CH_2CH_2CH(CH_3)CH_3$
3,3-Dimethyl Pentane	3.00E-12	e1	2	$CH_3CH_2C(CH_3)(CH_3)CH_2CH_3$
3-Methyl Hexane	7.17E-12	e1	2	$CH_3CH_2CH_2CH(CH_3)CH_2CH_3$
3-ethylpentane	7.58E-12	e1	2	$CH_3CH_2CH(CH_2CH_3)CH_2CH_3$
1,1-dimethylcyclopentane	3.98E-12	e1	2,A	$CH_3C*(CH_3)CH_2CH_2CH_2CH_2*$
1,2-dimethylcyclopentane	6.82E-12	e1	2,A	$CH_3CH*CH_2CH_2CH_2CH*CH_3$
1,3-Dimethyl Cyclopentane	6.82E-12	e1	2,A	$CH_3CH*CH_2CH_2CH(CH_3)CH_2*$
Cycloheptane	1.24E-11	1	2,A	$CH_2*CH_2CH_2CH_2CH_2CH_2CH_2*$
Ethyl Cyclopentane	7.27E-12	e1	2,A	$CH_3CH_2CH*CH_2CH_2CH_2CH_2*$
Methylcyclohexane	9.64E-12	1	2,A	$CH_3CH*CH_2CH_2CH_2CH_2CH_2*$
n-Octane	8.16E-12	1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
2,2,3,3-Tetramethyl Butane	9.89E-13	1	2	$CH_3C(CH_3)(CH_3)C(CH_3)(CH_3)CH_3$
2,2,4-Trimethyl Pentane	3.38E-12	1	2	$CH_3CH(CH_3)CH_2C(CH_3)(CH_3)CH_3$
2,2-Dimethyl Hexane	4.80E-12	2	2	$CH_3CH_2CH_2CH_2C(CH_3)(CH_3)CH_3$
2,3,4-Trimethyl Pentane	6.60E-12	1	2	$CH_3CH(CH_3)CH(CH_3)CH(CH_3)CH_3$
2,3-Dimethyl Hexane	8.57E-12	e1	2	$CH_3CH_2CH_2CH(CH_3)CH(CH_3)CH_3$
2,4-Dimethyl Hexane	8.57E-12	e1	2	$CH_3CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
2,5-Dimethyl Hexane	8.29E-12	e1	2	$CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_3$
2-Methyl Heptane	8.31E-12	e1	2	$CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_3$
3-Methyl Heptane	8.59E-12	e1	2	$CH_3CH_2CH_2CH_2CH(CH_3)CH_2CH_3$
4-Methyl Heptane	8.59E-12	e1	2	$CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_3$

Table B-4 (continued)

Compound	kOH [a]		Mec	Structure [c]
	k(300)	Ref	[b]	
2,3,3-trimethylpentane	4.40E-12	e1	2	$CH_3CH_2C(CH_3)(CH_3)CH(CH_3)CH_3$
3,3-dimethyl hexane	4.42E-12	e1	2	$CH_3CH_2CH_2C(CH_3)(CH_3)CH_2CH_3$
2,2,3-trimethyl-pentane	4.94E-12	e1	2	$CH_3CH_2CH(CH_3)C(CH_3)(CH_3)CH_3$
3,4-dimethylhexane	8.85E-12	e1	2	$CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_3$
3-Ethyl 2-Methyl Pentane	8.98E-12	e1	2	$CH_3CH_2CH(CH_2CH_3)CH(CH_3)CH_3$
1,1,2-trimethylcyclopentane	5.11E-12	e1	2	$CH_3CH*CH_2CH_2CH_2C*(CH_3)CH_3$
1,1,3-trimethylcyclopentane	5.11E-12	e1	2	$CH_3CH*CH_2CH_2C(CH_3)(CH_3)CH_2*$
1,1-Dimethyl Cyclohexane	7.44E-12	e1	2	$CH_3C*(CH_3)CH_2CH_2CH_2CH_2CH_2*$
1,2,3-trimethylcyclopentane	7.95E-12	e1	2	$CH_3CH*CH_2CH_2CH(CH_3)CH*CH_3$
1,2,4-trimethylcyclopentane	7.95E-12	e1	2	$CH_3CH*CH_2CH(CH_3)CH(CH_3)CH_2*$
1-methyl-3-ethylcyclopentane	8.40E-12	e1	2,A	$CH_3CH_2CH*CH_2CH_2CH(CH_3)CH_2*$
1,2-dimethylcyclohexane	1.19E-11	e1	2,A	$CH_3CH*CH_2CH_2CH_2CH_2CH*CH_3$
1,4-dimethylcyclohexane	1.19E-11	e1	2,A	$CH_3CH*CH_2CH_2CH(CH_3)CH_2CH_2*$
1,3-Dimethyl Cyclohexane	1.19E-11	e1	2,A	$CH_3CH*CH_2CH_2CH_2CH(CH_3)CH_2*$
Cyclooctane	1.33E-11	1	2,A	$CH_2*CH_2CH_2CH_2CH_2CH_2CH_2CH_2*$
Ethylcyclohexane	1.20E-11	e1	2	$CH_3CH_2CH*CH_2CH_2CH_2CH_2CH_2*$
Propyl Cyclopentane	8.69E-12	e1	2,A	$CH_3CH_2CH_2CH*CH_2CH_2CH_2CH_2*$
n-Nonane	9.75E-12	1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
2,2,5-Trimethyl Hexane	6.08E-12	e1	2	$CH_3CH(CH_3)CH_2CH_2C(CH_3)(CH_3)CH_3$
2,3,5-Trimethyl Hexane	7.90E-12	2	2,A	$CH_3CH(CH_3)CH_2CH(CH_3)CH(CH_3)CH_3$
2,4-Dimethyl Heptane	9.99E-12	e1	2	$CH_3CH_2CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
2-Methyl Octane	1.01E-11	2	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_3$
3,3-Diethyl Pentane	4.80E-12	1	2	$CH_3CH_2C(CH_2CH_3)(CH_2CH_3)CH_2CH_3$
3,5-Dimethyl Heptane	1.03E-11	e1	2	$CH_3CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH_3$
4-Ethyl Heptane	1.04E-11	e1	2	$CH_3CH_2CH_2CH(CH_2CH_3)CH_2CH_2CH_3$
4-Methyl Octane	9.70E-12	2	2	$CH_3CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_3$
2,4,4-trimethylhexane	5.82E-12	e1	2	$CH_3CH_2C(CH_3)(CH_3)CH_2CH(CH_3)CH_3$
3,3-dimethylheptane	5.84E-12	e1	2	$CH_3CH_2CH_2CH_2C(CH_3)(CH_3)CH_2CH_3$
4,4-dimethyl heptane	5.84E-12	e1	2	$CH_3CH_2CH_2C(CH_3)(CH_3)CH_2CH_2CH_3$
2,2-dimethyl heptane	6.10E-12	e1	2	$CH_3CH_2CH_2CH_2CH_2C(CH_3)(CH_3)CH_3$
2,2,4-trimethylhexane	6.36E-12	e1	2	$CH_3CH_2CH(CH_3)CH_2C(CH_3)(CH_3)CH_3$
2,6-dimethylheptane	9.71E-12	e1	2	$CH_3CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_3$
2,3-dimethylheptane	9.99E-12	e1	2	$CH_3CH_2CH_2CH_2CH(CH_3)CH(CH_3)CH_3$
2,5-dimethylheptane	9.99E-12	e1	2	$CH_3CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_3$
3-methyloctane	1.00E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_3$
3,4-dimethylheptane	1.03E-11	e1	2	$CH_3CH_2CH_2CH(CH_3)CH(CH_3)CH_2CH_3$
3-ethylheptane	1.04E-11	e1	2	$CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2CH_3$
Cis-hydrindane; Bicyclo[4.3.0]nonane	1.71E-11	e1	2,A	$CH_2*1CH_2CH_2CH*2CH_2CH_2CH_2CH*2CH_2*1$
1,2,3-trimethylcyclohexane	1.36E-11	e1	2,A	$CH_3CH*CH_2CH_2CH_2CH(CH_3)CH*CH_3$
1,3,5-trimethylcyclohexane	1.36E-11	e1	2	$CH_3CH*CH_2CH(CH_3)CH_2CH(CH_3)CH_2*$
1,1,3-Trimethyl Cyclohexane	8.70E-12	2	2	$CH_3CH*CH_2CH_2CH_2C(CH_3)(CH_3)CH_2*$
1-Ethyl-4-Methyl Cyclohexane	1.37E-11	e1	2,A	$CH_3CH_2CH*CH_2CH_2CH(CH_3)CH_2CH_2*$
Propyl Cyclohexane	1.34E-11	e1	2	$CH_3CH_2CH_2CH*CH_2CH_2CH_2CH_2CH_2*$
n-Decane	1.10E-11	1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
2,4,6-Trimethyl Heptane	1.14E-11	e1	2	$CH_3CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
2,4-Dimethyl Octane	1.14E-11	e1	2	$CH_3CH_2CH_2CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
2,6-Dimethyl Octane	1.29E-11	3	2	$CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_3$

Table B-4 (continued)

Compound	kOH [a]		Mec [b]	Structure [c]
	k(300)	Ref		
2-Methyl Nonane	1.28E-11	3	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_3$
3,4-Diethyl Hexane	6.92E-12	1	2	$CH_3CH_2CH(CH_2CH_3)CH(CH_2CH_3)CH_2CH_3$
3-Methyl Nonane	1.14E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_3$
4-Methyl Nonane	1.14E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_3$
4-Propyl Heptane	1.18E-11	e1	2	$CH_3CH_2CH_2CH(CH_2CH_2CH_3)CH_2CH_2CH_3$
2,4,4-trimethylheptane	7.24E-12	e1	2	$CH_3CH_2CH_2C(CH_3)(CH_3)CH_2CH(CH_3)CH_3$
2,5,5-trimethylheptane	7.24E-12	e1	2	$CH_3CH_2C(CH_3)(CH_3)CH_2CH_2CH(CH_3)CH_3$
3,3-dimethyloctane	7.26E-12	e1	2	$CH_3CH_2CH_2CH_2CH_2C(CH_3)(CH_3)CH_2CH_3$
4,4-dimethyloctane	7.26E-12	e1	2	$CH_3CH_2CH_2CH_2C(CH_3)(CH_3)CH_2CH_2CH_3$
2,2-dimethyloctane	7.52E-12	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2C(CH_3)(CH_3)CH_3$
2,2,4-trimethylheptane	7.78E-12	e1	2	$CH_3CH_2CH_2CH(CH_3)CH_2C(CH_3)(CH_3)CH_3$
2,2,5-trimethylheptane	7.78E-12	e1	2	$CH_3CH_2CH(CH_3)CH_2CH_2C(CH_3)(CH_3)CH_3$
2,3,6-trimethylheptane	1.14E-11	e1	2,A	$CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH(CH_3)CH_3$
2,3-dimethyloctane	1.14E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH(CH_3)CH_3$
2,5-dimethyloctane	1.14E-11	e1	2	$CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_3$
2-methyl-3-ethylheptane	1.18E-11	e1	2	$CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH(CH_3)CH_3$
4-ethyloctane	1.18E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2CH_2CH_3$
1,3-Diethyl-Cyclohexane	1.55E-11	e1	2,A	$CH_3CH_2CH*CH_2CH_2CH_2CH(CH_2CH_3)CH_2*$
1,4-Diethyl-Cyclohexane	1.55E-11	e1	2	$CH_3CH_2CH*CH_2CH_2CH(CH_2CH_3)CH_2CH_2*$
1-Methyl-3-Isopropyl Cyclohexane	1.51E-11	e1	2	$CH_3CH*CH_2CH_2CH_2CH(CH_2*)CH(CH_3)CH_3$
Butyl Cyclohexane	1.47E-11	1	2	$CH_3CH_2CH_2CH_2CH*CH_2CH_2CH_2CH_2CH_2*$
n-Undecane	1.23E-11	1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
2,3,4,6-Tetramethyl Heptane	1.31E-11	e1	2	$CH_3CH(CH_3)CH_2CH(CH_3)CH(CH_3)CH(CH_3)CH_3$
2,6-Dimethyl Nonane	1.28E-11	e1	2	$CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_3$
3,5-Diethyl Heptane	1.39E-11	e1	2	$CH_3CH_2CH(CH_2CH_3)CH_2CH(CH_2CH_3)CH_2CH_3$
3-Methyl Decane	1.29E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_3$
4-Methyl Decane	1.29E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_3$
1,3-Diethyl-5-Methyl Cyclohexane	1.72E-11	e1	2	$CH_3CH_2CH*CH_2CH(CH_3)CH_2CH(CH_2CH_3)CH_2*$
1-Ethyl-2-Propyl Cyclohexane	1.70E-11	e1	2,A	$CH_3CH_2CH_2CH*CH_2CH_2CH_2CH_2CH*CH_2CH_3$
Pentyl Cyclohexane	1.63E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH*CH_2CH_2CH_2CH_2CH_2*$
n-Dodecane	1.32E-11	1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
2,3,5,7-Tetramethyl Octane	1.45E-11	e1	2	$CH_3CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH(CH_3)CH_3$
2,6-Diethyl Octane	1.53E-11	e1	2	$CH_3CH_2CH(CH_2CH_3)CH_2CH_2CH(CH_2CH_3)CH_2CH_3$
3,6-Dimethyl Decane	1.45E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_2CH_3$
3-Methyl Undecane	1.43E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_3$
5-Methyl Undecane	1.43E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_3$
1,3,5-Triethyl Cyclohexane	1.90E-11	e1	2	$CH_3CH_2CH*CH_2CH(CH_2CH_3)CH_2CH(CH_2CH_3)CH_2*$
1-Methyl-4-Pentyl Cyclohexane	1.80E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH*CH_2CH_2CH(CH_3)CH_2CH_2*$
Hexyl Cyclohexane	1.78E-11	3	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH*CH_2CH_2CH_2CH_2CH_2*$
n-Tridecane	1.51E-11	1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
2,3,6-Trimethyl 4-Isopropyl Heptane	1.63E-11	e1	2	$CH_3CH(CH_3)CH_2CH(CH(CH_3)CH_3)CH(CH_3)CH(CH_3)CH_3$
2,4,6,8-Tetramethyl Nonane	1.59E-11	e1	2,A	$CH_3CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
3,6-Dimethyl Undecane	1.60E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_2CH_3$
3,7-Diethyl Nonane	1.68E-11	e1	2	$CH_3CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH(CH_2CH_3)CH_2CH_3$
3-Methyl Dodecane	1.57E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_3$

Table B-4 (continued)

Compound	kOH [a]		Mec [b]	Structure [c]
	k(300)	Ref		
5-Methyl Dodecane	1.57E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_3$
1,3-Diethyl-5-Propyl Cyclohexane	2.05E-11	e1	2	$CH_3CH_2CH_2CH*CH_2CH(CH_2CH_3)CH_2CH(CH_2CH_3)CH_2*$
1-Methyl-2-Hexyl-Cyclohexane	1.94E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH*CH_2CH_2CH_2CH_2CH*CH_3$
Heptyl Cyclohexane	1.91E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH*CH_2CH_2CH_2CH_2CH_2*$
n-Tetradecane	1.79E-11	1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
2,4,5,6,8-Pentamethyl Nonane	1.76E-11	e1	2	$CH_3CH(CH_3)CH_2CH(CH_3)CH(CH_3)CH(CH_3)CH_2CH(CH_3)CH_3$
2-Methyl 3,5-Diisopropyl Heptane	1.81E-11	e1	2,A	$CH_3CH_2CH(CH_2CH(CH(CH_3)CH_3)CH(CH_3)CH_3)CH(CH_3)CH_3$
3,7-Dimethyl Dodecane	1.74E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_3$
3,8-Diethyl Decane	1.82E-11	e1	2,A	$CH_3CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_2CH(CH_2CH_3)CH_2CH_3$
3-Methyl Tridecane	1.71E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_3$
6-Methyl Tridecane	1.71E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_2CH_3$
1,3-Dipropyl-5-Ethyl Cyclohexane	2.19E-11	e1	2	$CH_3CH_2CH_2CH*CH_2CH(CH_2CH_3)CH_2CH(CH_2CH_2CH_3)CH_2*$
trans 1-Methyl-4-Heptyl Cyclohexane	2.08E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH*CH_2CH_2CH(CH_3)CH_2CH_2*$
Octyl Cyclohexane	2.05E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH*CH_2CH_2CH_2CH_2CH_2*$
n-Pentadecane	2.07E-11	1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
2,6,8-Trimethyl 4-Isopropyl Nonane	1.91E-11	e1	2	$CH_3CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_2CH(CH_3)CH_3)CH(CH_3)CH_3$
3,7-Dimethyl Tridecane	1.88E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_3$
3,9-Diethyl Undecane	1.96E-11	e1	2	$CH_3CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_2CH_2CH(CH_2CH_3)CH_2CH_3$
3-Methyl Tetradecane	1.85E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_3$
6-Methyl Tetradecane	1.85E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_2CH_3$
1,3,5-Tripropyl Cyclohexane	2.33E-11	e1	2	$CH_3CH_2CH_2CH*CH_2CH(CH_2CH_2CH_3)CH_2CH(CH_2CH_2CH_3)CH_2*$
1-Methyl-2-Octyl Cyclohexane	2.22E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH*CH_2CH_2CH_2CH_2CH*CH_3$
Nonyl Cyclohexane	2.20E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH*CH_2CH_2CH_2CH_2CH_2*$
1,3-diethyl-5-pentyl cyclohexane	1.75E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH*CH_2CH_2CH_2C(CH_2CH_3)(CH_2CH_3)CH_2*$
n-C16	2.32E-11	1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
2,7-Dimethyl 3,5-Diisopropyl Heptane	2.09E-11	e1	2,A	$CH_3CH(CH_3)CH_2CH(CH_2CH(CH(CH_3)CH_3)CH(CH_3)CH_3)CH(CH_3)CH_3$
3-Methyl Pentadecane	2.00E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_3$

Table B-4 (continued)

Compound	kOH [a]		Mec [b]	Structure [c]
	k(300)	Ref		
4,8-Dimethyl Tetradecane	2.02E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_3$
7-Methyl Pentadecane	2.00E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_2CH_2CH_3$
1,3-Propyl-5-Butyl Cyclohexane	2.47E-11	e1	2	$CH_3CH_2CH_2CH_2CH*CH_2CH(CH_2CH_2CH_3)CH_2CH(CH_2CH_2CH_3)CH_2*$
1-Methyl-4-Nonyl Cyclohexane	2.36E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH*CH_2CH_2CH(CH_3)CH_2CH_2*$
Decyl Cyclohexane	2.34E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH*CH_2CH_2CH_2CH_2CH_2*$
Ethene	8.15E-12	1	1	
Propene	2.60E-11	1	2	$CH_2=CHCH_3$
1,2-propadiene (allene)	9.80E-12	1	3	$CH_2=C=CH_2$
1-Butene	3.11E-11	1	2	$CH_2=CHCH_2CH_3$
Isobutene	5.08E-11	1	2	$CH_2=C(CH_3)CH_3$
cis-2-Butene	5.58E-11	1	2	CH_3^$CH=CHvCH_3$
trans-2-Butene	6.32E-11	1	2	CH_3^$CH=CH$^CH_3
1,2-Butadiene	2.60E-11	1	3	$CH_2=C=CHCH_3$
1,3-Butadiene	6.59E-11	1	3	$CH_2=CHCH=CH_2$
1-Pentene	3.14E-11	1	2	$CH_2=CHCH_2CH_2CH_3$
3-Methyl-1-Butene	3.14E-11	1	2	$CH_2=CHCH(CH_3)CH_3$
2-Methyl-1-Butene	6.10E-11	1	2	$CH_2=C(CH_3)CH_2CH_3$
2-Methyl-2-Butene	8.60E-11	1	2	$CH_3CH=C(CH_3)CH_3$
cis-2-Pentene	6.50E-11	1	2	CH_3^$CH=CHvCH_2CH_3$
trans-2-Pentene	6.70E-11	1	2	CH_3^$CH=CH$^CH_2CH_3
Cyclopentene	6.70E-11	1	2	$CH*=CHCH_2CH_2CH_2*$
Trans 1,3-Pentadiene	1.01E-10	e2	3	$CH_2=CH$^$CH=CH$^CH_3
1,4-Pentadiene	5.30E-11	1	3	$CH_2=CHCH_2CH=CH_2$
1,2-Pentadiene	3.55E-11	1	3	$CH_2=C=CHCH_2CH_3$
3-Methyl-1,2-Butadiene	5.70E-11	1	3	$CH_2=C=C(CH_3)CH_3$
Isoprene	9.96E-11	1	1	
1-Hexene	3.70E-11	1	2	$CH_2=CHCH_2CH_2CH_2CH_3$
3,3-Dimethyl-1-Butene	2.80E-11	1	2	$CH_2=CHC(CH_3)(CH_3)CH_3$
3-Methyl-1-Pentene	3.55E-11	e1	2	$CH_2=CHCH(CH_3)CH_2CH_3$
4-Methyl-1-Pentene	3.55E-11	e1	2	$CH_2=CHCH_2CH(CH_3)CH_3$
2,3-Dimethyl-1-Butene	6.03E-11	e1	2	$CH_2=C(CH_3)CH(CH_3)CH_3$
2-Ethyl-1-Butene	6.01E-11	e1	2	$CH_2=C(CH_2CH_3)CH_2CH_3$
2-Methyl-1-Pentene	6.30E-11	1	2	$CH_2=C(CH_3)CH_2CH_2CH_3$
2,3-Dimethyl-2-Butene	1.10E-10	1	2	$CH_3C(CH_3)=C(CH_3)CH_3$
2-Methyl-2-Pentene	8.90E-11	1	2	$CH_3CH_2CH=C(CH_3)CH_3$
Cis-2-Hexene	6.60E-11	e1	2	CH_3^$CH=CHvCH_2CH_2CH_3$
Cis-3-Hexene	6.56E-11	e1	2	CH_3CH_2^$CH=CHvCH_2CH_3$
Cis-3-Methyl-2-Pentene	8.85E-11	e1	2	CH_3^$CH=C($^$CH_3)CH_2CH_3$
Trans 3-Methyl-2-Pentene	8.85E-11	e1	2	CH_3^$CH=C(vCH_3)CH_2CH_3$
Trans 4-Methyl-2-Pentene	5.98E-11	4	2	CH_3^$CH=CH$^$CH(CH_3)CH_3$
Trans-2-Hexene	6.60E-11	e1	2	CH_3^$CH=CH$^$CH_2CH_2CH_3$
Trans-3-Hexene	6.56E-11	e1	2	CH_3CH_2^$CH=CH$^CH_2CH_3
3-methylcyclopentene	6.67E-11	e1	2	$CH_3CH*CH=CHCH_2CH_2*$
1-Methyl cyclopentene	8.96E-11	e1	2,A	$CH_3C*=CHCH_2CH_2CH_2*$

Table B-4 (continued)

Compound	kOH [a]		Mec	Structure [c]
	k(300)	Ref	[b]	
Cyclohexene	6.77E-11	1	2	CH*=CHCH$_2$CH$_2$CH$_2$CH$_2$*
Trans 1,4-Hexadiene	9.10E-11	1	3	CH$_2$=CHCH$_2$^CH=CH^CH$_3$
1-Methyl Cyclohexene	9.40E-11	1	2	CH$_3$C*=CHCH$_2$CH$_2$CH$_2$CH$_2$*
4-Methyl Cyclohexene	7.02E-11	e1	2	CH$_3$CH*CH$_2$^CH=CHvCH$_2$CH$_2$*
1-Heptene	4.00E-11	1	2,A	CH$_2$=CHCH$_2$CH$_2$CH$_2$CH$_2$CH$_3$
3,4-dimethyl-1-pentene	3.69E-11	e1	2	CH$_2$=CHCH(CH$_3$)CH(CH$_3$)CH$_3$
3-methyl-1-hexene	3.69E-11	e1	2	CH$_2$=CHCH(CH$_3$)CH$_2$CH$_2$CH$_3$
2,4-dimethyl-1-pentene	6.19E-11	e1	2,A	CH$_2$=C(CH$_3$)CH$_2$CH(CH$_3$)CH$_3$
2,3-dimethyl-1-pentene	6.19E-11	e1	2	CH$_2$=C(CH$_3$)CH(CH$_3$)CH$_2$CH$_3$
3,3-dimethyl-1-pentene	3.33E-11	e1	2	CH$_2$=CHC(CH$_3$)(CH$_3$)CH$_2$CH$_3$
2-methyl-1-hexene	6.19E-11	e1	2	CH$_2$=C(CH$_3$)CH$_2$CH$_2$CH$_2$CH$_3$
2,3,3-trimethyl-1-Butene	5.86E-11	e1	2	CH$_2$=C(CH$_3$)C(CH$_3$)(CH$_3$)CH$_3$
4,4-dimethyl-cis-2-pentene	5.46E-11	e1	2	CH$_3$^CH=CHvC(CH$_3$)(CH$_3$)CH$_3$
2,4-dimethyl-2-pentene	8.97E-11	e1	2	CH$_3$C(CH$_3$)=CHCH(CH$_3$)CH$_3$
2-methyl-2-hexene	8.99E-11	e1	2	CH$_3$CH$_2$CH$_2$CH=C(CH$_3$)CH$_3$
3-ethyl-2-pentene	8.95E-11	e1	2	CH$_3$CH=C(CH$_2$CH$_3$)CH$_2$CH$_3$
3-methyl-trans-3-hexene	8.95E-11	e1	2	CH$_3$CH$_2$^CH=C(CH$_3$)vCH$_2$CH$_3$
cis-2-heptene	6.74E-11	e1	2	CH$_3$^CH=CHvCH$_2$CH$_2$CH$_2$CH$_3$
2-Methyl-trans-3-Hexene	6.68E-11	e1	2	CH$_3$CH$_2$^CH=CH^CH(CH$_3$)CH$_3$
3-methyl-cis-3-hexene	8.95E-11	e1	2	CH$_3$CH$_2$^CH=C(CH$_3$)^CH$_2$CH$_3$
3,4-dimethyl-cis-2-pentene	8.97E-11	e1	2	CH$_3$^CH=C(CH$_3$)^CH(CH$_3$)CH$_3$
2,3-Dimethyl-2-Pentene	1.03E-10	1	2	CH$_3$CH$_2$C(CH$_3$)=C(CH$_3$)CH$_3$
Cis-3-Heptene	6.70E-11	e1	2	CH$_3$CH$_2$^CH=CHvCH$_2$CH$_2$CH$_3$
Trans 4,4-dimethyl-2-Pentene	5.50E-11	1	2	CH$_3$^CH=CH^C(CH$_3$)(CH$_3$)CH$_3$
Trans-2-Heptene	6.80E-11	1	2	CH$_3$^CH=CH^CH$_2$CH$_2$CH$_2$CH$_3$
Trans-3-Heptene	6.70E-11	e1	2	CH$_3$CH$_2$^CH=CH^CH$_2$CH$_2$CH$_3$
cis-3-methyl-2-hexene	8.99E-11	e1	2	CH$_3$^CH=C(^CH$_3$)CH$_2$CH$_2$CH$_3$
trans 4-methyl-2-hexene	6.74E-11	e1	2	CH$_3$^CH=CH^CH(CH$_3$)CH$_2$CH$_3$
trans 3-methyl-2-hexene	8.99E-11	e1	2	CH$_3$^CH=C(vCH$_3$)CH$_2$CH$_2$CH$_3$
1,2-Dimethyl Cyclohexene	1.11E-10	e1	2	CH$_3$C*=C(CH$_3$)CH$_2$CH$_2$CH$_2$CH$_2$*
1-Octene	3.83E-11	e1	2	CH$_2$=CHCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$
2,4,4-trimethyl-1-pentene	5.97E-11	e1	2	CH$_2$=C(CH$_3$)CH$_2$C(CH$_3$)(CH$_3$)CH$_3$
3-Methyl-2-Isopropyl-1-Butene	6.25E-11	e1	2,A	CH$_2$=C(CH(CH$_3$)CH$_3$)CH(CH$_3$)CH$_3$
trans-2-octene	6.89E-11	e1	2	CH$_3$^CH=CH^CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$
2-Methyl-2-heptene	9.13E-11	e1	2	CH$_3$CH$_2$CH$_2$CH$_2$CH=C(CH$_3$)CH$_3$
Cis-4-Octene	6.84E-11	e1	2,A	CH$_3$CH$_2$CH$_2$^CH=CHvCH$_2$CH$_2$CH$_3$
Trans 2,2-Dimethyl 3-Hexene	6.50E-11	e1	2	CH$_3$CH$_2$^CH=CH^C(CH$_3$)(CH$_3$)CH$_3$
Trans 2,5-Dimethyl 3-Hexene	6.80E-11	e1	2,A	CH$_3$CH(CH$_3$)^CH=CH^CH(CH$_3$)CH$_3$
Trans-3-Octene	6.84E-11	e1	2,A	CH$_3$CH$_2$^CH=CH^CH$_2$CH$_2$CH$_2$CH$_3$
Trans-4-Octene	6.90E-11	1	2,A	CH$_3$CH$_2$CH$_2$^CH=CH^CH$_2$CH$_2$CH$_3$
2,4,4-trimethyl-2-Pentene	8.79E-11	e1	2	CH$_3$C(CH$_3$)=CHC(CH$_3$)(CH$_3$)CH$_3$
2,3-dimethyl-2-hexene	1.08E-10	e1	2	CH$_3$CH$_2$CH$_2$C(CH$_3$)=C(CH$_3$)CH$_3$
1-Nonene	3.98E-11	e1	2	CH$_2$=CHCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$
4,4-dimethyl-1-pentene	3.58E-11	e1	2	CH$_2$=CHCH$_2$C(CH$_3$)(CH$_3$)CH$_2$CH$_2$CH$_3$
Trans-4-Nonene	6.98E-11	e1	2,A	CH$_3$CH$_2$CH$_2$^CH=CH^CH$_2$CH$_2$CH$_2$CH$_3$
1-Decene	4.12E-11	e1	2	CH$_2$=CHCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$
3,4-Diethyl-2-Hexene	9.39E-11	e1	2	CH$_3$CH=C(CH$_2$CH$_3$)CH(CH$_2$CH$_3$)CH$_2$CH$_3$
Cis-5-Decene	7.12E-11	e1	2,A	CH$_3$CH$_2$CH$_2$CH$_2$^CH=CHvCH$_2$CH$_2$CH$_2$CH$_3$

Table B-4 (continued)

Compound	kOH [a]		Mec	Structure [c]
	k(300)	Ref	[b]	
Trans-4-Decene	7.12E-11	e1	2,A	$CH_3CH_2CH_2$^CH=CH^$CH_2CH_2CH_2CH_2CH_3$
3-Carene	8.80E-11	1	3	$CH_3C*1{=}CHCH_2CH*2CH(CH_2*1)C*2(CH_3)CH_3$
a-Pinene	5.18E-11	1	3	$CH_3C*1{=}CHCH_2CH*2CH_2CH*1C*2(CH_3)CH_3$
b-Pinene	7.35E-11	1	3	$CH_2{=}C*1CH_2CH_2CH*2CH_2CH*1C*2(CH_3)CH_3$
d-Limonene	1.63E-10	1	3	$CH_2{=}C(CH_3)CH*CH_2CH{=}C(CH_3)CH_2CH_2*$
Sabinene	1.17E-10	1	3	$CH_2{=}C*1CH_2CH_2C*2(CH_2CH*12)CH(CH_3)CH_3$
Terpinolene	1.96E-10	e1	3	$CH_3C(CH_3){=}C*CH_2CH{=}C(CH_3)CH_2CH_2*$
1-Undecene	4.26E-11	e1	2	$CH_2{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Trans-5-Undecene	7.26E-11	e1	2,A	$CH_3CH_2CH_2CH_2$^CH=CH^$CH_2CH_2CH_2CH_2CH_3$
1-Dodecene	4.40E-11	e1	2	$CH_2{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Trans-5-Dodecene	7.40E-11	e1	2,A	$CH_3CH_2CH_2CH_2$^CH=CH^$CH_2CH_2CH_2CH_2CH_2CH_3$
1-Tridecene	4.54E-11	e1	2	$CH_2{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Trans-5-Tridecene	7.55E-11	e1	2	$CH_3CH_2CH_2CH_2$^CH=CH^$CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
1-Tetradecene	4.69E-11	e1	2	$CH_2{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Trans-5-Tetradecene	7.69E-11	e1	2	$CH_3CH_2CH_2CH_2$^CH=CH^$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Trans-5-Pentadecene	7.83E-11	e1	2	$CH_3CH_2CH_2CH_2$^CH=CH^$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Benzene	1.22E-12	1	1	
Toluene	5.58E-12	1	5	
Ethyl Benzene	7.00E-12	1	5	
m-Xylene	2.31E-11	1	5	
o-Xylene	1.36E-11	1	5	
p-Xylene	1.43E-11	1	5	
Styrene	5.80E-11	1	4	
n-Propyl Benzene	5.80E-12	1	5	
Isopropyl Benzene (cumene)	6.30E-12	1	5	
m-Ethyl Toluene	1.86E-11	1	5	
o-Ethyl Toluene	1.19E-11	1	5	
p-Ethyl Toluene	1.18E-11	1	5	
1,2,3-Trimethyl Benzene	3.27E-11	1	5	
1,2,4-Trimethyl Benzene	3.25E-11	1	5	
1,3,5-Trimethyl Benzene	5.67E-11	1	5	
b-Methyl Styrene	5.70E-11	1	4	
C10 Monosubstituted Benzenes	9.58E-12	e3	5	
t-Butyl Benzene	4.50E-12	1	5	
m-c10 disubstituted benzenes	2.55E-11	e4	5	
o-c10 disubstituted benzenes	1.64E-11	e4	5	
p-c10 disubstituted benzenes	1.64E-11	e4	5	
1-methyl-4-isopropylbenzene (p-cymene)	1.45E-11	5	5	
1,2,3-c10 trisubstituted benzenes	3.41E-11	e5	5	
1,2,4-c10 trisubstituted benzenes	3.41E-11	e5	5	

Table B-4 (continued)

Compound	kOH [a]		Mec	Structure [c]
	k(300)	Ref	[b]	
1,3,5-c10 trisubstituted benzenes	5.77E-11	e5	5	
Tetralin	3.40E-11	1	6	
Naphthalene	2.30E-11	1	5	
C11 Monosubstituted Benzenes	1.10E-11	e3	5	
m-c11 disubstituted benzenes	2.74E-11	e4	5	
o-c11 disubstituted benzenes	1.82E-11	e4	5	
p-c11 disubstituted benzenes	1.82E-11	e4	5	
1,2,3-c11 trisubstituted benzenes	3.57E-11	e5	5	
1,2,4-c11 trisubstituted benzenes	3.57E-11	e5	5	
1,3,5-c11 trisubstituted benzenes	5.93E-11	e5	5	
Methyl Naphthalenes	1.59E-11	e6	6	
C12 Monosubstituted Benzenes	1.24E-11	e3	5	
m-c12 disubstituted benzenes	2.82E-11	e4	5	
o-c12 disubstituted benzenes	1.90E-11	e4	5	
p-c12 disubstituted benzenes	1.90E-11	e4	5	
1,2,3-c12 trisubstituted benzenes	3.66E-11	e5	5	
1,2,4-c12 trisubstituted benzenes	3.66E-11	e5	5	
1,3,5-c12 trisubstituted benzenes	6.01E-11	e5	5	
2,3-Dimethyl Naphthalene	7.68E-11	5	6	
C13 Monosubstituted Benzenes	1.38E-11	e3	5	
m-c13 disubstituted benzenes	2.96E-11	e4	5	
o-c13 disubstituted benzenes	2.05E-11	e4	5	
p-c13 disubstituted benzenes	2.05E-11	e4	5	
1,2,3-c13 trisubstituted benzenes	3.81E-11	e5	5	
1,2,4-c13 trisubstituted benzenes	3.81E-11	e5	5	
1,3,5-c13 trisubstituted benzenes	6.17E-11	e5	5	
C14 Monosubstituted Benzenes	1.53E-11	e3	5	
m-c14 disubstituted benzenes	3.11E-11	e4	5	
o-c14 disubstituted benzenes	2.19E-11	e4	5	
p-c14 disubstituted benzenes	2.19E-11	e4	5	
1,2,3-c14 trisubstituted benzenes	3.93E-11	e5	5	
1,2,4-c14 trisubstituted benzenes	3.93E-11	e5	5	

Table B-4 (continued)

Compound	kOH [a]		Mec [b]	Structure [c]
	k(300)	Ref		
1,3,5-c14 trisubstituted benzenes	6.28E-11	e5	5	
C15 Monosubstituted Benzenes	1.67E-11	e3	5	
m-c15 disubstituted benzenes	3.25E-11	e4	5	
o-c15 disubstituted benzenes	2.33E-11	e4	5	
p-c15 disubstituted benzenes	2.33E-11	e4	5	
1,2,3-c15 trisubstituted benzenes	4.04E-11	e5	5	
1,2,4-c15 trisubstituted benzenes	4.04E-11	e5	5	
1,3,5-c15 trisubstituted benzenes	6.40E-11	e5	5	
C16 Monosubstituted Benzenes	1.81E-11	e3	5	
m-c16 disubstituted benzenes	3.39E-11	e4	5	
o-c16 disubstituted benzenes	2.48E-11	e4	5	
p-c16 disubstituted benzenes	2.47E-11	e4	5	
1,2,3-c16 trisubstituted benzenes	4.17E-11	e5	5	
1,2,4-c16 trisubstituted benzenes	4.17E-11	e5	5	
1,3,5-c16 trisubstituted benzenes	6.52E-11	e5	5	
formaldehyde	8.47E-12	1	1	
methanol	9.02E-13	1	1	
formic acid	4.50E-13	29	1	
Ethylene Oxide	7.60E-14	20	2	CH_2*CH_2O*
acetaldehyde	1.49E-11	1	1	
Ethanol	3.21E-12	1	2	CH_3CH_2OH
Dimethyl Ether	2.83E-12	1	2	CH_3OCH_3
glyoxal	1.10E-11	1	1	
Methyl Formate	2.27E-13	19	2	CH_3OCHO
acetic acid	7.26E-13	29	1	
glycolaldehyde	1.49E-11	e18	24	
Ethylene Glycol	1.47E-11	8	2	$HOCH_2CH_2OH$
Glycolic Acid	3.08E-12	e1	2	$HOCH_2C(O)OH$
Acrolein	1.99E-11	20	8,A	$CH_2=CHCHO$
Trimethylene Oxide	1.03E-11	10	2	$CH_2*CH_2OCH_2*$
Propylene Oxide	5.20E-13	20	2	CH_3CH*CH_2O*
propionaldehyde	1.97E-11	1	1	
acetone	1.91E-13	1	1	
Isopropyl Alcohol	5.09E-12	1	2	$CH_3CH(CH_3)OH$
n-Propyl Alcohol	5.81E-12	1	2	$CH_3CH_2CH_2OH$
Acrylic Acid	2.85E-11	e1	2	$CH_2=CHC(O)OH$
methyl glyoxal	1.50E-11	1	1	
1,3-dioxolane	5.36E-11	e1	2	$CH_2*CH_2OCH_2O*$
Ethyl Formate	1.02E-12	19	2	CH_3CH_2OCHO

Table B-4 (continued)

Compound	kOH [a]		Mec	Structure [c]
	k(300)	Ref	[b]	
Methyl Acetate	3.49E-13	19	2	$CH_3C(O)OCH_3$
Propionic Acid	1.20E-12	29	1	$CH_3CH_2C(O)OH$
Hydroxy Acetone	3.02E-12	10	8	$CH_3C(O)CH_2OH$
Propylene Glycol	2.15E-11	8	2,A	$CH_3CH(OH)CH_2OH$
Dimethoxy methane	4.90E-12	11	2,A	$CH_3OCH_2OCH_3$
2-Methoxyethanol	1.33E-11	10	2	$CH_3OCH_2CH_2OH$
Dimethyl Carbonate	3.30E-13	11	2	$CH_3OC(O)OCH_3$
dihydroxyacetone	6.01E-12	e1	9	$HOCH_2C(O)CH_2OH$
Glycerol	1.87E-11	e1	2,A	$HOCH_2CH(OH)CH_2OH$
Furan	4.02E-11	5	7	
Crotonaldehyde	3.64E-11	33	8	$CH_3CH=CHCHO$
methacrolein	2.84E-11	1	1	
Cyclobutanone	8.70E-13	1	8	$CH_2{*}CH_2C(O)CH_2{*}$
methylvinyl ketone	1.99E-11	1	1	
Tetrahydrofuran	1.61E-11	6	2	$CH_2{*}CH_2CH_2OCH_2{*}$
1,2-Epoxybutane	1.91E-12	28	2	$CH_3CH_2CH{*}CH_2O{*}$
2-Methylpropanal	2.68E-11	1	2	$CH_3CH(CH_3)CHO$
Butanal	2.35E-11	1	2	$CH_3CH_2CH_2CHO$
methyl ethyl ketone	1.20E-12	1	1	
Isobutyl Alcohol	9.30E-12	1	2	$CH_3CH(CH_3)CH_2OH$
n-Butyl Alcohol	8.45E-12	1	2	$CH_3CH_2CH_2CH_2OH$
s-Butyl Alcohol	8.70E-12	1	2	$CH_3CH_2CH(CH_3)OH$
t-Butyl Alcohol	1.07E-12	1	2	$CH_3C(CH_3)(CH_3)OH$
Diethyl Ether	1.31E-11	1	2	$CH_3CH_2OCH_2CH_3$
gamma- butyrolactone	2.32E-12	e1	2	$CH_2{*}CH_2C(O)OCH_2{*}$
Methacrylic Acid	5.24E-11	e1	2	$CH_2=C(CH_3)C(O)OH$
Methyl Acrylate	2.87E-11	e1	2	$CH_2=CHC(O)OCH_3$
Vinyl Acetate	3.16E-11	e1	2	$CH_2=CHOC(O)CH_3$
Hydroxy Methacrolein	4.30E-11	e8	8	$CH_2=C(CHO)CH_2OH$
Biacetyl	0	51	1	
1,4-dioxane	3.83E-11	e1	2	$CH_2{*}CH_2OCH_2CH_2O{*}$
Ethyl Acetate	1.60E-12	20	2	$CH_3CH_2OC(O)CH_3$
Methyl Propionate	1.03E-12	19	2	$CH_3CH_2C(O)OCH_3$
n-Propyl Formate	2.38E-12	19	2	$CH_3CH_2CH_2OCHO$
Isopropyl Formate	2.09E-12	e1	2	$CH_3CH(CH_3)OCHO$
isobutyric acid	2.62E-12	e1	2	$CH_3CH(CH_3)C(O)OH$
butanoic acid	4.77E-12	e1	2	$CH_3CH_2CH_2C(O)OH$
Methoxy Acetone	6.77E-12	10	8	$CH_3C(O)CH_2OCH_3$
1,3-Butanediol	3.32E-11	9	2	$CH_3CH(OH)CH_2CH_2OH$
1,2-Butandiol	2.70E-11	9	2,A	$CH_3CH_2CH(OH)CH_2OH$
1,4-Butanediol	1.12E-11	e1	2	$HOCH_2CH_2CH_2CH_2OH$
2,3-Butanediol	2.36E-11	9	2,A	$CH_3CH(OH)CH(CH_3)OH$
1-Methoxy-2-Propanol	2.00E-11	15	2,A	$CH_3OCH_2CH(CH_3)OH$
2-Ethoxyethanol	1.87E-11	16	2	$CH_3CH_2OCH_2CH_2OH$
2-Methoxy-1-Propanol	2.53E-11	e1	2	$CH_3OCH(CH_3)CH_2OH$
3-methoxy-1-propanol	1.63E-11	e1	2	$CH_3OCH_2CH_2CH_2OH$
Propylene Carbonate	6.90E-13	24	2	$CH_3CH{*}CH_2OC(O)O{*}$
Methyl Lactate	2.76E-12	25	2	$CH_3OC(O)CH(CH_3)OH$

Table B-4 (continued)

Compound	kOH [a]		Mec [b]	Structure [c]
	k(300)	Ref		
Diethylene Glycol	2.75E-11	e1	2,A	$HOCH_2CH_2OCH_2CH_2OH$
malic acid	2.28E-11	e1	2	$HOC(O)CH_2CH(OH)C(O)OH$
2-methyl furan	6.19E-11	31	7	
3-methyl furan	9.35E-11	32	7	
Cyclopentanone	2.90E-12	1	8	$CH_2*CH_2CH_2C(O)CH_2*$
Cyclopentanol	1.10E-11	1	2	$HOCH*CH_2CH_2CH_2CH_2*$
Alpha-Methyltetrahydrofuran	2.20E-11	12	2	$CH_3CH*CH_2CH_2CH_2O*$
Tetrahydropyran	1.38E-11	10	2	$CH_2*CH_2CH_2OCH_2CH_2*$
2-Methyl-3-Butene-2-ol	6.26E-11	30	2	$CH_2=CHC(CH_3)(CH_3)OH$
2,2-Dimethylpropanal (pivaldehyde)	2.78E-11	1	2	$CH_3C(CH_3)(CH_3)CHO$
3-Methylbutanal (Isovaleraldehyde)	2.70E-11	1	2	$CH_3CH(CH_3)CH_2CHO$
Pentanal (Valeraldehyde)	2.78E-11	1	2	$CH_3CH_2CH_2CH_2CHO$
2-Pentanone	4.40E-12	1	8	$CH_3CH_2CH_2C(O)CH_3$
3-Pentanone	2.00E-12	1	8	$CH_3CH_2C(O)CH_2CH_3$
Methyl Isopropyl Ketone	3.01E-12	1	8	$CH_3C(O)CH(CH_3)CH_3$
2-Pentanol	1.20E-11	1	2	$CH_3CH_2CH_2CH(CH_3)OH$
3-Pentanol	1.30E-11	1	2	$CH_3CH_2CH(OH)CH_2CH_3$
Pentyl Alcohol	1.10E-11	1	2	$CH_3CH_2CH_2CH_2CH_2OH$
isoamyl alcohol (3-methyl-1-butanol)	1.30E-11	1	2	$CH_3CH(CH_3)CH_2CH_2OH$
2-methyl-1-butanol	8.61E-12	e1	2	$CH_3CH_2CH(CH_3)CH_2OH$
Ethyl Isopropyl Ether	2.44E-11	e1	2	$CH_3CH_2OCH(CH_3)CH_3$
Methyl n-Butyl Ether	1.48E-11	6	2	$CH_3CH_2CH_2CH_2OCH_3$
Methyl t-Butyl Ether	2.95E-12	1	2	$CH_3OC(CH_3)(CH_3)CH_3$
Ethyl Acrylate	3.01E-11	e1	2	$CH_2=CHC(O)OCH_2CH_3$
Methyl Methacrylate	5.25E-11	e1	2	$CH_2=C(CH_3)C(O)OCH_3$
Glutaraldehyde	4.16E-11	e1	2	$HCOCH_2CH_2CH_2CHO$
2,4-pentanedione	7.41E-13	e1	8	$CH_3C(O)CH_2C(O)CH_3$
tetrahydro-2-furanmethanol	2.77E-11	e1	2	$HOCH_2CH*CH_2CH_2CH_2O*$
Ethyl Propionate	2.14E-12	19	2	$CH_3CH_2C(O)OCH_2CH_3$
Isopropyl Acetate	3.40E-12	20	2	$CH_3C(O)OCH(CH_3)CH_3$
Methyl Butyrate	3.04E-12	19	2	$CH_3CH_2CH_2C(O)OCH_3$
Methyl Isobutyrate	1.73E-12	21	2	$CH_3OC(O)CH(CH_3)CH_3$
n-Butyl Formate	3.12E-12	19	2	$CH_3CH_2CH_2CH_2OCHO$
Propyl Acetate	3.40E-12	20	2	$CH_3CH_2CH_2OC(O)CH_3$
3-Methylbutanoic acid	8.81E-12	e1	2	$CH_3CH(CH_3)CH_2C(O)OH$
2,2-Dimethoxy Propane	2.65E-12	e1	2	$CH_3OC(CH_3)(CH_3)OCH_3$
1-Ethoxy-2-Propanol	2.62E-11	e1	2	$CH_3CH_2OCH_2CH(CH_3)OH$
2-Propoxyethanol	2.47E-11	e1	2,A	$CH_3CH_2CH_2OCH_2CH_2OH$
3-Ethoxy-1-Propanol	2.20E-11	10	2	$CH_3CH_2OCH_2CH_2CH_2OH$
3-Methoxy-1-Butanol	2.36E-11	10	2	$CH_3OCH(CH_3)CH_2CH_2OH$
2-Methoxyethyl Acetate	1.26E-11	e1	2	$CH_3C(O)OCH_2CH_2OCH_3$
Ethyl Lactate	3.91E-12	25	2	$CH_3CH_2OC(O)CH(CH_3)OH$
Methyl Isopropyl Carbonate	2.55E-12	26	2	$CH_3OC(O)OCH(CH_3)CH_3$
2-(2-Methoxyethoxy) Ethanol	3.41E-11	e1	2,A	$CH_3OCH_2CH_2OCH_2CH_2OH$
pentaerythritol	1.68E-11	e1	2,A	$HOCH_2C(CH_2OH)(CH_2OH)CH_2OH$
2,5-dimethyl furan	1.32E-10	31	7	

Table B-4 (continued)

Compound	kOH [a]		Mec	Structure [c]
	k(300)	Ref	[b]	
Cyclohexanone	6.40E-12	1	9	$CH_2*CH_2CH_2C(O)CH_2CH_2*$
Cyclohexanol	1.90E-11	1	2,A	$HOCH*CH_2CH_2CH_2CH_2CH_2*$
Hexanal	3.00E-11	1	2	$CH_3CH_2CH_2CH_2CH_2CHO$
4-Methyl-2-Pentanone	1.27E-11	1	8	$CH_3C(O)CH_2CH(CH_3)CH_3$
Methyl n-Butyl Ketone	9.10E-12	1	8	$CH_3CH_2CH_2CH_2C(O)CH_3$
Methyl t-Butyl Ketone	1.20E-12	1	8	$CH_3C(O)C(CH_3)(CH_3)CH_3$
1-Hexanol	1.50E-11	1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2OH$
2-Hexanol	1.20E-11	1	2,A	$CH_3CH_2CH_2CH_2CH(CH_3)OH$
4-methyl-2-pentanol (methyl isobutyl carbinol)	1.28E-11	e1	2,A	$CH_3CH(CH_3)CH_2CH(CH_3)OH$
Di n-Propyl Ether	1.85E-11	6	2	$CH_3CH_2CH_2OCH_2CH_2CH_3$
Ethyl n-Butyl Ether	2.13E-11	6	2	$CH_3CH_2CH_2CH_2OCH_2CH_3$
Ethyl t-Butyl Ether	8.68E-12	1	2	$CH_3CH_2OC(CH_3)(CH_3)CH_3$
Methyl t-Amyl Ether	6.06E-12	1	2	$CH_3CH_2C(CH_3)(CH_3)OCH_3$
diisopropyl ether	3.28E-11	e1	2	$CH_3CH(CH_3)OCH(CH_3)CH_3$
Ethyl Methacrylate	5.39E-11	e1	2	$CH_2=C(CH_3)C(O)OCH_2CH_3$
Ethyl Butyrate	4.94E-12	19	2	$CH_3CH_2CH_2C(O)OCH_2CH_3$
Isobutyl Acetate	4.61E-12	e1	2	$CH_3C(O)OCH_2CH(CH_3)CH_3$
Methyl Pivalate	1.20E-12	22	2	$CH_3OC(O)C(CH_3)(CH_3)CH_3$
n-Butyl Acetate	4.20E-12	20	2	$CH_3CH_2CH_2CH_2OC(O)CH_3$
n-Propyl Propionate	4.02E-12	19	2	$CH_3CH_2CH_2OC(O)CH_2CH_3$
s-Butyl Acetate	5.50E-12	20	2	$CH_3CH_2CH(CH_3)OC(O)CH_3$
t-Butyl Acetate	4.25E-13	23	2	$CH_3C(O)OC(CH_3)(CH_3)CH_3$
Diacetone Alcohol	1.49E-12	e1	9	$CH_3C(O)CH_2C(CH_3)(CH_3)OH$
methyl pentanoate; methyl valerate	3.33E-12	e1	2	$CH_3CH_2CH_2CH_2C(O)OCH_3$
1,2-Dihydroxy Hexane	1.87E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH(OH)CH_2OH$
2-Methyl-2,4-Pentanediol	2.77E-11	9	2	$CH_3CH(OH)CH_2C(CH_3)(CH_3)OH$
ethylene glycol diethyl ether; 1,2-diethoxyethane	3.51E-11	e1	2	$CH_3CH_2OCH_2CH_2OCH_2CH_3$
acetal (1,1-diethoxyethane)	1.49E-10	e1	2	$CH_3CH_2OCH(CH_3)OCH_2CH_3$
1-Propoxy-2-Propanol (Propylene glycol n-propyl ether)	2.91E-11	e1	2,A	$CH_3CH_2CH_2OCH_2CH(CH_3)OH$
2-Butoxyethanol	2.57E-11	17	2	$CH_3CH_2CH_2CH_2OCH_2CH_2OH$
3 methoxy -3 methyl-Butanol	1.64E-11	54	23	$CH_3OC(CH_3)(CH_3)CH_2CH_2OH$
n-propoxypropanol	2.61E-11	e1	2	$CH_3CH_2CH_2OCH_2CH_2CH_2OH$
hydroxypropyl acrylate	3.59E-11	e1	2	$CH_2=CHC(O)OCH_2CH_2CH_2OH$
1-Methoxy-2-Propyl Acetate	1.44E-11	7	2	$CH_3C(O)OCH(CH_3)CH_2OCH_3$
2-Ethoxyethyl Acetate	1.94E-11	e1	2	$CH_3CH_2OCH_2CH_2OC(O)CH_3$
2-Methyoxy-1-propyl Acetate	2.30E-11	e1	2	$CH_3C(O)OCH_2CH(CH_3)OCH_3$
methoxypropanol acetate	1.40E-11	e1	2	$CH_3C(O)OCH_2CH_2CH_2OCH_3$
2-(2-Ethoxyethoxy) Ethanol	5.08E-11	18	2	$CH_3CH_2OCH_2CH_2OCH_2CH_2OH$
Dipropylene Glycol Isomer (1-[2-hydroxypropyl]-2-propanol)	3.64E-11	e1	2,A	$CH_3CH(OH)CH_2OCH_2CH(CH_3)OH$
Dimethyl Succinate	1.50E-12	27	2	$CH_3OC(O)CH_2CH_2C(O)OCH_3$
Ethylene Glycol Diacetate	3.78E-12	e1	2	$CH_3C(O)OCH_2CH_2OC(O)CH_3$
adipic acid	1.09E-11	e1	2	$HOC(O)CH_2CH_2CH_2CH_2C(O)OH$

Table B-4 (continued)

Compound	kOH [a]		Mec	Structure [c]
	k(300)	Ref	[b]	
triethylene glycol	4.67E-11	e1	2	$HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$
benzaldehyde	1.20E-11	1	1	
o-cresol	4.03E-11	5	1	
Benzyl alcohol	2.29E-11	34	10	
Methoxybenzene; Anisole	1.73E-11	32	11	
Heptanal	3.00E-11	1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CHO$
2-methyl-hexanal	2.54E-11	e1	2	$CH_3CH_2CH_2CH_2CH(CH_3)CHO$
2-Heptanone	1.10E-11	1	8	$CH_3CH_2CH_2CH_2CH_2C(O)CH_3$
2-Methyl-3-Hexanone	7.21E-12	e1	8	$CH_3CH_2CH_2C(O)CH(CH_3)CH_3$
Di-Isopropyl Ketone	5.00E-12	1	8	$CH_3CH(CH_3)C(O)CH(CH_3)CH_3$
5-Methyl-2-Hexanone	1.16E-11	1	8,A	$CH_3C(O)CH_2CH_2CH(CH_3)CH_3$
3-Methyl-2-Hexanone	8.23E-12	e1	8	$CH_3CH_2CH_2CH(CH_3)C(O)CH_3$
1-Heptanol	1.40E-11	1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$
dimethylpentanol (2,3-dimethyl-1-pentanol)	1.17E-11	e1	2	$CH_3CH_2CH(CH_3)CH(CH_3)CH_2OH$
4,4-Dimethyl-3-oxahexane	9.63E-12	e1	2	$CH_3CH_2OC(CH_3)(CH_3)CH_2CH_3$
n-butyl acrylate	3.30E-11	e1	2	$CH_2=CHC(O)OCH_2CH_2CH_2CH_3$
isobutyl acrylate	3.30E-11	e1	2	$CH_2=CHC(O)OCH_2CH(CH_3)CH_3$
Butyl Propionate	5.06E-12	e1	2	$CH_3CH_2CH_2CH_2OC(O)CH_2CH_3$
Amyl Acetate	6.05E-12	e1	2,A	$CH_3CH_2CH_2CH_2CH_2OC(O)CH_3$
n-Propyl Butyrate	7.41E-12	19	2	$CH_3CH_2CH_2C(O)OCH_2CH_2CH_3$
isoamyl acetate (3-methylbutyl acetate)	6.03E-12	e1	2	$CH_3C(O)OCH_2CH_2CH(CH_3)CH_3$
2-methyl-1-butyl acetate	6.31E-12	e1	2	$CH_3CH_2CH(CH_3)CH_2OC(O)CH_3$
methyl hexanoate	4.75E-12	e1	2	$CH_3CH_2CH_2CH_2CH_2C(O)OCH_3$
1-tert-Butoxy-2-Propanol	1.87E-11	e1	2,A	$CH_3CH(OH)CH_2OC(CH_3)(CH_3)CH_3$
2-tert-Butoxy-1-Propanol	2.46E-11	e1	2	$CH_3CH(CH_2OH)OC(CH_3)(CH_3)CH_3$
n-Butoxy-2-Propanol (Propylene Glycol n-Butyl Ether)	3.76E-11	e1	2	$CH_3CH_2CH_2CH_2OCH_2CH(CH_3)OH$
Ethyl 3-Ethoxy Propionate	1.96E-11	e1	2,A	$CH_3CH_2OCH_2CH_2C(O)OCH_2CH_3$
Diisopropyl Carbonate	6.88E-12	e1	2	$CH_3CH(CH_3)OC(O)OCH(CH_3)CH_3$
2-(2-Propoxyethoxy) ethanol	4.38E-11	e1	2	$CH_3CH_2CH_2OCH_2CH_2OCH_2CH_2OH$
Dipropylene Glycol Methyl Ether isomer (1-methoxy-2-[2-hydroxypropoxy]-propane)	4.88E-11	e1	2,A	$CH_3OCH_2CH(CH_3)OCH_2CH(CH_3)OH$
Dipropylene Glycol Methyl Ether isomer (2-[2-methoxypropoxy]-1-propanol)	5.48E-11	e1	2,A	$CH_3OCH(CH_3)CH_2OCH(CH_3)CH_2OH$
1,2-Propylene glycol diacetate	5.91E-12	e1	2	$CH_3C(O)OCH_2CH(CH_3)OC(O)CH_3$
Dimethyl Glutarate	3.50E-12	27	2,A	$CH_3OC(O)CH_2CH_2CH_2C(O)OCH_3$
2-[2-(2-Methoxyethoxy) ethoxy] ethanol	5.32E-11	e1	2	$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2OH$
2-Butyl Tetrahydrofuran	2.76E-11	e1	2	$CH_3CH_2CH_2CH_2CH*CH_2CH_2CH_2O*$
Octanal	2.71E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CHO$
2-Octanone	1.10E-11	1	8	$CH_3CH_2CH_2CH_2CH_2CH_2C(O)CH_3$
1-Octanol	1.40E-11	1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$
2-Ethyl-1-Hexanol	1.33E-11	e1	2	$CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2OH$
2-Octanol	2.52E-11	7	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH(CH_3)OH$

Table B-4 (continued)

Compound	kOH [a]		Mec	Structure [c]
	k(300)	Ref	[b]	
3-Octanol	3.14E-11	7	2	$CH_3CH_2CH_2CH_2CH_2CH(OH)CH_2CH_3$
4-Octanol	2.87E-11	7	2,A	$CH_3CH_2CH_2CH_2CH(OH)CH_2CH_2CH_3$
5-methyl-1-heptanol	1.29E-11	e1	2,A	$CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH_2OH$
Di-Isobutyl Ether	2.60E-11	13	2	$CH_3CH(CH_3)CH_2OCH_2CH(CH_3)CH_3$
Di-n-butyl Ether	2.88E-11	6	2	$CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$
2-Phenoxyethanol; Ethylene glycol phenyl ether	2.99E-11	e9	11	
Butyl Methacrylate	5.68E-11	e1	2	$CH_2=C(CH_3)C(O)OCH_2CH_2CH_2CH_3$
Isobutyl Methacrylate	5.68E-11	e1	2	$CH_2=C(CH_3)C(O)OCH_2CH(CH_3)CH_3$
2,3-Dimethylbutyl Acetate	7.71E-12	e1	2	$CH_3C(O)OCH_2CH(CH_3)CH(CH_3)CH_3$
2-Methylpentyl Acetate	7.73E-12	e1	2	$CH_3CH_2CH_2CH(CH_3)CH_2OC(O)CH_3$
3-Methylpentyl Acetate	7.73E-12	e1	2,A	$CH_3CH_2CH(CH_3)CH_2CH_2OC(O)CH_3$
4-Methylpentyl Acetate	7.45E-12	e1	2	$CH_3C(O)OCH_2CH_2CH_2CH(CH_3)CH_3$
Isobutyl Isobutyrate	5.52E-12	e1	2	$CH_3CH(CH_3)CH_2OC(O)CH(CH_3)CH_3$
n-Butyl Butyrate	1.06E-11	19	2	$CH_3CH_2CH_2CH_2OC(O)CH_2CH_2CH_3$
n-Hexyl Acetate	7.47E-12	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2OC(O)CH_3$
methyl amyl acetate (4-methyl-2-pentanol acetate)	8.16E-12	e1	2	$CH_3C(O)OCH(CH_3)CH_2CH(CH_3)CH_3$
n-pentyl propionate	6.48E-12	e1	2,A	$CH_3CH_2CH_2CH_2CH_2OC(O)CH_2CH_3$
2-Ethyl Hexanoic Acid	1.33E-11	e1	2	$CH_3CH_2CH_2CH_2CH(CH_2CH_3)C(O)OH$
methyl heptanoate	6.17E-12	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2C(O)OCH_3$
2-Ethyl-1,3-hexanediol	2.22E-11	e1	2,A	$CH_3CH_2CH_2CH(OH)CH(CH_2CH_3)CH_2OH$
2-Hexyloxyethanol	2.89E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2OCH_2CH_2OH$
2,2,4-Trimethyl-1,3-Pentanediol	1.76E-11	e1	2	$CH_3CH(CH_3)CH(OH)C(CH_3)(CH_3)CH_2OH$
Phthalic Anhydride	4.00E-12	e10	11	
2-Butoxyethyl Acetate	2.38E-11	e1	2	$CH_3CH_2CH_2CH_2OCH_2CH_2OC(O)CH_3$
2-methoxy-1-(2-methoxy-1-methylethoxy)-propane	6.13E-11	e1	2,A	$CH_3OCH_2CH(CH_3)OCH_2CH(CH_3)OCH_3$
2-(2-Butoxyethoxy)-Ethanol	7.44E-11	e1	2	$CH_3CH_2CH_2CH_2OCH_2CH_2OCH_2CH_2OH$
dipropylene glycol ethyl ether	6.16E-11	e1	2	$CH_3CH_2OCH(CH_3)CH_2OCH(CH_3)CH_2OH$
Dimethyl Adipate	8.80E-12	27	2,A	$CH_3OC(O)CH_2CH_2CH_2CH_2C(O)OCH_3$
2-(2-Ethoxyethoxy) ethyl acetate	3.86E-11	e1	2,A	$CH_3CH_2OCH_2CH_2OCH_2CH_2OC(O)CH_3$
2-[2-(2-Ethoxyethoxy) ethoxy] Ethanol	6.00E-11	e1	2	$CH_3CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OH$
tetraethylene glycol	6.58E-11	e1	2	$HOCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OH$
2-propyl cyclohexanone	1.70E-11	e1	9,A	$CH_3CH_2CH_2CH*CH_2CH_2C(O)CH_2CH_2*$
4-propyl cyclohexanone	1.92E-11	e1	9	$CH_3CH_2CH_2CH*CH_2CH_2CH_2CH_2CO*$
1-nonene-4-one	4.04E-11	e1	9	$CH_2=CHCH_2C(O)CH_2CH_2CH_2CH_2CH_3$
trimethylcyclohexanol	2.25E-11	e1	2,A	$CH_3CH*CH_2CH_2CH(OH)CH(CH_3)CH*CH_3$
2-Nonanone	1.20E-11	1	9	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2C(O)CH_3$
Di-isobutyl ketone (2,6-dimethyl-4-heptanone)	2.60E-11	1	9	$CH_3CH(CH_3)CH_2C(O)CH_2CH(CH_3)CH_3$
dimethylheptanol (2,6-dimethyl-2-heptanol)	7.50E-12	e1	2	$CH_3CH(CH_3)CH_2CH_2CH_2C(CH_3)(CH_3)OH$
2,6-dimethyl-4-heptanol	1.86E-11	e1	2,A	$CH_3CH(CH_3)CH_2CH(OH)CH_2CH(CH_3)CH_3$
2,4-Dimethylpentyl Acetate	9.13E-12	e1	2	$CH_3C(O)OCH_2CH(CH_3)CH_2CH(CH_3)CH_3$
2-Methylhexyl Acetate	9.15E-12	e1	2,A	$CH_3CH_2CH_2CH_2CH(CH_3)CH_2OC(O)CH_3$

Table B-4 (continued)

Compound	kOH [a]		Mec [b]	Structure [c]
	k(300)	Ref		
3-Ethylpentyl Acetate	9.56E-12	e1	2	$CH_3CH_2CH(CH_2CH_3)CH_2CH_2OC(O)CH_3$
3-Methylhexyl Acetate	9.15E-12	e1	2	$CH_3CH_2CH_2CH(CH_3)CH_2CH_2OC(O)CH_3$
4-Methylhexyl Acetate	9.15E-12	e1	2	$CH_3CH_2CH(CH_3)CH_2CH_2CH_2OC(O)CH_3$
5-Methylhexyl Acetate	8.87E-12	e1	2,A	$CH_3C(O)OCH_2CH_2CH_2CH_2CH(CH_3)CH_3$
Isoamyl Isobutyrate	6.94E-12	e1	2	$CH_3CH(CH_3)CH_2CH_2OC(O)CH(CH_3)CH_3$
n-Heptyl Acetate	8.89E-12	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OC(O)CH_3$
methyl octanoate	7.59E-12	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2C(O)OCH_3$
1-(butoxyethoxy)-2-propanol	4.97E-11	e1	2,A	$CH_3CH_2CH_2CH_2OCH_2CH_2OCH_2CH(CH_3)OH$
Dipropylene glycol n-propyl ether isomer #1	5.86E-11	e1	2,A	$CH_3CH_2CH_2OCH_2CH(CH_3)OCH_2CH(CH_3)OH$
Dipropylene glycol methyl ether acetate isomer #1	4.42E-11	e1	2,A	$CH_3C(O)OCH(CH_3)CH_2OCH(CH_3)CH_2OCH_3$
Dipropylene glycol methyl ether acetate isomer #2	4.42E-11	e1	2,A	$CH_3C(O)OCH(CH_3)CH_2OCH_2CH(CH_3)OCH_3$
2-[2-(2-Propoxyethoxy) ethoxy] Ethanol	6.30E-11	e1	2	$CH_3CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OH$
tripropylene glycol	6.59E-11	e1	2	$CH_3CH(OH)CH_2OCH_2CH(CH_3)OCH_2CH(CH_3)OH$
2,5,8,11-Tetraoxatridecan-13-ol	7.24E-11	e1	2	$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OH$
glyceryl triacetate	8.49E-12	e1	2	$CH_3C(O)OCH_2CH(CH_2OC(O)CH_3)OC(O)CH_3$
Camphor	4.60E-12	e1	9	$CH_3C*1(CH_3)CH*2CH_2CH_2C*1(CH_3)C(O)CH_2*2$
a-terpineol	9.51E-11	e1	2	$CH_3C*{=}CHCH_2CH(CH_2CH_2*)C(CH_3)(CH_3)OH$
Citronellol (3,7-dimethy-6-octen-1-ol)	9.87E-11	e1	2	$CH_3C(CH_3){=}CHCH_2CH_2CH(CH_3)CH_2CH_2OH$
Hydroxycitronellal	2.80E-11	e1	2	$CH_3CH(CH_2CHO)CH_2CH_2CH_2C(CH_3)(CH_3)OH$
menthol	2.40E-11	e1	2	$CH_3CH(CH_3)CH*CH_2CH_2CH(CH_3)CH_2CH*OH$
Linalool	1.22E-10	e1	3	$CH_2{=}CHC(CH_3)(OH)CH_2CH_2CH{=}C(CH_3)CH_3$
2-Decanone	1.30E-11	1	9,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2C(O)CH_3$
8-Methyl-1-Nonanol (Isodecyl Alcohol)	1.54E-11	e1	2	$CH_3CH(CH_3)CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$
1-decanol	1.55E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$
3,7-dimethyl-1-octanol	1.57E-11	e1	2	$CH_3CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_2OH$
Di-n-Pentyl Ether	3.47E-11	14	2,A	$CH_3CH_2CH_2CH_2CH_2OCH_2CH_2CH_2CH_2CH_3$
1,2-Diacetyl benzene	4.00E-12	35	11	
2,4-Dimethylhexyl Acetate	1.08E-11	e1	2,A	$CH_3CH_2CH(CH_3)CH_2CH(CH_3)CH_2OC(O)CH_3$
2-Ethyl-Hexyl Acetate	1.10E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2OC(O)CH_3$
3,4-Dimethylhexyl Acetate	1.08E-11	e1	2,A	$CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_2OC(O)CH_3$
3,5-Dimethylhexyl Acetate	1.06E-11	e1	2	$CH_3C(O)OCH_2CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
3-Ethylhexyl Acetate	1.10E-11	e1	2	$CH_3CH_2CH_2CH(CH_2CH_3)CH_2CH_2OC(O)CH_3$
3-Methylheptyl Aceate	1.06E-11	e1	2	$CH_3CH_2CH_2CH_2CH(CH_3)CH_2CH_2OC(O)CH_3$
4,5-Dimethylhexyl Acetate	1.06E-11	e1	2,A	$CH_3C(O)OCH_2CH_2CH_2CH(CH_3)CH(CH_3)CH_3$
4-Methylheptyl Acetate	1.06E-11	e1	2	$CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_2OC(O)CH_3$
5-Methylheptyl Aceate	1.06E-11	e1	2,A	$CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH_2OC(O)CH_3$
n-Octyl Acetate	1.03E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OC(O)CH_3$
Geraniol	1.80E-10	e1	3	$CH_3C(CH_3){=}CHCH_2CH_2C(CH_3){=}CHCH_2OH$
methyl nonanoate	9.01E-12	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2C(O)OCH_3$
2-(2-Ethylhexyloxy) Ethanol	3.24E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2OCH_2CH_2OH$
2-(2-Hexyloxyethoxy) Ethanol	4.81E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2OCH_2CH_2OCH_2CH_2OH$

Table B-4 (continued)

Compound	kOH [a]		Mec [b]	Structure [c]
	k(300)	Ref		
glycol ether dpnb {1-(2-butoxy-1-methylethoxy)-2-propanol}	6.00E-11	e1	2,A	$CH_3CH_2CH_2CH_2OCH_2CH(CH_3)OCH_2CH(CH_3)OH$
2-(2-Butoxyethoxy) ethyl acetate	4.29E-11	e1	2	$CH_3CH_2CH_2CH_2OCH_2CH_2OCH_2CH_2OC(O)CH_3$
2-[2-(2-Butoxyethoxy) ethoxy] Ethanol	6.44E-11	e1	2	$CH_3CH_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OH$
Tripropylene Glycol Monomethyl Ether	7.83E-11	e1	2	$CH_3OCH_2CH(CH_3)OCH_2CH(CH_3)OCH_2CH(CH_3)OH$
2-Ethyl-Hexyl Acrylate	3.94E-11	e1	2	$CH_2=CHC(O)OCH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$
2,3,5-Teimethylhexyl Acetate	1.22E-11	e1	2,A	$CH_3C(O)OCH_2CH(CH_3)CH(CH_3)CH_2CH(CH_3)CH_3$
2,3-Dimethylheptyl Acetate	1.23E-11	e1	2	$CH_3CH_2CH_2CH_2CH(CH_3)CH(CH_3)CH_2OC(O)CH_3$
2,4-Dimethylheptyl Acetate	1.23E-11	e1	2,A	$CH_3CH_2CH_2CH(CH_3)CH_2CH(CH_3)CH_2OC(O)CH_3$
2,5-Dimethylheptyl Acetate	1.23E-11	e1	2	$CH_3CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_2OC(O)CH_3$
2-Methyloctyl Acetate	1.20E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH_2CH_2CH(CH_3)CH_2OC(O)CH_3$
3,5-Dimethylheptyl Acetate	1.23E-11	e1	2,A	$CH_3CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH_2OC(O)CH_3$
3,6-Dimethylheptyl Acetate	1.20E-11	e1	2	$CH_3C(O)OCH_2CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_3$
3-Ethylheptyl Acetate	1.24E-11	e1	2	$CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2CH_2OC(O)CH_3$
4,5-Dimethylheptyl Acetate	1.23E-11	e1	2,A	$CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_2CH_2OC(O)CH_3$
4,6-Dimethylheptyl Acetate	1.20E-11	e1	2	$CH_3C(O)OCH_2CH_2CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
4-Methyloctyl Acetate	1.20E-11	e1	2	$CH_3CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2OC(O)CH_3$
5-Methyloctyl Acetate	1.20E-11	e1	2,A	$CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_2OC(O)CH_3$
n-Nonyl Acetate	1.17E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OC(O)CH_3$
methyl decanoate	1.04E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C(O)OCH_3$
2,6,8-trimethyl-4-nonanone; Isobutyl heptyl ketone	2.31E-11	e1	9	$CH_3CH(CH_3)CH_2C(O)CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
Trimethylnonanolthreoerythro; 2,6,8-Trimethyl-4-nonanol	2.32E-11	e1	2,A	$CH_3CH(CH_3)CH_2CH(CH_3)CH_2CH(OH)CH_2CH(CH_3)CH_3$
3,6-Dimethyloctyl Acetate	1.37E-11	e1	2	$CH_3CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_2CH_2OC(O)CH_3$
3-Isopropylheptyl Acetate	1.38E-11	e1	2,A	$CH_3CH_2CH_2CH_2CH(CH_2CH_2OC(O)CH_3)CH(CH_3)CH_3$
4,6-Dimethyloctyl Acetate	1.37E-11	e1	2	$CH_3CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH_2CH_2OC(O)CH_3$
methyl undecanoate	1.19E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C(O)OCH_3$
1-Hydroxy-2,2,4-Trimethylpentyl-3-Isobutyrate	1.29E-11	e1	2	$CH_3CH(CH_3)C(O)OCH(CH(CH_3)CH_3)C(CH_3)(CH_3)CH_2OH$
3-Hydroxy-2,2,4-Trimethylpentyl-1-Isobutyrate	1.62E-11	e1	2,A	$CH_3CH(CH_3)C(O)OCH_2C(CH_3)(CH_3)CH(OH)CH(CH_3)CH_3$
diethylene glycol mono(2-ethylhexyl) ether	5.16E-11	e1	2	$CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2OCH_2CH_2OCH_2CH_2OH$
Diethyl Phthalate	5.67E-12	e11	11	
Dimethyl Sebacate	9.69E-12	e1	2	$CH_3OC(O)CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C(O)OCH_3$
diisopropyl adipate	1.04E-11	e1	2	$CH_3CH(CH_3)OC(O)CH_2CH_2CH_2CH_2C(O)OCH(CH_3)CH_3$
3,6,9,12-Tetraoxahexadecan-1-ol	8.35E-11	e1	2,A	$CH_3CH_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OH$
triethyl citrate	5.91E-12	e1	2	$CH_3CH_2OC(O)CH_2C(OH)(CH_2C(O)OCH_2CH_3)C(O)OCH_2CH_3$
3,5,7-Trimethyloctyl Acetate	1.51E-11	e1	2,A	$CH_3C(O)OCH_2CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
3-Ethyl-6-Methyloctyl Acetate	1.55E-11	e1	2,A	$CH_3CH_2CH(CH_3)CH_2CH_2CH(CH_2CH_3)CH_2CH_2OC(O)CH_3$
4,7-Dimethylnonyl Acetate	1.51E-11	e1	2,A	$CH_3CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_2CH_2CH_2OC(O)CH_3$
methyl dodecanoate {methyl laurate}	1.33E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C(O)OCH_3$

Table B-4 (continued)

