

**DETERMINATION OF ALDEHYDE AND PAN
FORMATION POTENTIALS FOR VOLATILE
ORGANIC COMPOUNDS**

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ABSTRACT

The SAPRC-99 chemical mechanism and the one-day EKMA model scenarios we employed previously for calculating the MIR and other ozone reactivity scales were used to derive numerical factors quantifying the impacts of different types volatile organic compounds (VOCs) on formation of selected VOC oxidation products. Formation potentials for 12 oxidation products, including formaldehyde, acetaldehyde, lumped higher aldehydes, PAN, higher PAN analogues, PBzN, acrolein, lumped organic nitrates, and lumped aromatic product species, were calculated for 694 types of VOCs and mixtures and for 348 of the 373 emissions profiles used in the current California Air Resources Board emissions inventory. The tabulated results give averages of the direct and total effects of the VOCs on hourly average concentrations of the products in the 39 base case scenarios employed in the study. The use of maximum or final product concentrations as impact quantification methods were found to be much more dependent on scenario conditions and did not provide as consistent a basis for comparison as using effects on average concentrations for this purpose. The scenario-to-scenario variability of the direct impacts on average concentrations in the base case scenarios for the VOCs with the highest was 10-15% for the aldehyde products, and 25-35% for PAN and PAN analogues, with higher variability for compounds with lower impacts. However, greater variability may result from use of a comprehensive set of scenarios. The effects of chemical mechanism uncertainty, the need to update the scenarios representing atmospheric conditions, and considerations involving use of alternative quantification methods are discussed.

Because of their size, the tables giving the mechanisms of the individual VOCs, the compositions of the emissions input and profiles, and the product formation potential results for the individual VOCs and emissions profiles, are available only in the electronic version of the Appendix to this report. This is available at <ftp.cert.ucr.edu/pub/carter/misc/oehha/appendx.xls>.

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TABLE OF CONTENTS

LIST OF TABLES	v
LIST OF FIGURES.....	vi
INTRODUCTION.....	1
Background and Statement of the Problem	1
Objectives and Overall Approach.....	2
METHODS.....	6
Chemical Mechanism Employed	6
Model Scenarios Employed.....	9
Base Case Scenarios.....	10
Modification to Base ROG Mixture.....	10
Adjusted NO _x scenarios and Variability of NO _x Conditions in the Base Case Scenarios.....	12
Averaged Conditions Scenarios	13
Modeling and Product Formation Potential Quantification Methods.....	13
Derivation of Product Formation Potentials for CARB Emissions Profiles.....	15
RESULTS AND DISCUSSION	16
Dependence of Results on Product Formation Quantification Method.....	16
Variability of Direct Product Formation Potentials with Scenario Conditions	19
Variability in Base Case Scenario Impacts Using Various Quantification Methods	19
Variability and Factors Affecting Indirect and Total Impacts	25
Correlations Between Indirect Impacts and Impacts on Radicals and Ozone.....	28
Correlation Between Direct and Total Impacts.....	28
Representative Results.....	29
Reported Data.....	29
Individual VOCs with Highest Product Impacts.....	33
Results for Emissions Profiles.....	40
CONCLUSIONS AND RECOMMENDATIONS.....	50
Chemical Mechanism Uncertainties	50
Representativeness of the Model Scenarios.....	51
Impact Quantification Methods	52
Compounds with Highest Product Formation Potentials.....	53
Product Formation Potentials for Emissions Profiles	54
REFERENCES.....	55
APPENDIX A.	57
MECHANISM LISTING AND RESULTS TABULATIONS	57

LIST OF TABLES

Table 1.	Listing of organic product compounds for which impacts were calculated in this study.....	3
Table 2.	List of organic product and radical species in the SAPRC-99 mechanism, indicating which were duplicated for the purpose of determining direct and indirect product formation.....	7
Table 3.	Summary of the conditions of the scenarios used for atmospheric reactivity assessment.....	11
Table 4.	Summary of model species assignments to the various VOC classifications in the preliminary SCOS-97 emissions inventory received from the CARB	12
Table 5.	Effects of quantification method on formaldehyde formation potentials for selected compounds relative to that for the base ROG mixture.	18
Table 6.	Effects of quantification method on PAN formation potentials for selected compounds relative to the PAN formation potential of the base ROG mixture.	18
Table 7.	Average direct, indirect, and total impacts of the base ROG mixture on all the product species studied for this project for the base case scenarios.	27
Table 8.	Correlation Coefficients for Indirect Product Formation Potentials for all VOCs in the mechanism with their effects on ozone and integrated OH radical levels for the averaged conditions adjusted NO _x scenarios.	29
Table 9.	Correlation coefficients between average direct and average total impacts for the base case scenarios for all product species, individual VOCs and emissions profiles considered in this project.	32
Table 10.	Average direct and total product formation potentials in the base case scenarios for the VOCs with the highest formation potentials for the various products, sorted by direct product formation potential.	34
Table 11.	Numbers and percentages of CARB emissions profiles with various ranges of mass percentages that have been assigned to SAPRC-99 detailed model species.....	41
Table 12.	Major Unidentified Components of the emissions profiles with over 50% of the mass unidentified.	42
Table 13.	Average direct and total product formation potentials in the base case scenarios for the 20 speciation profiles in the CARB emissions inventory with the highest direct formation potentials for the various products.	43
Table A-1.	Listing of model species used in the mechanism employed in this study. Except as indicated, the reactions of these species are given in Table A-2.	58
Table A-2.	Listing of the reactions of the inorganic, base case organic, and test compound product species in the mechanism used in this project.	62

LIST OF FIGURES

Figure 1.	Effects of test compound on concentration-time profiles for the formaldehyde or PAN directly formed from the reaction or introduction of the test compound in the averaged conditions MOIR scenario. The time dependence of the mixing height in the scenario is also shown.....	17
Figure 2.	Plots of standard deviations against average potentials for formation of selected products in the 38 base case scenarios for all VOCs and mixtures represented in the mechanism, with the formation potentials quantified in terms of effects on hourly average product concentrations.	20
Figure 3.	Plots of standard deviations against average potentials for formation of formaldehyde and PAN in the 38 base case scenarios for all VOCs and mixtures represented in the mechanism, with the formation potentials quantified in terms of effects on maximum formaldehyde or PAN concentrations.....	21
Figure 4.	Plots of standard deviations against average potentials for formation of formaldehyde and PAN in the 38 base case scenarios for all VOCs and mixtures represented in the mechanism, with the formation potentials quantified in terms of effects on final formaldehyde or PAN concentrations.....	21
Figure 5.	Distribution plots of direct average formaldehyde formation potentials calculated for selected VOCs and mixtures in the base case and the adjusted NO _x scenarios.	23
Figure 6.	Comparison of MIR with EBIR average direct average formaldehyde formation potentials calculated for all VOC classes currently represented in the mechanism. The lines of equal impacts for both types of scenarios are also shown.	24
Figure 7.	Dependences of direct average formaldehyde formation potentials on the maximum mixing height for the scenario for formaldehyde and ethylene.	25
Figure 8.	Distribution plots of direct average PAN formation potentials calculated for selected VOCs and mixtures in the base case and the adjusted NO _x scenarios.	26
Figure 9.	Comparison of MIR with EBIR average direct average PAN formation potentials calculated for all VOC classes currently represented in the mechanism. The line of equal impacts for both types of scenarios is also shown.	27
Figure 10.	Plots of indirect formation potentials for selected products for all VOCs in the current mechanism against their effects on integrated OH radical levels in the averaged conditions adjusted NO _x scenarios.	30
Figure 11.	Effects of added radical initiator species on concentration-time plots for ozone and the selected product species in the averaged conditions MOIR scenario. Numbers in parentheses are percentage change in average concentration caused by the added initiator.....	31
Figure 12.	Plots of average total impacts against average total impacts for representative product species in the base case scenarios for all VOCs in the mechanism. The self-formation potentials of the aldehydes are off scale and therefore are not shown.....	32

INTRODUCTION

Background and Statement of the Problem

The Office of Environmental Health Hazard Assessment (OEHHA) is characterizing health risks associated with exposure to various sources of air pollution in California. As part of this project, OEHHA must determine the proportion of ambient concentrations of toxic air pollutants that can be attributed to sources of interest. For toxic air pollutants whose only significant sources are primary emissions and that have relatively low atmospheric removal rates, this can be done by applying various source attribution methods. However, this approach does not work for toxic air pollutants that are introduced into the atmosphere significantly or exclusively from the gas-phase reactions of other emitted pollutants. Examples of such pollutants of interest to OEHHA include aldehydes such as formaldehyde, acetaldehyde and higher aldehydes, and acrolein, and organic nitrates such as peroxy acetyl nitrate (PAN) and its higher analogues, and other organic nitro compounds. These compounds are oxidation products formed in the gas-phase atmospheric reactions of the many types of volatile organic compounds (VOCs) that are emitted into the atmosphere from a wide variety of sources. Therefore, to assess the contributions of various types of sources to the atmospheric levels of these toxic pollutants that are also VOC oxidation products, one must have some measure or estimate of the relative potentials of each of the many types of emitted VOCs towards forming these products in the atmosphere.

The gas-phase atmospheric reactions most VOCs are complex (e.g., Atkinson, 1990, 1994, Carter, 2000a) and the amounts of oxidation products they form will depend not only on the reactivity and the reaction mechanism of the VOC, but may also depend, at least to some extent, on the nature of the environment in which they are reacting. The atmospheric reaction mechanism of the VOC is obviously important in that it determines the extent to which the oxidation product is formed when the VOC reacts and also the extent to which the product yield is affected by atmospheric conditions such as, for example, radical and NO_x levels. The rate at which the VOC reacts is also important in determining how much of the VOC reacts to form the toxic oxidation product before it is transported out of the region of interest, and also the amount of dilution occurring before the product is formed. Atmospheric conditions affect the overall radical levels that determine how rapidly the VOCs react to form the toxic products, but also the overall NO_x levels that can significantly affect yields of PAN analogues and other compounds, and to some effect can also affect aldehyde yields. All these factors need to be taken into account when assessing contributions of VOCs to atmospheric levels of their oxidation products.

The problem of quantifying the relative contributions of VOCs to formation of an organic oxidation product is similar in many ways to the problem of quantifying the relative reactivities of VOCs to formation of ozone. Ozone is not emitted directly, but is formed in a complex series of gas-phase reactions involving VOCs and NO_x in the atmosphere, and controlling VOCs is necessary to reduce ground-level ozone pollution in areas where ozone is not NO_x -limited. Since VOCs differ significantly in their effect on ozone formation, developing ozone reactivity scales quantifying the relative effects of the VOCs on O_3 in various environments provides a useful means to assess impacts of various VOC sources on ozone. The effects of VOCs on ozone depend on the rates and mechanism with which the VOC reacts, and also the nature of the environment in which the VOC reacts. These are the same factors that must be considered when assessing the effects of VOCs on other pollutants such as toxic organic products. The relative importance of the various mechanistic and environmental factors may be somewhat different, but the overall problem and tools needed to assess them are similar.

There has already been considerable research in developing reactivity scales for quantifying relative impacts of VOCs on ozone formation that can serve as the starting point for developing scales for quantifying impacts of VOCs on formation of other oxidation products. The author has previously developed detailed gas-phase atmospheric chemical mechanisms designed for representing the atmospheric reactions of the over 500 major types of VOCs that are emitted into the atmosphere (Carter, 1990, 2000a). These mechanisms were then used to calculate the relative ozone impacts of these VOCs under various types of conditions representing urban areas around the United States (Carter, 1994a, 2000a). The box model scenarios used to represent the urban areas in these calculations had highly simplified representations of the meteorology and transport and thus could not represent any specific episodes. Nevertheless, they were considered to be sufficient to represent the major chemical conditions affecting ozone and other product formation from the VOC reactions, and thus sufficient for developing general reactivity scales that will be applied to considering impacts in many different regions (Carter, 1994a). Because reactivities for ozone formation are strongly affected by NO_x conditions, several different ozone reactivity scales were developed to represent different NO_x conditions. One of these is the Maximum Incremental Reactivity (MIR) scale, which quantifies ozone impacts in the relatively high NO_x regions where ozone is most sensitive to changes in VOC emissions (Carter, 1994a). This scale was incorporated in several California Air Resources Board (CARB) regulations to regulate vehicle exhaust (CARB, 1993) and aerosol coatings (CARB, 2000) VOC emissions on the basis of their ozone impacts, and its use in regulating VOCs from other source categories is under consideration.

Although the mechanism and models used the most recent calculation of the MIR and other reactivity scales was designed primarily for calculating ozone impacts, they can also be used for calculating impacts on formation of many types of VOC oxidation products. The current mechanism, designated SAPRC-99, has explicit representation of formaldehyde, acetaldehyde, benzaldehyde, PAN and peroxy benzoyl nitrate (BPzN), has separate model species that can be used to represent higher aldehydes, cresols, nitrophenols, higher PAN analogues and other organic nitrates, and can be readily modified to explicitly represent acrolein and other toxic compounds if desired. The airshed scenarios used when calculating the ozone reactivity scales can also be used for calculating other impacts besides ozone, though perhaps updates and different impact quantification methods may be appropriate. Therefore, the tools developed for calculating the ozone can in principle also be used for calculating scales for quantifying impacts on other toxic pollutants.

Objectives and Overall Approach

In view of these considerations, the OEHHA contracted with the author to develop numerical factors or scales for quantifying impacts for the various types of emitted VOCs on formation of selected VOC oxidation products, using the tools developed previously for calculating ozone reactivity scales (Carter, 2000a) as the starting point. The specific types of oxidation products for which impacts are calculated in this work are listed Table 1. This table also indicates the extent to which their formation yields in the initial OH, O_3 or other reactions of the VOCs are expected to be dependent on reaction conditions, and also summarizes the types of VOCs forming them. As indicated on the table, the product species being considered in this work can be classified into two groups, based on the extent to which their yields in the initial oxidation reactions of the VOCs are expected to depend on reaction conditions. The first consists of the oxygenated products and alkyl nitrate species whose yields in the initial reactions are expected to be relatively independent of conditions, at least as long as some NO_x is present in the system. The second consists of the various acyl peroxy nitrate species that are not formed to a significant extent until most of the initially emitted NO is converted to NO_2 , and ozone formation begins. These groups

Table 1. Listing of organic product compounds for which impacts were calculated in this study.

Model Species	Description	Major types of precursor compounds
<u>Product species whose yields in the primary photooxidation reactions of most VOCs are predicted not to be highly dependent on reaction conditions in the current mechanism.</u>		
HCHO	Formaldehyde	Most VOCs at least as secondary product
CCHO	Acetaldehyde	Methyl-substituted alkenes and to some extent from many other aliphatic compounds.
RCHO	Lumped Higher Aldehydes	Alkyl-substituted alkenes and to some extent from most other aliphatic compounds.
BALD	Benzaldehyde and Other Aromatic Aldehydes	Aromatics
ACRO	Acrolein	1,3-Butadiene
CRES	Cresols	Aromatics
NPHE	Nitrophenols and Aromatic Nitro-compounds	Aromatics
RNO3	Lumped Alkyl Nitrates	Higher molecular weight aliphatics.
<u>Acyl Peroxynitrate species whose yields are predicted to be highly dependent on NO/NO₂ ratios and therefore correlated with ozone formation.</u>		
PAN	Peroxyacetyl Nitrate	Methyl-substituted alkenes, methylbenzenes, and to some extent from many other compounds.
PAN2	Higher Saturated Acyl Peroxynitrates	Alkyl-substituted alkenes, alkylbenzenes, and to some extent from many other compounds.
PBZN	Peroxybenzoyl Nitrate and Other Aromatic Acyl Peroxynitrates	Alkylbenzenes
MPAN	Unsaturated PAN Analogues such as that formed from methacrolein.	Acrolein, Methacrolein, 1,3-Butadiene, Crotonaldehyde, Isoprene

would therefore be expected to have some differences in how their direct and indirect formation potentials vary with scenario conditions, and this needs to be taken into account when interpreting the results.

Although many of the tools and procedures used when calculating the ozone reactivity scale could be applied directly to this project, there are some special considerations involved in this study that required some modifications to the mechanism, model scenarios, and calculation procedures. These are briefly summarized below.

The impacts of the various VOCs on product formation in a particular airshed scenario was determined by conducting a “base case” calculation designed to represent the conditions of the scenario, and then conducting separate “test” calculations for each VOC, where a small amount of the individual VOC of interest was added to the base case emissions. The impact of the VOC on formation of the product of

interest is then determined as the “incremental reactivity” of the VOC with respect to the product, which is defined as:

$$\begin{array}{l} \text{Incremental} \\ \text{Reactivity of VOC}_i \\ \text{for formation of} \\ \text{Product P} \\ \text{(Total Impact)} \end{array} = \lim_{\Delta[\text{VOC}]_i \rightarrow 0} \frac{\begin{array}{l} \text{Amount of Product P} \\ \text{Formed when VOC}_i \text{ is} \\ \text{Added to the Base Case} \end{array} - \begin{array}{l} \text{Amount of Product} \\ \text{P Formed in Base} \\ \text{Case Calculation} \end{array}}{\begin{array}{l} \Delta[\text{VOC}]_i, \text{ the Amount of VOC}_i \\ \text{Added in the Test Calculation} \end{array}} \quad (\text{I})$$

Note that this is a property of the scenario as well as of the test VOC and the product, P, whose impact is being calculated. This is the same general approach as used when quantifying ozone impacts.

Note also that the incremental reactivities defined as in Equation (I) also depend on how the “amount of product P formed” is quantified. For the MIR and other ozone reactivity scales the peak concentration is used as the metric, though other quantifications, such as the effect of the VOC on integrated ozone or the maximum 8-hour average can also be used. In the case of product formation potentials the use of the maximum product concentration is not appropriate, because as discussed below the time of the maximum can differ for different VOCs, meaning that these VOCs are not being compared on the same basis. The final product concentration was also judged not to be an appropriate measure for some products, because for rapidly reacting products such as formaldehyde it gave low product formation potentials for rapidly reacting VOCs that form the most of the product early in the simulation, leaving time for most of it to react away by the end of the simulation. After considering the alternatives, it was determined that the best measure was the average yield of the product throughout the simulation, specifically the averages of the concentrations calculated at the beginning and end of each hour. This gave an appropriate basis for comparing product formation potentials that impact formations of the products at different times in the simulation. This is discussed further below in the “Results” section.

It is also important to recognize that emissions of a VOC can have both a direct and an indirect effect on the formation of the oxidation product of interest. For example, if a VOC reacts to form formaldehyde as an oxidation product, or reacts to form an oxidation product that then reacts to form formaldehyde as a “second generation” product, then the VOC can be considered to have a *direct* effect on the formation of formaldehyde. However, a VOC that doesn’t form formaldehyde at all can still have a non-zero incremental reactivity for formaldehyde formation because its reactions may affect the reactions of the other VOCs present that form formaldehyde. For example, if the reactions of a VOC form radicals that cause other VOCs to react more rapidly than they would in its absence, the VOC causes increased formaldehyde formation from those other VOCs. This is referred to as the “*indirect*” effect of the VOC on product formation. Although this indirect effect can in many cases be a significant contributor to the overall impact of the product, for source attribution purposes it is useful to consider only the products formed directly from the VOCs reactions, or the VOCs *direct* impact on the product.

Because the OEHHA wanted a means to conduct direct source attribution analysis, it was necessary to modify the mechanism so that the direct and the total impacts could be separately calculated. This can be done by using different model species to represent the products formed from the reactions of the test VOC (the VOC_i in Equation I) than those used to represent the reactions of the products formed from the other VOCs that are present in the simulation. The effects of the test VOC on the former give the direct impact, their effects on the latter give the indirect impact, and the sum of these two impacts give the total impact, which is the same would be calculated if these were not represented separately. Because of the indirect impact effects, the compounds used to represent the total of all emitted VOCs in the base case

simulation (the *Base ROG* mixture) can potentially affect predictions of total product impacts of the various test VOCs. For that reason, the composition of the base ROG mixture was updated as part of this work.

The ozone reactivity scales we calculated previously (Carter, 1994a, 2000a) are based on 39 single-day box model scenarios that were developed previously by the EPA for regulatory risk analysis assessment purposes (Baugues, 1990). Because NO_x conditions are very important in affecting ozone reactivities, the MIR and other ozone reactivity scales were derived by adjusting NO_x inputs in these scenarios to yield well-defined NO_x conditions (such as NO_x giving the highest base ROG incremental reactivities in the case of MIR), and averaging the incremental reactivities derived in these adjusted NO_x scenarios. Although NO_x conditions may affect product formation potentials in most cases they are probably not as important as other variable scenario conditions. This is indicated by the data shown in the “Results” section, below. Therefore, although product potentials were calculated using adjusted NO_x scenarios for the purpose of assessing how NO_x levels affect these impacts, the primary product formation potential scales derived in this work were obtained by averaging the product formation potentials in the base case scenarios where no adjustments were made. The standard deviations of these averages, which in some cases were relatively large, provided a measure of the extent to which these product formation potentials vary with environmental conditions.

The modifications to the chemical mechanism and the scenarios employed and the various calculation and impact quantification methods employed are documented in the following section of this report, and selected results are given following that, together with a discussion of their implications on the relative merits of alternative methods to quantify product formation potentials of VOCs. The major output of this study consisted of tabulations of direct and total impacts of 693 types of VOCs and mixtures, and 348 of the 373 emissions profiles currently used in emissions inventories used for regulatory modeling in California. (Impacts were not calculated for the 25 other profiles with less than 50% of the mass in those profiles could be assigned to VOCs represented in the SAPRC-99 mechanism.) Complete tabulations of the results are given in appendices to this report, which are available in computer readable form.

METHODS

Chemical Mechanism Employed

The model simulations shown in this report were all carried out using the “SAPRC-99” mechanism that is documented in detail by Carter (2000a), with minor updates as indicated below, and with some modifications made for the purpose of this study as described below. This mechanism represents a complete update of the SAPRC-90 mechanism of Carter (1990), and incorporates recent reactivity data from a wide variety of VOCs. This includes assignments for ~400 types of VOCs, and can be used to estimate reactivities for almost 700 VOC categories. A unique feature of this mechanism is the use of a computerized system to estimate and generate complete reaction schemes for most non-aromatic hydrocarbons and oxygenates in the presence of NO_x, from which condensed mechanisms for the model can be derived. The mechanisms for the more reactive organic products of such VOC are also adjusted based on the generated reactions of the specific products they are predicted to form (Carter, 2000a). This is particularly useful for the purpose of this study, since it improves the accuracy of the predictions of the formation of the secondary products formed from the reactions of the more reactive primary products.

The mechanism was evaluated against the results of almost 1700 environmental chamber experiments carried out at the University of California at Riverside, including experiments to test ozone reactivity predictions for over 80 types of VOCs (Carter 2000a).

Some modifications were made to the mechanisms for certain VOCs and several additional types of VOCs were added to the SAPRC-99 mechanism since the documentation report of Carter (2000a) was completed, but prior to the work carried out for this study. Most of these modifications are described by Carter (2000b). The ozone reactivity tabulations available at the authors website¹ incorporate the results of these modifications. In addition, some minor changes were made to the mechanisms for the glycol ethers 1-butoxy-2-propanol, 2-(2-ethoxyethoxy) ethanol, and 2-(2-butoxyethoxy) ethanol based on new data obtained by Atkinson and co-workers (Atkinson et al, 2001, Carter et al, 2001). The ozone reactivity data currently available at the website may not yet incorporate the minor changes in the reactivities calculated for these three compounds.

Although the effects of the VOCs on total organic product formation could be determined using this mechanism, as indicated above the scope of work called for separate assessments of “direct” and “total” product formation potentials. To permit this, it was necessary to add a set of duplicate model species and reactions to the mechanism to separately represent products formed from the reactions of the test compounds whose product formation potentials are being assessed. This requires not only duplicating the species and reactions of the specific product compounds of interest, but also the intermediate radicals that form them, or that they form when they react whose subsequent reactions can form other products. Table 2 gives a listing of all the organic product and radical species in the SAPRC-99 mechanism that can be formed from the reactions of emitted VOCs, and indicates those whose reactions and model species were duplicated in the current study. Because of software and time limitations we were not able to calculate the formation potentials of all possible products in the current study, and the table indicates those whose direct and/or indirect formation potentials were assessed. Note that it is not necessary to

¹ The website address for the ozone reactivity data is <http://www.cert.ucr.edu/~carter/reactdat.htm>.

Table 2. List of organic product and radical species in the SAPRC-99 mechanism, indicating which were duplicated for the purpose of determining direct and indirect product formation.

Model Species	Description	Duplicated? [a]
<u>Radical Species and Operators.</u>		
C-O2.	Methyl Peroxy Radicals	X
RO2-N.	Peroxy Radical Operator representing NO consumption with organic nitrate formation.	X
CCO-O2.	Acetyl Peroxy Radicals	X
RCO-O2.	Peroxy Propionyl and higher peroxy acyl Radicals	X
BZCO-O2.	Peroxyacyl radical formed from Aromatic Aldehydes	X
MA-RCO3.	Peroxyacyl radicals formed from methacrolein and other acroleins.	X
TBU-O.	t-Butoxy Radicals	X
BZ-O.	Phenoxy Radicals	X
BZ(NO2)-O.	Nitro-substituted Phenoxy Radical	X
HOCOO.	Radical formed when Formaldehyde reacts with HO2	X
<u>Organic Product Species</u>		
HCHO	Formaldehyde	X
CCHO	Acetaldehyde	X
RCHO	Lumped C3+ Aldehydes	X
ACET	Acetone	X
MEK	Ketones and other non-aldehyde oxygenated products which react with OH radicals slower than $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-2} \text{ sec}^{-1}$.	X
MEOH	Methanol	X
COOH	Methyl Hydroperoxide	X
ROOH	Lumped higher organic hydroperoxides	X
GLY	Glyoxal	X
MGLY	Methyl Glyoxal	X
BACL	Biacetyl	X
PHEN	Phenol	X
CRES	Cresols	X
NPHE	Nitrophenols	X
BALD	Aromatic aldehydes (e.g., benzaldehyde)	X
ACRO	Acrolein [b]	X
MACR	Methacrolein	X
MVK	Methyl Vinyl Ketone	X
IPRD	Lumped isoprene product species	X
PRDX	Ketones and other non-aldehyde oxygenated products which react with OH radicals faster than $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-2} \text{ sec}^{-1}$.	X
RNO3	Lumped Organic Nitrates	X
DCB1	Reactive Aromatic Fragmentation Products that do not undergo significant photodecomposition to radicals.	X
DCB2	Reactive Aromatic Fragmentation Products which photolyze with alpha-dicarbonyl-like action spectrum.	X
DCB3	Reactive Aromatic Fragmentation Products which photolyze with acrolein action spectrum.	X
HCOOH	Formic Acid	

Table 2 (continued)

Model Species	Description	Duplicated? [a]
CCO-OH	Acetic Acid	
RCO-OH	Higher organic acids	
CCO-OOH	Peroxy Acetic Acid	
RCO-OOH	Higher organic peroxy acids	
PAN	Peroxy Acetyl Nitrate	X
PAN2	PPN and other higher alkyl PAN analogues	X
PBZN	PAN analogues formed from Aromatic Aldehydes	X
MPAN	PAN analogue formed from Methacrolein	X
<u>Primary Organics Represented explicitly</u>		
CH4	Methane	X
ETHENE	Ethene	X
ISOPRENE	Isoprene	X
<u>Organics Represented using the Lumped Parameter Approach</u>		
(varies)	Lumped parameter species (different species for base ROG components and test compounds or mixtures)	[c]

[a] “X” means that the compound reacts to form other products so a duplicate model species was added to the mechanism as part of this project for the purpose of calculating direct product formation potentials.

[b] Acrolein is not part of the standard SAPRC-99 mechanism, but was added to this mechanism for the purpose of calculating effects of VOCs on its formation.

[c] These have always been represented using separate model species for added test compounds than for base ROG components for reactivity calculation purposes, so no change was made in this regard. However, the mechanisms of the general species representing test compounds was changed so its reactions formed the duplicate species used for calculating direct product formation potentials.

include duplicate model species and reactions for product species that are treated as unreactive in the mechanism, or whose reactions do not form other organic species, unless their formation potentials are of specific interest. However, all reactive product species whose subsequent reactions may form products of interest have to be duplicated, even if its formation potentials are not the subject of the current assessment.

Note that it is also necessary to use separate model species to represent the explicitly represented primary organic species when their product formation potentials are being assessed or when they are present in mixtures that are being assessed. In the current SAPRC-99 mechanism the explicitly represented species include methane, ethene, and isoprene, and the explicitly represented organic products such as formaldehyde, etc. In the case of the latter the added duplicate product species are also used to represent their direct emissions, which means that emissions of a product is being treated as the same as its directly being formed with 100% yield. In the case of methane, ethane, and isoprene, it was necessary to add separate model species represent their reactions when their product formation potentials are assessed, with their reactions forming the duplicate organic model species used to assess direct product formation potentials.

Most of the emitted VOCs are represented in the mechanism using the “assigned parameter” approach, with general model species whose rate constants and product yield parameter values depending

on the compound being represented. For this study, the reactions of the general model species used to represent VOCs whose product potentials are being assessed were modified so they form the duplicate organic model species used to assess direct reactivities.

Because the OEHHA was interested in formation potentials for acrolein, this compound was added to the explicit product species represented in the mechanism. The mechanism employed is the same as used when calculating its ozone reactivity, as given by Carter (2000a). A duplicate acrolein model species was also added for the purpose of computing direct vs. indirect acrolein forming potentials. The only compound currently in the SAPRC-99 mechanism that is predicted to directly form acrolein to a significant extent is 1,3-butadiene, and its mechanism was modified appropriately to represent explicit formation of this product.

Test calculations were carried out to assure that the modified mechanism gave the same results as the original version except for the duplicated product species in added VOC test calculations, and that the total yields of the product species were the same as when they were not treated separately.

A complete listing of the modified SAPRC-99 mechanism, including the reactions of the duplicated product species, is given in Table A-1 through Table A-4 in the Appendix to this report, which is available in both printed and computer-readable form. The printed version gives Table A-1, the list of model species and Table A-2, the reactions in the “base” mechanism used to represent the inorganics and the reactive organic products. The computer-readable version gives these tables and includes Table A-3, which gives the reactions of the all the ~500 individual VOCs represented using the “assigned parameter” method. Because of its length this table, and also Table A-4, which gives the absorption cross sections and quantum yields of the photolysis reactions, are not included in the printed version. Except for 1,3-butadiene and those VOCs whose mechanisms have been modified as indicated by Carter (2000b) and Carter et al (2001), and the fact that model separate species are used to represent their products than used for the base case emissions, the mechanisms are the same as those given by Carter (2000a).

Model Scenarios Employed

Except for the change in the base ROG mixture used to represent the set of reactive organics emitted from all sources, the set of airshed scenarios employed to assess the reactivities for this study is the same as those used for calculating ozone reactivity scales in our previous work (Carter, 1994a, 2000a). These scenarios, and the reasons for using them, are briefly described below.

The objective is to use a set of scenarios that represents, as much as possible, a comprehensive distribution of the environmental conditions where unacceptable levels of ozone are formed. Although a set of scenarios has not been developed for the specific purpose of VOC reactivity assessment, the EPA developed an extensive set of scenarios for conducting analyses of effects of ROG and NO_x controls on ozone formation using the EKMA modeling approach (Gipson et al. 1981; Gipson and Freas, 1983; EPA, 1984; Gery et al. 1987; Baugues, 1990). The EKMA approach involves the use of single-cell box models to simulate how the ozone formation in one-day episodes is affected by changes in ROG and NO_x inputs. Although single-cell models cannot represent realistic pollution episodes in great detail, they can represent dynamic injection of pollutants, time-varying changes of inversion heights, entrainment of pollutants from aloft as the inversion height rises, and time-varying photolysis rates, temperatures, and humidities (Gipson and Freas, 1981; EPA, 1984; Gipson, 1984; Hogo and Gery, 1988). Thus, they can be used to simulate a wide range of the chemical conditions which affect ozone formation from ROG and NO_x, and which affect VOC reactivity. Therefore, at least to the extent they are suitable for their intended

purpose, an appropriate set of EKMA scenarios should also be suitable for assessing reactivities over a wide range of conditions.

Base Case Scenarios

The set of EKMA scenarios used in this study were developed by the United States EPA for assessing how various ROG and NO_x control strategies would affect ozone nonattainment in various areas of the country (Baugues, 1990). The characteristics of these scenarios and the methods used to derive their input data are described in more detail elsewhere (Baugues, 1990; Carter, 1994b). Briefly, 39 urban areas in the United States were selected based on geographical representativeness of ozone nonattainment areas and data availability, and a representative high ozone episode was selected for each. The initial non-methane organic carbon (NMOC) and NO_x concentrations, the aloft O₃ concentrations, and the mixing height inputs were based on measurement data for the various areas, the hourly emissions in the scenarios were obtained from the National Acid Precipitation Assessment Program emissions inventory (Baugues, 1990), and biogenic emissions were also included. Table 3 gives a summary of the urban areas represented and other selected characteristics of the scenarios.

This set of 39 EKMA scenarios are referred to as “base case” to distinguish them from the scenarios derived from them by adjusting NO_x inputs to yield standard conditions of NO_x availability as discussed below. No claim is made as to the accuracy of these scenarios in representing any real episode, but they are a result of an effort to represent, as accurately as possible given the available data and the limitations of the EKMA model, the range of conditions occurring in urban areas throughout the United States at the time the scenarios were developed. When developing general reactivity scales it is more important that the scenarios employed represent a realistic distribution of chemical conditions than accurately representing the details of any one particular episode.

Note that since these scenarios were designed primarily to represent conditions of high ozone pollution, they do not represent episodes of lower photochemical reactivity when ozone formation is less important. Since emitted VOCs may still react to some extent under those conditions to form the oxidation products of interest in this study, ideally such low photochemical reactivity conditions should also be represented in a comprehensive product formation potential assessment. Also, the episodes were developed some time ago and represent much higher ozone conditions than currently is the case, and updates to the mechanism has resulted in even higher predicted ozone concentrations for those episodes. However, updating these scenarios and developing new sets of scenarios to represent these lower photochemical reactivity days is well beyond the scope of this project.

Modification to Base ROG Mixture

The Base ROG mixture is the mixture of reactive organic gases used to represent the chemical composition of the initial and emitted anthropogenic reactive organic gases from all sources in the scenarios. Consistent with the approach used in the original EPA scenarios, the same mixture was used for all scenarios. Since the indirect product formation potentials of the test compounds depends on the products formed from the other VOCs present, the composition of the base ROG mixture used in the reactivity scenarios to represent the VOCs present in the base case was updated as part of this study. For this purpose, we used a composition representing summer weekday August 5, 1997 emissions into the SCOS-97 modeling region that was provided by Paul Allen of the CARB staff on February 20, 2001. He stated that some extremely large wildfires have been excluded from the data. The species in this mixture were associated wherever possible with SAPRC-99 model species. Although our previous assignments could be used in most cases, a number of new classes were found for which new assignments had to be

Table 3. Summary of the conditions of the scenarios used for atmospheric reactivity assessment.

Scenario		Max O ₃ (ppb)	ROG / NO _x	NO _x / MOIR NO _x	Max. Height (kM)	Init., Emit ROG (m. mol m ⁻²)	O ₃ aloft (ppb)	Integrated OH (ppt-min)
Avg.	MIR	200	3.1	1.6	1.8	15	70	133
Cond.	MOIR	263	4.5	1.0	1.8	15	70	238
	EBIR	239	6.4	0.6	1.8	15	70	228
Base	Atlanta, GA	192	7.3	0.6	2.1	12	63	222
Case	Austin, TX	188	9.3	0.5	2.1	11	85	198
	Baltimore, MD	372	5.2	0.9	1.2	17	84	229
	Baton Rouge, LA	269	6.8	0.8	1.0	11	62	215
	Birmingham, AL	261	6.9	0.5	1.8	13	81	233
	Boston, MA	207	6.5	0.5	2.6	14	105	283
	Charlotte, NC	148	7.8	0.3	3.0	7	92	223
	Chicago, IL	318	11.6	0.5	1.4	25	40	190
	Cincinnati, OH	219	6.4	0.7	2.8	17	70	245
	Cleveland, OH	279	6.6	0.8	1.7	16	89	221
	Dallas, TX	235	4.7	1.1	2.3	18	75	213
	Denver, CO	238	6.3	1.0	3.4	29	57	179
	Detroit, MI	265	6.8	0.7	1.8	17	68	265
	El Paso, TX	204	6.6	0.9	2.0	12	65	163
	Hartford, CT	183	8.4	0.4	2.3	11	78	240
	Houston, TX	342	6.1	0.8	1.7	25	65	264
	Indianapolis, IN	232	6.6	0.8	1.7	12	52	242
	Jacksonville, FL	167	7.6	0.6	1.5	8	40	226
	Kansas City, MO	168	7.1	0.5	2.2	9	65	255
	Lake Charles, LA	316	7.4	0.6	0.5	7	40	262
	Los Angeles, CA	653	7.6	0.8	0.5	23	100	167
	Louisville, KY	225	5.5	0.7	2.5	14	75	289
	Memphis, TN	246	6.8	0.6	1.8	15	58	280
	Miami, FL	141	9.6	0.4	2.7	9	57	196
	Nashville, TN	177	8.0	0.4	1.6	7	50	245
	New York, NY	419	8.1	0.6	1.5	39	103	195
	Philadelphia, PA	271	6.2	0.8	1.8	19	53	261
	Phoenix, AZ	313	7.6	0.9	3.3	40	60	185
	Portland, OR	175	6.5	0.6	1.6	6	66	252
	Richmond, VA	261	6.2	0.7	1.9	16	64	247
	Sacramento, CA	221	6.6	0.7	1.1	7	60	234
	St Louis, MO	367	6.1	0.9	1.6	26	82	215
	Salt Lake City, UT	199	8.5	0.5	2.2	11	85	204
	San Antonio, TX	141	3.9	1.0	2.3	6	60	209
San Diego, CA	215	7.1	0.8	0.9	8	90	164	
San Francisco, CA	394	4.8	1.5	0.7	25	70	88	
Tampa, FL	255	4.4	0.9	1.0	8	68	248	
Tulsa, OK	248	5.3	0.8	1.8	15	70	302	
Washington, DC	302	5.3	0.7	1.4	13	99	268	

Table 4. Summary of model species assignments to the various VOC classifications in the preliminary SCOS-97 emissions inventory received from the CARB

Type of VOC Classification	Wt %
Assigned the top 99 reactive species (by mole fraction)	97.5%
Petroleum Distillates, Naphtha, Mineral Spirits, etc. (included in total, above)	2.4%
Assigned the remaining 152 reactive species	0.6%
Assigned the INERT species	0.4%
Total of all assigned species	99.1%
Unknowns	0.3%
Other Categories with no SAPRC-99 species assigned	0.6%

made. A summary of the assignments is given in Table 4. The complete composition is given in Table A-5 in the Appendix to this report, which because of its length is only included in the computer-readable version of the Appendix.

As noted on Table 4, approximately 2.4% of the mass in this inventory consisted of various mixtures characterized as petroleum distillates, naphtha, or mineral spirits. These are represented by the mixture of compounds given in the CARB emissions inventory profile #1930, which was derived by Censullo et al. (1996) to represent an aggregate of such materials as used in California. This choice is based on recommendations provided by the CARB staff. The composition of this profile is given in Table A-6, which because of its length is included only in the electronic version of the Appendix to this report.

Adjusted NO_x scenarios and Variability of NO_x Conditions in the Base Case Scenarios

Because ozone reactivities depend significantly on relative NO_x levels, which vary widely in the base case scenarios, three separate sets of adjusted NO_x scenarios have been derived to obtain ozone reactivity scales for specified NO_x conditions (Carter, 1994a). These were also used in this study to assess the extent to which the product formation potentials depended on NO_x conditions. The three sets of NO_x conditions are designated MIR (for maximum incremental reactivity), MOIR (for maximum ozone incremental reactivity), and Equal Benefit Incremental Reactivity (EBIR), representing conditions of relatively high, optimum, and low NO_x availability with respect to ozone formation. In the MIR scenarios, the NO_x inputs were adjusted so the base ROG mixture has its highest incremental reactivity. Most other VOCs had their highest incremental reactivities at this same NO_x level. This is representative of the highest NO_x conditions of relevance to VOC reactivity assessment because at higher NO_x levels O₃ yields become significantly suppressed, but is also the condition where O₃ is most sensitive to VOC emissions. In the MOIR scenarios, the NO_x inputs were adjusted to yield the highest ozone concentration. In the EBIR scenarios, the NO_x inputs were adjusted so that the relative effects of NO_x reductions and total ROG reductions on peak ozone levels were equal. This represents the lowest NO_x condition of relevance for ozone reactivity assessment, because O₃ formation becomes more sensitive to NO_x emissions than VOC emissions at lower NO_x levels.

The ratio of the NO_x inputs in the base case scenarios to the NO_x inputs yielding maximum ozone concentrations (the MOIR NO_x) provides a good measure of the NO_x availability in the scenario with

respect to ozone formation. As discussed by Carter (1994a) the MIR and EBIR ROG/NO_x ratios are respectively ~1.5 and ~0.7 times those for the MOIR levels. This ratio for the base case scenarios, as shown on Table 2, indicate that the NO_x conditions for most (73%) of the base case scenarios are between MOIR and EBIR levels, with most of the remainder having lower NO_x levels than EBIR. Only two scenarios have higher NO_x than MOIR and only one has higher NO_x than MIR conditions. However, as discussed elsewhere (Carter, 1994a), this set of scenarios is based on near-worst-case conditions for ozone formation in each of the airsheds. Had scenarios representing less-than-worst-case conditions been included, one might expect a larger number of MIR or near MIR scenarios. This is because NO_x is consumed more slowly on days with lower light intensity or temperature, and thus the scenario is less likely to become NO_x-limited.