Compound	kOH [a]		Mec	Structure [c]
	k(300)	Ref	[b]	
tripropylene glycol n-butyl ether	9.54E-11	e1	2	$CH_3CH_2CH_2CH_2OCH_2CH(CH_3)OCH_2CH(CH_3)OCH(CH_3)CH_2OH$
2,3,5,7-Tetramethyloctyl Acetate	1.68E-11	e1	2	$CH_3C(O)OCH_2CH(CH_3)CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
3,5,7-Trimethylnonyl Acetate	1.68E-11	e1	2,A	$CH_3CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH_2OC(O)CH_3$
3,6,8-Trimethylnonyl Acetate	1.65E-11	e1	2,A	$CH_3C(O)OCH_2CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
methyl tridecanoate	1.47E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C(O)OCH_3$
2-ethylhexyl benzoate	1.37E-11	e12	11	
2,4,6,8-Tetramethylnonyl Acetate	1.82E-11	e1	2,A	$CH_3C(O)OCH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
3-Ethyl-6,7-Dimethylnonyl Acetate	1.86E-11	e1	2,A	$CH_3CH_2CH(CH_2CH_2OC(O)CH_3)CH_2CH_2CH(CH_3)CH(CH_3)CH_2CH_3$
4,7,9-Trimethyldecyl Acetate	1.79E-11	e1	2,A	$CH_3C(O)OCH_2CH_2CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
methyl myristate {methyl tetradecanoate}	1.61E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C(O)OCH_3$
methyl cis-9-pentadecenoate	7.76E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2C(O)OCH_3$
methyl pentadecanoate	2.10E-11	e1	2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C(O)CH_3$
2,3,5,6,8-Pentaamethylnonyl Acetate	1.99E-11	e1	2	$CH_3C(O)OCH_2CH(CH_3)CH(CH_3)CH_2CH(CH_3)CH(CH_3)CH_2CH(CH_3)CH_3$
3,5,7,9-Tetramethyldecyl Acetate	1.96E-11	e1	2,A	$CH_3C(O)OCH_2CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
5-Ethyl-3,6,8-Trimethylnonyl Acetate	2.00E-11	e1	2,A	$CH_3CH_2CH(CH_2CH(CH_3)CH_2CH_2OC(O)CH_3)CH(CH_3)CH_2CH(CH_3)CH_3$
Dibutyl phthalate	8.59E-12	e11	11	
2,2,4-trimethyl-1,3-pentanediol diisobutyrate	1.15E-11	e1	2	$CH_3CH(CH_3)C(O)OCH_2C(CH_3)(CH_3)CH(OC(O)CH(CH_3)CH_3)CH(CH_3)CH_3$
methyl linolenate; methyl cis,cis,cis-9,12,15-octadecatrienoate	2.02E-10	e1	2	CH_3CH_2^$CH{=}CHvCH_2$^$CH{=}CHvCH_2$^$CH{=}CHvCH_2CH_2CH_2CH_2CH_2CH_2CH_2C(O)OCH_3$
methyl linoelate; methyl cis,cis-9,12-octadecadienoate	1.42E-10	e1	2	$CH_3CH_2CH_2CH_2CH_2$^$CH{=}CHvCH_2$^$CH{=}CHvCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C(O)OCH_3$
Methylamine	1.97E-11	38	3,12	CH_3NH_2
Methyl Chloride	4.48E-14	6	3	CH_3Cl
Methyl nitrite	1.20E-13	20	13	
nitromethane	1.30E-13	6	26	
Carbon disulfide	2.76E-12	48	19	
Dichloromethane	1.45E-13	20	3	$ClCH_2Cl$
Methyl Bromide	4.12E-14	20	17	
Chloroform	1.06E-13	20	3	$ClCH(Cl)Cl$
methyl iodide	1.03E-13	29	20	CH_3I
Chloropicrin	0	51	18	
Acetylene	7.56E-13	6	1	
Dimethyl Amine	6.52E-11	38	3,12	CH_3NHCH_3

Table B-4 (continued)

Compound	kOH [a]		Mec	Structure [c]
	k(300)	Ref	[b]	
Ethyl Amine	2.58E-11	38	3,12	$CH_3CH_2NH_2$
Ethanolamine	4.41E-11	e14	3,12	$NH_2CH_2CH_2OH$
Vinyl Chloride	6.90E-12	6	3	CH_2=CHCl
Ethyl Chloride	4.18E-13	6	3	CH_3CH_2Cl
1,1-difluoroethane; HFC-152a	3.47E-14	55	28	
Methyl isothiocyanate	1.72E-12	49	19	
nitroethane	1.50E-13	6	27	
Dimethyl Sulfoxide	6.20E-11	20	19	
Chloroacetaldehyde	3.10E-12	47	1	
1,1-Dichloroethene	1.09E-11	2	3	CH_2=C(Cl)Cl
Trans-1,2-Dichloroethene	2.32E-12	6	3	ClCH=CH^Cl
1,1-Dichloroethane	2.60E-13	20	3	CH_3CH(Cl)Cl
1,2-Dichloroethane	2.53E-13	6	3	$ClCH_2CH_2Cl$
1,1,1,2-tetrafluoroethane; HFC-134a	4.59E-15	55	29	
Ethyl Bromide	3.08E-13	20	17	
Trichloroethylene	2.34E-12	6	3	ClCH=C(Cl)Cl
1,1,1-Trichloroethane	1.24E-14	20	3	CH_3C(Cl)(Cl)Cl
1,1,2-Trichloroethane	2.00E-13	6	3	$ClCH_2$CH(Cl)Cl
Perchloroethylene	1.71E-13	6	3	ClC(Cl)=C(Cl)Cl
1,2-Dibromoethane	2.27E-13	6	17	
Methyl Acetylene	5.90E-12	6	2	HC#CCH$_3$
Acrylonitrile	4.90E-12	42	14	
Trimethyl Amine	4.84E-11	38	3,12	$CH_3N(CH_3)CH_3$
isopropylamine	3.78E-11	e14	3,12	$CH_3CH(CH_3)NH_2$
1-amino-2-propanol	4.85E-11	e1	3,12	$CH_3CH(OH)CH_2NH_2$
3-Chloropropene	3.20E-11	e1	3	CH_2=$CHCH_2Cl$
1-nitropropane	1.33E-12	e1	3	$CH_3CH_2CH_2NO_2$
2-nitropropane	2.57E-13	58	27	
chloroacetone	0	51	1	
trans-1,3-dichloropropene	1.44E-11	45	3	Cl^CH=CH^CH$_2$Cl
cis-1,3-dichloropropene	8.45E-12	45	3	Cl^CH=CHvCH$_2$Cl
1,2-Dichloropropane	4.50E-13	e1	3	$CH_3CH(Cl)CH_2Cl$
trans 1,3,3,3-tetrafluoropropene	9.25E-13	52	21	
2,3,3,3-tetrafluoropropene	1.05E-12	53	22	
n-Propyl Bromide	1.18E-12	44	17	
1,1,1,3,3-pentafluoropropane	7.24E-15	55	30	
3,3-dichloro-1,1,1,2,2-pentafluoropropane;HCFC-225ca	2.57E-14	55	31	
1,3-dichloro-1,1,2,2,3-pentafluoropropane;HCFC-225cb	9.11E-15	55	31	
1,3-butadiyne	2.13E-11	e7	36	
2-Butyne	2.72E-11	6	2	CH$_3$C#CCH$_3$
Ethyl Acetylene	8.00E-12	6	2	HC#CCH$_2$CH$_3$
t-butyl amine	1.18E-11	39	3,12	$CH_3C(CH_3)(CH_3)NH_2$

Table B-4 (continued)

Compound	kOH [a]		Mec	Structure [c]
	k(300)	Ref	[b]	
morpholine	1.12E-10	e1	2	$CH_2{*}CH_2OCH_2CH_2NH{*}$
ethyl methyl ketone oxime	5.14E-12	e15	15	$CH_3CH_2C(CH_3){=}NOH$
Dimethylaminoethanol	6.85E-11	40	3,12	$CH_3N(CH_3)CH_2CH_2OH$
2-amino-1-butanol	5.32E-11	e14	3,12	$CH_3CH_2CH(NH_2)CH_2OH$
2-Amino-2-Methyl-1-Propanol	2.80E-11	41	3,12	$CH_3C(CH_3)(NH_2)CH_2OH$
1-Chlorobutane	2.19E-12	e1	3	$CH_3CH_2CH_2CH_2Cl$
Diethanol Amine	1.01E-10	e14	3,12	$HOCH_2CH_2NHCH_2CH_2OH$
2-(Cl-methyl)-3-Cl-Propene	3.16E-11	2	3	$CH_2{=}C(CH_2Cl)CH_2Cl$
n-Butyl Bromide	2.46E-12	44	17	
1,1,1,3,3-pentafluorobutane; HFC-365mfc	7.12E-15	55	32	
2-amino-2-ethyl-1,3-propanediol	2.70E-11	e1	3,12	$CH_3CH_2C(NH_2)(CH_2OH)CH_2OH$
N-Methyl-2-Pyrrolidone	2.15E-11	43	16	
methyl nonafluorobutyl ether	1.15E-12	e1	3	$CH_3OC(F)(F)C(F)(F)C(F)(F)C(F)(F)F$
methoxy-perfluoro-n-butane	1.20E-14	57	35	
1,1,1,2,2,3,4,5,5,5-decafluoropentane; HFC-43-10mee	3.50E-15	55	33	
Triethyl Amine	5.57E-11	e14	3,12	$CH_3CH_2N(CH_2CH_3)CH_2CH_3$
Monochlorobenzene	7.70E-13	20	11	
Nitrobenzene	1.41E-13	5	11	
p-Dichlorobenzene	5.55E-13	e16	11	
Triethanolamine	8.04E-11	e14	3,12	$HOCH_2CH_2N(CH_2CH_2OH)CH_2CH_2OH$
Hexamethyldisiloxane	1.38E-12	20	11	
Hydroxymethyldisiloxane	1.89E-12	20	11	
Hexafluorobenzene	1.74E-13	6	11	
ethoxy-perfluoro-n-butane	6.40E-14	56	34	
ethoxy-perfluoro-isobutane	7.70E-14	56	34	
ethyl nonafluorobutyl ether	7.97E-12	e1	3	$CH_3CH_2OC(F)(F)C(F)(F)C(F)(F)C(F)(F)F$
m-Nitrotoluene	1.24E-12	5	11	
Benzotrifluoride	4.60E-13	46	11	
p-Trifluoromethyl-Cl-Benzene	2.40E-13	46	11	
Para Toluene Isocyanate	5.90E-12	36	6	
D4 Cyclosiloxane	1.00E-12	20	11	
2,4-Toluene Diisocyanate	7.40E-12	37	6	
Molinate	2.42E-11	e17	19	
Ethyl di-n-Propyl-Thiolcarbamate	2.12E-11	50	19	
triisopropanolamine	9.37E-11	e14	3,12	$CH_3CH(OH)CH_2N(CH_2CH(CH_3)OH)CH_2CH(CH_3)OH$
Pebulate	2.26E-11	e17	19	
D5 Cyclosiloxane	1.55E-12	20	11	
thiobencarb	1.87E-11	e17	19	
Methylene Diphenylene Diisocyanate	1.18E-11	e13	6	
PROD2 Species #1	9.63E-12	e1	8	$CH_3C(O)CH_2CH_2CH_2OH$
PROD2 Species #2	1.45E-11	e1	8	$CH_3C(O)CH_2CH(CH_3)CH_2OH$

Table B-4 (continued)

Compound	kOH [a]		Mec	Structure [c]
	k(300)	Ref	[b]	
PROD2 Species #3	1.52E-11	e1	8	$CH_3CH_2C(O)CH_2CH_2CH(CH_3)OH$
PROD2 Species #4	1.83E-11	e1	8	$CH_3CH_2C(O)CH_2CH_2CH(OH)CH_2CH_3$
PROD2 Species #5	1.97E-11	e1	8	$CH_3CH_2CH_2CH(OH)CH_2CH_2C(O)CH_2CH_3$
RNO3 Species #1	1.60E-12	e1	8	$CH_3CH_2CH(CH_3)ONO_2$
RNO3 Species #2	1.15E-11	e1	8	$CH_3CH(OH)CH_2CH_2CH_2ONO_2$
RNO3 Species #3	4.70E-12	e1	8	$CH_3CH_2CH(CH_3)CH(CH_3)ONO_2$
RNO3 Species #4	9.89E-12	e1	8	$CH_3CH_2CH_2CH_2CH_2CH(ONO_2)CH_2OH$
RNO3 Species #5	5.64E-12	e1	8	$CH_3CH_2C(CH_3)(ONO_2)CH_2CH(CH_3)CH_3$
RNO3 Species #6	9.87E-12	e1	8	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH(ONO_2)CH_2CH_3$

[a] Rate constant for reaction with OH radicals at 300°K in units of cm^3 $molec^{-1}$ s^{-1}. See the complete mechanism listing in the electronic version of the report for the temperature dependences, where available. Footnotes for measured rate constants are as follows:

1 As recommended or tabulated by Atkinson and Arey (2003)
2 Atkinson (1997) Recommendation
3 Carter et al (2000a)
4 298K Rate constant as recommended by Calvert et al (2000). Temperature dependence estimated from k(T)=A exp(500/T), where A is adjusted to yield the recommended 298K rate constant, based on data for those alkenes for which temperature dependence data are available.
5 As recommended or tabulated by Calvert et al (2002)
6 Rate constant expression recommended by Atkinson (1994)
7 Carter et al (2000b).
8 Aschmann and Atkinson (1998).
9 Bethel et al, (2001).
10 Dagaut et al (1989)
11 Rate constant used is average of various measurements tabulated by Sidebottom et al (1997).
12 Wallington et al (1990).
13 Bennett and Kerr (1989).
14 Wallington et al (1988a).
15 Average of values of Porter et al (1995) and Aschmann and Atkinson (1998)
16 Rate constant of Dagaut et al (1988a) used. Value of Hartmann et al (1986) is not consistent with chamber data (Carter et al, 1993)
17 Average of values of Dagaut et al (1988a), Stemmler et al (1996) and Aschmann and Atkinson (1998).
18 Carter et al (1993).
19 Wallington et al (1988b).
20 Rate constant expression recommended by Atkinson (1989). Recommendation not changed in evaluation updates.
21 Wyatt et al. (1999).
22 Wallington et al (2001)
23 Smith et al (1992). Average of values relative to propane and n-butane
24 Carter et al (1996b).
25 Atkinson and Carter (1995).
26 Carter et al (2000c)
27 Carter et al (1997c).
28 Wallington et al (1988c).
29 IUPAC (2006) Recommendation
30 Rudich et al (1995), as recommended by Atkinson (personal communication, 2000). Good agreement with data of Ferronato et al (1998).
31 Bierbach et al (1992)
32 Atkinson et al (1989)
33 Atkinson et al (1983).
34 As tabulated by Atkinson (1989) (Cited reference not available).

Table B-4 (continued)

35 Wang et al (2006).
36 Carter et al (1999a)
37 Becker et al (1988).
38 Average of values tabulated by Carl and Crowley (1998).
39 Koch et al (1996)
40 Average of values of Harris and Pitts (1983) and Anderson and Stephens (1988), as tabulated by Atkinson (1989).
41 Harris and Pitts (1983)
42 Harris et al (1981). Rate constant is pressure dependent and was measured at lower than atmospheric pressures, and extrapolated to atmospheric pressure.
43 Aschmann and Atkinson (1999).
44 Donaghy et al. (1993).
45 Tuazon et al (1988).
46 Atkinson et al (1985).
47 Rate constants from Scollard et al (1993)
48 Mechanism is complex and depends on pressure, temperature, and O2 content. Rate constant given is for 1 atm air and 298oK only, and derived from the IUPAC (2006) rate constants recommended for CS2 and HOCS2 (the species assumed to be initially formed in the reaction). See Carter and Malkina (2007).
49 Rate constant from Carter and Malkina (2007).
50 Rate constant from Carter and Malkina (2007). This is somewhat higher than the value determined by Kwok et al (1992), but is used as the basis for evaluating the mechanism against chamber data.
51 Reaction expected to be slow and is neglected.
52 Søndergaard et al (2007)
53 Nielsen et al (2007)
54 Carter et al (2010)
55 NASA (2006) recommendation.
56 Christensen et al (1998)
57 Wallington et al (1997). Rate constant for mixture of isomers, which couldn't be separated.
58 Liu et al (1990)

Footnotes for estimated rate constants are as follows:

e1 Estimated using the group-additivity estimation assignments implemented in the current mechanism generation system. See Carter (2000a) and Table 3.
e2 Assumed to have the same rate constant as the cis isomer.
e3 Rate constant estimated using rate constant for ring addition for toluene, derived based on the observed benzaldehyde + belzyl nitrate yields, and estimated rate constants for abstraction reactions for additions at various positions of the molecules of the mixture of alkylbenzenes used to represent those with this carbon number. Partial rate constant for reaction at the -CH2- group next to the aromatic derived from the rate constant for ethylbenzene and the ring addition rate constant for toluene. Partial rate constants for reactions at other positions based on standard structure-reactivity methods used in the mechanism generation system. (Carter, 2000a). The compounds used to represent the lumped monoalkylbenzenes are given with the aromatics mechanism documentation.
e4 Rate constant estimated using the estimated rate constants for ring addition for the xylene isomers, derived based on the observed tolualdenyde yields and estimated nitrate yields, and based on estimated rate constants for abstraction reactions for additions at various positions of the molecules of the mixture of alkylbenzenes used to represent those with this carbon number. Separate ring addition estimates are made for o-, m-, and p-configurations. Partial rate constant for reaction at the -CH2- or -CH- groups next to the aromatic derived from the rate constants for ethylbenzene or isopropyl benzene, respectively and the ring addition rate constant for toluene. Partial rate constants for reactions at other positions based on standard structure-reactivity methods used in the mechanism generation system. (Carter, 2000a). The compounds used to represent the lumped dialkylbenzenes are given in Table 10.
e5 Rate constant estimated using the estimated rate constants for ring addition for the trimethylbenzene isomers, derived based on the observed aromatic aldehyde yields and estimated nitrate yields, and based on estimated rate constants for abstraction reactions for additions at various positions of the molecules of the mixture of alkylbenzenes used to represent those with this carbon number. Separate estimates are made for 1,2,3 (3CnnBEN3), 1,3,4 (4CnnBEN3) and 1,3,5 (5CnnBEN3) substituent configurations, based on the

trimethylbenzenes. (Aromatic aldehyde yields for 1,2,3-trimethylbenzene are not available. The ring addition rate constant for this compound is estimated to be the same as that for 1,2,4-trimethylbenzene.) Partial rate constant for reaction at the -CH2- or -CH- groups next to the aromatic derived from the rate constants for ethylbenzene or isopropyl benzene, respectively, and the ring addition rate constant for toluene. Partial rate constants for reactions at other positions based on standard structure-reactivity methods used in the mechanism generation system (Carter, 2000a). The compounds used to represent the lumped trialkylbenzenes are given in are given in Table 10.

e6 Average of rate constants for 1-methyl and 2-methyl naphthalenes

e7 Estimated to have a similar rate constant as 2-butyne, on the basis of the fact that the rate constant for 1,3-butadiene is similar to that for the 2-butenes. This estimate is highly uncertain.

e8 Rate constant estimated by Carter and Atkinson (1996).

e9 Rate constant for reaction at the aromatic ring assumed to be the same as that for anisole. Rate constant for reaction at the anisole aromatic ring estimated from the total OH rate constant and the rate constant for reaction at methoxy group estimated using the structure-reactivity estimation methods used in the mechanism generation system (Carter, 2000). Rate constants for reactions at other positions in this molecule also estimated using the structure-reactivity estimation methods used in the mechanism generation system (Carter, 2000).

e10 Estimated to have the same rate constant as 1,2-diacetyl pthallate on the basis of similar substitution around the aromatic ring, and the expectation that for both compound the reaction would be primarily at the aromatic ring.

e11 Rate constant for reaction at the aromatic ring assumed to be the same as measured for 1,2-diacetyl phthalate. Rate constant for reaction at groups off the aromatic ring estimated using the group-additivity methods incorporated in the mechanism generation system (Carter, 2000).

e12 Rate constant for reaction at the aromatic ring estimated to be the same as the total rate constant for acetophenone (Atkinson, 1989), assuming that ring addition is the major reaction for that compound. The rate constant for reaction at groups off the aromatic ring based on those estimated for 2-ethyl hexyl acetate, since reaction at the acetate group is estimated to be negligible for that compound.

e13 Estimated to have a rate constant that it twice that of pare-toluene isocyanate, based on the structure of the molecule (Carter et al, 1999a).

e14 Derived from structure-reactivity methods, where group rate constants for reactions at HN, NH2, at groups adjacent to the amino group were derived based on rate constants for the simple amines for which rate constant data are available.

e15 The rate constant for addition of OH to the C=N double bond is estimated by the rate constant for OH + isobutene x the average of the ratio of the rate constants for CH2=NOH / Ethene and CH3CH=NOH / Propene, with abstractions from the methyl group subtracted off. The CH2=NOH and CH3CH=NOH rate constants are from the tabulation of Atkinson (1989). The rate constants for addition to the methyl groups were estimated using the structure-reactivity methods incorporated in the mechanism generation system.

e16 Average of values for o-, m- and p- isomers tabulated by Atkinson (1989).

e17 Rate constant as estimated by Carter and Malkina (2007).

e18 Assumed to have the same rate constant as acetaldehyde.

[b] Codes for types of mechanisms that were derived are as follows. See the complete mechanism listing Table B-2 of this report for the mechanisms.

1 Reactions in the base mechanism or the base chlorine mechanism. See Table A-2 or Table A-5 for documentation.

2 Mechanism derived using the mechanism generation system. Rate constants and branching ratios may have been assigned based on available data or estimates for individual cases. See documentation of the mechanism generation system. In most cases these mechanisms should be the same as or similar to those in SAPRC-99.

3 Mechanism derived using the mechanism generation system using enhanced capabilities and additional assignments that were developed for this project. Rate constants and branching ratios may have been assigned based on available data or estimates for individual cases. See documentation of the mechanism generation system. Note that these mechanisms could not be generated using the SAPRC-99 version of the mechanism generation system.

Table B-4 (continued)

4 The styrene mechanism is based on that derived by Carter et al, (1999b) except for some rate constants updates and re-adjustment of the nitrate yields based on the chamber data. Mechanisms for other styrenes were estimated based on that developed for styrene.

5 The mechanisms for alkylbenzenes were derived as discussed in the documentation of the updated aromatics mechanism. The general ring opening mechanism is as shown on Figure 2.

6 The mechanism for this aromatic compound is a simplified and parameterized representation that was either adjusted to fit chamber data or was derived based on mechanism(s) adjusted to fit chamber data. See Table 14 on non-alkylbenzene aromatics for further information.

7 The furans are assumed to react primarily to form the monounsaturated 1,4-dicarbonyl resulting from OH addition adjacent to the oxygen, followed by ring opening. These were represented by the AFG1 and AFG2 model species with their relative yields adjusted to fit available chamber data where such data are available, as used in the general aromatic hydrocarbon mechanism discussed in the text.

8 Portions of the mechanism for this photoreactive compound were derived using the mechanism generation system, with appropriate assignments for rate constants and branching ratios as applicable. The photolysis reactions were estimated, with absorption cross-sections and quantum yields derived as indicated on Table A-3 or A-6. The mechanism generation system is described by Carter (2000a), with updates and extensions as described by in the text.

9 Photolysis reactions of C_{9+} ketones are assumed to be negligible, based on the apparent decline in overall quantum yields with carbon number in mechanisms that give the best fits to environmental chamber data. The mechanisms for the other reactions are estimated using the mechanism generation system.

10 The benzyl alcohol mechanism is based on that derived by Carter et al (2005a). The measured benzaldehyde in the chamber experiments are consistent with a fraction reacted by abstraction from the -CH_2OH of 30%, and the products formed following the addition to the aromatic ring are assumed to be the same as used for ethylbenzene. The nitrate yield factor derived for toluene for the peroxy reactions involved in the ring addition mechanism gives results in reasonably good fits to the data and was not adjusted.

11 The mechanism for this aromatic compound was derived by analogy to the reactions of benzene or the alkylbenzenes. See text for more details.

12 See Carter (2008a) for a discussion of the mechanisms for the amines and the associated uncertainties and evaluation problems. The magnitudes of the calculated atmospheric reactivities must be considered to be upper limits because of the possibility of removal of the amines by reaction with atmospheric nitric acid is assumed to be negligible in the calculations, which might not be the case. The evaluations against chamber data is uncertain because the amount of amine present in the gas phase at the beginning of the chamber experiments could not be determined, and are expected to be lower than the calculated amounts reacted because of the tendency of the amines to go to surfaces. The amount of initially present amine in the experiments had to be adjusted to fit the initial rates of NO oxidation in the experiments, and the adjusted amounts were always less than the calculated amount injected.

13 The reaction with OH is assumed to proceed by abstraction from the methyl group, followed by decomposition to form NO and formaldehyde. The photolysis absorption cross sections are from Calvert and Pitts (1966). The major reaction pathway is photolysis, which is assumed to form methyl radicals and NO with unit quantum yields.

14 The data of Hashimoto et al (1984) indicate that the products are formaldehyde and HCO-CN after an NO to NO_2 conversion. HCO-CN is assumed to be relatively unreactive, which is supported by the concentration-time profiles reported by Hashimoto et al (1984). Reactions with NO_3 and O_3 are assumed to be relatively slow, though no data are available concerning these reactions.

15 An estimated mechanism was derived explicitly for this compound. About 24% of the reaction is assumed to occur at the methyl or CH2 groups, with the subsequent reactions estimated using the procedures in the mechanism generation system. The remainder of the reaction is assumed to be addition of OH to the C=N double bond, which is assumed to form primarily C2H2C(CH3)(OH)N(.)OH, which is assumed to react with O_2 to form $C_2H_5C(CH_3)(OH)NO + HO_2$. The rate constant is estimated by the rate constant for OH + isobutene x the average of the ratio of the rate constants for CH_2=NOH / Ethene and CH_3CH=NOH / Propene, with abstractions from the methyl group subtracted off. The CH2=NOH and CH3CH=NOH rate constants are from the tabulation of Atkinson (1989). The $C_2H_5C(CH_3)(OH)NO$ is assumed to photolyze rapidly, forming NO + an alpha-hydroxy radical that reacts with O_2 to form MEK and HO_2. The absorption

cross-sections and quantum yields are unknown, but photolysis is assumed to be relatively rapid, and estimated to be comparable to that of methyl nitrite.

16 The N-methyl 2-pyrrolidone mechanism is based on that derived by Carter et al (1996b).

17 The mechanism for bromine-containing compound were derived based on that estimated using the mechanism generation system for the corresponding chlorine-containing compound, but using the appropriate rate constant for the individual compound. The mechanisms were not optimized to fit the chamber data and no mechanisms were found to simulate the data particularly well (Carter and Tuazon, 2000).

18 The mechanism for chloropicrin is based on that of Carter et al (1997b), updated as discussed by Carter and Malkina (2007).

19 The mechanisms for these pesticide compounds were derived as discussed by Carter and Malkina (2007), but updated to the current version of the mechanism.

20 The mechanism used for methyl iodide, including the reactions of the inorganic iodine species formed, is given by Carter (2007).

21 The mechanism, and its evaluation against chamber data, is documented by Carter (2009a).

22 The mechanism, and its evaluation against chamber data, is documented by Carter (2009b).

23 The mechanism, and its evaluation against chamber data, is documented by Carter et al (2010).

24 Assumed to have an analogous mechanism as that for acetaldehyde, except that the absorption cross-sections and quantum yields are those recommended by IUPAC (2006) for glycolaldehyde.

26 Mechanism estimated for this compound based on the following assumptions. Mechanism assumed to involve formation of $CH_3N(OH)(O)O$, which thermally decomposes to HNO_3 + CH_3. Pressure dependence and rate constants for other nitro compounds suggest that H-abstraction not important for alpha-nitro compounds.

27 Mechanism estimated for this compound based on the following assumptions. Reaction at group not adjacent to the nitro group, followed by O_2 reaction with the alkoxy radical formed assumed to dominate. Nitrate formation ignored. $HCOCH_2NO_2$ represented by Acetaldehyde + XN, and $CH_3CH(NO_2)CHO$ represented by RCHO + XN.

28 Mechanism estimated for this compound based on the following assumptions. Reaction assumed to occur at the CH_3 group, followed by reaction of the alkoxy radical formed with O_2, forming CHF_2CHO. The latter is represented by acetaldehyde (which probably overestimates its reactivity).

29 Mechanism estimated for this compound based on the following assumptions. Decomposition of alkoxy radical, forming CF_3 and inert F_2CO assumed. CF_3O assumed to react with other VOCs to form CF_3OH, which is treated as inert. The effect of the CF3O + VOC reaction is represented by the formation of OH.

30 Mechanism estimated for this compound based on the following assumptions. Overall nitrate yield estimated by assuming it is the same as the alkyl peroxy radical with the same number of carbons. Products formed assumed to be unreactive. Reaction of alkoxy radical with O_2 assumed to dominate.

31 Mechanism estimated for this compound based on the following assumptions. Overall nitrate yield estimated by assuming it is the same as the alkyl peroxy radical with the same number of carbons. Products formed assumed to be unreactive. Decomposition to form chlorine atoms assumed to dominate.

32 Mechanism estimated for this compound based on the following assumptions. Most of reaction is assumed to occur at CH_2 group, with the alkoxy radical formed assumed to react with O_2 to form a relatively unreactive fluorinated carbonyl product. Overall nitrate yield estimated by assuming it is the same as the alkyl peroxy radical with the same number of carbons.

33 Mechanism estimated for this compound based on the following assumptions. Alkoxy radical formed following abstraction from either hydrogen is assumed to decompose forming an alpha-hydrogen-substituted radical that reacts to form an alkoxy radical that reacts with O_2 forming HO_2 and an unreactive carbonyl fluoride. Nitrate yields in peroxy radical reactions assumed to be the same as in the corresponding alkylperoxy radical with the same number of carbons.

34 Mechanism estimated for this compound based on the following assumptions. Reaction assumed to occur primarily at the CH_2 group, ultimately giving rise to methyl radicals and C_4F_9OCHO, which is assumed to be unreactive. Nitrate yield from peroxy radical formed assumed to be the same as that formed from ethyl propyl ether.

35 Mechanism estimated for this compound based on the following assumptions. Alkoxy radical formed assumed to react with O_2 forming HO_2 and a perfluoro formate, which is assumed to be unreactive. Nitrate yield from peroxy radical formed assumed to be the same as that formed from ethyl propyl ether.

Table B-4 (continued)

36 It is assumed that the primary reaction is OH or NO_3 adding to terminal position, forming an allylic-stabilized radical. In the case of the OH reaction, the 1,2-unsaturated alpha-hydroxy radical reacts with O_2 to form HO2 and 1,2-butadien-4-al, and in the case of the NO_3 reaction the analogous compound reacts unimolecularly to form NO_2 and the same aldehyde. The aldehyde is represented by RCHO, on the basis that this is probably not as bad an approximation as MACR. It is assumed that the reaction with O_3 is slow.

A The atmospheric reactivity values were derived using the "Adjusted Products" version of the mechanism, where the major oxidation products are represented explicitly using mechanisms derived using the mechanism generation system. See Carter (2000a, 2009) for more details concerning how adjusted products mechanisms are derived.

LM This compound is represented using the "lumped molecule" approach, where the atmospheric reactivity of this compound is assumed to have the same per-molecule atmospheric impact as another compound. See Table B-9 for the compounds used to represent other compounds using the lumped molecule approach.

[c] Structures used when deriving the mechanism using the mechanism generation system. If no structure is given then the mechanism generation system was not used to derive the mechanisms. "*", "*1", "*2" indicate join points for cyclic or bicyclic compounds. "^" and "v" are used to indicate cis/trans isomerization for alkenes (cis/trans isomerization for cyclic compounds isn't recognized by the system). "#" indicates a triple bond.

Table B-5. Listing of compounds for which mechanisms have been derived. 2. Rate constants for reactions with O_3, NO_3, and O^3P at 300^{o}K, where applicable.

Compound	Rate constant at 300 K (cm^3 $molec^{-1}$ s^{-1}) [a]					
	O_3		NO_3		O^3P	
Propene	1.05E-17	1	9.73E-15	1	4.01E-12	2
1-Butene	9.08E-18	1	1.38E-14	1	4.17E-12	2
Isobutene	1.17E-17	1	3.44E-13	1	1.68E-11	2
cis-2-Butene	1.28E-16	1	3.52E-13	1	1.75E-11	2
trans-2-Butene	1.95E-16	1	3.93E-13	1	1.99E-11	2
1,3-Butadiene	6.64E-18	1	1.00E-13	1	1.98E-11	2
1-Pentene	1.10E-17	1	1.50E-14	1	4.69E-12	2
3-Methyl-1-Butene	9.87E-18	3	1.39E-14	e1	4.19E-12	2
2-Methyl-1-Butene	1.48E-17	1	3.32E-13	e1	1.80E-11	2
2-Methyl-2-Butene	4.11E-16	1	9.37E-12	1	5.08E-11	2
cis-2-Pentene	1.31E-16	1	3.70E-13	e1	1.70E-11	2
trans-2-Pentene	1.63E-16	1	3.70E-13	e1	2.10E-11	2
Cyclopentene	5.61E-16	1	4.20E-13	1	2.10E-11	2
Trans 1,3-Pentadiene	1.33E-17	e2	5.69E-13	e1	4.76E-11	e3
1,4-Pentadiene	1.51E-17	3	2.76E-14	e1	1.41E-11	e3
Isoprene	1.34E-17	1	6.81E-13	1	3.50E-11	2
1-Hexene	1.17E-17	1	1.80E-14	1	5.03E-12	2
3,3-Dimethyl-1-Butene	4.08E-18	3	1.38E-14	e1	4.80E-12	2
3-Methyl-1-Pentene	3.97E-18	3	1.39E-14	e1	5.60E-12	e1
4-Methyl-1-Pentene	1.04E-17	3	1.39E-14	e1	5.60E-12	e1
2,3-Dimethyl-1-Butene	1.04E-17	4	3.32E-13	e1	1.73E-11	e1
2-Ethyl-1-Butene	1.35E-17	4	4.52E-13	1	1.73E-11	e1
2-Methyl-1-Pentene	1.66E-17	4	3.32E-13	e1	2.03E-11	e1
2,3-Dimethyl-2-Butene	1.14E-15	1	5.72E-11	1	7.64E-11	2
2-Methyl-2-Pentene	3.48E-16	e1	9.37E-12	e1	3.86E-11	e1
Cis-2-Hexene	1.08E-16	1	3.70E-13	e1	2.05E-11	e1
Cis-3-Hexene	1.43E-16	6	3.70E-13	e1	2.05E-11	e1
Cis-3-Methyl-2-Pentene	4.58E-16	7	9.37E-12	e1	3.71E-11	e1
Trans 3-Methyl-2-Pentene	5.69E-16	7	9.37E-12	e1	3.71E-11	e1
Trans 4-Methyl-2-Pentene	1.15E-16	e1	3.70E-13	e1	1.84E-11	e1
Trans-2-Hexene	1.57E-16	1	3.70E-13	e1	2.05E-11	e1
Trans-3-Hexene	1.64E-16	8	3.70E-13	e1	2.05E-11	e1
3-methylcyclopentene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
1-Methyl cyclopentene	6.81E-16	10	9.37E-12	e1	3.71E-11	e1
Cyclohexene	8.30E-17	1	5.10E-13	1	2.00E-11	2
Trans 1,4-Hexadiene	1.69E-16	e4	3.84E-13	e1	3.91E-11	e3
1-Methyl Cyclohexene	1.64E-16	1	1.00E-11	1	9.00E-11	11
4-Methyl Cyclohexene	9.04E-17	1	3.70E-13	e1	2.05E-11	e1
1-Heptene	1.21E-17	1	2.00E-14	1	8.70E-12	e1
3,4-dimethyl-1-pentene	1.01E-17	e1	1.40E-14	e1	5.60E-12	e1
3-methyl-1-hexene	1.01E-17	e1	1.40E-14	e1	5.60E-12	e1
2,4-dimethyl-1-pentene	1.18E-17	e1	3.32E-13	e1	1.73E-11	e1
2,3-dimethyl-1-pentene	1.18E-17	e1	3.32E-13	e1	1.73E-11	e1
3,3-dimethyl-1-pentene	1.01E-17	e1	1.38E-14	e1	5.60E-12	e1
2-methyl-1-hexene	1.18E-17	e1	3.32E-13	e1	1.73E-11	e1
2,3,3-trimethyl-1-Butene	8.09E-18	4	3.32E-13	e1	1.73E-11	e1

Table B-5 (continued)

Compound	Rate constant at 300 K (cm^3 $molec^{-1}$ s^{-1}) [a]					
	O_3		NO_3		O^3P	
4,4-dimethyl-cis-2-pentene	1.15E-16	e1	3.70E-13	e1	1.55E-11	e1
2,4-dimethyl-2-pentene	3.48E-16	e1	9.37E-12	e1	3.71E-11	e1
2-methyl-2-hexene	3.48E-16	e1	9.37E-12	e1	3.71E-11	e1
3-ethyl-2-pentene	3.48E-16	e1	9.37E-12	e1	3.71E-11	e1
3-methyl-trans-3-hexene	3.48E-16	e1	9.37E-12	e1	3.71E-11	e1
cis-2-heptene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
2-Methyl-trans-3-Hexene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
3-methyl-cis-3-hexene	3.48E-16	e1	9.37E-12	e1	3.71E-11	e1
3,4-dimethyl-cis-2-pentene	3.48E-16	e1	9.37E-12	e1	3.71E-11	e1
2,3-Dimethyl-2-Pentene	6.74E-16	e1	5.72E-11	e1	5.07E-11	e1
Cis-3-Heptene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
Trans 4,4-dimethyl-2-Pentene	1.15E-16	e1	3.70E-13	e1	1.57E-11	e1
Trans-2-Heptene	1.15E-16	e1	3.70E-13	e1	2.34E-11	e1
Trans-3-Heptene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
cis-3-methyl-2-hexene	3.48E-16	e1	9.37E-12	e1	3.71E-11	e1
trans-4-methyl-2-hexene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
trans-3-methyl-2-hexene	3.48E-16	e1	9.37E-12	e1	3.71E-11	e1
1,2-Dimethyl Cyclohexene	2.11E-16	12	5.72E-11	e1	5.29E-11	e1
1-Octene	1.45E-17	3	1.39E-14	e1	5.60E-12	e1
2,4,4-trimethyl-1-pentene	1.18E-17	e1	3.32E-13	e1	1.73E-11	e1
3-Methyl-2-Isopropyl-1-Butene	3.45E-18	5	3.32E-13	e1	1.73E-11	e1
trans-2-octene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
2-Methyl-2-heptene	3.48E-16	e1	9.37E-12	e1	3.71E-11	e1
Cis-4-Octene	9.22E-17	6	3.70E-13	e1	2.05E-11	e1
Trans 2,2-Dimethyl 3-Hexene	4.34E-17	9	3.70E-13	e1	2.05E-11	e1
Trans 2,5-Dimethyl 3-Hexene	4.24E-17	9	3.70E-13	e1	2.05E-11	e1
Trans-3-Octene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
Trans-4-Octene	1.34E-16	8	3.70E-13	e1	2.40E-11	e1
2,4,4-trimethyl-2-Pentene	1.44E-16	10	9.37E-12	e1	3.71E-11	e1
2,3-dimethyl-2-hexene	6.74E-16	e1	5.72E-11	e1	5.29E-11	e1
1-Nonene	1.01E-17	e1	1.39E-14	e1	5.60E-12	e1
4,4-dimethyl-1-pentene	1.01E-17	e1	1.39E-14	e1	5.60E-12	e1
Trans-4-Nonene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
1-Decene	9.68E-18	3	1.40E-14	e1	5.60E-12	e1
3,4-Diethyl-2-Hexene	4.28E-18	7	9.37E-12	e1	3.71E-11	e1
Cis-5-Decene	1.13E-16	6	3.70E-13	e1	2.05E-11	e1
Trans-4-Decene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
3-Carene	3.76E-17	13	9.10E-12	1	3.20E-11	2
a-Pinene	8.55E-17	1	6.09E-12	1	3.20E-11	2
b-Pinene	1.57E-17	1	2.51E-12	1	2.70E-11	2
d-Limonene	2.17E-16	1	1.22E-11	1	7.20E-11	2
Sabinene	8.40E-17	13	1.00E-11	1	6.27E-11	e3
Terpinolene	1.02E-15	e1	6.66E-11	e1	1.63E-10	e1
1-Undecene	1.01E-17	e1	1.40E-14	e1	5.60E-12	e1
Trans-5-Undecene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
1-Dodecene	1.01E-17	e1	1.40E-14	e1	5.60E-12	e1
Trans-5-Dodecene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
1-Tridecene	1.01E-17	e1	1.41E-14	e1	5.60E-12	e1

Table B-5 (continued)

Compound	Rate constant at 300 K (cm^3 $molec^{-1}$ s^{-1}) [a]					
	O_3		NO_3		O^3P	
Trans-5-Tridecene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
1-Tetradecene	1.01E-17	e1	1.41E-14	e1	5.60E-12	e1
Trans-5-Tetradecene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
Trans-5-Pentadecene	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
Styrene	1.76E-17	3	1.50E-13	1	1.75E-11	e5
b-Methyl Styrene	3.25E-16	e6	3.92E-13	e7	1.62E-11	e3
Glyoxal			1.02E-15	e8		
glycolaldehyde			2.84E-15	e17		
Acrolein	3.07E-19	17	1.18E-15	18	2.37E-12	e1
Acrylic Acid	1.01E-17	e1	2.76E-18	e1	4.60E-12	e1
Methyl Glyoxal			2.53E-15	e8		
Crotonaldehyde	1.58E-18	19	5.12E-15	20	7.29E-12	e1
Methacrolein	1.28E-18	1	3.54E-15	1	6.34E-12	e8
Methylvinyl ketone	5.36E-18	1			4.32E-12	e8
2-Methylpropanal			1.15E-14	1		
Butanal			1.15E-14	1		
Methacrylic Acid	1.18E-17	e1	6.71E-17	e1	1.42E-11	e1
Methyl Acrylate	1.01E-17	e1	2.76E-18	e1	4.60E-12	e1
Vinyl Acetate	1.01E-17	e1	1.38E-14	e1	5.60E-12	e1
Hydroxy Methacrolein	1.28E-18	e9	3.40E-15	e10	9.95E-12	e1
2-Methyl-3-Butene-2-ol	9.68E-18	15	1.21E-14	16	2.01E-11	e1
2,2-Dimethylpropanal (pivaldehyde)			2.40E-14	1		
3-Methylbutanal (Isovaleraldehyde)			1.90E-14	1		
Pentanal (Valeraldehyde)			1.50E-14	1		
Ethyl Acrylate	1.01E-17	e1	3.70E-18	e1	4.60E-12	e1
Methyl Methacrylate	1.18E-17	e1	6.71E-17	e1	1.42E-11	e1
Glutaraldehyde			7.63E-15	e1		
Hexanal			1.60E-14	1		
Ethyl Methacrylate	1.18E-17	e1	6.80E-17	e1	1.42E-11	e1
hydroxypropyl acrylate	1.01E-17	e1	2.96E-17	e1	4.60E-12	e1
Benzaldehyde			2.73E-15	21		
o-Cresol			1.40E-11	2		
Heptanal			1.90E-14	1		
2-methyl-hexanal			3.90E-15	e1		
n-butyl acrylate	1.01E-17	e1	5.06E-17	e1	4.60E-12	e1
isobutyl acrylate	1.01E-17	e1	1.14E-16	e1	4.60E-12	e1
Octanal			1.70E-14	1		
Butyl Methacrylate	1.18E-17	e1	1.15E-16	e1	1.42E-11	e1
Isobutyl Methacrylate	1.18E-17	e1	1.79E-16	e1	1.42E-11	e1
a-terpineol	3.48E-16	e1	9.37E-12	e1	3.71E-11	e1
Citronellol (3,7-dimethy-6-octen-1-ol)	3.48E-16	e1	9.37E-12	e1	3.71E-11	e1
Hydroxycitronellal			4.03E-15	e1		
Linalool	3.58E-16	e1	9.38E-12	e1	6.60E-11	e1
Geraniol	6.96E-16	e1	1.87E-11	e1	1.35E-10	e1
2-Ethyl-Hexyl Acrylate	1.01E-17	e1	2.95E-16	e1	4.60E-12	e1
methyl cis-9-pentadecenoate	1.15E-16	e1	3.70E-13	e1	2.05E-11	e1
methyl linolenate (methyl cis,cis,cis-9,12,15-octadecatrienoate)	3.45E-16	e1	1.11E-12	e1	1.59E-10	e1

Table B-5 (continued)

Compound	Rate constant at 300 K (cm^3 molec^{-1} s^{-1}) [a]					
	O$_3$		NO$_3$		O^{3}P	
methyl linoelate (methyl cis,cis-9,12-octadecadienoate)	2.30E-16	e1	7.40E-13	e1	7.47E-11	e1
Methylamine	7.40E-21	22	9.60E-14	e11		
Acetylene	1.16E-20	14				
Dimethyl Amine	1.67E-18	22	2.03E-13	e11		
Ethyl Amine	2.09E-20	e12	1.16E-13	e11		
Ethanolamine	6.86E-20	e12	1.35E-13	e11		
Dimethyl Sulfoxide			3.00E-13	27		
Trichloroethylene			2.99E-16	18	4.37E-14	e1
Trimethyl Amine	7.84E-18	22	1.56E-13	e11		
isopropylamine	3.48E-20	e12	1.21E-13	e11		
1-amino-2-propanol	6.58E-20	e18	1.35E-13	e1		
trans-1,3-dichloropropene	7.12E-19	24	9.13E-17	e13	1.30E-12	e14
cis-1,3-dichloropropene	1.60E-19	25	5.57E-18	e13	4.79E-13	e14
1,3-butadiyne			1.00E-15	e7		
t-butyl amine	0	e12	5.88E-14	e11		
morpholine	3.77E-18	e18	3.30E-13	e1		
Dimethylaminoethanol	6.76E-18	22	1.80E-13	e11		
2-amino-1-butanol	3.74E-19	e12	1.70E-13	e11		
2-Amino-2-Methyl-1-Propanol	0	e12	5.88E-14	e11		
Diethanol Amine	3.78E-18	e12	3.30E-13	e11		
2-(Cl-methyl)-3-Cl-Propene	4.14E-19	26	1.00E-15	e15	5.60E-12	e1
2-amino-2-ethyl-1,3-propanediol			5.89E-14	e1		
N-Methyl-2-Pyrrolidone			1.26E-13	23		
Triethyl Amine	1.20E-17	e12	1.71E-13	e11		
Triethanolamine	3.94E-17	e12	2.29E-13	e11		
Molinate			9.20E-15	e16		
EPTC (S-Ethyl Dipropylthiocarbamate)			9.20E-15	28		
triisopropanolamine	3.94E-17	e12	2.29E-13	e11		
Pebulate			9.20E-15	e16		
Thiobencarb			9.20E-15	e16		

[a] See the complete mechanism listing in the electronic version of the report for the temperature dependences, where available. Footnotes for measured rate constants are as follows:

1 As recommended or tabulated by Atkinson and Arey (2003)

2 As recommended or tabulated by Calvert et al (2002)

3 Rate constant at 298K as recommended or tabulated by Atkinson and Arey (2003). Temperature dependence estimated by assuming that the A factor is the same as that for 1 butene.

4 Rate constant at 298K as recommended or tabulated by Atkinson and Arey (2003). Temperature dependence estimated by assuming that the A factor is the same as that for 2 methyl-1-butene.

5 T=298K rate constant recommended by Atkinson (1997). Temperature dependence estimated by assuming the A factor is the same as for isobutene.

6 Rate constant at 298K as recommended or tabulated by Atkinson and Arey (2003). Temperature dependence estimated by assuming that the A factor is the same as that for cis-2-butene.

7 Rate constant at 298K as recommended by Atkinson (1997). Temperature dependence estimated by assuming that the A factor is the same as that for 2-methyl-1-butene.

8 Rate constant at 298K as recommended or tabulated by Atkinson and Arey (2003). Temperature dependence estimated by assuming that the A factor is the same as that for trans-2-butene.

Table B-5 (continued)

9 Rate constant at 298K as recommended by Atkinson (1997). Temperature dependence estimated by assuming that the A factor is the same as that for trans-2-butene.
10 Rate constant at 298K as recommended or tabulated by Atkinson and Arey (2003). Temperature dependence estimated by assuming that the A factor is the same as that for 2-methyl-2-butene.
11 Atkinson (1997) Recommendation
12 Rate constant at 298K as recommended by Atkinson (1997). Temperature dependence estimated by assuming that the A factor is the same as that for 2,3-dimethyl-2-butene.
13 Rate constant at 298K as recommended or tabulated by Atkinson and Arey (2003). Temperature dependence estimated by assuming that the A factor is the same as that for alpha-pinene.
14 Rate constant at 298K recommended by IUPAC (2006). A factor estimated to be approximately 2 times that for ethene, as assumed by Carter (2000a).
15 Rate constant at 298K is average of 291K rate constant of Grosjean and Grosjean (1994) and the 298K rate constant of Fantechi et al (1998). Temperature dependence estimated by assuming that the A factor is the same as that for 1-butene
16 Rate expression of Rudich et al (1996), as recommended by Atkinson (private communication, 2000). Reasonable agreement with data of Fantechi et al (1998).
17 Rate constant at 298K recommended by Atkinson (1994). Temperature dependence estimated by assuming that the A factor is the same as that for methacrolein.
18 Rate constant relative to ethene from Atkinson et al (1987). Placed on an absolute basis using 300K rate constant for ethene recommended by Atkinson and Arey (2003).
19 Sato et al (2004b).
20 Rate constant relative to propene from Atkinson et al (1987). Placed on an absolute basis using 300K rate constant for propene recommended by Atkinson and Arey (2003).
21 The T=298K rate constant recommended by Atkinson (1994). Temperature dependence estimated by assuming the reaction has the same A factor as the reaction of NO3 with acetaldehyde. This gives the same 298K rate constant but a slightly different temperature dependence than used in SAPRC-99.
22 Rate constant from Tuazon et al (1994)
23 Rate constant from Aschmann and Atkinson (1999)
24 Rate constant at 298K from Tuazon et al (1984). Temperature dependence estimated by assuming that the A factor is the same as that for trans-2-butene.
25 Rate constant at 298K from Tuazon et al (1984). Temperature dependence estimated by assuming that the A factor is the same as that for cis-2-butene.
26 Rate constant at 298K from Atkinson and Carter (1984). Temperature dependence estimated by assuming that the A factor is the same as that for isobutene.
27 Rate constant is geometric mean of measurements of Barnes et al (1989) and Falbe-Hansen et al (2000), as used by Carter et al (2000).
28 Rate constant from Kwok et al (1992)

Footnotes for estimated rate constants are as follows:

e1 Estimated using the group-additivity estimation assignments implemented in the current mechanism generation system. See Carter (2000a).
e2 Rate constant unknown. Roughly estimate that it is similar to that for isoprene
e3 Estimated from correlation between measured OH and O^3P rate constants (with ethene, allene, and some other outliers excluded) at 300K.
e4 Estimated as the sum of the 300K rate constants for 1-hexene and trans-2-hexene.
e5 Assumed to have the same rate constant as cis-2-butene on the basis of their having similar OH radical rate constants.
e6 Estimated from the 300K styrene, propene, and trans-2-butene rate constants by assuming that the styrene/b-methyl styrene ratio is the same as the ratio for propene to trans-2-butene.
e7 Estimated from the correlation between OH and NO_3 rate constants, using the assigned 300K OH rate constant for this compound.
e8 Estimated value used in SAPRC-99 mechanism. See base mechanism listing and Carter (2000a).
e9 Estimated to have the same rate constant and kinetic parameters as methacrolein, as assumed by Carter and Atkinson (1996).
e10 Rate constant assumed to be the same as for methacrolein (Carter and Atkinson, 1996)

Table B-5 (continued)

e11 Estimated based on the NO_3 + NMP rate constant and assuming ratios of rate constants for reactions of NO_3 at various types of amine groups is the same as those estimated for the reactions of OH with those groups. Reaction assumed to occur only from NH or NH_2 or from C-H bonds on carbons bonded to the amino group.

e12 Estimated from the estimated rate of reaction of OH at the alpha position, and correlations between this and the measured O_3 rate constants of Tuazon et al (1994) for the methylamines and DMAE. Reaction assumed to be slow if no abstractable hydrogens in a group adjacent to the amino group.

e13 Estimated by Carter and Malkina (2007) based on correlation between O3 and NO3 rate constants.

e14 Estimated by Carter and Malkina (2007) based on correlation between O3 and NO3 rate constants.

e15 This rate constant estimated by Atkinson (private communication, 1997) based on the rate constant for NO_3 + Allyl chloride (Atkinson, 1991)

e16 Estimated by Carter and Malkina (2007) to have the same rate constant as EPTC.

e17 Assumed to have the same rate constant as acetaldehyde.

e18 Estimated from estimated rate of reaction of OH at the alpha position, and correlations between this and the measured O_3 rate constants of Tuazon et al (1994) for the methylamines and DMAE.

Table B-6. Listing of compounds for which mechanisms have been derived. 3. Absorption cross-sections, quantum yields, and mechanisms for photolysis reactions, where applicable.

Compound	Phot Data [a]			Mechanism
glycolaldehyde	HOCCHO		6	GLCLALD + HV = CO + #2 HO2 + HCHO
Acrolein	MACR-06		e2	ACROLEIN + HV = #.178 OH + #1.066 HO2 + #.234 MEO2 + #.33 MACO3 + #1.188 CO + #.102 CO2 + #.34 HCHO + #.05 CCOOH + #-.284 XC
Hydroxy Acetone	MEK-06	0.175	e3	HOACET + HV = HO2 + MECO3 + HCHO
Crotonaldehyde	MACR-06		e2	CROTALD + HV = #2 HO2 + #2 CO + CCHO
2-Methylpropanal	C2CHO		e1	2MEC3AL + HV = HO2 + #.96 RO2C + #.04 RO2XC + #.04 zRNO3 + CO + #.96 xHO2 + #.96 xACET + yROOH + #-.12 XC
Butanal	C2CHO		e1	1C4RCHO + HV = HO2 + #.98 RO2C + #.02 RO2XC + #.02 zRNO3 + CO + #.98 xHO2 + #.98 xRCHO + yROOH + #-.06 XC
Hydroxy Methacrolein	MACR-06		e2	HOMACR + HV = HO2 + RCO3 + CO + HCHO + #-1 XC
Methoxy Acetone	MEK-06	0.1	e3	MEOACET + HV = MECO3 + RO2C + xHO2 + #.079 xHCHO + yROOH + #1.921 XC
2,2-Dimethylpropanal (pivaldehyde)	C2CHO		e1	22DMC3AL + HV = HO2 + #.961 RO2C + #.039 RO2XC + #.039 zRNO3 + CO + #.961 xTBUO + yR6OOH + #-.079 XC
3-Methylbutanal (Isovaleraldehyde)	C2CHO		e1	3MC4RCHO + HV = HO2 + #1.294 RO2C + #.053 RO2XC + #.053 zRNO3 + CO + #.947 xHO2 + #.348 xHCHO + #.613 xRCHO + #.334 xACET + yR6OOH + #.492 XC
Pentanal (Valeraldehyde)	C2CHO		e1	1C5RCHO + HV = HO2 + #1.686 RO2C + #.069 RO2XC + #.069 zRNO3 + CO + #.931 xHO2 + #.931 xRCHO + yR6OOH + #.792 XC
2-Pentanone	MEK-06	0.1	e3	MPK + HV = MECO3 + #.98 RO2C + #.02 RO2XC + #.02 zRNO3 + #.98 xHO2 + #.98 xRCHO + yR6OOH + #-.06 XC
3-Pentanone	MEK-06	0.1	e3	DEK + HV = RCO3 + RO2C + xHO2 + xCCHO + yR6OOH
Methyl Isopropyl Ketone	MEK-06	0.1	e3	MIPRK + HV = MECO3 + #.96 RO2C + #.04 RO2XC + #.04 zRNO3 + #.96 xHO2 + #.96 xACET + yR6OOH + #-.12 XC
Glutaraldehyde	C2CHO		e1	GLTRALD + HV = HO2 + #.961 RO2C + #.039 RO2XC + #.039 zRNO3 + CO + #.961 xRCO3 + yR6OOH + #.882 XC
2,4-pentanedione	MEK-06	0.1	e3	24C5-K + HV = MECO3 + RO2C + xMECO3 + xHCHO + yR6OOH
Hexanal	C2CHO		e1	1C6RCHO + HV = HO2 + #1.809 RO2C + #.126 RO2XC + #.126 zRNO3 + CO + #.874 xHO2 + #.874 xRCHO + yR6OOH + #1.623 XC
4-Methyl-2-Pentanone	MEK-06	0.02	e3	MIBK + HV = MECO3 + #1.294 RO2C + #.053 RO2XC + #.053 zRNO3 + #.947 xHO2 + #.348 xHCHO + #.613 xRCHO + #.334 xACET + yR6OOH + #.492 XC
Methyl n-Butyl Ketone	MEK-06	0.02	e3	MNBK + HV = MECO3 + #1.686 RO2C + #.069 RO2XC + #.069 zRNO3 + #.931 xHO2 + #.931 xRCHO + yR6OOH + #.792 XC
Methyl t-Butyl Ketone	MEK-06	0.02	e3	MTBK + HV = MECO3 + #.961 RO2C + #.039 RO2XC + #.039 zRNO3 + #.961 xTBUO + yR6OOH + #-.079 XC
Heptanal	C2CHO		e1	1C7RCHO + HV = HO2 + #1.717 RO2C + #.186 RO2XC + #.186 zRNO3 + CO + #.814 xHO2 + #.814 xRCHO + yR6OOH + #2.443 XC
2-methyl-hexanal	C2CHO		e1	2MEXAL + HV = HO2 + #1.608 RO2C + #.237 RO2XC + #.237 zRNO3 + CO + #.763 xHO2 + #.763 xPROD2 + yR6OOH

Table B-6 (continued)

Compound	Phot Data [a]			Mechanism
2-Heptanone	MEK-06	0.004	e3	C7-KET-2 + HV = MECO3 + #1.809 RO2C + #.126 RO2XC + #.126 zRNO3 + #.874 xHO2 + #.874 xRCHO + yR6OOH + #1.623 XC
2-Methyl-3-Hexanone	MEK-06	0.004	e3	2M-3-HXO + HV = RCO3 + #.98 RO2C + #.02 RO2XC + #.02 zRNO3 + #.98 xHO2 + #.98 xRCHO + yR6OOH + #.94 XC
Di-Isopropyl Ketone	MEK-06	0.004	e3	DIPK + HV = RCO3 + #.96 RO2C + #.04 RO2XC + #.04 zRNO3 + #.96 xHO2 + #.96 xACET + yR6OOH + #.88 XC
5-Methyl-2-Hexanone	MEK-06	0.004	e3	5M2HXO + HV = MECO3 + #1.722 RO2C + #.119 RO2XC + #.119 zRNO3 + #.881 xHO2 + #.881 xRCHO + yR6OOH + #1.642 XC
3-Methyl-2-Hexanone	MEK-06	0.004	e3	3M2HXO + HV = MECO3 + #1.612 RO2C + #.165 RO2XC + #.165 zRNO3 + #.835 xHO2 + #.029 xCCHO + #.029 xRCHO + #.107 xMEK + #.699 xPROD2 + yR6OOH + #-.758 XC
Octanal	C2CHO		e1	1C8RCHO + HV = HO2 + #1.613 RO2C + #.252 RO2XC + #.252 zRNO3 + CO + #.748 xHO2 + #.748 xRCHO + yR6OOH + #3.244 XC
2-Octanone	MEK-06	0.0001	e3	C8-KET-2 + HV = MECO3 + #1.717 RO2C + #.186 RO2XC + #.186 zRNO3 + #.814 xHO2 + #.814 xRCHO + yR6OOH + #2.443 XC
Hydroxycitronellal	C2CHO		e1	HYCITRLL + HV = HO2 + #1.43 RO2C + #.372 RO2XC + #.372 zRNO3 + CO + #.628 xHO2 + #.006 xHCHO + #.622 xRCHO + #.006 xPROD2 + yR6OOH + #4.86 XC
Methyl Nitrite	CONO		1	ME-NITRT + HV = HCHO + HO2 + NO
Carbon Disulfide	CS2	0.012	3	CS2 + HV = SO2 + O3P + XC
methyl iodide	CH3I		5	CH3I + OH = RO2C + xHO2 + xHCHO + I
Chloropicrin	CLPICERI	0.87	2	CCL3NO2 + HV = NO2 + RO2C + xCL + XC
Methyl Isothiocyanate	MITC		4	MITC + HV = XC + SO2 + #2 O3P
Methyl Isothiocyanate	MITC		4	MITC + HV = XC + SO2 + #2 O3P
PROD2 Species #1	MEK-06	0.02	e3	PROD2-1 + HV = MECO3 + #1.013 RO2C + xHO2 + #.033 xHCHO + #.002 xCCHO + #.987 xRCHO + yR6OOH
PROD2 Species #2	MEK-06	0.004	e3	PROD2-2 + HV = MECO3 + #1.697 RO2C + #.051 RO2XC + #.051 zRNO3 + #.949 xHO2 + #1.484 xHCHO + #.736 xCCHO + #.213 xRCHO + yR6OOH + #.1 XC
PROD2 Species #3	MEK-06	0.0001	e3	PROD2-3 + HV = RCO3 + #1.715 RO2C + #.07 RO2XC + #.07 zRNO3 + #.93 xHO2 + #.93 xRCHO + yR6OOH + #.789 XC
PROD2 Species #4	MEK-06	0.0001	e3	PROD2-4 + HV = RCO3 + #1.809 RO2C + #.126 RO2XC + #.126 zRNO3 + #.874 xHO2 + #.077 xCCHO + #.874 xRCHO + yR6OOH + #1.469 XC
PROD2 Species #5	MEK-06	0.0001	e3	PROD2-5 + HV = RCO3 + #1.717 RO2C + #.186 RO2XC + #.186 zRNO3 + #.814 xHO2 + #.898 xRCHO + yR6OOH + #2.193 XC
RNO3 Species #1	IC3ONO2		e4	RNO3-1 + HV = NO2 + #.606 HO2 + #.394 RO2C + #.394 CCHO + #.606 MEK + #.394 xHO2 + #.394 xCCHO + #.394 yROOH
RNO3 Species #2	IC3ONO2		e4	RNO3-2 + HV = NO2 + HO2 + PROD2 + #-1 XC
RNO3 Species #3	IC3ONO2		e4	RNO3-3 + HV = NO2 + #.016 HO2 + #1.226 RO2C + #.081 RO2XC + #.081 zRNO3 + #.89 CCHO + #.016 PROD2 + #.904 xHO2 + #.645 xCCHO + #.495 xMEK + #.085 xPROD2 + #.984 yR6OOH + #-.143 XC

Table B-6 (continued)

Compound	Phot Data [a]		Mechanism
RNO3 Species #4	IC3ONO2	e4	RNO3-4 + HV = NO2 + #.441 HO2 + #.483 RO2C + #.075 RO2XC + #.075 zRNO3 + #.441 HCHO + #.441 RCHO + #.483 xHO2 + #.483 xPROD2 + #.559 yR6OOH + #1.882 XC
RNO3 Species #5	IC3ONO2	e4	RNO3-5 + HV = NO2 + #1.422 RO2C + #.215 RO2XC + #.215 zRNO3 + #.137 MEK + #.124 PROD2 + #.785 xHO2 + #.367 xHCHO + #.341 xCCHO + #.379 xRCHO + #.046 xACET + #.236 xPROD2 + yR6OOH + #1.678 XC
RNO3 Species #6	IC3ONO2	e4	RNO3-6 + HV = NO2 + #.802 RO2C + #.24 RO2XC + #.24 zRNO3 + #.76 xHO2 + #.76 xPROD2 + yR6OOH + #4 XC

[a] The first column gives the photolysis set name that refers to the set of absorption cross-sections and (in some cases) quantum yields. The second column gives the overall quantum yield, if quantum yields are not given in the photolysis set. If blank, then unit quantum yields are used. The third column gives the footnote for the measured or estimated absorption cross-sections and quantum yields. Footnotes for measured data are as follows. In all these cases, the absorption cross sections are given in Table B-8.

1 Absorption cross-sections from Calvert and Pitts (1966). Unit quantum yields assumed.
2 Absorption cross-sections and quantum yields from Carter et al (1997b).
3 Absorption cross-sections from current IUPAC (2006) recommendation. Quantum yield is IUPAC (2006) upper limit recommendation, but chamber data are best fit is this upper limit is used. See Carter and Malkina (2007).
4 Based on data from Alvarez (1993) and Alvarez and Moore (1994).
5 IUPAC (2006) recommendation. Unit quantum yields assumed.
6 IUPAC (2006) recommendation for absorption cross-sections and overall quantum yield.

Footnotes for estimated absorption cross-sections and quantum yields are as follows. In all these cases, the photolysis sets are associated with the base mechanism, and the corresponding absorption cross sections and quantum yields are given in Table A-3 in Appendix A. See footnotes to Table A-2 for the documentation for the values used.

e1 Assumed to have the same photolysis rate as propionaldehyde (model species RCHO).
e2 Assumed to have the same photolysis rate as methacrolein (model species MACR)
e3 Assumed to have the same absorption cross sections of methyl ethyl ketone, but with overall quantum yields depending on the carbon number, based on quantum yields that give the best simulations of the chamber data for methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, and 2-heptanol. Based on these data, overall quantum yields for simple ketones with carbon numbers of 4, 5, 6, 8, and ≥8 are assumed to be 0.174, 0.1, 0.02, 0.004, and ~0, respectively. For oxygenated ketones such as hydroxyacetone or the PROD2 species, the effective carbon number is the sum of the carbons + OH groups. For the purpose of computing an average quantum yield and a photolysis mechanism for PROD2, quantum yields of 0.0001 were used for PROD2 species with 8 or more carbons + OH groups. This was necessary in order for the mechanisms for these species to be generated.
e4 Assumed to have the same photolysis rate as isopropyl nitrate, as used in the base mechanism for RNO3.

Table B-7. Listing of compounds for which mechanisms have been derived. 4. Rate constants and mechanisms for reactions with chlorine atoms, where used.