Averaged Conditions Scenarios

For the purpose of sensitivity calculations, three “averaged conditions” adjusted NO_x scenarios were derived to represent average or typical conditions of the 39 scenarios representing the various urban areas. As discussed by Carter (1994a,b), these were derived by using average or typical values of most of the inputs to obtain an averaged conditions base case scenario, and then adjusting the NO_x inputs as described above to obtain MIR, MOIR, or EBIR conditions. The ozone reactivities derived using these scenarios were very close to the averages for the corresponding 39 adjusted NO_x scenarios, indicating that these scenarios are useful for sensitivity and exploratory calculations at least for ozone reactivity. However, this may not be the case for product formation potential calculations, as discussed in the Results section, below.

Modeling and Product Formation Potential Quantification Methods

The procedures for carrying out the model simulations for this project were generally the same as employed when calculating the ozone reactivity scales (Carter, 1994a, 2000a), except that product yield data were also saved and used in the analysis. For each scenario a “base case” simulation was carried out to determine the levels of product species formed without the added test compounds. The maximum, integrated and hourly O₃ concentrations, the integrated OH radical levels, and the maximum, final, and sum of the hourly concentrations of each of the product species were saved. Then for each test VOC or test mixture represented in the SAPRC-99 mechanism, a separate calculation was carried out for each scenario where a small amount of the test VOC or mixture was added, and the same data were saved as in the base case simulations. The amount of test VOC added was derived such that the estimated amount reacted in the simulations was 0.005 millimoles m⁻², where the emitted VOC reacting was derived based on its rate constants and parameters relating these to amounts reacted that were derived in the base case simulations.

The results were then used to determine the molar product formation potentials, computed as follows:

$$\begin{array}{l} \text{Direct Product} \\ \text{Formation} \\ \text{Potential of} \\ \text{Test VOC} \\ \text{(mole per mole)} \end{array} = \begin{array}{l} \text{Scenario-dependent} \\ \text{Conversion Factor} \\ \text{(millimoles m}^{-2} \text{ ppm}^{-1}) \end{array} \cdot \frac{\begin{array}{l} \text{Concentration of product formed from test} \\ \text{VOCs in the added VOC calculation (ppm)} \end{array}}{\begin{array}{l} \text{Amount of test VOC added (millimoles m}^{-2}) \end{array}} \quad \text{(II)}$$

$$\begin{array}{r}
 \text{Indirect} \\
 \text{Product} \\
 \text{Formation} \\
 \text{Potential of} \\
 \text{Test VOC} \\
 \text{(mole per} \\
 \text{mole)}
 \end{array}
 =
 \begin{array}{r}
 \text{Scenario-} \\
 \text{dependent} \\
 \text{Conversion} \\
 \text{Factor} \\
 \text{(millimoles} \\
 \text{m}^{-2} \text{ ppm}^{-1})
 \end{array}
 \cdot
 \frac{
 \begin{array}{r}
 \text{Concentration of} \\
 \text{product formed from} \\
 \text{base case species in} \\
 \text{the added VOC} \\
 \text{calculation (ppm)}
 \end{array}
 -
 \begin{array}{r}
 \text{Concentration of} \\
 \text{product formed from} \\
 \text{base case species in} \\
 \text{the base case} \\
 \text{calculation (ppm)}
 \end{array}
 }{
 \text{Amount of test VOC added (millimoles m}^{-2})
 }
 \quad \text{(III)}$$

The “concentration of product formed” can be either maximum, final, or hourly average product concentration, depending on the product quantification method used. As discussed below, the results (both relative and absolute) can differ significantly depending on which product quantification method is used. For reasons discussed below the major quantification method used in most of this work is effects on average product concentration, which is computed by summing the concentrations at the beginning or end of each hour, then dividing by the number of hours in the simulations, which are always 11 hours in these one-day simulations.

Since the model computes the model species concentrations in ppm, while the VOC inputs are given in units of moles per unit area per day, a conversion factor between ppm and moles per unit area is used to make the formation potentials unitless quantities. This conversion factor is given by

$$\begin{aligned}
 \text{Conversion Factor (millimoles m}^{-2} \text{ ppm}^{-1}) &= 12.19 \cdot H \text{ (meters)} / T \text{ (}^{\circ}\text{K)} \\
 &= 4.06 \times 10^{-2} \cdot H \text{ (meters) at } T = 300^{\circ}\text{K}
 \end{aligned}
 \quad \text{(IV)}$$

where H is the maximum and final mixing height in meters, and T is the temperature used for computing the conversion factor, for which 300°K was used for all scenarios. These conversions are appropriate for 1 atmosphere total pressure, which is assumed to be the case in all the scenarios. Note that the mixing height increases throughout the day in these EKMA scenarios, so the maximum and final mixing heights are the same. These are given in Table 3 for each of the scenarios.

As with ozone formation potentials, the relative product formation potentials will depend on whether the VOC is quantified on a mass or mole basis. The equations above all show how the product formation potentials are computed on a mole basis, since these are what are calculated in the simulations. However, because VOC emissions are quantified by mass in regulatory applications, it is appropriate to convert these mole-based product formation potentials to mass-based units, so they give products formed per unit mass of VOC emissions. These are the units that must be used when quantifying product formation potentials from mass-based emissions inventories. This conversion is done as follows.

$$\begin{array}{r}
 \text{Direct or Indirect} \\
 \text{Product Formation} \\
 \text{Potential of VOC} \\
 \text{(mass basis)}
 \end{array}
 =
 \begin{array}{r}
 \text{Direct or Indirect Product} \\
 \text{Formation Potential of VOC} \\
 \text{(mole basis)}
 \end{array}
 \cdot
 \frac{
 \text{Molecular weight of product}
 }{
 \text{Molecular weight of VOC}
 }
 \quad \text{(V)}$$

Note that it is not strictly necessary to use the molecular weight of the product in the conversion when considering relative impacts because the factor is the same for all VOCs, but this is used so the formation potentials are still unitless quantities. Except as noted the product formation potential results given in this report will all be given in mass-based units because this is the most appropriate for regulatory assessment applications, and is the most useful in assessments using mass-based emissions inventories.

Derivation of Product Formation Potentials for CARB Emissions Profiles

Although the fundamental quantities of interest to be calculated in this project are the product formation potentials of the individual classes of emitted VOCs, from an applied standpoint the OEHHA is interested in determining the product formation potentials of various types of emissions sources. The OEHHA analysis will be using emissions databases maintained by the CARB, which uses various speciation profiles that give the chemical compositions of the various emissions sources. Therefore, the specific quantities of practical interest to the OEHHA analysis are the product formation potentials of the various emissions *profile*, rather than of the individual compounds themselves. This requires (1) assigning SAPRC-99 model species to the various chemical categories that are used in the CARB emissions profile database, and (2) using these assignments, together with the product formation potentials calculated for the various model species, to calculate the product formation potentials of these profiles. The assignments and procedures used for doing this are summarized in this section.

The CARB speciation databases used in this work were provided by Beth Schwehr of the CARB in February of 2001, and the file provided was dated 11/29/2000. (The file name was ORGPROF_11_30_00.xls, and is also available at <http://www.arb.ca.gov/emisinv/speciate/speciate.htm>. Note that this is characterized as a “draft”, and is therefore subject to change. However, this same speciation profile dataset was still available at the CARB web site as of early September 2001. The relevant data from this file are given in Table A-6Table A-5, which because of its length is included only with the electronic version of the Appendix to this report.

This CARB speciation databases use a 6-digit numeric “ChemCodes” to define the chemical classes in the various speciation profiles. These ChemCodes are similar to, but not the same as, the SAROAD categorization system used by the U.S. EPA. These categories include not only well defined chemical compounds, they also include various types of mixtures, general categories of chemicals, and an “unidentified” category. Many of these CARB chemical categories have been assigned to SAPRC detailed model species in previous projects, but the CARB had added additional categories that needed to be assigned, and some categories had to be re-assigned because of new model species that have been added to the mechanism as part of recent projects (e.g., see Carter, 2000b).

Therefore, as part of this project we reviewed the assignments of SAPRC-99 model species to ARB’s ChemCode categories, made as many additional assignments as possible, and made revisions to previous assignments. These assignments are given with the listing of the speciation database in Table A-6Table A-5 in the electronic version of the Appendix to this report. The most significant revision was to the “distillates/naphtha/mineral spirits” category, which were assigned to the mixture of compounds derived by Censullo et al. (1996) to represent an aggregate of such materials as used in California (profile #1930). Note that it was not possible to assign model species to all chemical categories used in the CARB emissions databases. In addition to the “unassigned” category, there are categories whose chemical structures are too poorly defined to be assigned model species, and also chemicals whose mechanisms are unknown. The mass emissions of most of these categories were generally small in most of the profiles, but a few profiles had a significant fraction of the mass that could not be assigned model species.

The assignments of model species to the various CARB profiles were made on a mass basis, so the mass-based product formation impacts were used to derive the mass-based product formation impacts of the various profiles. No product formation impact estimates were made for profiles that had less than 50% of the mass assigned to model species. If a profile had greater than 50% but less than 100% of the mass assigned, the fraction that was assigned was used to represent the entire mass of the profile, i.e., the impacts per unit mass of the entire profile was assumed to be the same as the impacts per unit mass of the assigned fraction.

RESULTS AND DISCUSSION

Dependence of Results on Product Formation Quantification Method

As indicated above, the effects of VOCs on formation of a particular product species depends on how the amount of product formed is quantified. Different results can be obtained if the formation potentials are given relative to peak, average, or final concentrations of the products. These are illustrated by the formaldehyde and PAN formation potentials of selected compounds in a representative scenario, as discussed in this section. Formaldehyde and PAN are taken as representative of the two major types of product species considered in this work as indicated in Table 1, and the averaged conditions MOIR scenario is taken as representative of the various scenarios employed in this study. The results for the other compounds and scenarios should be representative of the examples discussed here, at least in terms of the general types of dependences observed. Effects of quantification method on scenario-to-scenario variability of product formation potentials are discussed separately in the following section.

The effects of product yield quantification on formaldehyde and PAN formation potentials of selected representative compounds in the averaged conditions MOIR scenario are shown on Figure 1 and Table 5 and Table 6. The various compounds are chosen to be representatives of different types of mechanisms in terms of rates of reaction and whether the products are formed as primary or secondary products, with the base ROG mixture being shown for comparison. Figure 1 shows how the shapes of the concentration-time plots for the directly formed (or added) formaldehyde or PAN varies depending on which compound is added, and Table 5 and Table 6 show how the formaldehyde or PAN impacts of these compounds, relative to the formaldehyde or PAN impacts of the base ROG mixture, varies depending on the quantification method. Figure 1 also shows how the mixing height in this scenario varies with time in this scenario, which is typical of its behavior in all the scenarios employed in this study. As discussed below the time variation of the mixing height is an important factor affecting the product yield quantification method because it relates how the instantaneous concentrations of the product are related to the moles of products actually introduced, and is used in the computations of the magnitudes of the yields (see Equations II and IV, above).

Figure 1 shows that there are significant differences in concentration-time profiles in the directly formed (or added) formaldehyde in the simulations, depending on the test compound used. When the test compound is formaldehyde itself, the directly added formaldehyde peak is at the initial time in the simulation and it falls off to very low values by the end of the simulation. The decline in concentration is both because of the relatively rapid chemical reaction of formaldehyde and also because of dilution caused of the increase of the mixing height (also shown on the figure). A very rapidly reacting compound such as 2,3-dimethyl-2-butene gives a very similar profile for the directly formed formaldehyde, with the peak forming very early in the simulation (though not initially), then falling rapidly throughout the day. Ethene, which reacts at a more moderate rate forming formaldehyde as one of its primary products, is more typical of most VOCs with high direct formaldehyde formation potentials, which dominates the formaldehyde-forming potentials of the mixture of all emitted VOCs. The formaldehyde formed from such compounds tend to peak in the middle of the simulation, then decline to lower values at the end. Finally, n-octane is representative of compounds that form formaldehyde only as secondary products, which means that the peak direct formaldehyde formation from it comes at the end of the simulation.

Figure 1 shows that similar results are obtained when comparing the PAN formation potentials of the representative PAN-forming compounds. Here, 2,3-dimethyl-2-butene and methylglyoxal are the

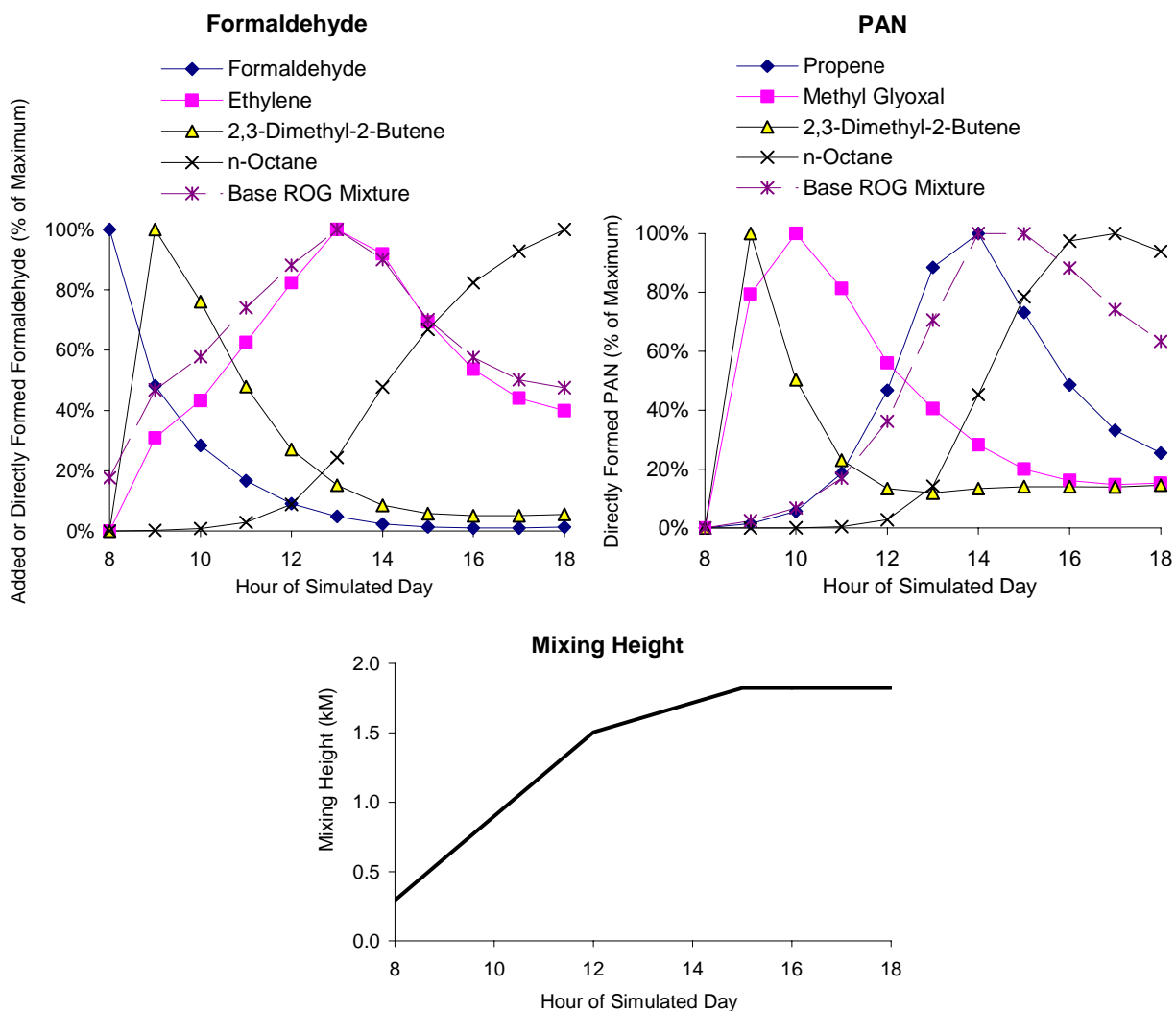


Figure 1. Effects of test compound on concentration-time profiles for the formaldehyde or PAN directly formed from the reaction or introduction of the test compound in the averaged conditions MOIR scenario. The time dependence of the mixing height in the scenario is also shown.

compounds that form PAN rapidly, n-octane forms PAN primarily from secondary reactions of product, and propene is a moderately reactive compound that forms PAN from reactions of its primary products. The PAN formation in the base ROG mixture is attributed primarily in part to moderately reactive compounds like propene that form PAN from its primary products, and to compounds like n-octane that form it from secondary products, so the concentration-time profile for PAN directly formed from the base ROG mixture is intermediate between those two compounds.

Table 5 shows that the relative formaldehyde impacts of the compounds can be significantly different depending on the formaldehyde quantification method used, with the ordering as well as the magnitude being affected in some cases. All these differences can be understood in terms of the different formaldehyde concentration-time profile shapes shown on Figure 1. Although the ordering of relative

Table 5. Effects of quantification method on formaldehyde formation potentials for selected compounds relative to that for the base ROG mixture.

Compound	Relative Impact (Normalized to Base ROG)		
	Average	Peak	Final
Formaldehyde	3.5	11.5	0.3
2,3-Dimethyl-2-Butene	2.1	5.0	0.6
Ethylene	1.1	1.3	1.1
Base ROG Mixture	1	1	1
n-Octane	0.3	0.5	1.2

Table 6. Effects of quantification method on PAN formation potentials for selected compounds relative to the PAN formation potential of the base ROG mixture.

Compound	Relative Impact (Normalized to Base ROG)		
	Average	Peak	Final
Methyl Glyoxal	2.2	2.8	0.7
Propene	2.0	2.6	1.0
2,3-Dimethyl-2-Butene	1.8	3.8	0.9
n-Octane	1.5	2.0	2.9
Base ROG Mixture	1	1	1

impacts tend to be similar regardless of whether the average or peak concentration quantification method is used, the peak concentration quantification method tends to give greater impacts for the most rapidly reacting compounds (or the self-impacts of the product itself) than is the case for the average concentration method. This is because the directly produced (or injected) formaldehyde peaks early in the simulation when the mixing height is low, and thus concentrations are highest relative to the number of moles emitted. Because of this mixing height effect, the compounds that form formaldehyde later in the day have less of an effect on the peak formaldehyde concentration than those forming it early, even if the same number of moles were formed. Although a mixing height correction factor is used when computing the product formation potentials regardless of the quantification method used (see Equations II and IV, above), it cannot correct to the fact that the products formed from the different VOCs may peak at times when the mixing heights are different.

Table 6 shows that the relative PAN formation impacts also differ, and can have different orderings, depending on the quantification method used. In general, the patterns seen are analogous to those seen for formaldehyde, discussed above, though the effect is somewhat less dramatic because in most cases the differences in the concentration-time profiles are somewhat less (see Figure 1).

The fact that peak concentrations of products formed from the VOCs may be occurring at times with different mixing heights means that use of the maximum concentration quantification method results in product formation potentials not always being compared on the same basis for different VOCs. This would also cause greater scenario-to-scenario variability in the formation potentials, because the variation in inversion heights among the scenarios (see Table 3). This is less of a problem with the average concentration quantification method, which gives equal weight to all the times (and mixing heights) in the simulations, or the final concentration method, which uses the same mixing height for all VOCs, is considered to be more appropriate. For this reason, use of the peak concentrations to quantify impacts is probably not appropriate.

Because most of the products being considered in this report undergo relatively rapid reaction, the final concentrations of the directly formed or added formaldehyde concentrations tend to be much lower if the product is formed early in the experiment than is the case if it were formed later. For this reason, the formaldehyde forming potentials of formaldehyde itself and the PAN and formaldehyde forming potentials of rapidly reacting species such as 2,3-dimethyl-2-butene, tend to be much lower when quantified by the final concentration than when quantified by the average or peak levels. Conversely, compounds like n-octane, which form PAN precursors or formaldehyde only as a secondary products, tend to have quite high impacts on peak concentrations than compounds that form formaldehyde directly, because of the formaldehyde formed as a secondary product has less time to react. Therefore, using final product concentrations as the quantification method tends to quite different orderings of formation potentials than using peak or average concentrations, and the results are generally not consistent with the total amounts of product that the various VOCs actually produce.

Because of these considerations, we conclude that for most applications the using effects on average concentrations of the product of interest is a better quantification method than using the maximum or final concentrations of these products. For that reason, most of the results discussed in the remainder of this report will focus on formation potentials quantified by effects on average concentrations, except in the following section where scenario-to-scenario variability for all three quantification methods are compared.

Variability of Direct Product Formation Potentials with Scenario Conditions

Before presenting the full set of results of the calculations of the direct, indirect, and total product formation potentials for the various classes of VOCs and profiles, it is useful to get a sense of the extent to which these impacts vary with scenario conditions, and of which scenario conditions are the most important in affecting this variability. In addition to varying NO_x levels, the base case scenarios have varying maximum mixing heights, total pollution levels, initial and hourly emissions fractions, and other varying conditions (see, for example, Table 3, above). The adjusted NO_x scenarios provide a means for removing the variability in NO_x conditions, but the other conditions such as mixing heights are still as variable as in the base case scenarios. Therefore, the differences in the product formation potentials between the base case and various adjusted NO_x scenarios give an indication of the extent to which NO_x conditions affect the product formation potentials, and the variabilities among the scenarios with the same NO_x conditions give an indication of the effects of the other variable scenario conditions.