Compound	Rate const. [a]		Mechanism [b]
Ethane	5.95E-11	1	ETHANE + CL = xHO2 + RO2C + HCL + xCCHO + yROOH
Propane	1.37E-10	2	PROPANE + CL = #.97 xHO2 + #.97 RO2C + #.03 RO2XC + #.03 zRNO3 + HCL + #.482 xRCHO + #.488 xACET + yROOH + #-.09 XC
n-Butane	2.05E-10	1	N-C4 + CL = HCL + #1.418 RO2C + #.077 RO2XC + #.077 zRNO3 + #.923 xHO2 + #.481 xCCHO + #.313 xRCHO + #.37 xMEK + yROOH + #.16 XC
n-Pentane	2.80E-10	2	N-C5 + CL = HCL + #1.577 RO2C + #.143 RO2XC + #.143 zRNO3 + #.857 xHO2 + #.105 xCCHO + #.328 xRCHO + #.177 xMEK + #.352 xPROD2 + yR6OOH + #.127 XC
n-Hexane	3.40E-10	2	N-C6 + CL = HCL + #1.591 RO2C + #.22 RO2XC + #.22 zRNO3 + #.78 xHO2 + #.009 xCCHO + #.215 xRCHO + #.585 xPROD2 + yR6OOH + #.51 XC
n-Heptane	3.90E-10	2	N-C7 + CL = HCL + #1.519 RO2C + #.29 RO2XC + #.29 zRNO3 + #.71 xHO2 + #.143 xRCHO + #.575 xPROD2 + yR6OOH + #1.386 XC
n-Octane	4.60E-10	2	N-C8 + CL = HCL + #1.449 RO2C + #.352 RO2XC + #.352 zRNO3 + #.648 xHO2 + #.088 xRCHO + #.561 xPROD2 + yR6OOH + #2.263 XC
n-Nonane	4.80E-10	2	N-C9 + CL = HCL + #1.393 RO2C + #.398 RO2XC + #.398 zRNO3 + #.602 xHO2 + #.068 xRCHO + #.535 xPROD2 + yR6OOH + #3.203 XC
n-Decane	5.50E-10	2	N-C10 + CL = HCL + #1.355 RO2C + #.428 RO2XC + #.428 zRNO3 + #.572 xHO2 + #.057 xRCHO + #.515 xPROD2 + yR6OOH + #4.17 XC
n-Undecane	6.27E-10	e1	N-C11 + CL = HCL + #1.331 RO2C + #.448 RO2XC + #.448 zRNO3 + #.552 xHO2 + #.049 xRCHO + #.503 xPROD2 + yR6OOH + #5.147 XC
n-Dodecane	6.89E-10	e1	N-C12 + CL = HCL + #1.315 RO2C + #.46 RO2XC + #.46 zRNO3 + #.54 xHO2 + #.044 xRCHO + #.497 xPROD2 + yR6OOH + #6.131 XC
n-Tridecane	7.51E-10	e1	N-C13 + CL = HCL + #1.305 RO2C + #.467 RO2XC + #.467 zRNO3 + #.533 xHO2 + #.039 xRCHO + #.494 xPROD2 + yR6OOH + #7.118 XC
Isobutane	1.43E-10	2	2-ME-C3 + CL = HCL + #1.19 RO2C + #.049 RO2XC + #.049 zRNO3 + #.651 xHO2 + #.3 xTBUO + #.239 xHCHO + #.422 xRCHO + #.23 xACET + yROOH + #.314 XC
Iso-Pentane	2.20E-10	2	2-ME-C4 + CL = HCL + #1.734 RO2C + #.123 RO2XC + #.123 zRNO3 + #.869 xHO2 + #.008 xMEO2 + #.044 xHCHO + #.482 xCCHO + #.381 xRCHO + #.439 xACET + #.042 xMEK + yR6OOH + #.623 XC
2,2-Dimethyl Butane	1.96E-10	e1	22-DM-C4 + CL = HCL + #2.068 RO2C + #.167 RO2XC + #.167 zRNO3 + #.549 xHO2 + #.016 xMEO2 + #.268 xTBUO + #.409 xHCHO + #.638 xCCHO + #.185 xRCHO + #.363 xACET + #.016 xMEK + yR6OOH + #.513 XC
2,3-Dimethyl Butane	2.30E-10	2	23-DM-C4 + CL = HCL + #1.733 RO2C + #.164 RO2XC + #.164 zRNO3 + #.836 xHO2 + #.047 xHCHO + #.039 xCCHO + #.456 xRCHO + #.734 xACET + #.001 xMEK + yR6OOH + #1.315 XC
2-Methyl Pentane	2.90E-10	2	2-ME-C5 + CL = HCL + #1.661 RO2C + #.193 RO2XC + #.193 zRNO3 + #.807 xHO2 + #.001 xHCHO + #.004 xCCHO + #.625 xRCHO + #.234 xACET + #.006 xMEK + #.183 xPROD2 + yR6OOH + #1.139 XC
3-Methylpentane	2.80E-10	2	3-ME-C5 + CL = HCL + #1.832 RO2C + #.191 RO2XC + #.191 zRNO3 + #.809 xHO2 + #.019 xHCHO + #.784 xCCHO + #.282 xRCHO + #.344 xMEK + #.047 xPROD2 + yR6OOH + #.762 XC
2,3-Dimethyl Pentane	2.79E-10	e1	23-DM-C5 + CL = HCL + #1.846 RO2C + #.253 RO2XC + #.253 zRNO3 + #.747 xHO2 + #.038 xHCHO + #.415 xCCHO + #.313 xRCHO + #.41 xACET + #.203 xMEK + #.047 xPROD2 + yR6OOH + #1.351 XC

Table B-7 (continued)

Compound	Rate const. [a]		Mechanism [b]
2,4-Dimethyl Pentane	2.90E-10	2	24-DM-C5 + CL = HCL + #1.857 RO2C + #.234 RO2XC + #.234 zRNO3 + #.766 xHO2 + #.213 xHCHO + #.009 xCCHO + #.661 xRCHO + #.23 xACET + #.008 xMEK + #.082 xPROD2 + yR6OOH + #2.163 XC
2-Methyl Hexane	3.50E-10	2	2-ME-C6 + CL = HCL + #1.585 RO2C + #.267 RO2XC + #.267 zRNO3 + #.733 xHO2 + #.008 xHCHO + #.019 xCCHO + #.362 xRCHO + #.121 xACET + #.378 xPROD2 + yR6OOH + #1.633 XC
3-Methyl Hexane	3.30E-10	e1	3-ME-C6 + CL = HCL + #1.67 RO2C + #.269 RO2XC + #.269 zRNO3 + #.731 xHO2 + #.005 xHCHO + #.171 xCCHO + #.433 xRCHO + #.133 xMEK + #.289 xPROD2 + yR6OOH + #1.479 XC
2,4-Dimethyl Hexane	3.41E-10	e1	24-DM-C6 + CL = HCL + #1.752 RO2C + #.34 RO2XC + #.34 zRNO3 + #.66 xHO2 + #.103 xHCHO + #.212 xCCHO + #.427 xRCHO + #.055 xACET + #.065 xMEK + #.227 xPROD2 + yR6OOH + #2.365 XC
2-Methyl Heptane	3.91E-10	e1	2-ME-C7 + CL = HCL + #1.489 RO2C + #.338 RO2XC + #.338 zRNO3 + #.662 xHO2 + #.006 xHCHO + #.01 xCCHO + #.229 xRCHO + #.021 xACET + #.45 xPROD2 + yR6OOH + #2.494 XC
4-Methyl Heptane	3.92E-10	e1	4-ME-C7 + CL = HCL + #1.542 RO2C + #.338 RO2XC + #.338 zRNO3 + #.662 xHO2 + #.002 xHCHO + #.004 xCCHO + #.326 xRCHO + #.041 xMEK + #.411 xPROD2 + yR6OOH + #2.353 XC
2,4-Dimethyl Heptane	4.03E-10	e1	24-DM-C7 + CL = HCL + #1.588 RO2C + #.396 RO2XC + #.396 zRNO3 + #.604 xHO2 + #.071 xHCHO + #.007 xCCHO + #.387 xRCHO + #.019 xACET + #.014 xMEK + #.339 xPROD2 + yR6OOH + #3.226 XC
2-Methyl Octane	4.53E-10	e1	2-ME-C8 + CL = HCL + #1.447 RO2C + #.4 RO2XC + #.4 zRNO3 + #.6 xHO2 + #.001 xHCHO + #.136 xRCHO + #.013 xACET + #.469 xPROD2 + yR6OOH + #3.336 XC
4-Methyl Octane	4.54E-10	e1	4-ME-C8 + CL = HCL + #1.472 RO2C + #.395 RO2XC + #.395 zRNO3 + #.605 xHO2 + #.001 xHCHO + #.012 xCCHO + #.188 xRCHO + #.004 xMEK + #.482 xPROD2 + yR6OOH + #3.132 XC
2,6-Dimethyl Octane	4.64E-10	e1	26DM-C8 + CL = HCL + #1.507 RO2C + #.429 RO2XC + #.429 zRNO3 + #.571 xHO2 + #.001 xHCHO + #.071 xCCHO + #.262 xRCHO + #.054 xACET + #.036 xMEK + #.318 xPROD2 + yR6OOH + #4.283 XC
2-Methyl Nonane	5.14E-10	e1	2-ME-C9 + CL = HCL + #1.399 RO2C + #.435 RO2XC + #.435 zRNO3 + #.565 xHO2 + #.106 xRCHO + #.012 xACET + #.46 xPROD2 + yR6OOH + #4.279 XC
4-Methyl Nonane	5.15E-10	e1	4-ME-C9 + CL = HCL + #1.418 RO2C + #.429 RO2XC + #.429 zRNO3 + #.571 xHO2 + #.001 xHCHO + #.007 xCCHO + #.161 xRCHO + #.002 xMEK + #.466 xPROD2 + yR6OOH + #4.121 XC
2,6-Dimethyl Nonane	5.26E-10	e1	26DM-C9 + CL = HCL + #1.455 RO2C + #.458 RO2XC + #.458 zRNO3 + #.542 xHO2 + #.001 xHCHO + #.001 xCCHO + #.219 xRCHO + #.049 xACET + #.003 xMEK + #.371 xPROD2 + yR6OOH + #5.21 XC
3-Methyl Decane	5.77E-10	e1	3-ME-C10 + CL = HCL + #1.391 RO2C + #.458 RO2XC + #.458 zRNO3 + #.542 xHO2 + #.001 xHCHO + #.032 xCCHO + #.096 xRCHO + #.01 xMEK + #.449 xPROD2 + yR6OOH + #5.166 XC
4-Methyl Decane	5.77E-10	e1	4-ME-C10 + CL = HCL + #1.396 RO2C + #.458 RO2XC + #.458 zRNO3 + #.542 xHO2 + #.001 xHCHO + #.001 xCCHO + #.118 xRCHO + #.002 xMEK + #.462 xPROD2 + yR6OOH + #5.118 XC
3,6-Dimethyl Decane	5.89E-10	e1	36DM-C10 + CL = HCL + #1.46 RO2C + #.482 RO2XC + #.482 zRNO3 + #.518 xHO2 + #.001 xHCHO + #.056 xCCHO + #.165 xRCHO + #.029 xMEK + #.406 xPROD2 + yR6OOH + #5.955 XC
3-Methyl Undecane	6.39E-10	e1	3-ME-C11 + CL = HCL + #1.367 RO2C + #.469 RO2XC + #.469 zRNO3 + #.531 xHO2 + #.001 xHCHO + #.029 xCCHO + #.084 xRCHO + #.009 xMEK + #.449 xPROD2 + yR6OOH + #6.146 XC

Table B-7 (continued)

Compound	Rate const. [a]		Mechanism [b]
5-Methyl Undecane	6.39E-10	e1	5-ME-C11 + CL = HCL + #1.366 RO2C + #.469 RO2XC + #.469 zRNO3 + #.531 xHO2 + #.003 xCCHO + #.098 xRCHO + #.464 xPROD2 + yR6OOH + #6.098 XC
2,4,6,8-Tetramethyl Nonane	5.49E-10	e1	2468TMC9 + CL = #.488 xHO2 + #1.531 RO2C + #.512 RO2XC + #.512 zRNO3 + HCL + #.011 xHCHO + #.001 xCCHO + #.35 xRCHO + #.038 xACET + #.001 xMEK + #.28 xPROD2 + yR6OOH + #7.067 XC
3,6-Dimethyl Undecane	6.51E-10	e1	36DM-C11 + CL = HCL + #1.428 RO2C + #.488 RO2XC + #.488 zRNO3 + #.512 xHO2 + #.001 xHCHO + #.046 xCCHO + #.152 xRCHO + #.023 xMEK + #.406 xPROD2 + yR6OOH + #6.993 XC
3-Methyl Dodecane	7.01E-10	e1	3-ME-C12 + CL = HCL + #1.351 RO2C + #.476 RO2XC + #.476 zRNO3 + #.524 xHO2 + #.001 xHCHO + #.026 xCCHO + #.076 xRCHO + #.008 xMEK + #.45 xPROD2 + yR6OOH + #7.13 XC
5-Methyl Dodecane	7.01E-10	e1	5-ME-C12 + CL = HCL + #1.352 RO2C + #.478 RO2XC + #.478 zRNO3 + #.522 xHO2 + #.003 xCCHO + #.087 xRCHO + #.461 xPROD2 + yR6OOH + #7.099 XC
Cyclopentane	3.09E-10	e1	CYCC5 + CL = HCL + #2.438 RO2C + #.224 RO2XC + #.224 zRNO3 + #.776 xHO2 + #.054 xCO + #.756 xRCHO + #.02 xMEK + yR6OOH + #1.255 XC
Cyclohexane	3.50E-10	2	CYCC6 + CL = HCL + #1.272 RO2C + #.201 RO2XC + #.201 zRNO3 + #.799 xHO2 + #.203 xRCHO + #.597 xPROD2 + yR6OOH + #.608 XC
Methylcyclopentane	3.21E-10	e1	ME-CYCC5 + CL = HCL + #2.241 RO2C + #.31 RO2XC + #.31 zRNO3 + #.596 xHO2 + #.092 xMECO3 + #.003 xRCO3 + #.028 xCO + #.052 xHCHO + #.679 xRCHO + #.001 xMEK + #.007 xPROD2 + yR6OOH + #1.785 XC
1,2-dimethylcyclopentane	3.32E-10	e1	2468TMC9 + CL = #.488 xHO2 + #1.531 RO2C + #.512 RO2XC + #.512 zRNO3 + HCL + #.011 xHCHO + #.001 xCCHO + #.35 xRCHO + #.038 xACET + #.001 xMEK + #.28 xPROD2 + yR6OOH + #7.067 XC
Ethyl Cyclopentane	3.83E-10	e1	2468TMC9 + CL = #.488 xHO2 + #1.531 RO2C + #.512 RO2XC + #.512 zRNO3 + HCL + #.011 xHCHO + #.001 xCCHO + #.35 xRCHO + #.038 xACET + #.001 xMEK + #.28 xPROD2 + yR6OOH + #7.067 XC
Methylcyclohexane	3.90E-10	2	ME-CYCC6 + CL = HCL + #1.6 RO2C + #.318 RO2XC + #.318 zRNO3 + #.682 xHO2 + #.044 xHCHO + #.003 xCCHO + #.377 xRCHO + #.31 xPROD2 + yR6OOH + #2.057 XC
Ethylcyclohexane	4.45E-10	e1	ET-CYCC6 + CL = HCL + #1.528 RO2C + #.365 RO2XC + #.365 zRNO3 + #.634 xHO2 + #.002 xHCHO + #.135 xCCHO + #.298 xRCHO + #.34 xPROD2 + yR6OOH + #2.602 XC
Propene	2.67E-10	3	PROPENE + CL = #.124 HCL + #.971 RO2C + #.029 RO2XC + #.029 zRNO3 + #.971 xHO2 + #.124 xMACR + yROOH + #2.328 XC
1-Butene	3.39E-10	4	2468TMC9 + CL = #.488 xHO2 + #1.531 RO2C + #.512 RO2XC + #.512 zRNO3 + HCL + #.011 xHCHO + #.001 xCCHO + #.35 xRCHO + #.038 xACET + #.001 xMEK + #.28 xPROD2 + yR6OOH + #7.067 XC (Mechanism is average of those for propene and 1-butene)
1-Pentene	4.05E-10	4	1-PENTEN + CL = #.408 HCL + #1.666 RO2C + #.136 RO2XC + #.136 zRNO3 + #.864 xHO2 + #.039 xHCHO + #.225 xCCHO + #.079 xRCHO + #.223 xMACR + #.021 xMVK + #.042 xIPRD + yR6OOH + #2.271 XC
3-Methyl-1-Butene	3.52E-10	5	Use mechanism derived for the 2-butenes
1-Hexene			Use mechanism and rate constant of 1-pentene
1-Heptene			Use mechanism and rate constant of 1-pentene
1-Octene			Use mechanism and rate constant of 1-pentene
1-Nonene			Use mechanism and rate constant of 1-pentene
1-Decene			Use mechanism and rate constant of 1-pentene
1-Undecene			Use mechanism and rate constant of 1-pentene

Table B-7 (continued)

Compound	Rate const. [a]		Mechanism [b]
Isobutene	3.25E-10	5	2468TMC9 + CL = #.488 xHO2 + #1.531 RO2C + #.512 RO2XC + #.512 zRNO3 + HCL + #.011 xHCHO + #.001 xCCHO + #.35 xRCHO + #.038 xACET + #.001 xMEK + #.28 xPROD2 + yR6OOH + #7.067 XC
2-Methyl-1-Butene	3.82E-10	5	2468TMC9 + CL = #.488 xHO2 + #1.531 RO2C + #.512 RO2XC + #.512 zRNO3 + HCL + #.011 xHCHO + #.001 xCCHO + #.35 xRCHO + #.038 xACET + #.001 xMEK + #.28 xPROD2 + yR6OOH + #7.067 XC
cis-2-Butene	3.88E-10	5	C-2-BUTE + CL = #.199 HCL + #.971 RO2C + #.079 RO2XC + #.079 zRNO3 + #.919 xHO2 + #.002 xMEO2 + #.047 xHCHO + #.104 xMVK + #.08 xIPRD + yROOH + #2.66 XC
trans-2-Butene	3.55E-10	3	T-2-BUTE + CL = #.199 HCL + #.923 RO2C + #.077 RO2XC + #.077 zRNO3 + #.921 xHO2 + #.002 xMEO2 + #.104 xMVK + #.082 xIPRD + yROOH + #2.709 XC
2-Methyl-2-Butene	3.23E-10	5	Use mechanism derived for the 2-butenes
cis-2-Pentene	3.94E-10	e1	C-2-PENT + CL = #.33 HCL + #1.729 RO2C + #.14 RO2XC + #.14 zRNO3 + #.282 xHO2 + #.001 xMEO2 + #.577 xCL + #.116 xHCHO + #.742 xCCHO + #.577 xRCHO + #.052 xMVK + #.231 xIPRD + yR6OOH + #-.535 XC
trans-2-Pentene	3.94E-10	e1	T-2-PENT + CL = #.33 HCL + #1.634 RO2C + #.134 RO2XC + #.134 zRNO3 + #.287 xHO2 + #.002 xMEO2 + #.577 xCL + #.078 xHCHO + #.687 xCCHO + #.577 xRCHO + #.052 xMVK + #.237 xIPRD + yR6OOH + #-.381 XC
Cis-2-Hexene			Use mechanism and rate constant derived for the 2-pentenes
Trans-2-Hexene			Use mechanism and rate constant derived for the 2-pentenes
Trans-2-Heptene			Use mechanism and rate constant derived for the 2-pentenes
Trans-3-Heptene			Use mechanism and rate constant derived for the 2-pentenes
Trans-4-Octene			Use mechanism and rate constant derived for the 2-pentenes
Trans-4-Nonene			Use mechanism and rate constant derived for the 2-pentenes
3,4-Diethyl-2-Hexene			Use mechanism and rate constant derived for the 2-pentenes
Trans-4-Decene			Use mechanism and rate constant derived for the 2-pentenes
Trans-5-Undecene			Use mechanism and rate constant derived for the 2-pentenes
Cyclohexene			Use mechanism and rate constant derived for the 2-pentenes
1,3-Butadiene	4.90E-10	2	13-BUTDE + CL = #.39 xHO2 + #.541 xCL + #1.884 RO2C + #.069 RO2XC + #.069 zRNO3 + #.863 xHCHO + #.457 xMACR + #.473 xIPRD + yROOH + #-1.47 XC
alpha Pinene	5.46E-10	e1	A-PINENE + CL = #.548 HCL + #2.258 RO2C + #.582 RO2XC + #.582 zRNO3 + #.252 xHO2 + #.034 xMECO3 + #.05 xRCO3 + #.016 xMACO3 + #.068 xCL + #.035 xCO + #.158 xHCHO + #.185 xRCHO + #.274 xACET + #.007 xGLY + #.003 xBACL + #.006 xAFG1 + #.006 xAFG2 + #.003 xMVK + #.158 xIPRD + yROOH + #-6.231 XC
Toluene	6.20E-11	6	TOLUENE + CL = #.894 RO2C + #.106 RO2XC + #.106 zRNO3 + #.894 xHO2 + #.894 xBALD + yR6OOH + #.106 XC
Ethyl Benzene	1.70E-10	e1	C2-BENZ + CL = #.864 RO2C + #.136 RO2XC + #.136 zRNO3 + #.864 xHO2 + #.864 xPROD2 + yR6OOH + #2 XC
n-Propyl Benzene	2.28E-10	e1	N-C3-BEN + CL = #.838 RO2C + #.162 RO2XC + #.162 zRNO3 + #.838 xHO2 + #.838 xPROD2 + yR6OOH + #3 XC
Isopropyl Benzene (cumene)	1.56E-10	e1	I-C3-BEN + CL = #.838 RO2C + #.162 RO2XC + #.162 zRNO3 + #.838 xHO2 + #.838 xPROD2 + yR6OOH + #3 XC
C10 Monosubstituted Benzenes	2.48E-10	e1	C10-BEN1 + CL = #.82 RO2C + #.18 RO2XC + #.18 zRNO3 + #.82 xHO2 + #.82 xPROD2 + yR6OOH + #4 XC
t-Butyl Benzene	9.82E-11	e1	T-C4-BEN + CL = #.82 RO2C + #.18 RO2XC + #.18 zRNO3 + #.82 xHO2 + #.82 xPROD2 + yR6OOH + #4 XC

Table B-7 (continued)

Compound	Rate const. [a]		Mechanism [b]
C11 Monosubstituted Benzenes	3.10E-10	e1	C11-BEN1 + CL = #.808 RO2C + #.192 RO2XC + #.192 zRNO3 + #.808 xHO2 + #.808 xPROD2 + yR6OOH + #5 XC
C12 Monosubstituted Benzenes	3.72E-10	e1	C12-BEN1 + CL = #.8 RO2C + #.2 RO2XC + #.2 zRNO3 + #.8 xHO2 + #.8 xPROD2 + yR6OOH + #6 XC
C13 Monosubstituted Benzenes	4.33E-10	e1	C13-BEN1 + CL = #.795 RO2C + #.205 RO2XC + #.205 zRNO3 + #.795 xHO2 + #.795 xPROD2 + yR6OOH + #7 XC
C14 Monosubstituted Benzenes	4.95E-10	e1	C14-BEN1 + CL = #.792 RO2C + #.208 RO2XC + #.208 zRNO3 + #.792 xHO2 + #.792 xPROD2 + yR6OOH + #8 XC
C15 Monosubstituted Benzenes	5.57E-10	e1	C15-BEN1 + CL = #.791 RO2C + #.209 RO2XC + #.209 zRNO3 + #.791 xHO2 + #.791 xPROD2 + yR6OOH + #9 XC
C16 Monosubstituted Benzenes	6.19E-10	e1	C16-BEN1 + CL = #.789 RO2C + #.211 RO2XC + #.211 zRNO3 + #.789 xHO2 + #.789 xPROD2 + yR6OOH + #10 XC
m-Xylene	1.35E-10	6	M-XYLENE + CL = #.864 RO2C + #.136 RO2XC + #.136 zRNO3 + #.864 xHO2 + #.864 xBALD + yR6OOH + #1.136 XC
o-Xylene	1.40E-10	6	O-XYLENE + CL = #.864 RO2C + #.136 RO2XC + #.136 zRNO3 + #.864 xHO2 + #.864 xBALD + yR6OOH + #1.136 XC
p-Xylene	1.44E-10	6	P-XYLENE + CL = #.864 RO2C + #.136 RO2XC + #.136 zRNO3 + #.864 xHO2 + #.864 xBALD + yR6OOH + #1.136 XC
m-Ethyl Toluene	2.39E-10	e1	M-ET-TOL + CL = #.838 RO2C + #.162 RO2XC + #.162 zRNO3 + #.838 xHO2 + #.243 xBALD + #.595 xPROD2 + yR6OOH + #2.757 XC
o-Ethyl Toluene	2.39E-10	e1	O-ET-TOL + CL = #.838 RO2C + #.162 RO2XC + #.162 zRNO3 + #.838 xHO2 + #.243 xBALD + #.595 xPROD2 + yR6OOH + #2.757 XC
p-Ethyl Toluene	2.39E-10	e1	P-ET-TOL + CL = #.838 RO2C + #.162 RO2XC + #.162 zRNO3 + #.838 xHO2 + #.243 xBALD + #.595 xPROD2 + yR6OOH + #2.757 XC
m-c10 disubstituted benzenes	3.02E-10	e1	MC10BEN2 + CL = #.82 RO2C + #.18 RO2XC + #.18 zRNO3 + #.82 xHO2 + #.094 xBALD + #.725 xPROD2 + yR6OOH + #3.906 XC
o-c10 disubstituted benzenes	3.02E-10	e1	OC10BEN2 + CL = #.82 RO2C + #.18 RO2XC + #.18 zRNO3 + #.82 xHO2 + #.094 xBALD + #.725 xPROD2 + yR6OOH + #3.906 XC
p-c10 disubstituted benzenes	3.02E-10	e1	PC10BEN2 + CL = #.82 RO2C + #.18 RO2XC + #.18 zRNO3 + #.82 xHO2 + #.094 xBALD + #.725 xPROD2 + yR6OOH + #3.906 XC
1-methyl-4-isopropylbenzene (p-cymene)	2.25E-10	e1	P-CYMENE + CL = #.82 RO2C + #.18 RO2XC + #.18 zRNO3 + #.82 xHO2 + #.253 xBALD + #.567 xPROD2 + yR6OOH + #3.747 XC
m-c11 disubstituted benzenes	3.53E-10	e1	MC11BEN2 + CL = #.808 RO2C + #.192 RO2XC + #.192 zRNO3 + #.808 xHO2 + #.054 xBALD + #.754 xPROD2 + yR6OOH + #4.946 XC
o-c11 disubstituted benzenes	3.53E-10	e1	OC11BEN2 + CL = #.808 RO2C + #.192 RO2XC + #.192 zRNO3 + #.808 xHO2 + #.054 xBALD + #.754 xPROD2 + yR6OOH + #4.946 XC
p-c11 disubstituted benzenes	3.53E-10	e1	PC11BEN2 + CL = #.808 RO2C + #.192 RO2XC + #.192 zRNO3 + #.808 xHO2 + #.054 xBALD + #.754 xPROD2 + yR6OOH + #4.946 XC
m-c12 disubstituted benzenes	4.00E-10	e1	MC12BEN2 + CL = #.8 RO2C + #.2 RO2XC + #.2 zRNO3 + #.8 xHO2 + #.035 xBALD + #.765 xPROD2 + yR6OOH + #5.965 XC
o-c12 disubstituted benzenes	4.00E-10	e1	OC12BEN2 + CL = #.8 RO2C + #.2 RO2XC + #.2 zRNO3 + #.8 xHO2 + #.035 xBALD + #.765 xPROD2 + yR6OOH + #5.965 XC
p-c12 disubstituted benzenes	4.00E-10	e1	PC12BEN2 + CL = #.8 RO2C + #.2 RO2XC + #.2 zRNO3 + #.8 xHO2 + #.035 xBALD + #.765 xPROD2 + yR6OOH + #5.965 XC
m-c13 disubstituted benzenes	4.58E-10	e1	MC13BEN2 + CL = #.795 RO2C + #.205 RO2XC + #.205 zRNO3 + #.795 xHO2 + #.795 xPROD2 + yR6OOH + #7 XC
o-c13 disubstituted benzenes	4.58E-10	e1	OC13BEN2 + CL = #.795 RO2C + #.205 RO2XC + #.205 zRNO3 + #.795 xHO2 + #.795 xPROD2 + yR6OOH + #7 XC
p-c13 disubstituted benzenes	4.58E-10	e1	PC13BEN2 + CL = #.795 RO2C + #.205 RO2XC + #.205 zRNO3 + #.795 xHO2 + #.795 xPROD2 + yR6OOH + #7 XC

Table B-7 (continued)

Compound	Rate const. [a]		Mechanism [b]
m-c14 disubstituted benzenes	5.20E-10	e1	MC14BEN2 + CL = #.792 RO2C + #.208 RO2XC + #.208 zRNO3 + #.792 xHO2 + #.792 xPROD2 + yR6OOH + #8 XC
o-c14 disubstituted benzenes	5.20E-10	e1	OC14BEN2 + CL = #.792 RO2C + #.208 RO2XC + #.208 zRNO3 + #.792 xHO2 + #.792 xPROD2 + yR6OOH + #8 XC
p-c14 disubstituted benzenes	5.20E-10	e1	PC14BEN2 + CL = #.792 RO2C + #.208 RO2XC + #.208 zRNO3 + #.792 xHO2 + #.792 xPROD2 + yR6OOH + #8 XC
m-c15 disubstituted benzenes	5.81E-10	e1	MC15BEN2 + CL = #.791 RO2C + #.209 RO2XC + #.209 zRNO3 + #.791 xHO2 + #.791 xPROD2 + yR6OOH + #9 XC
o-c15 disubstituted benzenes	5.81E-10	e1	OC15BEN2 + CL = #.791 RO2C + #.209 RO2XC + #.209 zRNO3 + #.791 xHO2 + #.791 xPROD2 + yR6OOH + #9 XC
p-c15 disubstituted benzenes	5.81E-10	e1	PC15BEN2 + CL = #.791 RO2C + #.209 RO2XC + #.209 zRNO3 + #.791 xHO2 + #.791 xPROD2 + yR6OOH + #9 XC
m-c16 disubstituted benzenes	6.43E-10	e1	MC16BEN2 + CL = #.789 RO2C + #.211 RO2XC + #.211 zRNO3 + #.789 xHO2 + #.789 xPROD2 + yR6OOH + #10 XC
o-c16 disubstituted benzenes	6.43E-10	e1	OC16BEN2 + CL = #.789 RO2C + #.211 RO2XC + #.211 zRNO3 + #.789 xHO2 + #.789 xPROD2 + yR6OOH + #10 XC
p-c16 disubstituted benzenes	6.43E-10	e1	PC16BEN2 + CL = #.789 RO2C + #.211 RO2XC + #.211 zRNO3 + #.789 xHO2 + #.789 xPROD2 + yR6OOH + #10 XC
1,2,3-Trimethyl Benzene	2.42E-10	e2	123-TMB + CL = #.838 RO2C + #.162 RO2XC + #.162 zRNO3 + #.838 xHO2 + #.838 xBALD + yR6OOH + #2.162 XC
1,2,4-Trimethyl Benzene	2.42E-10	e2	124-TMB + CL = #.838 RO2C + #.162 RO2XC + #.162 zRNO3 + #.838 xHO2 + #.838 xBALD + yR6OOH + #2.162 XC
1,3,5-Trimethyl Benzene	2.42E-10	7	135-TMB + CL = #.838 RO2C + #.162 RO2XC + #.162 zRNO3 + #.838 xHO2 + #.838 xBALD + yR6OOH + #2.162 XC
1,2,3-c10 trisubstituted benzenes	3.09E-10	e1	3C10BEN3 + CL = #.808 RO2C + #.192 RO2XC + #.192 zRNO3 + #.808 xHO2 + #.363 xBALD + #.445 xPROD2 + yR6OOH + #3.637 XC
1,2,4-c10 trisubstituted benzenes	3.09E-10	e1	4C10BEN3 + CL = #.808 RO2C + #.192 RO2XC + #.192 zRNO3 + #.808 xHO2 + #.363 xBALD + #.445 xPROD2 + yR6OOH + #3.637 XC
1,3,5-c10 trisubstituted benzenes	3.09E-10	e1	5C10BEN3 + CL = #.808 RO2C + #.192 RO2XC + #.192 zRNO3 + #.808 xHO2 + #.363 xBALD + #.445 xPROD2 + yR6OOH + #3.637 XC
1,2,3-c11 trisubstituted benzenes	3.88E-10	e1	3C11BEN3 + CL = #.8 RO2C + #.2 RO2XC + #.2 zRNO3 + #.8 xHO2 + #.215 xBALD + #.585 xPROD2 + yR6OOH + #4.785 XC
1,2,4-c11 trisubstituted benzenes	3.88E-10	e1	4C11BEN3 + CL = #.8 RO2C + #.2 RO2XC + #.2 zRNO3 + #.8 xHO2 + #.215 xBALD + #.585 xPROD2 + yR6OOH + #4.785 XC
1,3,5-c11 trisubstituted benzenes	3.88E-10	e1	5C11BEN3 + CL = #.8 RO2C + #.2 RO2XC + #.2 zRNO3 + #.8 xHO2 + #.215 xBALD + #.585 xPROD2 + yR6OOH + #4.785 XC
1,2,3-c12 trisubstituted benzenes	4.13E-10	e1	3C12BEN3 + CL = #.795 RO2C + #.205 RO2XC + #.205 zRNO3 + #.795 xHO2 + #.179 xBALD + #.616 xPROD2 + yR6OOH + #5.821 XC
1,2,4-c12 trisubstituted benzenes	4.13E-10	e1	4C12BEN3 + CL = #.795 RO2C + #.205 RO2XC + #.205 zRNO3 + #.795 xHO2 + #.179 xBALD + #.616 xPROD2 + yR6OOH + #5.821 XC
1,3,5-c12 trisubstituted benzenes	4.13E-10	e1	5C12BEN3 + CL = #.795 RO2C + #.205 RO2XC + #.205 zRNO3 + #.795 xHO2 + #.179 xBALD + #.616 xPROD2 + yR6OOH + #5.821 XC
1,2,3-c13 trisubstituted benzenes	4.87E-10	e1	3C13BEN3 + CL = #.792 RO2C + #.208 RO2XC + #.208 zRNO3 + #.792 xHO2 + #.113 xBALD + #.679 xPROD2 + yR6OOH + #6.887 XC
1,2,4-c13 trisubstituted benzenes	4.87E-10	e1	4C13BEN3 + CL = #.792 RO2C + #.208 RO2XC + #.208 zRNO3 + #.792 xHO2 + #.113 xBALD + #.679 xPROD2 + yR6OOH + #6.887 XC
1,3,5-c13 trisubstituted benzenes	4.87E-10	e1	5C13BEN3 + CL = #.792 RO2C + #.208 RO2XC + #.208 zRNO3 + #.792 xHO2 + #.113 xBALD + #.679 xPROD2 + yR6OOH + #6.887 XC
1,2,3-c14 trisubstituted benzenes	5.50E-10	e1	3C14BEN3 + CL = #.792 RO2C + #.208 RO2XC + #.208 zRNO3 + #.792 xHO2 + #.075 xBALD + #.717 xPROD2 + yR6OOH + #7.925 XC

Table B-7 (continued)

Compound	Rate const. [a]		Mechanism [b]
1,2,4-c14 trisubstituted benzenes	5.50E-10	e1	4C14BEN3 + CL = #.792 RO2C + #.208 RO2XC + #.208 zRNO3 + #.792 xHO2 + #.075 xBALD + #.717 xPROD2 + yR6OOH + #7.925 XC
1,3,5-c14 trisubstituted benzenes	5.50E-10	e1	5C14BEN3 + CL = #.792 RO2C + #.208 RO2XC + #.208 zRNO3 + #.792 xHO2 + #.075 xBALD + #.717 xPROD2 + yR6OOH + #7.925 XC
1,2,3-c15 trisubstituted benzenes	5.88E-10	e1	3C15BEN3 + CL = #.791 RO2C + #.209 RO2XC + #.209 zRNO3 + #.791 xHO2 + #.047 xBALD + #.744 xPROD2 + yR6OOH + #8.953 XC
1,2,4-c15 trisubstituted benzenes	5.88E-10	e1	4C15BEN3 + CL = #.791 RO2C + #.209 RO2XC + #.209 zRNO3 + #.791 xHO2 + #.047 xBALD + #.744 xPROD2 + yR6OOH + #8.953 XC
1,3,5-c15 trisubstituted benzenes	5.88E-10	e1	5C15BEN3 + CL = #.791 RO2C + #.209 RO2XC + #.209 zRNO3 + #.791 xHO2 + #.047 xBALD + #.744 xPROD2 + yR6OOH + #8.953 XC
1,2,3-c16 trisubstituted benzenes	6.49E-10	e1	3C16BEN3 + CL = #.789 RO2C + #.211 RO2XC + #.211 zRNO3 + #.789 xHO2 + #.021 xBALD + #.768 xPROD2 + yR6OOH + #9.979 XC
1,2,4-c16 trisubstituted benzenes	6.49E-10	e1	4C16BEN3 + CL = #.789 RO2C + #.211 RO2XC + #.211 zRNO3 + #.789 xHO2 + #.021 xBALD + #.768 xPROD2 + yR6OOH + #9.979 XC
1,3,5-c16 trisubstituted benzenes	6.49E-10	e1	5C16BEN3 + CL = #.789 RO2C + #.211 RO2XC + #.211 zRNO3 + #.789 xHO2 + #.021 xBALD + #.768 xPROD2 + yR6OOH + #9.979 XC
PROD2 Species #1	1.35E-10	e1	PROD2-1 + CL = HCL + #.512 HO2 + #.456 RO2C + #.032 RO2XC + #.032 zRNO3 + #.512 RCHO + #.429 xHO2 + #.018 xMECO3 + #.009 xRCO3 + #.438 xHCHO + #.447 xRCHO + #.488 yR6OOH + #1.431 XC
PROD2 Species #2	1.46E-10	e1	PROD2-2 + CL = HCL + #.476 HO2 + #.651 RO2C + #.063 RO2XC + #.063 zRNO3 + #.476 RCHO + #.445 xHO2 + #.016 xMECO3 + #.621 xHCHO + #.208 xRCHO + #.253 xMEK + #.524 yR6OOH + #1.904 XC
PROD2 Species #3	1.78E-10	e1	PROD2-3 + CL = HCL + #.255 HO2 + #.687 RO2C + #.107 RO2XC + #.107 zRNO3 + #.255 PROD2 + #.568 xHO2 + #.069 xRCO3 + #.124 xHCHO + #.313 xCCHO + #.624 xRCHO + #.745 yR6OOH + #1.994 XC
PROD2 Species #4	2.41E-10	e1	PROD2-4 + CL = HCL + #.18 HO2 + #.782 RO2C + #.164 RO2XC + #.164 zRNO3 + #.18 PROD2 + #.629 xHO2 + #.027 xRCO3 + #.231 xCCHO + #.882 xRCHO + #.002 xPROD2 + #.82 yR6OOH + #2.73 XC
PROD2 Species #5	3.02E-10	e1	PROD2-5 + CL = HCL + #.146 HO2 + #.821 RO2C + #.214 RO2XC + #.214 zRNO3 + #.146 PROD2 + #.634 xHO2 + #.007 xRCO3 + #.796 xRCHO + #.2 xPROD2 + #.854 yR6OOH + #3.237 XC
RNO3 Species #1	5.05E-11	e1	RNO3-1 + CL = HCL + #.105 NO2 + #1.408 RO2C + #.065 RO2XC + #.065 zRNO3 + #.105 MEK + #.115 xNO2 + #.715 xHO2 + #.23 xCCHO + #.715 xRNO3 + #.895 yROOH + #.065 XN + #-1.559 XC
RNO3 Species #2	1.56E-10	e1	RNO3-2 + CL = HCL + #.052 NO2 + #.291 HO2 + #.837 RO2C + #.058 RO2XC + #.058 zRNO3 + #.052 RCHO + #.291 RNO3 + #.599 xHO2 + #.003 xHCHO + #.373 xCCHO + #.599 xRNO3 + #.657 yR6OOH + #.058 XN + #-1.594 XC
RNO3 Species #3	1.45E-10	e1	RNO3-3 + CL = HCL + #.037 NO2 + #1.511 RO2C + #.185 RO2XC + #.185 zRNO3 + #.037 PROD2 + #.405 xNO2 + #.373 xHO2 + #.077 xHCHO + #.991 xCCHO + #.05 xRCHO + #.031 xMEK + #.06 xPROD2 + #.373 xRNO3 + #.963 yR6OOH + #.185 XN + #-.261 XC
RNO3 Species #4	2.43E-10	e1	RNO3-4 + CL = HCL + #.021 NO2 + #.036 HO2 + #1.158 RO2C + #.178 RO2XC + #.178 zRNO3 + #.021 PROD2 + #.036 RNO3 + #.159 xNO2 + #.605 xHO2 + #.008 xCCHO + #.011 xRCHO + #.159 xPROD2 + #.605 xRNO3 + #.943 yR6OOH + #.178 XN + #.952 XC
RNO3 Species #5	1.61E-10	e1	RNO3-5 + CL = HCL + #1.449 RO2C + #.304 RO2XC + #.304 zRNO3 + #.27 xNO2 + #.426 xHO2 + #.188 xHCHO + #.197 xCCHO + #.058 xRCHO + #.016 xACET + #.216 xMEK + #.054 xPROD2 + #.426 xRNO3 + yR6OOH + #.304 XN + #1.625 XC

Table B-7 (continued)

Compound	Rate const. [a]		Mechanism [b]
RNO3 Species #6	3.99E-10	e1	RNO3-6 + CL = HCL + #.013 NO2 + #1.33 RO2C + #.42 RO2XC + #.42 zRNO3 + #.013 PROD2 + #.003 xNO2 + #.564 xHO2 + #.003 xPROD2 + #.564 xRNO3 + #.987 yR6OOH + #.42 XN + #4 XC

[a] Rate constant for the reaction with Cl atoms in cm^3 $molec^{-1}$ s^{-1}. The temperature dependences are unknown, so they are assumed to be temperature independent. Footnotes for measured rate constants are as follows:

1 IUPAC (2006) Recommendation
2 Atkinson (1997) Recommendation
3 Average of values tabulated by Wang et al (2002). Value of Wang et al (2002) placed on an absolute basis using the Atkinson (1997)-recommended rate constant for n-heptane.
4 Average of value of Coquet et al (2000), placed on an absolute basis using the Atkinson (1997)-recommended n-hexane rate constant, and the value of Wang et al (2002), placed on an absolute basis using the Atkinson (1997)-recommended rate constant for n-heptane.
5 Value of Wang et al (2002), placed on an absolute basis using the Atkinson (1997)-recommended rate constant for n-heptane.
6 Average of values tabulated by Wang et al (2005).
7 Wang et al (2005)

Footnotes for estimated rate constants are as follows:

e1 Estimated using the group-additivity estimation assignments as indicated on Table 3.
e2 Estimated to have the same rate constant as 1,3,5-trimethylbenzene.

[b] Mechanisms derived for the mechanism generation system except for the aromatics, whose mechanisms were derived as discussed in the "Updated Aromatics Mechanisms" section.

Table B-8. Absorption cross sections used for the photolysis reactions for represented photoreactive VOCs that are not in the base mechanism.

a) Phot set <u>HOCCHO</u>: Glycolaldehyde photolysis
Note: Quantum yield of 0.75 is used for all wavelengths (not shown below)

wl	abs	wl	abs	wl	abs	wl	abs	wl	abs	wl	abs
205	3.91E-19	228	6.37E-21	251	2.50E-20	274	5.40E-20	297	3.29E-20	320	3.29E-21
206	3.37E-19	229	6.37E-21	252	2.65E-20	275	5.41E-20	298	3.17E-20	321	2.85E-21
207	2.87E-19	230	6.49E-21	253	2.82E-20	276	5.39E-20	299	3.02E-20	322	2.49E-21
208	2.46E-19	231	6.44E-21	254	2.97E-20	277	5.42E-20	300	2.90E-20	323	2.13E-21
209	2.12E-19	232	6.80E-21	255	3.09E-20	278	5.37E-20	301	2.74E-20	324	1.85E-21
210	1.81E-19	233	7.23E-21	256	3.21E-20	279	5.34E-20	302	2.51E-20	325	1.47E-21
211	1.53E-19	234	7.85E-21	257	3.39E-20	280	5.34E-20	303	2.26E-20	326	1.28E-21
212	1.30E-19	235	8.33E-21	258	3.59E-20	281	5.37E-20	304	2.07E-20	327	1.05E-21
213	1.12E-19	236	8.80E-21	259	3.75E-20	282	5.37E-20	305	1.91E-20	328	8.70E-22
214	9.40E-20	237	9.39E-21	260	3.89E-20	283	5.25E-20	306	1.77E-20	329	8.40E-22
215	7.84E-20	238	1.03E-20	261	4.02E-20	284	5.12E-20	307	1.64E-20	330	6.80E-22
216	6.49E-20	239	1.11E-20	262	4.13E-20	285	5.01E-20	308	1.50E-20	331	5.80E-22
217	5.30E-20	240	1.20E-20	263	4.24E-20	286	4.93E-20	309	1.36E-20	332	4.30E-22
218	4.26E-20	241	1.28E-20	264	4.40E-20	287	4.80E-20	310	1.25E-20	333	4.00E-22
219	3.37E-20	242	1.38E-20	265	4.60E-20	288	4.67E-20	311	1.15E-20	334	4.00E-22
220	2.65E-20	243	1.50E-20	266	4.75E-20	289	4.58E-20	312	1.03E-20	335	3.90E-22
221	2.13E-20	244	1.59E-20	267	4.85E-20	290	4.50E-20	313	8.84E-21	336	0.00E+00
222	1.65E-20	245	1.71E-20	268	4.92E-20	291	4.41E-20	314	7.71E-21		
223	1.36E-20	246	1.83E-20	269	4.99E-20	292	4.19E-20	315	6.89E-21		
224	1.12E-20	247	1.95E-20	270	5.05E-20	293	3.96E-20	316	5.97E-21		
225	9.33E-21	248	2.09E-20	271	5.14E-20	294	3.76E-20	317	5.16E-21		
226	7.83E-21	249	2.22E-20	272	5.23E-20	295	3.59E-20	318	4.55E-21		
227	6.91E-21	250	2.36E-20	273	5.36E-20	296	3.46E-20	319	3.96E-21		

Wavelengths in nm and absorption cross-sections in cm^{-2}. IUPAC (2006) recommendation (including 0.75 overall quantum yield)

b) Phot set CONO: Absorption cross-sections for methyl nitrite

wl	abs	wl	abs	wl	abs	wl	abs	wl	abs	wl	abs
250	1.55e-18	295	8.60e-20	320	1.45e-19	345	1.45e-19	370	1.24e-19	395	2.70e-20
260	1.00e-18	300	7.00e-20	325	9.70e-20	350	2.91e-19	375	9.70e-20	400	1.10e-20
280	1.83e-19	305	6.50e-20	330	2.37e-19	355	1.78e-19	380	4.90e-20	405	1.40e-20
285	1.49e-19	310	9.10e-20	335	1.19e-19	360	1.62e-19	385	4.30e-20	410	-
290	1.08e-19	315	8.10e-20	340	3.07e-19	365	1.67e-19	390	4.30e-20		

Wavelengths in nm and absorption cross-sections in cm^{-2}. Absorption cross-sections from Calvert and Pitts (1966). Unit quantum yields assumed.

Table B-8 (continued)

c) Phot set CS2: Absorption cross-sections for carbon disulfide

wl	abs	wl	abs	wl	abs	wl	abs	wl	abs	wl	abs
280	5.30e-22	296	1.13e-20	312	6.69e-20	328	2.85e-20	344	5.56e-21	360	1.19e-21
281	6.20e-22	297	1.86e-20	313	8.15e-20	329	2.85e-20	345	3.53e-21	361	4.20e-22
282	8.00e-22	298	2.29e-20	314	7.84e-20	330	3.80e-20	346	3.50e-21	362	4.80e-22
283	1.03e-21	299	2.02e-20	315	9.44e-20	331	1.30e-20	347	3.28e-21	363	2.10e-22
284	1.22e-21	300	1.88e-20	316	7.04e-20	332	3.06e-20	348	1.09e-21	364	3.70e-22
285	1.58e-21	301	3.27e-20	317	9.46e-20	333	1.55e-20	349	3.68e-21	365	1.20e-22
286	2.09e-21	302	3.17e-20	318	7.16e-20	334	1.51e-20	350	2.39e-21	366	3.60e-22
287	2.54e-21	303	3.13e-20	319	9.80e-20	335	1.38e-20	351	1.27e-21	367	2.30e-22
288	3.09e-21	304	4.44e-20	320	4.52e-20	336	8.61e-21	352	2.55e-21	368	2.00e-22
289	4.45e-21	305	4.46e-20	321	6.12e-20	337	1.38e-20	353	6.60e-22	369	1.10e-22
290	4.38e-21	306	3.66e-20	322	4.22e-20	338	5.91e-21	354	1.72e-21	370	1.80e-22
291	6.35e-21	307	5.12e-20	323	5.18e-20	339	1.12e-20	355	2.47e-21	371	
292	6.40e-21	308	7.10e-20	324	3.52e-20	340	4.89e-21	356	5.20e-22		
293	8.78e-21	309	4.93e-20	325	8.63e-20	341	3.86e-21	357	1.33e-21		
294	8.01e-21	310	8.84e-20	326	5.02e-20	342	5.73e-21	358	5.50e-22		
295	1.14e-20	311	5.61e-20	327	3.48e-20	343	3.87e-21	359	5.90e-22		

Wavelengths in nm and absorption cross-sections in cm^{-2}. IUPAC (2006) recommendation for absorption cross-sections. Unit quantum yields assumed.

d) Phot set CH3I: Absorption cross-sections for methyl iodide

wl	Abs	wl	Abs	wl	abs	wl	abs	wl	abs
280	2.80e-19	300	2.03e-20	320	2.15e-21	340	2.30e-22	360	1.30e-23
285	1.52e-19	305	1.09e-20	325	1.24e-21	345	1.27e-22	365	4.00e-24
290	7.79e-20	310	6.19e-21	330	7.00e-22	350	6.70e-23	370	-
295	3.92e-20	315	3.56e-21	335	3.30e-22	355	2.60e-23		

Wavelengths in nm and absorption cross-sections in cm^{-2}. IUPAC (2006) recommendation.

e) Phot set BRNO2: Absorption cross-sections for BrNO2 used in the methyl iodide mechanism for INO2

wl	Abs	wl	Abs	wl	abs	wl	abs	wl	abs	wl	abs
280	8.80e-19	310	1.10e-19	340	1.60e-19	370	1.70e-19	400	1.40e-19	430	9.00e-20
285	6.30e-19	315	1.10e-19	345	1.50e-19	375	1.80e-19	405	1.40e-19	435	8.00e-20
290	4.40e-19	320	1.00e-19	350	1.60e-19	380	1.70e-19	410	1.30e-19	440	7.00e-20
295	3.00e-19	325	1.20e-19	355	1.60e-19	385	1.70e-19	415	1.20e-19	445	7.00e-20
300	2.00e-19	330	1.30e-19	360	1.80e-19	390	1.60e-19	420	1.10e-19	450	6.00e-20
305	1.50e-19	335	1.40e-19	365	1.90e-19	395	1.50e-19	425	1.00e-19	480	-

Wavelengths in nm and absorption cross-sections in cm^{-2}. IUPAC (2006) recommendation.

f) Phot set HI: Absorption cross-sections for HI used in the methyl iodide mechanism.

wl	Abs	wl	Abs	wl	abs	wl	abs	wl	abs
280	8.94e-20	295	3.17e-20	310	1.01e-20	325	2.47e-21	340	4.70e-22
285	6.37e-20	300	2.23e-20	315	6.53e-21	330	1.45e-21	347	-
290	4.51e-20	305	1.52e-20	320	4.09e-21	335	8.30e-22		

Wavelengths in nm and absorption cross-sections in cm^{-2}. IUPAC (2006) recommendation.

Table B-8 (continued)

g) Phot set HOI: Absorption cross-sections for HOI used in the methyl iodide mechanism.

wl	Abs	wl	Abs	wl	abs	wl	abs	wl	abs	wl	abs
280	7.70e-21	320	2.07e-18	360	2.58e-18	400	3.22e-18	440	1.13e-18	480	2.96e-20
285	2.26e-20	325	2.72e-18	365	2.21e-18	405	3.32e-18	445	8.13e-19	485	1.61e-20
290	5.89e-20	330	3.29e-18	370	1.98e-18	410	3.27e-18	450	5.63e-19	490	8.60e-21
295	1.37e-19	335	3.70e-18	375	1.94e-18	415	3.07e-18	455	3.76e-19	496	-
300	2.86e-19	340	3.85e-18	380	2.07e-18	420	2.75e-18	460	2.42e-19		
305	5.41e-19	345	3.77e-18	385	2.33e-18	425	2.35e-18	465	1.50e-19		
310	9.26e-19	350	3.47e-18	390	2.66e-18	430	1.92e-18	470	9.04e-20		
315	1.45e-18	355	3.04e-18	395	2.98e-18	435	1.50e-18	475	5.25e-20		

Wavelengths in nm and absorption cross-sections in cm^{-2}. IUPAC (2006) recommendation.

h) Phot set CLPICERI: Absorption cross-sections for chloropicrin

wl	abs	wl	abs	wl	abs	wl	abs	wl	abs	wl	abs
280	1.67e-19	300	6.44e-20	320	1.38e-20	340	5.20e-21	360	1.54e-21	380	5.57e-22
282	1.62e-19	302	5.47e-20	322	1.23e-20	342	4.80e-21	362	2.13e-21	382	4.66e-22
284	1.54e-19	304	4.68e-20	324	1.10e-20	344	4.36e-21	364	1.78e-21	384	4.68e-22
286	1.44e-19	306	3.97e-20	326	9.94e-21	346	4.00e-21	366	1.25e-21	386	1.70e-22
288	1.34e-19	308	3.33e-20	328	8.98e-21	348	3.68e-21	368	1.28e-21	388	5.02e-22
290	1.23e-19	310	2.79e-20	330	8.18e-21	350	3.34e-21	370	1.04e-21	390	3.50e-22
292	1.10e-19	312	2.36e-20	332	7.54e-21	352	3.05e-21	372	1.08e-21	392	-
294	9.82e-20	314	2.03e-20	334	6.82e-21	354	2.70e-21	374	7.13e-22		
296	8.71e-20	316	1.77e-20	336	6.27e-21	356	2.51e-21	376	6.96e-22		
298	7.57e-20	318	1.55e-20	338	5.69e-21	358	2.30e-21	378	5.85e-22		

Wavelengths in nm and absorption cross-sections in cm^{-2}. Absorption cross-sections from Carter et al (1997b). Unit quantum yields assumed.

i) Phot set MITC: Absorption cross-sections for methyl isothiocyanate.

wl	abs	wl	abs	wl	abs	wl	abs
285.6	3.44e-20	302.5	1.23e-20	317.5	3.48e-21	332.5	4.00e-22
290.0	2.66e-20	307.5	8.52e-21	322.5	1.96e-21	337.5	1.70e-22
297.5	1.70e-20	312.5	5.63e-21	327.5	9.60e-22	340.0	-

Wavelengths in nm and absorption cross-sections in cm^{-2}. Absorption cross-sections from Alvarez and Moore (1994). Unit quantum yields assumed.

Table B-8 (continued)

j) Phot set PAA: Peroxy acetic acid absorption cross-sections

wl	abs	wl	abs	wl	abs	wl	abs	wl	abs	wl	abs
210	3.81E-19	234	7.03E-20	258	1.93E-20	282	4.44E-21	306	7.80E-22	330	9.00E-23
212	3.31E-19	236	6.31E-20	260	1.71E-20	284	3.86E-21	308	6.90E-22	332	1.10E-22
214	2.95E-19	238	5.61E-20	262	1.53E-20	286	3.34E-21	310	6.20E-22	334	1.10E-22
216	2.54E-19	240	5.03E-20	264	1.35E-20	288	2.97E-21	312	4.50E-22	336	9.00E-23
218	2.17E-19	242	4.83E-20	266	1.21E-20	290	2.56E-21	314	4.40E-22	338	9.00E-23
220	1.89E-19	244	4.31E-20	268	1.06E-20	292	2.26E-21	316	4.00E-22	340	6.00E-23
222	1.60E-19	246	3.82E-20	270	9.45E-21	294	1.93E-21	318	3.50E-22	342	3.00E-23
224	1.39E-19	248	3.41E-20	272	8.35E-21	296	1.70E-21	320	2.50E-22	344	0.00E+00
226	1.20E-19	250	3.05E-20	274	7.42E-21	298	1.41E-21	322	2.00E-22		
228	1.05E-19	252	2.71E-20	276	6.51E-21	300	1.23E-21	324	2.00E-22		
230	9.10E-20	254	2.42E-20	278	5.74E-21	302	1.07E-21	326	1.70E-22		
232	8.01E-20	256	2.16E-20	280	5.06E-21	304	9.40E-22	328	1.40E-22		

Wavelengths in nm and absorption cross-sections in cm^{-2}. Orlando and Tyldall (2003)

Table B-9. Lumped molecule representations used in the SAPRC-07 mechanism.

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
Branched C5 Alkanes	1	Iso-Pentane				
Branched C6 Alkanes	0.5	2,3-Dimethyl Butane	0.25	3-Methylpentane	0.25	2-Methyl Pentane
C6 Cycloalkanes	1	Cyclohexane				
Branched C7 Alkanes	0.5	2,4-Dimethyl Pentane	0.25	3-Methyl Hexane	0.25	2-Methyl Hexane
C7 Cycloalkanes	1	Methylcyclohexane				
Branched C8 Alkanes	0.5	2,4-Dimethyl Hexane	0.25	4-Methyl Heptane	0.25	2-Methyl Heptane
C8 Bicycloalkanes	1	Methylcyclohexane				
C8 Cycloalkanes	1	Ethylcyclohexane				
Branched C9 Alkanes	0.5	2,4-Dimethyl Heptane	0.25	4-Methyl Octane	0.25	2-Methyl Octane
C9 Bicycloalkanes	0.5	Propyl Cyclohexane	0.5	1-Ethyl-4-Methyl Cyclohexane		
C9 Cycloalkanes	0.5	Propyl Cyclohexane	0.5	1-Ethyl-4-Methyl Cyclohexane		
Branched C10 Alkanes	0.5	2,6-Dimethyl Octane	0.25	4-Methyl Nonane	0.25	2-Methyl Nonane
C10 Bicycloalkanes	0.34	Butyl Cyclohexane	0.33	1-Methyl-3-Isopropyl Cyclohexane	0.33	1,4-Diethyl-Cyclohexane
isobutylclohexane; (2-methylpropyl) cyclohexane	1	Butyl Cyclohexane				
sec-butylcyclohexane	1	Butyl Cyclohexane				
C10 Cycloalkanes	0.34	Butyl Cyclohexane	0.33	1-Methyl-3-Isopropyl Cyclohexane	0.33	1,4-Diethyl-Cyclohexane
Branched C11 alkanes	0.5	2,6-Dimethyl Nonane	0.25	4-Methyl Decane	0.25	3-Methyl Decane
C11 Bicycloalkanes	0.34	Pentyl Cyclohexane	0.33	1,3-Diethyl-5-Methyl Cyclohexane	0.33	1-Ethyl-2-Propyl Cyclohexane
C11 Cycloalkanes	0.34	Pentyl Cyclohexane	0.33	1,3-Diethyl-5-Methyl Cyclohexane	0.33	1-Ethyl-2-Propyl Cyclohexane
Branched C12 Alkanes	0.5	3,6-Dimethyl Decane	0.25	5-Methyl Undecane	0.25	3-Methyl Undecane
C12 Tricycloalkanes	0.34	Hexyl Cyclohexane	0.33	1,3,5-Triethyl Cyclohexane	0.33	1-Methyl-4-Pentyl Cyclohexane
C12 Bicycloalkanes	0.34	Hexyl Cyclohexane	0.33	1,3,5-Triethyl Cyclohexane	0.33	1-Methyl-4-Pentyl Cyclohexane
C12 Cycloalkanes	0.34	Hexyl Cyclohexane	0.33	1,3,5-Triethyl Cyclohexane	0.33	1-Methyl-4-Pentyl Cyclohexane

Table B-9 (continued)

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
Branched C13 Alkanes	0.5	3,6-Dimethyl Undecane	0.25	5-Methyl Dodecane	0.25	3-Methyl Dodecane
C13 Tricycloalkanes	0.34	Heptyl Cyclohexane	0.33	1,3-Diethyl-5-Propyl Cyclohexane	0.33	1-Methyl-2-Hexyl-Cyclohexane
C13 Bicycloalkanes	0.34	Heptyl Cyclohexane	0.33	1,3-Diethyl-5-Propyl Cyclohexane	0.33	1-Methyl-2-Hexyl-Cyclohexane
C13 Cycloalkanes	0.34	Heptyl Cyclohexane	0.33	1,3-Diethyl-5-Propyl Cyclohexane	0.33	1-Methyl-2-Hexyl-Cyclohexane
Branched C14 Alkanes	0.5	3,7-Dimethyl Dodecane	0.25	6-Methyl Tridecane	0.25	3-Methyl Tridecane
C14 Tricycloalkanes	0.34	Octyl Cyclohexane	0.33	1,3-Dipropyl-5-Ethyl Cyclohexane	0.33	trans 1-Methyl-4-Heptyl Cyclohexane
C14 Bicycloalkanes	0.34	Octyl Cyclohexane	0.33	1,3-Dipropyl-5-Ethyl Cyclohexane	0.33	trans 1-Methyl-4-Heptyl Cyclohexane
C14 Cycloalkanes	0.34	Octyl Cyclohexane	0.33	1,3-Dipropyl-5-Ethyl Cyclohexane	0.33	trans 1-Methyl-4-Heptyl Cyclohexane
Branched C15 Alkanes	0.5	3,7-Dimethyl Tridecane	0.25	6-Methyl Tetradecane	0.25	3-Methyl Tetradecane
C15 Tricycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C15 Bicycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C15 Cycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
Branched C16 Alkanes	0.5	4,8-Dimethyl Tetradecane	0.25	7-Methyl Pentadecane	0.25	3-Methyl Pentadecane
C16 Tricycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C16 Bicycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C16 Cycloalkanes	0.34	Decyl Cyclohexane	0.33	1,3-Propyl-5-Butyl Cyclohexane	0.33	1-Methyl-4-Nonyl Cyclohexane
n-C17	1	n-C16				
Branched C17 Alkanes	0.5	4,8-Dimethyl Tetradecane	0.25	7-Methyl Pentadecane	0.25	3-Methyl Pentadecane
C17 Tricycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C17 Bicycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane

Table B-9 (continued)

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
C17 Cycloalkanes	0.34	Decyl Cyclohexane	0.33	1,3-Propyl-5-Butyl Cyclohexane	0.33	1-Methyl-4-Nonyl Cyclohexane
n-C18	1	n-C16				
Branched C18 Alkanes	0.5	4,8-Dimethyl Tetradecane	0.25	7-Methyl Pentadecane	0.25	3-Methyl Pentadecane
C18 Tricycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C18 Bicycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C18 Cycloalkanes	0.34	Decyl Cyclohexane	0.33	1,3-Propyl-5-Butyl Cyclohexane	0.33	1-Methyl-4-Nonyl Cyclohexane
n-C19	1	n-C16				
Branched C19 Alkanes	0.5	4,8-Dimethyl Tetradecane	0.25	7-Methyl Pentadecane	0.25	3-Methyl Pentadecane
C19 Tricycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C19 Bicycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C19 Cycloalkanes	0.34	Decyl Cyclohexane	0.33	1,3-Propyl-5-Butyl Cyclohexane	0.33	1-Methyl-4-Nonyl Cyclohexane
n-C20	1	n-C16				
Branched C20 Alkanes	0.5	4,8-Dimethyl Tetradecane	0.25	7-Methyl Pentadecane	0.25	3-Methyl Pentadecane
C20 Tricycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C20 Bicycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C20 Cycloalkanes	0.34	Decyl Cyclohexane	0.33	1,3-Propyl-5-Butyl Cyclohexane	0.33	1-Methyl-4-Nonyl Cyclohexane
n-C21	1	n-C16				
Branched C21 Alkanes	0.5	4,8-Dimethyl Tetradecane	0.25	7-Methyl Pentadecane	0.25	3-Methyl Pentadecane
C21 Tricycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C21 Bicycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C21 Cycloalkanes	0.34	Decyl Cyclohexane	0.33	1,3-Propyl-5-Butyl Cyclohexane	0.33	1-Methyl-4-Nonyl Cyclohexane
n-C22	1	n-C16				

Table B-9 (continued)

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
Branched C22 Alkanes	0.5	4,8-Dimethyl Tetradecane	0.25	7-Methyl Pentadecane	0.25	3-Methyl Pentadecane
C22 Tricycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C22 Bicycloalkanes	0.34	Nonyl Cyclohexane	0.33	1,3,5-Tripropyl Cyclohexane	0.33	1-Methyl-2-Octyl Cyclohexane
C22 Cycloalkanes	0.34	Decyl Cyclohexane	0.33	1,3-Propyl-5-Butyl Cyclohexane	0.33	1-Methyl-4-Nonyl Cyclohexane
C4 Terminal Alkenes	1	1-Butene				
C4 Internal Alkenes	0.5	trans-2-Butene	0.5	cis-2-Butene		
C4 Alkenes	0.5	1-Butene	0.25	trans-2-Butene	0.25	cis-2-Butene
C5 Terminal Alkenes	1	1-Pentene				
2-Pentenes	0.5	cis-2-Pentene	0.5	trans-2-Pentene		
C5 Internal Alkenes	0.5	cis-2-Pentene	0.5	trans-2-Pentene		
Cis 1,3-Pentadiene	1	Trans 1,3-Pentadiene				
Cyclopentadiene	1	Cyclopentene				
C5 Alkenes	0.5	1-Pentene	0.25	cis-2-Pentene	0.25	trans-2-Pentene
C6 Terminal Alkenes	1	1-Hexene				
Cis 4-Methyl-2-Pentene	1	Trans 4-Methyl-2-Pentene				
2-Hexenes	0.5	Cis-2-Hexene	0.5	Trans-2-Hexene		
C6 Internal Alkenes	0.5	Cis-2-Hexene	0.5	Trans-2-Hexene		
trans,trans-2,4-hexadiene	1	Trans-2-Hexene				
Trans 1,3-Hexadiene	1	Trans 1,3-Pentadiene				
C6 Cyclic or di-olefins	0.5	Cis-2-Hexene	0.5	Trans-2-Hexene		
C6 Alkenes	0.5	1-Heptene	0.25	Cis-2-Hexene	0.25	Trans-2-Hexene
C7 Cyclic or di-olefins	1	Trans-2-Heptene				
2-Heptenes	0.5	Trans-3-Heptene	0.5	Cis-3-Heptene		
C7 Terminal Alkenes	1	1-Heptene				
C7 Internal Alkenes	1	Trans-3-Heptene				
C7 Alkenes	0.5	1-Heptene	0.5	Trans-3-Heptene		
C8 Cyclic or di-olefins	1	Trans-4-Octene				
3-Octenes	1	Trans-3-Octene				
C8 Terminal Alkenes	1	1-Octene				
C8 Internal Alkenes	1	Trans-4-Octene				
C8 Alkenes	0.5	1-Octene	0.5	Trans-4-Octene		

Table B-9 (continued)

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
C9 Terminal Alkenes	1	1-Nonene				
4-Nonene	1	Trans-4-Nonene				
3-Nonenes	1	Trans-4-Nonene				
C9 Internal Alkenes	1	Trans-4-Nonene				
C9 Cyclic or di-olefins	1	Trans-4-Nonene				
C9 Alkenes	0.5	1-Nonene	0.5	Trans-4-Nonene		
C10 Terminal Alkenes	1	1-Decene				
C10 3-Alkenes	1	Trans-4-Decene				
C10 Internal Alkenes	1	Trans-4-Decene				
C10 Cyclic or di-olefins	1	Trans-4-Decene				
Camphene	1	a-pinene				
Terpene	0.4	a-Pinene	0.25	b-Pinene	0.1	d-Limonene
	0.15	3-Carene	0.1	Sabinene		
C10 Alkenes	0.333	1-Decene	0.667	Trans-4-Decene		
C11 Terminal Alkenes	1	1-Undecene				
C11 3-Alkenes	1	Trans-5-Undecene				
C11 Internal Alkenes	1	Trans-5-Undecene				
C11 Cyclic or di-olefins	1	Trans-5-Undecene				
C11 Alkenes	0.5	1-Undecene	0.5	Trans-5-Undecene		
C12 Terminal Alkenes	1	1-Dodecene				
C12 2-Alkenes	1	Trans-5-Dodecene				
C12 3-Alkenes	1	Trans-5-Dodecene				
C12 Internal Alkenes	1	Trans-5-Dodecene				
C12 Cyclic or di-olefins	1	Trans-5-Dodecene				
C12 Alkenes	0.5	1-Dodecene	0.5	Trans-5-Dodecene		
C13 Terminal Alkenes	1	1-Tridecene				
C13 3-Alkenes	1	Trans-5-Tridecene				
C13 Internal Alkenes	1	Trans-5-Tridecene				
C13 Cyclic or di-olefins	1	Trans-5-Tridecene				
C13 Alkenes	0.5	1-Tridecene	0.5	Trans-5-Tridecene		
C14 Terminal Alkenes	1	1-Tetradecene				
C14 3-Alkenes	1	Trans-5-Tetradecene				
C14 Internal Alkenes	1	Trans-5-Tetradecene				
C14 Cyclic or di-olefins	1	Trans-5-Tetradecene				

Table B-9 (continued)

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
C14 Alkenes	0.5	1-Tetradecene	0.5	Trans-5-Tetradecene		
1-pentadecene	1	1-Tetradecene				
C15 Terminal Alkenes	1	1-Tetradecene				
C15 3-Alkenes	1	Trans-5-Pentadecene				
C15 Internal Alkenes	1	Trans-5-Pentadecene				
C15 Cyclic or di-olefins	1	Trans-5-Pentadecene				
C15 Alkenes	0.5	1-Tetradecene	0.5	Trans-5-Pentadecene		
C8 Disubstituted Benzenes	0.34	m-Xylene	0.33	o-Xylene	0.33	p-Xylene
Isomers of Ethylbenzene	0.25	m-Xylene	0.25	o-Xylene	0.25	p-Xylene
	0.25	Ethyl Benzene				
C9 Monosubstituted Benzenes	1	n-Propyl Benzene				
C9 Disubstituted Benzenes	0.334	m-Ethyl Toluene	0.333	o-Ethyl Toluene	0.333	p-Ethyl Toluene
C9 Trisubstituted Benzenes	0.334	1,2,4-Trimethyl Benzene	0.333	1,2,3-Trimethyl Benzene	0.333	1,3,5-Trimethyl Benzene
Isomers of Propylbenzene	0.111	1,3,5-Trimethyl Benzene	0.111	1,2,3-Trimethyl Benzene	0.111	1,2,4-Trimethyl Benzene
	0.334	n-Propyl Benzene	0.111	m-Ethyl Toluene	0.111	o-Ethyl Toluene
	0.111	p-Ethyl Toluene				
Indene	1	Styrene				
Indan	1	Tetralin				
Allylbenzene	1	Styrene				
a-Methyl Styrene	1	Styrene				
C9 Styrenes	1	Styrene				
n-Butyl Benzene	1	C10 Monosubstituted Benzenes				
s-Butyl Benzene	1	C10 Monosubstituted Benzenes				
o-cymene; 1-methyl-2-(1-methylethyl)benzene	1	o-c10 disubstituted benzenes				
1-methyl-2-n-propylbenzene	1	o-c10 disubstituted benzenes				
m-cymene; 1-methyl-3-(1-methylethyl)benzene	1	m-c10 disubstituted benzenes				
1-methyl-3-n-propylbenzene	1	m-c10 disubstituted benzenes				
1-methyl-4-n-propylbenzene	1	p-c10 disubstituted benzenes				
C10 Disubstituted Benzenes	0.334	m-c10 disubstituted benzenes	0.333	o-c10 disubstituted benzenes	0.333	p-c10 disubstituted benzenes
m-Diethyl Benzene	1	m-c10 disubstituted benzenes				
o-Diethyl Benzene	1	o-c10 disubstituted benzenes				
p-Diethyl Benzene	1	p-c10 disubstituted benzenes				

Table B-9 (continued)

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
1,2,3,4-tetramethylbenzene	0.334	1,2,4-c10 trisubstituted benzenes	0.333	1,2,3-c10 trisubstituted benzenes	0.333	1,3,5-c10 trisubstituted benzenes
1,2,4,5-tetramethylbenzene	0.334	1,2,4-c10 trisubstituted benzenes	0.333	1,2,3-c10 trisubstituted benzenes	0.333	1,3,5-c10 trisubstituted benzenes
1,2-dimethyl-3-ethylbenzene	1	1,2,3-c10 trisubstituted benzenes				
1,2-dimethyl-4-ethylbenzene	1	1,2,4-c10 trisubstituted benzenes				
1,3-dimethyl-2-ethylbenzene	1	1,2,3-c10 trisubstituted benzenes				
1,3-dimethyl-4-ethylbenzene	1	1,2,4-c10 trisubstituted benzenes				
1,3-dimethyl-5-ethylbenzene	1	1,3,5-c10 trisubstituted benzenes				
1,4-dimethyl-2-ethylbenzene	1	1,2,4-c10 trisubstituted benzenes				
1,2,3,5 Tetramethyl Benzene	0.334	1,2,4-c10 trisubstituted benzenes	0.333	1,2,3-c10 trisubstituted benzenes	0.333	1,3,5-c10 trisubstituted benzenes
C10 Trisubstituted Benzenes	0.334	1,2,4-c10 trisubstituted benzenes	0.333	1,2,3-c10 trisubstituted benzenes	0.333	1,3,5-c10 trisubstituted benzenes
C10 Tetrasubstituted Benzenes	0.334	1,2,4-c10 trisubstituted benzenes	0.333	1,2,3-c10 trisubstituted benzenes	0.333	1,3,5-c10 trisubstituted benzenes
Isomers of Butylbenzene	0.334	C10 Monosubstituted Benzenes	0.111	o-c10 disubstituted benzenes	0.111	m-c10 disubstituted benzenes
	0.111	p-c10 disubstituted benzenes	0.111	1,2,3-c10 trisubstituted benzenes	0.111	1,2,4-c10 trisubstituted benzenes
	0.111	1,3,5-c10 trisubstituted benzenes				
Methyl Indans	1	Tetralin				
C10 Styrenes	1	Styrene				
n-pentylbenzene	1	C11 Monosubstituted Benzenes				
1-butyl-2-methylbenzene	1	o-c11 disubstituted benzenes				
1-ethyl-2-n-propylbenzene	1	o-c11 disubstituted benzenes				
o-t-butyl toluene; 1-(1,1-dimethylethyl)-2-methylbenzene	1	o-c11 disubstituted benzenes				
1-methyl-3-n-butyl-benzene	1	m-c11 disubstituted benzenes				
p-Isobutyl toluene; 1-methyl-4(2-methylpropyl) benzene	1	p-c11 disubstituted benzenes				
C11 Disubstituted Benzenes	0.334	m-c11 disubstituted benzenes	0.333	o-c11 disubstituted benzenes	0.333	p-c11 disubstituted benzenes
Pentamethylbenzene	0.334	1,2,4-c11 trisubstituted benzenes	0.333	1,2,3-c11 trisubstituted benzenes	0.333	1,3,5-c11 trisubstituted benzenes
1-methyl-3,5-diethylbenzene	1	1,3,5-c11 trisubstituted benzenes				

Table B-9 (continued)

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
C11 Trisubstituted Benzenes	0.334	1,2,4-c11 trisubstituted benzenes	0.333	1,2,3-c11 trisubstituted benzenes	0.333	1,3,5-c11 trisubstituted benzenes
C11 Tetrasubstituted Benzenes	0.334	1,2,4-c11 trisubstituted benzenes	0.333	1,2,3-c11 trisubstituted benzenes	0.333	1,3,5-c11 trisubstituted benzenes
C11 Pentasubstituted Benzenes	0.334	1,2,4-c11 trisubstituted benzenes	0.333	1,2,3-c11 trisubstituted benzenes	0.333	1,3,5-c11 trisubstituted benzenes
Isomers of Pentylbenzene	0.334	C10 Monosubstituted Benzenes	0.111	o-c11 disubstituted benzenes	0.111	o-c11 disubstituted benzenes
	0.111	p-c11 disubstituted benzenes	0.111	1,2,3-c11 trisubstituted benzenes	0.111	1,2,4-c11 trisubstituted benzenes
	0.111	1,3,5-c11 trisubstituted benzenes				
C11 Tetralin or Indan	1	Tetralin				
1-Methyl Naphthalene	1	Methyl Naphthalenes				
2-Methyl Naphthalene	1	Methyl Naphthalenes				
1,3-di-n-propylbenzene	1	o-c12 disubstituted benzenes				
1,4 diisopropyl benzene	1	p-c12 disubstituted benzenes				
3-Isopropyl Cumene; 1,3-diisopropyl benzene	1	m-c12 disubstituted benzenes				
C12 Disubstituted Benzenes	0.334	m-c12 disubstituted benzenes	0.333	o-c12 disubstituted benzenes	0.333	p-c12 disubstituted benzenes
1-(1,1-dimethylethyl)-3,5-dimethylbenzene	1	1,3,5-c12 trisubstituted benzenes				
C12 Trisubstituted Benzenes	0.334	1,2,4-c12 trisubstituted benzenes	0.333	1,2,3-c12 trisubstituted benzenes	0.333	1,3,5-c12 trisubstituted benzenes
C12 Tetrasubstituted Benzenes	0.334	1,2,4-c12 trisubstituted benzenes	0.333	1,2,3-c12 trisubstituted benzenes	0.333	1,3,5-c12 trisubstituted benzenes
C12 Pentasubstituted Benzenes	0.334	1,2,4-c12 trisubstituted benzenes	0.333	1,2,3-c12 trisubstituted benzenes	0.333	1,3,5-c12 trisubstituted benzenes
C12 Hexasubstituted Benzenes	0.334	1,2,4-c12 trisubstituted benzenes	0.333	1,2,3-c12 trisubstituted benzenes	0.333	1,3,5-c12 trisubstituted benzenes
Isomers of Hexylbenzene	0.334	C10 Monosubstituted Benzenes	0.111	o-c12 disubstituted benzenes	0.111	o-c12 disubstituted benzenes
	0.111	p-c12 disubstituted benzenes	0.111	1,2,3-c12 trisubstituted benzenes	0.111	1,2,4-c12 trisubstituted benzenes
	0.111	1,3,5-c12 trisubstituted benzenes				
C12 Tetralin or Indan	1	Tetralin				
1-Ethylnaphthalene	1	Methyl Naphthalenes				
C12 Naphthalenes	0.5	Methyl Naphthalenes	0.5	2,3-Dimethyl Naphthalene		

Table B-9 (continued)

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
C12 Monosubstituted Naphthalene	1	Methyl Naphthalenes				
C12 Disubstituted Naphthalenes	1	2,3-Dimethyl Naphthalene				
Dimethyl Naphthalenes	1	2,3-Dimethyl Naphthalene				
C13 Disubstituted Benzenes	0.334	m-c13 disubstituted benzenes	0.333	o-c13 disubstituted benzenes	0.333	p-c13 disubstituted benzenes
C13 Trisubstituted Benzenes	0.334	1,2,4-c13 trisubstituted benzenes	0.333	1,2,3-c13 trisubstituted benzenes	0.333	1,3,5-c13 trisubstituted benzenes
C13 Tetralin or Indan	1	Tetralin				
C13 Naphthalenes	0.5	Methyl Naphthalenes	0.5	2,3-Dimethyl Naphthalene		
C13 Monosubstituted Naphthalene	1	Methyl Naphthalenes				
C13 Disubstituted Naphthalenes	1	2,3-Dimethyl Naphthalene				
C13 Trisubstituted Naphthalenes	1	2,3-Dimethyl Naphthalene				
C14 Disubstituted Benzenes	0.334	m-c14 disubstituted benzenes	0.333	o-c14 disubstituted benzenes	0.333	p-c14 disubstituted benzenes
C14 Trisubstituted Benzenes	0.334	1,2,4-c14 trisubstituted benzenes	0.333	1,2,3-c14 trisubstituted benzenes	0.333	1,3,5-c14 trisubstituted benzenes
C14 Tetralin or Indan	1	Tetralin				
C14 Naphthalenes	0.5	Methyl Naphthalenes	0.5	2,3-Dimethyl Naphthalene		
C15 Disubstituted Benzenes	0.334	m-c15 disubstituted benzenes	0.333	o-c15 disubstituted benzenes	0.333	p-c15 disubstituted benzenes
C15 Trisubstituted Benzenes	0.334	1,2,4-c15 trisubstituted benzenes	0.333	1,2,3-c15 trisubstituted benzenes	0.333	1,3,5-c15 trisubstituted benzenes
C15 Tetralin or Indan	1	Tetralin				
C15 Naphthalenes	0.5	Methyl Naphthalenes	0.5	2,3-Dimethyl Naphthalene		
C16 Disubstituted Benzenes	0.334	m-c16 disubstituted benzenes	0.333	o-c16 disubstituted benzenes	0.333	p-c16 disubstituted benzenes
C16 Trisubstituted Benzenes	0.334	1,2,4-c16 trisubstituted benzenes	0.333	1,2,3-c16 trisubstituted benzenes	0.333	1,3,5-c16 trisubstituted benzenes
C16 Tetralin or Indan	1	Tetralin				
C16 Naphthalenes	0.5	Methyl Naphthalenes	0.5	2,3-Dimethyl Naphthalene		
C17 Monosubstituted Benzenes	1	C16 Monosubstituted Benzenes				
C17 Disubstituted Benzenes	0.334	m-c16 disubstituted benzenes	0.333	o-c16 disubstituted benzenes	0.333	p-c16 disubstituted benzenes
C17 Trisubstituted Benzenes	0.334	1,2,4-c16 trisubstituted benzenes	0.333	1,2,3-c16 trisubstituted benzenes	0.333	1,3,5-c16 trisubstituted benzenes
C17 Tetralin or Indan	1	Tetralin				
C17 Naphthalenes	0.5	Methyl Naphthalenes	0.5	2,3-Dimethyl Naphthalene		
C18 Monosubstituted Benzenes	1	C16 Monosubstituted Benzenes				
C18 Disubstituted Benzenes	0.334	m-c16 disubstituted benzenes	0.333	o-c16 disubstituted benzenes	0.333	p-c16 disubstituted benzenes

Table B-9 (continued)

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
C18 Trisubstituted Benzenes	0.334	1,2,4-c16 trisubstituted benzenes	0.333	1,2,3-c16 trisubstituted benzenes	0.333	1,3,5-c16 trisubstituted benzenes
C18 Tetralin or Indan	1	Tetralin				
C18 Naphthalenes	0.5	Methyl Naphthalenes	0.5	2,3-Dimethyl Naphthalene		
C19 Monosubstituted Benzenes	1	C16 Monosubstituted Benzenes				
C19 Disubstituted Benzenes	0.334	m-c16 disubstituted benzenes	0.333	o-c16 disubstituted benzenes	0.333	p-c16 disubstituted benzenes
C19 Trisubstituted Benzenes	0.334	1,2,4-c16 trisubstituted benzenes	0.333	1,2,3-c16 trisubstituted benzenes	0.333	1,3,5-c16 trisubstituted benzenes
C19 Tetralin or Indan	1	Tetralin				
C19 Naphthalenes	0.5	Methyl Naphthalenes	0.5	2,3-Dimethyl Naphthalene		
C20 Monosubstituted Benzenes	1	C16 Monosubstituted Benzenes				
C20 Disubstituted Benzenes	0.334	m-c16 disubstituted benzenes	0.333	o-c16 disubstituted benzenes	0.333	p-c16 disubstituted benzenes
C20 Trisubstituted Benzenes	0.334	1,2,4-c16 trisubstituted benzenes	0.333	1,2,3-c16 trisubstituted benzenes	0.333	1,3,5-c16 trisubstituted benzenes
C20 Tetralin or Indan	1	Tetralin				
C20 Naphthalenes	0.5	Methyl Naphthalenes	0.5	2,3-Dimethyl Naphthalene		
C21 Monosubstituted Benzenes	1	C16 Monosubstituted Benzenes				
C21 Disubstituted Benzenes	0.334	m-c16 disubstituted benzenes	0.333	o-c16 disubstituted benzenes	0.333	p-c16 disubstituted benzenes
C21 Trisubstituted Benzenes	0.334	1,2,4-c16 trisubstituted benzenes	0.333	1,2,3-c16 trisubstituted benzenes	0.333	1,3,5-c16 trisubstituted benzenes
C21 Tetralin or Indan	1	Tetralin				
C21 Naphthalenes	0.5	Methyl Naphthalenes	0.5	2,3-Dimethyl Naphthalene		
C22 Monosubstituted Benzenes	1	C16 Monosubstituted Benzenes				
C22 Disubstituted Benzenes	0.334	m-c16 disubstituted benzenes	0.333	o-c16 disubstituted benzenes	0.333	p-c16 disubstituted benzenes
C22 Trisubstituted Benzenes	0.334	1,2,4-c16 trisubstituted benzenes	0.333	1,2,3-c16 trisubstituted benzenes	0.333	1,3,5-c16 trisubstituted benzenes
C22 Tetralin or Indan	1	Tetralin				
C22 Naphthalenes	0.5	Methyl Naphthalenes	0.5	2,3-Dimethyl Naphthalene		
Peroxyacetic Acid	1	Acetic Acid				
C4 aldehydes	1	Butanal				
C5 Cyclic Ketones	1	Cyclopentanone				
C5 Aldehydes	1	Pentanal (Valeraldehyde)				
C5 Ketones	1	2-Pentanone				
Phenol	1	o-Cresol				

Table B-9 (continued)

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
2-Ethyl furan	1	2-methyl furan				
C6 Cyclic Ketones	1	Cyclohexanone				
mesityl oxide (2-methyl-2-penten-4-one)	1	Lumped product model species ISO-PROD				
C6 Aldehydes	1	Hexanal				
C6 Ketones	1	Methyl n-Butyl Ketone				
C7 Alkyl Phenols	1	o-Cresol				
m-Cresol	1	o-Cresol				
p-Cresol	1	o-Cresol				
C7 Cyclic Ketones	1	Cyclohexanone				
C7 Aldehydes	1	Heptanal				
C7 Ketones	1	2-Heptanone				
Tolualdehyde	1	Benzaldehyde				
4-vinylphenol	1	styrene				
2,4-Dimethyl Phenol	1	o-Cresol				
2,5-Dimethyl Phenol	1	o-Cresol				
3,4-Dimethyl Phenol	1	o-Cresol				
2,3-Dimethyl Phenol	1	o-Cresol				
2,6-Dimethyl Phenol	1	o-Cresol				
C8 Alkyl Phenols	1	o-Cresol				
beta-phenethyl alcohol	1	benzyl alcohol				
C8 Cyclic Ketones	1	Cyclohexanone				
C8 Aldehydes	1	Octanal				
C8 Ketones	1	2-Octanone				
Hexyl Acetates	0.5	n-Hexyl Acetate	0.125	2-Methylpentyl Acetate		
	0.125	3-Methylpentyl Acetate	0.125	4-Methylpentyl Acetate	0.125	2,3-Dimethylbutyl Acetate
methylparaben (4-Hydroxybenzoic acid, methyl ester)	1	o-cresol				
Cinnamic aldehyde	1	lumped c5+ unsaturated carbonyl species				
Cinnamic alcohol	1	b-methyl styrene				
2,3,5-Trimethyl Phenol	1	o-Cresol				
2,3,6-Trimethyl Phenol	1	o-Cresol				
C9 Alkyl Phenols	1	o-Cresol				

Table B-9 (continued)

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
isophorone {3,5,5-trimethyl-2-cyclohexenone}	1	Lumped product model species ISO-PROD				
C9 Cyclic Ketones	1	Cyclohexanone				
C9 Ketones	1	2-Nonanone				
1-phenoxy-2-propanol	1	n-Propyl Benzene				
Dipropylene glycol methyl ether acetate isomers	0.5	Dipropylene glycol methyl ether acetate isomer #1	0.5	Dipropylene glycol methyl ether acetate isomer #2		
anethol	1	b-methyl styrene				
C10 Alkyl Phenols	1	o-Cresol				
C10 Cyclic Ketones	1	Cyclohexanone				
C10 Ketones	1	2-Decanone				
propylparaben	1	o-cresol				
C11 Alkyl Phenols	1	o-Cresol				
C12 Alkyl Phenols	1	o-Cresol				
Texanol isomers	0.67	3-Hydroxy-2,2,4-Trimethylpentyl-1-Isobutyrate	0.33	1-Hydroxy-2,2,4-Trimethylpentyl-3-Isobutyrate		
Substituted C7 ester (C12)	0.67	3-Hydroxy-2,2,4-Trimethylpentyl-1-Isobutyrate	0.33	1-Hydroxy-2,2,4-Trimethylpentyl-3-Isobutyrate		
Substituted C9 Ester (C12)	0.67	3-Hydroxy-2,2,4-Trimethylpentyl-1-Isobutyrate	0.33	1-Hydroxy-2,2,4-Trimethylpentyl-3-Isobutyrate		
Amyl cinnamal	1	lumped c5+ unsaturated carbonyl species				
isobornyl methacrylate	1	isobutyl methacrylate				
Hexyl cinnamal	1	lumped c5+ unsaturated carbonyl species				
2,6-di-tert-butyl-p-cresol	1	o-cresol				
methyl cis-9-hexadecenoate (methyl palmitoleate)	1	methyl cis-9-pentadecenoate				
methyl hexadecanoate; methyl palmitate	1	methyl pentadecanoate				
Methyl cis-9-heptadecenoate	1	methyl cis-9-pentadecenoate				

Table B-9 (continued)

Compound or Mixture	Representation					
	Mol	Compound	Mol	Compound	Mol	Compound
methyl heptadecanoate; methyl margarate	1	methyl pentadecanoate				
methyl cis-9-octadecenoate; methyl oleate	1	methyl cis-9-pentadecenoate				
methyl octadecanoate; methyl stearate	1	methyl pentadecanoate				
Carbon Tetrachloride	1	Represented as inert				
Methylene Bromide	1	Represented as inert				
Cis-1,2-Dichloroethene	1	Trans-1,2-Dichloroethene				
1,3-dichloropropene mixture	0.56	cis-1,3-dichloropropene	0.44	trans-1,3-dichloropropene		
1-buten-3-yne (vinyl acetylene)	1	1-Butene				
methyl nonafluoroisobutyl ether	1	methyl nonafluorobutyl ether				
Methoxy perfluoro isobutane	1	Methoxy perfluoro n-butane				
triethylene diamine	1	triethyl amine				
o-dichlorobenzene	1	p-dichlorobenzene				
ethyl nonafluoroisobutyl ether	1	ethyl nonafluorobutyl ether				
Perfluorohexane	1	Represented as inert				
2-chlorotoluene	1	toluene				
3-(Chloromethyl)-Heptane	1	3-Methyl Heptane				
2,6-Toluene Diisocyanate	1	2,4-Toluene Diisocyanate				
Toluene Diisocyanate (mixed isomers)	1	2,4-Toluene Diisocyanate				
lauryl pyrrolidone	1	n-methyl-2-pyrrolidone				

Table B-10. Listing of components of complex mixtures for which atmospheric reactivities have been calculated. (Available in electronic form only)

Because of the size of this table, it is only available in as supplementary material in electronic form. See Appendix D.

Table B-11. Assignments of explicitly represented compounds to lumped model species in the fixed parameter mechanism. (Available in electronic form only)

Because of the size of this table, it is only available in as supplementary material in electronic form. See Appendix D.

APPENDIX C. MECHANISM EVALUATION TABULATIONS AND PLOTS

This appendix contains the plots of the results of the model simulations of the environmental chamber experiments. The data presented in these plots are described in the "Data Presented" subsection of the "Mechanism Evaluation" section of the report. Reference is made to Table C-1, which contains the list of environmental chamber experiments used in this mechanism evaluation. Because of its size, this table is available only as supplementary material in the Excel file that also contains the tabulations in the other appendices to this report. This is described in Appendix D.

Table C-1. List of environmental chamber experiments used in the mechanism evaluation. . (Available in electronic form only)

Because of the size of this table, it is only available in as supplementary material in electronic form. See Appendix D.

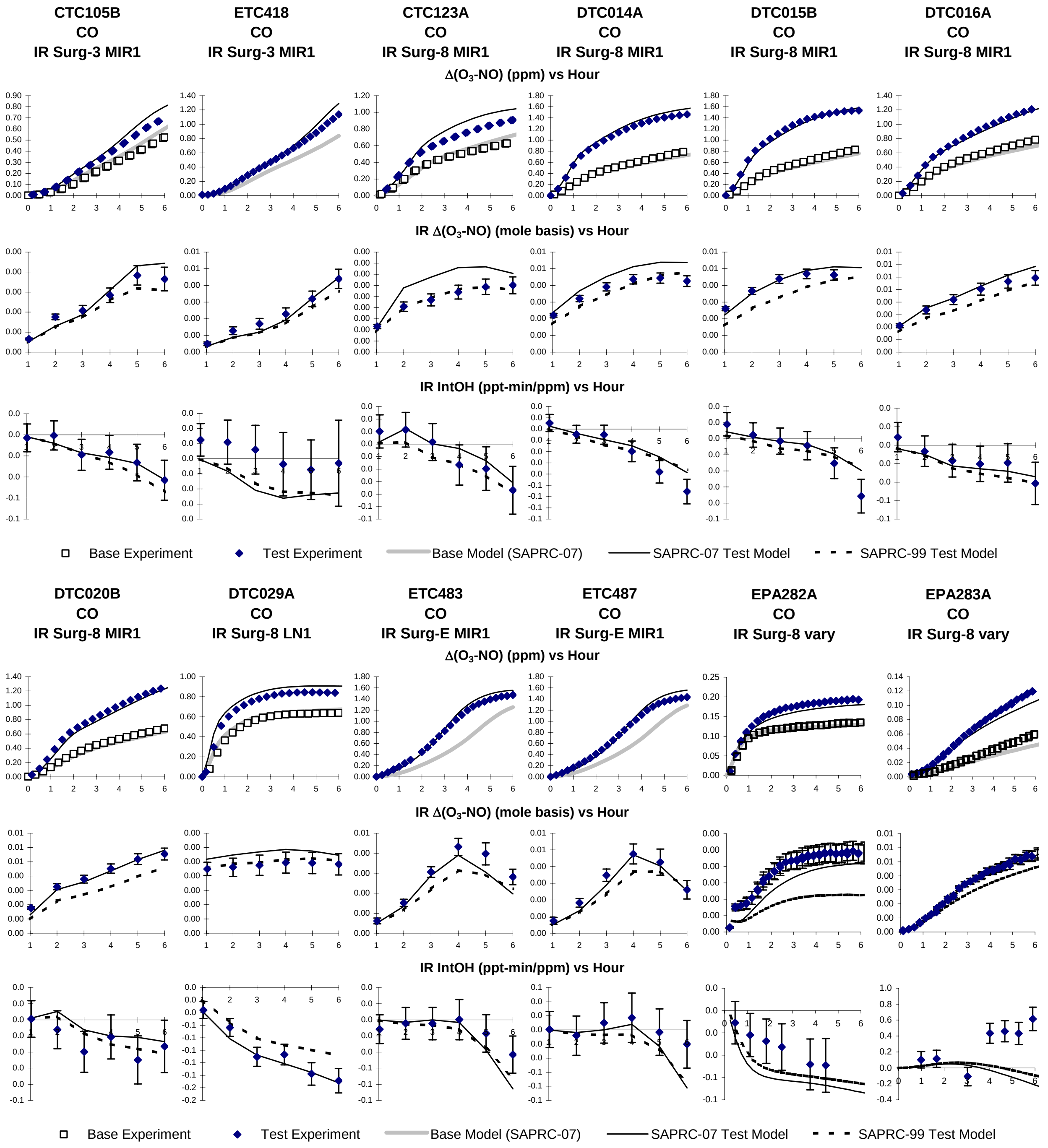


Figure C-1. Plots of experimental and calculated environmental chamber reactivity results for carbon monoxide.

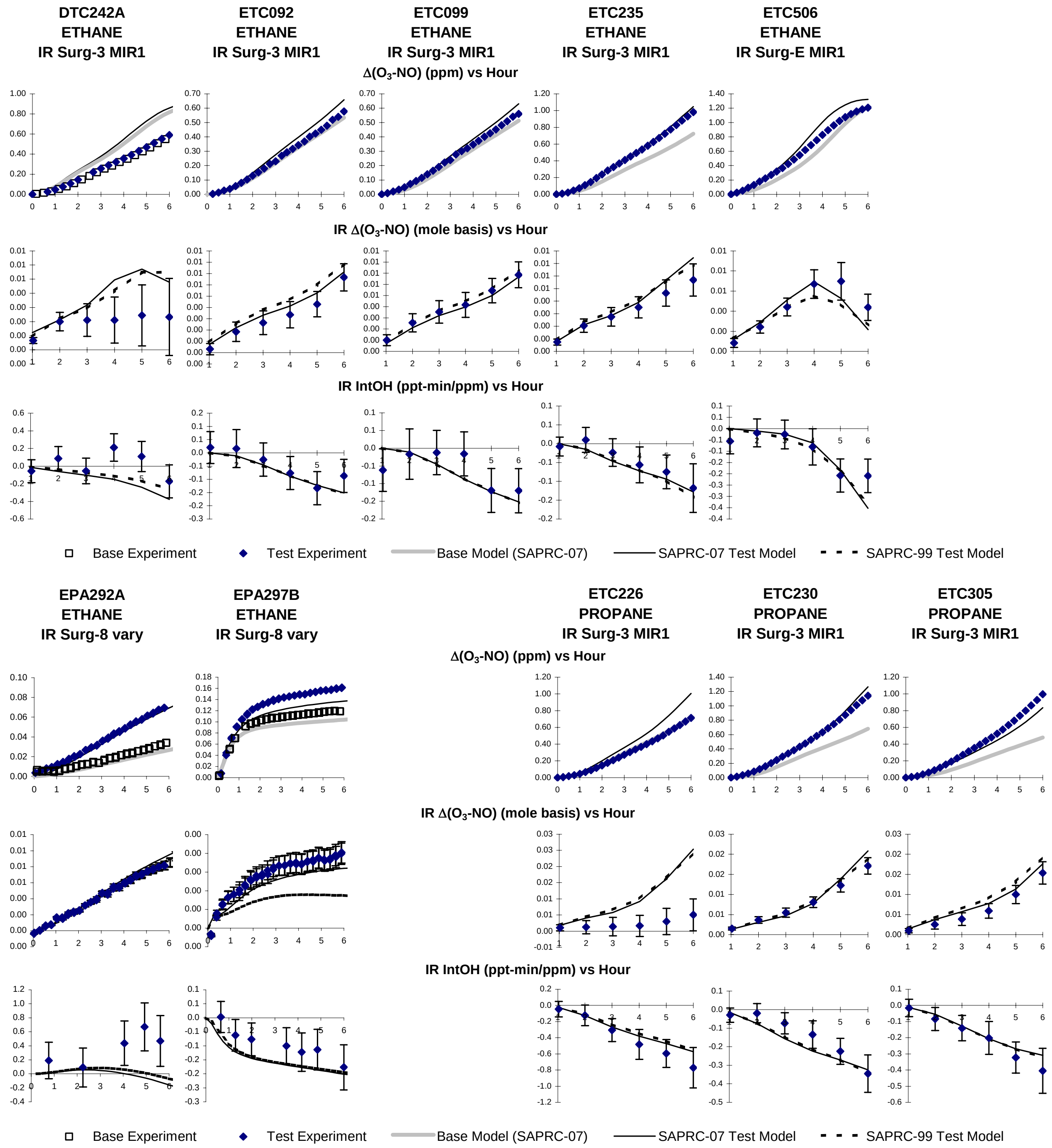


Figure C-2. Plots of experimental and calculated environmental chamber reactivity results for ethane and propane

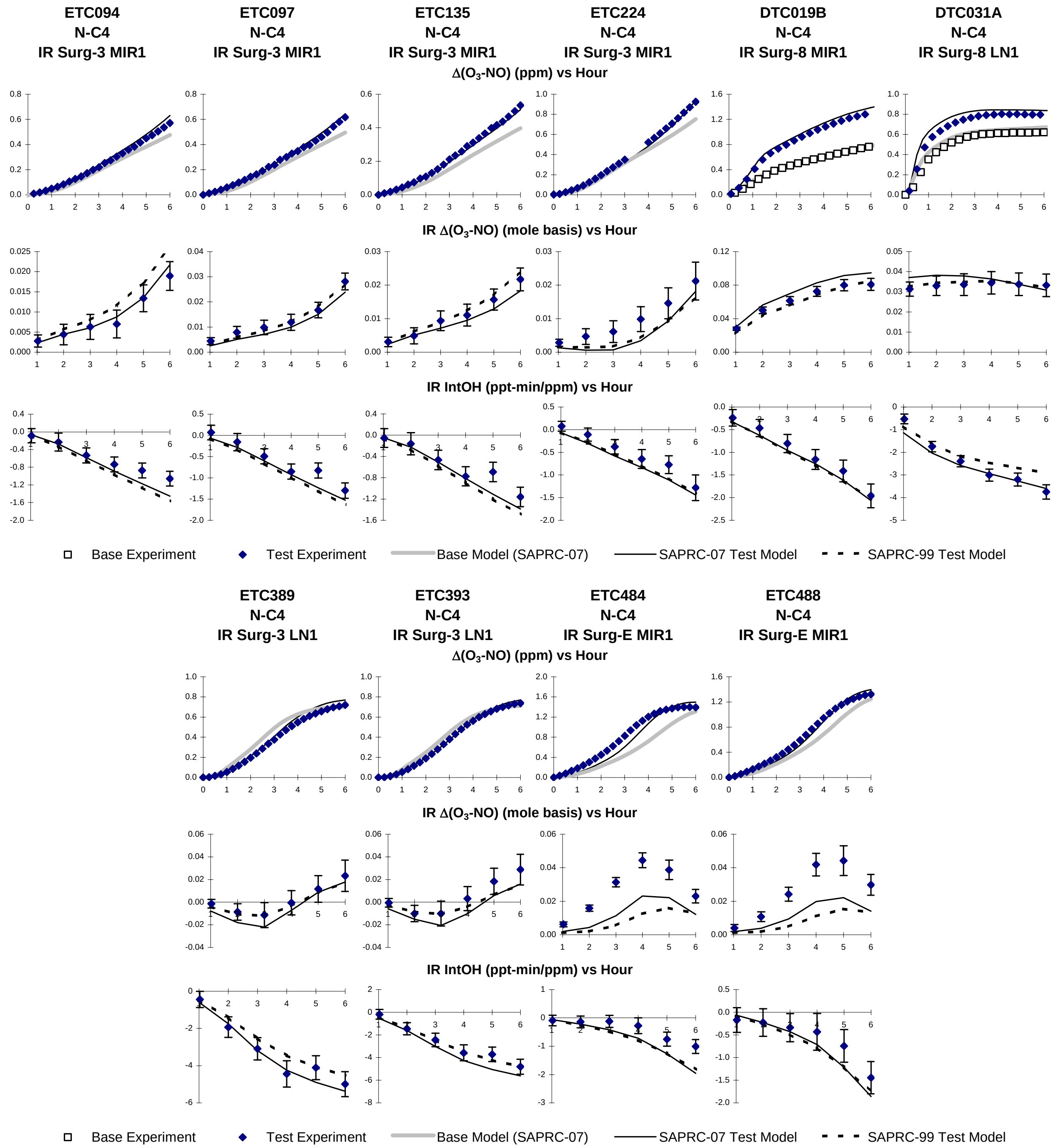
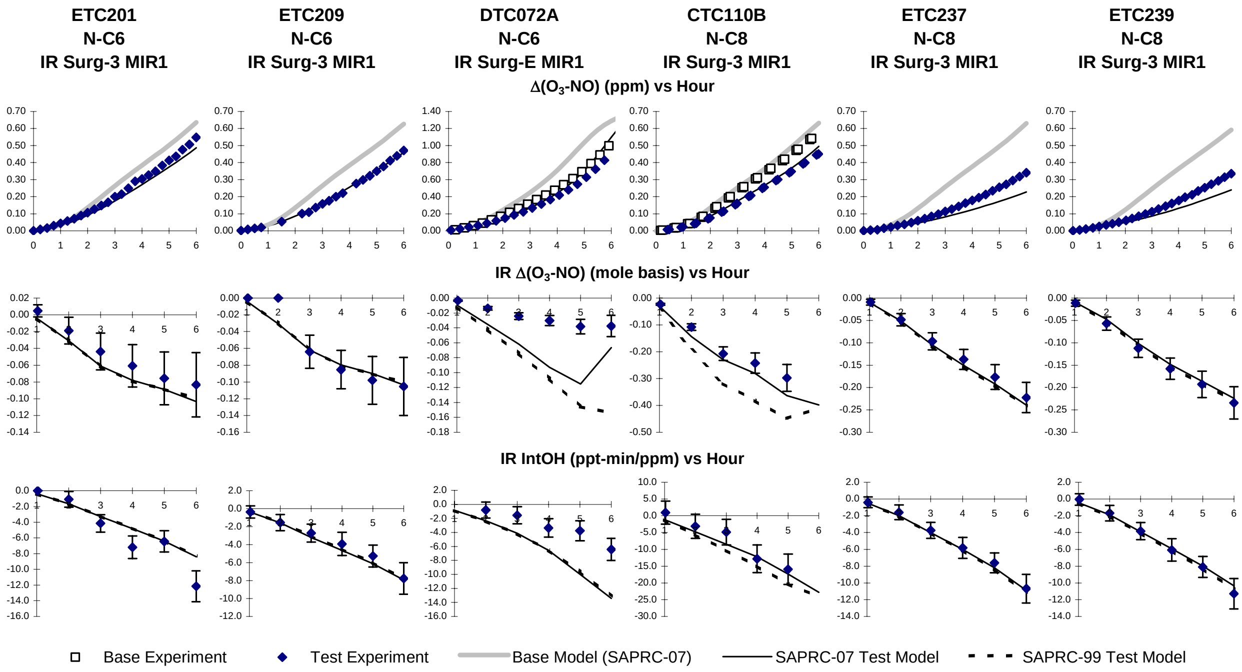


Figure C-3. Plots of experimental and calculated environmental chamber reactivity results for n-butane


ETC201 N-C6 IR Surg-3 MIR1
ETC209 N-C6 IR Surg-3 MIR1
DTC072A N-C6 IR Surg-E MIR1
CTC110B N-C8 IR Surg-3 MIR1
ETC237 N-C8 IR Surg-3 MIR1
ETC239 N-C8 IR Surg-3 MIR1

Δ(O_3-NO) (ppm) vs Hour

IR Δ(O_3-NO) (mole basis) vs Hour

IR IntOH (ppt-min/ppm) vs Hour

Figure C-4. Plots of experimental and calculated environmental chamber reactivity results for n-hexane and the Surg-3 MIR1 experiments for n-octane.

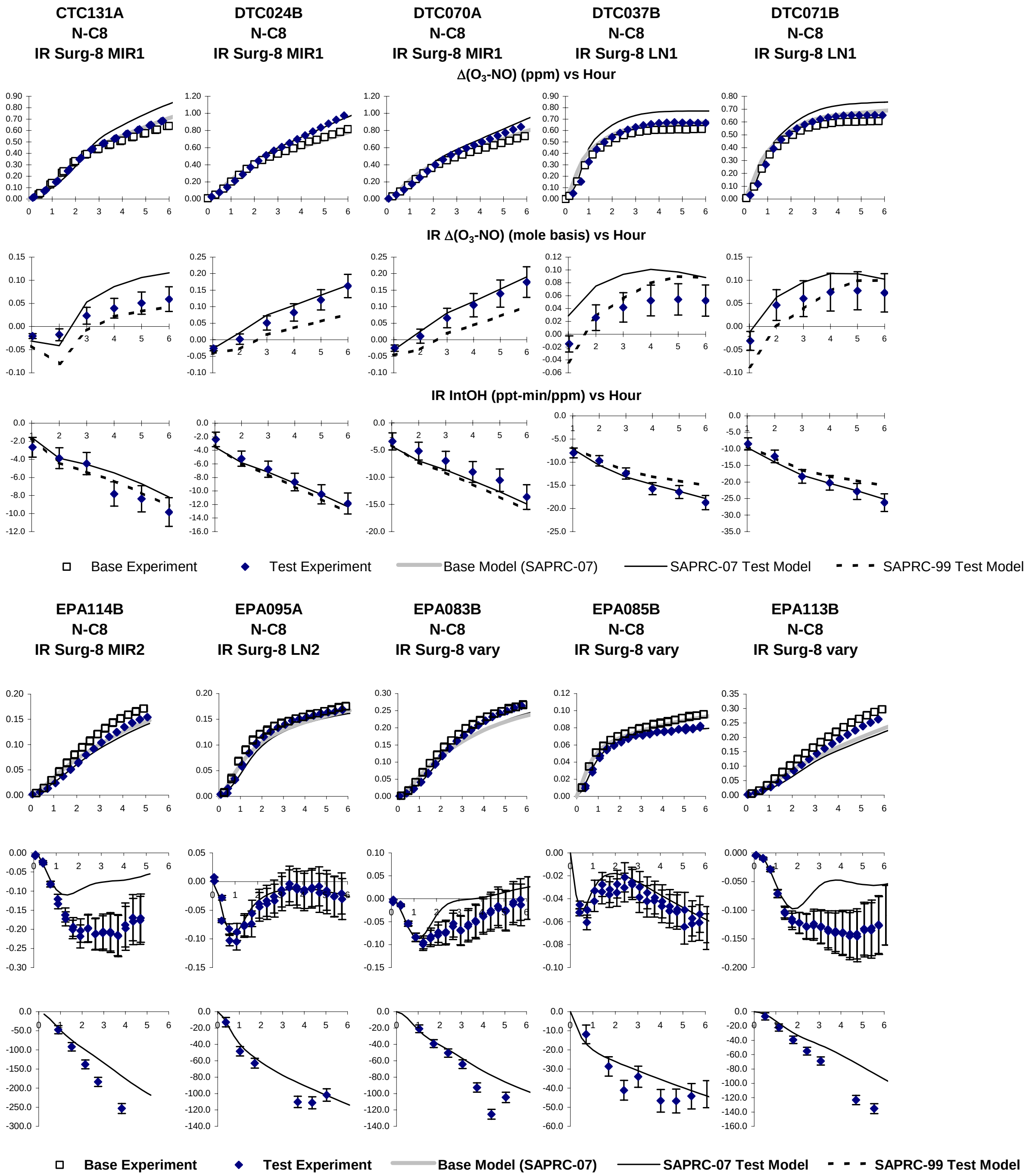


Figure C-5. Plots of experimental and calculated environmental chamber reactivity results for n-octane (excluding the Surg-3 MIR1 experiments, which are on Figure C-4).

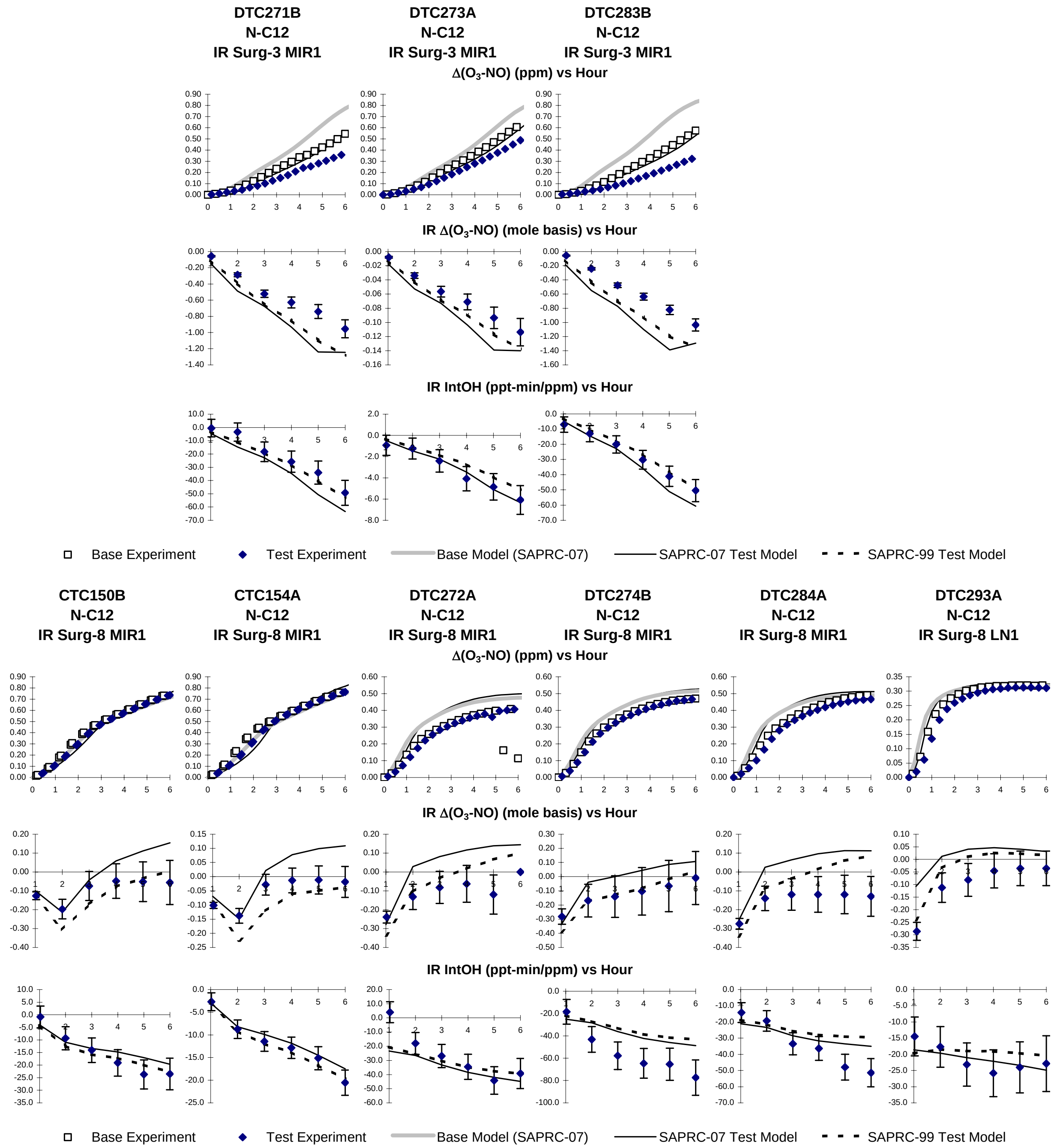
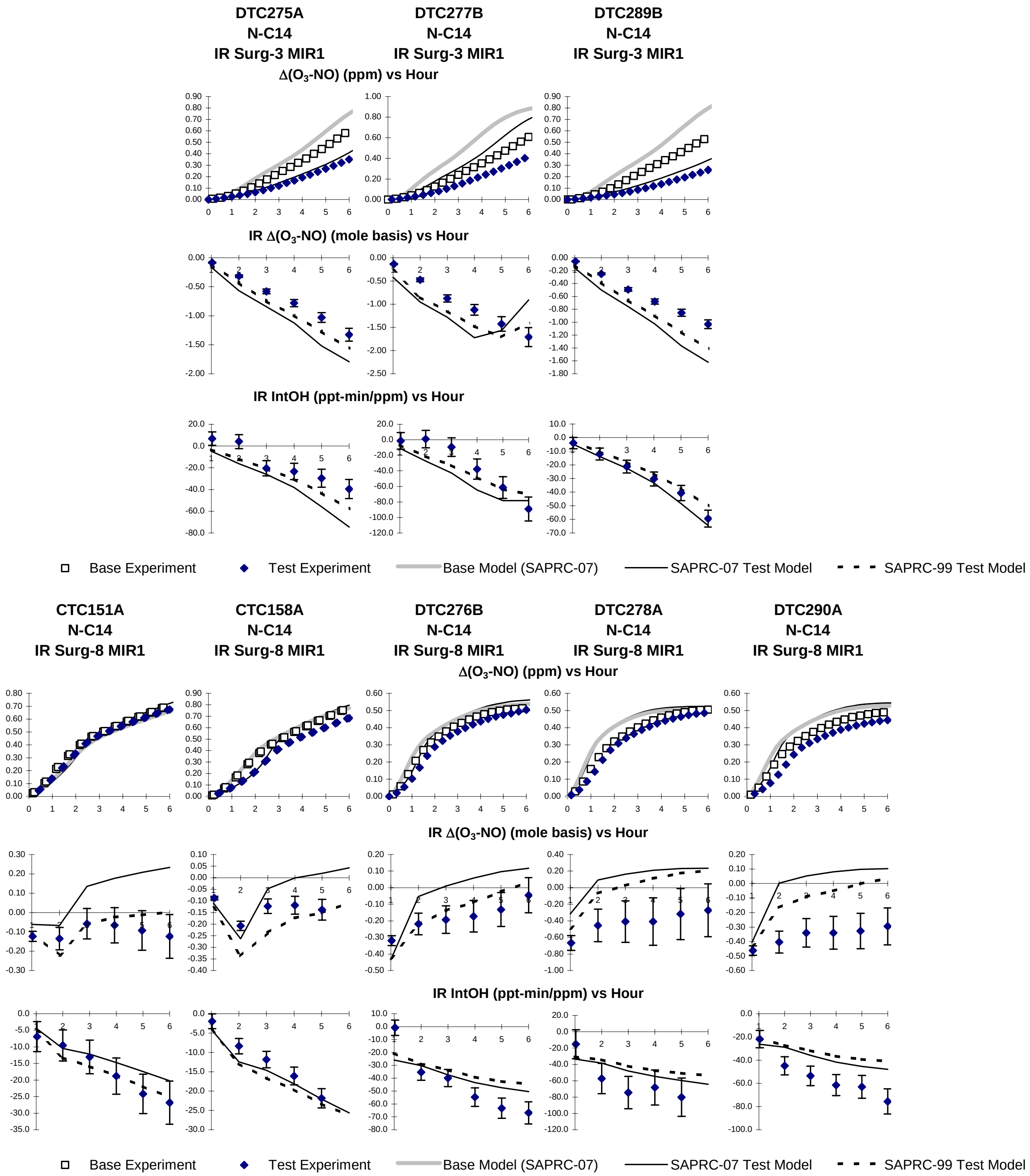


Figure C-6. Plots of experimental and calculated environmental chamber reactivity results for n-dodecane.


DTC275A N-C14 IR Surg-3 MIR1

DTC277B N-C14 IR Surg-3 MIR1

DTC289B N-C14 IR Surg-3 MIR1

CTC151A N-C14 IR Surg-8 MIR1

CTC158A N-C14 IR Surg-8 MIR1

DTC276B N-C14 IR Surg-8 MIR1

DTC278A N-C14 IR Surg-8 MIR1

DTC290A N-C14 IR Surg-8 MIR1

Figure C-7. Plots of experimental and calculated environmental chamber reactivity results for n-tetradecane

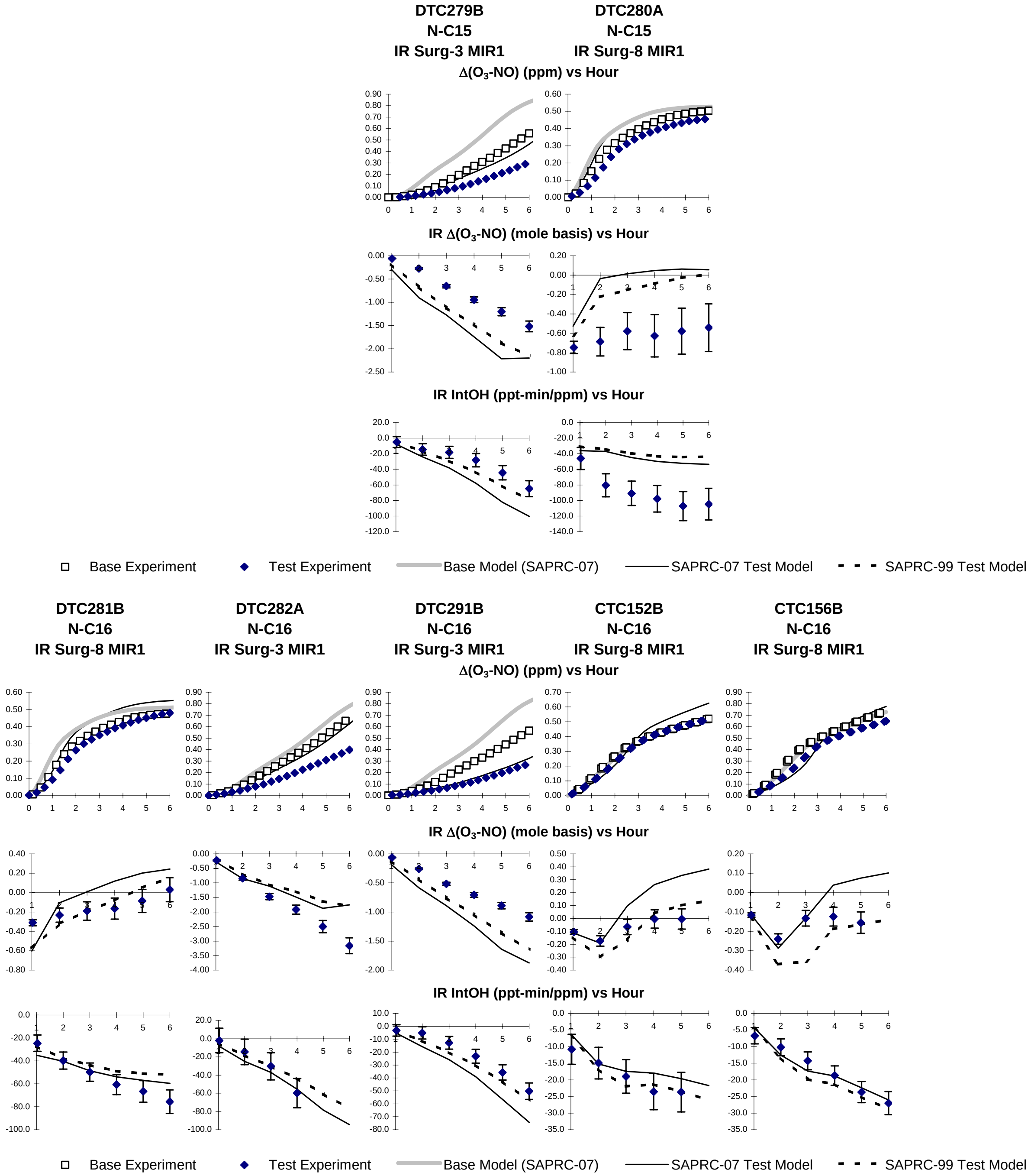


Figure C-8. Plots of experimental and calculated environmental chamber reactivity results for n-pentadecane and n-hexadecane.

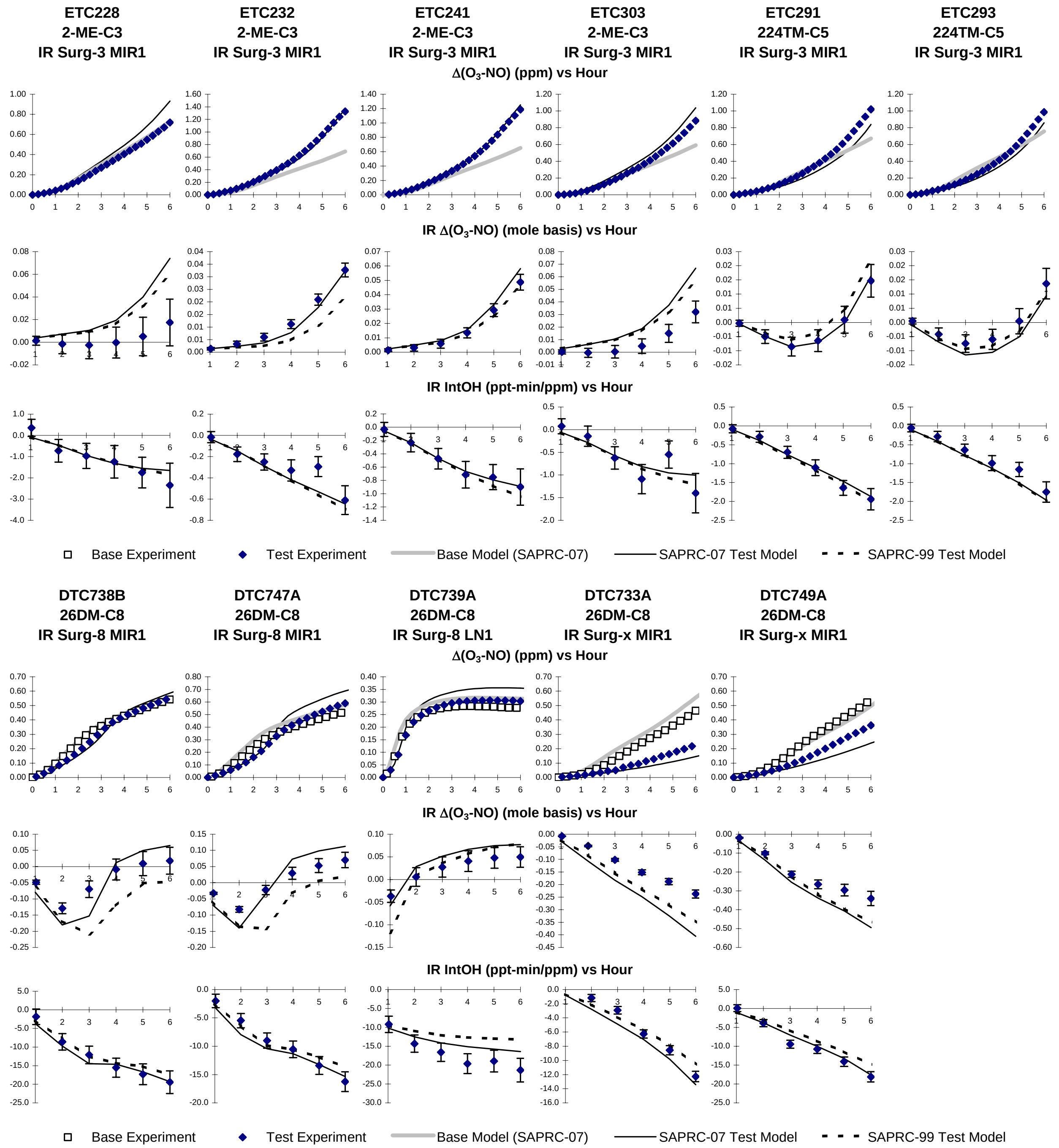


Figure C-9. Plots of experimental and calculated environmental chamber reactivity results for isobutane, 2,2,4-trimethyl pentane, and 2,6-dimethyl octane.

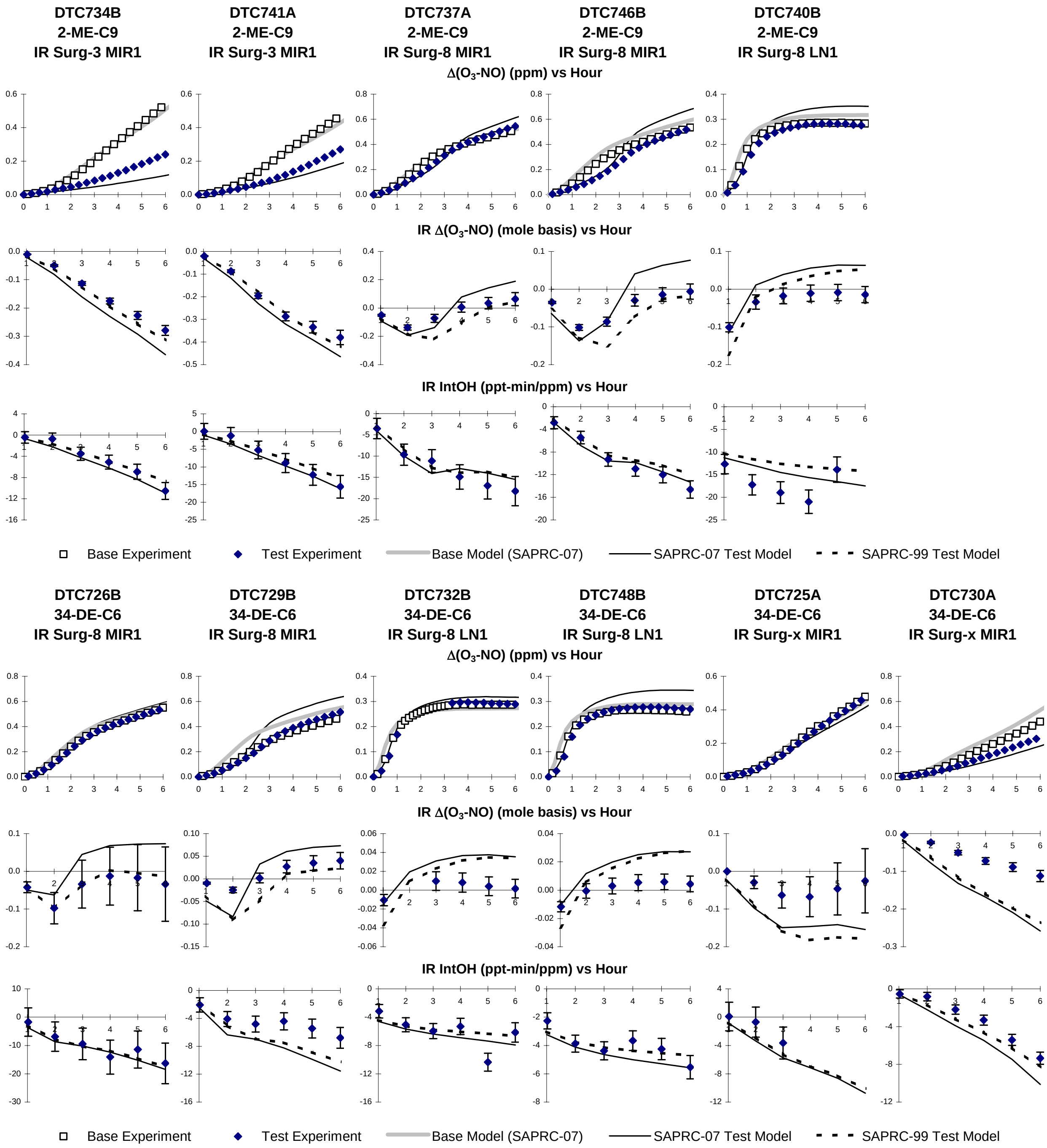


Figure C-10. Plots of experimental and calculated environmental chamber reactivity results for 2-methyl nonane and 3,4-diethyl hexane.

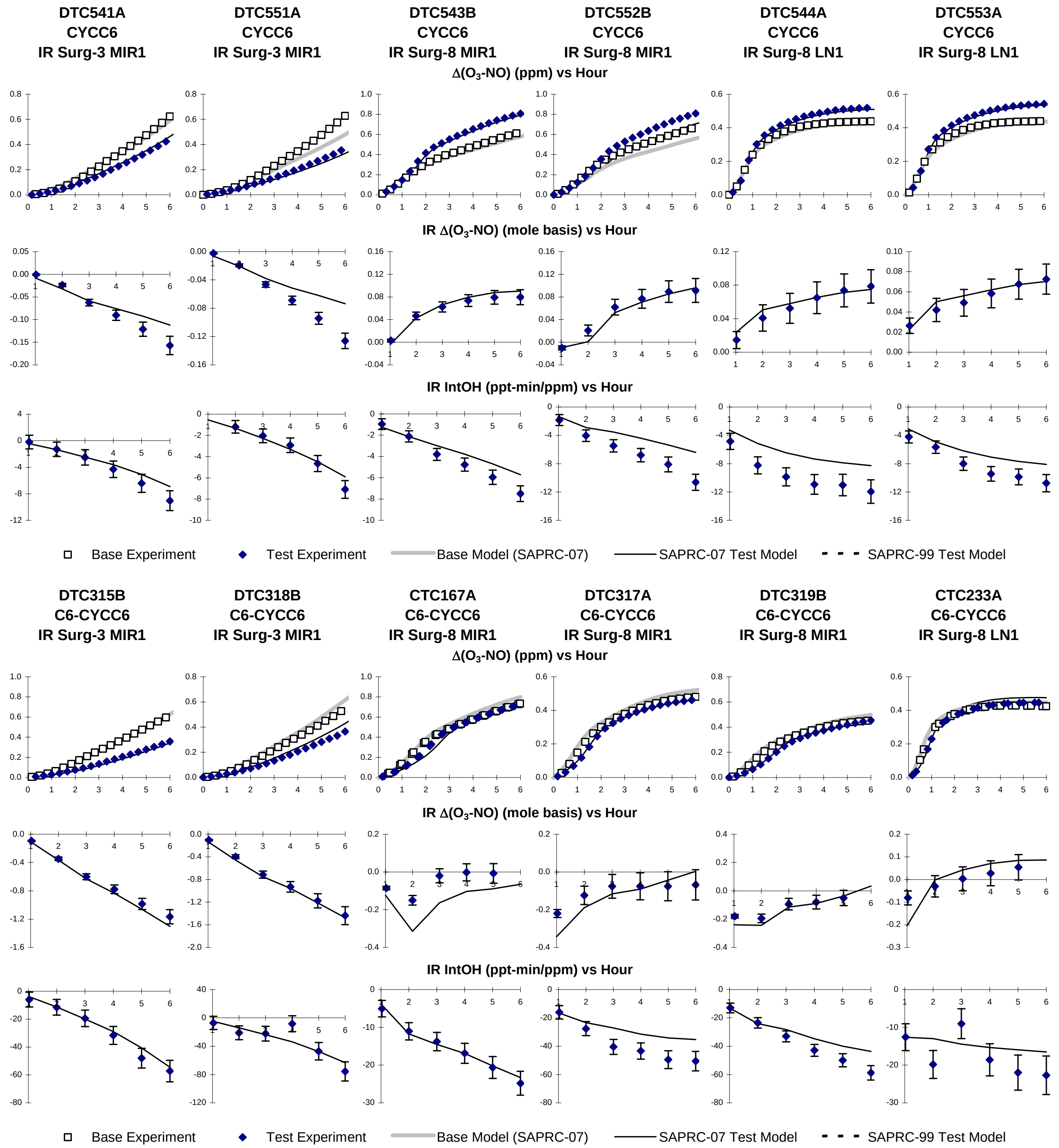


Figure C-11. Plots of experimental and calculated environmental chamber reactivity results for cyclohexane and hexyl cyclohexane.

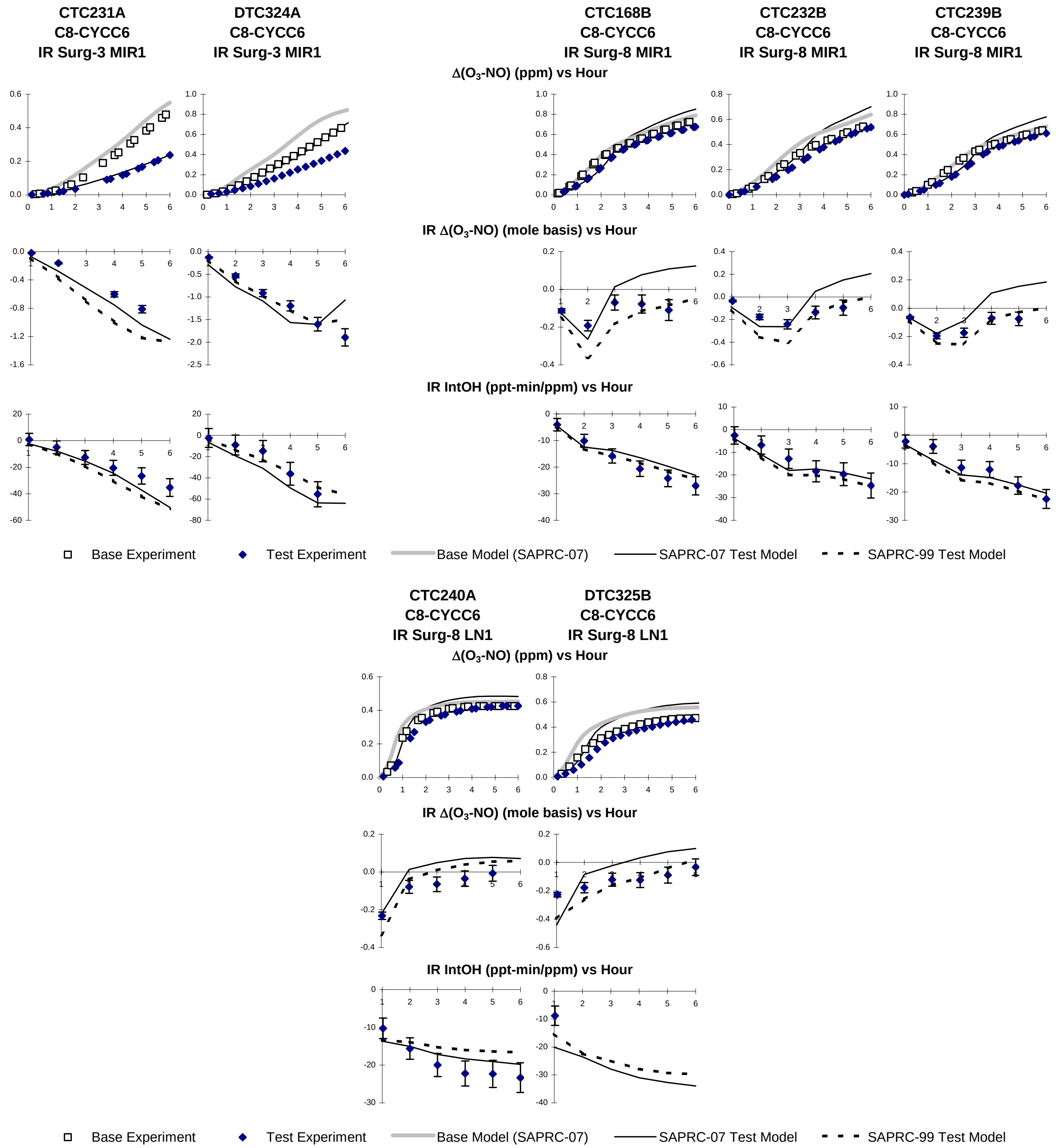


Figure C-12. Plots of experimental and calculated environmental chamber reactivity results for octyl cyclohexane.

Ethene - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
UCR Arc Light	10	-3%	-2%	-6%	-5%
UCR Blacklight	29	24%	9%	22%	10%
TVA chamber	3	-6%	4%	-16%	-4%
OTC Chamber	7	-30%	-22%	-28%	-23%

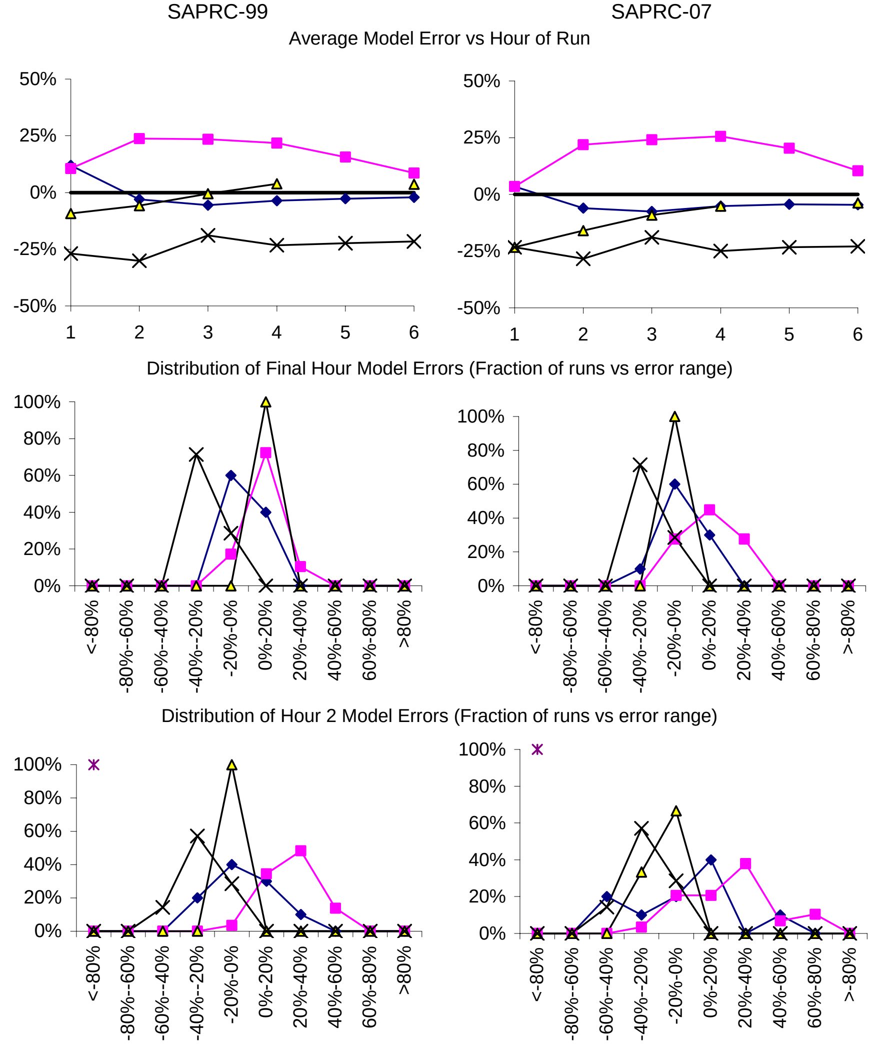


Figure C-13. Plots of model errors in simulations of the ethene - NO_x environmental chamber experiments.

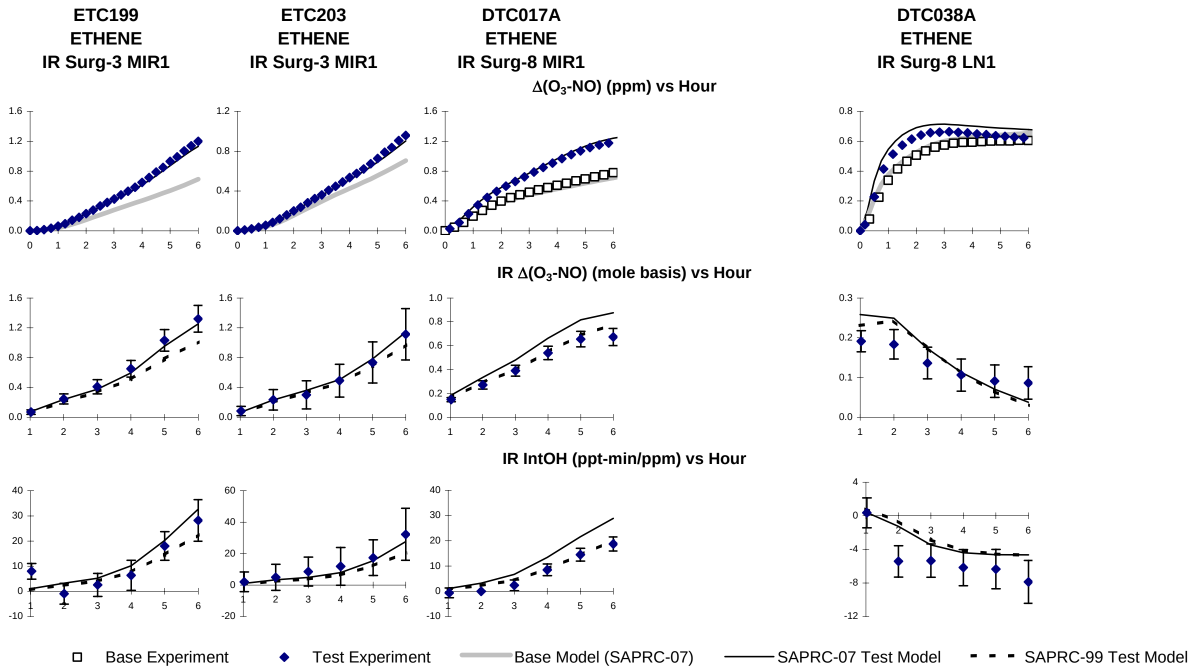


Figure C-14. Plots of experimental and calculated environmental chamber reactivity results for ethene.

Propene - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
UCR Arc Light	74	-9%	-1%	-8%	2%
UCR Blacklight	84	-5%	-1%	5%	3%
TVA chamber	4	8%	13%	2%	6%
OTC Chamber	6	-19%	1%	-3%	1%
UNC Chamber	20	58%	19%	61%	22%
Added CO	2	3%	-12%	23%	-5%

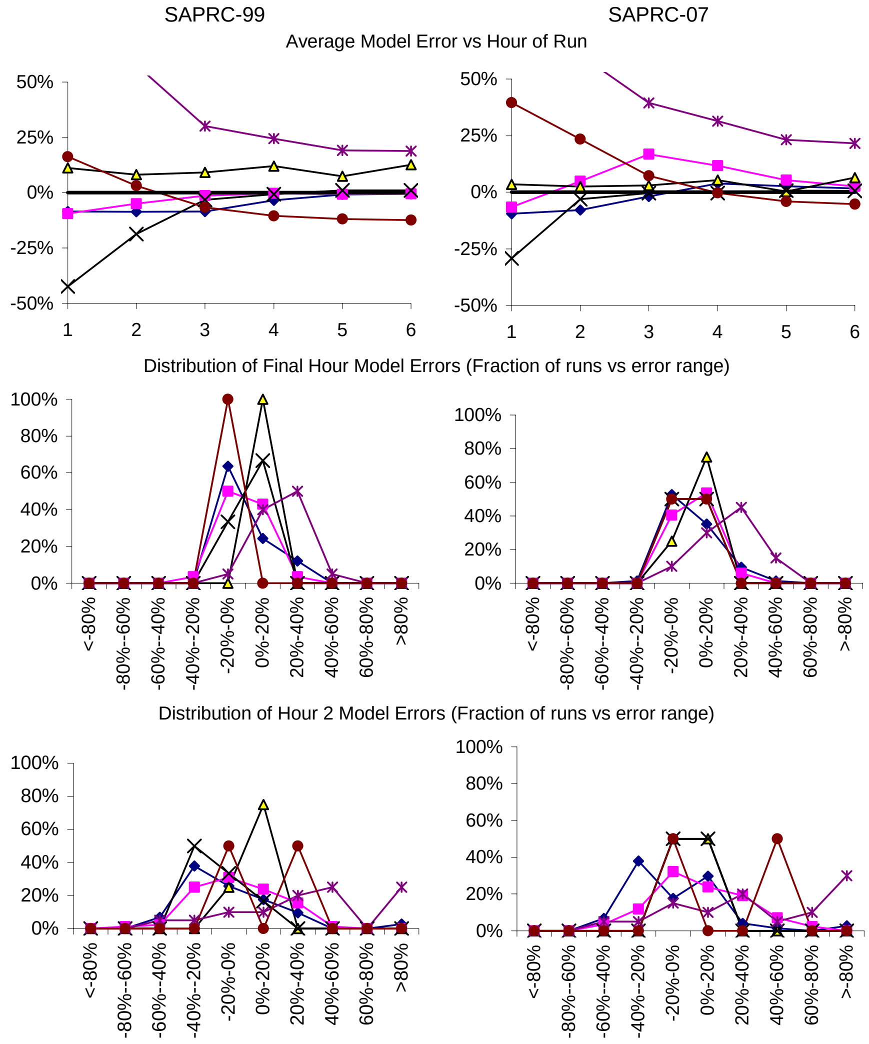


Figure C-15. Plots of model errors in simulations of the propene - NO_x environmental chamber experiments.

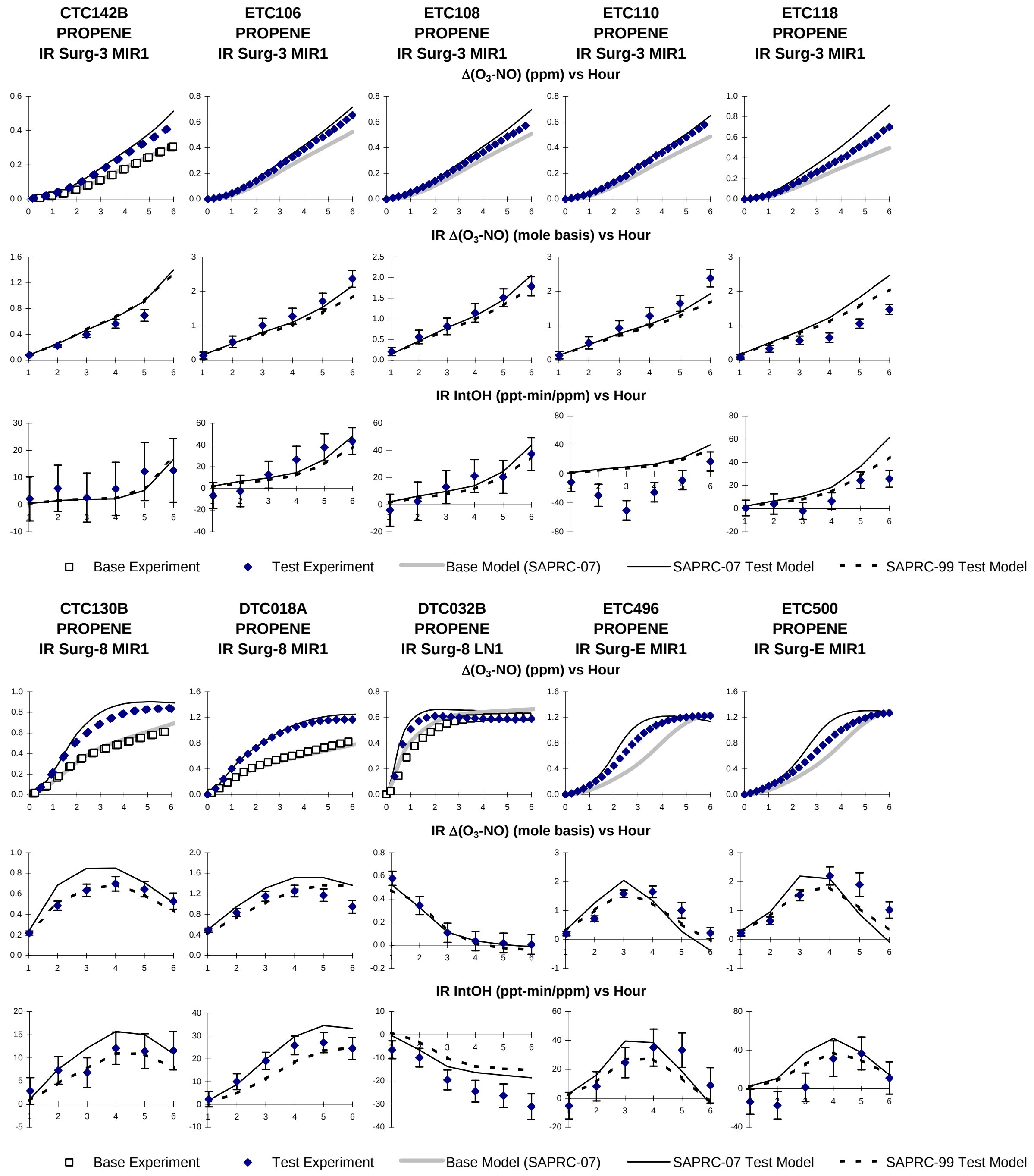


Figure C-16. Plots of experimental and calculated environmental chamber reactivity results for propene.

1-Butene - NOx and 1-Hexene - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	 Final	 SAPRC-07 2-Hr	 Final
1-Butene, Black	3	18%	-1%	7%	-9%
1-Butene, Arc	3	-11%	-8%	-34%	-22%
1-Hexene, Black	3	1%	15%	16%	17%

◆ 1-Butene, Black
■ 1-Butene, Arc
△ 1-Hexene, Black

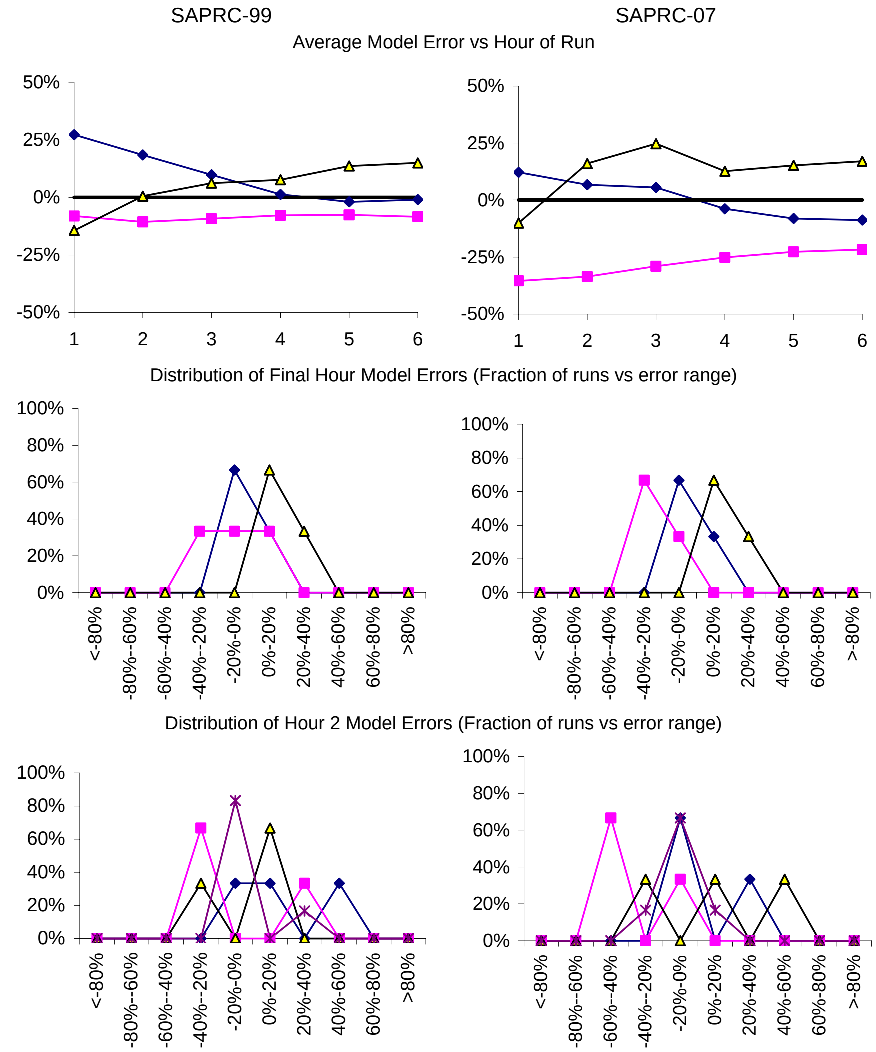


Figure C-17. Plots of model errors in simulations of the 1-buteme and 1-hexene - NO_x environmental chamber experiments.

Trans-2-Butene - NOx and Isobutene - NOx

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
Isobutene, Black	2	0%	13%	-7%	9%
Trans-2-Butene, TVA	3	1%	8%	0%	3%
Trans-2-Butene, EC	3	5%	1%	8%	0%

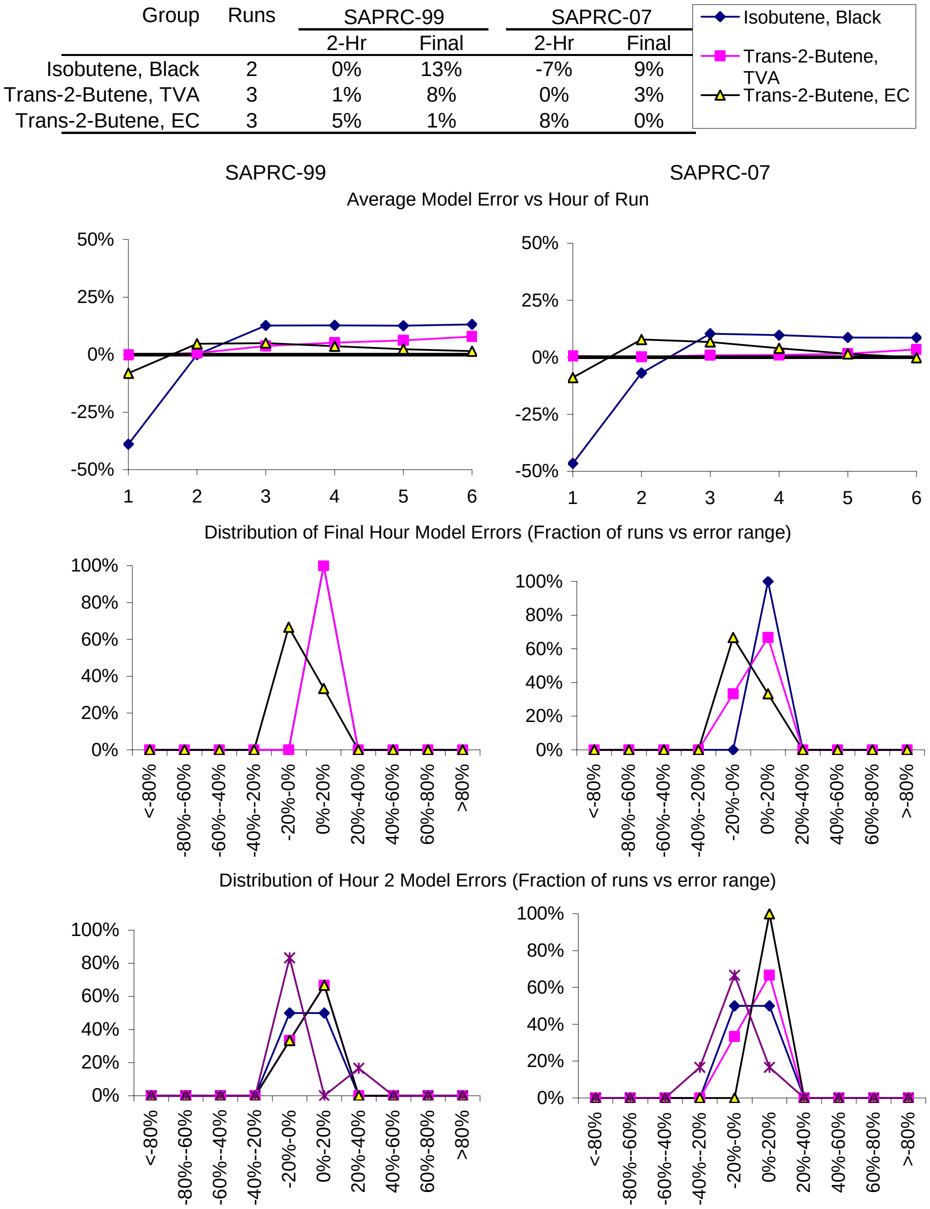
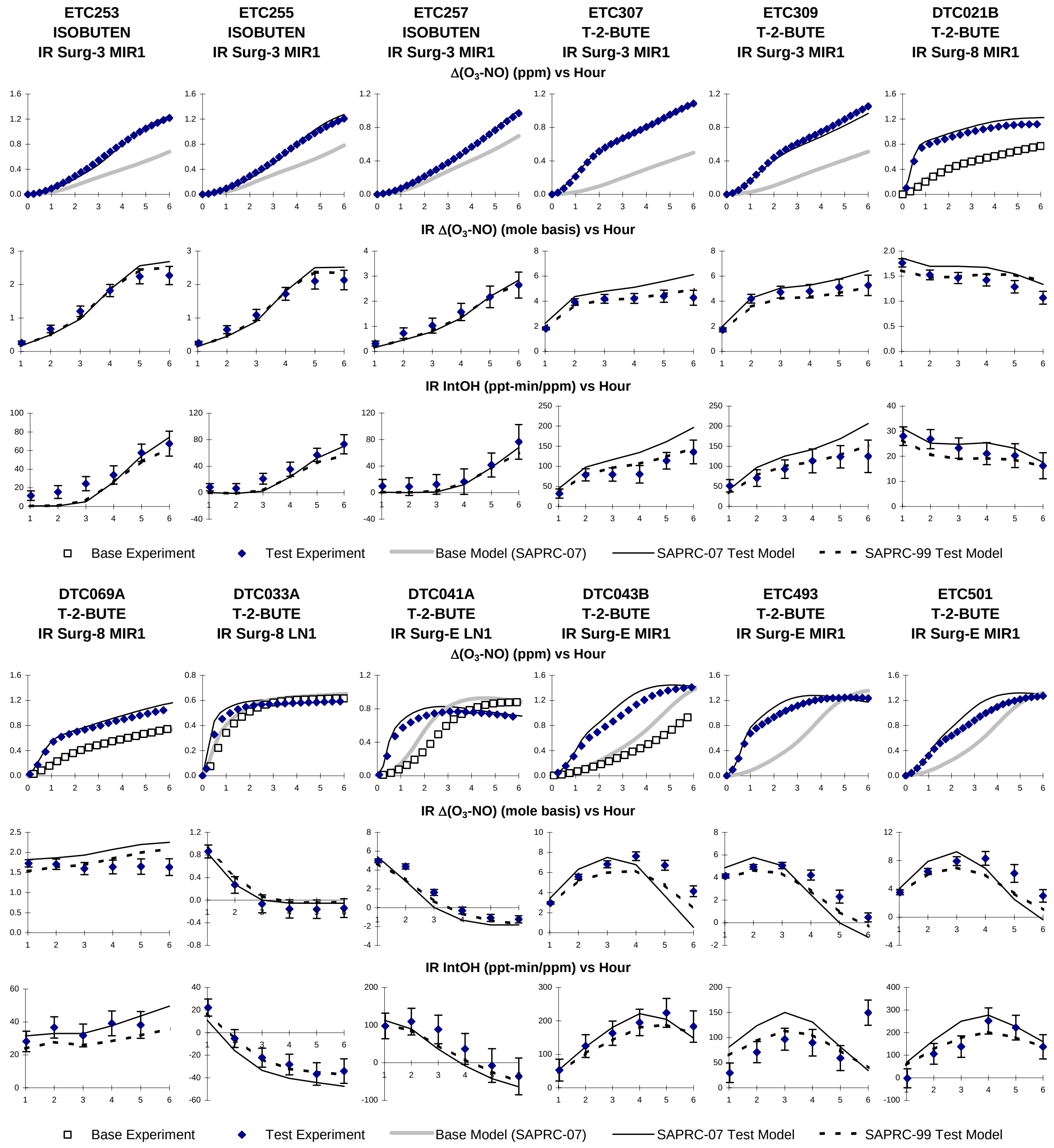


Figure C-18. Plots of model errors in simulations of the trans-2-butene and isobutene - NO_x environmental chamber experiments.



ETC253 ISOBUTEN IR Surg-3 MIR1

ETC255 ISOBUTEN IR Surg-3 MIR1

ETC257 ISOBUTEN IR Surg-3 MIR1

ETC307 T-2-BUTE IR Surg-3 MIR1

ETC309 T-2-BUTE IR Surg-3 MIR1

DTC021B T-2-BUTE IR Surg-8 MIR1

DTC069A T-2-BUTE IR Surg-8 MIR1

DTC033A T-2-BUTE IR Surg-8 LN1

DTC041A T-2-BUTE IR Surg-E LN1

DTC043B T-2-BUTE IR Surg-E MIR1

ETC493 T-2-BUTE IR Surg-E MIR1

ETC501 T-2-BUTE IR Surg-E MIR1

Figure C-19. Plots of experimental and calculated environmental chamber reactivity results for isobutene and trans-2-butene.