Variability in Base Case Scenario Impacts Using Various Quantification Methods

One measure of the variability of product impacts with scenario conditions is the standard deviations of the averages of the impacts for the 39 base case scenarios. Plots of these standard deviations against the averages for representative product formation potentials for all the VOCs in the base case

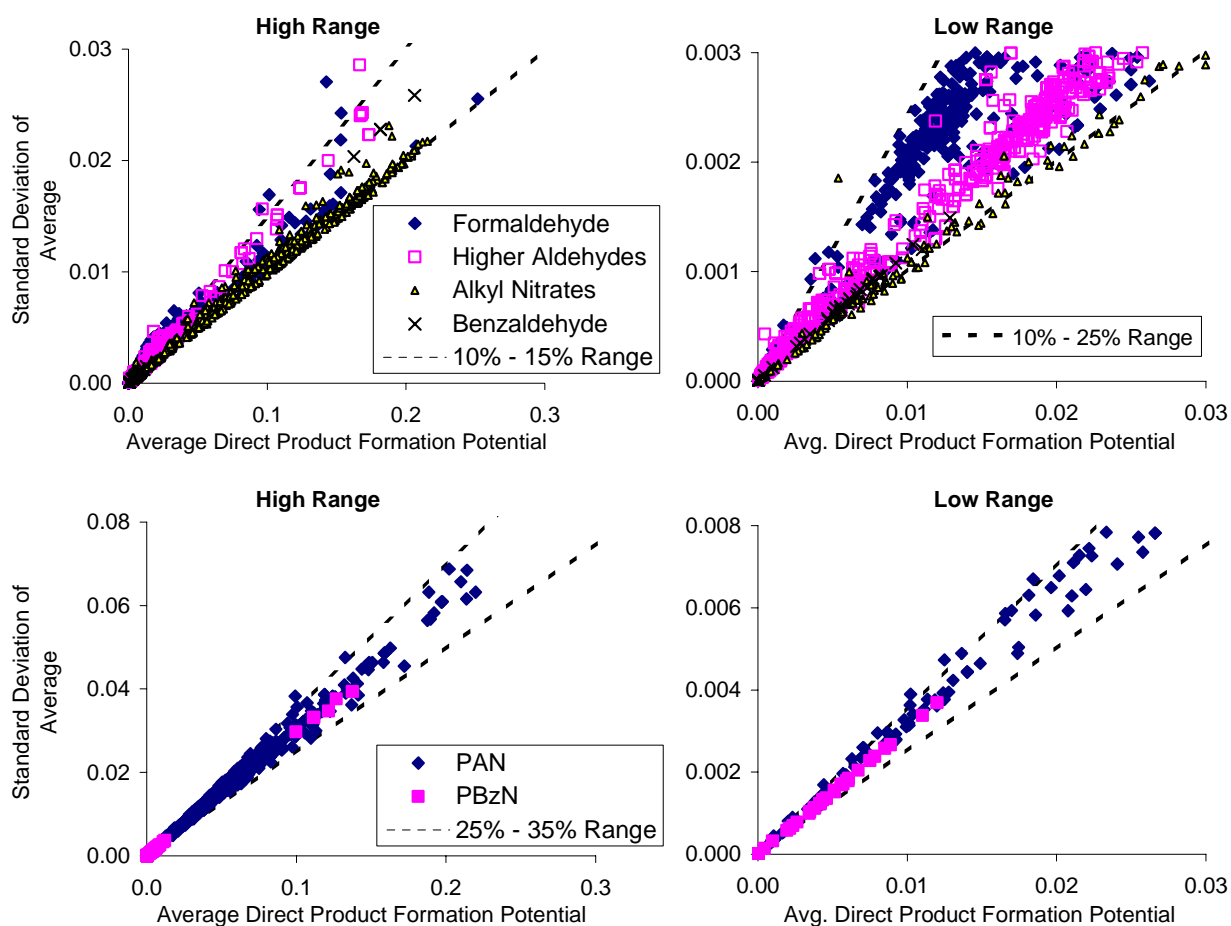


Figure 2. Plots of standard deviations against average potentials for formation of selected products in the 38 base case scenarios for all VOCs and mixtures represented in the mechanism, with the formation potentials quantified in terms of effects on hourly average product concentrations.

scenarios shown on Figure 2 through Figure 4, where. Figure 2 shows the results quantified based on hourly average concentrations, and Figure 3 and Figure 4 show the results quantified using maximum and final concentrations, respectively. In all three cases the results for formaldehyde or the representative aldehyde and alkyl nitrate products are shown on the top plots, or for PAN or the representative PAN analogues are shown on the bottom.

A comparison of Figure 2 with Figure 3 and Figure 4 indicate that much lower standard deviations are obtained when the product impacts are quantified on an hourly average basis rather than on the basis of maximum or final concentrations. For the oxygenated and organic nitrate products, the standard deviations of the compounds with the highest product formation potentials are generally in the 10-15% range when quantified in terms of average concentrations, while they are somewhat more variable, being in the 10-25% or 10-35% range when quantified in terms of maximum or final concentrations, respectively. For PAN analogues the difference is even greater, with the standard deviations when quantified in terms of hourly averages being fairly narrowly distributed in the 25-25% range, but being in the 15-50% or 50-80% when quantified in terms of maximum or final yields. This can

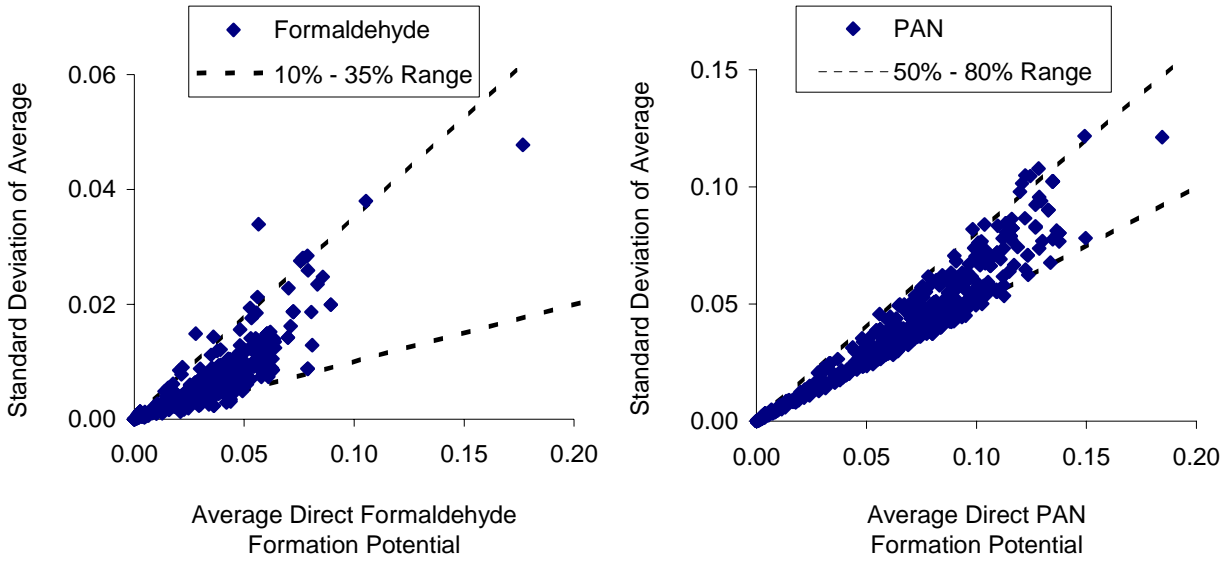


Figure 3. Plots of standard deviations against average potentials for formation of formaldehyde and PAN in the 38 base case scenarios for all VOCs and mixtures represented in the mechanism, with the formation potentials quantified in terms of effects on maximum formaldehyde or PAN concentrations.

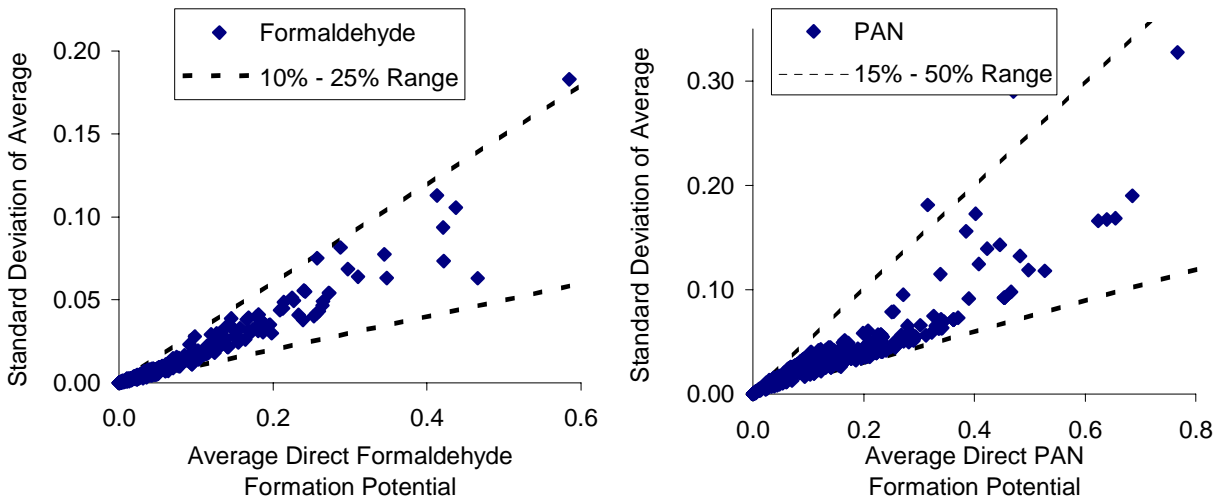


Figure 4. Plots of standard deviations against average potentials for formation of formaldehyde and PAN in the 38 base case scenarios for all VOCs and mixtures represented in the mechanism, with the formation potentials quantified in terms of effects on final formaldehyde or PAN concentrations.

be attributed primarily to effects of variable mixing heights and the other factors that were discussed in the previous section. Because of this, combined with the other reasons discussed in the previous section, in the remainder of this report we will focus primarily on results obtained using the hourly average quantification method.

Figure 2 indicates that the standard deviations for impacts based on average concentrations tend to fall in the same ranges for products of the same type. As expected, the variability tends to be less for the oxygenated and alkyl nitrate products whose yields tend to be less dependent on NO_x conditions than it is for the PAN analogues. It is interesting to note that the variability in formaldehyde and (to a lesser extent) higher aldehyde impacts tend to be greater on a relative basis for those compounds with low formation potentials for these products than those with the higher formation potentials, though this is not the case for impacts on alkyl nitrates. This may be because the direct aldehyde formation from compounds with low direct aldehyde impacts tends to be primarily due to secondary reactions of the VOCs products, whose relative rates would tend to be more scenario-dependent. This is consistent with the fact that the highest variability is seen for formaldehyde, which has a greater tendency to be a secondary product. On the other hand, the relative variabilities in the hourly average PAN and PAN analogue impacts tend to fall in a very narrow range, independently of the magnitude of the total impact.

Although the standard deviations in the base case scenarios give an indication of the relative magnitudes of the scenario-to-scenario variability, they give no indication of the distributions of the variability or of the factors that cause the variability. Figure 5 shows distribution plots for hourly average formaldehyde forming potentials of selected compounds for selected compounds for the base case and the adjusted NO_x scenarios, for both absolute impacts and (for ethylene) impacts relative to those of the base ROG mixture. The data for ethylene is typical of the compounds with the higher formaldehyde forming potential that tend to have standard deviations in the 10-15% range as indicated on Figure 2. Similar distributions are observed for the base ROG mixture, which is expected since the direct product formation potentials for this mixture is dominated by those for its components with the highest formation potentials. For these compounds, essentially the same distribution is obtained in the adjusted NO_x scenarios as in the base cases, indicating that NO_x effects are not significant in affecting formaldehyde-forming potentials for these compounds. The distributions of the product formation potentials relative to the base ROG mixture is somewhat narrower than the absolute product formation potentials, but not significantly so.

On the other hand, the two compounds shown with low formaldehyde forming potentials, n-octane and methane, have significantly lower formaldehyde forming potentials in the MIR scenarios than in the base case and the lower NO_x scenarios. In both cases, this can be attributed to the lower overall OH radical levels in the MIR scenarios compared to those representing lower NO_x conditions, since the relatively high NO_x in the MIR scenarios inhibits OH radicals due to the $\text{OH} + \text{NO}_2$ reaction. In the case of methane, which forms 100% formaldehyde as the primary product when it reacts but has a low formation potential because of its very slow rate of reaction, the lower OH means that less of it reacts during the period of the simulation, so less formaldehyde is formed. In the case of n-octane, where formaldehyde is formed only as a secondary product, the lower radical levels tend to cause less of the primary product to react during the time frame of the simulation. Although mechanisms for formaldehyde formation are quite different for these two compounds, the net effects of NO_x levels on their formaldehyde forming potentials are therefore very similar.

This effect of NO_x on direct formaldehyde forming potentials is shown further on Figure 6, which gives plots of the average potentials in the relatively high NO_x MIR scenarios against those in the much lower NO_x EBIR scenarios. The line shown is the 1:1 line where all points would fall if they were the same in both types of scenarios. Consistent with the results discussed above, the formaldehyde impacts

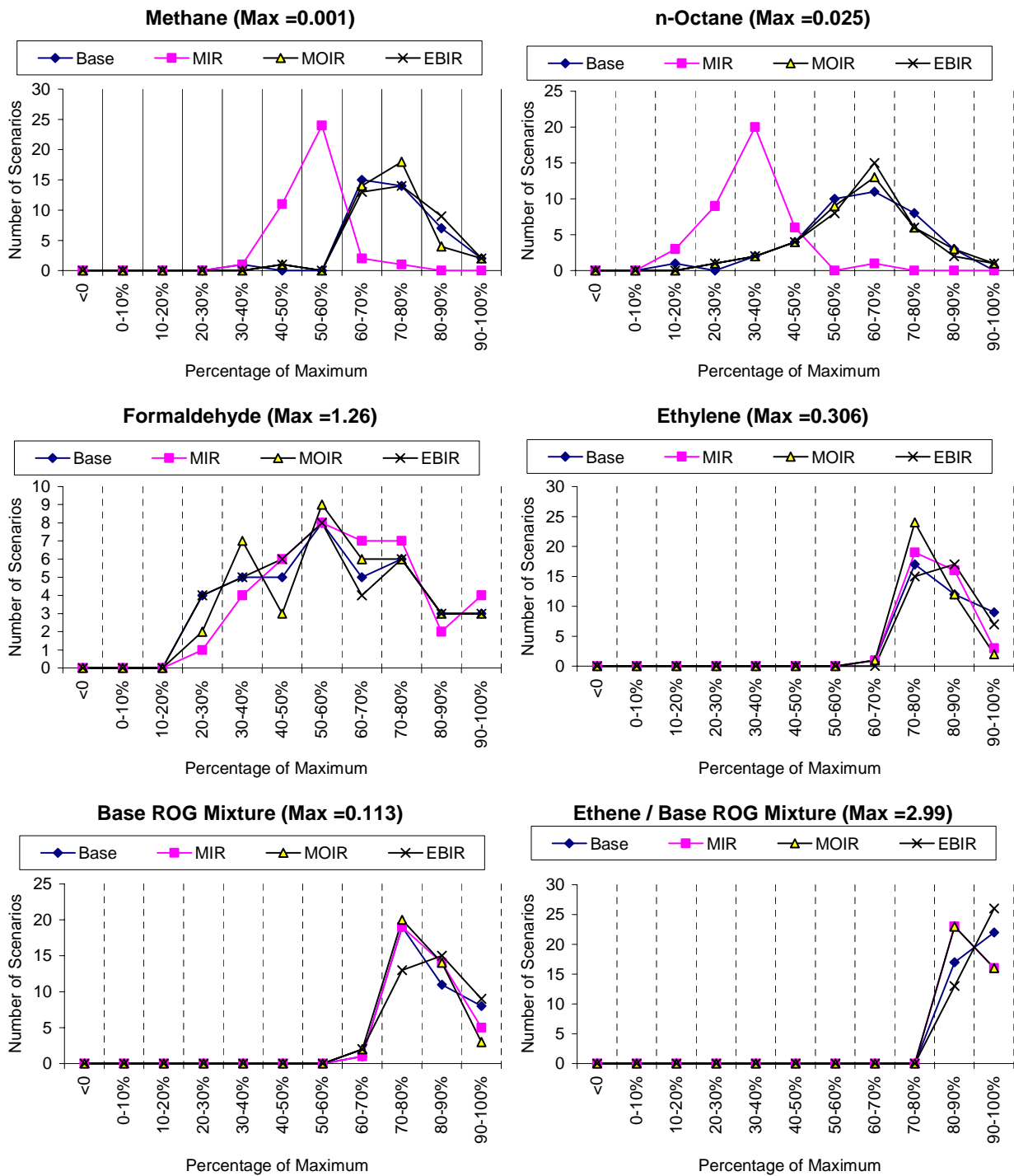


Figure 5. Distribution plots of direct average formaldehyde formation potentials calculated for selected VOCs and mixtures in the base case and the adjusted NO_x scenarios.

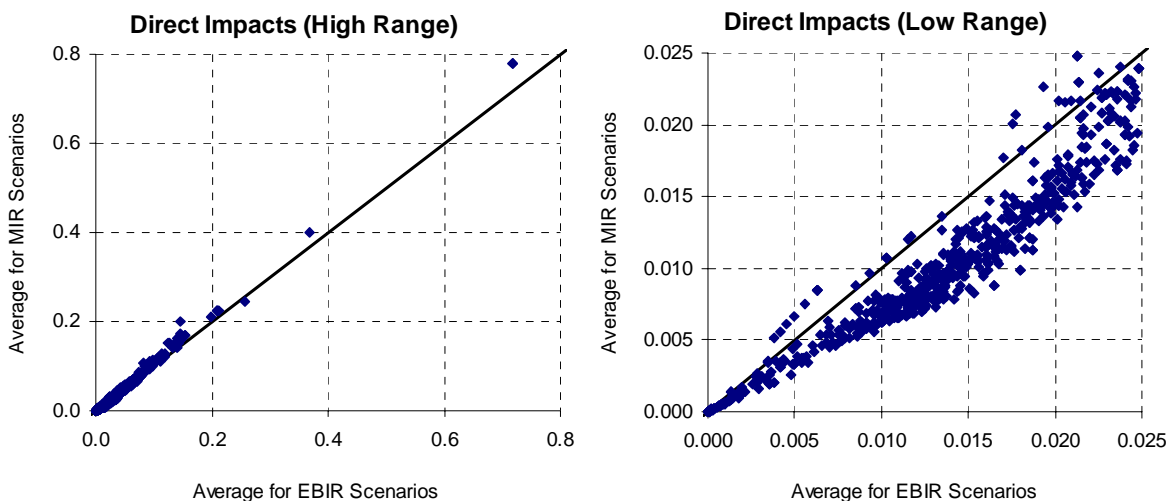


Figure 6. Comparison of MIR with EBIR average direct average formaldehyde formation potentials calculated for all VOC classes currently represented in the mechanism. The lines of equal impacts for both types of scenarios are also shown.

for the compounds with the highest impacts tend to be the same at both NO_x levels, but for the compounds with lower formaldehyde potentials the impacts are much lower in the higher NO_x scenario. This probably contributes to the higher variability of the formaldehyde impacts of these compounds, as indicated on Figure 2, above.

It is interesting to note that the scenario-to-scenario variability for the self-formation potentials of the aldehyde products that are also emitted (e.g., the formaldehyde formation potential of formaldehyde itself, etc.) is greater than the aldehyde-forming potentials of the VOCs that form them. This can be seen by comparing the distribution plots for formaldehyde on Figure 5 with those for ethene and the base ROG. The standard deviations for the self-formation potentials of the aldehydes are ~33%, about twice as high as the 10-15% range shown on Figure 2 for the compounds that form it when they react. This can be attributed to the fact that the self-forming potentials of the aldehydes tend to be more sensitive to the maximum mixing heights than is the case for the VOCs that form them as products. This is shown on Figure 7, which shows plots of the formaldehyde-forming potential of formaldehyde itself and of ethylene in the base case scenarios against the mixing heights in those scenarios. In the case of the compounds forming formaldehyde by reaction, the effects on the average formaldehyde levels tend to occur around the end of the simulation, where the mixing height is at its maximum. Because the maximum mixing height is used to convert the moles reactant emitted to concentration units for comparison with concentration of products formed when computing the product formation potentials, the effect of mixing height tends to cancel out in this calculation. However, in the self-formation potential calculation, the greatest effect of the added aldehyde on the aldehyde concentration is during the initial period of the simulation, when the mixing heights are much less variable. Because the units conversion is done in terms of the much more variable final mixing height, it tends to over-correct for the effect of mixing height, resulting in an increase in the computed self-forming potential with mixing height.