Isoprene - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
Arc Light	3	-4%	-5%	-9%	-8%
Blacklight	6	-6%	-7%	-11%	-11%
EC Chamber	5	8%	19%	-7%	12%
OTC Chamber	4	-3%	-1%	-4%	-2%
UNC Chamber	10	-2%	1%	-1%	4%

◆ Arc Light
■ Blacklight
△ EC Chamber
✕ OTC Chamber
✳ UNC Chamber

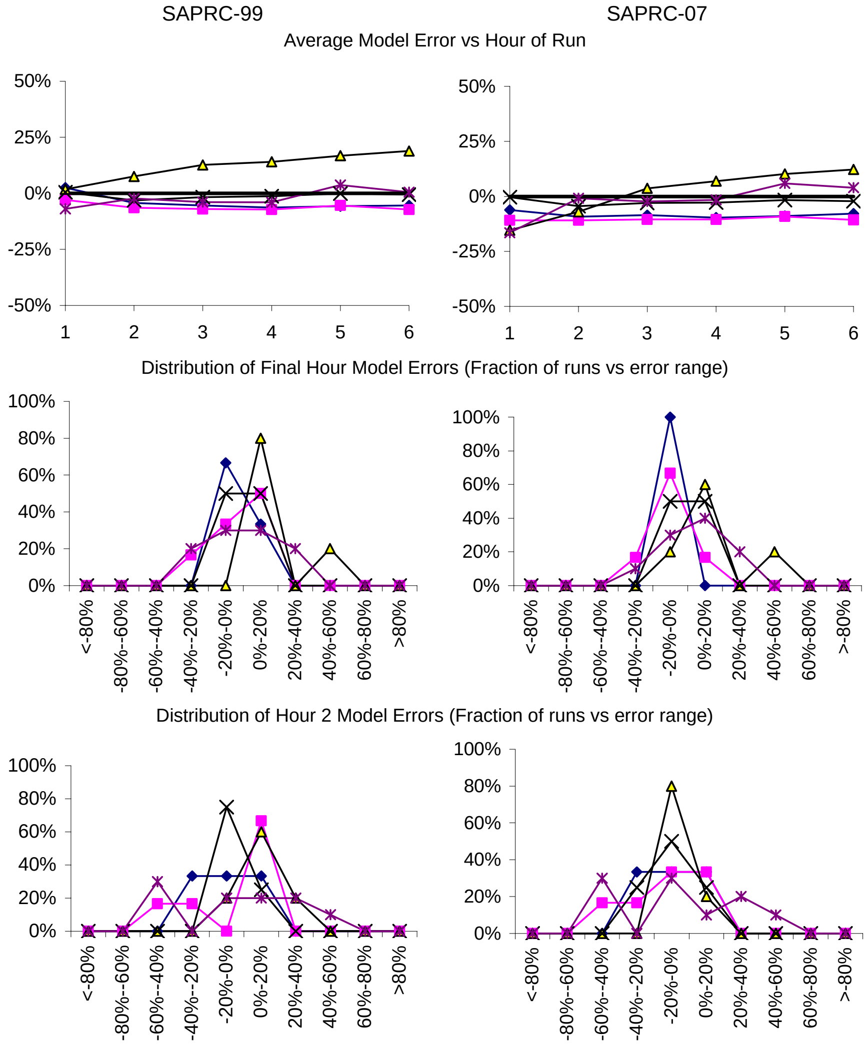


Figure C-20. Plots of model errors in simulations of the isoprene - NO_x environmental chamber experiments.

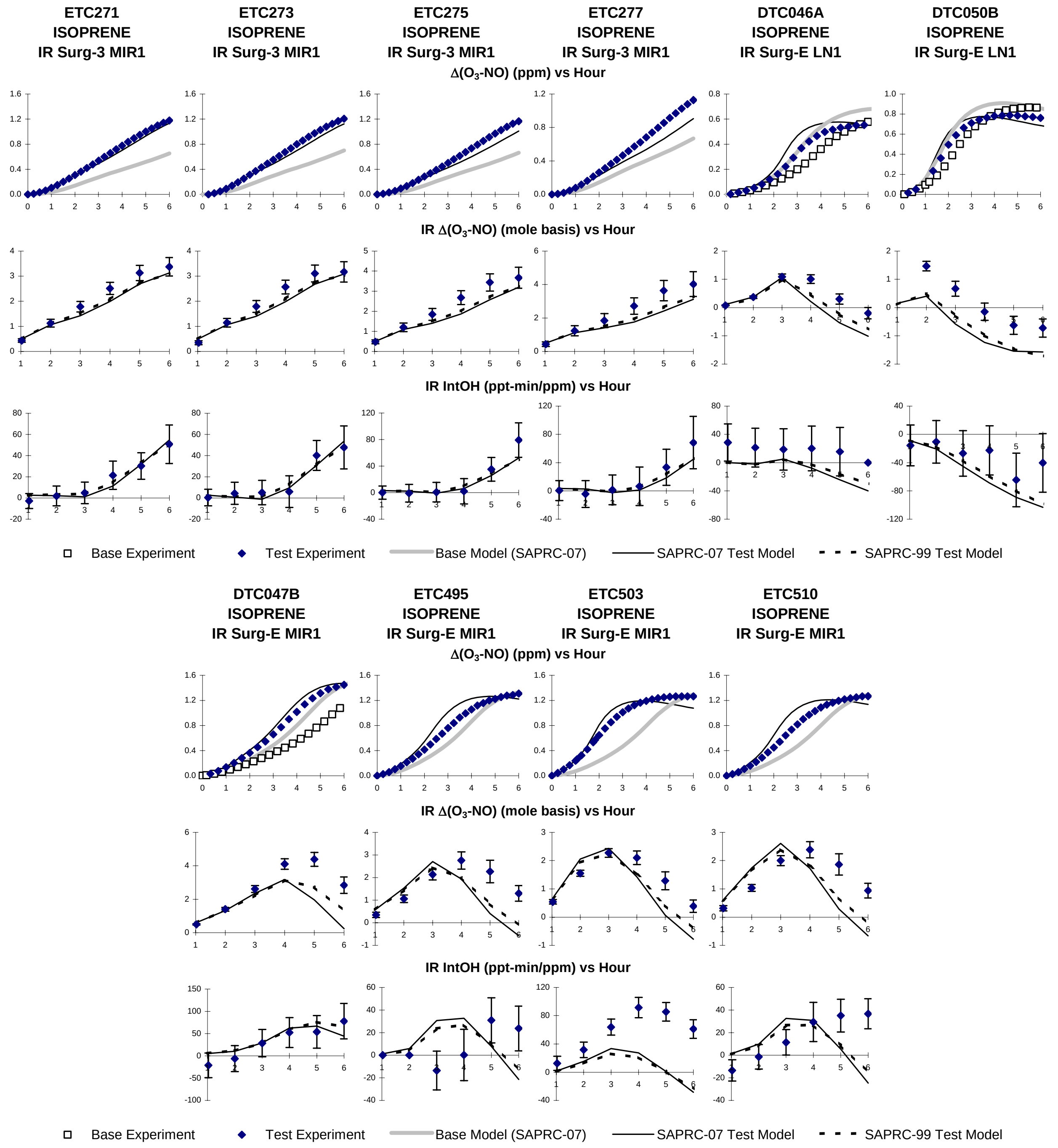


Figure C-21. Plots of experimental and calculated environmental chamber reactivity results for isoprene

Terpene - NOx Experiments

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
a-Pinene	6	6%	2%	1%	-1%
b-Pinene	6	-8%	44%	-13%	41%
d-Limonene	7	-7%	-6%	-2%	-4%
Sabinene	3	54%	3%	6%	4%
3-Carene	4	-12%	-15%	-9%	-22%

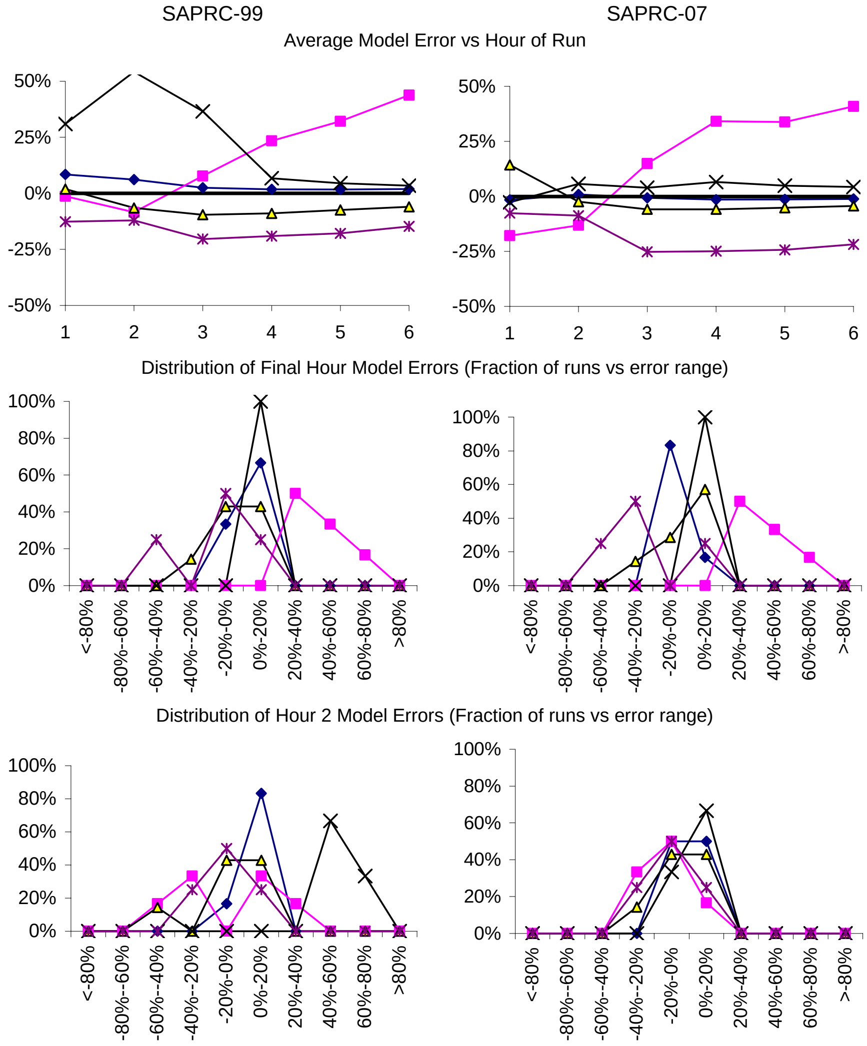


Figure C-22. Plots of model errors in simulations of the terpene - NO_x environmental chamber experiments.

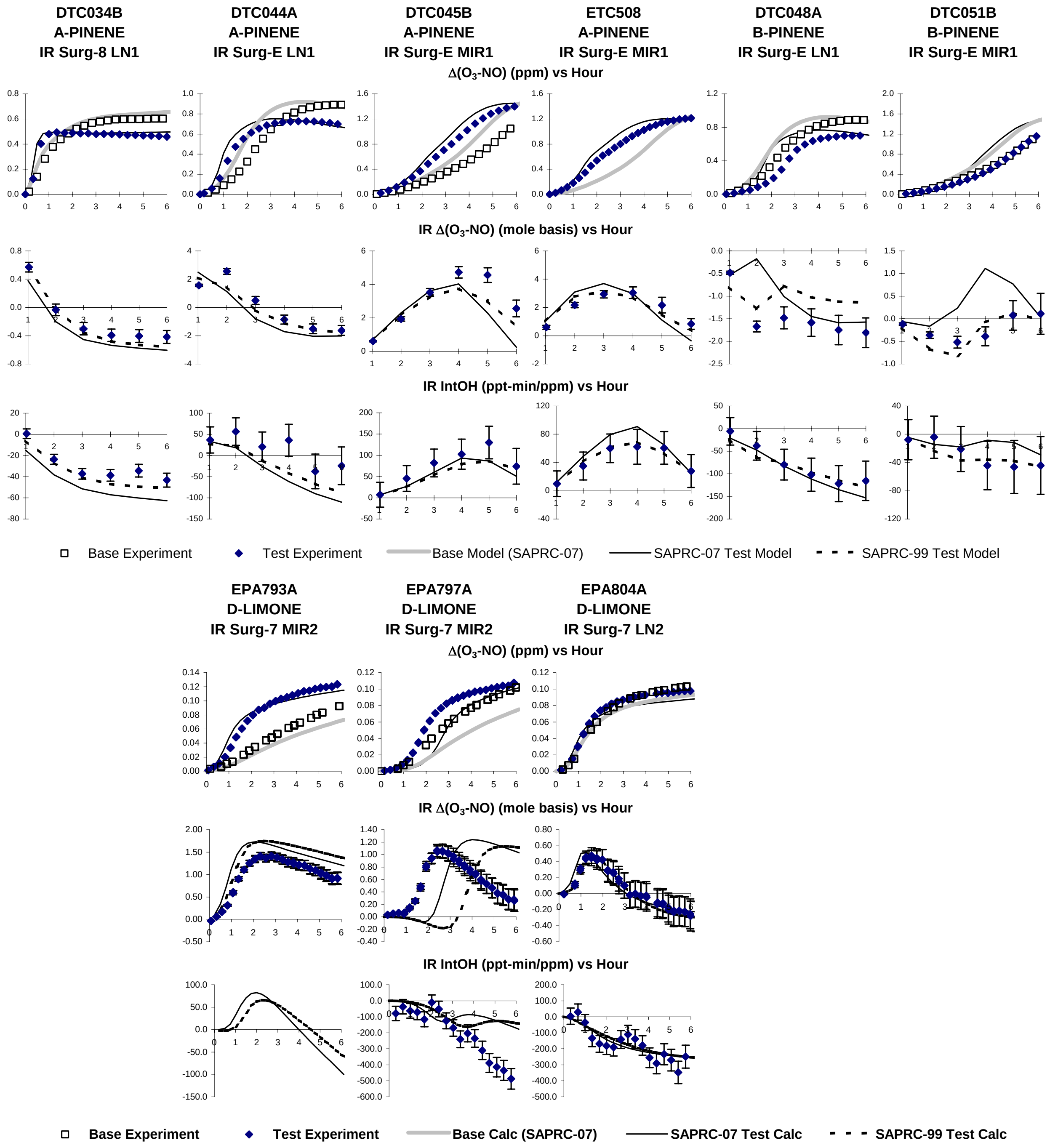


Figure C-23. Plots of experimental and calculated environmental chamber reactivity results for α- and β-pinene and d-limonene.

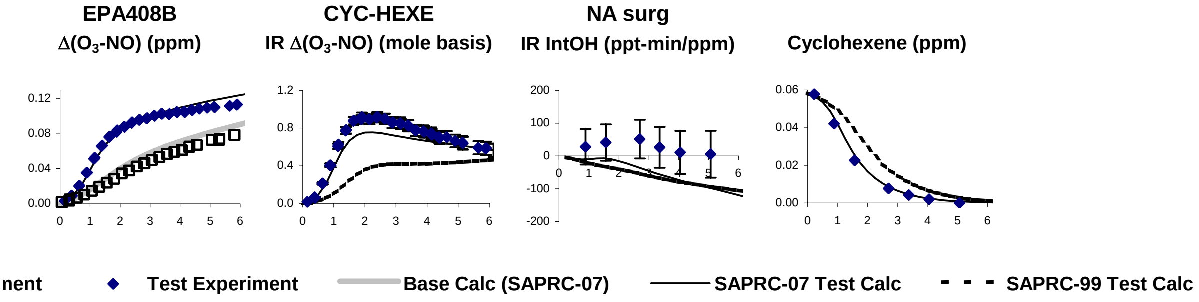


Figure C-24. Plots of experimental and calculated environmental chamber reactivity results for cyclohexene.

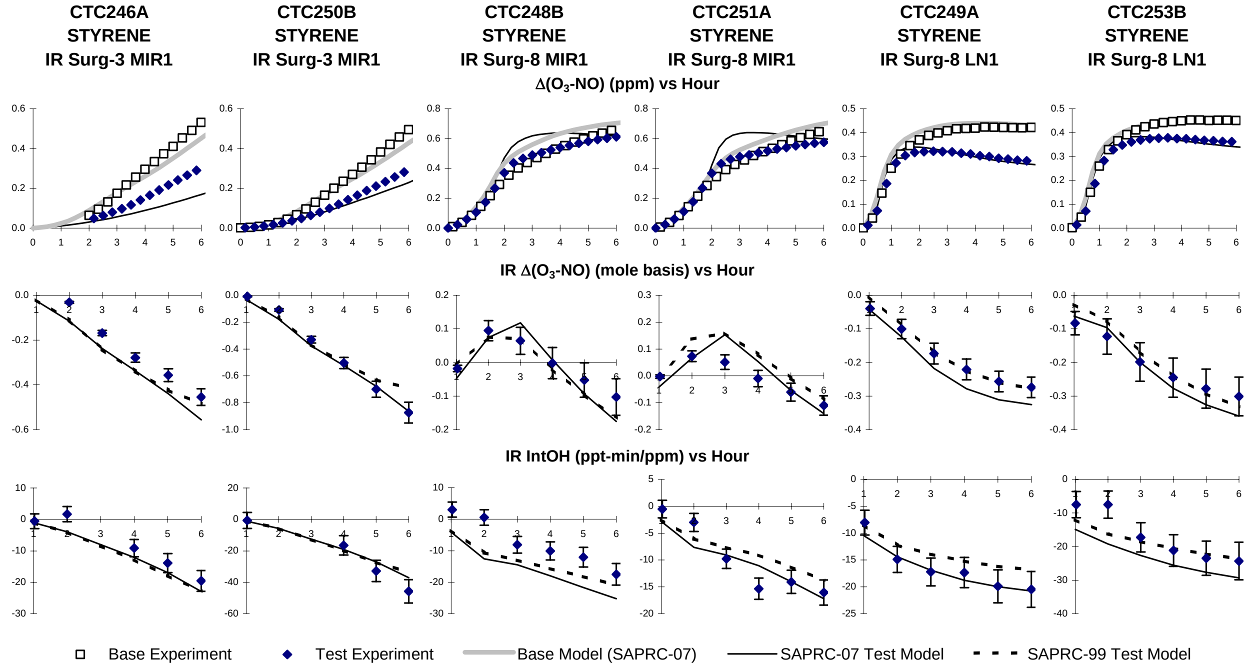


Figure C-25. Plots of experimental and calculated environmental chamber reactivity results for styrene.

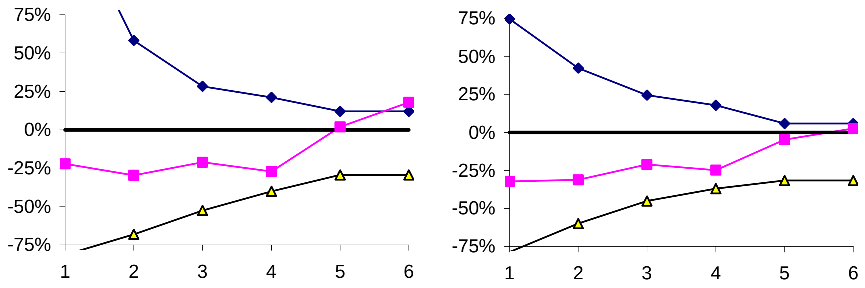
Benzene - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
Arc Light	4	58%	12%	42%	6%
Blacklight	4	-30%	18%	-31%	3%
Added CO	1	-68%	-29%	-60%	-32%

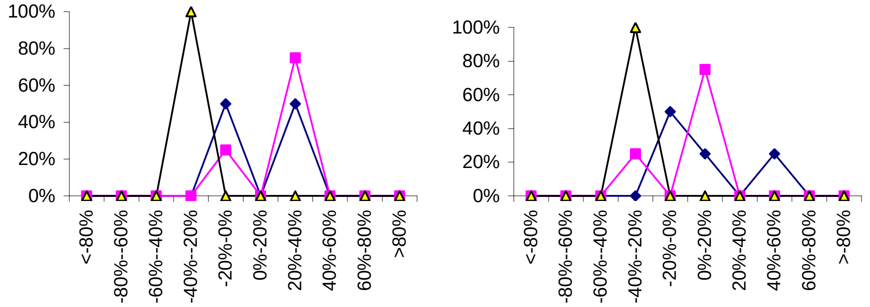
◆ Arc Light
■ Blacklight
▲ Added CO

SAPRC-99 SAPRC-07

Average Model Error vs Hour of Run



Distribution of Final Hour Model Errors (Fraction of runs vs error range)



Distribution of Hour 2 Model Errors (Fraction of runs vs error range)

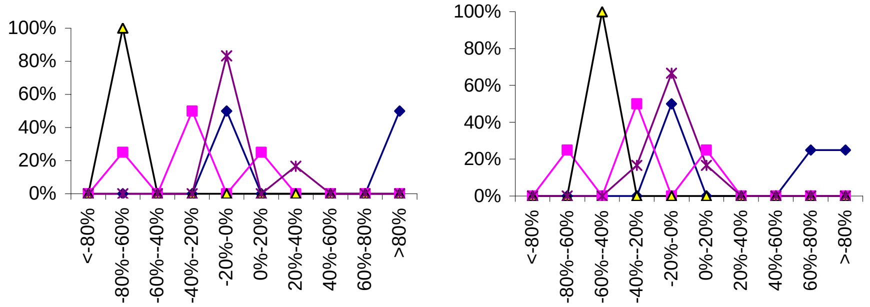


Figure C-26. Plots of model errors in simulations of the benzene and benzene + CO - NO_x environmental chamber experiments.

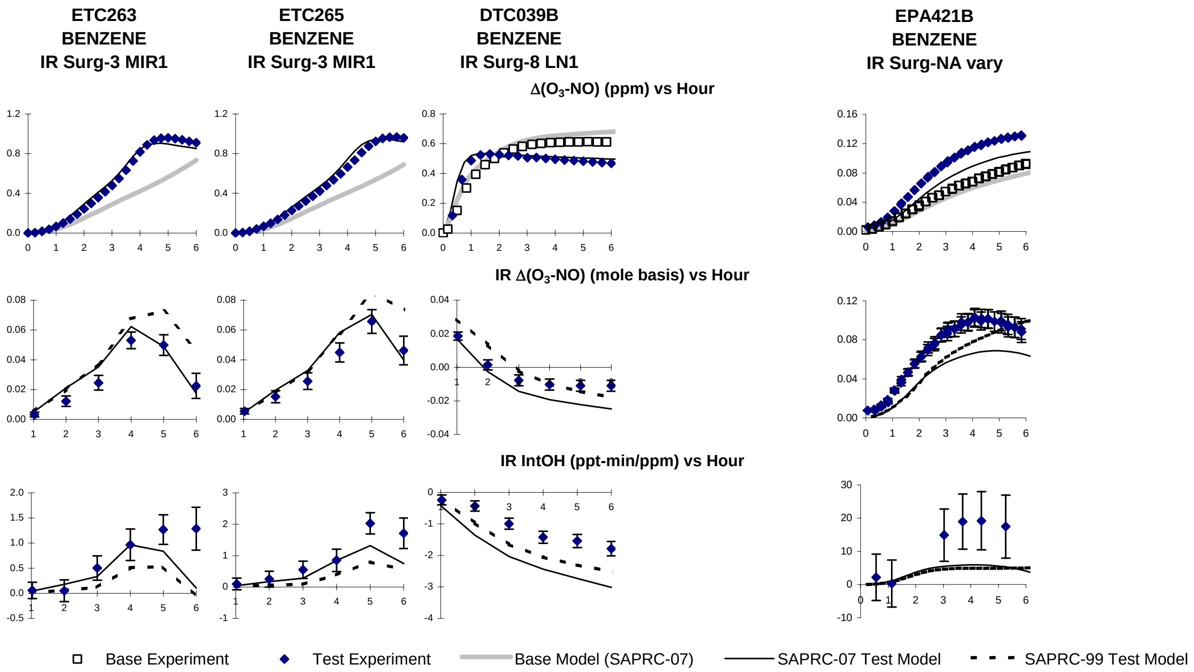


Figure C-27. Plots of experimental and calculated environmental chamber reactivity results for benzene.

Toluene - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
Arc Light	22	3%	11%	-13%	7%
Blacklight	19	-7%	-3%	28%	2%
TVA chamber	3	-3%	-2%	-5%	1%
OTC Chamber	4	-4%	7%	-11%	15%
UNC Chamber	5	53%	68%	27%	88%
Added CO	7	-20%	-19%	-18%	-13%

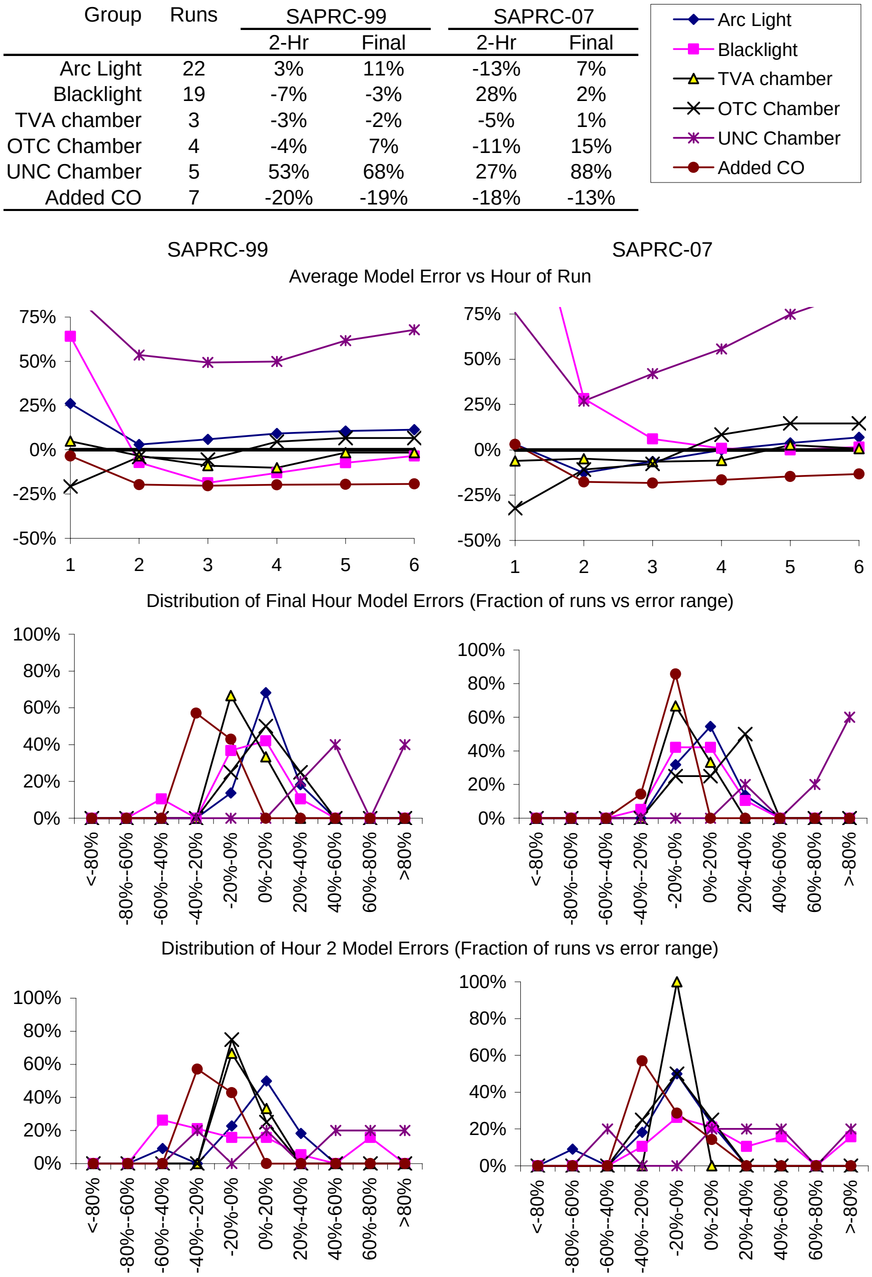


Figure C-28. Plots of model errors in simulations of the toluene and toluene + CO - NO_x environmental chamber experiments.

Ethylbenzene - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	 Final	 SAPRC-07 2-Hr	 Final
Arc Light	4	5%	5%	-18%	14%
Blacklight	4	16%	-10%	-3%	-10%

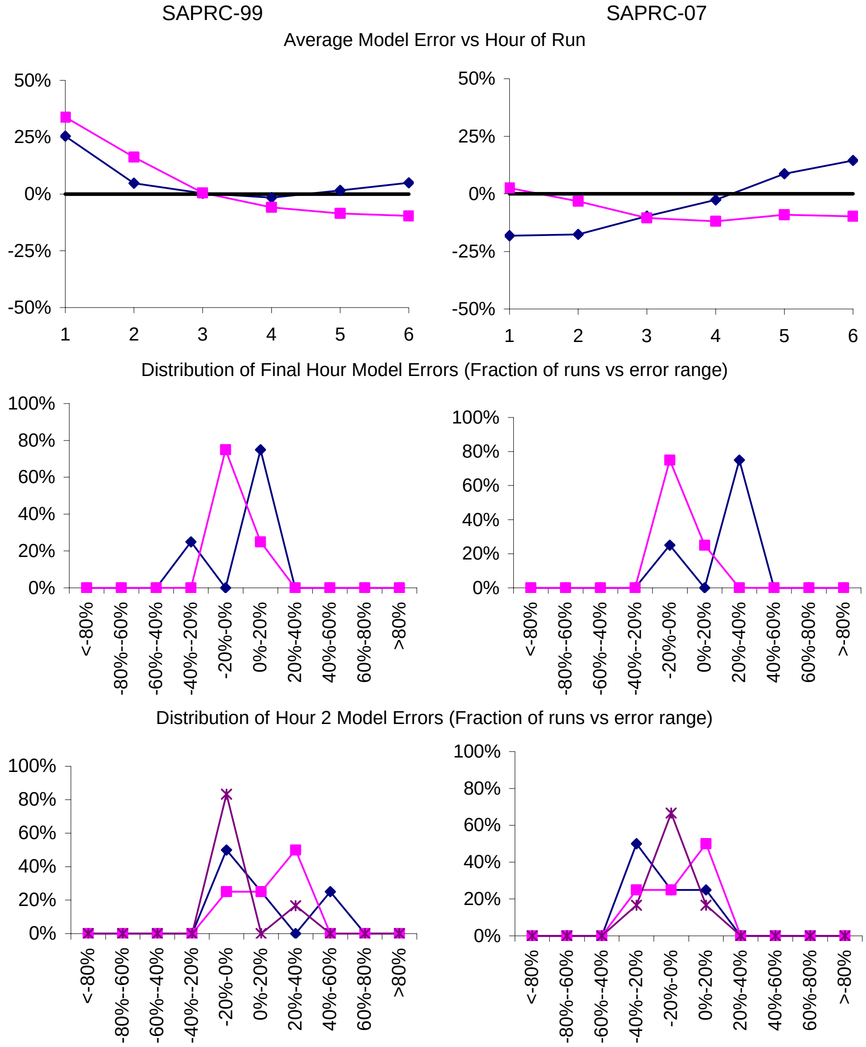


Figure C-29. Plots of model errors in simulations of the ethylbenzene - NO_x environmental chamber experiments.

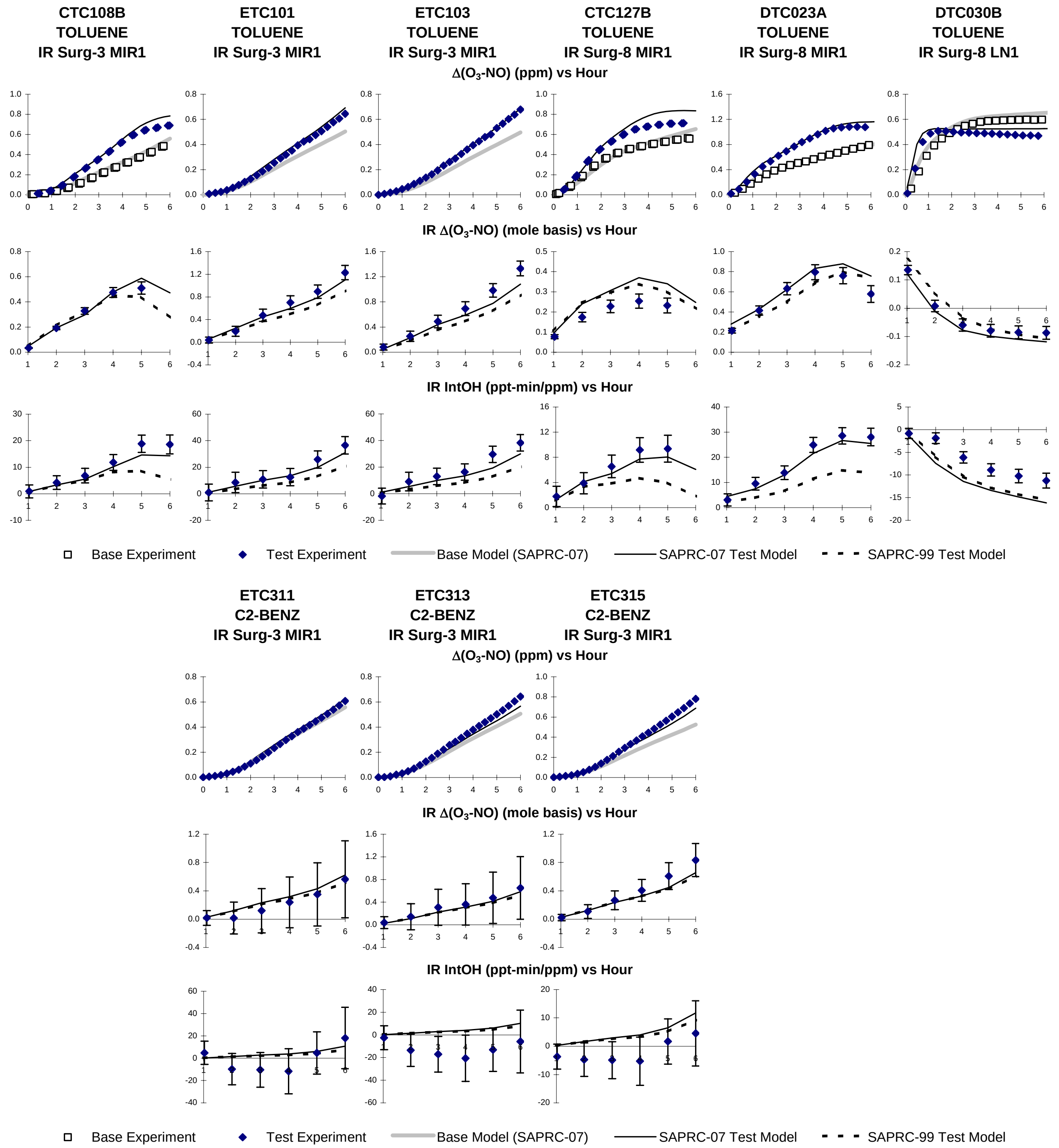
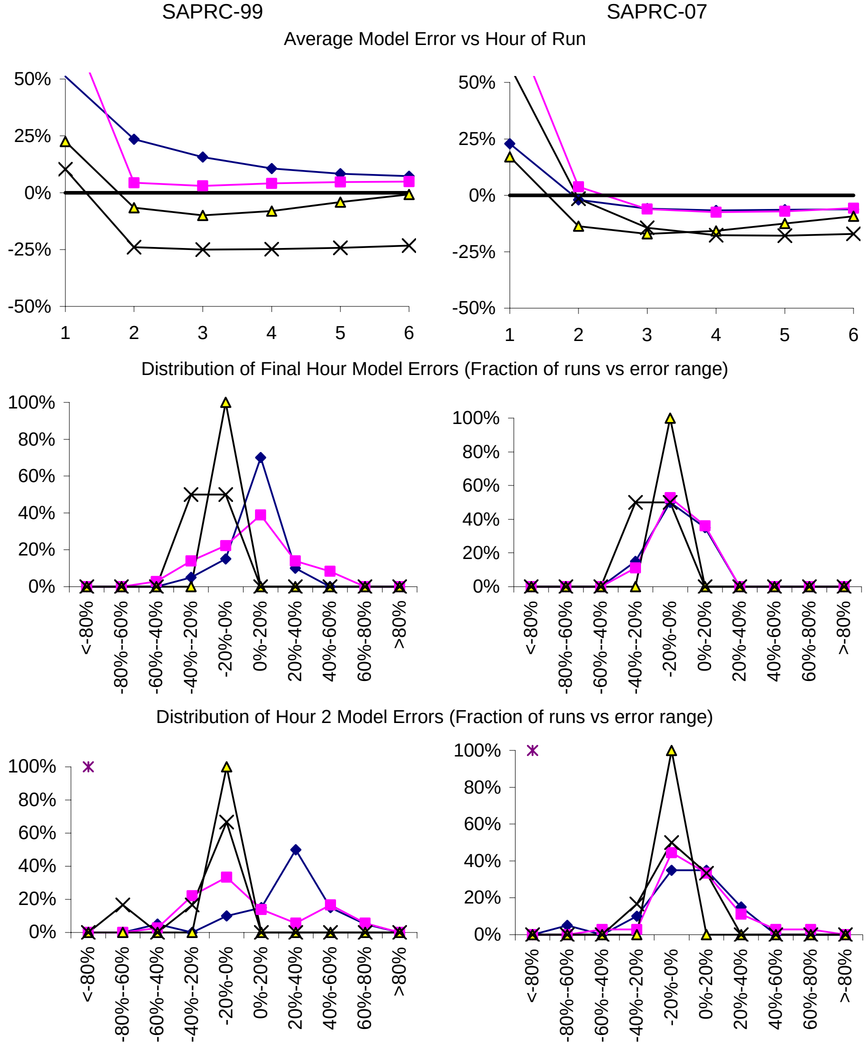


Figure C-30. Plots of experimental and calculated environmental chamber reactivity results for toluene and ethylbenzene.

M-Xylene - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
Arc Light	20	24%	7%	-2%	-6%
Blacklight	36	4%	5%	4%	-6%
TVA chamber	2	-7%	-1%	-14%	-9%
Added CO	6	-24%	-23%	-2%	-17%


SAPRC-99

SAPRC-07

Average Model Error vs Hour of Run

Distribution of Final Hour Model Errors (Fraction of runs vs error range)

Distribution of Hour 2 Model Errors (Fraction of runs vs error range)

Figure C-31. Plots of model errors in simulations of the m-xylene and m-xylene + CO - NO_x environmental chamber experiments.

O-Xylene - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
Arc Light	6	15%	4%	-2%	-6%
Blacklight	6	10%	-3%	-3%	-12%
EC Chamber	2	-1%	7%	-15%	1%
UNC Chamber	4	54%	16%	45%	24%

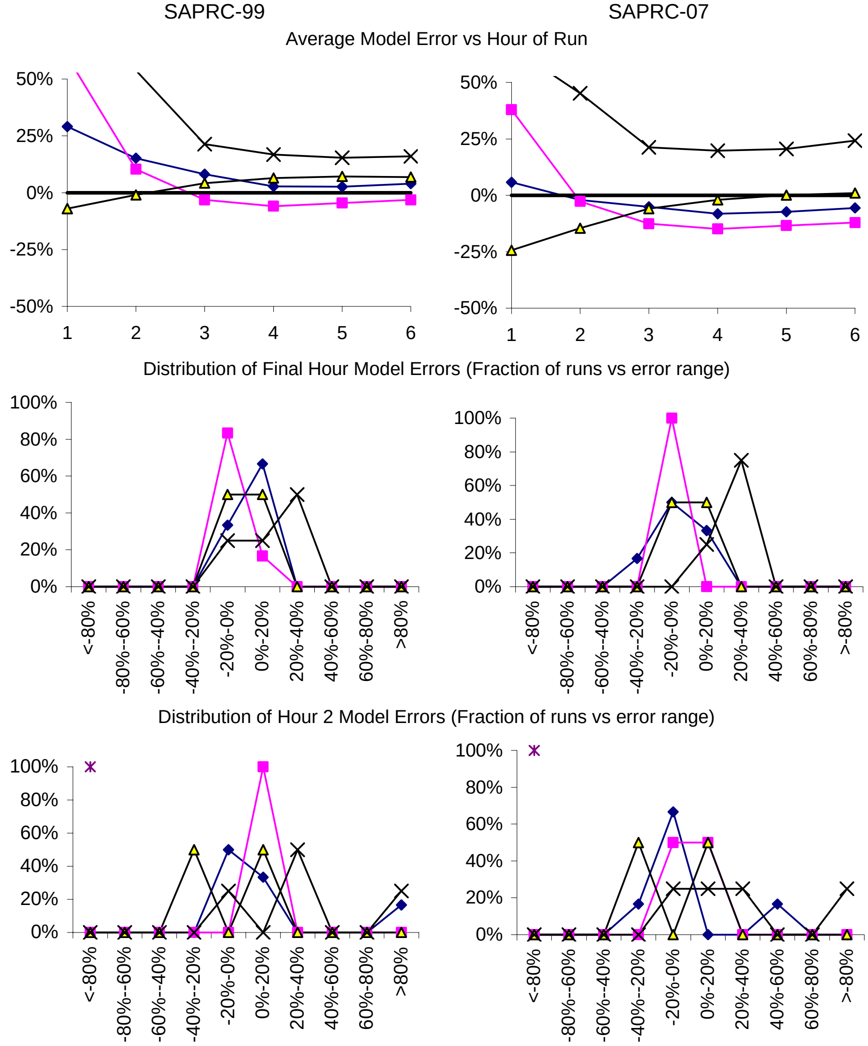


Figure C-32. Plots of model errors in simulations of the o-xylene - NO_x environmental chamber experiments.

P-Xylene - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
Arc Light	6	52%	-10%	6%	6%
Blacklight	7	10%	-15%	-3%	-4%
Added CO	1	-38%	-30%	-54%	-27%

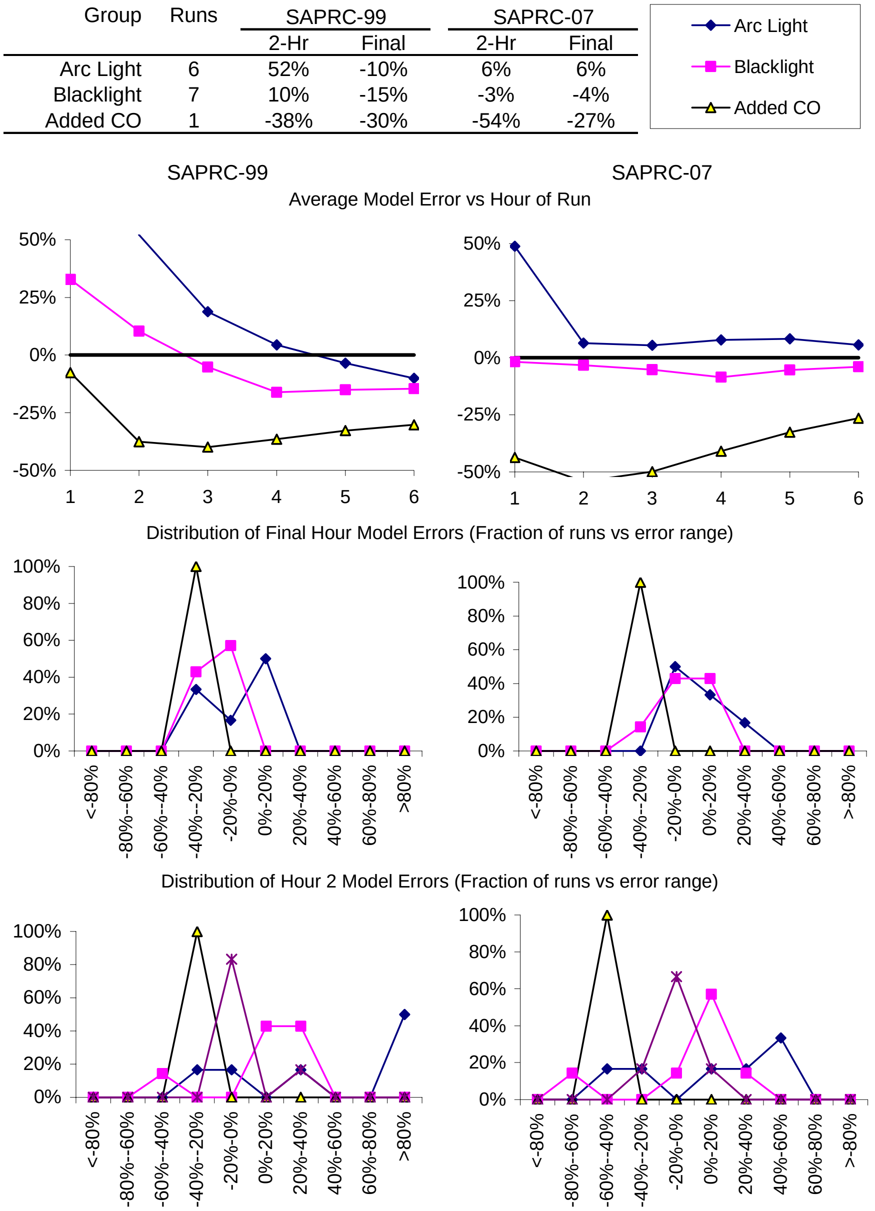


Figure C-33. Plots of model errors in simulations of the p-xylene - NO_x environmental chamber experiments.

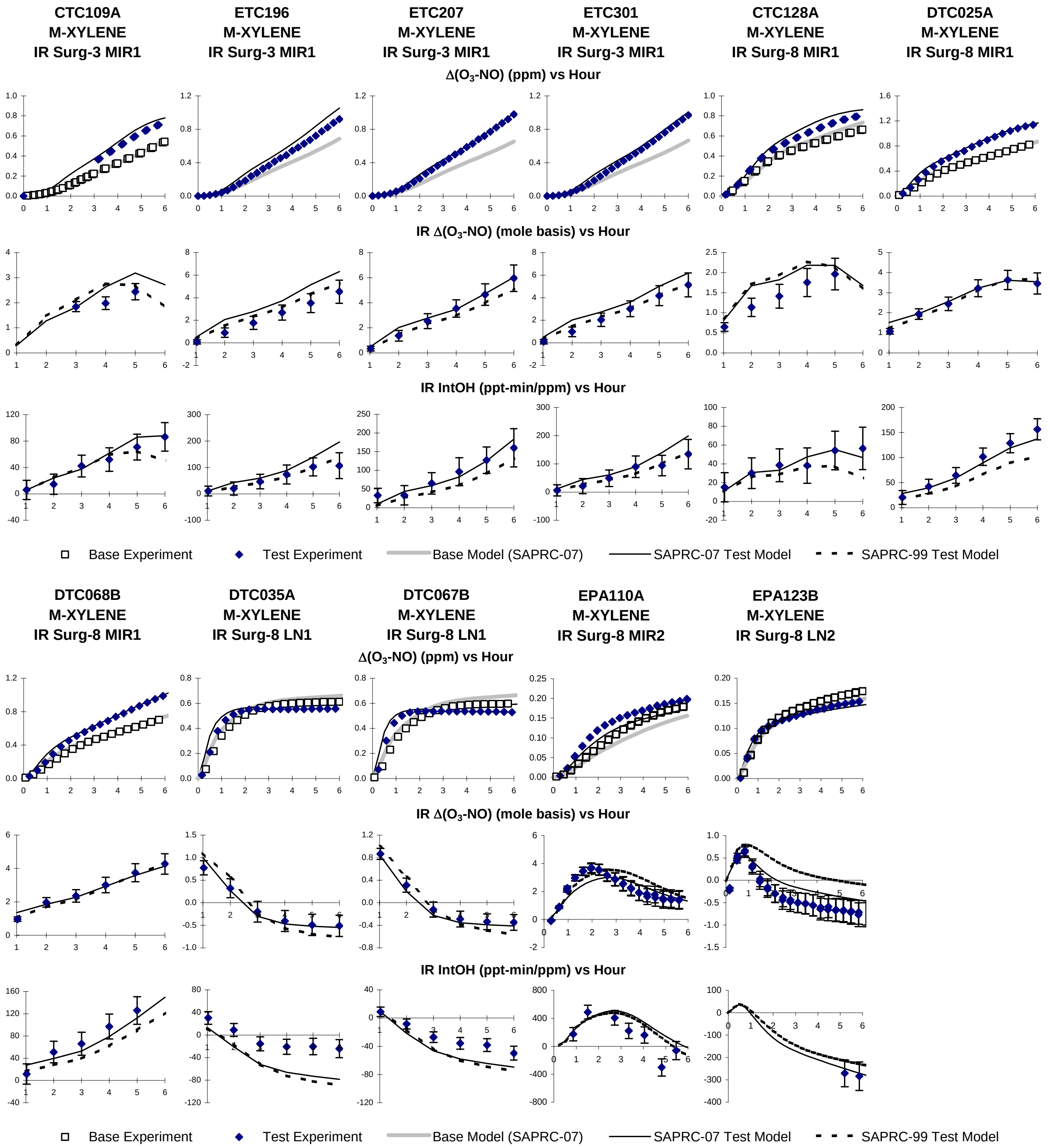
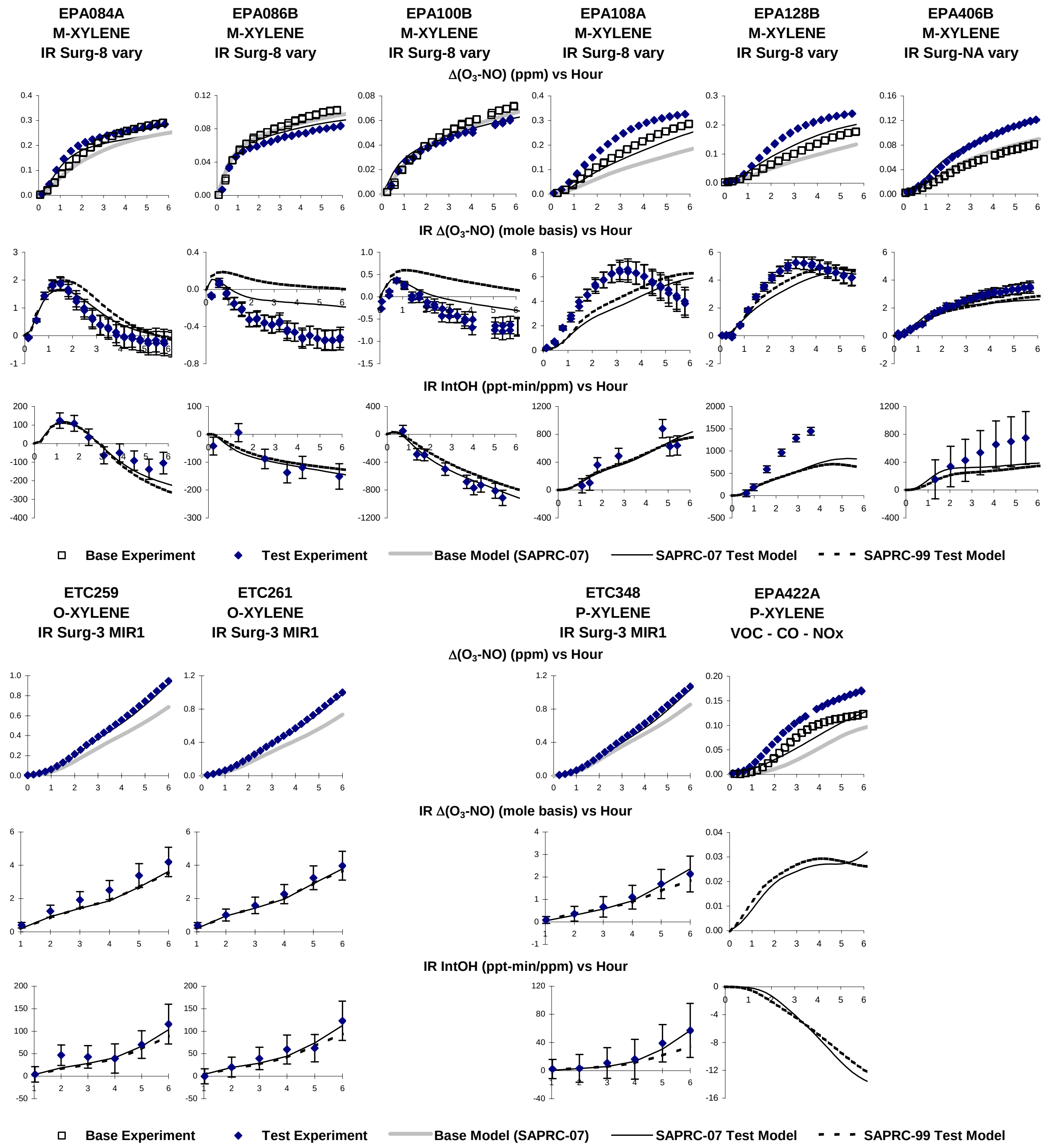


Figure C-34. Plots of experimental and calculated environmental chamber reactivity results for m-xylene (additional experiments shown on Figure C-35).


EPA084A M-XYLENE IR Surg-8 vary

EPA086B M-XYLENE IR Surg-8 vary

EPA100B M-XYLENE IR Surg-8 vary

EPA108A M-XYLENE IR Surg-8 vary

EPA128B M-XYLENE IR Surg-8 vary

EPA406B M-XYLENE IR Surg-NA vary

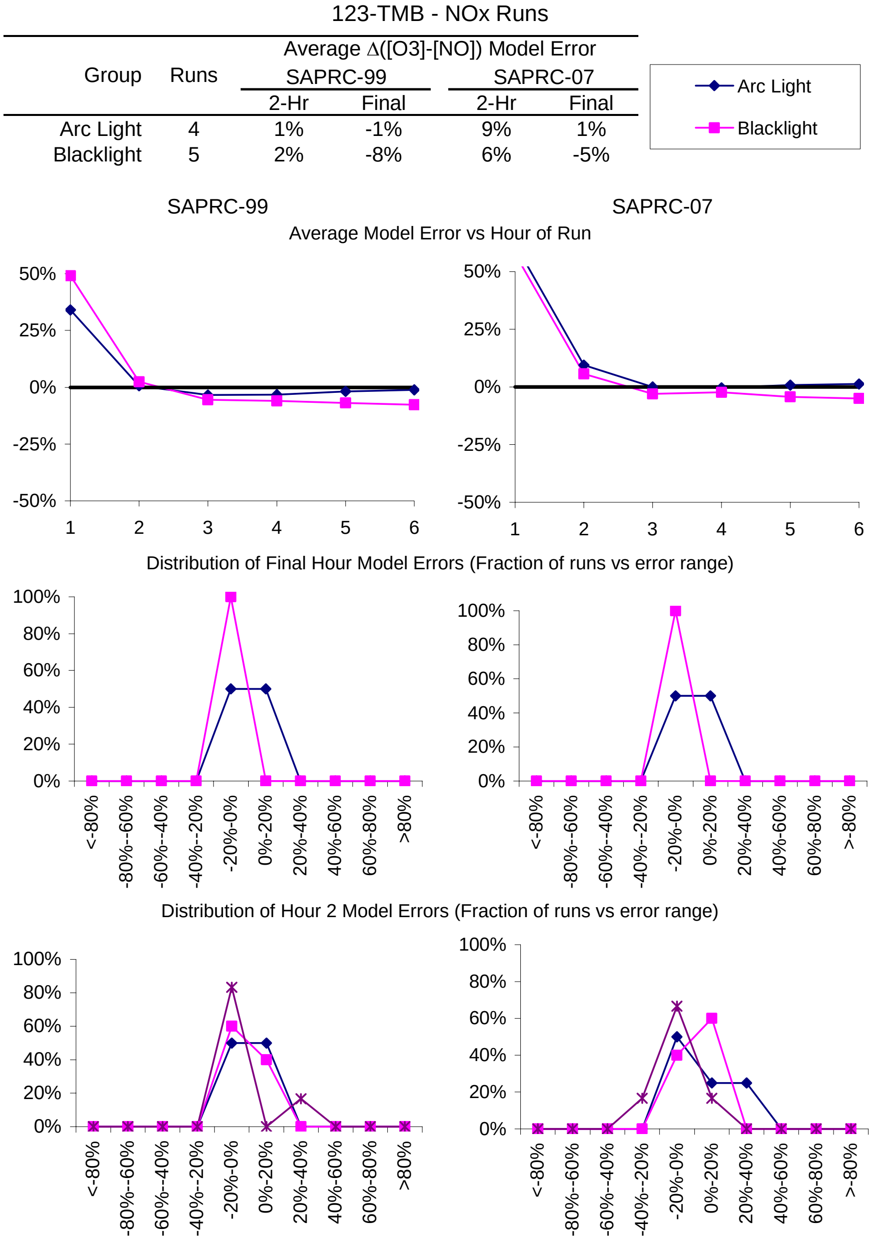
ETC259 O-XYLENE IR Surg-3 MIR1

ETC261 O-XYLENE IR Surg-3 MIR1

ETC348 P-XYLENE IR Surg-3 MIR1

EPA422A P-XYLENE VOC - CO - NOx

Figure C-35. Plots of experimental and calculated environmental chamber reactivity results for m-xylene (with variable surrogate conditions), o-xylene, and p-xylene.



123-TMB - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
Arc Light	4	1%	-1%	9%	1%
Blacklight	5	2%	-8%	6%	-5%

Figure C-36. Plots of model errors in simulations of the 1,2,3-trimethylbenzene - NO_x environmental chamber experiments.

124-TMB - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
Arc Light	4	23%	-2%	5%	14%
Blacklight	6	17%	-9%	-5%	-8%
Added CO	1	-8%	-19%	-36%	-21%

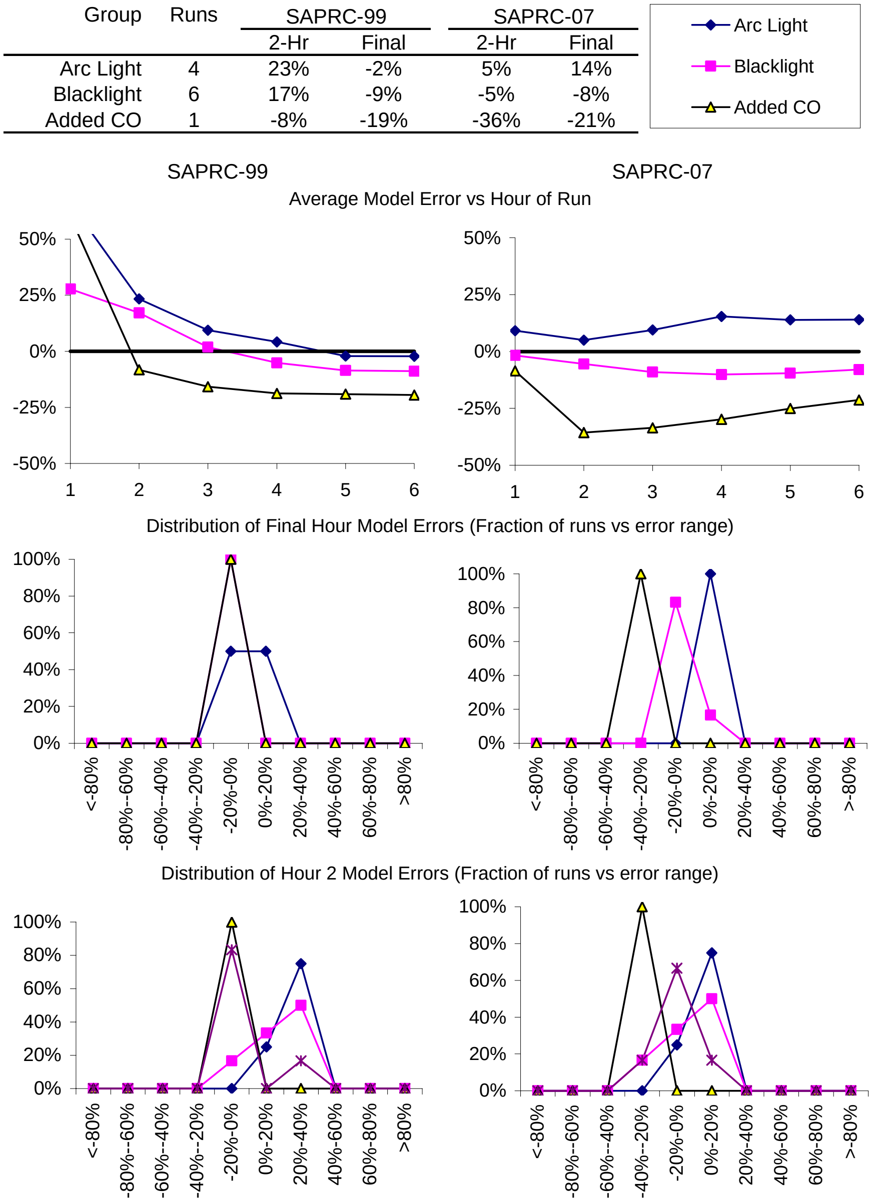


Figure C-37. Plots of model errors in simulations of the 1,2,4-trimethylbenzene - NO_x environmental chamber experiments.

135-TMB - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
Arc Light	5	0%	3%	1%	5%
Blacklight	12	0%	0%	-2%	1%
EC Chamber	2	21%	33%	14%	35%
Added CO	2	0%	-15%	-1%	-7%

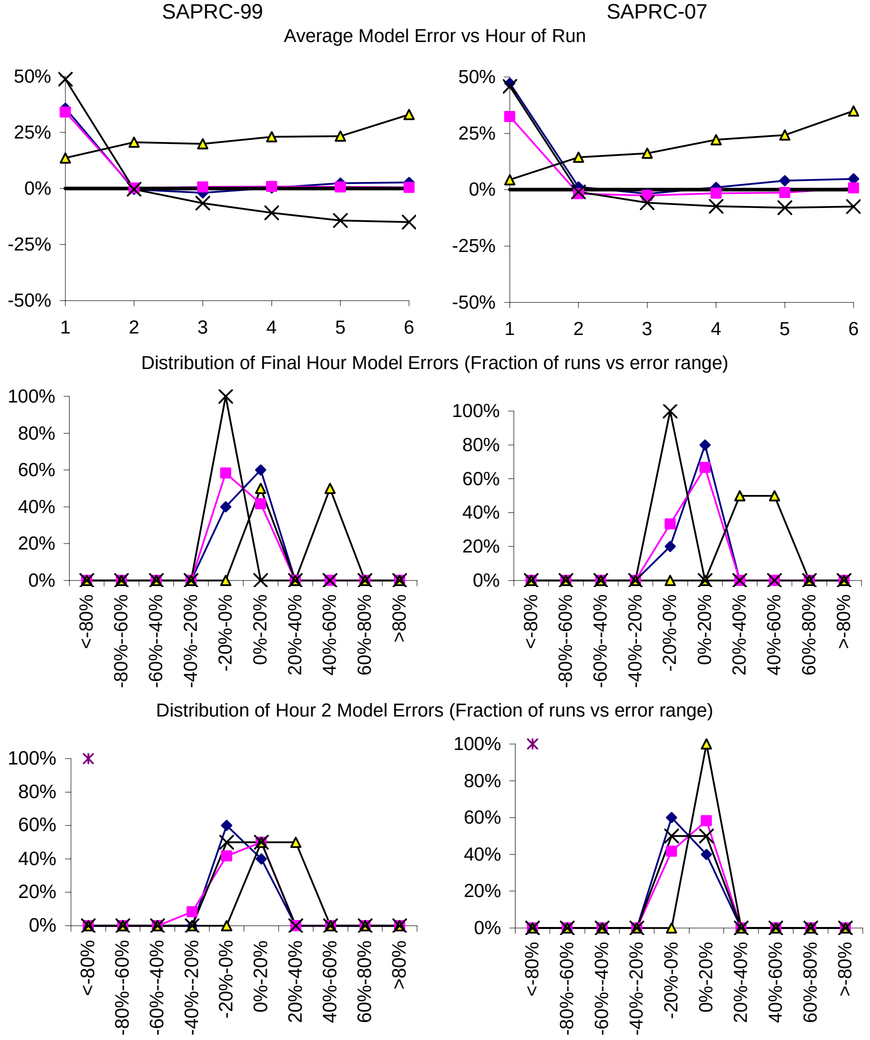


Figure C-38. Plots of model errors in simulations of the 1,3,5-trimethylbenzene and 1,3,5-trimethylbenzene + CO - NO_x environmental chamber experiments.

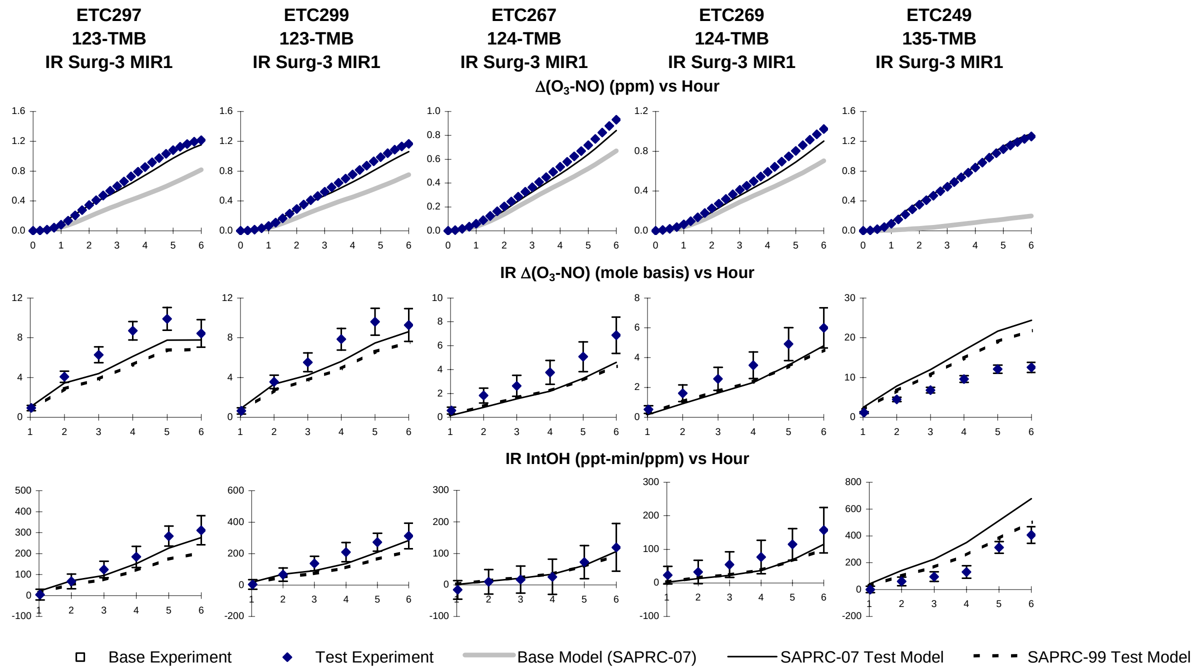


Figure C-39. Plots of experimental and calculated environmental chamber reactivity results for 1,2,3-, 1,2,4- and 1,3,4-trimethylbenzenes.

Naphtlanenes and Tetralin NOx Experiments

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
Naphthalene	5	15%	5%	17%	3%
Tetralin	5	-14%	7%	4%	16%
2,3-Dime.naphth.	4	14%	0%	10%	-2%

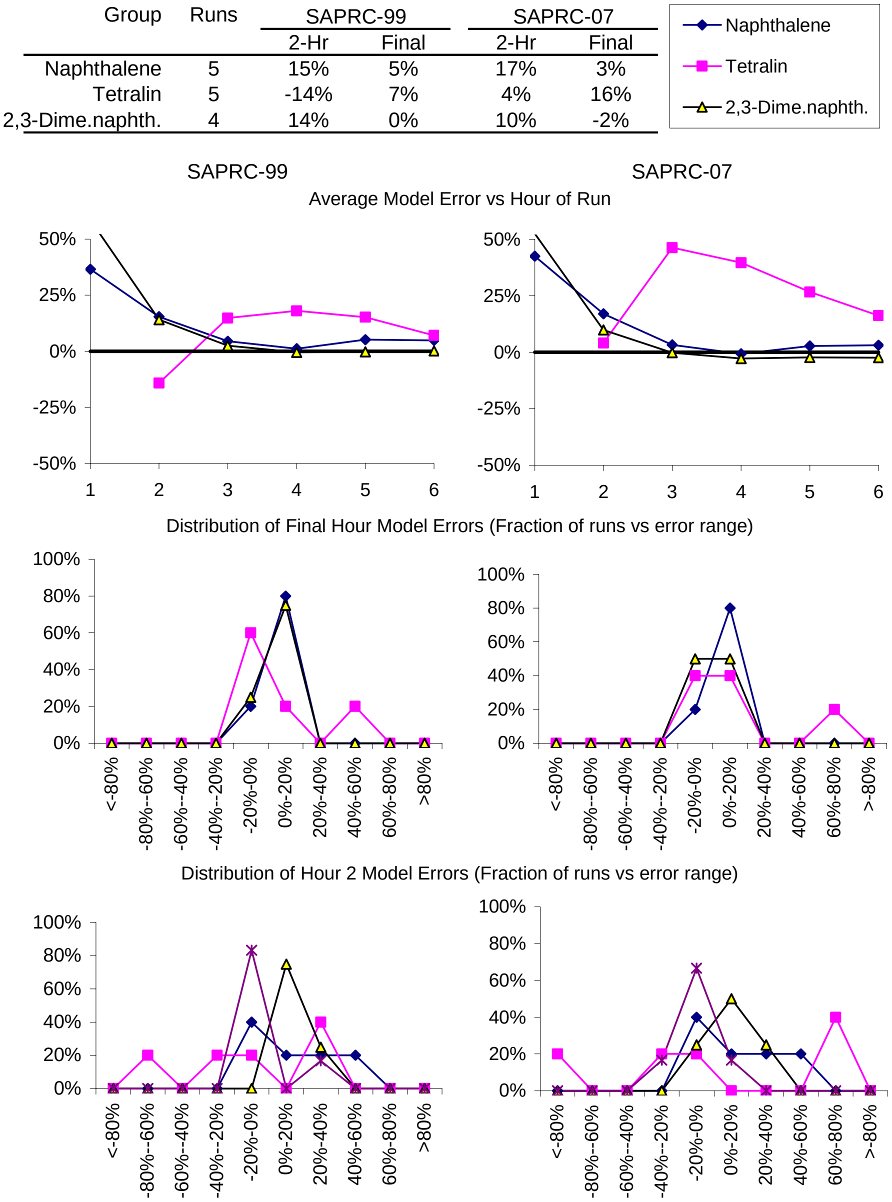


Figure C-40. Plots of model errors in simulations of the naphthalene, 2,3-dimethylnaphthalene, and tetralin - NO_x environmental chamber experiments.

Acetyllene - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
Arc Light	2	25%	-5%	-35%	-23%
Blacklight	2	2%	2%	-16%	-19%

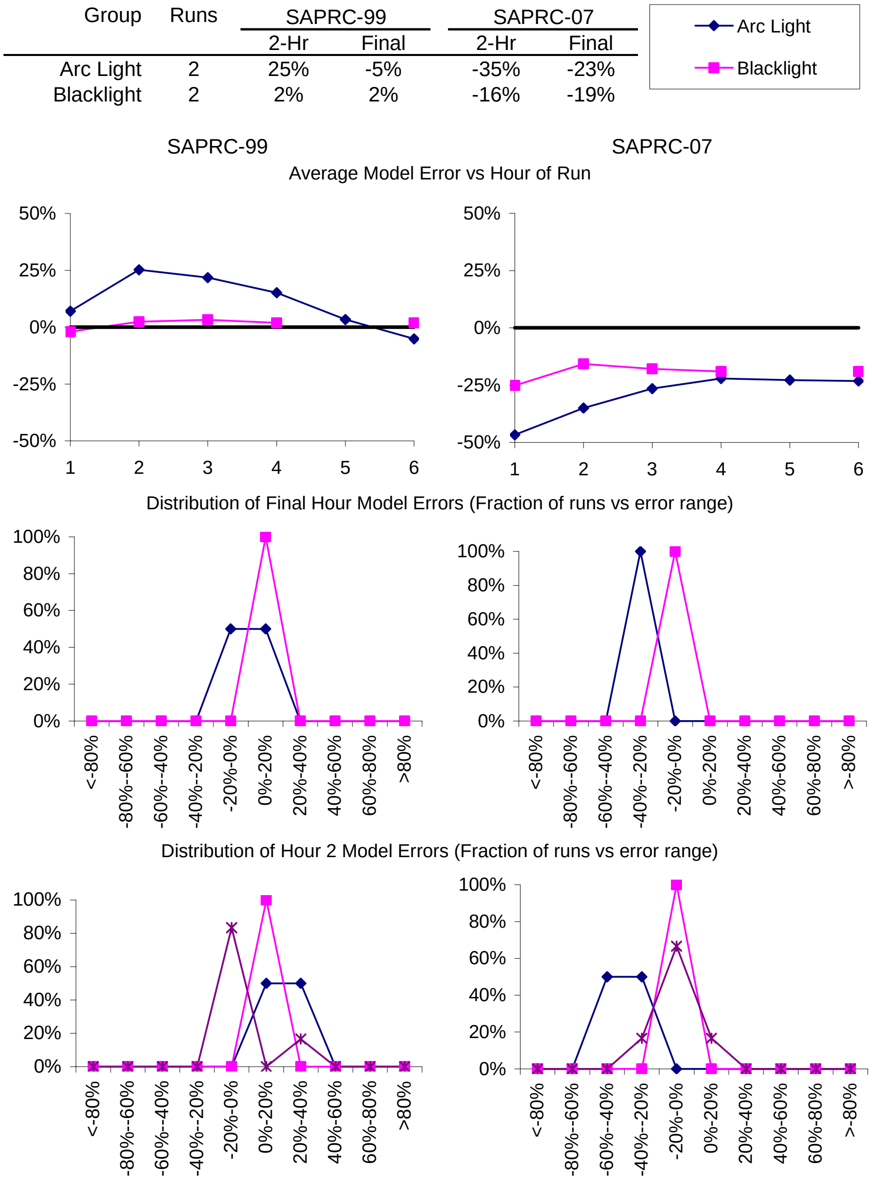


Figure C-41. Plots of model errors in simulations of the acetylene - NO_x environmental chamber experiments.

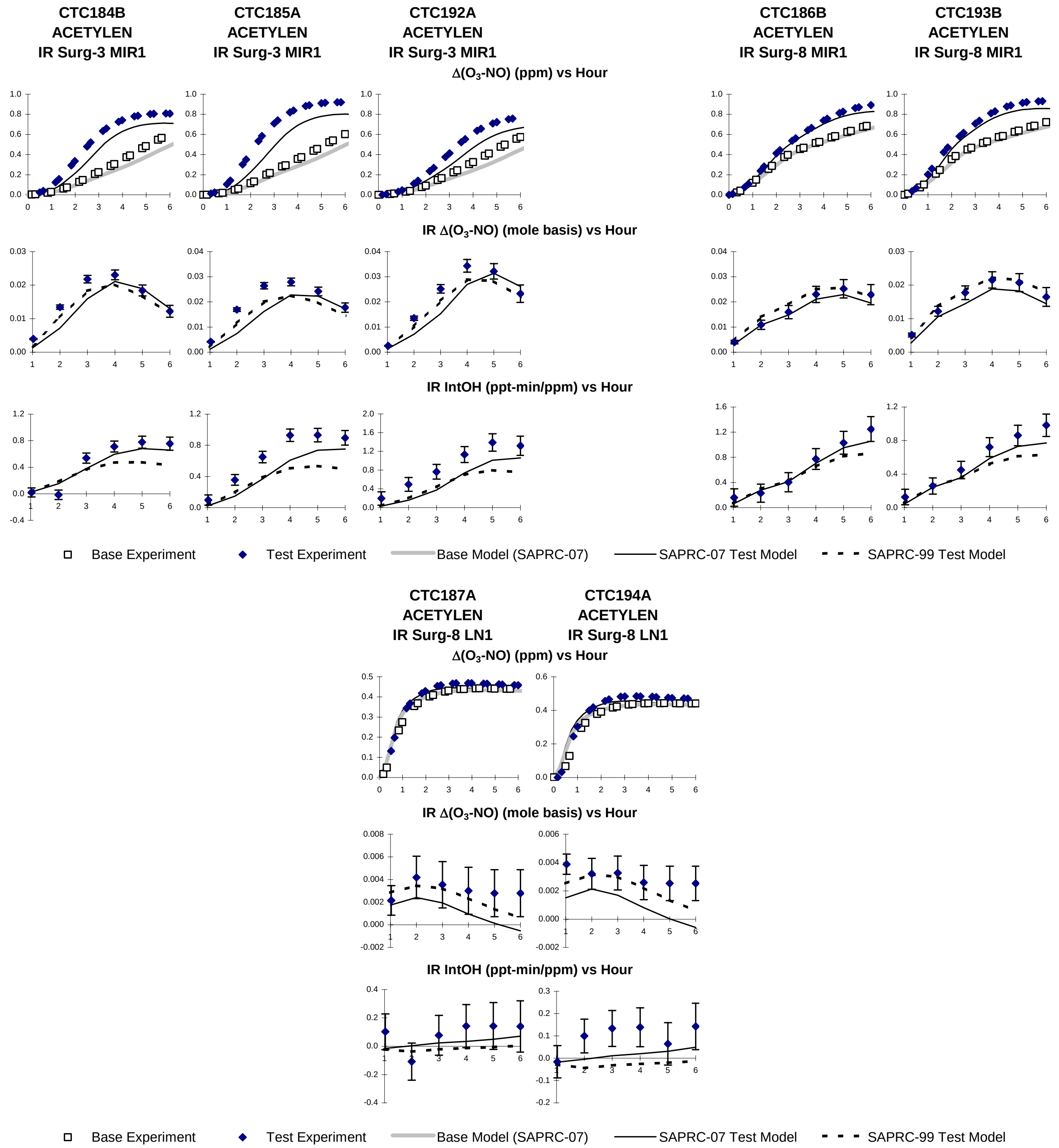


Figure C-42. Plots of experimental and calculated environmental chamber reactivity results for acetylene.

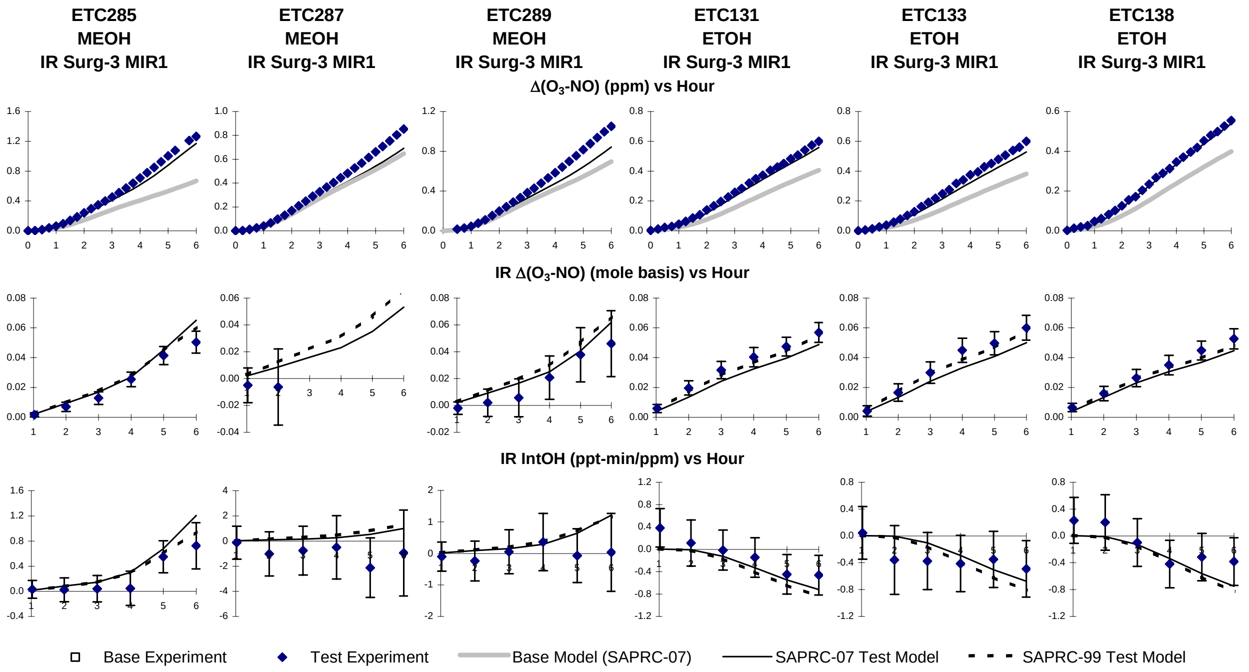


Figure C-43. Plots of experimental and calculated environmental chamber reactivity results for methanol and ethanol.

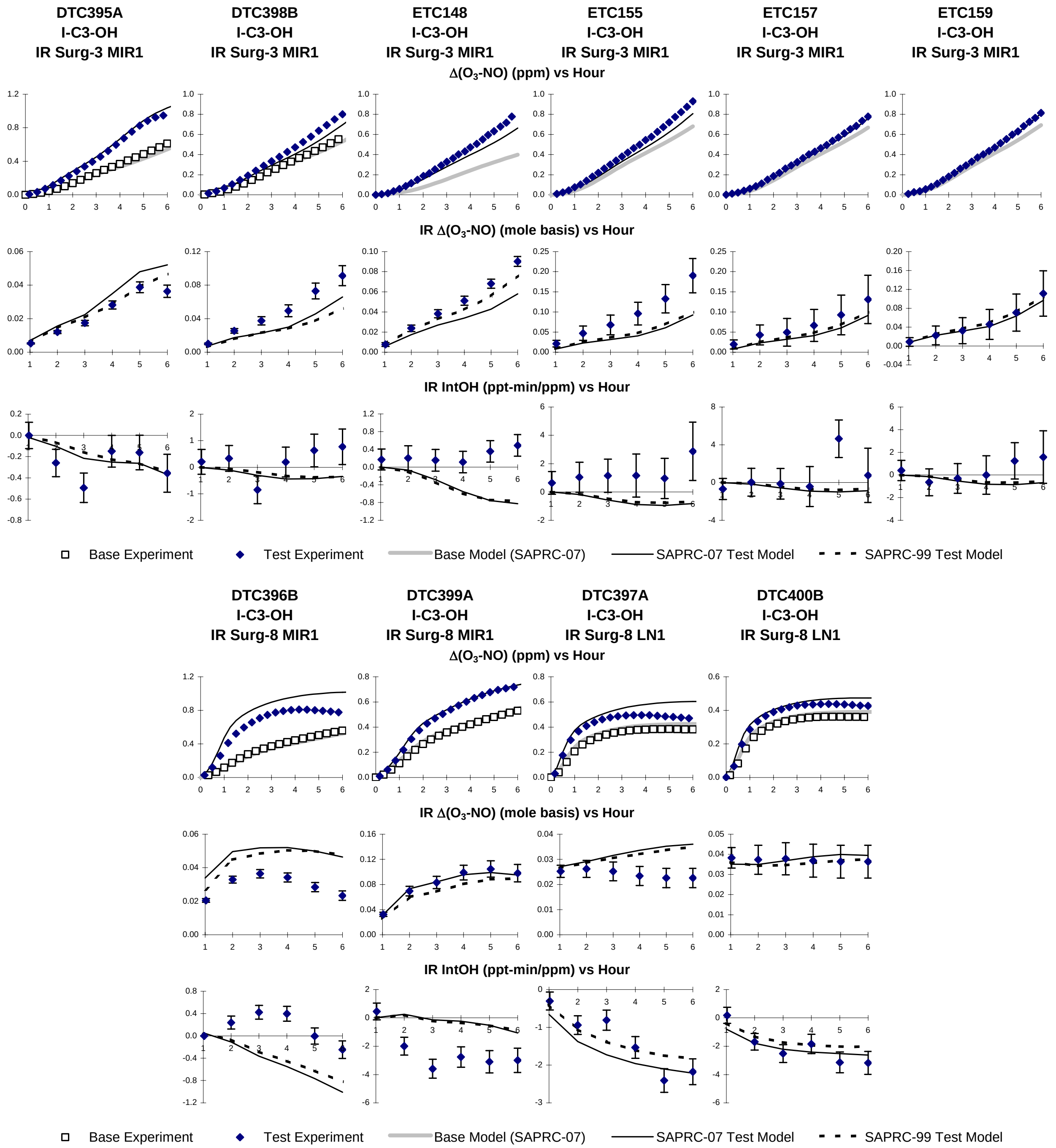


Figure C-44. Plots of experimental and calculated environmental chamber reactivity results for isopropyl alcohol.

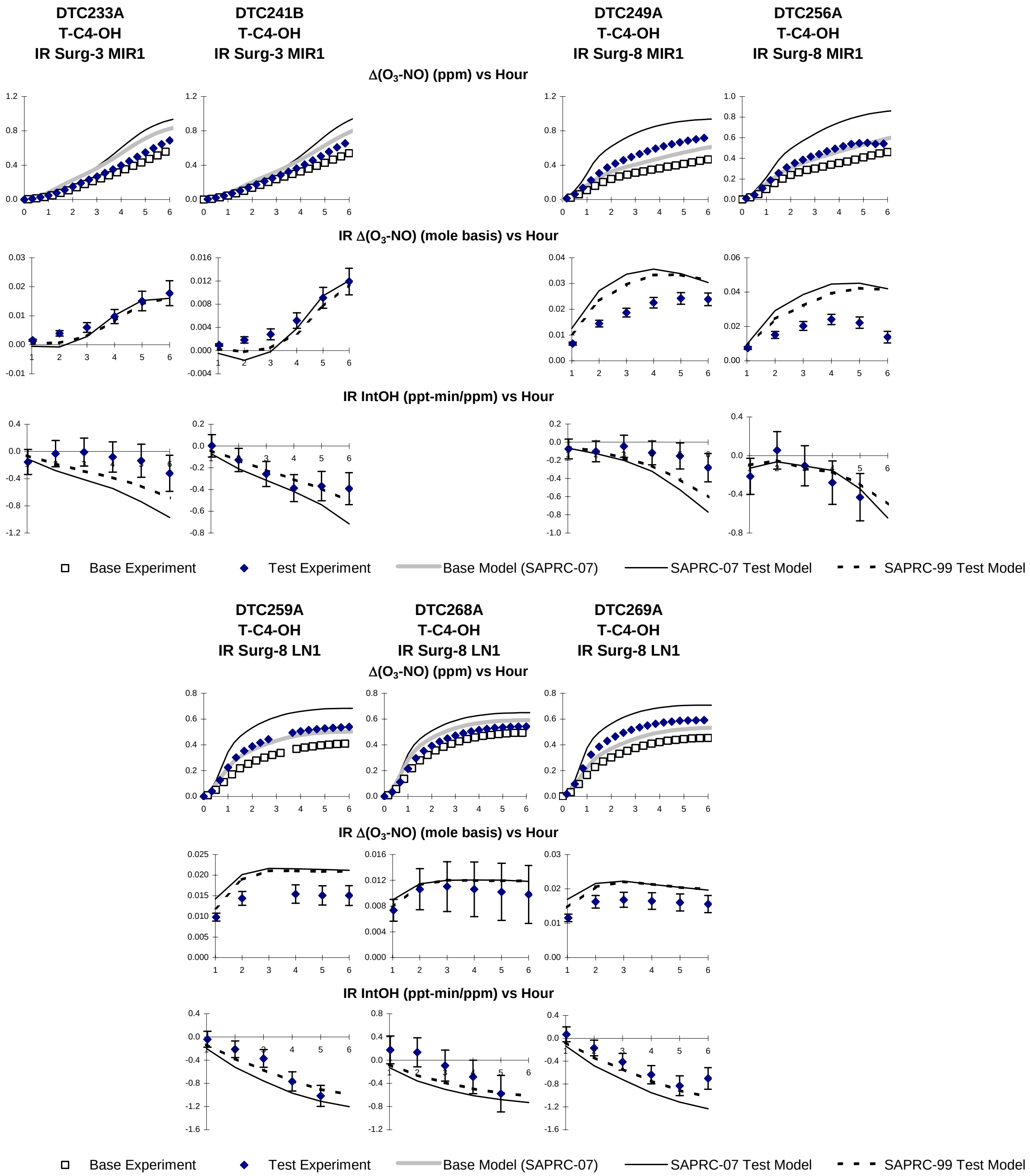


Figure C-45. Plots of experimental and calculated environmental chamber reactivity results for t-butyl alcohol.

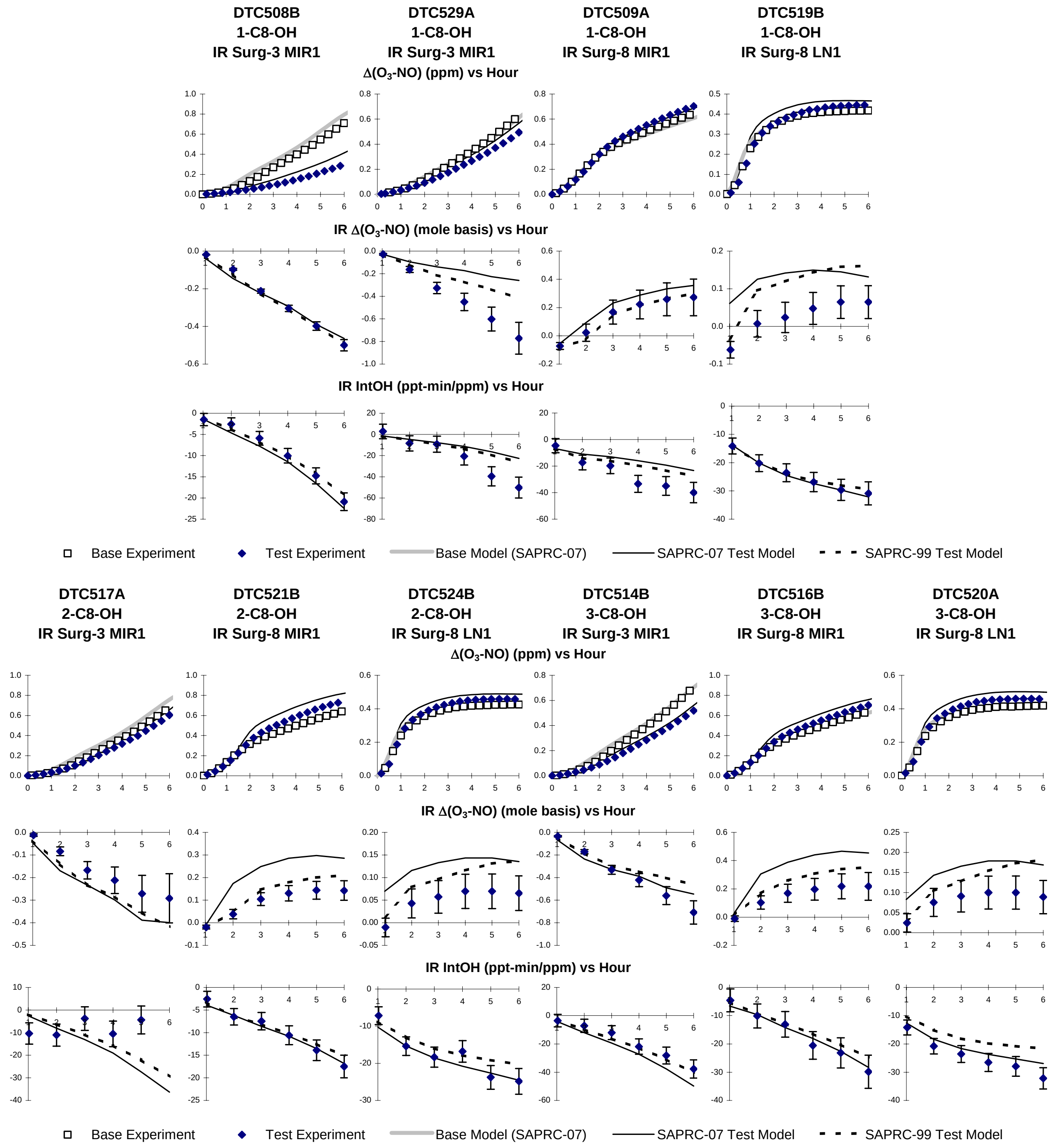


Figure C-46. Plots of experimental and calculated environmental chamber reactivity results for 1-, 2-, and 3-octanol.

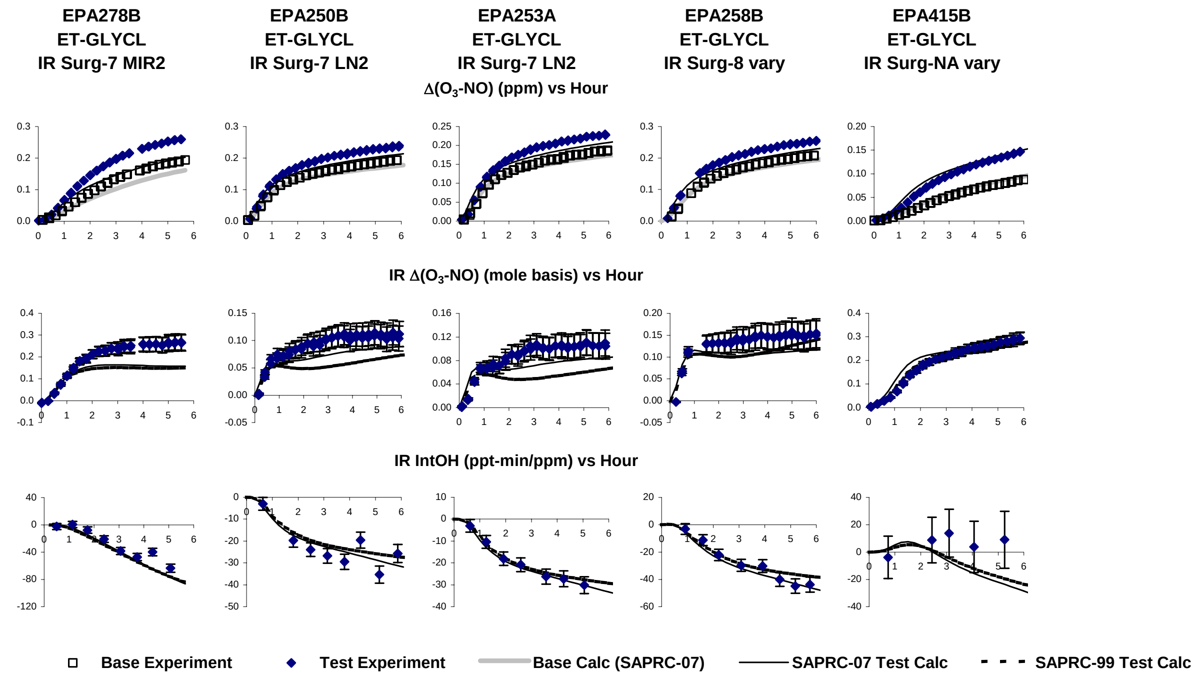


Figure C-47. Plots of experimental and calculated environmental chamber reactivity results for ethylene glycol.

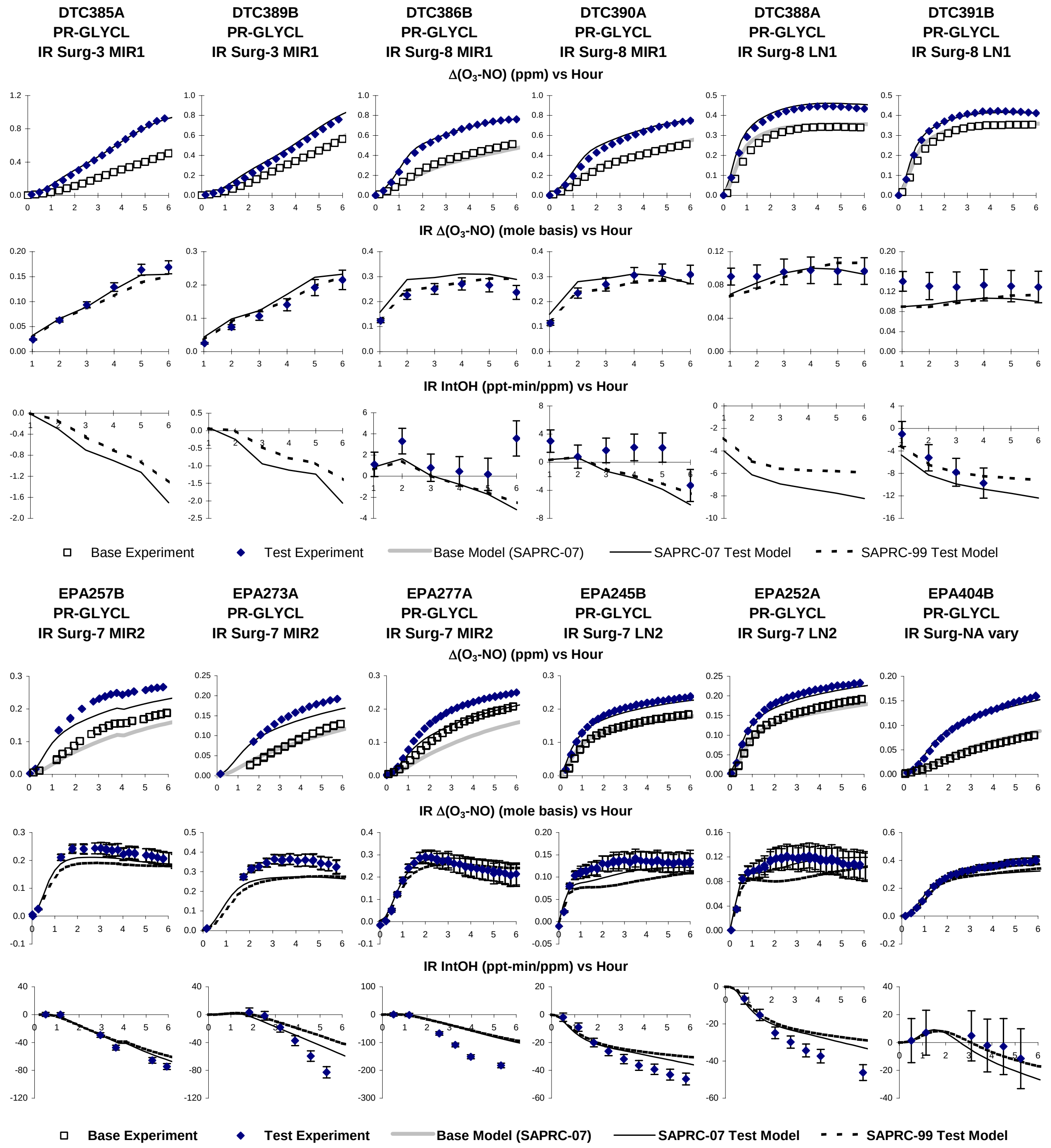


Figure C-48. Plots of experimental and calculated environmental chamber reactivity results for propylene glycol.

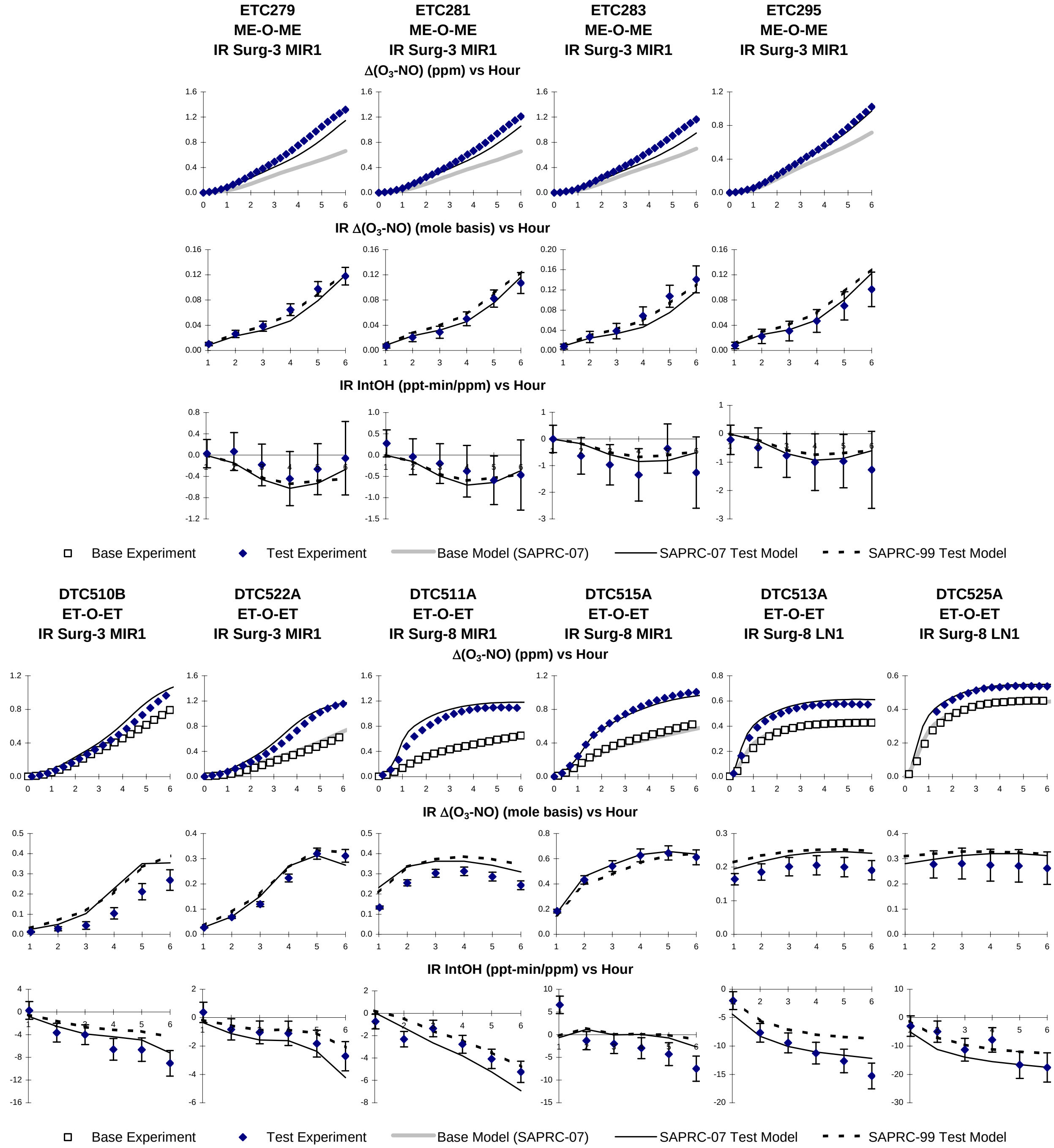


Figure C-49. Plots of experimental and calculated environmental chamber reactivity results for dimethyl ether and diethyl ether.

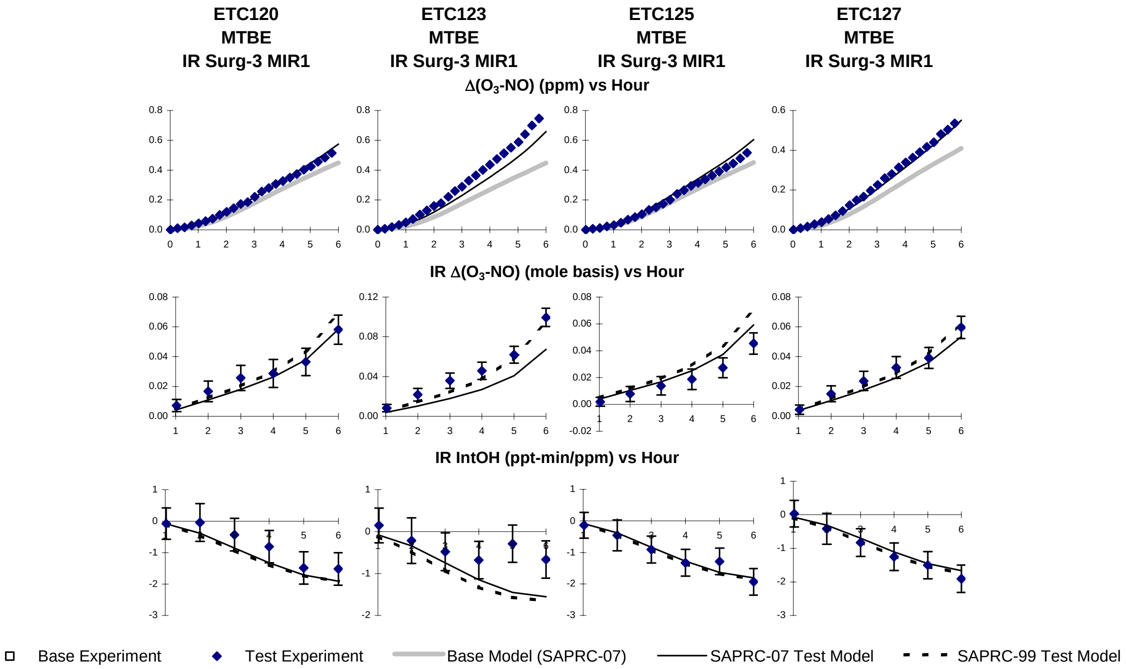


Figure C-50. Plots of experimental and calculated environmental chamber reactivity results for methyl t-butyl ether.

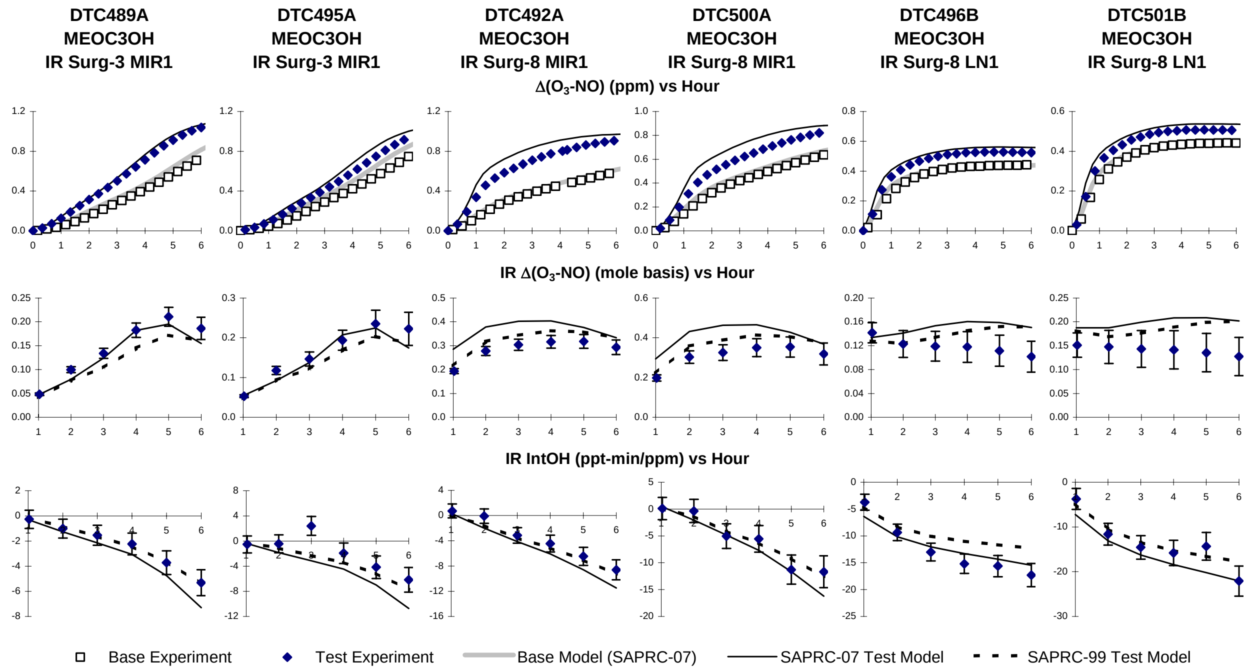


Figure C-51. Plots of experimental and calculated environmental chamber reactivity results for 1-methoxy-2-propanol.

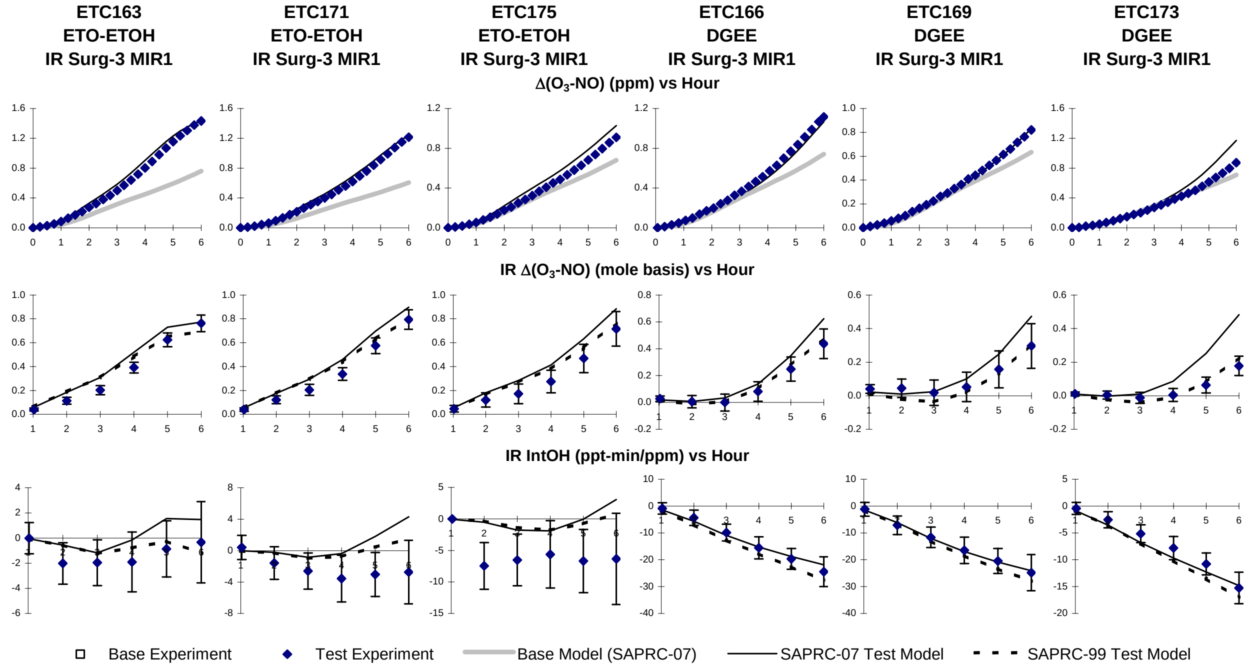


Figure C-52. Plots of experimental and calculated environmental chamber reactivity results for 2-ethoxyethanol and 2-(2-ethoxyethoxy) ethanol (DGEE).

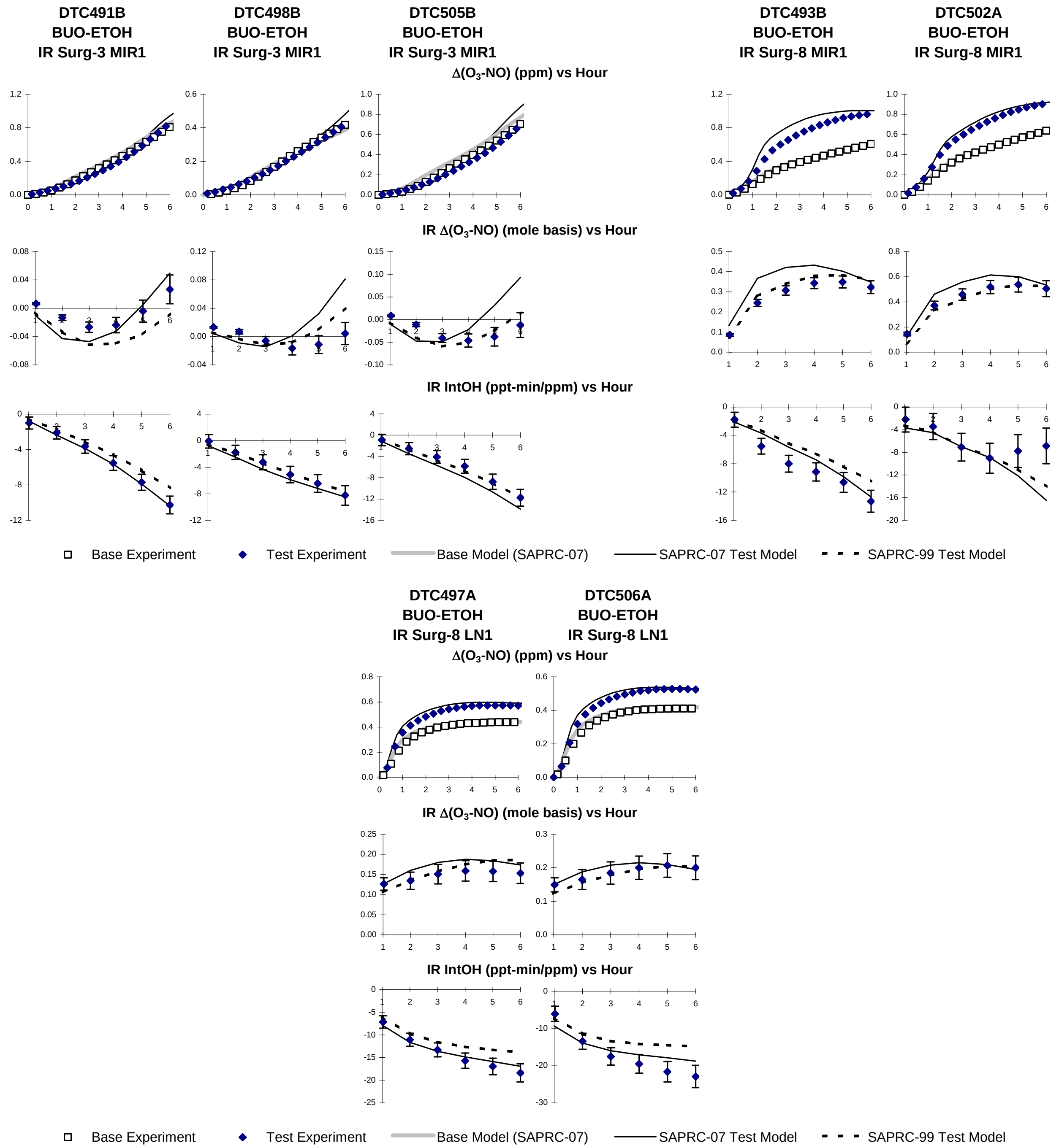


Figure C-53. Plots of experimental and calculated environmental chamber reactivity results for 2-butoxyethanol.

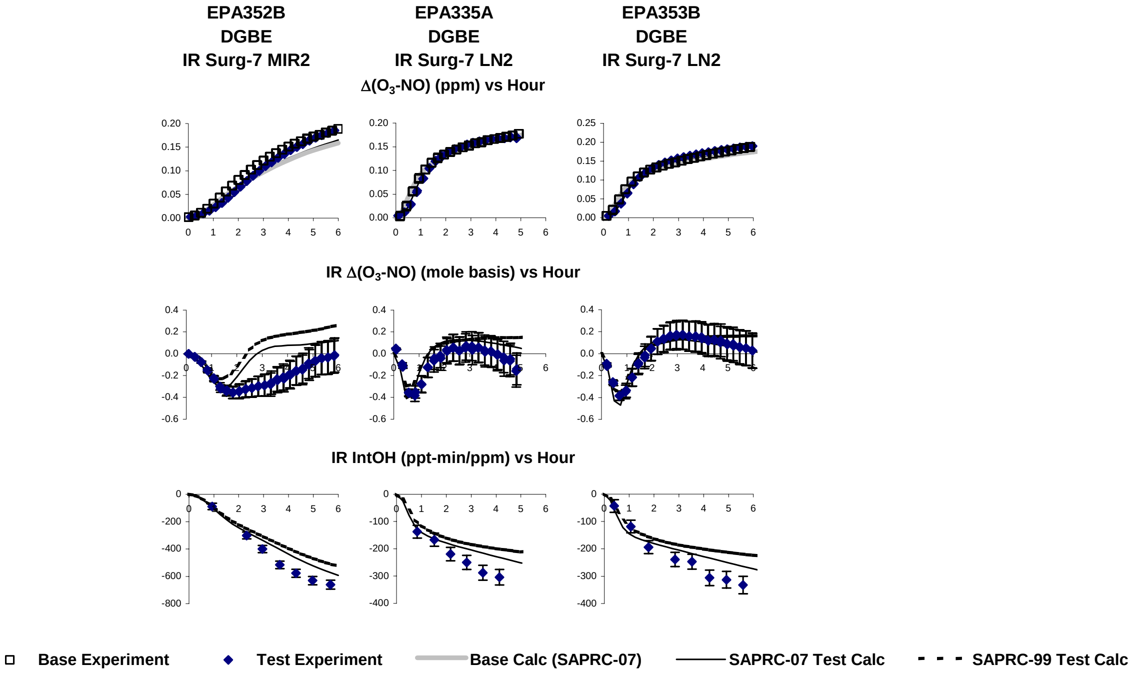


Figure C-54. Plots of experimental and calculated environmental chamber reactivity results for 2-(2-butoxyethoxy)-ethanol.

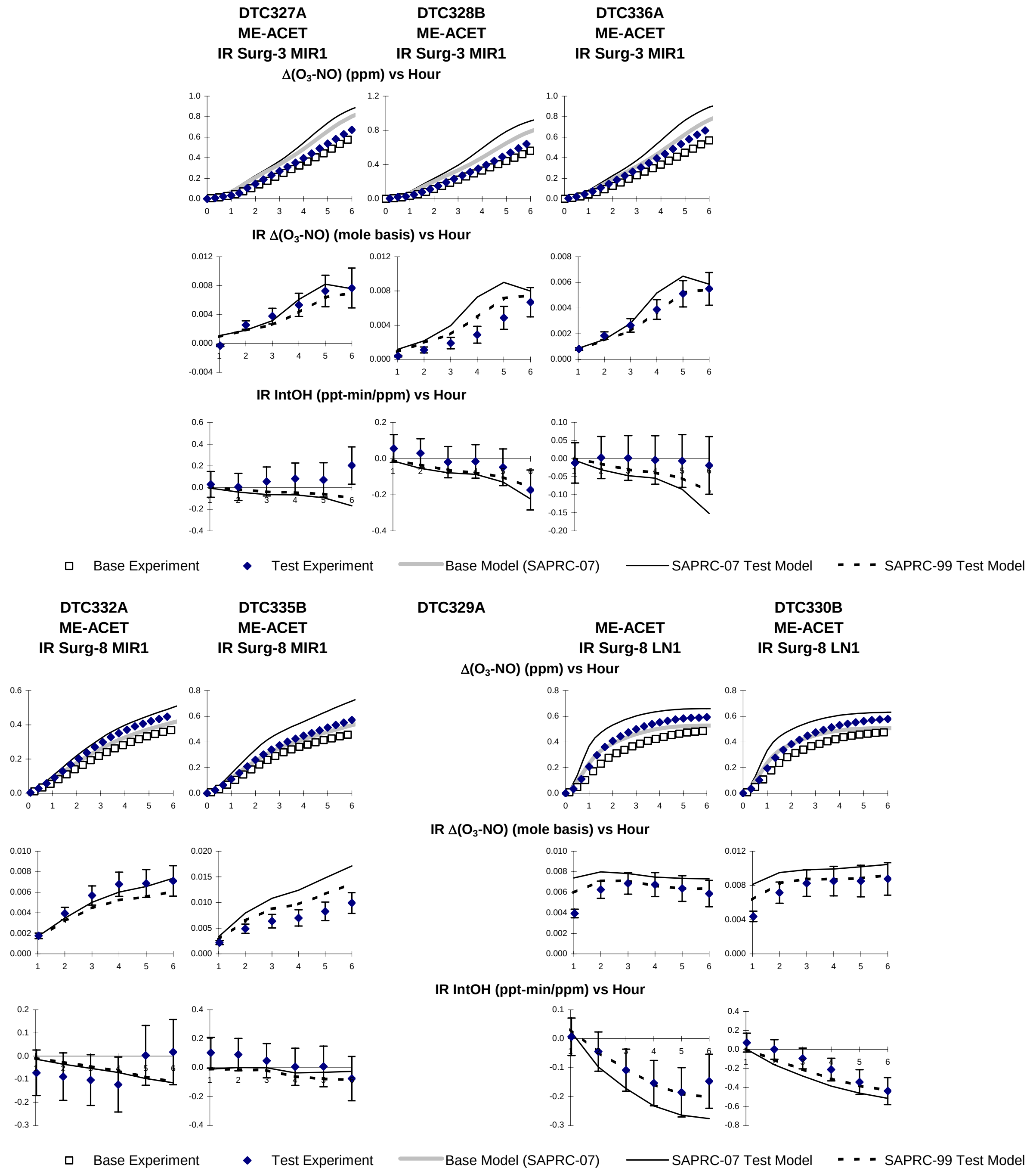


Figure C-55. Plots of experimental and calculated environmental chamber reactivity results for methyl acetate.

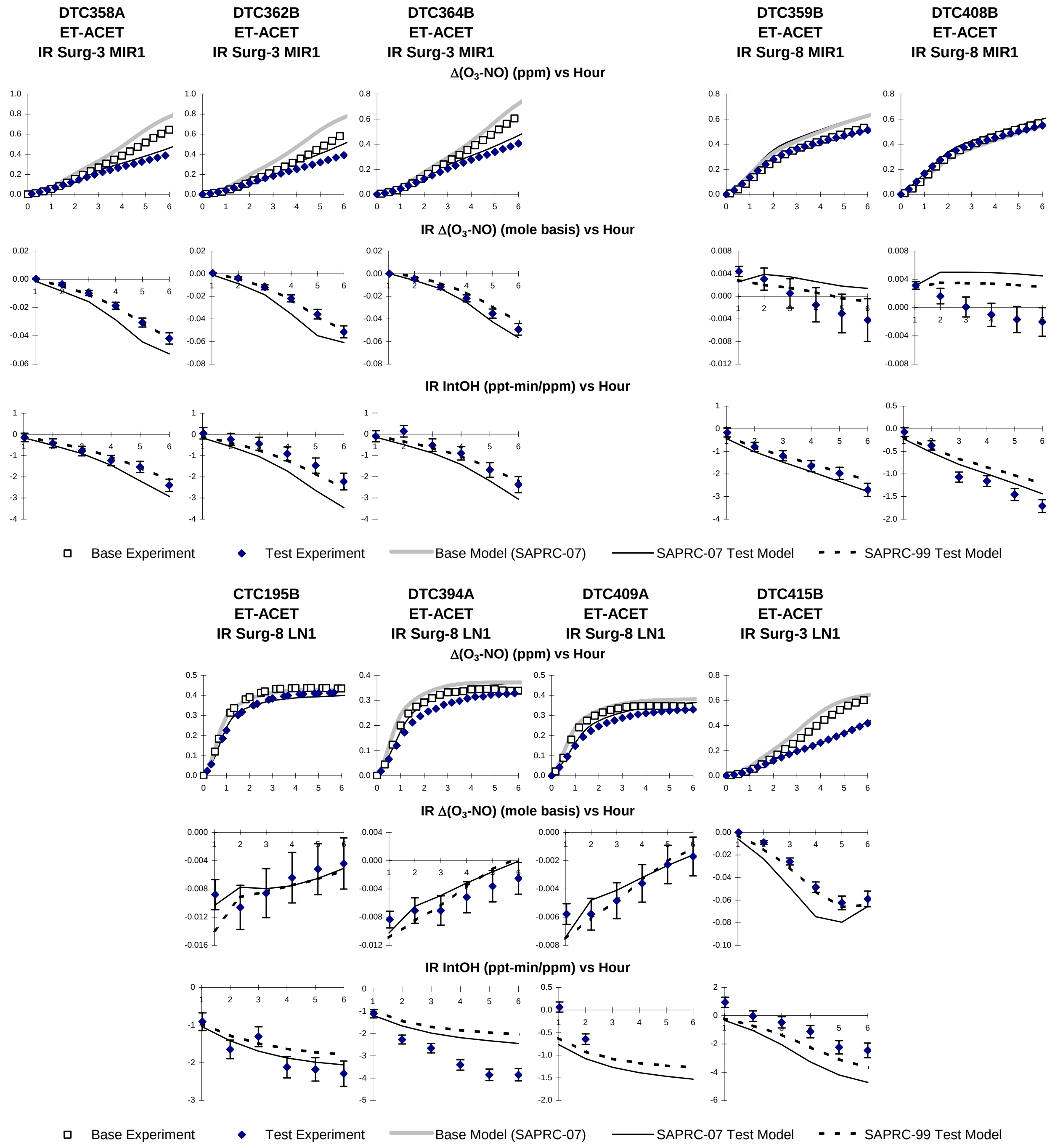


Figure C-56. Plots of experimental and calculated environmental chamber reactivity results for ethyl acetate.

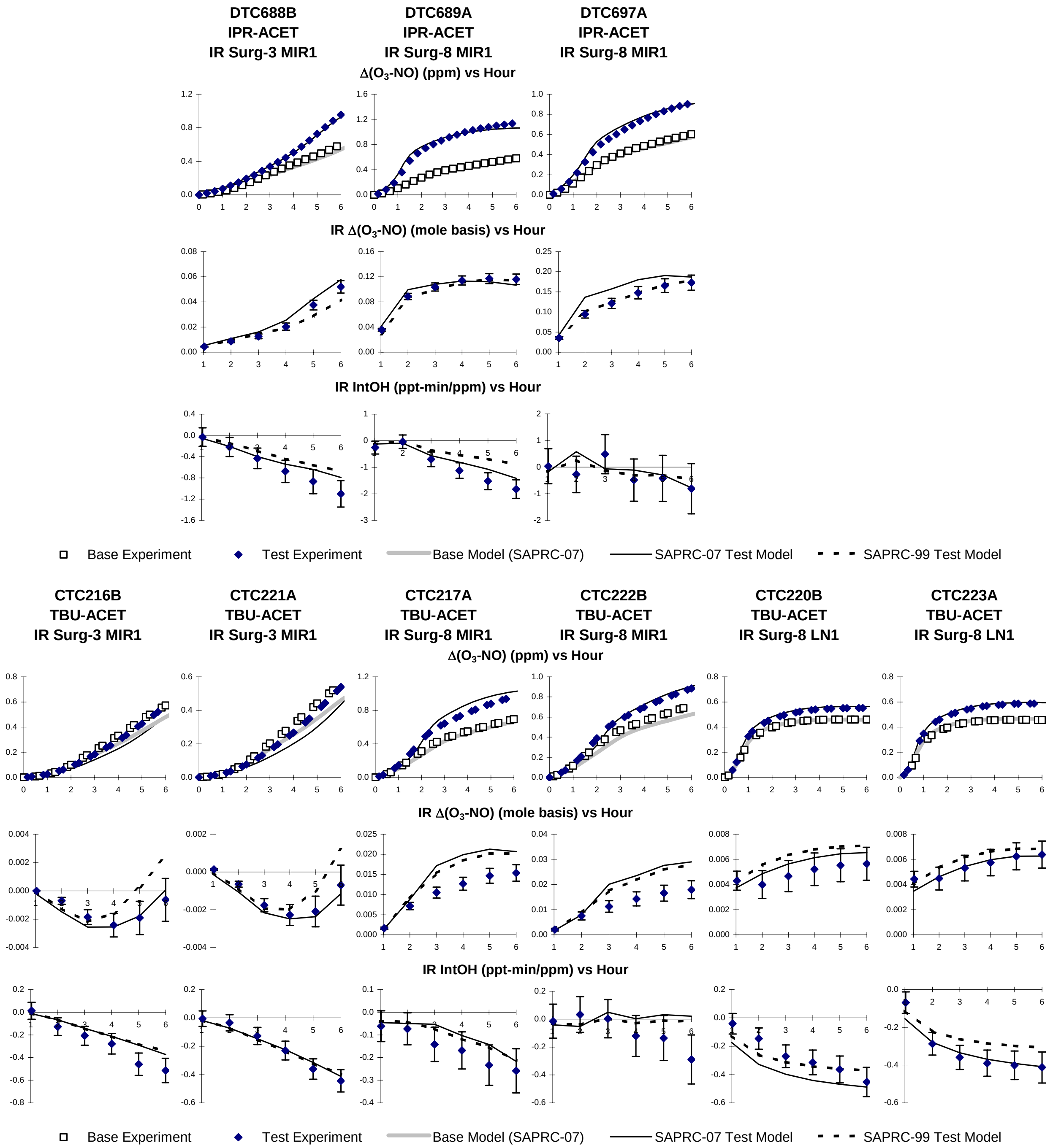


Figure C-57. Plots of experimental and calculated environmental chamber reactivity results for isopropyl and t-butyl acetates.

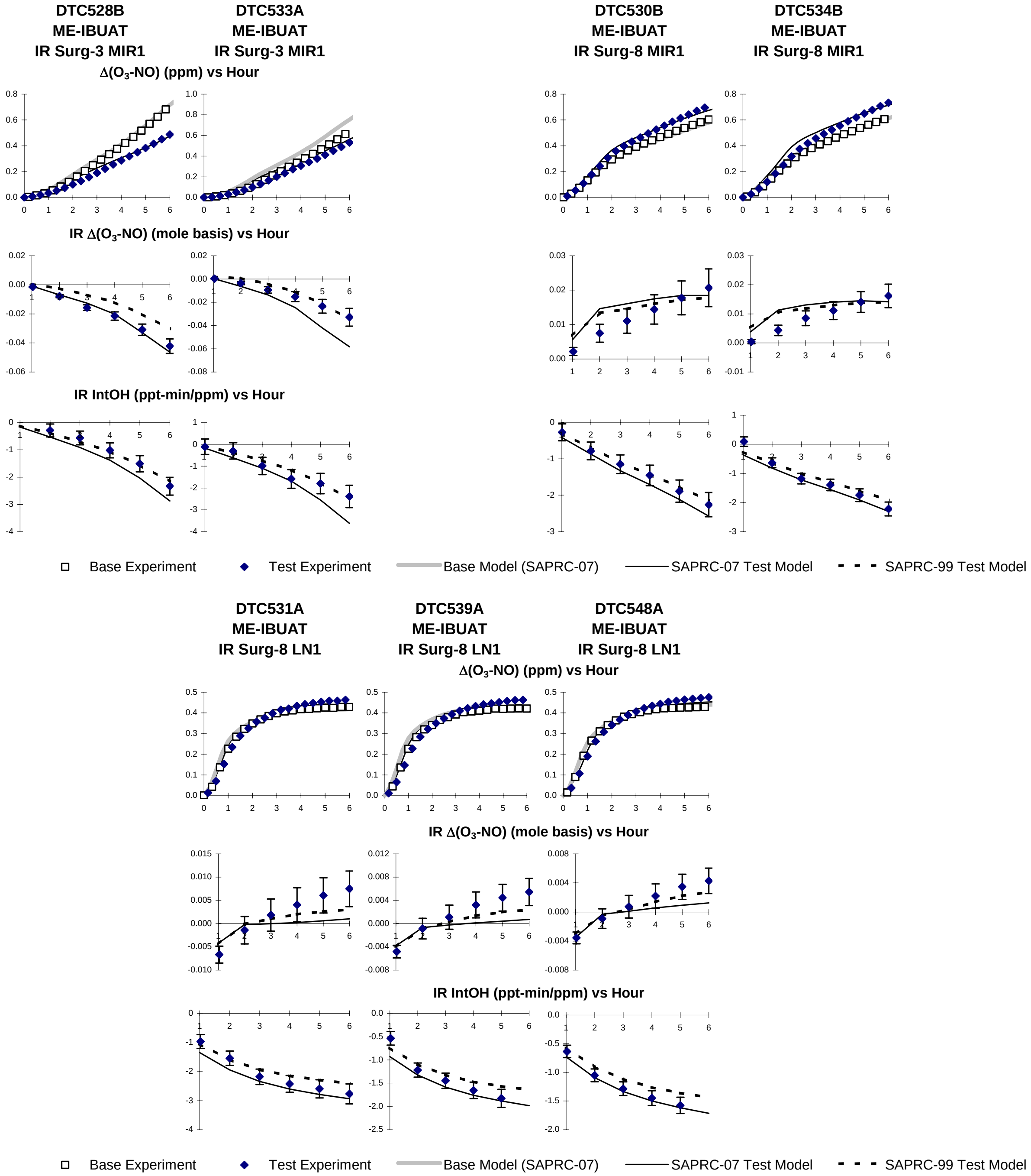


Figure C-58. Plots of experimental and calculated environmental chamber reactivity results for methyl isobutyrate.

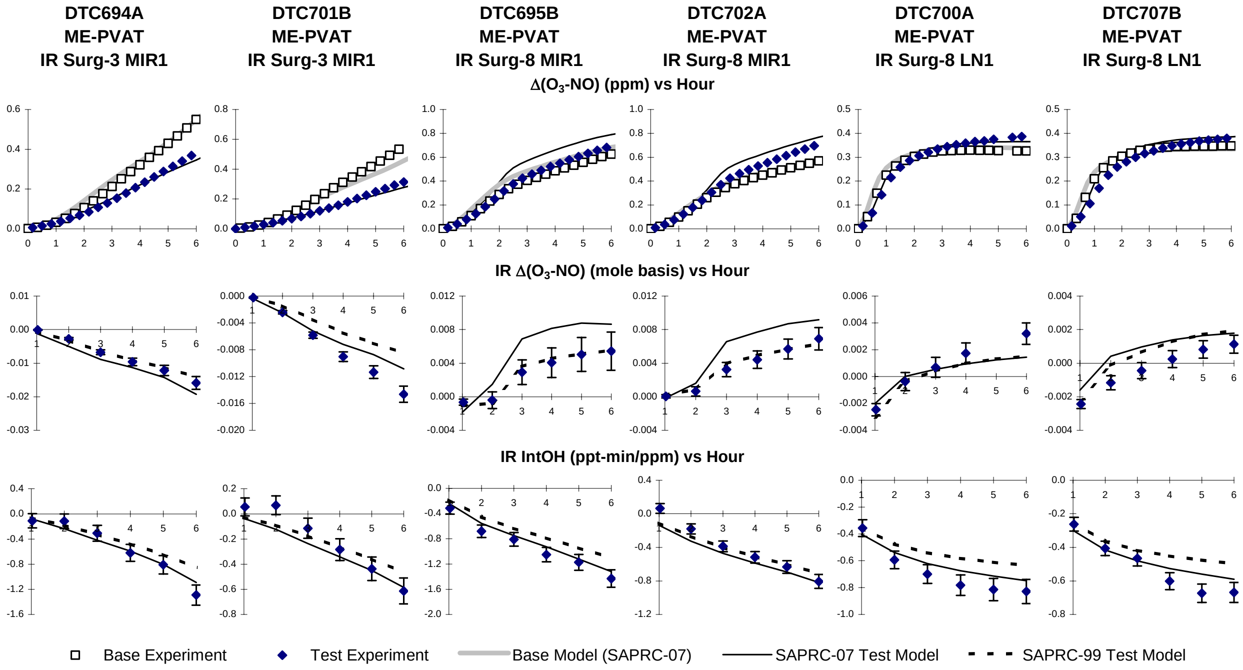


Figure C-59. Plots of experimental and calculated environmental chamber reactivity results for methyl pivalate.

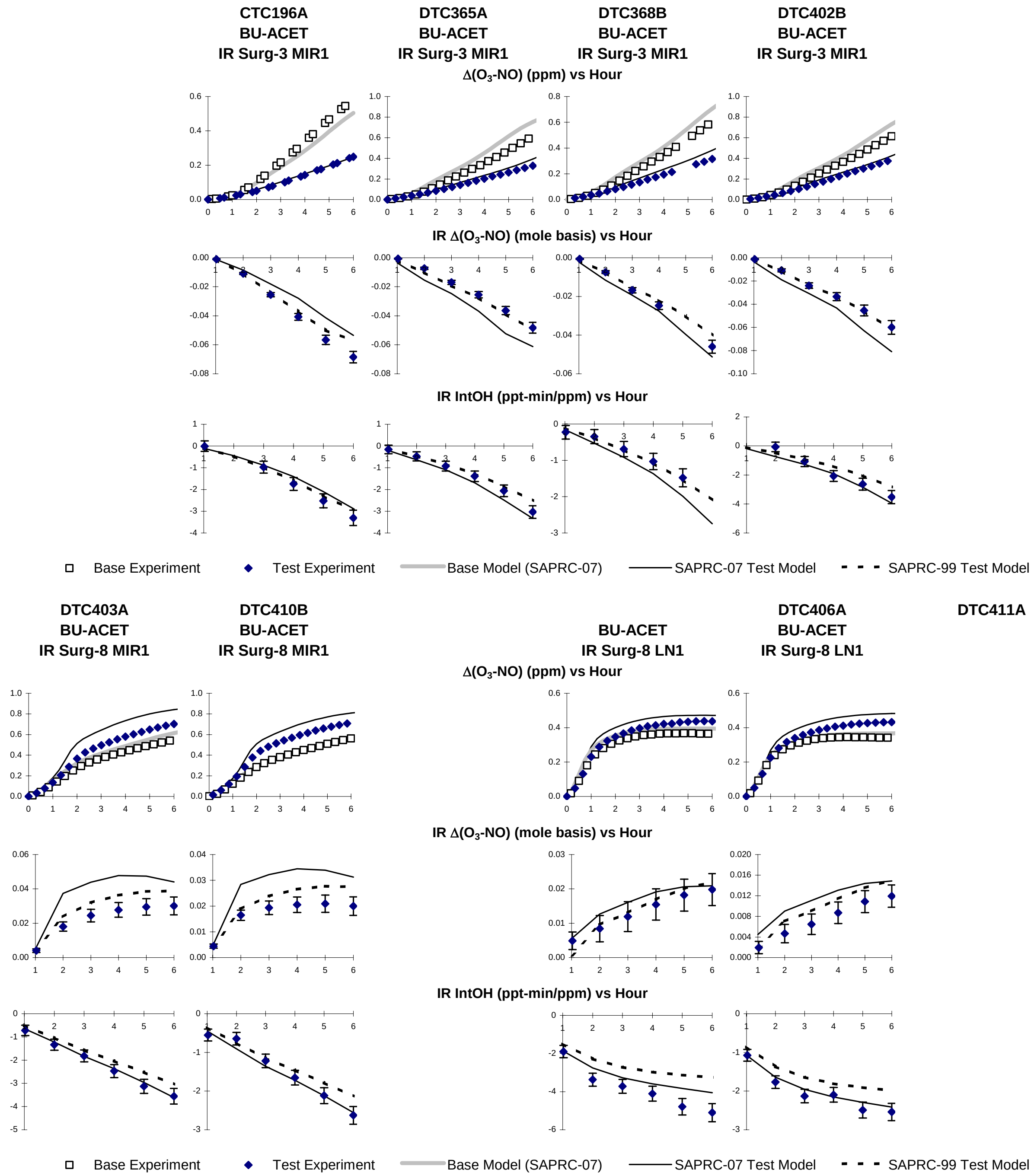


Figure C-60. Plots of experimental and calculated environmental chamber reactivity results for n-butyl acetate.

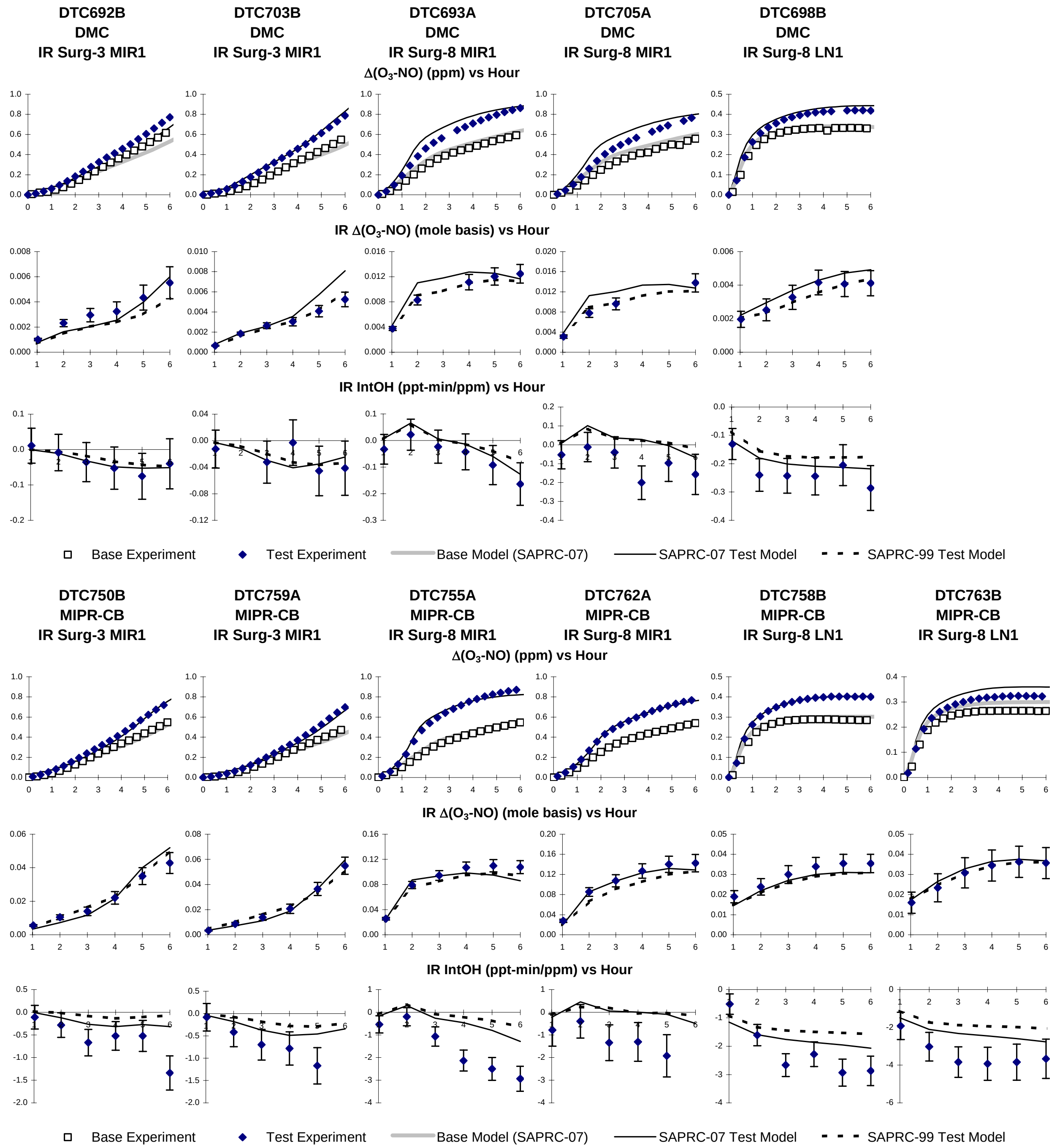


Figure C-61. Plots of experimental and calculated environmental chamber reactivity results for dimethyl carbonate and methyl isopropyl carbonate.

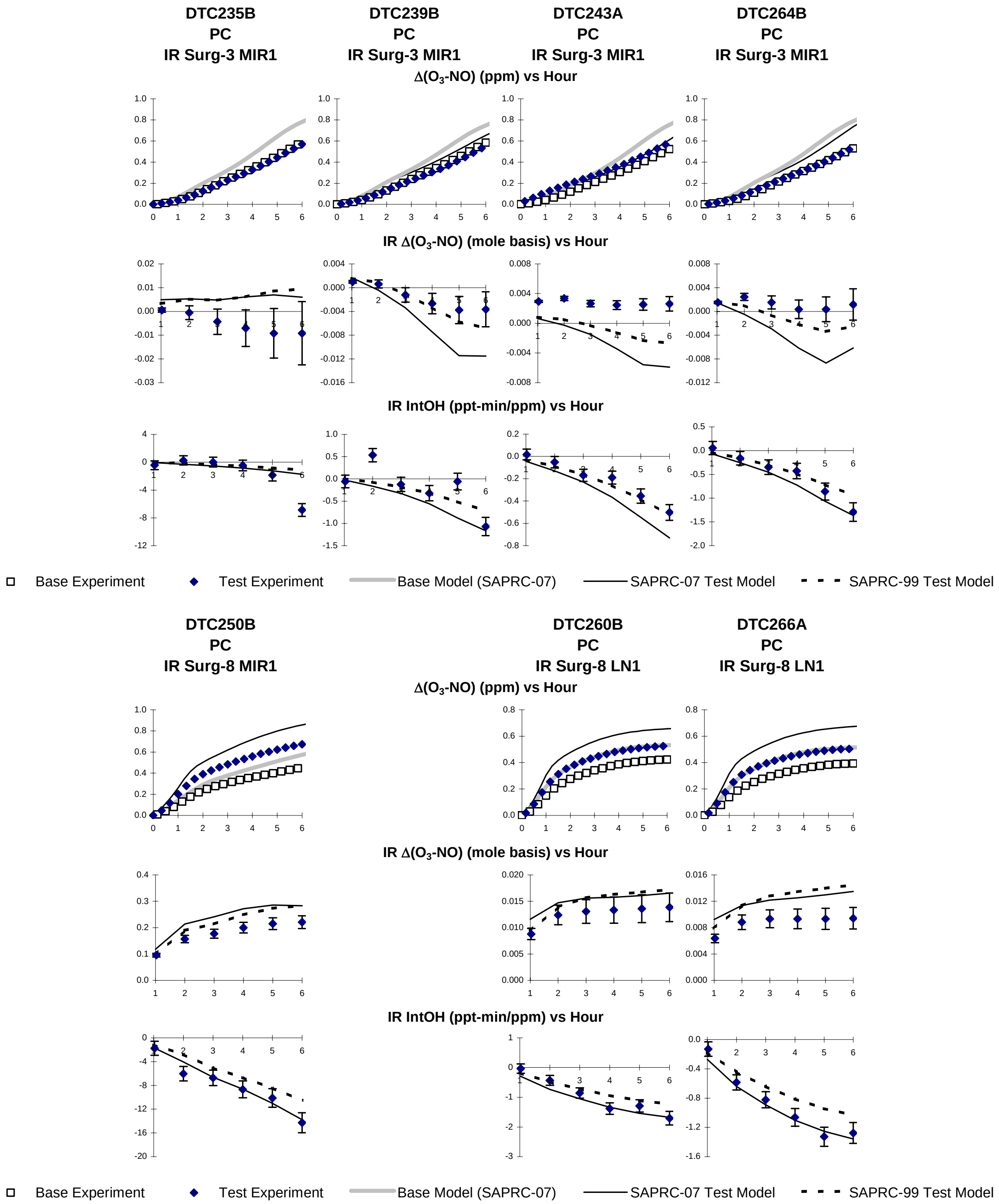


Figure C-62. Plots of experimental and calculated environmental chamber reactivity results for propylene carbonate.

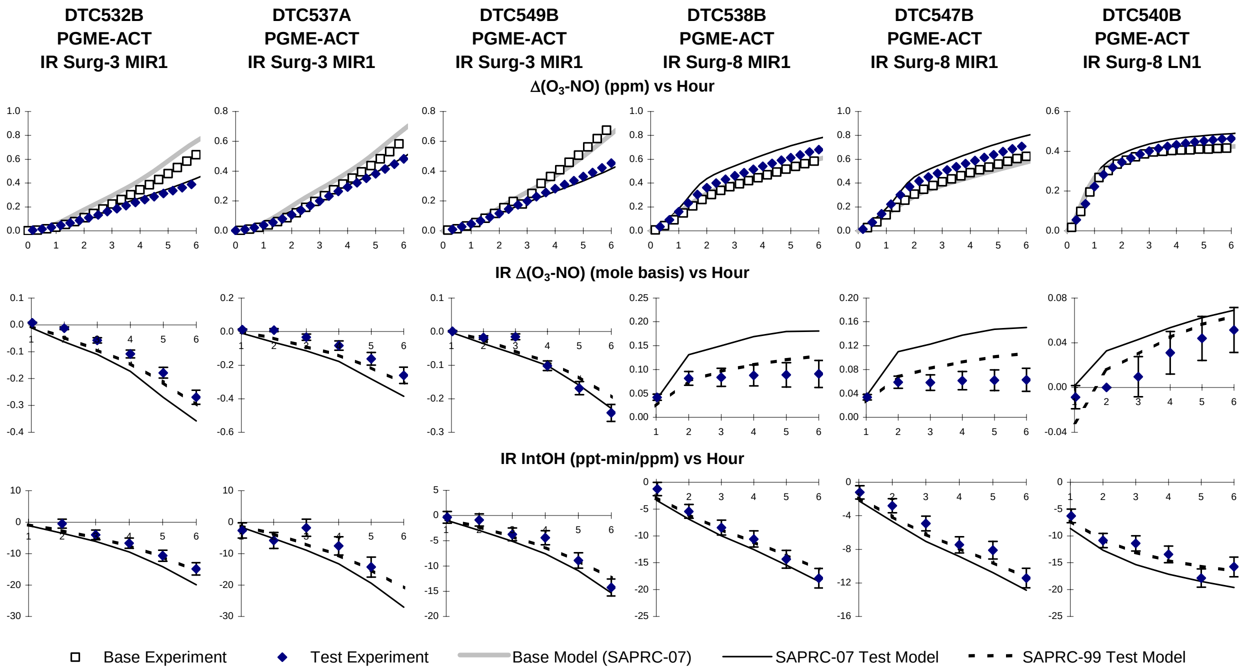


Figure C-63. Plots of experimental and calculated environmental chamber reactivity results for 1-methoxy-2-propyl acetate.

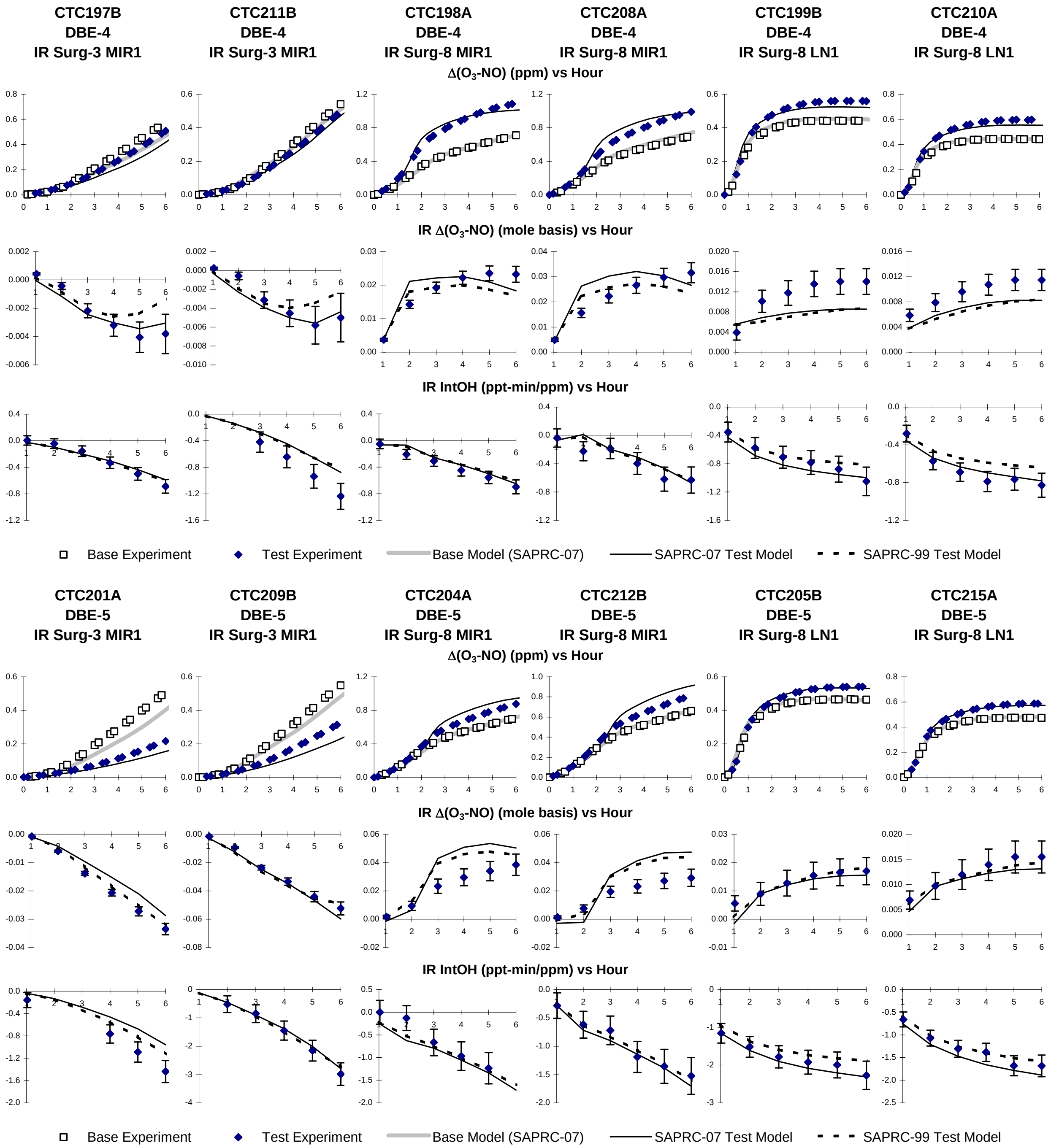


Figure C-64. Plots of experimental and calculated environmental chamber reactivity results for dimethyl succinate and dimethyl glutarate.