Figure 8 shows the distribution plots for the PAN formation potentials for selected compounds for the base case and adjusted NO_x scenarios, and Figure 9 shows a comparison of the average PAN formation potentials in the high NO_x MIR scenarios to those in the much lower NO_x EBIR scenarios. In

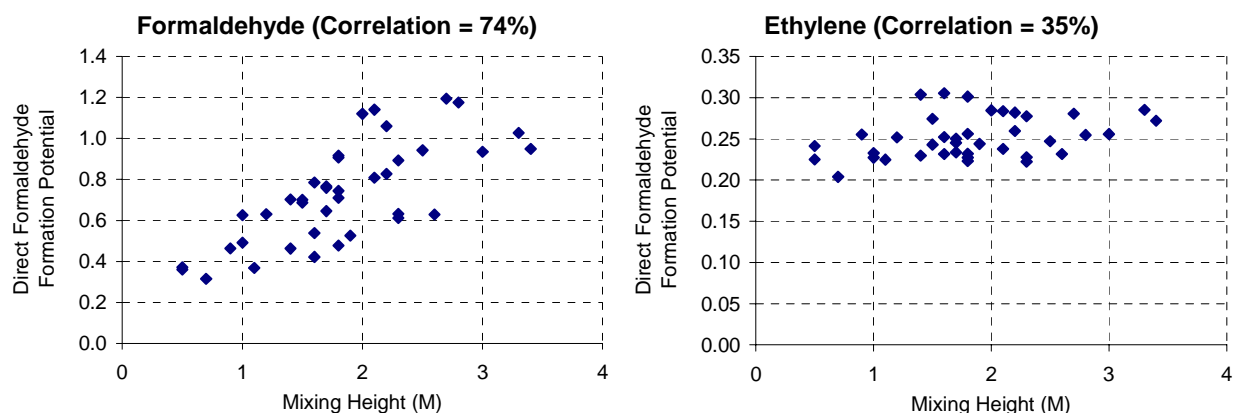


Figure 7. Dependences of direct average formaldehyde formation potentials on the maximum mixing height for the scenario for formaldehyde and ethylene.

this case, the impacts are lower for the MIR scenarios for essentially all the compounds, with much less difference between high and low impact compounds than is the case for formaldehyde. In addition, the relative impacts tend to be much narrower for the absolute impacts, as shown on Figure 8 for propene, which is typical of compounds with relatively high PAN impacts.

This greater variability and dependence on NO_x conditions for PAN (and its analogues) compared to formaldehyde and other aldehydes and alkyl nitrates is attributed to the PAN formation occurs to a significant extent only after all the NO is converted to NO_2 . The higher NO_x MIR scenarios tend to have a longer time period required for the NO to be converted, so the PAN formation potentials tend to be lower. However, the fact that the variability in PAN formation potentials is also relatively high in the adjusted NO_x scenarios indicates that other factors are also involved in causing this variability.

Variability and Factors Affecting Indirect and Total Impacts

The above discussion concerned the variability and factors affecting only the product formation resulting directly from the reactions of the added VOC or mixture. As discussed above, the indirect effects on product formation, due to the reactions of the added VOC or mixture affecting product formation from the reactions of the other VOCs present in the scenario, may also be significant. These indirect impacts need to be taken into account if the total impacts of the various VOCs or mixtures on the formation of the product species are of interest.

The relative importance of indirect impacts on the total product formation potentials would obviously vary significantly from compound to compound, depending on the total impacts. If the total impact is zero or low the indirect effect would dominate, with the direct effects dominating for compounds with high direct impacts. However, an overall indication of the relative importance of indirect impacts is shown on Table 7, which summarizes average direct, indirect, and total impacts on all the product species considered in this project for the mixture of all emitted VOCs in the base case scenarios. The ratios of indirect to total impacts are also shown.

Table 7 shows that the indirect effects can range from 3% to over 50% of the total impacts for the mixture of compounds in the base ROG mixture, indicating that indirect effects are indeed non-negligible

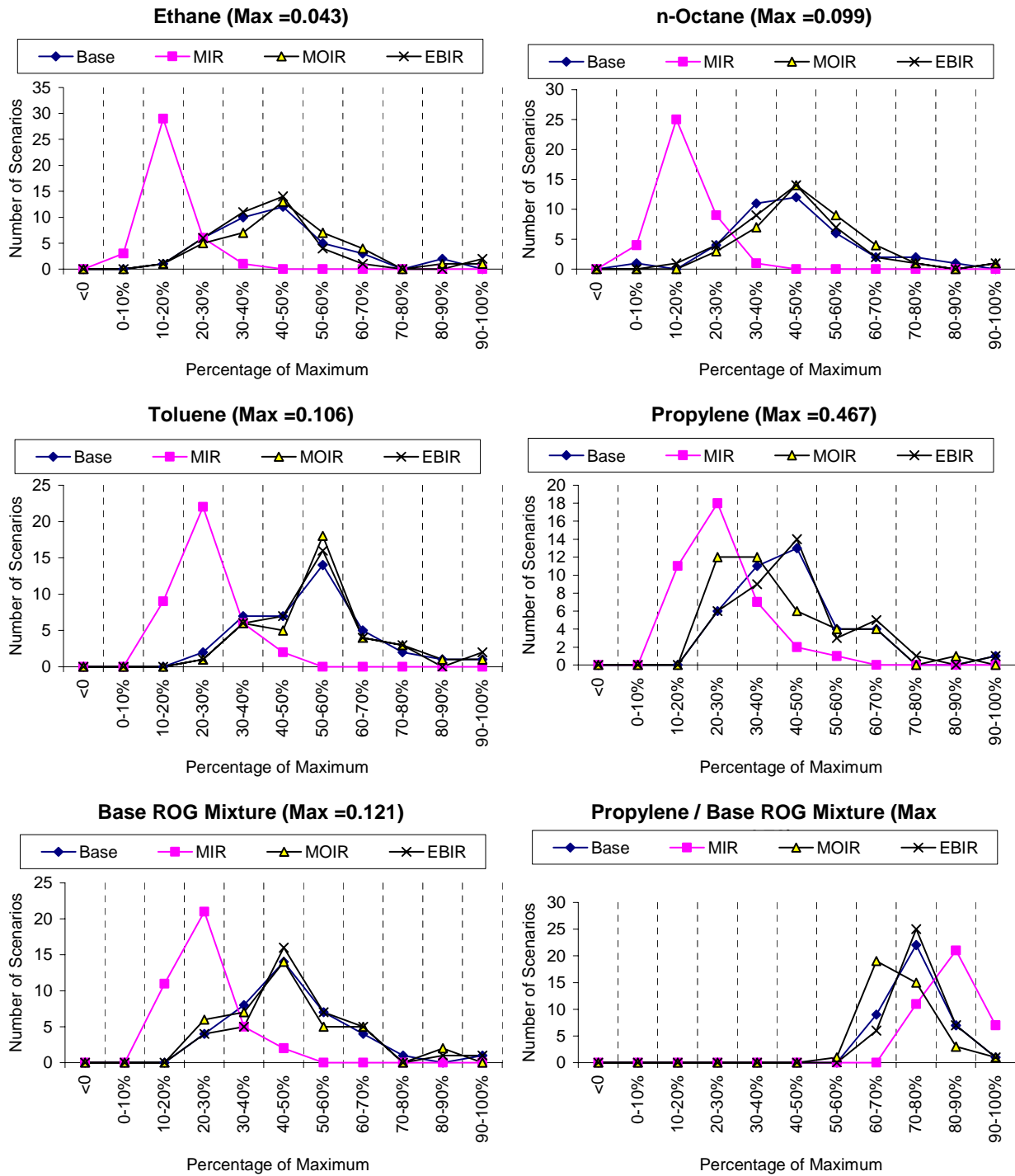


Figure 8. Distribution plots of direct average PAN formation potentials calculated for selected VOCs and mixtures in the base case and the adjusted NO_x scenarios.

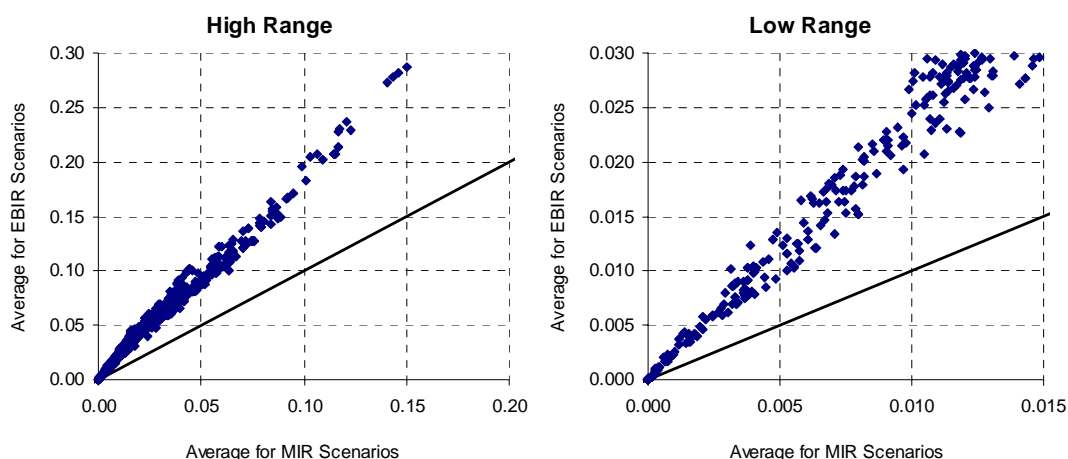


Figure 9. Comparison of MIR with EBIR average direct average PAN formation potentials calculated for all VOC classes currently represented in the mechanism. The line of equal impacts for both types of scenarios is also shown.

Table 7. Average direct, indirect, and total impacts of the base ROG mixture on all the product species studied for this project for the base case scenarios.

Description	Impacts on Hourly Average Concentrations in the Base Case Scenarios for the Base ROG Mixture (mass basis)			Ratio of Indirect to Total
	Direct	Indirect	Total	
Formaldehyde	0.0928 ($\pm 11\%$)	0.0060 ($\pm 71\%$)	0.0988 ($\pm 12\%$)	6%
Acetaldehyde	0.0431 ($\pm 12\%$)	0.0084 ($\pm 61\%$)	0.0515 ($\pm 17\%$)	16%
Lumped Higher Aldehydes	0.0140 ($\pm 12\%$)	0.0128 ($\pm 36\%$)	0.0268 ($\pm 21\%$)	48%
Benzaldehyde and Other Aromatic Aldehydes	0.0016 ($\pm 21\%$)	0.0001 ($\pm 172\%$)	0.0017 ($\pm 22\%$)	3%
Acrolein	0.0011 ($\pm 18\%$)	-0.0001 ($\pm 242\%$)	0.0011 ($\pm 23\%$)	-6%
Cresols	0.0008 ($\pm 17\%$)	-0.0002 ($\pm 81\%$)	0.0006 ($\pm 40\%$)	-29%
Nitrophenols and Aromatic Nitro-compounds	0.0026 ($\pm 33\%$)	-0.0005 ($\pm 29\%$)	0.0020 ($\pm 46\%$)	-27%
Lumped Alkyl Nitrates	0.0282 ($\pm 10\%$)	0.0015 ($\pm 89\%$)	0.0297 ($\pm 11\%$)	5%
Peroxyacetyl Nitrate (PAN)	0.0570 ($\pm 32\%$)	0.0224 ($\pm 81\%$)	0.0794 ($\pm 30\%$)	28%
Higher Saturated Acyl Peroxynitrates (PAN analogues)	0.0194 ($\pm 32\%$)	0.0204 ($\pm 36\%$)	0.0398 ($\pm 29\%$)	51%
Peroxybenzoyl Nitrate (PBzN) and Other Aromatic Acyl Peroxynitrates	0.0008 ($\pm 29\%$)	0.0003 ($\pm 73\%$)	0.0012 ($\pm 28\%$)	29%
Unsaturated PAN Analogues such as that formed from methacrolein.	0.0028 ($\pm 30\%$)	0.0022 ($\pm 42\%$)	0.0050 ($\pm 29\%$)	44%

when considering overall emissions effects. The indirect effects tend to be relatively higher for the PAN analogues compared to the aldehyde or alkyl nitrate species, and are also the highest for the lumped higher aldehyde and lumped higher PAN species used to represent a wide variety of products. Note that the indirect effects are negative in some cases, indicating that the addition of the base ROG to the emissions causes decreased formation of some products from the other VOCs present. Negative indirect effects are in fact quite common for many VOCs and products, as discussed below.

Correlations Between Indirect Impacts and Impacts on Radicals and Ozone

One way the addition of a VOC could affect the product formation from other compounds would be to inhibit or enhance overall levels of the OH radicals that initiate the product-formation reactions for most VOCs. Thus, one would expect the indirect product formation potentials to correlate with the effect of the VOC on integrated OH. A correlation between indirect product formation potentials and ozone reactivity might also be expected, since ozone reactivity is another measure of the extent to which the addition of the VOC affects the overall system.

The correlation coefficients between indirect impacts and effects on ozone or integrated OH levels for all VOCs in the mechanism for the adjusted NO_x averaged conditions scenarios are given on Table 8, and plots of indirect impacts for selected products against effect on OH for these VOCs and scenarios are shown on Figure 10. It can be seen that good correlations are obtained in some cases, but there are a number of cases where very low or even high negative correlations are seen. Negative and low correlations can be attributed to the fact that if a VOC has positive effects on radical levels (or O₃) it is also likely to have positive effects on the rate the product is consumed in the scenario once it is formed. Thus if the compound is present initially or formed early in the simulation, the increased OH levels caused by an added VOC with a high positive OH impact may cause the average concentration of the product to decline, even if it increases the concentrations initially.

Figure 11 shows the concentration-time plots of all the product species considered in this study calculated for a representative scenario, and also the concentration-time plots caused by adding a hypothetical test compound whose only direct impact is to increase total OH levels. Numbers in the parentheses show the percentage changes in the hourly average concentrations caused by adding this OH initiator. It can be seen that the added initiator always increases the concentrations of the product species during the initial period of the irradiation, but it also tends to increase the rates at which the products are consumed during the latter stages of the experiment, and causes the consumption to begin earlier. Therefore, OH initiators tend to have less of an effect (or a negative effect) on compounds that are present initially to a significant extent or are formed earlier in the simulation than is the case for other compounds. Also radical levels tend to have much less of an effect on the consumption rates of PAN and PAN analogues than is the case for the aldehyde and alkyl nitrate species, so indirect impacts on these compounds tend to have the highest correlations with impacts on OH levels and ozone.

Correlation Between Direct and Total Impacts

The correlations coefficients between average direct and total impacts for all the product species of interest the base case scenarios calculated for all the VOCs in the current mechanism are shown on Table 9, and Figure 12 shows plots of average direct vs. total impacts for representative compounds in these scenarios. Correlation coefficients for direct vs. total impacts for the mixtures used in the current CARB emissions inventories are also shown in Table 9. Table 9 shows that very good correlations are obtained for the individual compounds and even better correlations are obtained for the emissions mixtures, with the worst correlations (still greater than 85%) being obtained for formation of formaldehyde, PAN, and higher PAN analogues. However, Figure 12 shows that for many, though not all,

Table 8. Correlation Coefficients for Indirect Product Formation Potentials for all VOCs in the mechanism with their effects on ozone and integrated OH radical levels for the averaged conditions adjusted NO_x scenarios.

Product	Correlation with Ozone Reactivity			Correlation with Effect on Integrated OH		
	MIR	MOIR	EBIR	MIR	MOIR	EBIR
<u>Effect on Integrated OH</u>	97%	64%	25%			
<u>Indirect Formation Potentials</u>						
Formaldehyde	78%	40%	38%	90%	73%	63%
Acetaldehyde	-29%	40%	42%	-12%	64%	47%
Higher Aldehydes	-31%	76%	50%	-16%	81%	29%
Acrolein	-96%	-59%	18%	-96%	-66%	-17%
Benzaldehyde	-75%	-29%	37%	-66%	-25%	18%
Cresols	-62%	-31%	-6%	-46%	19%	52%
Nitrophenols	-11%	-1%	-18%	12%	65%	58%
Alkyl Nitrates	74%	35%	35%	86%	66%	60%
PAN	99%	84%	59%	99%	95%	83%
Higher PANs	99%	86%	66%	99%	92%	71%
PBzN	98%	83%	54%	100%	95%	82%
Methacrolein's PAN	98%	84%	56%	99%	91%	67%

of the product species there can be significant differences between direct and total reactivities, even for species with relatively high direct and total reactivities. The indirect effects, and thus the differences between direct and total impacts, appear to be most important for formaldehyde, PAN and the PAN analogues other than PBzN, but appear to be relatively unimportant for most of the other product species.

Representative Results

Reported Data

The primary deliverable for this project is the formation potentials calculated for all the product species listed on Table 1, above, for all the VOC species currently represented in the SAPRC-99 mechanism, and for the emissions speciation profiles used in the current CARB database. The data reported are the averages and standard deviations of the effects of the VOCs or profiles on the hourly average product concentrations in the 39 base case scenarios. The hourly average product concentrations are used for the primary basis for reporting the impacts because it gives a more consistent basis for comparison that is less variable from scenario-to-scenario, as discussed in the previous sections. The base case scenarios are used because there is no consistent strong and consistent dependence of these product formation potentials on NO_x conditions, and because (unlike the case for quantifying ozone impacts) there is no compelling basis for using adjusted NO_x scenarios when assessing these impacts. The standard deviations are reported with the averages to provide an indication of the scenario-to-scenario variability of the results, which provides *minimum* uncertainty level for the data. The impacts are quantified on a mass

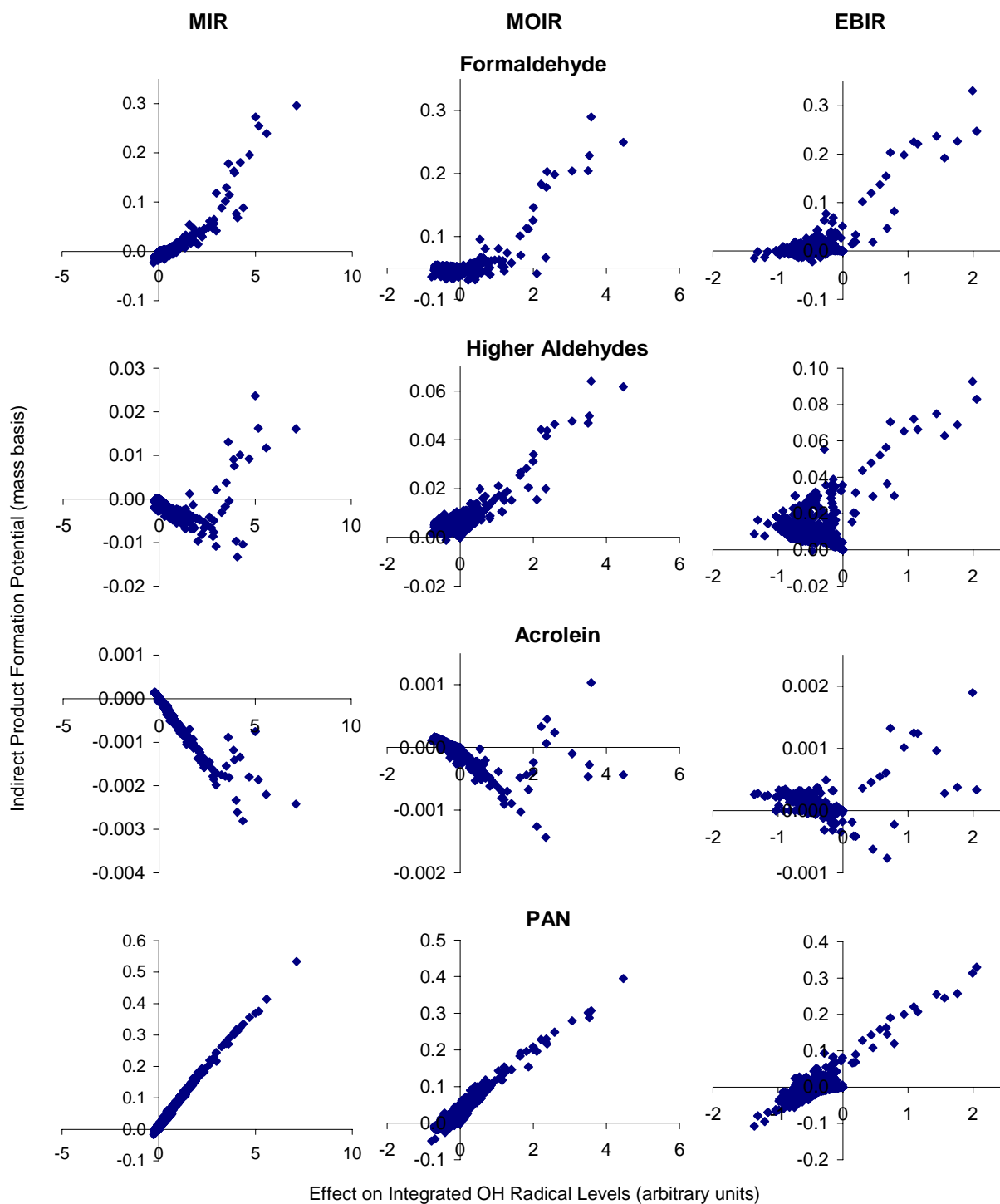


Figure 10. Plots of indirect formation potentials for selected products for all VOCs in the current mechanism against their effects on integrated OH radical levels in the averaged conditions adjusted NO_x scenarios.