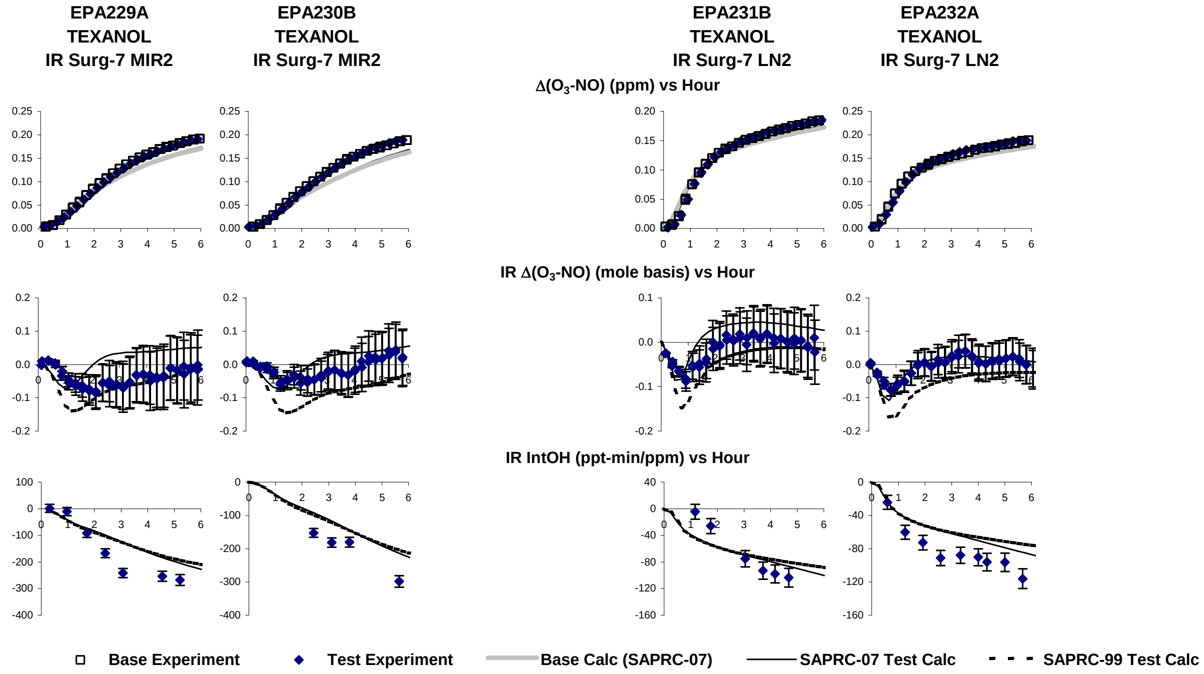


Figure C-65. Plots of experimental and calculated environmental chamber reactivity results for the Texanol®[1] isomers.

---

[1] Texanol is a trademark of Eastman Chemical Company.

Furan - NOx Experiments

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
EPA Chm., Arc	2	-29%	1%	-28%	-25%
EPA Chm, Black	2	-55%	-26%	12%	-26%
ITC Chamber	4	-20%	47%	-15%	1%

◆ EPA Chm., Arc

■ EPA Chm, Black

▲ ITC Chamber

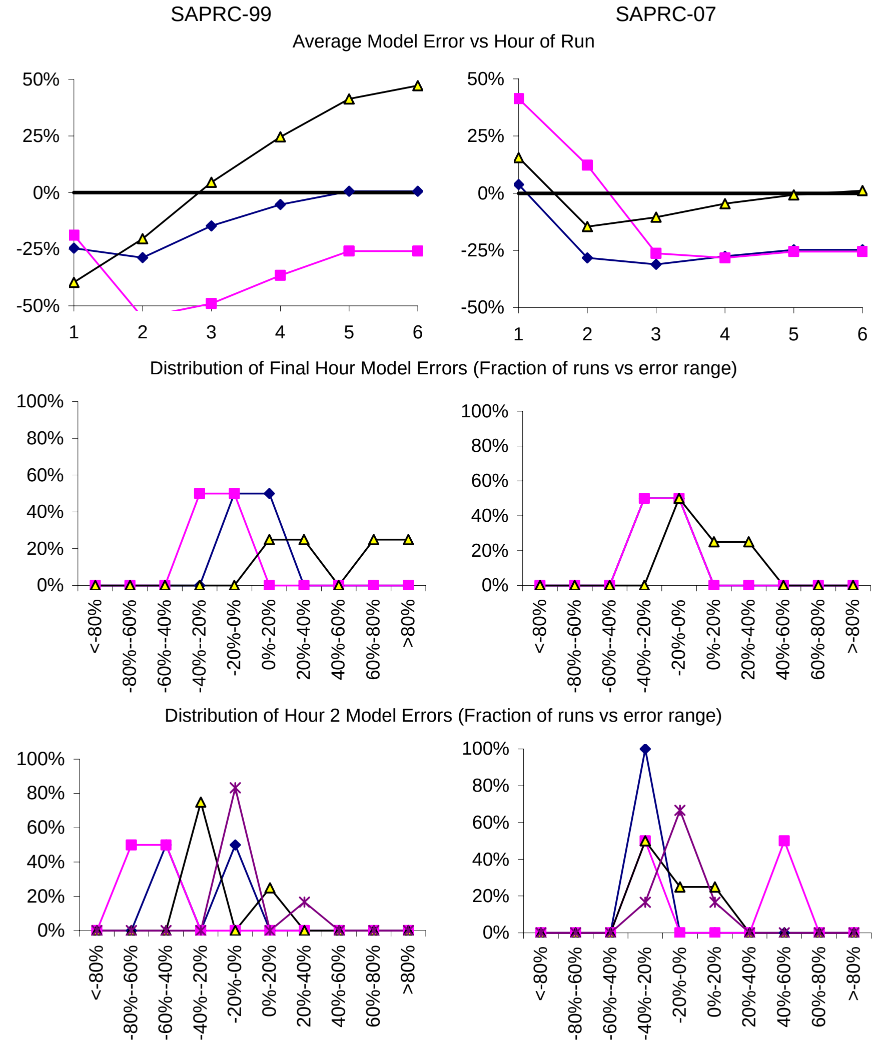


Figure C-66. Plots of model errors in simulations of the furan - NO_x environmental chamber experiments.

Methylfuran - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99	SAPRC-07 2-Hr	 Final
2-Methyl, Arc	2	(Not represented)	-13%	-12%
3-Methyl, Arc	4		-15%	-23%
3-Methyl, Black	2		-3%	-21%
2,5-Dimethyl, Arc	2		-19%	-24%

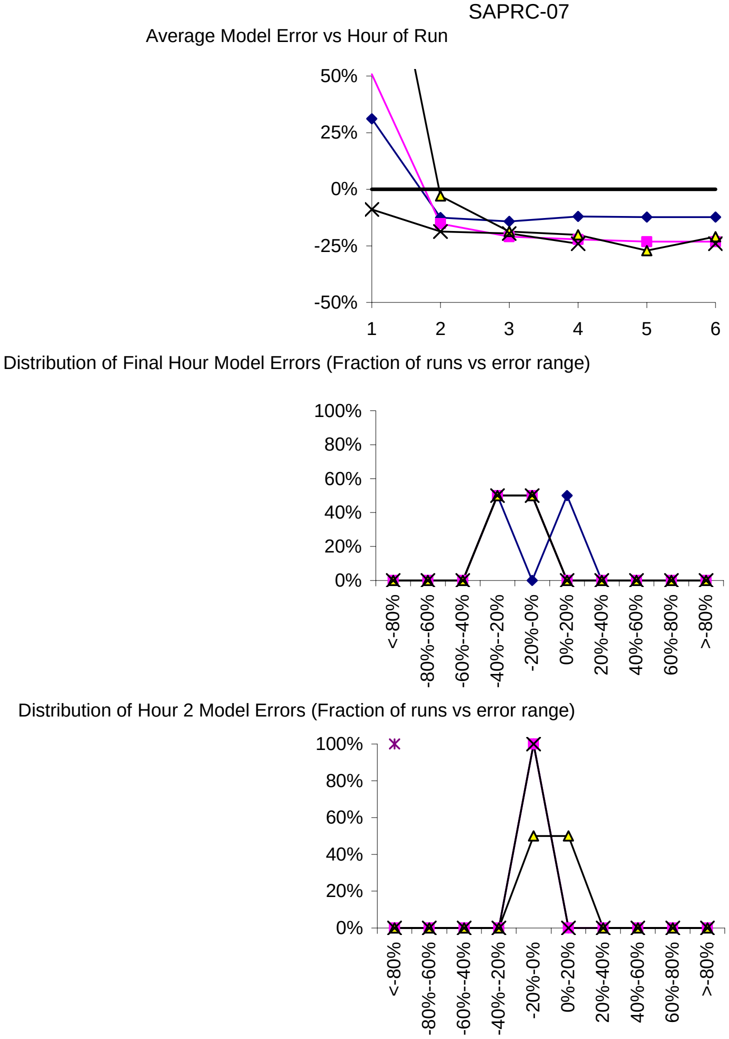


Figure C-67. Plots of model errors in simulations of the methyl furan - NO_x environmental chamber experiments.

Benzyl Alcohol - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
Arc Light	3	7%	18%	-1%	10%
Blacklight	2	-17%	11%	20%	7%
Added CO	1	-11%	3%	-14%	19%

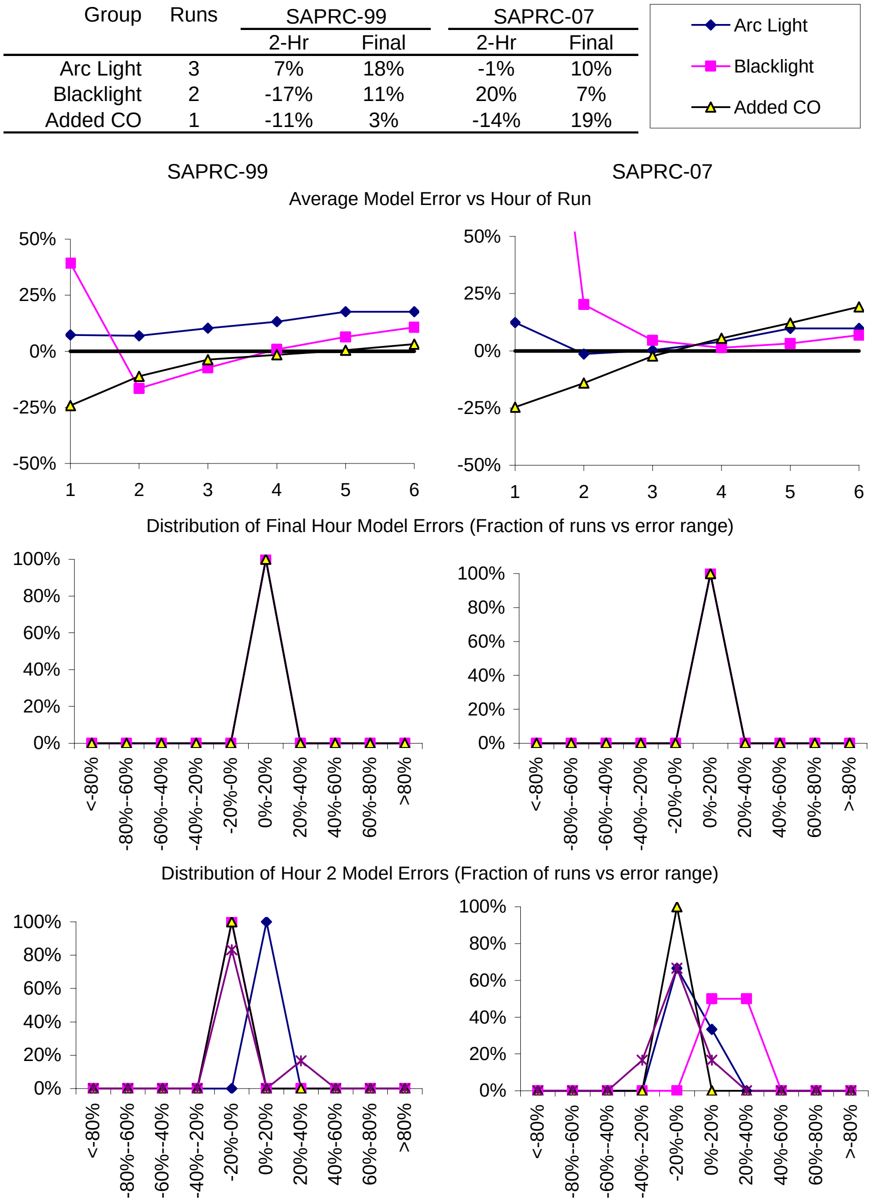


Figure C-68. Plots of model errors in simulations of the benzyl alcohol and benzyl alcohol + CO - NO_x environmental chamber experiments.

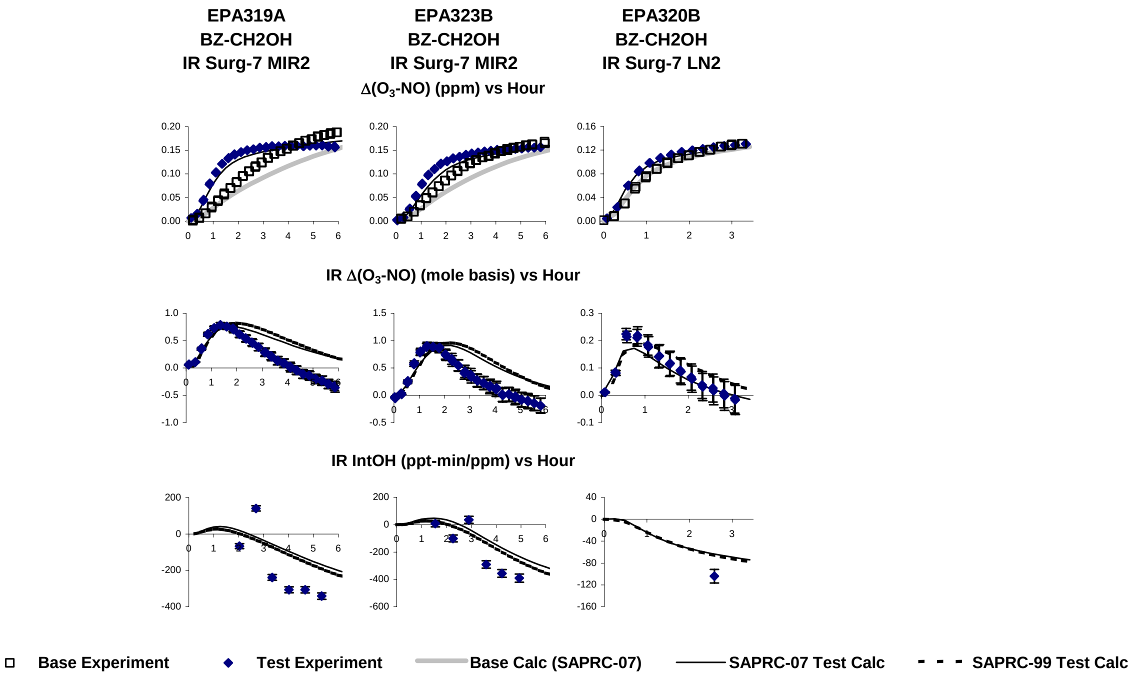
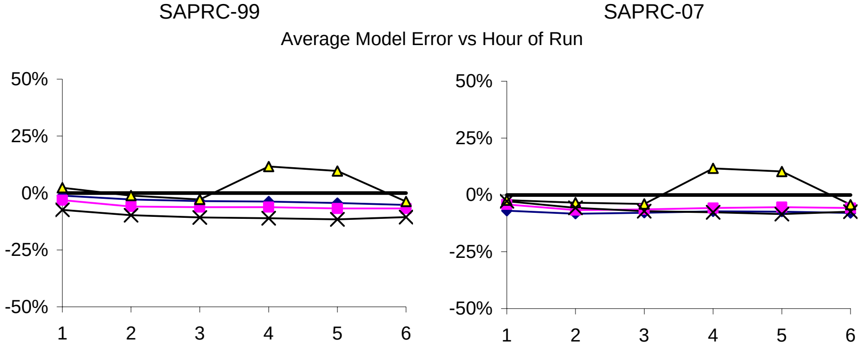


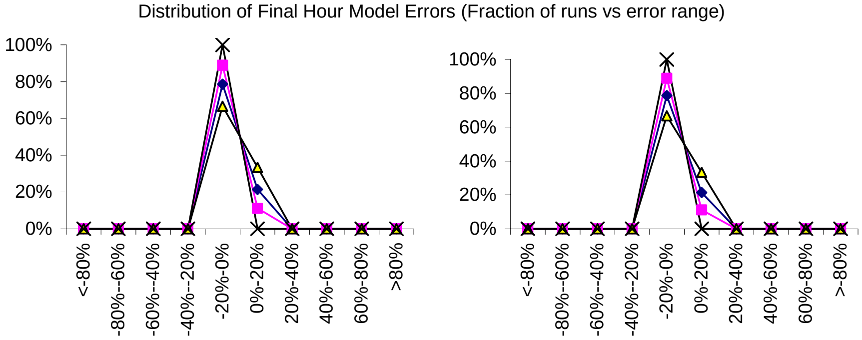
Figure C-69. Plots of experimental and calculated environmental chamber reactivity results for benzyl alcohol.

Formaldehyde - NOx Runs

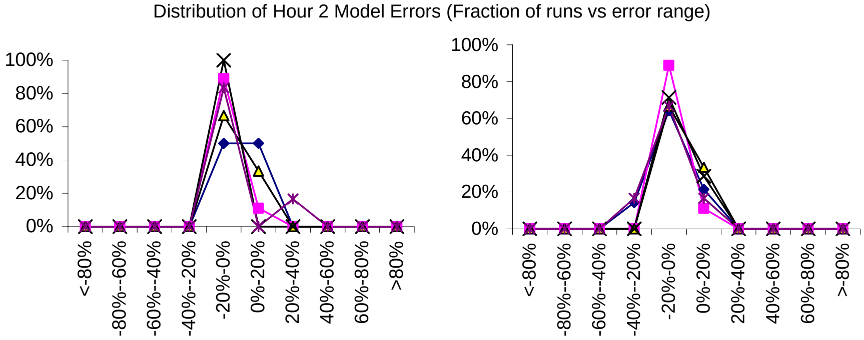
Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
UCR Arc Light	14	-3%	-5%	-8%	-8%
UCR Blacklight	9	-6%	-7%	-7%	-6%
TVA chamber	3	-1%	-4%	-3%	-4%
Added CO	7	-10%	-11%	-6%	-7%



Average Model Error vs Hour of Run



Distribution of Final Hour Model Errors (Fraction of runs vs error range)



Distribution of Hour 2 Model Errors (Fraction of runs vs error range)

Figure C-70. Plots of model errors in simulations of the formaldehyde - NO_x environmental chamber experiments.

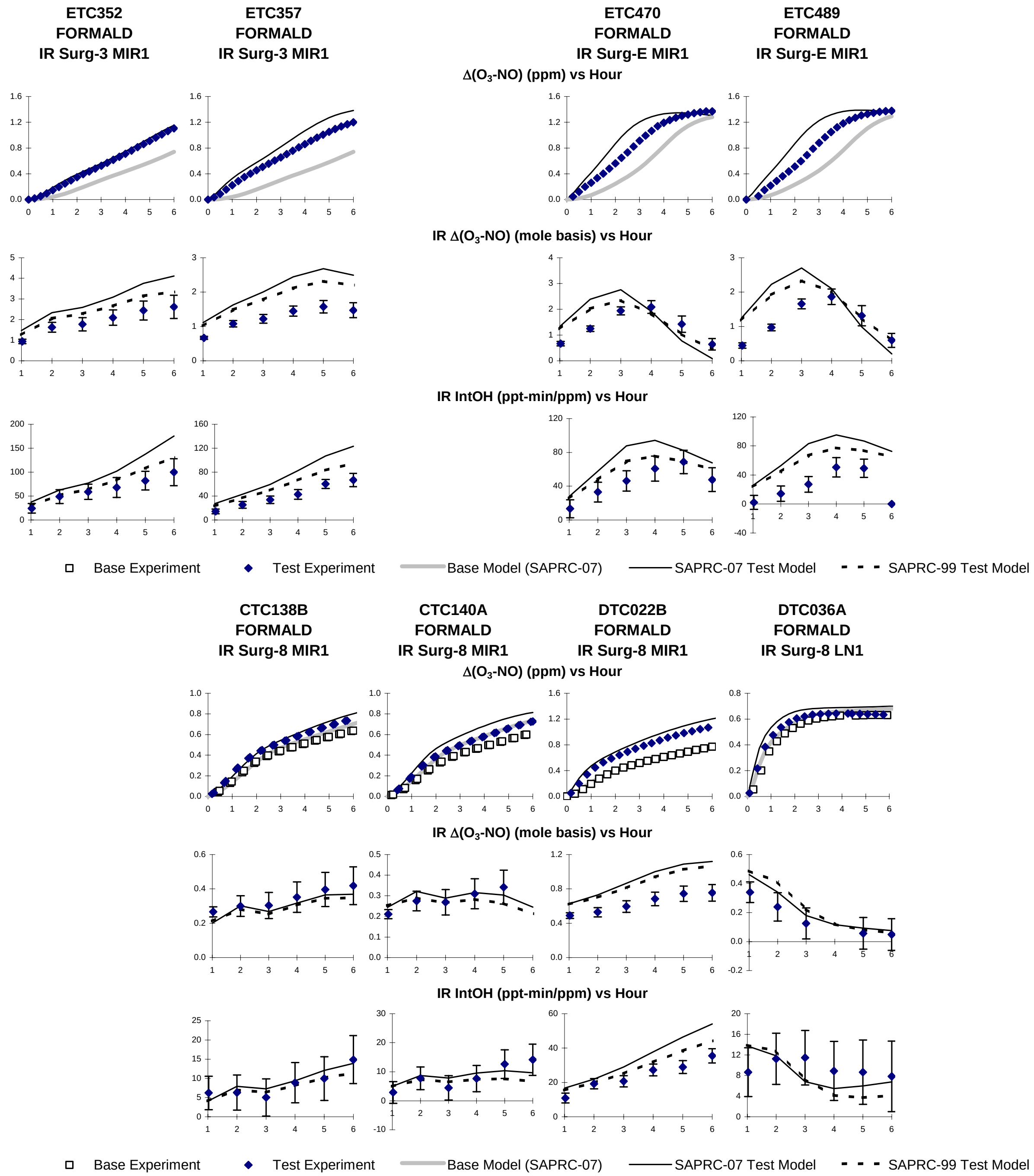


Figure C-71. Plots of experimental and calculated environmental chamber reactivity results for formaldehyde.

Acetaldehyde - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	SAPRC-99 Final	SAPRC-07 2-Hr	SAPRC-07 Final
Arc Light	8	17%	16%	5%	5%
Blacklight	5	8%	4%	2%	-1%
OTC Chamber	4	-2%	1%	-5%	-1%
Added CO	1	6%	-5%	6%	-5%

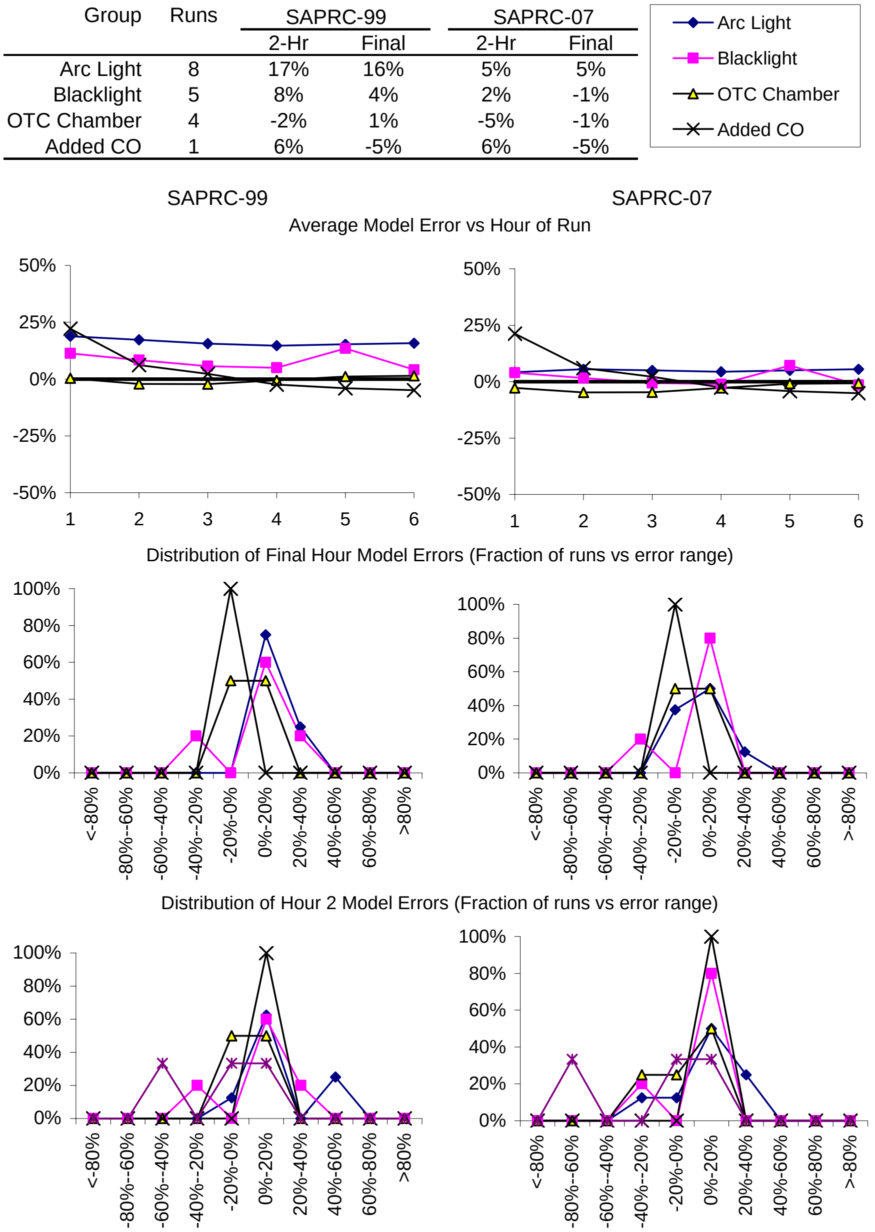


Figure C-72. Plots of model errors in simulations of the acetaldehyde - NO_x environmental chamber experiments.

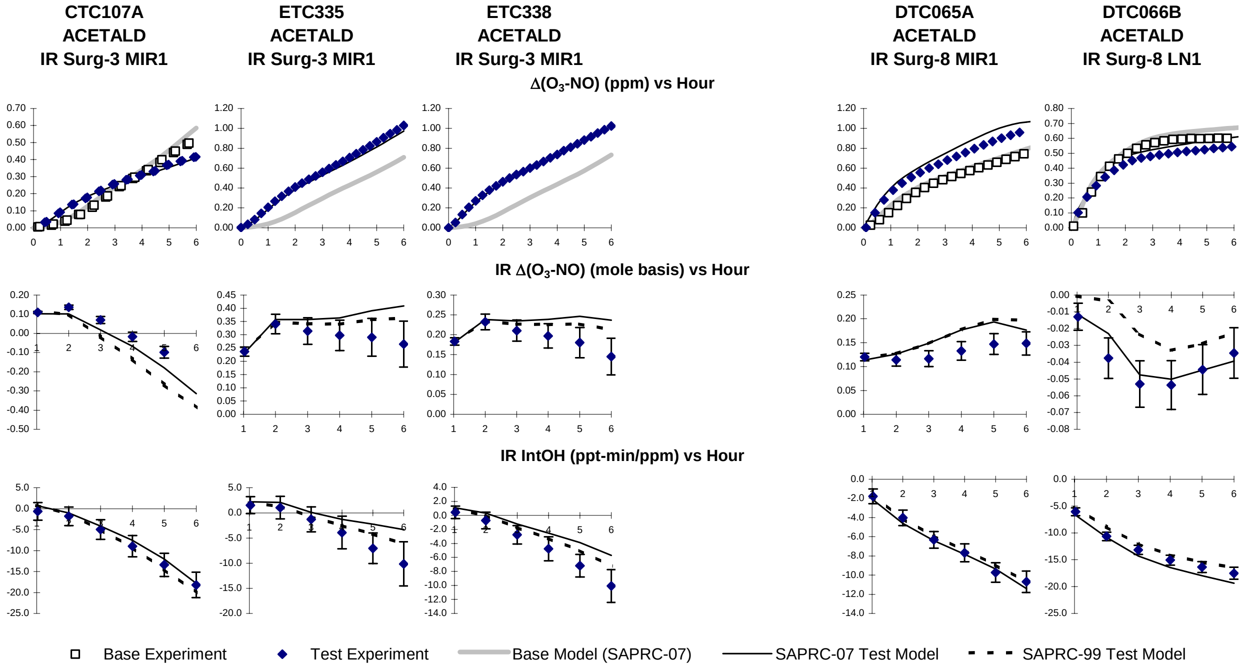


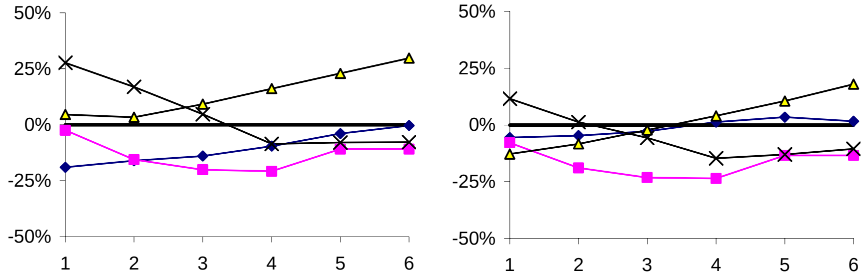
Figure C-73. Plots of experimental and calculated environmental chamber reactivity results for acetaldehyde.

Acrolein, Methacrolein - NOx Runs

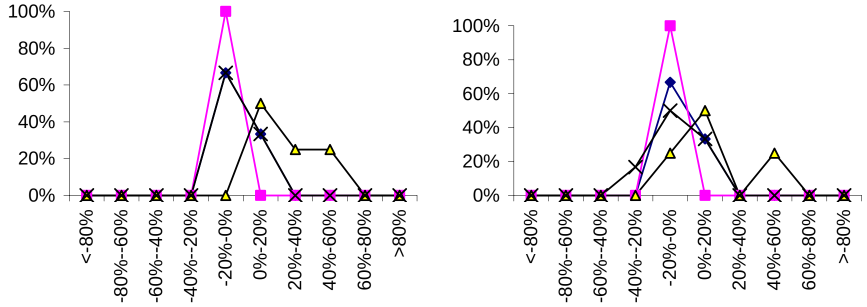
Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
Acrolein	3	-16%	0%	-5%	2%
MA, XTC Chamber	2	-16%	-11%	-19%	-13%
MA, EC Chamber	4	3%	30%	-8%	18%
MA, Blacklights	6	17%	-8%	1%	-11%

SAPRC-99 SAPRC-07

Average Model Error vs Hour of Run



Distribution of Final Hour Model Errors (Fraction of runs vs error range)



Distribution of Hour 2 Model Errors (Fraction of runs vs error range)

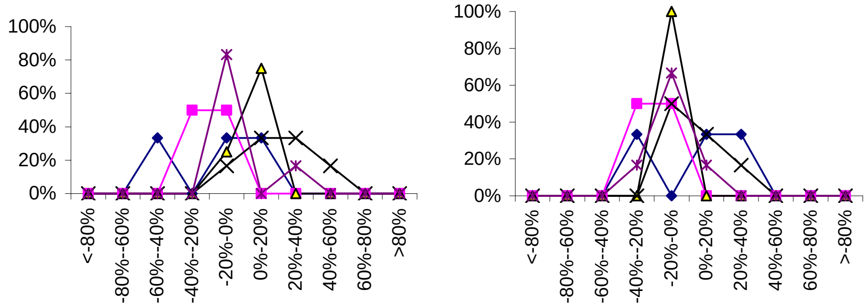


Figure C-74. Plots of model errors in simulations of the acrolein and methacrolein (MA) - NO_x environmental chamber experiments.

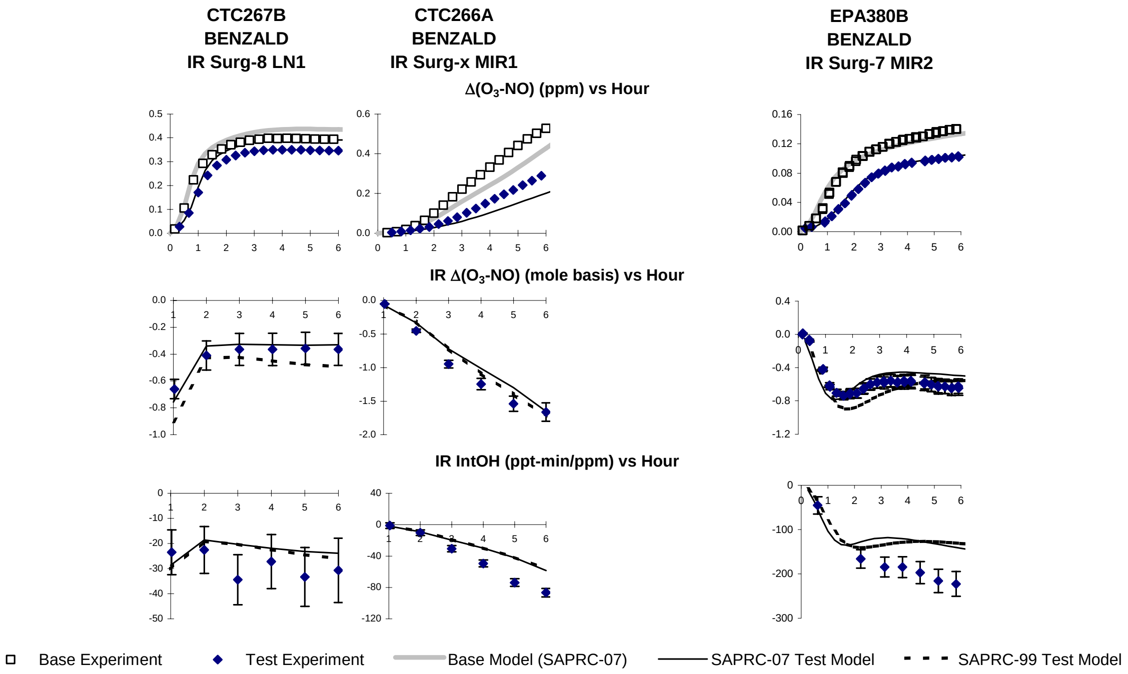
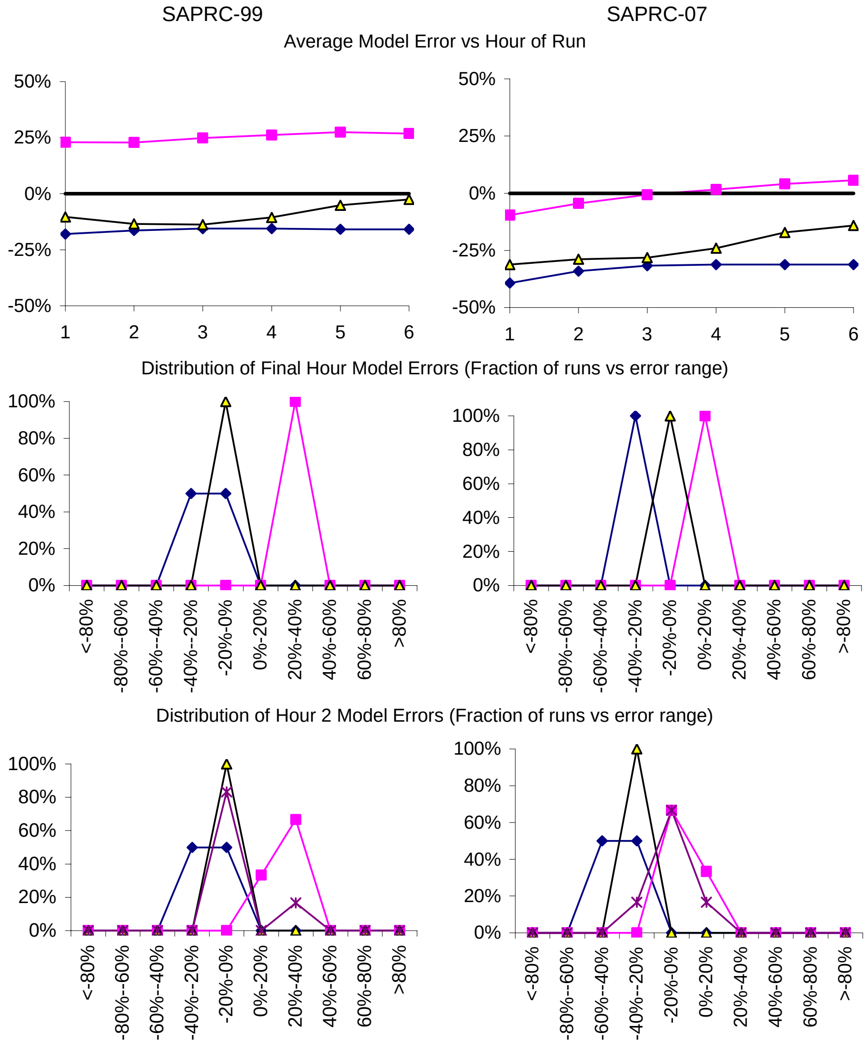


Figure C-75. Plots of experimental and calculated environmental chamber reactivity results for benzaldehyde.

Acetone - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
Arc Light	2	-16%	-16%	-34%	-31%
Blacklight	3	23%	27%	-4%	6%
OTC Chamber	2	-13%	-3%	-29%	-14%



SAPRC-99

SAPRC-07

Average Model Error vs Hour of Run

Distribution of Final Hour Model Errors (Fraction of runs vs error range)

Distribution of Hour 2 Model Errors (Fraction of runs vs error range)

Figure C-76. Plots of model errors in simulations of the acetone - NO_x environmental chamber experiments.

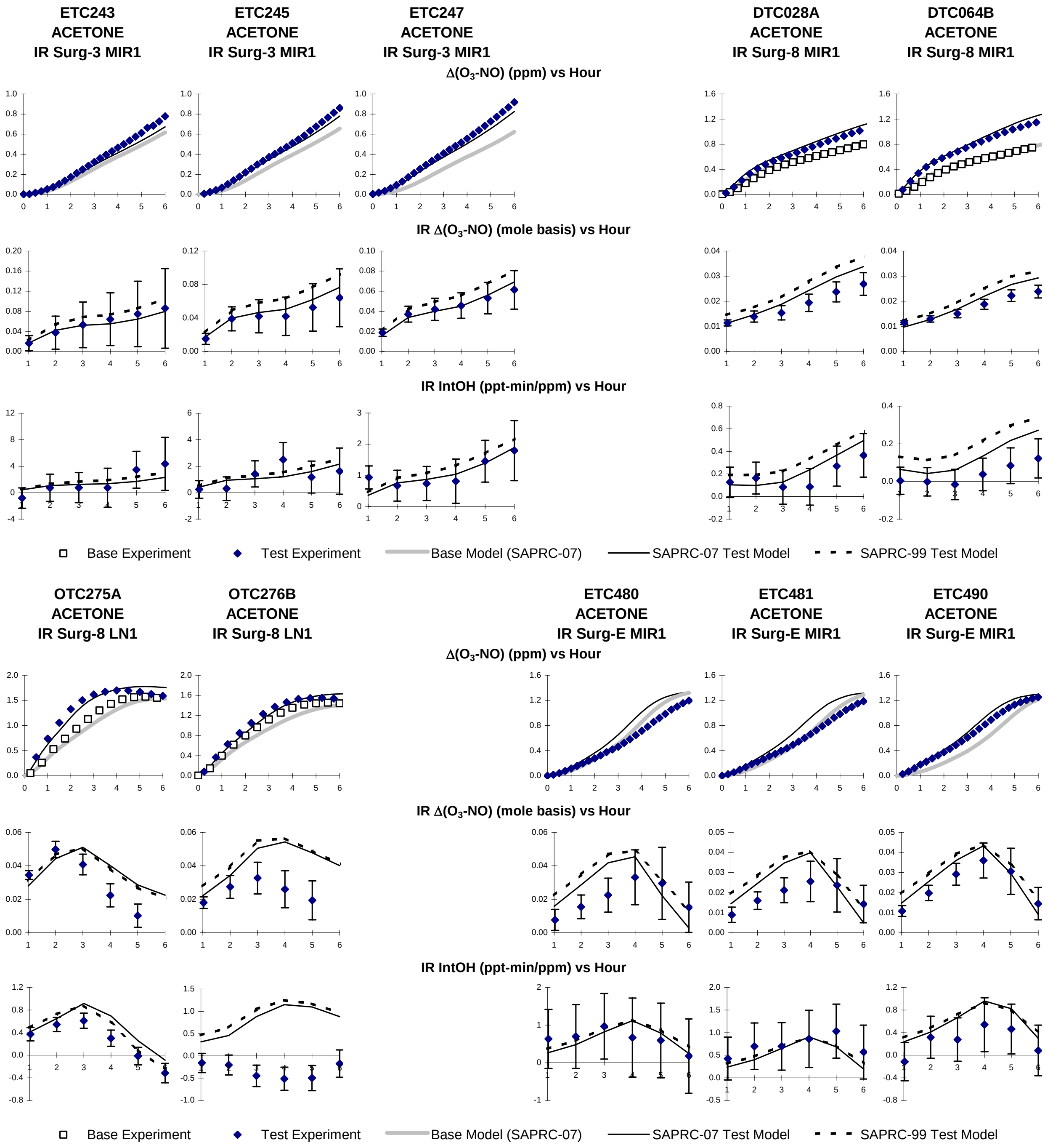


Figure C-77. Plots of experimental and calculated environmental chamber reactivity results for acetone.

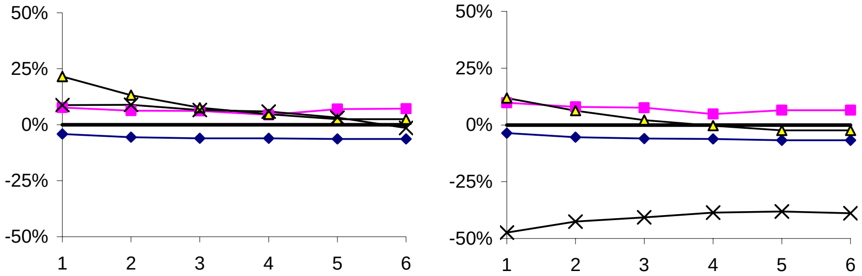
Ketone - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
MEK, Arc	2	-6%	-6%	-5%	-7%
MEK, Black	4	6%	7%	8%	7%
MPK	1	13%	2%	6%	-2%
2-Heptanone	1	9%	-1%	-43%	-39%

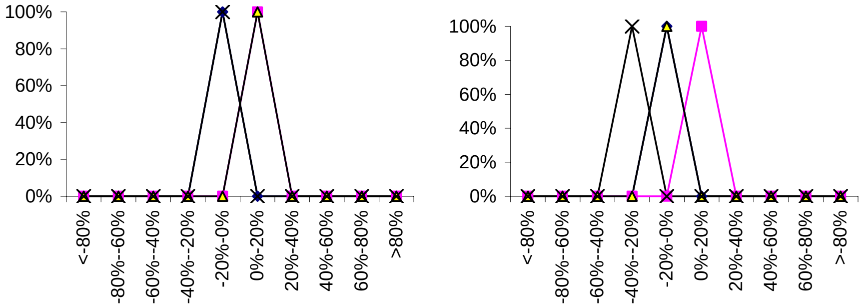
◆ MEK, Arc
■ MEK, Black
△ MPK
× 2-Heptanone

SAPRC-99 SAPRC-07

Average Model Error vs Hour of Run



Distribution of Final Hour Model Errors (Fraction of runs vs error range)



Distribution of Hour 2 Model Errors (Fraction of runs vs error range)

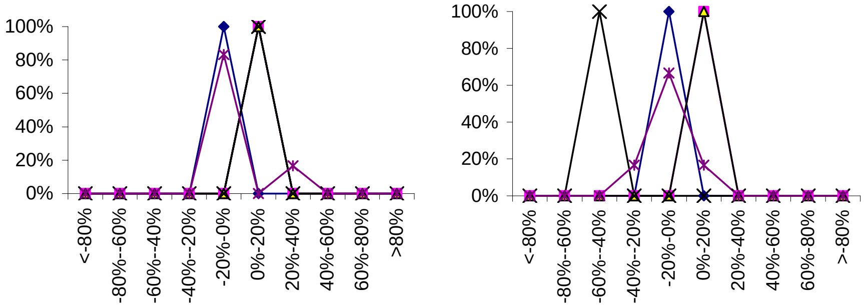


Figure C-78. Plots of model errors in simulations of the methyl ethyl ketone (MEK), 2-pentanone (MPK) and 2-heptanone - NO_x environmental chamber experiments.

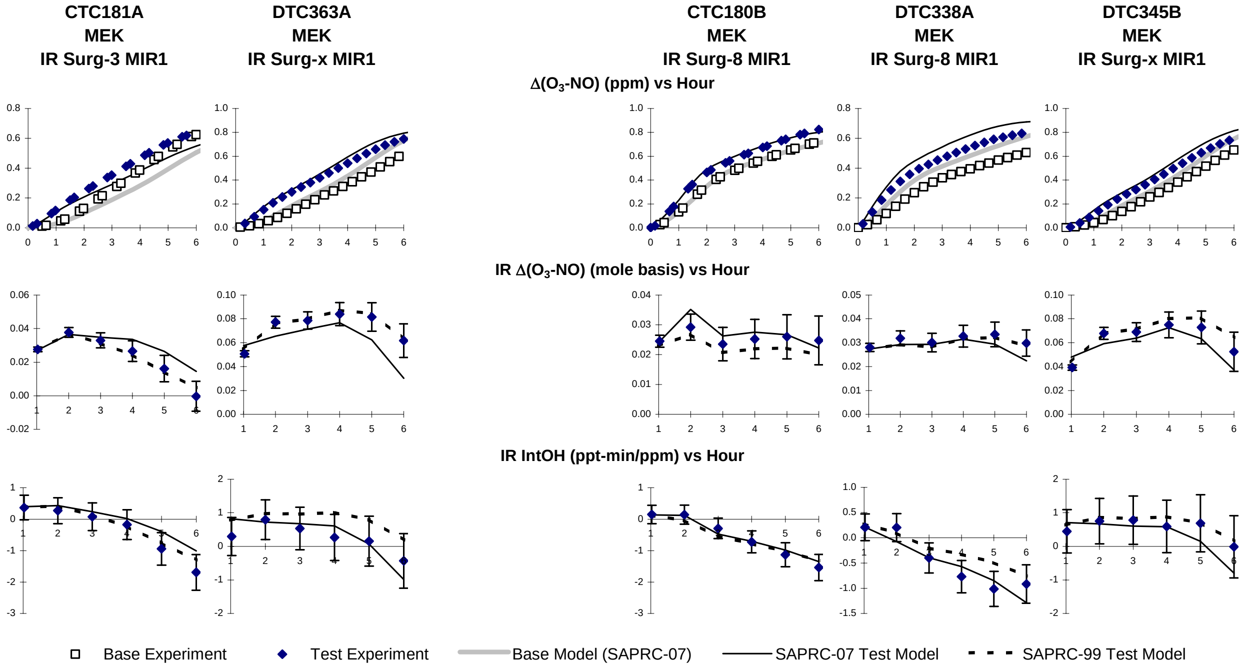


Figure C-79. Plots of experimental and calculated environmental chamber reactivity results for methyl ethyl ketone.

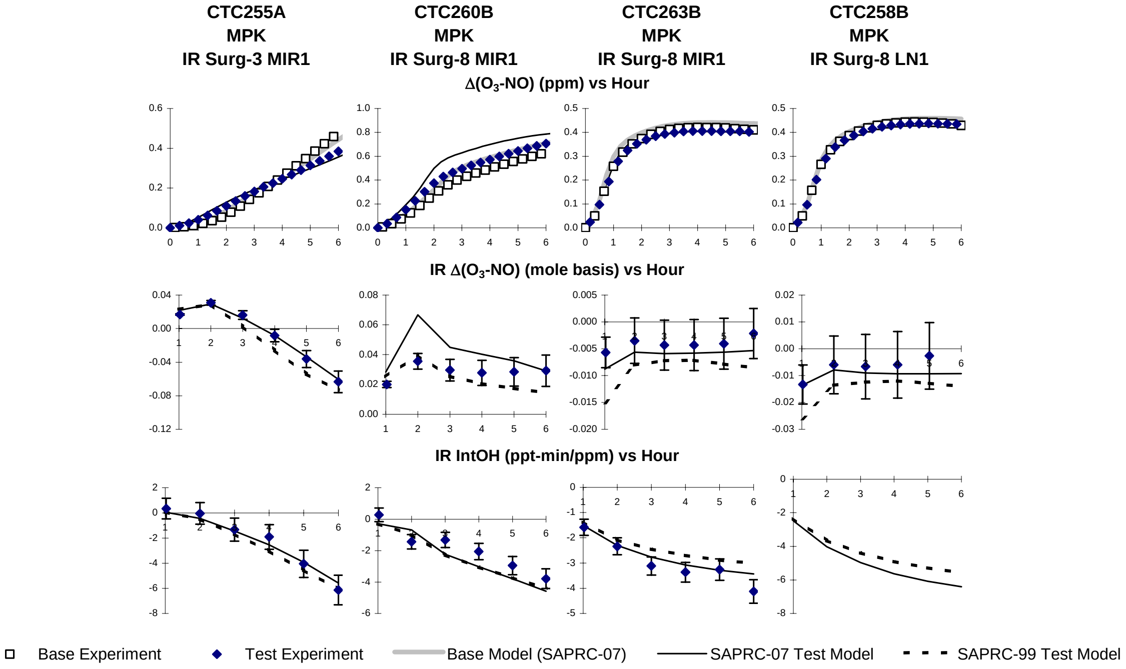


Figure C-80. Plots of experimental and calculated environmental chamber reactivity results for 2-pentanone.

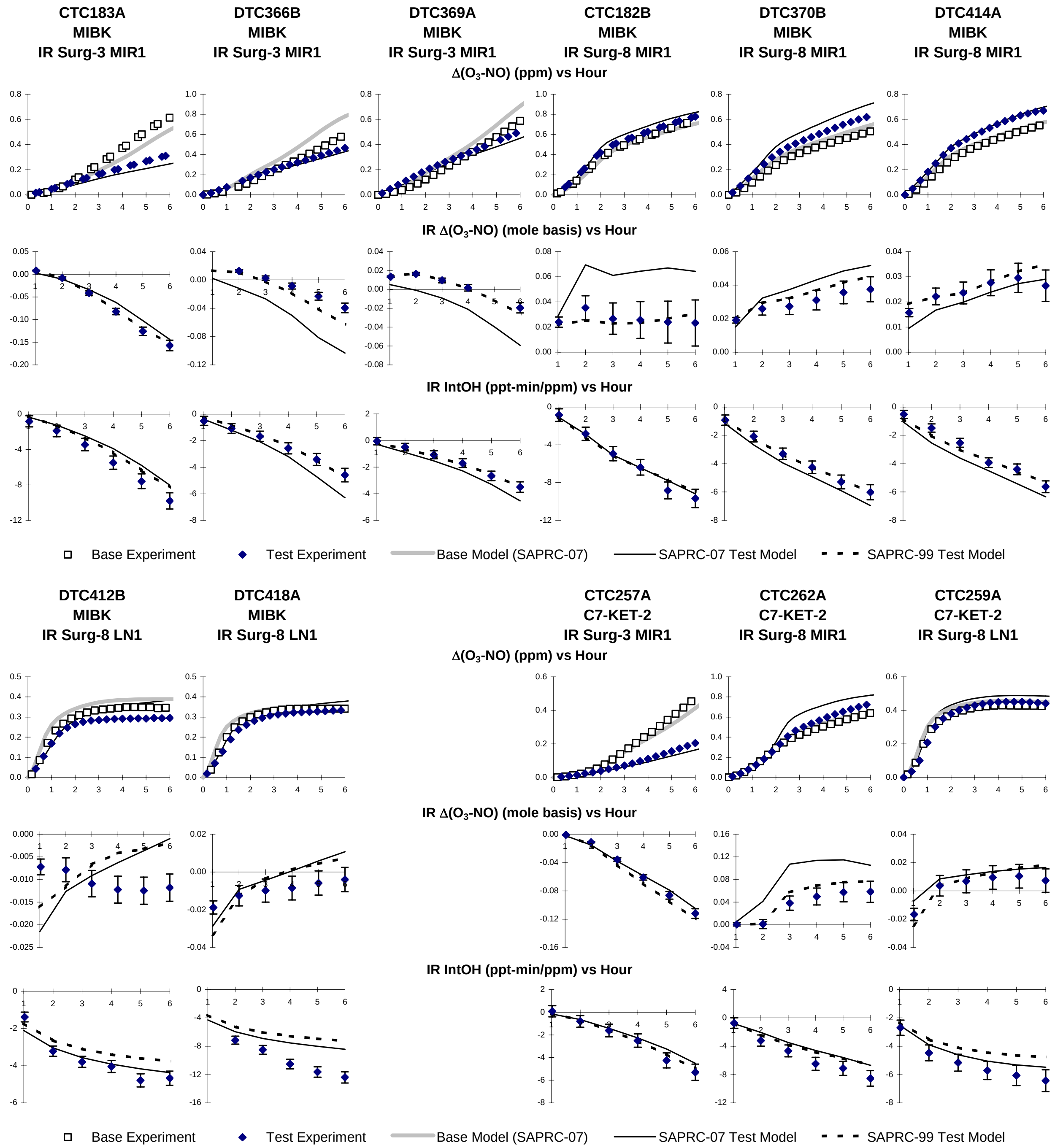


Figure C-81. Plots of experimental and calculated environmental chamber reactivity results for 4-methyl-2-pentanone and 2-heptanone.

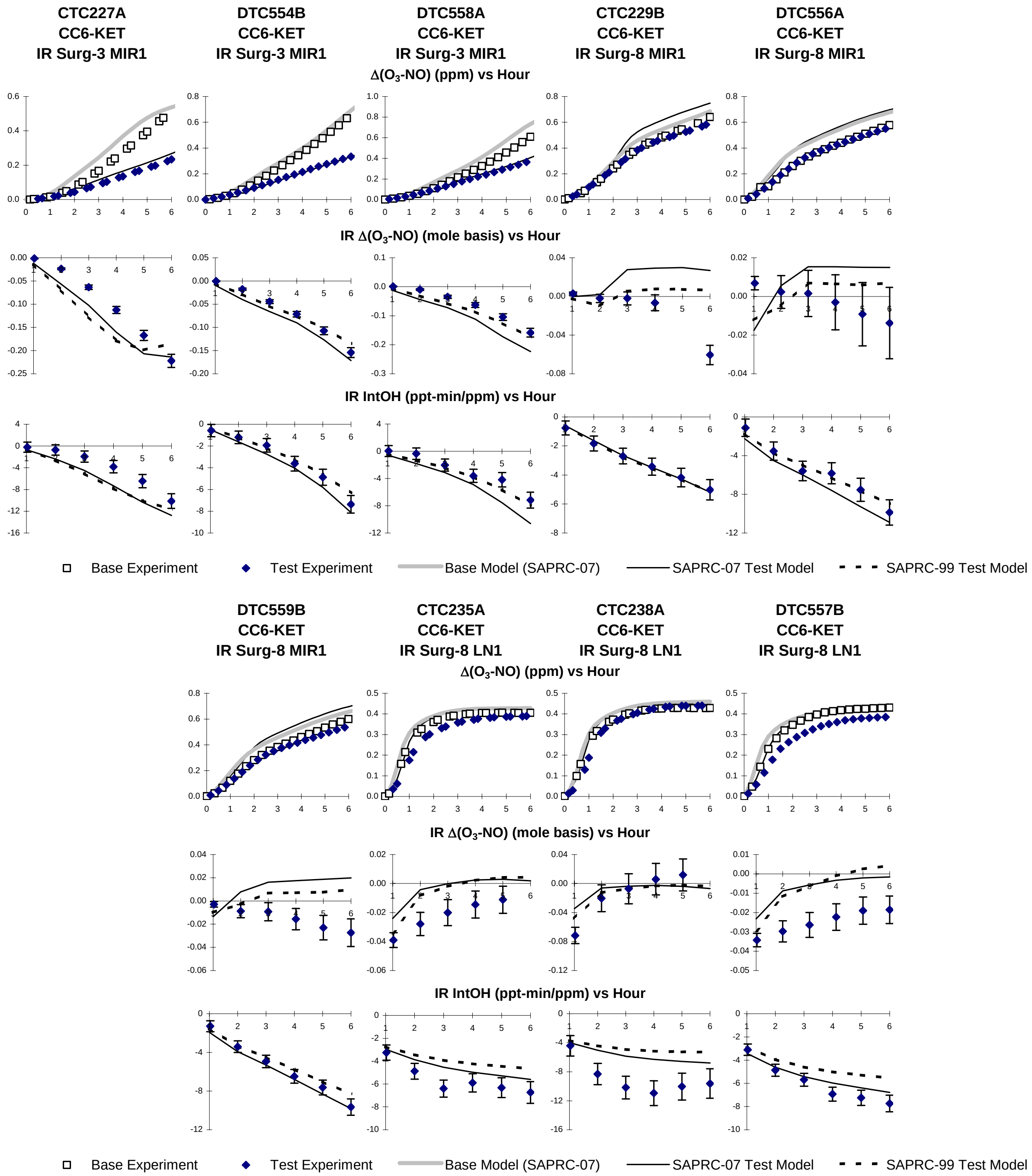


Figure C-82. Plots of experimental and calculated environmental chamber reactivity results for cyclohexanone.

MVK - NOx Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
EC Chamber	3	-3%	17%	-10%	11%
Blacklight	3	0%	-6%	-15%	-11%

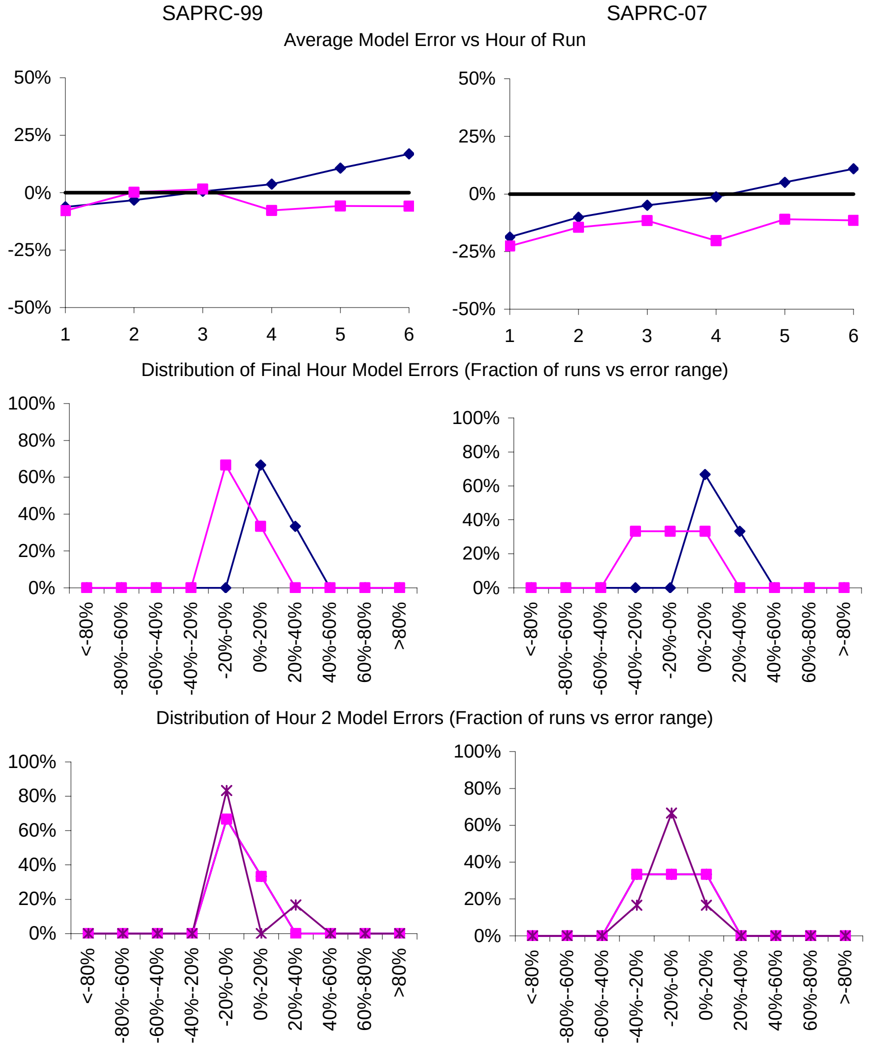


Figure C-83. Plots of model errors in simulations of the methyl vinyl ketone - NO_x environmental chamber experiments.

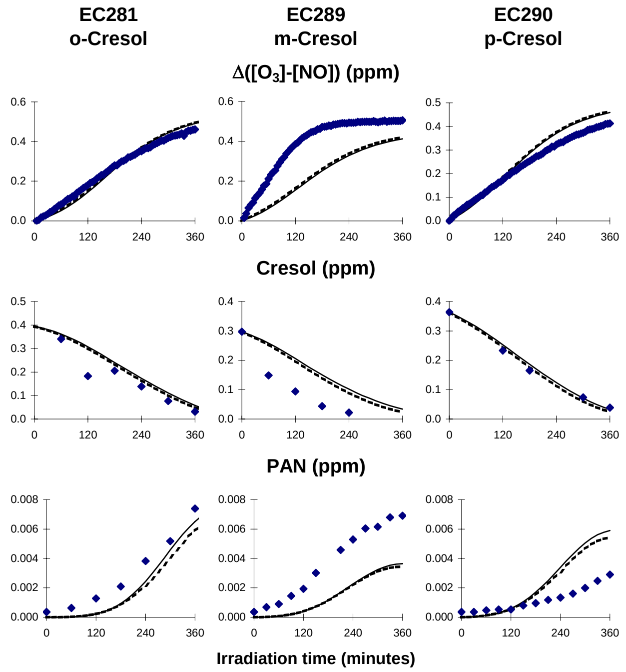


Figure C-84. Plots of experimental and calculated Δ([O_3]-[NO]), cresol, and PAN concentrations in the cresol - NO_x environmental chamber experiments.

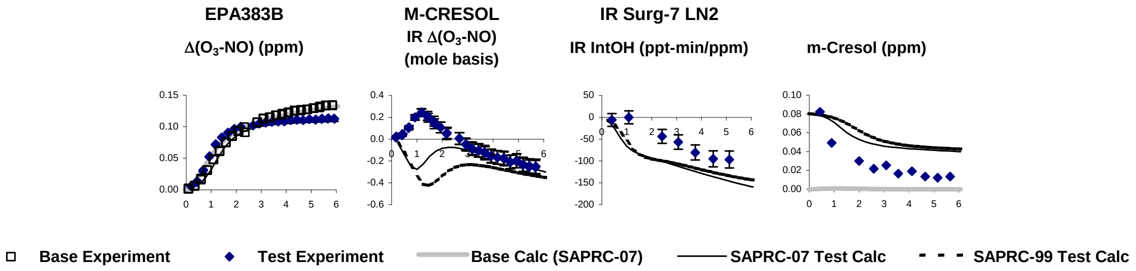


Figure C-85. Plots of experimental and calculated environmental chamber reactivity results for m-cresol.

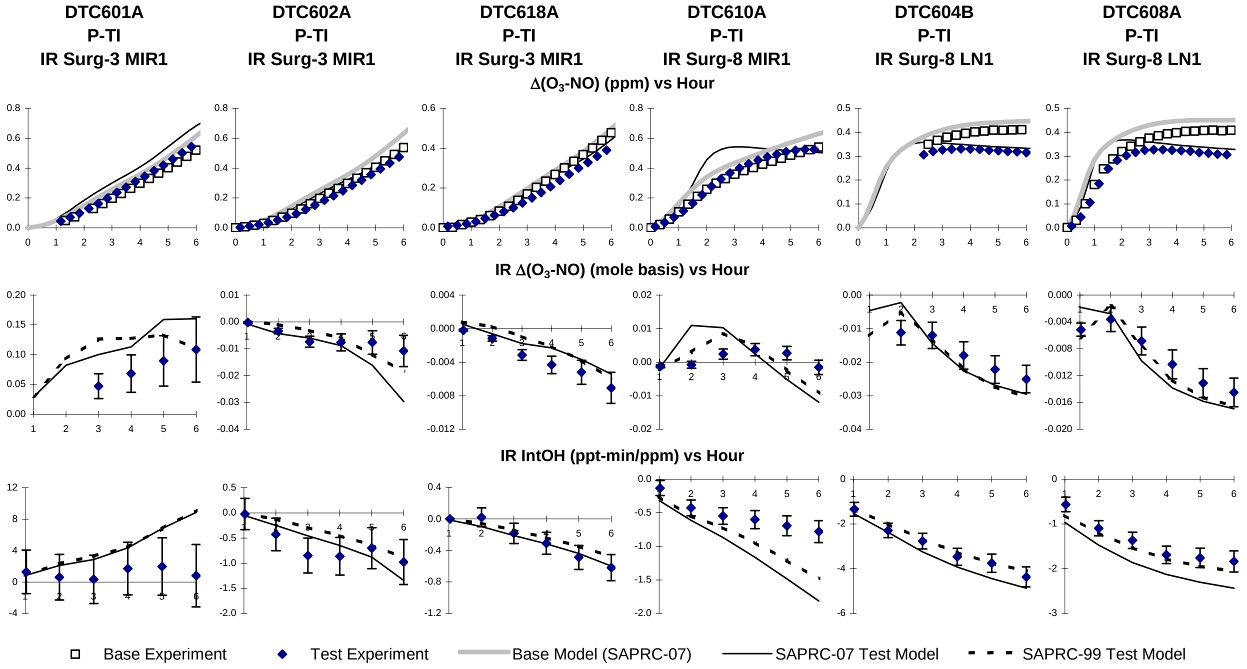


Figure C-86. Plots of experimental and calculated environmental chamber reactivity results for para toluene isocyanate.

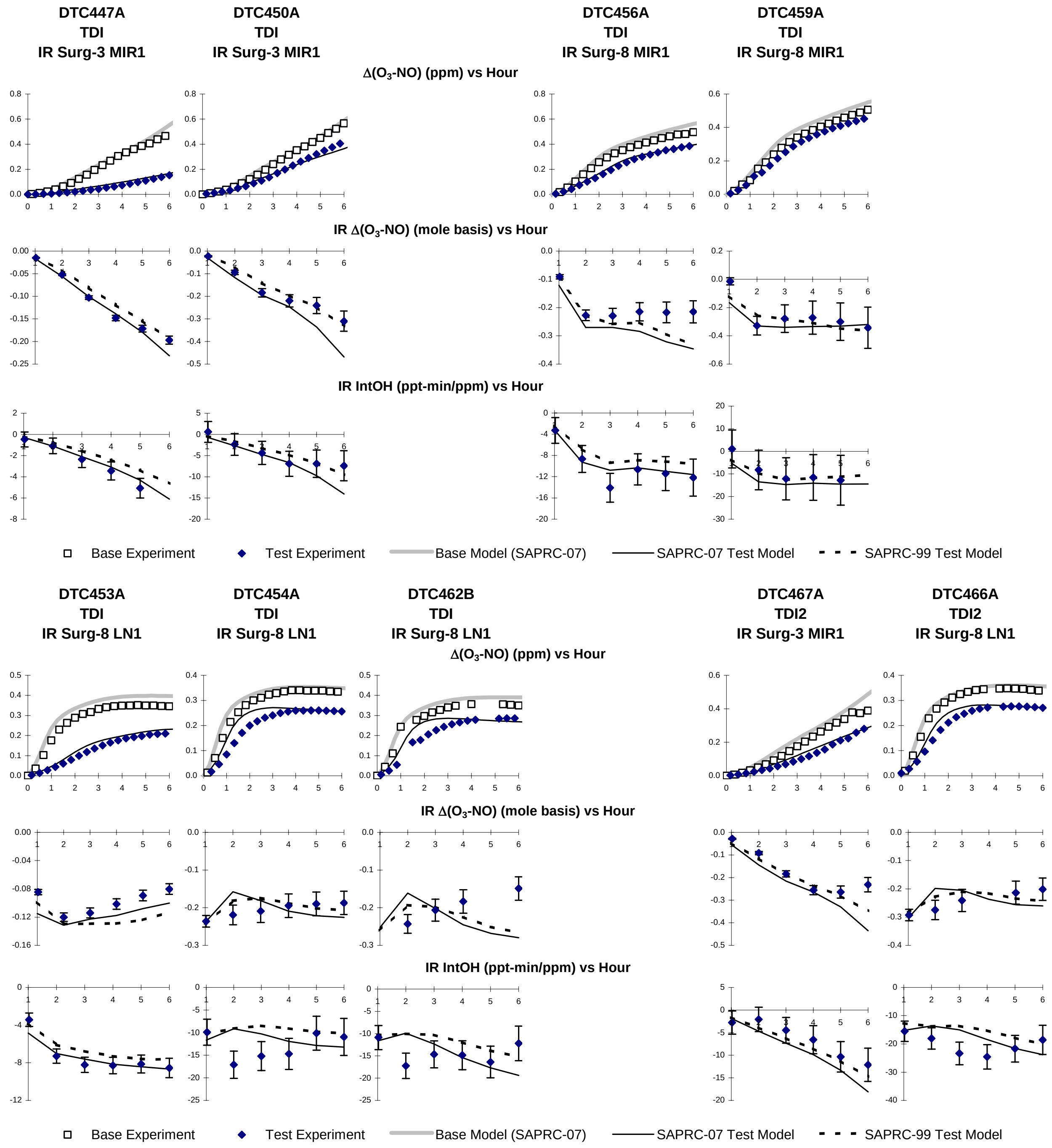


Figure C-87. Plots of experimental and calculated environmental chamber reactivity results for 2,4-toluene diisocyanate (TDI1) and 2,6-toluene diisocyanate (TDI2).

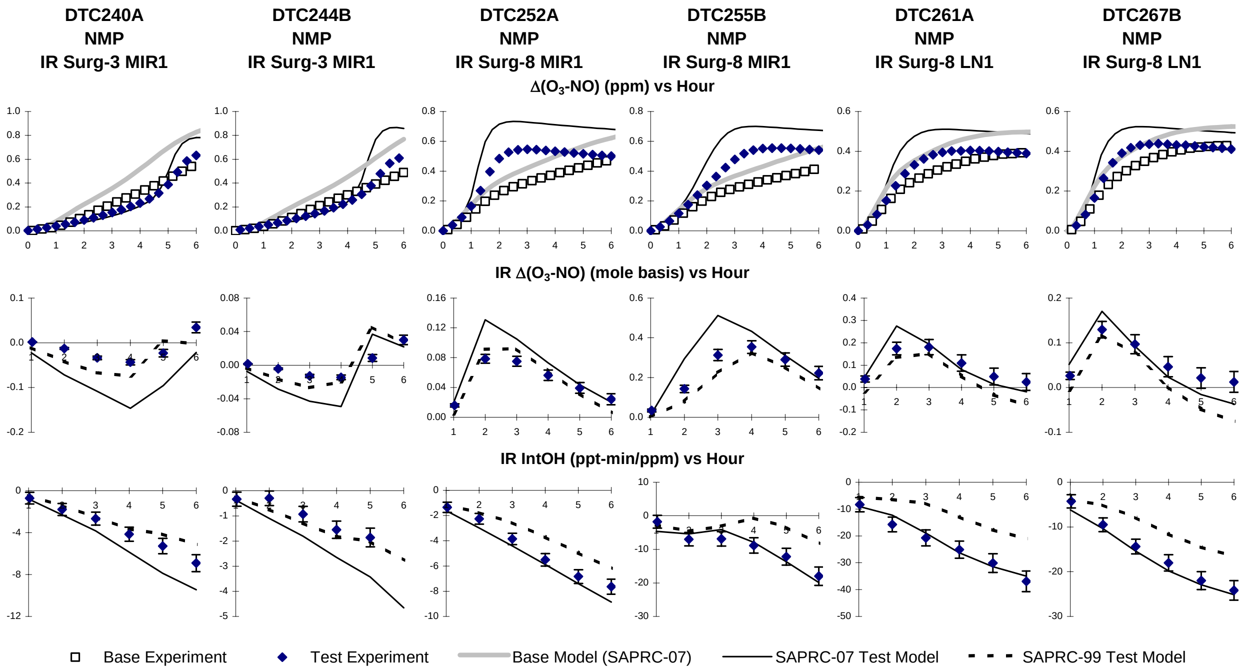


Figure C-88. Plots of experimental and calculated environmental chamber reactivity results for n-methyl-2-pyrrolidone.

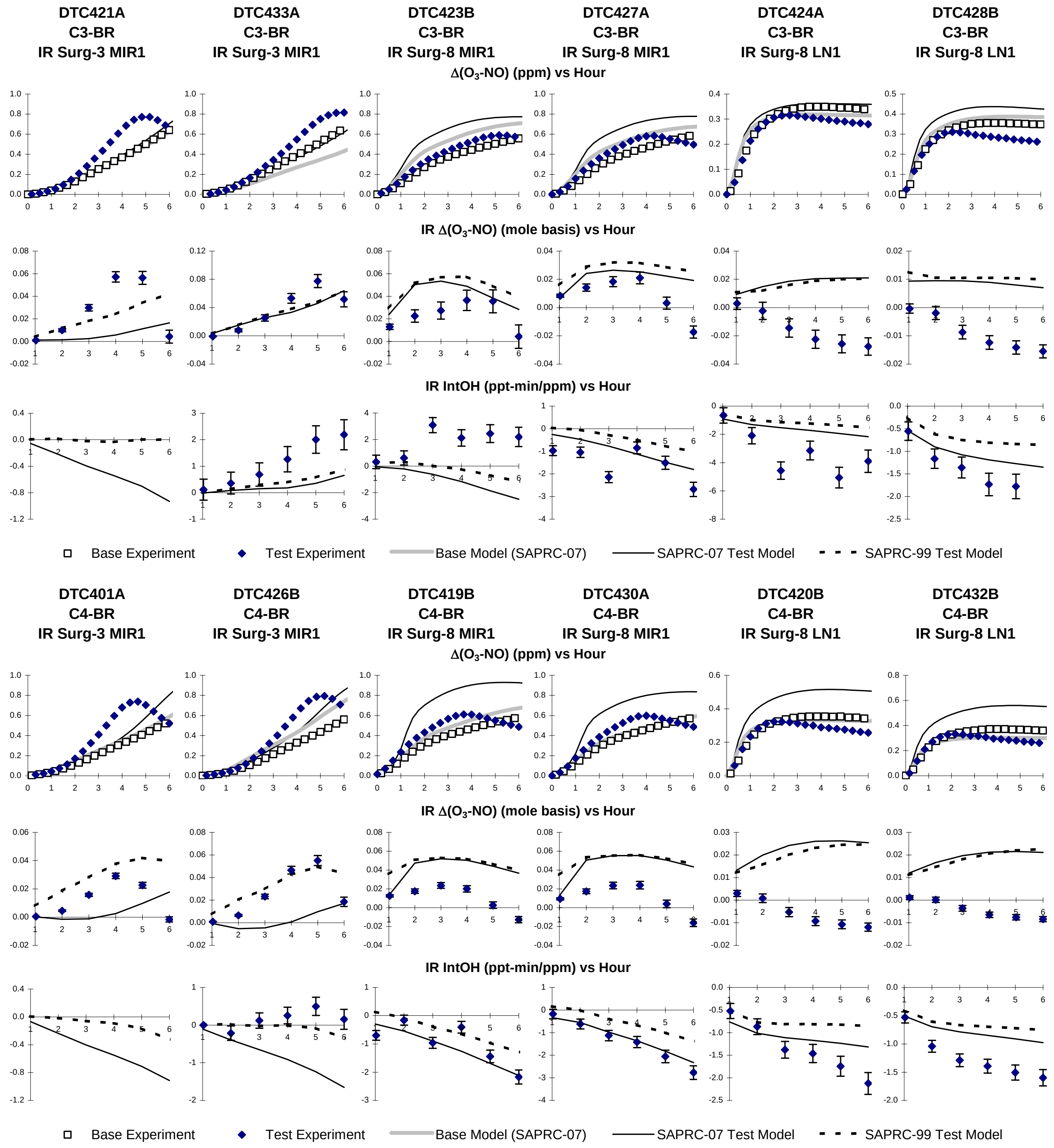
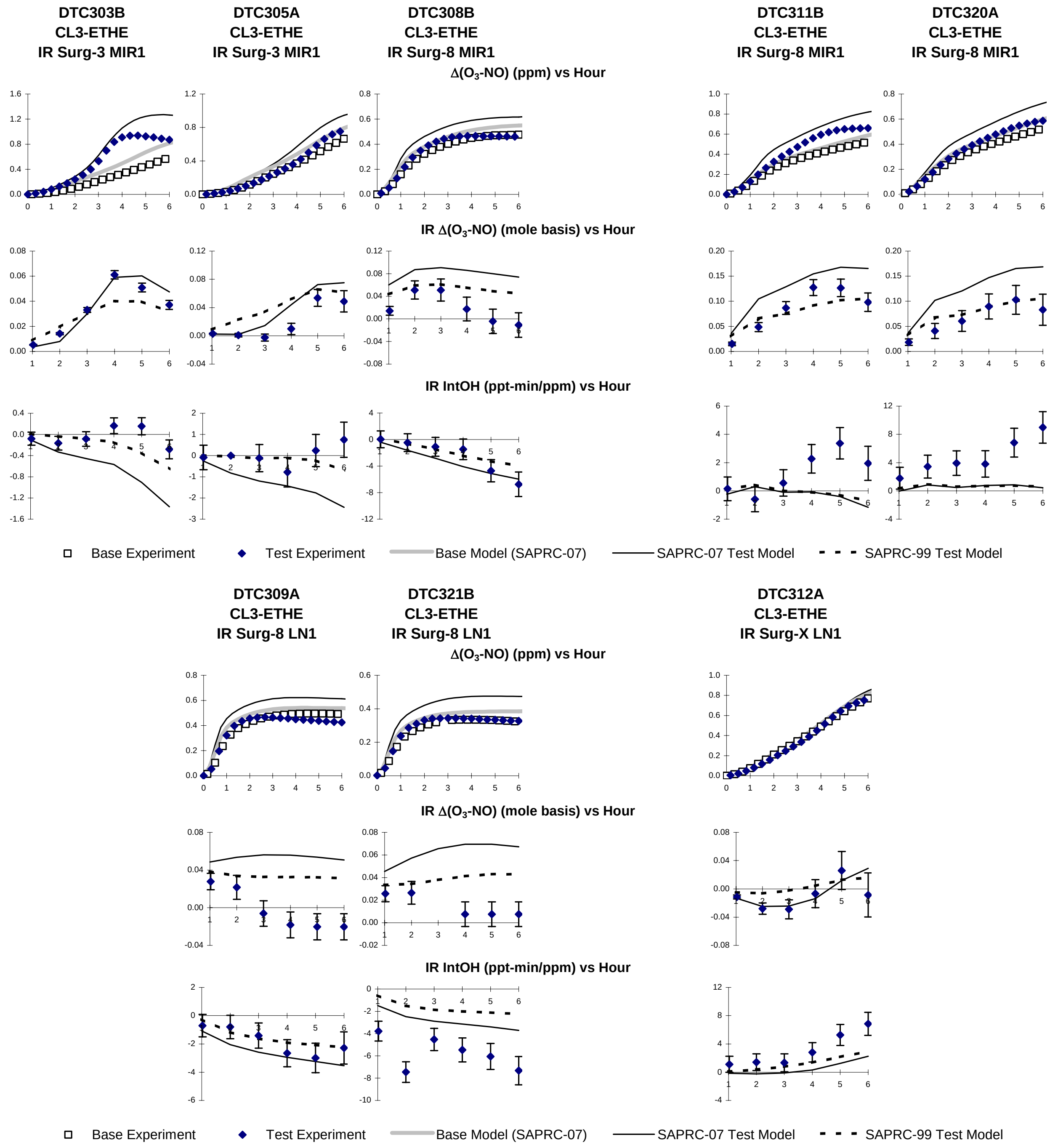


Figure C-89. Plots of experimental and calculated environmental chamber reactivity results for n-propyl bromide and n-butyl bromide.



DTC303B CL3-ETHE IR Surg-3 MIR1

DTC305A CL3-ETHE IR Surg-3 MIR1

DTC308B CL3-ETHE IR Surg-8 MIR1

DTC311B CL3-ETHE IR Surg-8 MIR1

DTC320A CL3-ETHE IR Surg-8 MIR1

DTC309A CL3-ETHE IR Surg-8 LN1

DTC321B CL3-ETHE IR Surg-8 LN1

DTC312A CL3-ETHE IR Surg-X LN1

Figure C-90. Plots of experimental and calculated environmental chamber reactivity results for trichloroethylene.

1,3-Dichloropropene Runs

Group	Runs	Average Δ([O3]-[NO]) Model Error			
		SAPRC-99		SAPRC-07	
		2-Hr	Final	2-Hr	Final
13-DCP - NOx	4	0%	0%	-18%	-9%
DCP + n-C4 - NOx	2	0%	0%	-24%	-13%

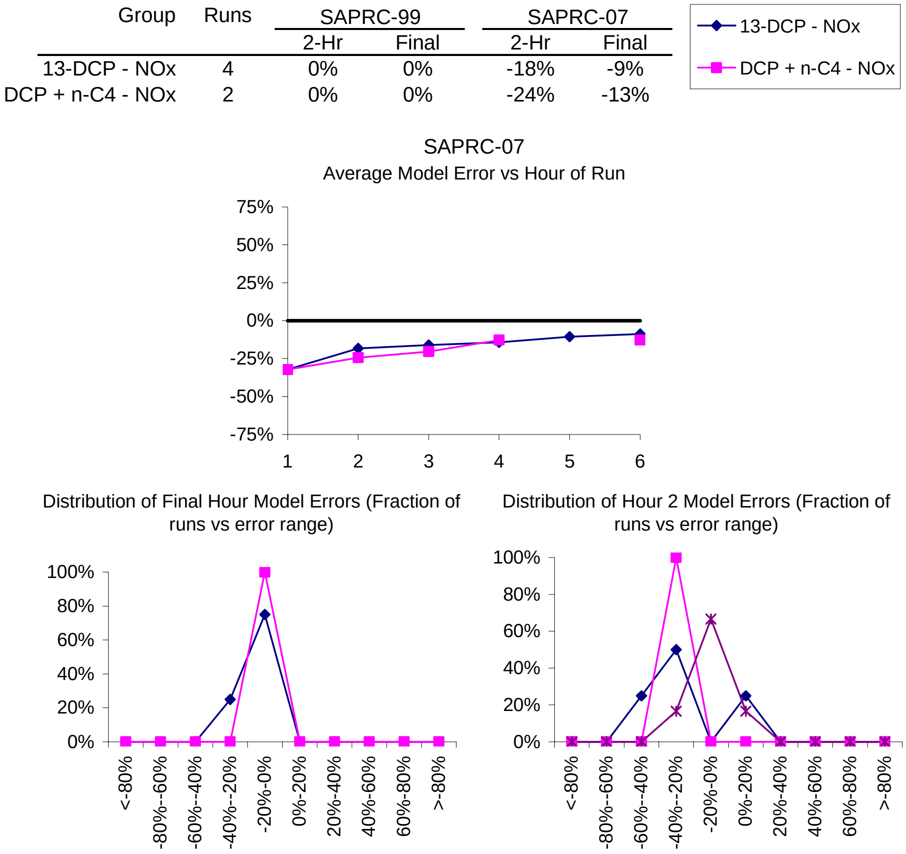


Figure C-91. Plots of model errors in simulations of the 1,3-dichloropropene and 1,3-dichloropropene + n-butane - NO_x environmental chamber experiments.

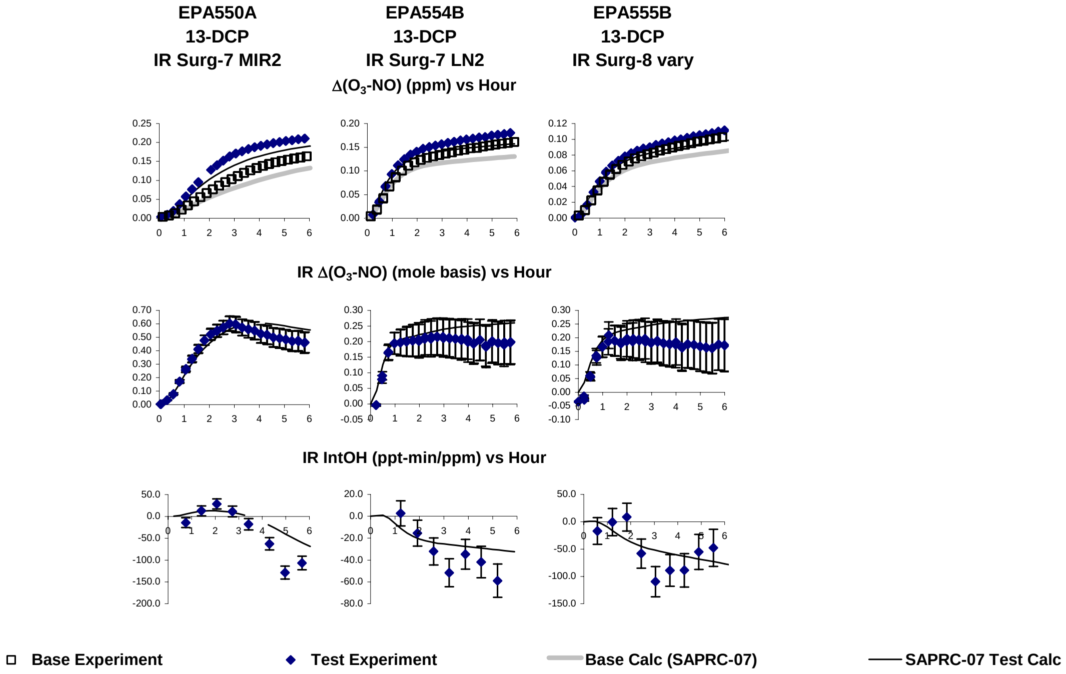


Figure C-92. Plots of experimental and calculated environmental chamber reactivity results for the 1,3-dichloropropenes.

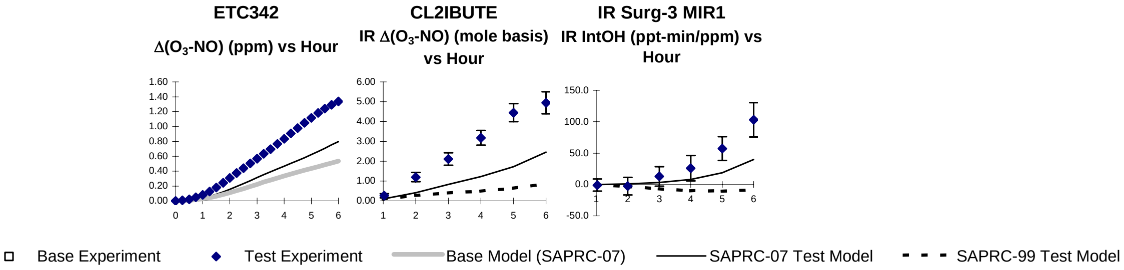


Figure C-93. Plots of experimental and calculated environmental chamber reactivity results for 2-(chloromethyl)-3-chloro-propene.

Chlorine and Chloropicrin

Group	Runs	Average Δ([O3]-[NO]) Model Error SAPRC-99 2-Hr	Final	SAPRC-07 2-Hr	Final
Cl2 + n-C4 - NOx	2			4%	5%
CP + n-C4 - NOx	2			14%	8%
CP + C2 + NOx	2			1%	2%
CP + n-C4 - Air	2			-1%	-6%

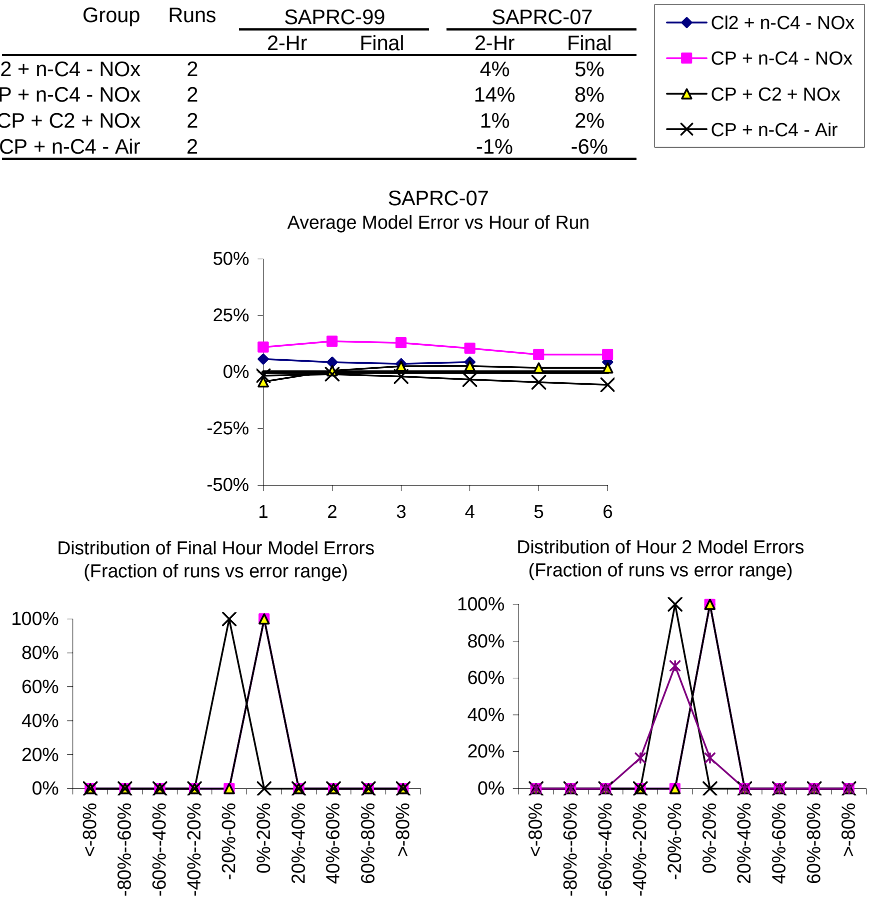


Figure C-94 Plots of model errors in simulations of the chloropicrin (CP) – alkane - NO_x and the chlorine + alkane - NO_x experiments.

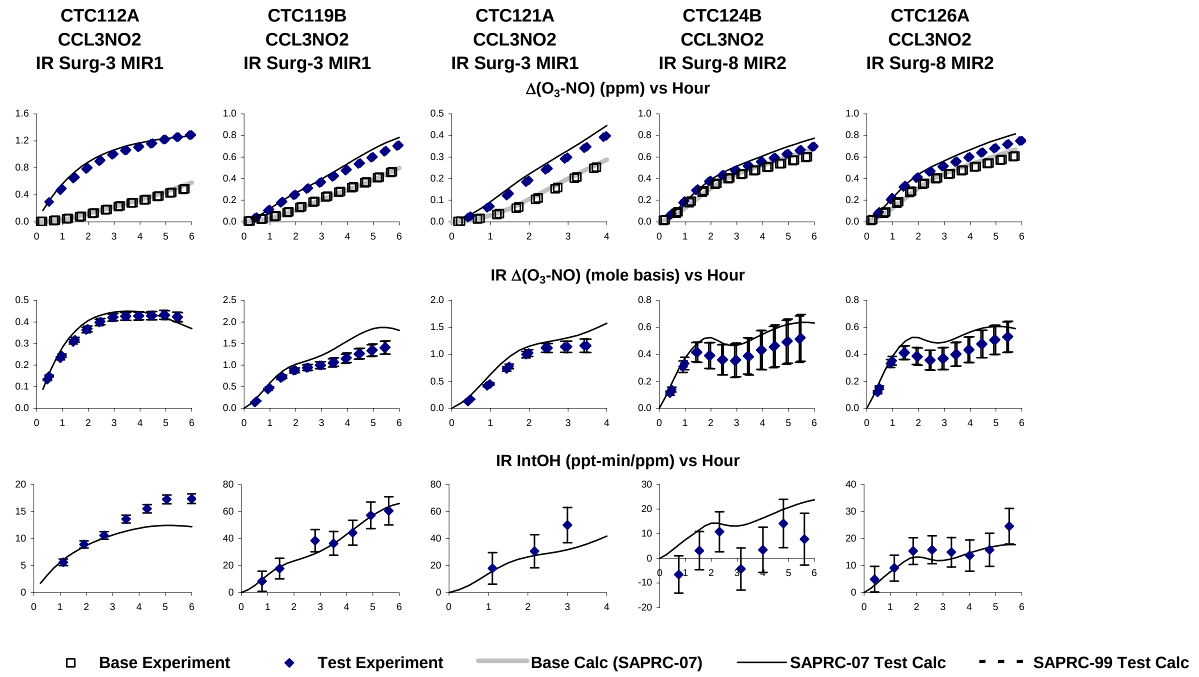
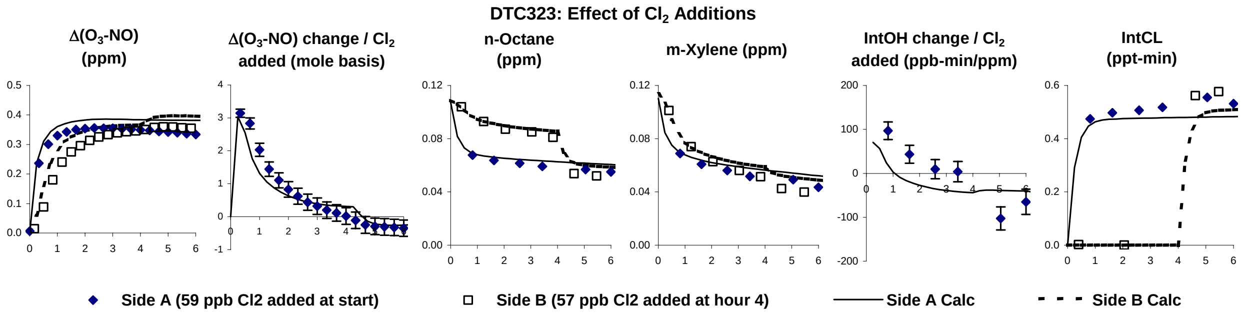


Figure C-95. Plots of experimental and calculated environmental chamber reactivity results for chloropicrin.



(IntCl is integrated chlorine calculated from the consumption rate for n-octane relative to the consumption rate of m-xylene)

Figure C-96. Plots of experimental and calculated environmental chamber reactivity results for chlorine. Note that chlorine was added to the "base case" experiment after four hours of irradiation.

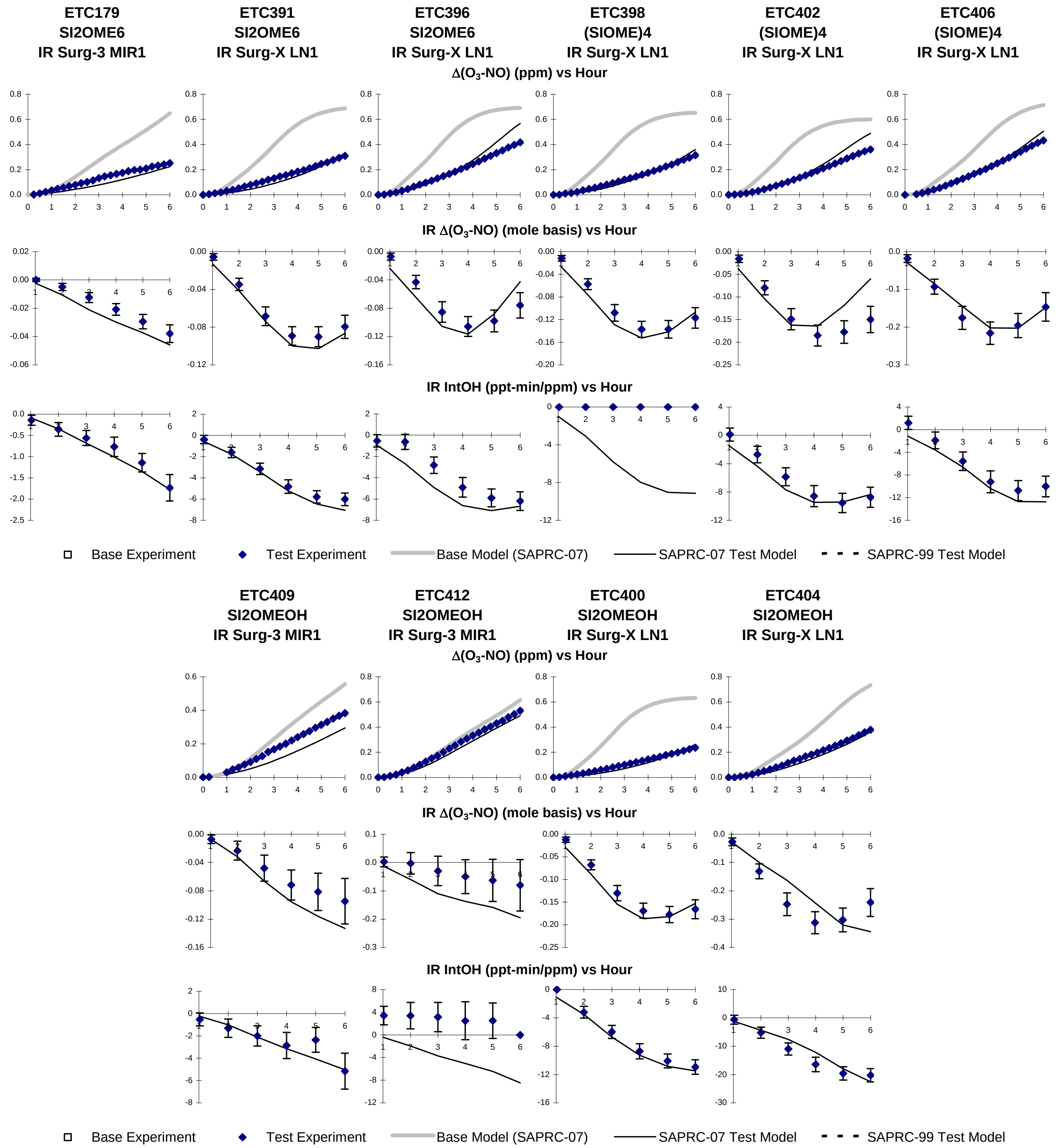


Figure C-97. Plots of experimental and calculated environmental chamber reactivity results for hexamethyldisiloxane, d4 cyclosiloxane, and hydroxymethyldisiloxane.

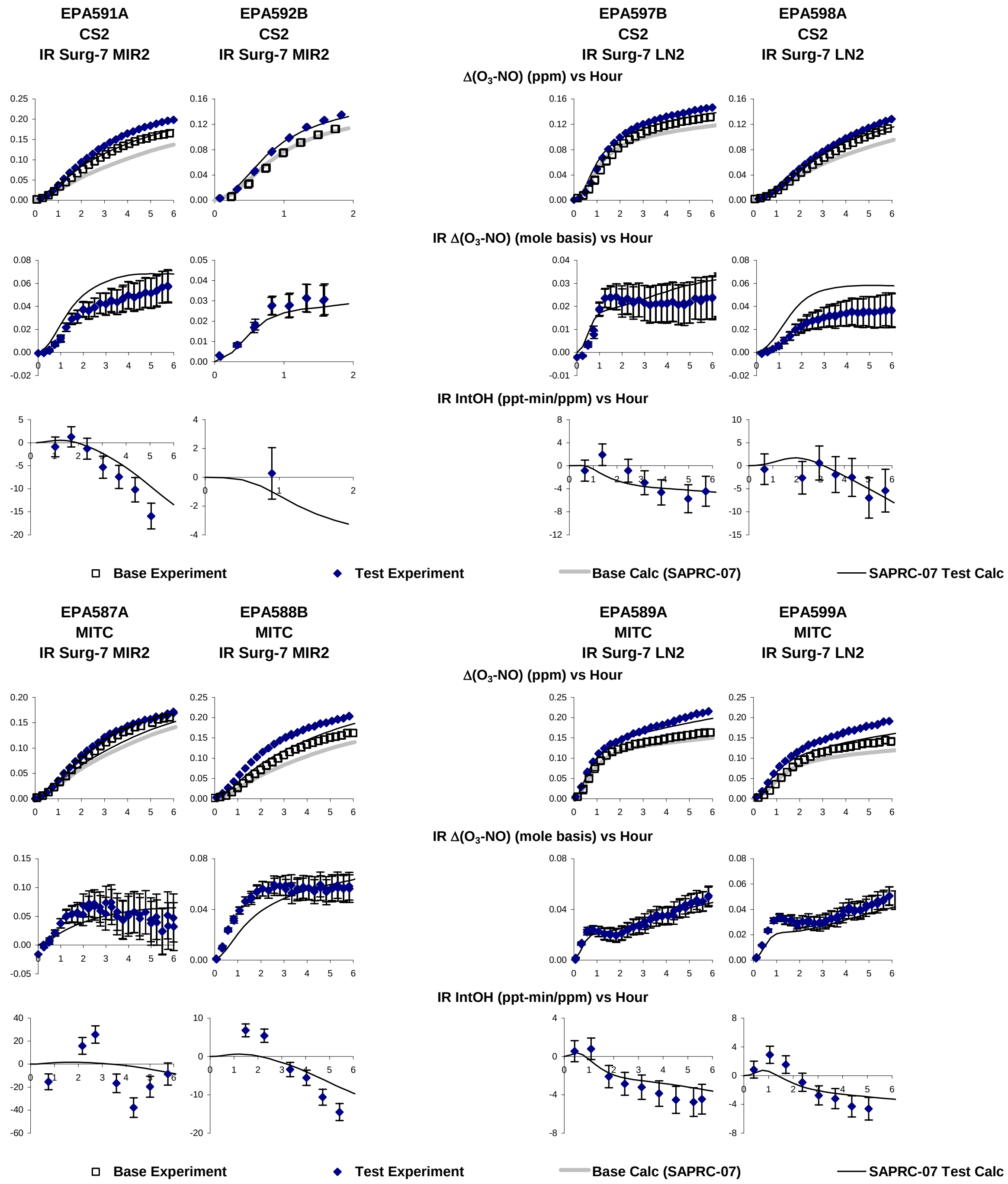


Figure C-98. Plots of experimental and calculated environmental chamber reactivity results for carbon disulfide and methyl isothiocyanate.

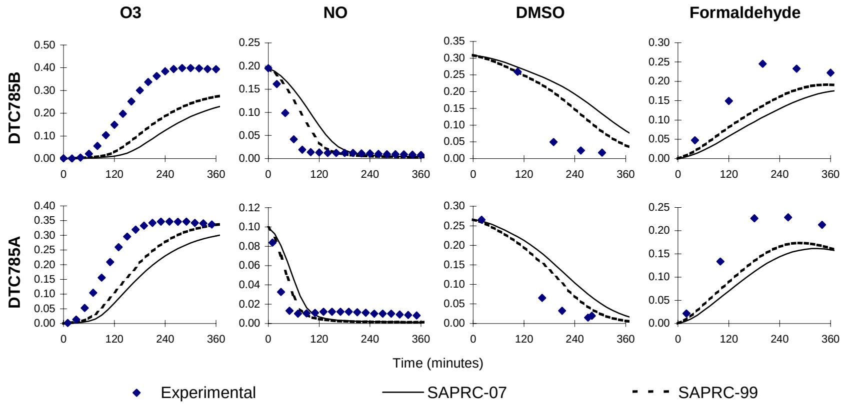


Figure C-99. Plots of experimental and calculated O_3, NO, DMSO and formaldehyde in the dimethyl sulfoxide - NO_x environmental chamber experiments.

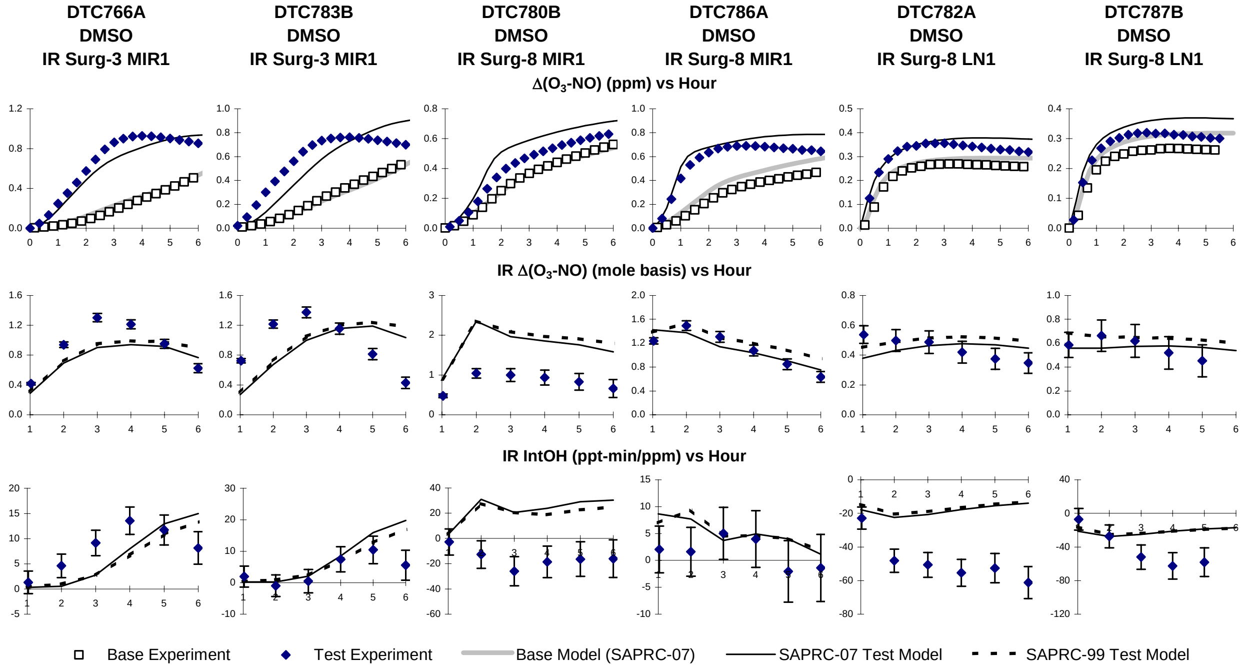


Figure C-100. Plots of experimental and calculated environmental chamber reactivity results for dimethyl sulfoxide.

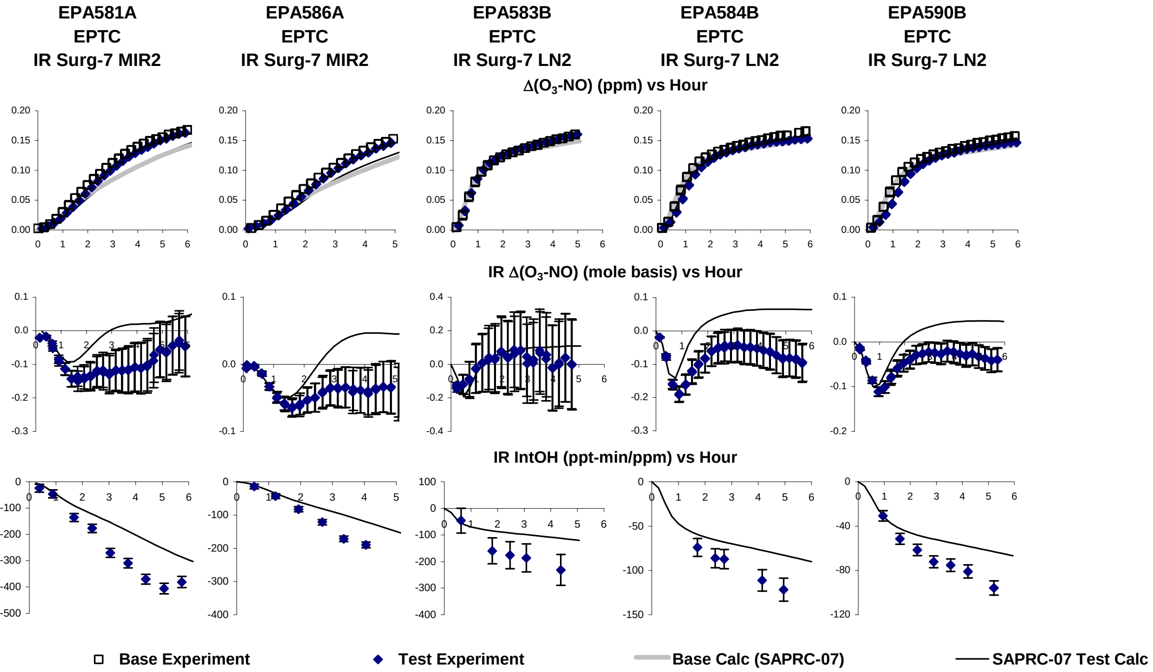


Figure C-101. Plots of experimental and calculated environmental chamber reactivity results for s-ethyl dipropylthiocarbamate (EPTC).

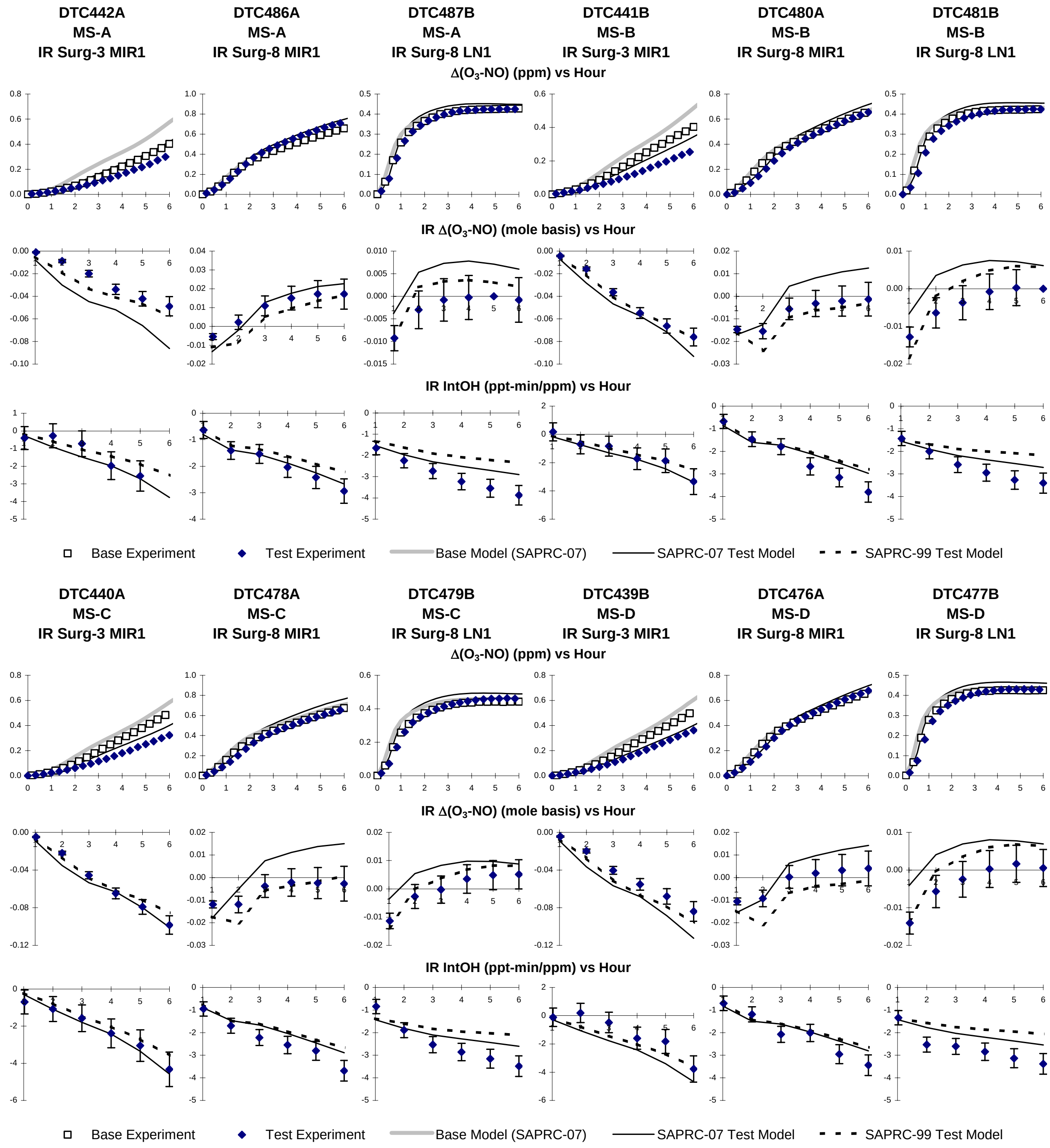


Figure C-102. Plots of experimental and calculated environmental chamber reactivity results for the mineral spirits samples studied for Safety-Kleen (Carter et al, 1997e).

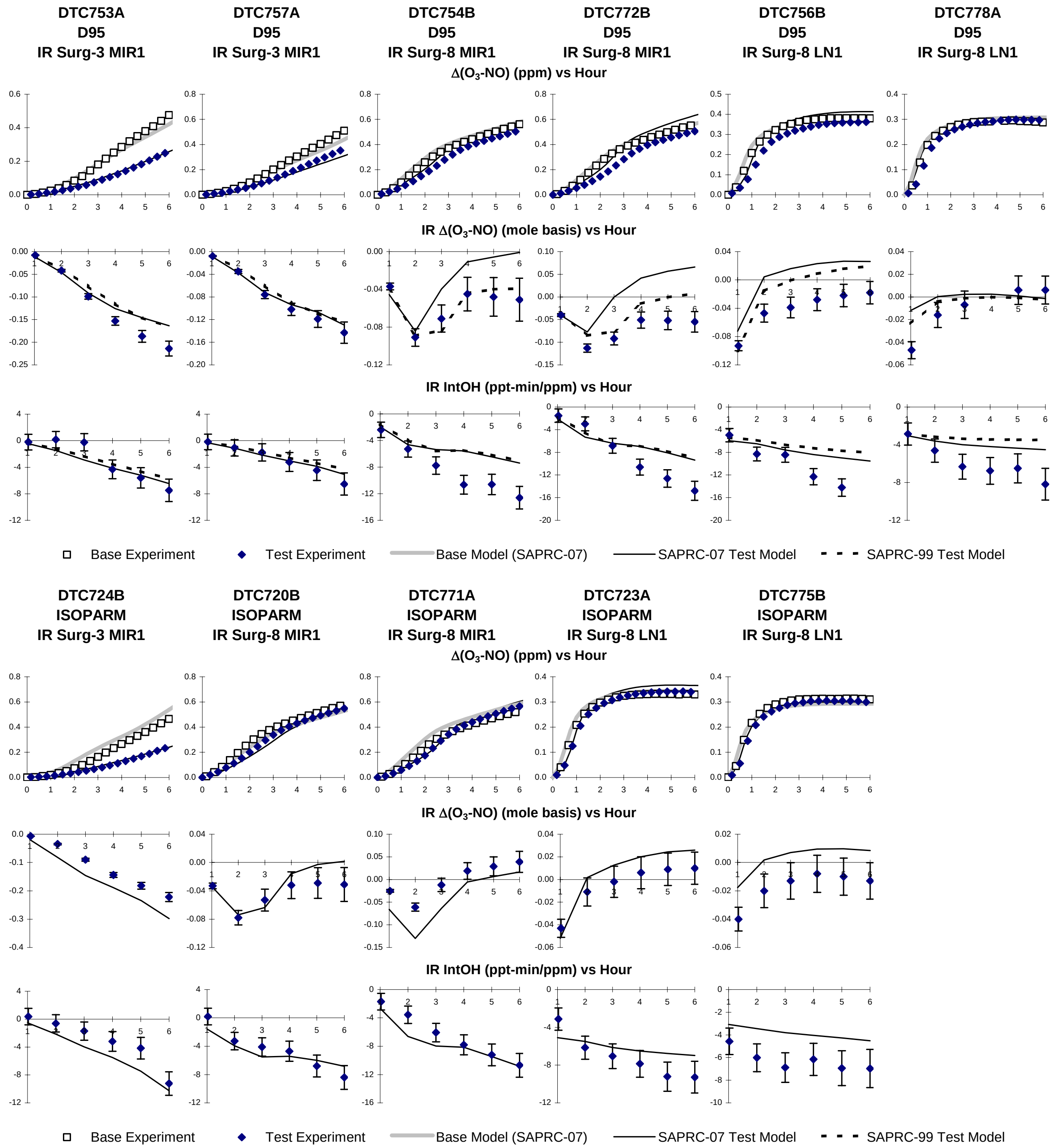


Figure C-103. Plots of experimental and calculated environmental chamber reactivity results for Exxon Exxol® D95 Fluid and Exxon Isopar® M Fluid studied for ExxonMobil (Carter et al, 2000e)[1].

---

[1] Exxol and Isopar are trademarks of ExxonMobil Chemical Company.

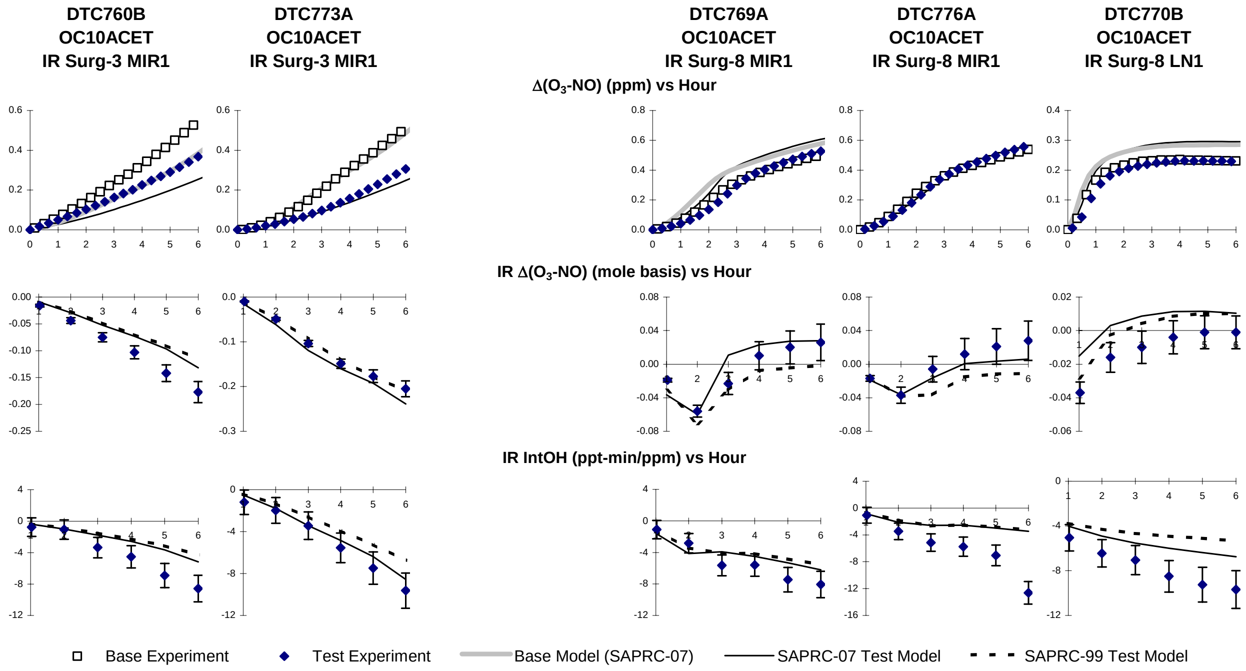


Figure C-104. Plots of experimental and calculated environmental chamber reactivity results for oxo-decyl Acetate fluid studied for ExxonMobil (Carter et al, 2000e).

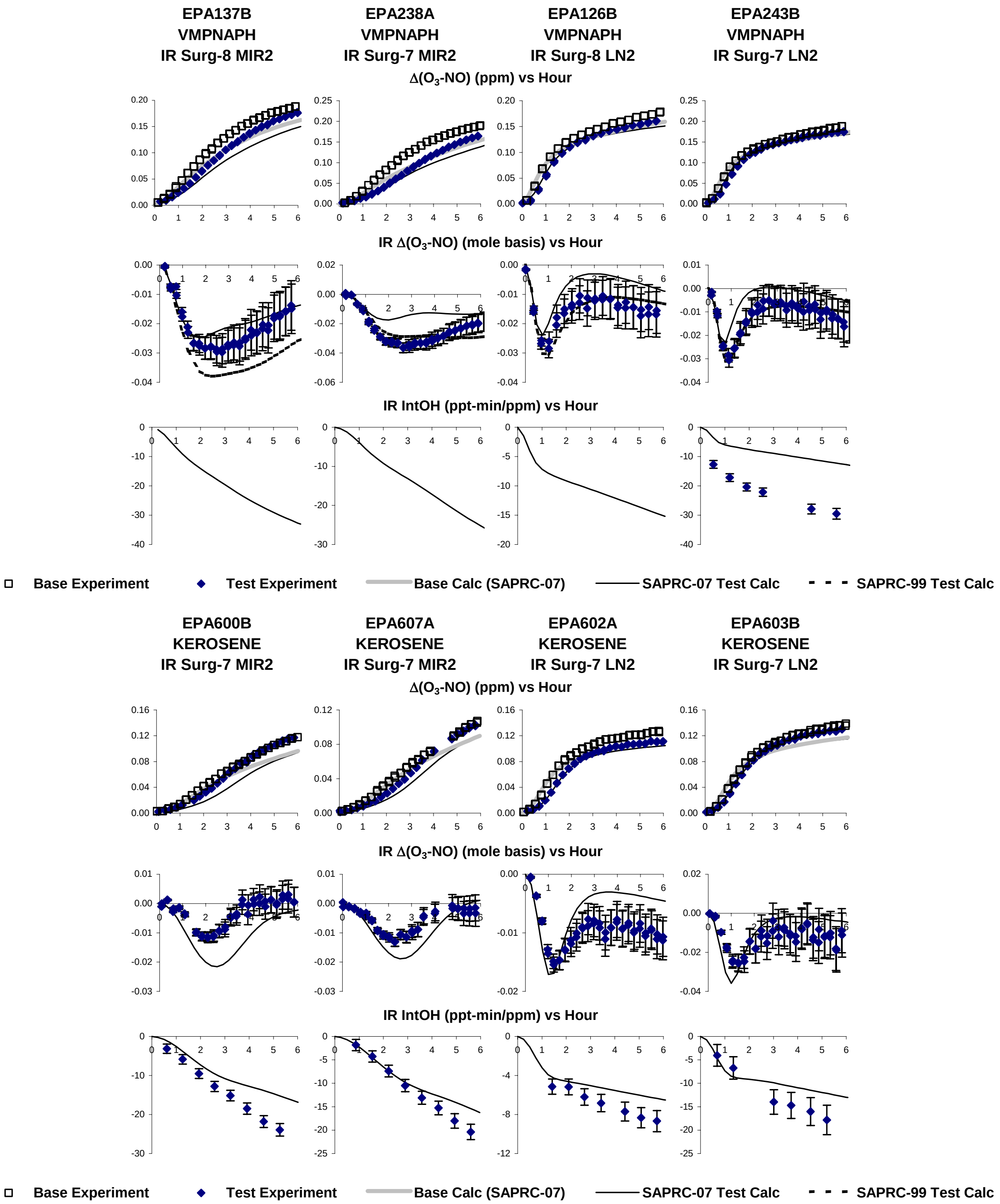


Figure C-105. Plots of experimental and calculated environmental chamber reactivity results for VMP Naphtha sample studied by Carter and Malkina (2005) and the Kerosene sample studied by Carter and Malkina (2007).

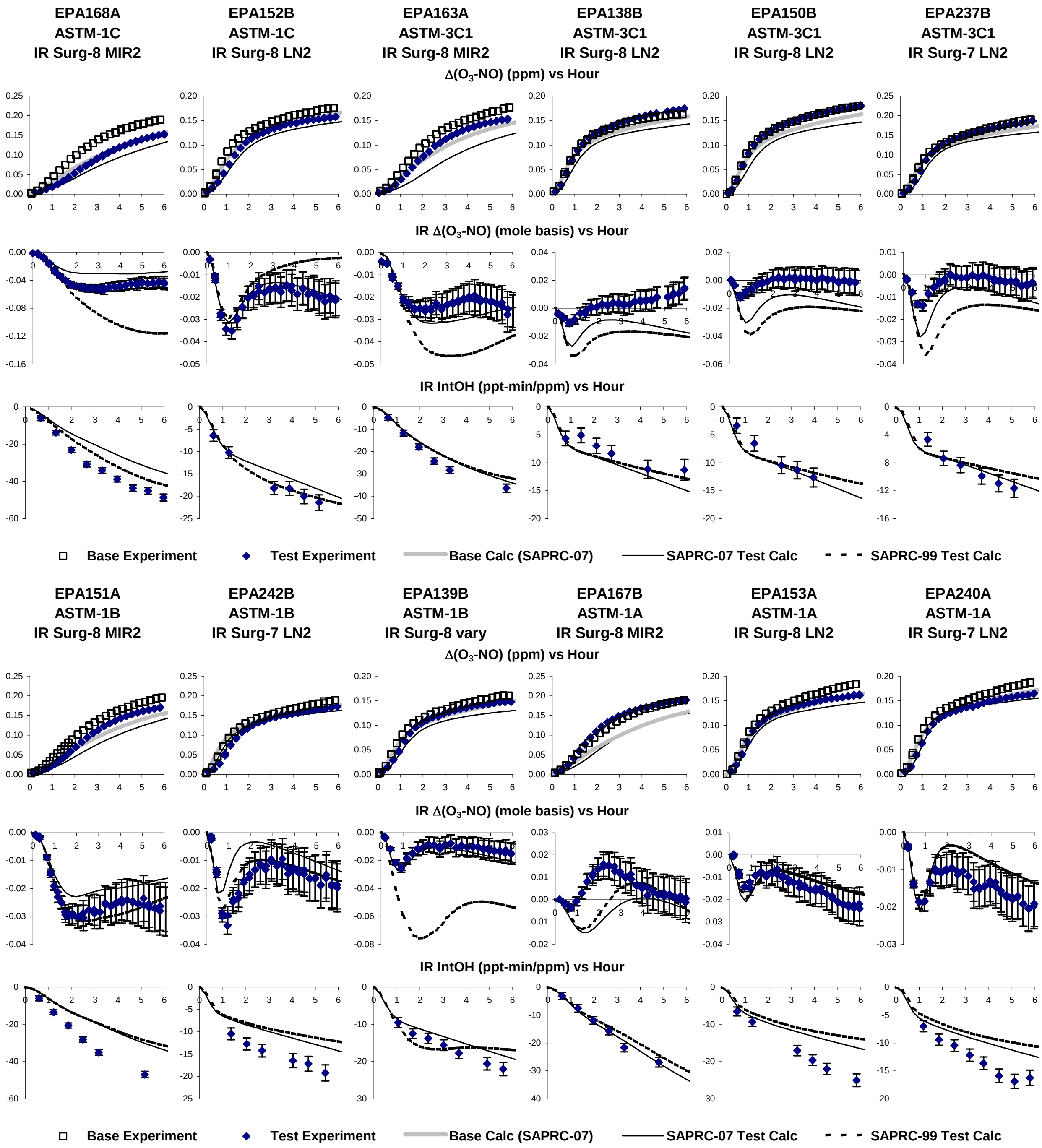


Figure C-106. Plots of experimental and calculated environmental chamber reactivity results for the dearomatized alkanes mixed, predominately C_{10}-C_{12} (ASTM-1C), synthetic isoparaffinic alkane mixture, predominately C_{10}-C_{12} (ASTM-3C1), Reduced Aromatics Mineral Spirits (ASTM-1B), and Regular mineral spirits (ASTM-1A) solvents studied by Carter and Malkina (2005).

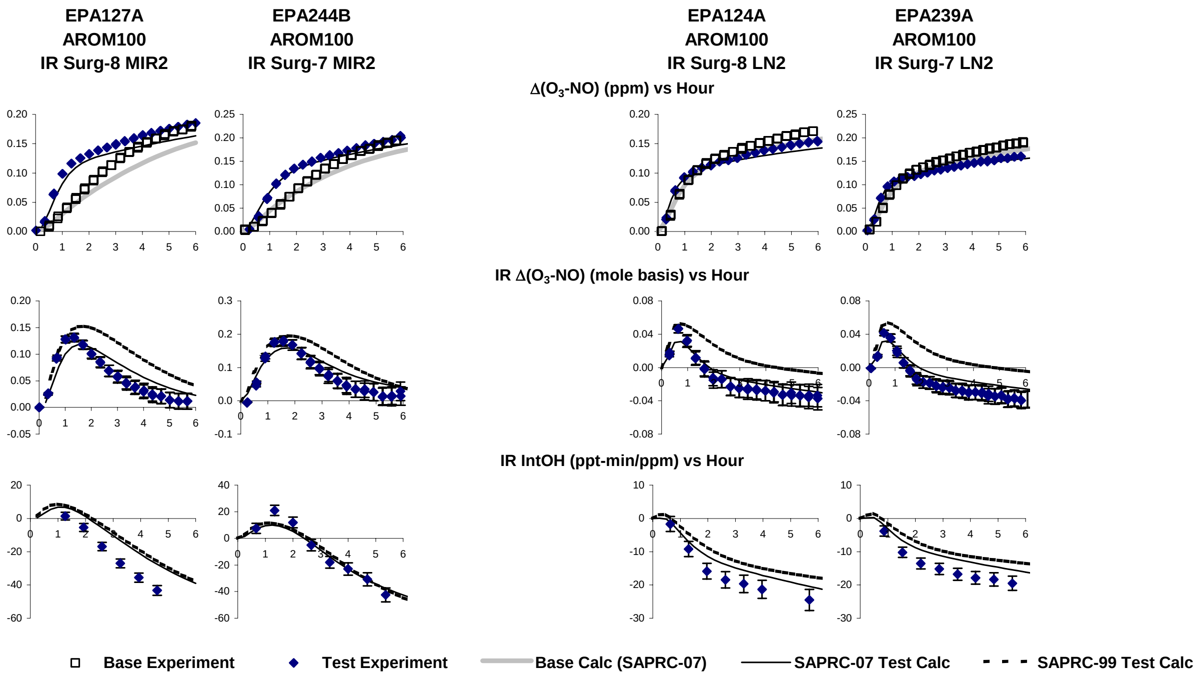


Figure C-107. Plots of experimental and calculated environmental chamber reactivity results for the aromatic-100 solvent studied by Carter and Malkina (2005).

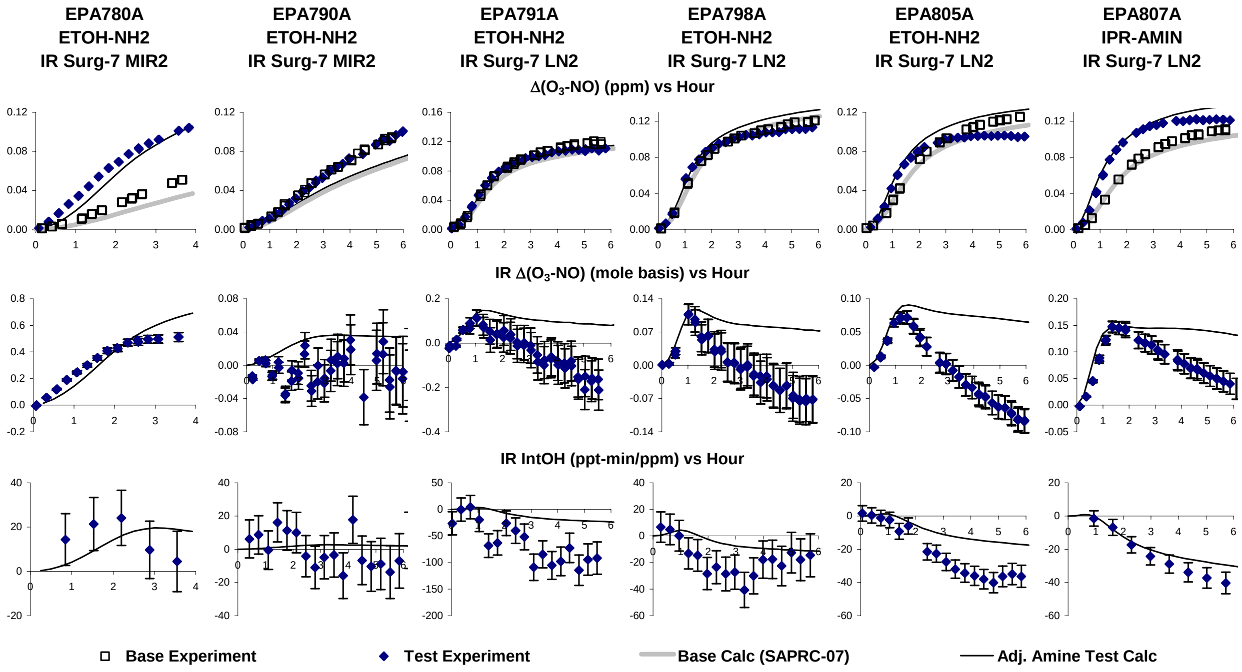


Figure C-108. Plots of experimental and calculated environmental chamber reactivity results for ethanolamine and isopropyl amine. In order to obtain the fits shown, the initial amine concentrations had to be adjusted to optimize the model fits to the reactivity data.

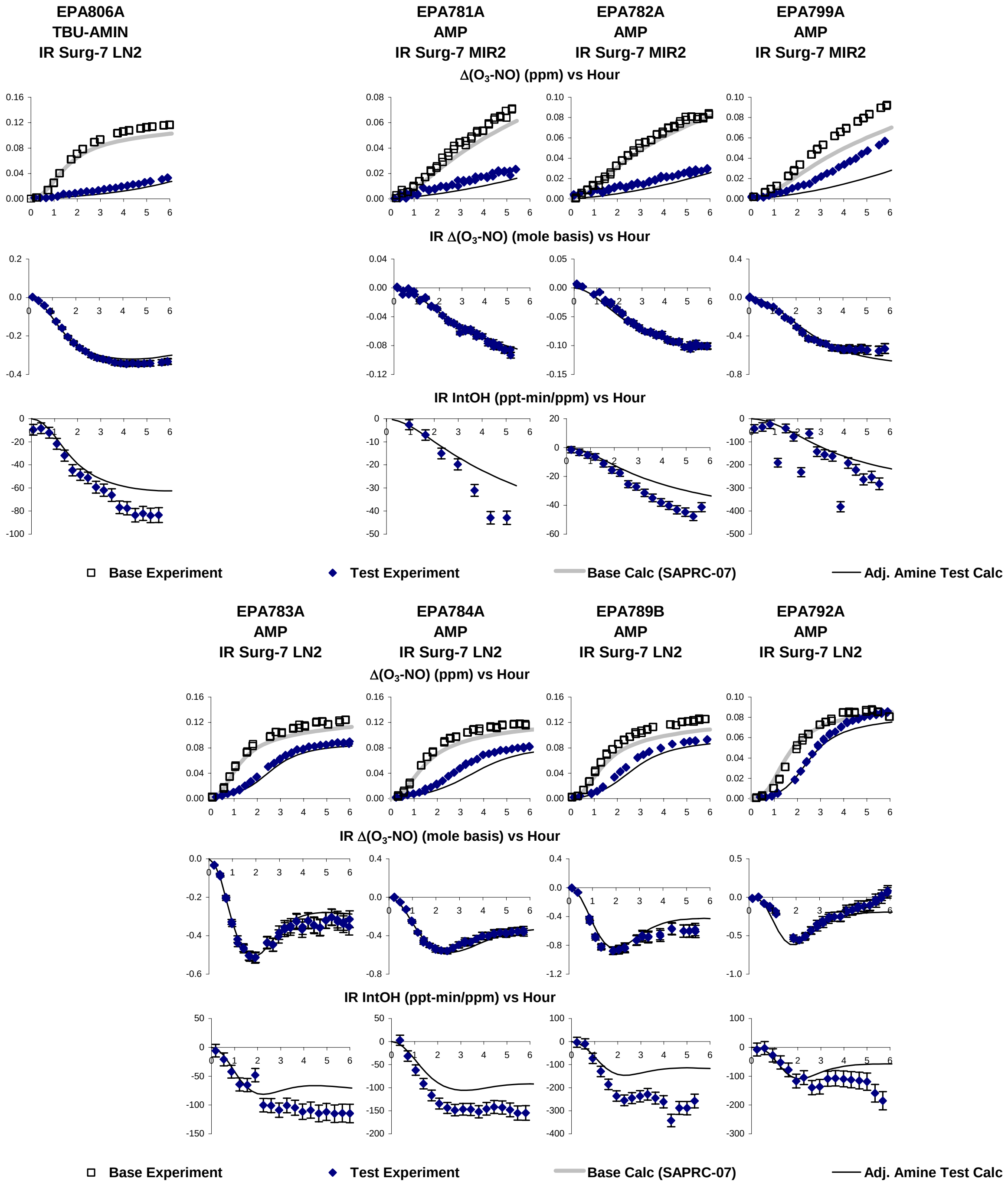


Figure C-109. Plots of experimental and calculated environmental chamber reactivity results for t-butyl amine and 2-amino-2-methyl-1-propanol. In order to obtain the fits shown, the initial amine concentrations had to be adjusted to optimize the model fits to the reactivity data.

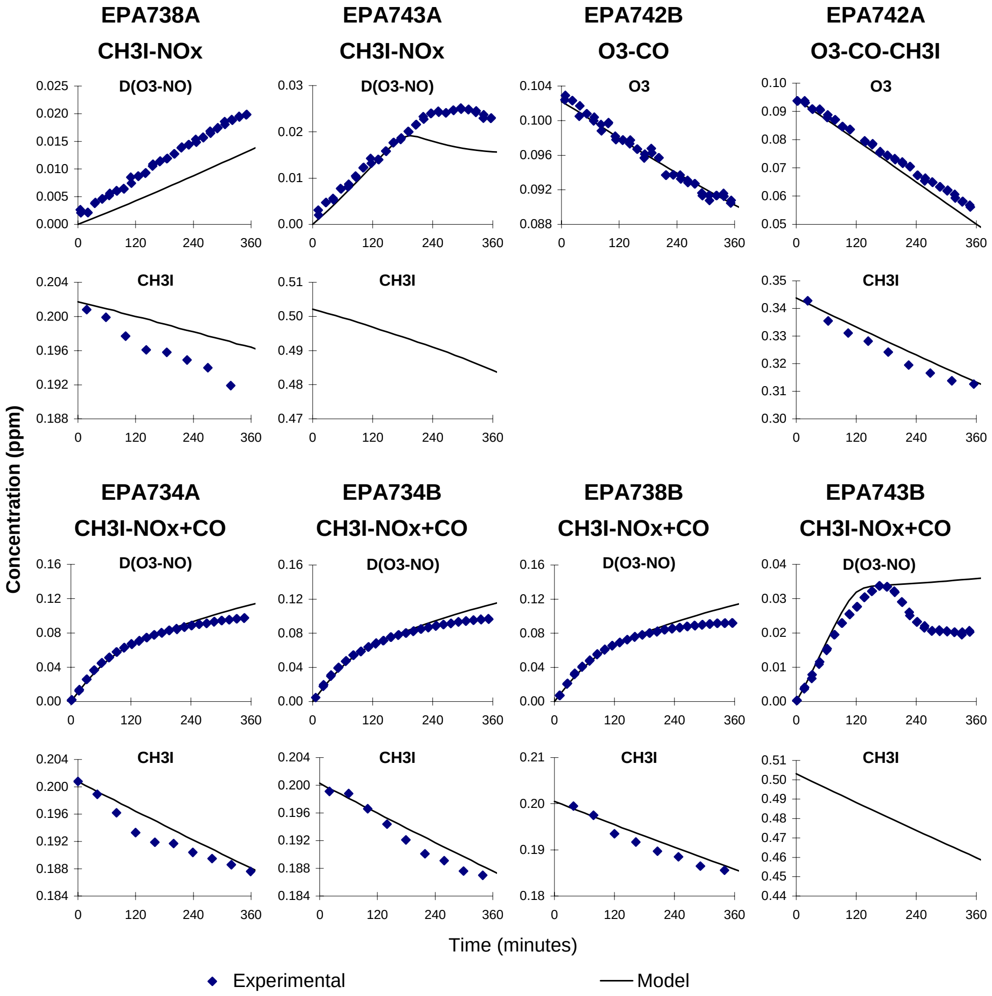


Figure C-110. Plots of selected experimental and calculated concentration-time plots for the methyl iodide - NO_x, methyl iodide - CO - NO_x, and methyl iodide - O_3 experiments.

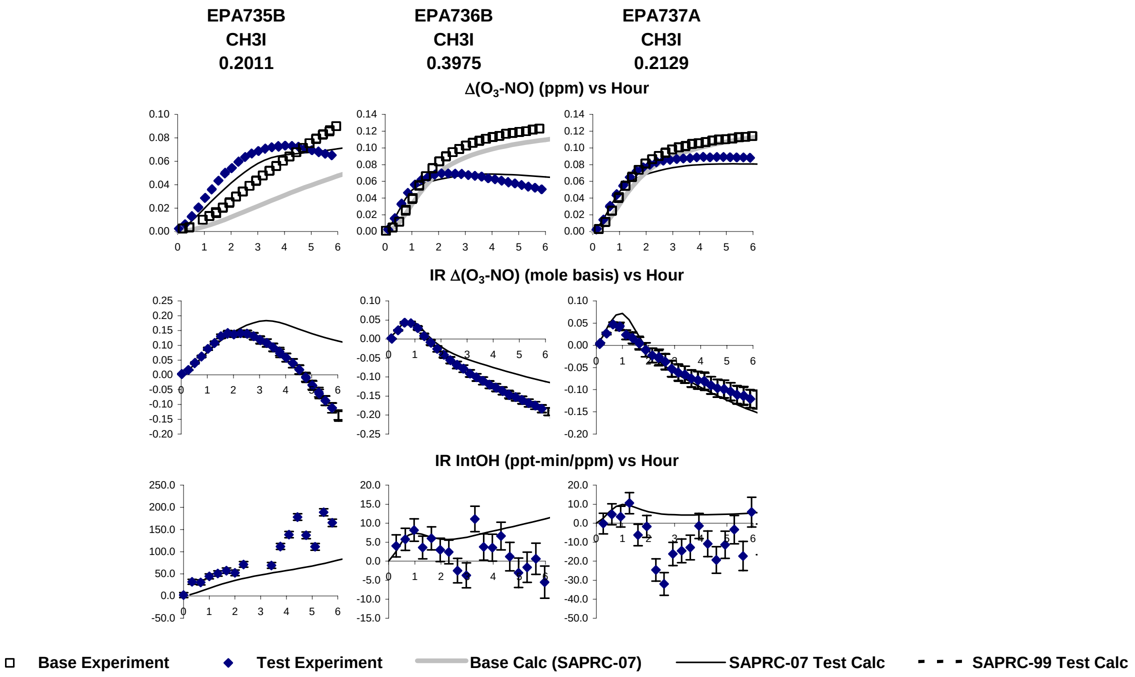


Figure C-111. Plots of experimental and calculated environmental chamber reactivity results for the methyl iodide experiments of Carter (2007).

APPENDIX D. SUPPLEMENTARY MATERIAL AVAILABLE

Complete documentation of this mechanism and its evaluation requires several tables that are too extensive to be appropriate for a printed report. These include the following:

Table A-3	Absorption cross-sections and quantum yields for all photolysis reactions in the base mechanism.
Table B-2	Listing of mechanisms for all VOCs for which mechanism assignments have been derived.
Table B-3	Listing of adjustable product mechanisms for all VOCs for which such mechanisms have been derived.
Table B-10	Listing of components of complex mixtures for which atmospheric reactivities have been calculated.
Table B-11	Assignments of explicitly represented compounds to lumped model species in the fixed parameter mechanism.
Table C-1	List of environmental chamber experiments used in the mechanism evaluation.

These are available in Excel files that can be downloaded using links at the SAPRC mechanism web site at http://www.cert.ucr.edu/~carter/SAPRC. These consist of saprc07.xls, that contains all the tables in Appendix A through Appendix C, and Table-A1.xls, Table-B2.xls, through Table-C1.xls that contain only the tables indicated. Because these files contain documentation information not included in the printable version of this report, these files must be considered to be an integral part of the SAPRC-07 mechanism documentation.

The SAPRC mechanism web site at http://www.cert.ucr.edu/~carter/SAPRC is currently under development. At present it contains this report document (as a Microsoft Word and a PDF file), the files containing the supplementary material as discussed above, and the files to implement the mechanism and conduct the simulations of the chamber experiments and other test calculations. Additional files will be added as time permits if requested. The web site will contain documentation concerning the format and use of the available files.

APPENDIX E. CHANGE LOG

In this Appendix, the changes to the mechanism and the mechanism documentation that was distributed or made available at the SAPRC mechanism web site are listed. If the mechanism needs to be changed or corrected in the future, this report and the supplementary material will be changed accordingly, and the modifications will be listed in this section.

6/15/07 This is the version documented in the final report that was submitted as the deliverable for CARB Contract 03-318.

12/31/07 This revised version was prepared as part of work on CARB project 06-408. The modifications are as follows:

- The mechanisms for the amines were revised or added as a result of CARB project 06-408. This resulted in substantial changes in the reactivities for these compounds.
- Results of modeling chamber experiments carried out for CARB project 06-408 was added to the "Mechanism Evaluation Results" section. These were primarily amine experiments but included a few other compounds.
- A minor error in the representation of the peroxy + HO_2 reactions was corrected.
- The reactivity scales were re-calculated after these changes were made. The effects of the changes were insignificant except for the amines..

5/21/08 This revised version was prepared as part of work on documenting the condensed version of SAPRC-07 and incorporates corrections of errors or omissions found during the course of the preparation of the condensed mechanism and other work. The reactivity scales were recalculated after these errors were corrected but the changes in the simulations of the chamber experiments were judged to be too small to revise the presentation of the fits of the model simulations to the chamber data. The modifications to the mechanism and the report were as follows:

- This Appendix E, giving the change log, was added to the report.
- An error in the rate constant for OH with 1,1-dichloroethene was corrected. This resulted in a decrease in the MIR of this compound from 2.76 to 1.69.
- The reactions of amines with O_3 were added. This resulted in changes in MIR's for in certain amines of up to ~30%.
- The photolysis reactions for PAN2 and the other high PAN analogues were added, based on analogy with the photolysis of PAN that was already in the mechanism. This shouldn't significantly affect environmental chamber and atmospheric reactivity simulations in this report but may non-negligibly affect regional airshed model predictions under some conditions.
- The derivation of the lumped model species whose parameters depend on the base ROG mixture (e.g., ALKn, OLEn, AROn) were re-derived because the original values of the mole fractions of the components used as the weighting factors could not be exactly reproduced. This was necessary to derive a standardized spreadsheet to derive weighting factors based on this mixture for mechanisms with other lumping schemes. The changes were small and only affect the fixed parameter version of the mechanism, but may have up

to ~10% effects on MIR's for compounds whose reactivities are highly sensitive to the base mechanism.

- The OLE2 + Cl mechanism was revised to incorporate explicitly generated mechanisms for reactions of chlorine with 1,3-butadiene and 2-methyl-1-butene. This would not affect the reactivity results for these compounds.
- Minor errors in the zRNO3 yields in the AFGn reactions were corrected. These shouldn't significantly affect model results.
- A minor error in the rate constant for the NRAD + HO2 rate constant was corrected. This shouldn't significantly affect model results.
- The files implementing the mechanism did not specify yRAOOH as a steady state species as documented, and this was corrected. This shouldn't affect model simulation results but might have a small effect on computer time, depending on how the mechanism is implemented.
- The reactivity scales were recalculated after these changes were made. Except for 1,1-dichloroethene and amines discussed above the changes were relatively minor. The MIR for TDI, changed by about 12% and the MIRs for certain higher alkanes changed by as much as 8% but usually less than 5%. For most compounds the change in MIRs were less than 2%.

6/3/08 The CARB hydrocarbon bin reactivities (Kwok et al, 2000; Carter and Malkina, 2005) have been added to the reactivity tabulation in Table B-1 and the compositions used to calculate the reactivities of these bins have been added to Table B-10 (Table B-10 available with the supplementary materials only). A footnote was added to Table B-1 referencing the relevant hydrocarbon bin work. No change was made to the main body of the report text.

6/19/08 Minor editorial corrections made to the documentation in several places, and some updates made to the references.

7/7/08 An error in the spreadsheet used to derive the aromatics mechanism was found that affected computation of ratio of BALD and PROD2 yields used to represent aromatic aldehydes and ketones formed from abstractions on alkyl groups on alkylbenzenes. This affected the BALD and PROD2 yields in ARO2 and in alkylbenzenes with groups other than methyl, but had relatively small effects on reactivity and other calculation results. In addition, several xPROD species (xHNO3, xHCOOH, xCCOOH, xRCOOH) were found not to be needed in the lumped atmospheric mechanism and were deleted. For reactivity calculations, these are replaced by their corresponding product species. Because of the relatively low reactivity of these species, the effects of this approximation on reactivity calculations, especially for MIR conditions, should be negligible. The mechanism listings were updated and the reactivity scales on Table B-1 were recomputed using the current version of the mechanism.

3/13/09 Several corrections and revisions were made as a result of problems discovered during the peer review of the mechanism. These are as follows:

- An error in the activation energy for the $HO_2 + O_3$ reaction was corrected. This resulted in 20% increase in this rate constant at 300^{o}K.
- The reaction of formaldehyde with HO_2 was deleted from the mechanism because as formulated in the mechanism it should be negligible under all relevant atmospheric and environmental chamber conditions. This permitted removal of one intermediate species from the mechanism.

- The rate constant expression for the reaction of OH radicals with methyl hydroperoxide was changed to that recommended by the NASA (2006) evaluation. This gives a 300^{o}K rate constant that is 35% higher than that previously used, which was from the IUPAC (2006) evaluation. The IUPAC recommendation has since been changed to an expression that gives an even higher rate constant than the current NASA (2006) recommendation. The branching ratios for the two competing reactions were also changed slightly to be consistent with the NASA (2006) recommendation.
- The group additivity parameters used in the mechanism generation system to estimate rate constants for reactions of OH radicals with organic hydroperoxides were modified to be consistent with the revised rate constant and branching ratio used for OH + methyl hydroperoxide. The methyl hydroperoxide data indicate an unusually large group additivity correction for OOH substitution on alkyl groups, and also indicates a much higher rate constant for reaction at the OOH group in organic hydroperoxides than for H_2O_2. The parameters used in the previous version of the mechanism were in error and were not consistent even with the previously used IUPAC (2006) rate constant for OH + methyl hydroperoxide. The revised group additivity parameters resulted in changes in the rate constants and the product distributions derived for the reactions of OH with the lumped higher hydroperoxide species ROOH, R6OOH and RAOOH. The products of the CL + RAOOH reaction were also revised, since they were estimated based on those for the OH reaction.
- Composition assignments were revised for several mixtures for consistency with the speciation database, resulting in slight changes in reactivities calculated for these mixtures. The affected mixtures, listed in order of reactivity changes, were "isomers of ethylbenzene", "C10 alkenes", and "isomers of butyl benzene", and Table B-9 has been modified accordingly. The MIR changes caused by these reassignments these were 20%, 9%, and 3%, respectively.

The plots and tables in this report giving model performance results in simulating these data have been updated using the current revised mechanism. However, these changes had minor or insignificant effect on model simulations of most of the chamber experiments, and did not require any revisions of parameters adjusted to fit the chamber data.

The atmospheric reactivities summarized have been recalculated using the current version of the mechanism and the reactivity tabulations in Table B-1 and the Supplementary Materials have been updated accordingly. These changes did not have significant affects on any calculated MIR values (changes being less than 4% for all compounds), but did cause changes of up to 25-30% for a few compounds in the lower NO_x scenarios. This is consistent with the fact that the HO_2 + O_3 and the hydroperoxide reactions become more important under low NO_x conditions.

6/8/09 Several fluoropropenes were added to the list of compounds with mechanisms and reactivity estimates based on the results of Carter (2009a,b), and a few minor corrections and additions were made to some of the footnotes in Table B-4.

6/10/09 Table 22 modified to include the values of all the chamber characterization parameters, not just RN-I.

6/22/09 The hydrocarbon bin reactivities and uncertainty classifications on Table B-1 were updated as discussed by Carter (2009c), which was added to the reference list. Some higher unspeciated aromatics compositions and reactivities on Table B-1 were also modified. Table B-10 in the electronic version was updated to give the revised bin and unspeciated aromatic compositions.

1/15/10 Several corrections and revisions were incorporated as a result of problems found with the mechanism or its documentation to date. These are summarized below.

- An error in the mechanism of the acyl peroxy + methyl peroxy reaction (Reaction BR24 in Table A-2) was corrected. The previous version had the alkoxy radical products forming in 10% yields when they should have been 90%. This correction required changing the mechanisms for all the peroxy + acyl peroxy reactions to be consistent with this. This correction affected the predictions of some low NO$_x$ products but had insignificant effects on ozone predictions. Nevertheless, all the reactivity scales were recalculated.
- Several other errors in various peroxy + peroxy reactions were corrected. These had no significant effect on ozone and had only minor effects for some species under low NO$_x$ conditions.
- Errors in the calculations of the atmospheric reactivities of the tertiary amines were corrected. The previous atmospheric reactivity calculations did not take into account the NO$_x$ loss involved in their mechanisms, though the radical loss was taken into account. This resulted in the MIRs for these compounds becoming positive rather than negative, but low NO$_x$ reactivities becoming more negative. This only affects 2-amino-2-methyl-1-propanol, t-butyl amine, and 2-amino-2-ethyl-1,3-propanediol. This did not affect the simulations of environmental chamber experiments with these compounds.
- Numerous errors in Table 1 were corrected.
- A number of VOCs were added to the reactivity tabulation in previous revisions but information about their mechanisms was not included in the tables in Appendix B. This information has now been added.
- The methods for reactivity values for mixtures was revised to be derived from those given for their components, rather than calculated for each mixture directly, since this approach does not involve the lumping of compounds that can occur when directly computing reactivities of complex mixtures.
- The mechanism and reactivity values for 3-methoxy-3-methyl-1-butanol were updated based on recent data from our laboratory (Carter et al, 2010).
- Several minor errors or omissions found in various tables or the text were corrected.

1/27/10 An error in the files implementing the mechanism, resulting in the rate constant for the O^{1}D+H$_2$O reaction being low by ~18%, was corrected, and all calculations were redone. This had no significant effects on the simulations of the chamber experiments used in the mechanism evaluations, but had small but nonnegligible effects (on the order of ~10%) on ambient simulations and atmospheric reactivity values. Affected tables and plots, including Table B-1 giving the reactivity vales, werer updated.