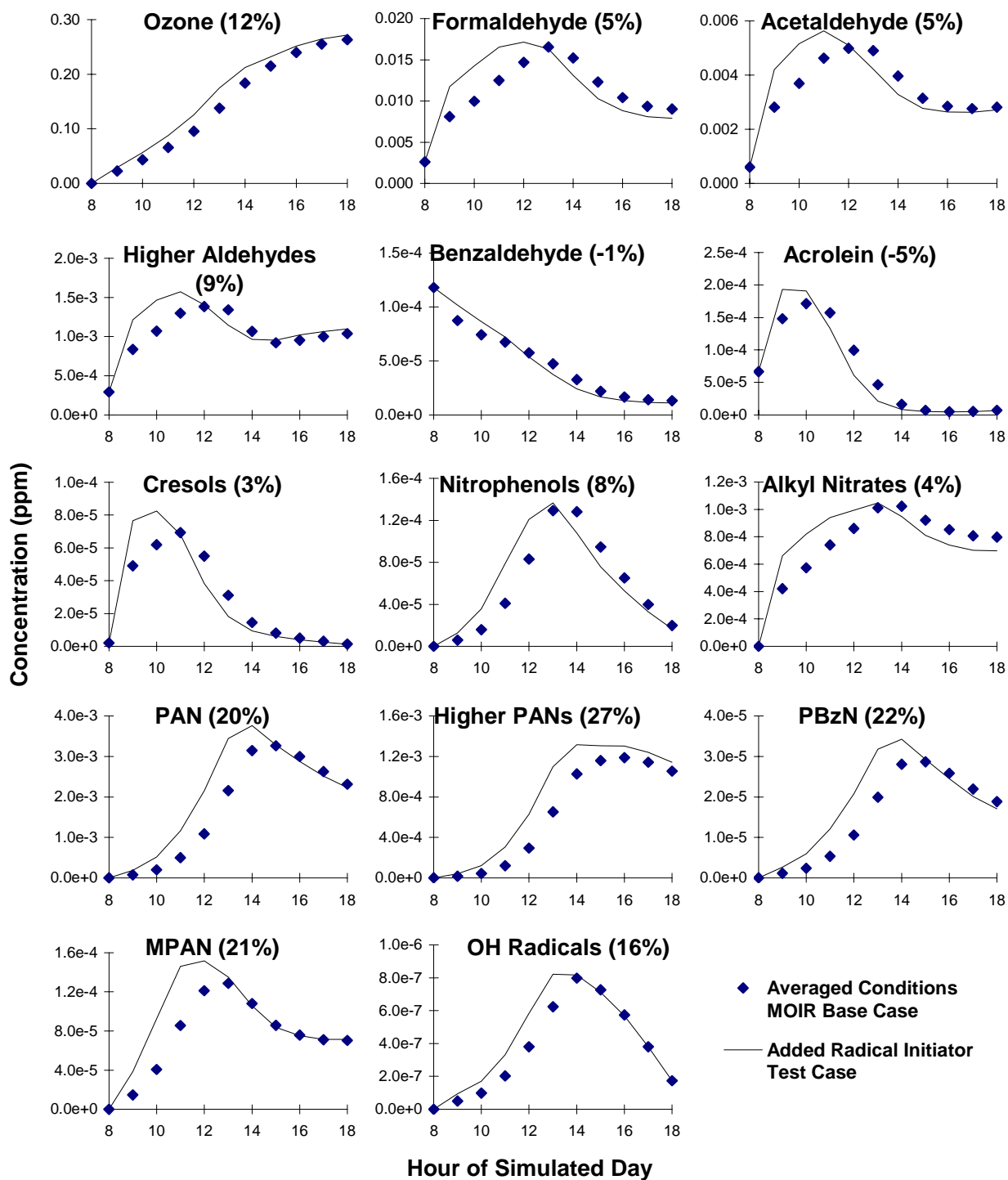


Figure 11. Effects of added radical initiator species on concentration-time plots for ozone and the selected product species in the averaged conditions MOIR scenario. Numbers in parentheses are percentage change in average concentration caused by the added initiator.

Table 9. Correlation coefficients between average direct and average total impacts for the base case scenarios for all product species, individual VOCs and emissions profiles considered in this project.

Product	Individual VOCs	Emissions Profiles
Formaldehyde	91%	100%
Acetaldehyde	98%	100%
Higher Aldehydes	99%	99%
Benzaldehyde	100%	100%
Acrolein	100%	100%
Cresols	100%	100%
Nitrophenols	100%	100%
Organic Nitrates	99%	100%
PAN	89%	86%
Higher PAN Analogues	85%	90%
PBzN	100%	100%
Methacrolein's PAN	95%	98%

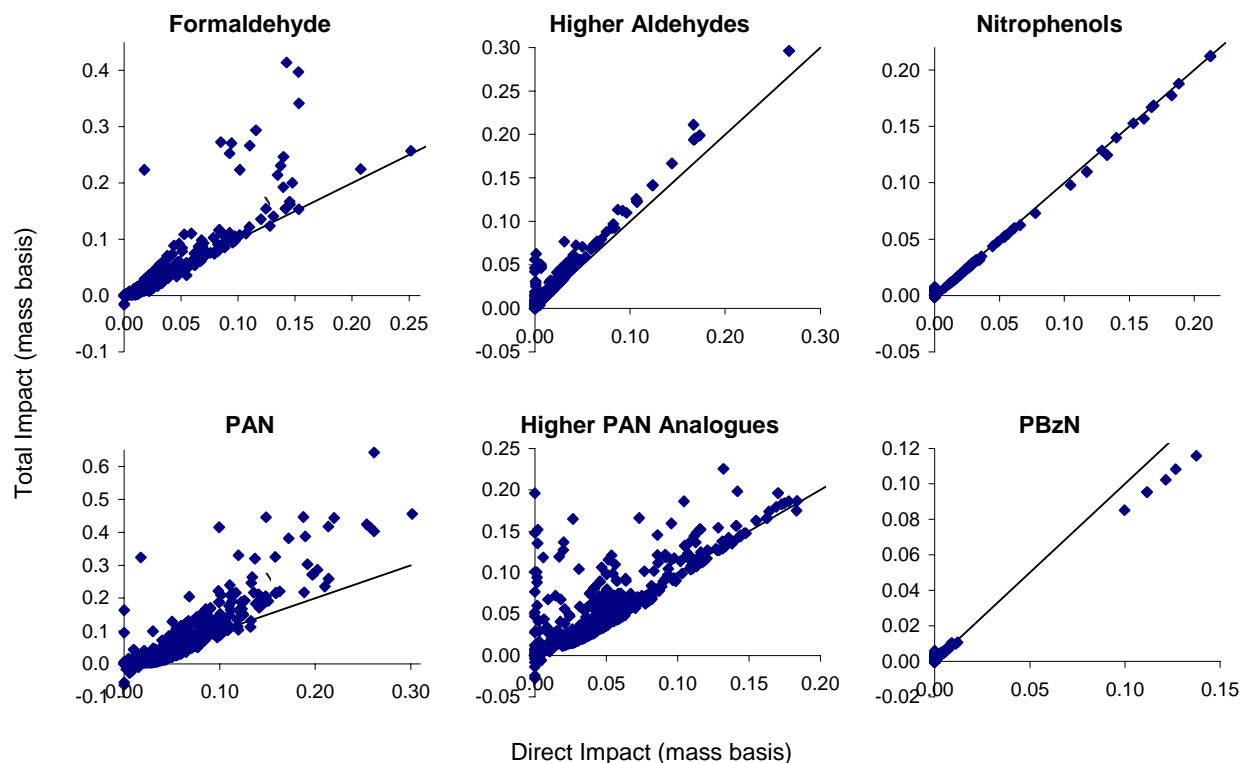


Figure 12. Plots of average total impacts against average total impacts for representative product species in the base case scenarios for all VOCs in the mechanism. The self-formation potentials of the aldehydes are off scale and therefore are not shown.

basis because this is the quantification used for emissions profiles, and for many profiles the number of moles is not well defined or unknown.

Individual VOCs with Highest Product Impacts

The average and the standard deviations for the product yield potentials of all the types of VOCs currently represented in the SAPRC-99 mechanism are tabulated in Table A-7 in the electronic version of the appendix to this report, and the data for the VOCs with the highest impacts are summarized on Table 10. The results for the various types of products are briefly summarized below.

Formaldehyde. The compound with the highest impact on average formaldehyde levels in the base case scenarios is formaldehyde itself, with an impact about three times higher than the compound with the next highest impact. Other than that, the compounds with the highest formaldehyde forming potentials are those with =CH₂ groups, as is expected since reactions at double bonds are relatively rapid, and =CH₂ groups are precursors for formaldehyde formation. Ethene has the highest formaldehyde impact of these compounds because it forms almost two moles of formaldehyde when it reacts, but the 1-alkenes and most other compounds with =CH₂ groups, which form about half as much formaldehyde on a molar basis, are not significantly lower because of their higher reaction rates. Other compounds with high formaldehyde-forming potentials include DMSO, which forms formaldehyde in high yields as a primary product (Carter et al, 2000), and very rapidly reacting compounds such as biacetyl and 2,3-dimethyl-2-butene that form formaldehyde as a secondary product. Note that almost all VOCs directly form formaldehyde to at least some extent as a secondary if not a primary product.

Acetaldehyde and Glycolaldehyde. After acetaldehyde itself, which like formaldehyde has about three times the impact on its average concentration as the compound with the next highest impact, the compounds with the highest acetaldehyde forming potentials are alkenes with =CH-CH₃ groups. This is expected because reaction at this group to form acetaldehyde is expected to be relatively rapid. The 2-butenes have the highest impact because they have two such groups, and also react quite rapidly. The other compounds with high computed acetaldehyde impacts are propionaldehyde and ethylene glycol. However, note that ethylene glycol is actually predicted to form glycolaldehyde when it reacts, but glycolaldehyde is represented by acetaldehyde in the current mechanism, which is why it is represented as forming acetaldehyde. A separate model species would have to be added to the mechanism if it is desired to consider glycolaldehyde and acetaldehyde impacts separately.

Lumped Higher Aldehydes. As with formaldehyde and acetaldehyde, propionaldehyde itself (which represents the higher aldehydes in the mechanism) is predicted to have about three times the impact on the average higher aldehyde concentration than any compound that forms them as products. As expected, the aldehyde-forming compounds with the highest higher-aldehyde formation potentials are those with =CHR groups, where R = ethyl or higher. Note amines are relatively high on the list because of the nature of the “placeholder” mechanism used to represent them in models (Carter, 2000a), and not necessarily because they actually are predicted to form these compounds. The actual atmospheric reaction mechanisms are unknown, and highly simplified mechanisms, which use the lumped higher aldehyde species to represent their products, are used so they can be represented in models. This is also the case for furan.

Benzaldehyde and Lumped Aromatic Aldehydes. Only aromatic compounds can have nonzero aromatic aldehyde forming potentials. After benzaldehyde and tolualdehyde (which is represented by benzaldehyde in the model and has a lower benzaldehyde-forming impact only because of its higher molecular weight), the compounds with the highest aromatic aldehyde-forming potentials are the styrenes. The other aromatics have about an order of magnitude lower aromatic aldehyde forming potentials than is

Table 10. Average direct and total product formation potentials in the base case scenarios for the VOCs with the highest formation potentials for the various products, sorted by direct product formation potential.

Compound	Direct		Total	
	Average	St.Dev	Average	St.Dev
Impact on Formaldehyde				
Formaldehyde	0.73	34%	0.82	30%
Ethene	0.25	10%	0.26	11%
Propene	0.21	10%	0.22	14%
2-Methyl-2-Butene	0.15	16%	0.34	24%
Isoprene	0.15	11%	0.15	17%
Biacetyl	0.15	14%	0.40	28%
Methyl Methacrylate	0.15	11%	0.20	27%
Dimethyl Sulfoxide	0.15	13%	0.16	18%
1,3-Butadiene	0.15	11%	0.17	20%
2,3-Dimethyl-2-Butene	0.14	19%	0.41	25%
1-Butene	0.14	11%	0.15	14%
trans-2-Butene	0.14	11%	0.25	22%
cis-2-Butene	0.13	10%	0.21	21%
Isobutene	0.13	12%	0.14	16%
Acrolein	0.13	11%	0.12	21%
2-Butyne	0.12	11%	0.15	33%
2-Methyl-1-Butene	0.12	12%	0.14	16%
Trans 3-Methyl-2-Hexene	0.12	13%	0.29	24%
Cis-3-Methyl-2-Hexene	0.11	13%	0.27	24%
Dimethyl Amine	0.11	12%	0.12	17%
Methylvinyl ketone	0.11	10%	0.11	18%
2-Methyl-2-Pentene	0.10	17%	0.22	25%
1-Pentene	0.10	11%	0.11	13%
2,3-Dimethyl-2-Hexene	0.09	17%	0.27	25%
1-Methyl cyclopentene	0.09	13%	0.25	25%
Butyl Methacrylate	0.09	11%	0.11	27%
Isobutyl Methacrylate	0.09	11%	0.11	26%
Methyl Glyoxal	0.08	13%	0.27	30%
2-Pentenes	0.08	11%	0.12	19%
Furan	0.06	11%	0.11	32%
1,2-Dimethyl Cyclohexene	0.05	14%	0.11	24%
Glyoxal	0.02	13%	0.22	32%
Impact on Acetaldehyde				
Acetaldehyde	0.77	31%	0.80	31%
2-Butenes	0.37	14%	0.44	16%
Trans 3-Methyl-2-Hexene	0.24	17%	0.33	20%
Cis-3-Methyl-2-Hexene	0.23	17%	0.31	20%
2-Pentenes	0.22	13%	0.25	14%
Propene	0.20	13%	0.22	13%
2-Methyl-2-Butene	0.18	16%	0.28	22%
2-Hexenes	0.18	13%	0.20	13%
Trans 4-Methyl-2-Hexene	0.17	13%	0.19	13%
2-Heptenes	0.16	13%	0.17	13%
3,4-Diethyl-2-Hexene	0.13	12%	0.13	11%
Propionaldehyde	0.13	14%	0.14	15%

Table 10 (continued)

Compound	Direct		Total	
	Average	St.Dev	Average	St.Dev
3-Hexenes	0.12	13%	0.13	13%
Ethylene Glycol	0.11	13%	0.12	13%
Trans 4,4-dimethyl-2-Pentene	0.11	13%	0.12	14%
2-Methyl-3-Butene-2-ol	0.10	13%	0.11	13%
Cyclopentene	0.10	13%	0.11	13%
Butanal	0.10	13%	0.11	14%
3-Heptenes	0.10	13%	0.11	13%
1-Methyl cyclopentene	0.08	13%	0.16	26%
2-Methyl-2-Pentene	0.07	13%	0.13	26%
2,3-Dimethyl-2-Hexene	0.06	16%	0.14	31%
2,3-Dimethyl-2-Butene	0.00	19%	0.13	44%
Impact on Lumped Higher Aldehydes				
Propionaldehyde	0.72	33%	0.76	32%
3-Hexenes	0.27	15%	0.30	15%
1-Butene	0.17	13%	0.20	12%
trans-2-Pentene	0.17	14%	0.20	14%
2-Pentenes	0.17	14%	0.19	14%
cis-2-Pentene	0.17	14%	0.19	14%
2-Methyl-2-Pentene	0.17	17%	0.21	17%
Dimethyl Amine	0.14	14%	0.17	13%
3-Heptenes	0.12	14%	0.14	14%
2-Heptenes	0.12	14%	0.14	14%
3-Octenes	0.11	14%	0.12	13%
Trimethyl Amine	0.11	14%	0.12	13%
Ethyl Amine	0.11	13%	0.13	12%
d-Limonene	0.10	16%	0.11	16%
3-Carene	0.08	14%	0.09	14%
Ethanolamine	0.08	13%	0.10	12%
Dimethylaminoethanol	0.08	14%	0.09	14%
2-Amino-2-Methyl-1-Propanol	0.08	14%	0.09	14%
Diethanol Amine	0.07	14%	0.08	14%
n-Propyl Alcohol	0.07	11%	0.07	12%
a-Pinene	0.07	13%	0.08	13%
Di-n-butyl Ether	0.06	12%	0.07	11%
N-Methyl-2-Pyrrolidone	0.06	12%	0.07	11%
Methyl n-Butyl Ether	0.06	12%	0.07	12%
Furan	0.04	13%	0.07	35%
1-Methyl cyclopentene	0.03	14%	0.08	30%
Impact on Benzaldehyde and Lumped Aromatic Aldehydes				
Benzaldehyde	0.73	33%	0.75	32%
Tolualdehyde	0.65	33%	0.67	32%
Styrene	0.21	13%	0.22	14%
a-Methyl Styrene	0.18	13%	0.19	14%
C9 Styrenes	0.18	13%	0.19	14%
C10 Styrenes	0.16	13%	0.17	14%
p-Xylene	0.013	12%	0.013	11%
Toluene	0.011	11%	0.011	10%
Impact on Acrolein				
Acrolein	0.74	33%	0.77	32%

Table 10 (continued)

Compound	Direct		Total	
	Average	St.Dev	Average	St.Dev
1,3-Butadiene	0.12	14%	0.13	18%
2,3-Dimethyl-2-Butene	0.000	-	0.001	255%
Impact on Alkyl Phenols				
C7 Alkyl Phenols	0.59	38%	0.62	37%
C8 Alkyl Phenols	0.52	38%	0.55	37%
C9 Alkyl Phenols	0.47	38%	0.49	37%
Para Toluene Isocyanate	0.029	21%	0.030	20%
Furan	0.026	16%	0.027	21%
Toluene Diisocyanate	0.025	20%	0.027	19%
Methylene Diphenylene Diisocyanate	0.023	18%	0.024	19%
C12 Disubstituted Naphthalenes	0.022	17%	0.024	23%
Dimethyl Naphthalenes	0.022	17%	0.024	23%
Methyl Naphthalenes	0.020	16%	0.022	22%
1,3,5-Trimethyl Benzene	0.020	17%	0.021	22%
m-Xylene	0.016	16%	0.017	21%
Impact on Nitrophenols				
C7 Alkyl Phenols	0.21	27%	0.21	24%
C8 Alkyl Phenols	0.19	27%	0.19	24%
Benzaldehyde	0.18	37%	0.18	31%
C9 Alkyl Phenols	0.17	27%	0.17	24%
Phenol	0.17	26%	0.17	21%
Tolualdehyde	0.16	37%	0.16	31%
Styrene	0.13	45%	0.12	39%
C9 Styrenes	0.12	45%	0.11	39%
C10 Styrenes	0.10	45%	0.10	39%
Para Toluene Isocyanate	0.078	30%	0.073	28%
Toluene Diisocyanate	0.066	30%	0.062	27%
Furan	0.056	30%	0.054	27%
Tetralin	0.054	28%	0.053	23%
Methylene Diphenylene Diisocyanate	0.054	29%	0.052	25%
m-Xylene	0.036	30%	0.035	27%
p-Xylene	0.035	34%	0.032	30%
Toluene	0.034	34%	0.031	34%
1,3,5-Trimethyl Benzene	0.032	28%	0.032	25%
Impact on Lumped Alkyl Nitrates				
3,4-Diethyl-2-Hexene	0.23	13%	0.22	12%
Cyclooctane	0.22	10%	0.21	9%
1,3-Diethyl-5-Methyl Cyclohexane	0.21	10%	0.21	9%
1,3,5-Triethyl Cyclohexane	0.21	10%	0.21	9%
1,3-Diethyl-Cyclohexane	0.21	10%	0.21	9%
1-Ethyl-2-Propyl Cyclohexane	0.21	10%	0.21	9%
1-Ethyl-4-Methyl Cyclohexane	0.20	10%	0.20	9%
1,4-Diethyl-Cyclohexane	0.20	10%	0.20	9%
1,3-Dimethyl Cyclohexane	0.20	10%	0.20	9%
1,3-Diethyl-5-Propyl Cyclohexane	0.20	10%	0.20	9%
Cycloheptane	0.20	10%	0.20	9%
1-Methyl-3-Isopropyl Cyclohexane	0.19	10%	0.19	9%
1,3-Dipropyl-5-Ethyl Cyclohexane	0.19	10%	0.19	9%
Butyl Cyclohexane	0.19	10%	0.19	9%

Table 10 (continued)

Compound	Direct		Total	
	Average	St.Dev	Average	St.Dev
1,2-Dimethyl Cyclohexene	0.19	12%	0.21	12%
1-Methyl-2-Hexyl-Cyclohexane	0.19	10%	0.19	9%
Sabinene	0.19	12%	0.19	12%
Pentyl Cyclohexane	0.19	10%	0.19	9%
Hexyl Cyclohexane	0.19	10%	0.19	9%
3,5-Diethyl Heptane	0.19	10%	0.18	9%
Propyl Cyclohexane	0.18	10%	0.18	9%
Ethylcyclohexane	0.18	10%	0.18	9%
Heptyl Cyclohexane	0.18	10%	0.18	9%
1,3,5-Tripropyl Cyclohexane	0.18	10%	0.18	9%
2-Butyl Tetrahydrofuran	0.18	11%	0.18	10%
1,1,3-Trimethyl Cyclohexane	0.18	10%	0.17	9%
2-Methyl Nonane	0.18	10%	0.17	9%
1,3-Propyl-5-Butyl Cyclohexane	0.17	10%	0.17	9%
Impact on PAN				
2-Butyne	0.30	32%	0.46	33%
cis-2-Butene	0.26	32%	0.40	32%
Biacetyl	0.26	32%	0.64	35%
trans-2-Butene	0.25	32%	0.42	32%
Trans 3-Methyl-2-Hexene	0.22	29%	0.44	32%
Methylvinyl ketone	0.21	32%	0.26	30%
Cis-3-Methyl-2-Hexene	0.21	29%	0.42	32%
Acetaldehyde	0.21	31%	0.23	28%
Propene	0.20	34%	0.29	34%
2-Pentenes	0.20	31%	0.27	30%
Methyl Methacrylate	0.19	30%	0.39	36%
Methyl Acetylene	0.19	34%	0.22	31%
2-Methyl-2-Butene	0.19	30%	0.45	33%
1-Methyl cyclopentene	0.17	26%	0.38	32%
2-Hexenes	0.16	31%	0.22	30%
Furan	0.16	29%	0.33	40%
Methyl Glyoxal	0.15	31%	0.45	41%
Trans 4-Methyl-2-Hexene	0.15	31%	0.20	30%
Trans-2-Heptene	0.15	31%	0.19	29%
3-Hexenes	0.15	31%	0.19	32%
Acrolein	0.14	27%	0.17	28%
Isoprene	0.14	29%	0.21	34%
Propionaldehyde	0.14	31%	0.18	35%
2-Methyl-2-Pentene	0.14	26%	0.32	32%
Crotonaldehyde	0.14	29%	0.22	35%
1,3-Butadiene	0.13	30%	0.26	37%
1,2,3-Trimethyl Benzene	0.13	29%	0.25	37%
Ethylene Glycol	0.13	36%	0.13	32%
3,4-Diethyl-2-Hexene	0.13	31%	0.11	26%
Impact on Lumped Higher PAN Analogues				
Ethyl Acetylene	0.18	32%	0.19	34%
Trimethylene Oxide	0.18	31%	0.17	32%
3-Hexenes	0.18	30%	0.19	30%
Propionaldehyde	0.17	29%	0.18	29%
1-Butene	0.17	32%	0.20	32%

Table 10 (continued)

Compound	Direct		Total	
	Average	St.Dev	Average	St.Dev
Cyclopentene	0.16	30%	0.17	29%
3-Heptenes	0.16	31%	0.17	30%
2-Heptenes	0.16	31%	0.17	30%
Butanal	0.16	30%	0.16	29%
4-Octenes	0.15	31%	0.15	30%
3-Octenes	0.14	30%	0.14	30%
Methyl Acrylate	0.14	30%	0.20	32%
1-Pentene	0.14	32%	0.16	32%
Tetrahydrofuran	0.14	34%	0.14	33%
Trans 2,5-Dimethyl 3-Hexene	0.14	31%	0.13	30%
2-Methylpropanal	0.14	29%	0.14	29%
1-Methyl cyclopentene	0.13	28%	0.23	33%
Pentanal (Valeraldehyde)	0.13	29%	0.14	28%
3-Nonenes	0.13	31%	0.13	30%
Trans-4-Nonene	0.13	31%	0.13	30%
Cyclohexene	0.13	31%	0.13	29%
2,2-Dimethylpropanal (pivaldehyde)	0.12	29%	0.13	29%
Cis-5-Decene	0.12	30%	0.12	29%
Trans-4-Decene	0.12	31%	0.11	30%
Impact on PBzN				
Benzaldehyde	0.14	29%	0.12	40%
Styrene	0.13	30%	0.11	40%
Tolualdehyde	0.12	29%	0.10	40%
a-Methyl Styrene	0.11	30%	0.10	40%
p-Xylene	0.012	31%	0.011	36%
Toluene	0.011	31%	0.010	38%
Impact on Unsaturated PAN Analogues				
Acrolein	0.19	30%	0.17	36%
Methacrolein	0.10	29%	0.09	36%
1,3-Butadiene	0.10	31%	0.09	37%
Crotonaldehyde	0.09	29%	0.09	35%
Hydroxy Methacrolein	0.06	29%	0.06	35%
Isoprene	0.05	30%	0.05	34%
Methylvinyl ketone	0.0004	33%	0.00	47%
Biacetyl	0	-	0.03	42%
2,3-Dimethyl-2-Butene	0	-	0.02	44%

the case for styrenes. Although the trimethylbenzenes react more rapidly than toluene or xylenes, they have lower aromatic aldehyde forming potentials because of lower yields of such products in their reactions.

Acrolein. The only compound in the current SAPRC-99 mechanism predicted to form acrolein in significant quantities is 1,3-butadiene. Its impact on average acrolein levels in the base case scenarios is predicted to be about 1/6 that of acrolein itself. For comparison, Table 10 also lists the compound with the highest indirect acrolein forming impact, which can be seen to be insufficient to give it a significant total acrolein-forming impact compared to acrolein itself and 1,3-butadiene.

Alkyl Phenols (Cresols). Other than the alkyl phenols themselves, the compounds predicted to have the highest alkyl phenol impact are various isocyanates, furan, and naphthalenes. However, the alkyl phenol formation potentials of these compounds are relatively low compared to the formation potentials for other products from reacting VOCs. These compounds may not actually form alkyl phenols, but the “Cresol” model species is used in parameterized mechanisms for these compounds that are adjusted to fit chamber data (Carter, 2000a, and references therein). For that reason, the predicted “cresol” impacts for these compounds are actually predicted impacts of primarily uncharacterized compounds that are assumed to have similar reactivity characteristics. On the other hand, alkyl phenols are known to be formed from the reactions of the alkylbenzenes, so the alkyl phenol formation potentials for these compounds are less uncertain.

Nitrophenols. The “nitrophenol” model species is used primarily to represent uncharacterized aromatic ring-retaining nitrogenous products formed after phenolic compounds react with NO_3 radicals. The compounds actually formed in these reactions are unknown, and probably include compounds other than nitrophenols. In any case, the compounds with the highest formation potential for this model species are primarily phenols and compounds that form phenols in the highest yields. The one exception is benzaldehyde, which is believed to form phenyl radicals directly, and the current mechanism assumes that the primary fate of phenyl radicals in the presence of NO_x is formation of nitrophenols. The actual fate of phenyl radicals may be different, however.

Alkyl Nitrates. The alkyl nitrate model species is used primarily to represent the nitrate formation product that results when higher molecular weight peroxy radicals react with NO , which include hydroxynitrates and other oxygen-containing nitrates formed from high molecular weight oxygenates as well as the unsubstituted alkyl nitrates formed from alkanes. The compounds with the highest alkyl nitrate impacts are the high molecular weight alkanes, alkenes, and oxygenates that form high molecular weight peroxy radicals that have relatively high nitrate yields when they react with NO . There are a relatively large number of such compounds in the current mechanism, which is why the organic nitrate impacts for the compounds listed on Table 10 are all relatively high.

PAN. The compounds with the highest PAN formation potentials are those rapidly reacting compounds that either form the PAN precursor acetyl peroxy radicals in their initial reactions, or compounds that form high yields of such rapidly reacting PAN precursor compounds as products. Examples of the former include 2-butyne, biacetyl, methyl vinyl ketone, acetaldehyde, and alkenes with $=\text{C}(\text{CH}_3)\text{-R}$, and examples of the latter include 2-butenes and other 2-alkenes, which form high yields of acetaldehyde when they react, and 2-butyne, which is predicted to form biacetyl as a product as well as forming the PAN precursor radical. As indicated on Table 10, there are a relatively large number of compounds with these characteristics, and thus relatively high PAN formation potentials.

Lumped Higher PAN Analogues. The factors causing high higher PAN formation potentials are analogous to those discussed above for PAN. Ethyl acetylene, trimethylene oxide, and propionaldehyde

and higher aldehydes are examples of the former, and alkenes with =CHR groups (where R = ethyl or greater), which form higher aldehydes when they react, are examples of the latter. Again, there are a relatively large number of such compounds with relatively high formation potentials for these higher PAN analogues, though the levels of such compounds tend to be lower in the emissions. This is indicated by the data on Table 7, above, where the direct PAN formation potential of the base ROG mixture derived from the emissions data is approximately three times higher than its formation potential for the higher PAN analogues.

PBzN and Lumped Aromatic PAN Analogues. The compounds with the highest PBzN formation are benzaldehyde and other aromatics aldehydes, which form the PBzN precursor radical in high yields when they react, and the styrenes, which form high yields of the benzaldehyde model species. It is perhaps surprising that the PBzN formation potential of styrene is almost as high as that of benzaldehyde; this may be due in part to benzaldehyde PAN precursor reacting later in the simulation when the conditions are more favorable for formation of PAN analogues. The NO concentrations, which suppress PAN analogue formation by reacting with the precursor radicals to form other products, are relatively high early in the simulations, making PAN analogue formation less efficient. Although the alkylbenzenes such as xylenes and toluene also have direct PBzN formation potentials through their formation of aromatic aldehyde products, the yields of these products are relatively low, giving these compounds PBzN formation potentials that are about an order of magnitude lower than the styrenes.

Unsaturated PAN Analogues. The compounds with the highest formation potentials for the unsaturated PAN analogue model species are acrolein, methacrolein, and other unsaturated aldehydes that form the unsaturated PAN precursor radical directly, and 1,3-butadiene isoprene, which form such aldehydes as products. Methyl vinyl ketone has a small direct formation potential for this product because the model assumes the precursor forms during its photolysis, which is relatively slow. Table 10 lists all the compounds in the current mechanism predicted to have nonzero direct formation potentials for these products, together with the two compounds with the highest total formation potentials, which are 3-5 times lower than those for the compounds with the highest direct formation potentials.

Results for Emissions Profiles

Table 11 indicates the extent to which we were able to assign the mass in the emissions profiles currently used in California emissions inventory to model species for which the product formation potentials have been calculated. As indicated in the Methods section, above, product formation potentials were calculated only for those profiles that had at least 50% of the mass assigned to SAPRC model species, and Table 11 indicates that this is the case for all but ~6% of the profiles in the inventory. A vast majority (over 80%) of the profiles had more than 85% of the mass assigned, indicating that most are sufficiently well characterized for the purpose of this study.

Table 12 lists the profiles that had insufficient mass assigned to determine product yield potentials, and indicated their major unassigned chemical categories. Those that were nearly 100% unassigned used species that are not in the current mechanism. In most cases, this is because their mechanism is unknown and no attempt was made to derive a “placeholder” mechanism for them, though volatile methyl siloxanes have been studied previously (Carter et al, 1992), but are represented in the current mechanism. However, a number of other profiles are unassigned because they contain poorly characterized chemical classifications such as “misc other VOCs”, “fragrances”, and “PAR”. Profiles containing large amounts of such chemical classifications obviously need to be improved before they can be assigned.

Table 11. Numbers and percentages of CARB emissions profiles with various ranges of mass percentages that have been assigned to SAPRC-99 detailed model species.

Mass Fraction Assigned	Number of Profiles	Percentage of Profiles
Less than 10%	9	2%
10-50%	16	4%
50-85%	49	13%
85-98%	121	32%
98-99+%	113	30%
100%	65	17%

Examples of the results obtained for the emissions profiles that could be assigned are given in Table 13, which lists, for each of the product species considered in this study, the average and standard deviations direct and total formation potentials in the base case scenarios for 20 profiles that have the highest direct formation potentials for those products. Consistent with the results shown on Table 10, indicating that the species with the highest potentials depend on the product being considered, this is the case for the profiles as well.

A complete listing of the averages and standard deviations of the impacts of all the profiles on average concentrations of all the products in the base case scenarios is given in Table A-8 in the electronic version of the Appendix to this report.

Table 12. Major Unidentified Components of the emissions profiles with over 50% of the mass unidentified.

No.	Profile Description	Major Unidentified Components	
		Wt. %	Description
554	Ethylene Dibromide	100%	Ethylene Dibromide
558	Acrylonitrile	100%	Acrylonitrile
789	Dimethyl Formamide	100%	Dimethyl Formamide
941	Aniline	100%	Aniline {Aminobenzene}
942	Adipic Acid	100%	Adipic Acid
1406	Synthetic Organic Fiber Prod - Average (EPA 9006)	100%	Hexamethylenediamine
1731	[Draft] Consumer Prd: Underarm Antiperspirants - Non-Aerosols	94%	Volatile Methyl Siloxanes (VMS)
537	Crude Oil - Sumps/ Wells/ Hots - Kern County	86%	PAR (a Carbon Bond model species)
763	Phthalic Anhydride Mfg.-Xylene Oxidation	60%	Phthalic Anhydride
1416	Textile Products - Average (EPA 9016)	21%	Butyl Benzoate
		20%	Palmitic Acid {N-Hexadecanoic Acid}
		11%	Methyl Stearate {Methyl Octadecanoate}
1660	[Draft] Consumer Prd: Toilet Bowl Cleaners	64%	Fragrances
12	Iron Production - Blast Furnace - Ore Charging	84%	Trimethylfluorosilane
306	Open Hearth With Oxygen Lance- Steel Production	84%	Trimethylfluorosilane
1601	[Draft] Consumer Prd: Selective Herbicides / Defoliants	81%	Misc./Other Voc
1637	[Draft] Consumer Prd: Carpet Deodorizers	80%	Fragrances
1741	[Draft] Consumer Prd: Hand And Body Lotions	32%	Volatile Methyl Siloxanes (VMS)
		27%	Fragrances
		7%	Witch Hazel
1432	Organic Chem/Fixed Roof:Misc Amines - Avg (EPA 9032)	33%	Misc. Ethyleneamines
		33%	Aniline {Aminobenzene}
1410	Secondary Metal Production - Average (EPA 9010)	35%	Aniline {Aminobenzene}
1539	[Draft] Consumer Prd: Tire Cleaners	39%	Volatile Methyl Siloxanes (VMS)
		16%	Hydrocarbon Propellant (LPG)
1537	[Draft] Consumer Prd: Rubber And Vinyl Protectants - Non-Aerosols	61%	Volatile Methyl Siloxanes (VMS)
1791	[Draft] Consumer Prd: Hand Dishwashing Soap	45%	Fragrances
		15%	Voc Ingredients < 0.1%
1520	[Draft] Consumer Prd: Sealants & Caulking Compounds	23%	Misc. Esters
		19%	Volatile Methyl Siloxanes (VMS)
		7%	Other, Lumped Vocs, Individually < 2% Of Category
		2%	Misc. Alcohols
1713	[Draft] Consumer Prd: Liquid/Pump Spray Air Fresheners	40%	Fragrances
		6%	Lemon Oil
		4%	Orange Oil
		2%	Other, Lumped Vocs, Individually < 2% Of Category
1610	[Draft] Consumer Prd: Flea And Tick Insecticide	46%	Hydrocarbon Propellant {Lpg, Sweetened}
		3%	Misc. Hydrocarbon Propellants
		2%	Other, Lumped VOCs, Individually < 2% Of Category

Table 13. Average direct and total product formation potentials in the base case scenarios for the 20 speciation profiles in the CARB emissions inventory with the highest direct formation potentials for the various products.

Profile No.	Description	Direct		Total	
		Average	St.Dev	Average	St.Dev
Impact on Formaldehyde					
797	Formaldehyde	0.73	34%	0.82	30%
29	Refinery Co Boiler - FCC	0.37	33%	0.42	30%
586	Composite Jet Exhaust Jp-5 (EPA 1097-1099)	0.21	22%	0.24	21%
511	Plastics Mfg- Polypropylene	0.21	10%	0.22	14%
818	Farm Equipment - Diesel - Light & Heavy - (EMS=Actual Weight)	0.20	24%	0.22	22%
51	Refinery Flares- Natural Gas	0.15	33%	0.17	30%
555	Methyl Methacrylate	0.15	11%	0.20	20%
944	Butadiene	0.15	11%	0.17	20%
9	Industrial Ice- Distillate Oil	0.14	10%	0.15	12%
79	Flares- Chemical Manufacturing	0.12	12%	0.13	14%
784	Synthetic Rubber Mfg-Styrene-Butadiene Rubber	0.11	11%	0.12	18%
307	Forest Fires	0.11	10%	0.12	11%
4	External Combustion Boiler - Process Gas	0.10	22%	0.11	21%
1405	Plastics Production - Average (EPA 9005)	0.089	11%	0.091	12%
778	Methyl Isobutyl Ketone	0.082	10%	0.079	12%
401	Gasoline - Non-Cat - Stabilized Exhaust - ARB IUS Summer 1996	0.080	15%	0.089	16%
1412	Petroleum Industry - Average (EPA 9012)	0.080	28%	0.089	26%
557	Methyl Acrylate	0.078	11%	0.103	27%
11	Coke Oven Stack Gas - Primary Metals	0.076	10%	0.078	11%
798	Ethyl Ether	0.070	10%	0.071	11%
Impact on Acetaldehyde					
511	Plastics Mfg- Polypropylene	0.20	13%	0.22	13%
946	Ethylene Glycol	0.11	13%	0.12	13%
818	Farm Equipment - Diesel - Light & Heavy - (EMS=Actual Weight)	0.10	24%	0.11	23%
1592	[Draft] Consumer Prd: Sterilants (Not Including Ethylene Oxide)	0.085	14%	0.091	18%
586	Composite Jet Exhaust Jp-5 (EPA 1097-1099)	0.079	20%	0.093	21%
211	Beer Fermentation- Ethanol	0.078	11%	0.079	12%
226	Surface Coating Solvent- Ethyl Alcohol	0.078	11%	0.079	12%
1733	[Draft] Consumer Prd: Underarm Deodorants - Non-Aerosols	0.078	11%	0.079	12%
1751	[Draft] Consumer Prd: Personal Fragrance Product (Fragrance > 20%)	0.078	11%	0.079	12%
79	Flares- Chemical Manufacturing	0.078	13%	0.088	16%
1510	[Draft] Consumer Prd: Woodworking Glues	0.077	11%	0.078	12%
1740	[Draft] Consumer Prd: Astringents/Toners	0.077	11%	0.078	12%
1767	[Draft] Consumer Prd: Hair Styling Gels	0.077	11%	0.078	12%
1750	[Draft] Consumer Prd: Personal Fragrance Product (Fragrance <= 20%)	0.076	11%	0.077	12%
1591	[Draft] Consumer Prd: Sanitizers	0.076	11%	0.076	12%
1590	[Draft] Consumer Prd: Disinfectants	0.072	11%	0.073	12%
557	Methyl Acrylate	0.072	14%	0.081	22%

Table 13 (continued)

Profile No.	Description	Direct		Total	
		Average	St.Dev	Average	St.Dev
1732	[Draft] Consumer Prd: Underarm Deodorants - Aerosols	0.070	11%	0.070	13%
1625	[Draft] Consumer Prd: Insect Repellants - Aerosols	0.068	11%	0.068	12%
1760	[Draft] Consumer Prd: Hair Spray	0.067	11%	0.068	12%
Impact on Lumped Higher Aldehydes					
926	Degreasing: Cold Cleaning (Batch, Conveyor, Spray Gun)	0.081	16%	0.092	16%
927	Degreasing: Handwiping	0.081	16%	0.092	16%
1790	[Draft] Consumer Prd: Laundry Detergent	0.079	13%	0.093	12%
781	N-Propyl Alcohol	0.067	11%	0.075	12%
1413	Pulp And Paper Industry - Average (EPA 9013)	0.056	13%	0.065	13%
1947	[Draft] Consumer Prd Composite: Soaps And Detergent Products	0.053	13%	0.063	12%
1659	[Draft] Consumer Prd: Oven Cleaners - Liquid And Other	0.049	12%	0.058	12%
549	Red Oak Combustion - Wood Stove (W/O Catalyst)	0.048	31%	0.054	28%
510	Plastics Mfg- Vinyl Chloride	0.047	12%	0.056	15%
1792	[Draft] Consumer Prd: Heavy Duty Hand Cleaner Or Soap	0.045	12%	0.053	13%
945	Butyl Carbitol	0.040	12%	0.046	11%
1650	[Draft] Consumer Prd: Floor Wax Strippers	0.039	12%	0.047	12%
1654	[Draft] Consumer Prd: General Purpose Degreasers - Non-Aerosols	0.037	12%	0.043	13%
1530	[Draft] Consumer Prd: Bug And Tar Removers	0.035	12%	0.042	16%
1653	[Draft] Consumer Prd: General Purpose Degreasers - Aerosols	0.034	12%	0.040	14%
223	Surface Coating Evaporation- Xylene Solvent	0.034	13%	0.050	26%
1502	[Draft] Consumer Prd: Arts And Crafts Adhesives	0.034	11%	0.043	20%
1449	Fabricated Metal (Us EPA #2466)	0.034	13%	0.049	26%
1428	Organic Chemical Storage - Average (EPA 9028)	0.032	19%	0.039	19%
230	Petro Storage- Fixed Roof- Hexane	0.030	14%	0.036	29%
Impact on Benzaldehyde and Lumped Aromatic Aldehydes					
753	Styrene	0.21	13%	0.22	14%
1405	Plastics Production - Average (EPA 9005)	0.11	13%	0.11	14%
784	Synthetic Rubber Mfg-Styrene-Butadiene Rubber	0.082	13%	0.086	14%
1414	Rubber/Misc. Plastics Productn - Average (EPA 9014)	0.027	13%	0.029	14%
90	Degreasing- Toluene	0.011	11%	0.011	10%
922	Degreasing: Handwiping	0.010	11%	0.010	10%
921	Degreasing: Cold Cleaning (Batch, Conveyor, Spray Gun)	0.010	11%	0.010	10%
401	Gasoline - Non-Cat - Stabilized Exhaust - ARB IUS Summer 1996	0.010	29%	0.010	28%
1404	Chemical Manufacturing - Average (EPA 9004)	0.010	13%	0.010	14%
223	Surface Coating Evaporation- Xylene Solvent	0.009	12%	0.009	12%
1449	Fabricated Metal (Us EPA #2466)	0.009	12%	0.009	12%
79	Flares- Chemical Manufacturing	0.008	12%	0.008	13%
1403	Industrial Processes - Average (EPA 9003)	0.008	13%	0.008	14%
818	Farm Equipment - Diesel - Light & Heavy - (EMS=Actual Weight)	0.007	31%	0.007	31%
829	Gasoline - Catalyst - Ftp Bag 1-3 Starts - ARB IUS Summer 1994	0.006	20%	0.007	20%
1502	[Draft] Consumer Prd: Arts And Crafts Adhesives	0.006	11%	0.006	10%

Table 13 (continued)

Profile No.	Description	Direct		Total	
		Average	St.Dev	Average	St.Dev
412	Gasoline - Non-Cat - Ftp Bag 1-3 Starts - ARB IUS Summer 1994	0.006	21%	0.006	20%
413	Gasoline - Non-Cat - Ftp Composite - ARB IUS Summer 1994	0.006	22%	0.006	21%
1506	[Draft] Consumer Prd: Contact Adhesive	0.006	11%	0.006	10%
586	Composite Jet Exhaust Jp-5 (EPA 1097-1099)	0.006	29%	0.006	29%
Impact on Acrolein					
944	Butadiene	0.12	14%	0.13	18%
784	Synthetic Rubber Mfg-Styrene-Butadiene Rubber	0.071	14%	0.076	18%
1414	Rubber/Misc. Plastics Productn - Average (EPA 9014)	0.024	14%	0.025	18%
586	Composite Jet Exhaust Jp-5 (EPA 1097-1099)	0.021	30%	0.022	31%
1404	Chemical Manufacturing - Average (EPA 9004)	0.014	33%	0.015	32%
1428	Organic Chemical Storage - Average (EPA 9028)	0.014	33%	0.015	32%
1403	Industrial Processes - Average (EPA 9003)	0.011	31%	0.011	31%
9	Industrial Ice- Distillate Oil	0.008	14%	0.009	16%
412	Gasoline - Non-Cat - Ftp Bag 1-3 Starts - ARB IUS Summer 1994	0.003	20%	0.003	21%
401	Gasoline - Non-Cat - Stabilized Exhaust - ARB IUS Summer 1996	0.002	23%	0.002	26%
411	Gasoline - Non-Cat - Stabilized Exhaust - ARB IUS Summer 1994	0.002	21%	0.002	23%
533	Daytime Biogenic Profile- Kern County Crops	0.002	14%	0.002	15%
402	Gasoline - Non-Cat - Ftp Bag1-3 Starts - ARB IUS Summer 1996	0.002	22%	0.002	24%
413	Gasoline - Non-Cat - Ftp Composite - ARB IUS Summer 1994	0.002	23%	0.002	25%
829	Gasoline - Catalyst - Ftp Bag 1-3 Starts - ARB IUS Summer 1994	0.002	20%	0.002	22%
861	Gasoline - Catalyst - Stabilized Exhaust - ARB IUS Summer 1987	0.002	21%	0.002	24%
430	Gasoline - Catalyst - Stabilized Exhaust - ARB IUS Summer 1988	0.002	21%	0.002	24%
431	Gasoline - Catalyst - Stabilized Exhaust - ARB IUS Summer 1989	0.002	21%	0.002	24%
876	Gasoline - Catalyst - Stabilized Exhaust - ARB IUS Summer 1996	0.002	24%	0.002	26%
436	Gasoline - Catalyst - Stabilized Exhaust - ARB IUS Summer 1997	0.002	24%	0.002	26%
Impact on Phenols					
1447	Organic Solvent Evaporation - Misc. - Avg (EPA 9047)	0.099	38%	0.103	38%
223	Surface Coating Evaporation- Xylene Solvent	0.012	17%	0.013	20%
921	Degreasing: Cold Cleaning (Batch, Conveyor, Spray Gun)	0.011	18%	0.012	20%
1449	Fabricated Metal (Us EPA #2466)	0.011	17%	0.011	20%
922	Degreasing: Handwiping	0.011	19%	0.011	20%
90	Degreasing- Toluene	0.010	21%	0.010	20%
1502	[Draft] Consumer Prd: Arts And Crafts Adhesives	0.006	20%	0.006	20%
1506	[Draft] Consumer Prd: Contact Adhesive	0.005	20%	0.005	20%
1448	Auto Refinishing (Us EPA #2402)	0.005	17%	0.005	20%

Table 13 (continued)

Profile No.	Description	Direct		Total	
		Average	St.Dev	Average	St.Dev
1803	[Draft] Aerosol Ctg: Metallic Pigmented Coatings	0.005	20%	0.005	20%
711	Industrial Surface Coating-Composite Laquer	0.005	20%	0.005	20%
713	Industrial Surface Coating-Composite Primer	0.005	20%	0.005	20%
815	Utility Equipment - Gasoline - 2 Cycle - Calpoly 1991	0.005	17%	0.005	20%
783	Industrial Surface Coating-Solvent Based Paint	0.005	20%	0.005	20%
1812	[Draft] Aerosol Ctg: High Temperature Coatings	0.005	19%	0.005	20%
712	Industrial Surface Coating-Composite Enamel	0.004	18%	0.005	20%
716	Medium Cure Asphalt	0.004	17%	0.005	20%
1582	[Draft] Consumer Prd: Adhesive Remover	0.004	17%	0.004	20%
420	Cbg - Hot Soak - Mtbe/Etoh Program - Ldv	0.004	17%	0.004	20%
1503	[Draft] Consumer Prd: Automotive Adhesives	0.004	20%	0.004	20%
Impact on Nitrophenols					
552	Phenol	0.17	26%	0.17	21%
753	Styrene	0.13	45%	0.12	39%
1405	Plastics Production - Average (EPA 9005)	0.070	44%	0.065	40%
1447	Organic Solvent Evaporation - Misc. - Avg (EPA 9047)	0.064	26%	0.064	23%
784	Synthetic Rubber Mfg-Styrene-Butadiene Rubber	0.053	45%	0.049	40%
90	Degreasing- Toluene	0.034	34%	0.031	34%
922	Degreasing: Handwiping	0.034	34%	0.031	32%
921	Degreasing: Cold Cleaning (Batch, Conveyor, Spray Gun)	0.033	33%	0.031	31%
223	Surface Coating Evaporation- Xylene Solvent	0.033	32%	0.031	29%
1449	Fabricated Metal (Us EPA #2466)	0.030	33%	0.028	30%
1502	[Draft] Consumer Prd: Arts And Crafts Adhesives	0.020	34%	0.018	34%
1414	Rubber/Misc. Plastics Productn - Average (EPA 9014)	0.018	44%	0.016	41%
1506	[Draft] Consumer Prd: Contact Adhesive	0.018	34%	0.016	34%
1803	[Draft] Aerosol Ctg: Metallic Pigmented Coatings	0.017	34%	0.015	33%
711	Industrial Surface Coating-Composite Laquer	0.017	34%	0.015	34%
713	Industrial Surface Coating-Composite Primer	0.016	34%	0.015	34%
783	Industrial Surface Coating-Solvent Based Paint	0.016	34%	0.014	33%
1812	[Draft] Aerosol Ctg: High Temperature Coatings	0.015	34%	0.013	33%
1448	Auto Refinishing (Us EPA #2402)	0.015	33%	0.013	31%
712	Industrial Surface Coating-Composite Enamel	0.013	33%	0.012	31%
Impact on Lumped Alkyl Nitrates					
274	Synthetic Rubber Auto Tire Production	0.17	10%	0.17	9%
86	Stoddard Cleaning Solvent	0.16	10%	0.16	9%
100	Jet Fuel Evaporation (Jet A)	0.16	10%	0.16	9%
1413	Pulp And Paper Industry - Average (EPA 9013)	0.16	12%	0.16	12%
1430	Organic Chem/Fixed Roof:Misc Alkanes - Avg (EPA 9030)	0.15	10%	0.15	9%
563	Jet Fuel Evaporation (Jp-4)	0.15	10%	0.15	9%
21	Asphalt Roofing - Blowing Operation	0.14	10%	0.14	10%
1792	[Draft] Consumer Prd: Heavy Duty Hand Cleaner Or Soap	0.13	10%	0.14	9%
301	Petro Storage- Fixed Roof- Heptane	0.13	10%	0.13	11%
926	Degreasing: Cold Cleaning (Batch, Conveyor, Spray Gun)	0.13	12%	0.13	14%
927	Degreasing: Handwiping	0.13	12%	0.13	14%
919	Degreasing: Cold Cleaning (Batch, Conveyor, Spray Gun)	0.12	10%	0.12	9%
920	Degreasing: Handwiping	0.12	10%	0.12	9%
1720	[Draft] Consumer Prd: Charcoal Lighter Materials	0.12	10%	0.12	9%
1611	[Draft] Consumer Prd: Flying Insect Insecticide - Aerosols	0.12	10%	0.12	9%

Table 13 (continued)

Profile No.	Description	Direct		Total	
		Average	St.Dev	Average	St.Dev
1600	[Draft] Consumer Prd: Non-Selective Herbicides/Defoliants	0.12	10%	0.12	9%
1684	[Draft] Consumer Prd: Wood Floor Wax/Polish	0.12	10%	0.12	9%
299	Petro Storage- Fixed Roof- Cyclohexane	0.12	10%	0.12	12%
551	Ocs - Oil Seeps - Volatile Fraction	0.12	10%	0.12	9%
1671	[Draft] Consumer Prd: Laundry Prewash - Other Forms	0.11	10%	0.11	9%
Impact on PAN					
511	Plastics Mfg- Polypropylene	0.20	34%	0.29	34%
555	Methyl Methacrylate	0.19	30%	0.39	36%
944	Butadiene	0.13	30%	0.26	37%
946	Ethylene Glycol	0.13	36%	0.13	32%
778	Methyl Isobutyl Ketone	0.10	31%	0.11	28%
211	Beer Fermentation- Ethanol	0.10	36%	0.087	36%
226	Surface Coating Solvent- Ethyl Alcohol	0.10	36%	0.087	36%
1733	[Draft] Consumer Prd: Underarm Deodorants - Non-Aerosols	0.10	36%	0.087	36%
1751	[Draft] Consumer Prd: Personal Fragrance Product (Fragrance > 20%)	0.10	36%	0.087	36%
1510	[Draft] Consumer Prd: Woodworking Glues	0.099	36%	0.086	35%
1740	[Draft] Consumer Prd: Astringents/Toners	0.099	36%	0.086	36%
1767	[Draft] Consumer Prd: Hair Styling Gels	0.099	36%	0.086	36%
557	Methyl Acrylate	0.099	29%	0.222	41%
1750	[Draft] Consumer Prd: Personal Fragrance Product (Fragrance <= 20%)	0.098	35%	0.085	36%
1591	[Draft] Consumer Prd: Sanitizers	0.097	36%	0.084	36%
1590	[Draft] Consumer Prd: Disinfectants	0.093	36%	0.081	35%
1732	[Draft] Consumer Prd: Underarm Deodorants - Aerosols	0.090	35%	0.077	35%
1449	Fabricated Metal (Us EPA #2466)	0.088	30%	0.141	38%
1625	[Draft] Consumer Prd: Insect Repellants - Aerosols	0.087	35%	0.076	35%
1760	[Draft] Consumer Prd: Hair Spray	0.087	35%	0.076	35%
Impact on Lumped Higher PAN Analogues					
557	Methyl Acrylate	0.14	30%	0.20	32%
289	Surface Coating Evaporation- Solvent- Butyl Alcohol	0.11	33%	0.11	35%
1592	[Draft] Consumer Prd: Sterilants (Not Including Ethylene Oxide)	0.11	29%	0.12	27%
781	N-Propyl Alcohol	0.099	33%	0.090	36%
777	Methyl Amyl Ketone	0.081	33%	0.073	33%
1790	[Draft] Consumer Prd: Laundry Detergent	0.080	33%	0.098	33%
1440	Organic Chem/Fixed Roof:Misc Ketones - Avg (EPA 9040)	0.080	32%	0.070	33%
1627	[Draft] Consumer Prd: Fungicides And Nematicides	0.079	32%	0.069	34%
274	Synthetic Rubber Auto Tire Production	0.070	33%	0.057	35%
795	Glycol Ethers (Diethylene Glycol)	0.068	33%	0.073	34%
510	Plastics Mfg- Vinyl Chloride	0.066	33%	0.069	36%
299	Petro Storage- Fixed Roof- Cyclohexane	0.063	33%	0.051	40%
1429	Organic Chem/Fixed Roof:Alcohols - Avg (EPA 9029)	0.062	33%	0.057	35%
1659	[Draft] Consumer Prd: Oven Cleaners - Liquid And Other	0.062	32%	0.070	32%
1509	[Draft] Consumer Prd: Pipe Cements And Primers	0.060	33%	0.059	32%
1413	Pulp And Paper Industry - Average (EPA 9013)	0.058	30%	0.068	29%
945	Butyl Carbitol	0.057	32%	0.056	31%

Table 13 (continued)

Profile No.	Description	Direct		Total	
		Average	St.Dev	Average	St.Dev
230	Petro Storage- Fixed Roof- Hexane	0.057	35%	0.046	43%
223	Surface Coating Evaporation- Xylene Solvent	0.057	34%	0.090	34%
1947	[Draft] Consumer Prd Composite: Soaps And Detergent Products	0.057	32%	0.066	32%
Impact on PBzN					
753	Styrene	0.13	30%	0.11	40%
1405	Plastics Production - Average (EPA 9005)	0.066	30%	0.057	39%
784	Synthetic Rubber Mfg-Styrene-Butadiene Rubber	0.051	30%	0.044	38%
1414	Rubber/Misc. Plastics Productn - Average (EPA 9014)	0.017	30%	0.015	38%
90	Degreasing- Toluene	0.011	31%	0.010	38%
922	Degreasing: Handwiping	0.010	30%	0.009	36%
921	Degreasing: Cold Cleaning (Batch, Conveyor, Spray Gun)	0.010	30%	0.009	35%
223	Surface Coating Evaporation- Xylene Solvent	0.008	30%	0.008	34%
1449	Fabricated Metal (Us EPA #2466)	0.008	30%	0.008	33%
1502	[Draft] Consumer Prd: Arts And Crafts Adhesives	0.006	31%	0.006	36%
1404	Chemical Manufacturing - Average (EPA 9004)	0.006	30%	0.005	36%
1506	[Draft] Consumer Prd: Contact Adhesive	0.006	31%	0.005	37%
711	Industrial Surface Coating-Composite Laquer	0.005	31%	0.005	37%
713	Industrial Surface Coating-Composite Primer	0.005	31%	0.005	37%
1803	[Draft] Aerosol Ctg: Metallic Pigmented Coatings	0.005	30%	0.005	37%
79	Flares- Chemical Manufacturing	0.005	30%	0.005	33%
783	Industrial Surface Coating-Solvent Based Paint	0.005	31%	0.004	36%
1403	Industrial Processes - Average (EPA 9003)	0.005	30%	0.004	36%
1812	[Draft] Aerosol Ctg: High Temperature Coatings	0.004	30%	0.004	36%
1448	Auto Refinishing (Us EPA #2402)	0.004	30%	0.004	33%
Impact on Unsaturated PAN Analogues					
944	Butadiene	0.097	31%	0.094	37%
784	Synthetic Rubber Mfg-Styrene-Butadiene Rubber	0.058	31%	0.056	37%
1414	Rubber/Misc. Plastics Productn - Average (EPA 9014)	0.019	31%	0.019	36%
533	Daytime Biogenic Profile- Kern County Crops	0.011	30%	0.012	33%
586	Composite Jet Exhaust Jp-5 (EPA 1097-1099)	0.010	29%	0.013	33%
9	Industrial Ice- Distillate Oil	0.007	31%	0.010	33%
1428	Organic Chemical Storage - Average (EPA 9028)	0.005	30%	0.006	30%
1404	Chemical Manufacturing - Average (EPA 9004)	0.004	30%	0.004	31%
1403	Industrial Processes - Average (EPA 9003)	0.003	30%	0.004	31%
534	Nighttime Biogenic Profile - Kern County Crops	0.002	30%	0.003	31%
412	Gasoline - Non-Cat - Ftp Bag 1-3 Starts - ARB IUS Summer 1994	0.002	31%	0.004	33%
401	Gasoline - Non-Cat - Stabilized Exhaust - ARB IUS Summer 1996	0.002	30%	0.004	33%
816	Utility Equipment - Gasoline - 4 Cycle - Calpoly 1991	0.0014	31%	0.004	34%
411	Gasoline - Non-Cat - Stabilized Exhaust - ARB IUS Summer 1994	0.0013	30%	0.004	34%
402	Gasoline - Non-Cat - Ftp Bag1-3 Starts - ARB IUS Summer 1996	0.0013	30%	0.003	33%
829	Gasoline - Catalyst - Ftp Bag 1-3 Starts - ARB IUS Summer 1994	0.0013	31%	0.003	34%

Table 13 (continued)

Profile No.	Description	Direct		Total	
		Average	St.Dev	Average	St.Dev
413	Gasoline - Non-Cat - Ftp Composite - ARB IUS Summer 1994	0.0012	30%	0.003	34%
861	Gasoline - Catalyst - Stabilized Exhaust - ARB IUS Summer 1987	0.0012	30%	0.003	34%
430	Gasoline - Catalyst - Stabilized Exhaust - ARB IUS Summer 1988	0.0012	30%	0.003	34%
877	Gasoline - Catalyst - Ftp Bag 1-3 Starts - ARB IUS Summer 1996	0.0012	30%	0.003	33%

CONCLUSIONS AND RECOMMENDATIONS

This project achieved its objective in providing numerical factors to quantify the relative impacts of various types of VOC emissions on atmospheric levels of various organic oxidation products of potential concern to OEHHA. However, it is important to recognize that the results depend significantly on the choice of chemical mechanism, model scenarios, and product impact quantification method to use in the analysis. Probably the most important of these is the product impact quantification method, since making different choices in this regard leads to significantly different results in not only the magnitude but also the ordering of the product formation potential results. However, the choice in scenarios used to represent ambient conditions affect the representativeness of the data, and the uncertainties and limitations in the chemical mechanism affect the accuracy and applicability of the predictions. These factors, and their implications concerning the results of this project, are discussed further below.

Chemical Mechanism Uncertainties

Although the chemical mechanism employed in this study was designed and evaluated primarily for predicting effects of VOCs on ozone formation, it is probably the best available for use in this study because of its detailed representation of the many types of emitted VOCs and because it represents organic products using more model species than most. However, it is not without uncertainties and limitations that impact the results of this study. Experimental product yield information is available only for the best-studied compounds, and for the majority of the compounds the product yields are estimated or approximated. Predictions of secondary products are particularly uncertain, and the many of the photooxidation products of aromatics are unknown and are represented in the model by lumped species with parameterized mechanisms. Although environmental chamber data have been used to test predictions of effects of VOCs on ozone and radical levels, evaluations of effects on organic product levels are extremely limited.

In general, product impact predictions are probably the most reliable for formation of formaldehyde, higher aldehydes and PAN from the simpler alkenes, formation of PAN from the simple aldehydes, alkenes, and methylbenzenes, formation of benzaldehyde from methylbenzenes and styrenes, and formation of acrolein from 1,3-butadiene. They are more uncertain but probably not too unreliable for formation of alkyl nitrates from high molecular weight aliphatics, PBzN from benzaldehyde and styrenes and unsaturated PAN from acrolein and methacrolein. These are generally the compounds with the highest formation potentials of these products. The lumped higher aldehyde predictions must be considered to be highly approximate because the model species represent a wide range of compounds and are used as surrogate species in a number of highly uncertain mechanisms where the actual products are unknown. The “cresol” and “nitrophenol” model species are used in many aromatic mechanisms to represent products whose chemical structures are unknown, particularly for those compounds with the highest predicted formation potentials for these model species. Therefore, the predicted impacts on these model species must be considered to be only very approximate upper-limit indications of the amount of such products that *might* be formed.

Except for the “cresol” and “nitrophenol” impacts, in most cases the chemical mechanistic uncertainties in the formation potentials for a product are the lowest for the compounds with the highest impacts on the product, and increase as the impacts decrease. This is because a low formation potential usually means that the formation is dominated by secondary reactions, which tend to be most uncertain. This suggests that the mechanism uncertainties of product impacts of complex mixtures of many organics

may be relatively low, since the impacts of mixtures tend to be dominated by those components with the highest individual impacts. Also, some statistical cancellation of errors occurs when the products are formed from reactions of sufficiently large number of compounds.

If reduced mechanism uncertainty is desired for predictions of impacts of VOCs on formation of a particular product, then it is necessary to experimentally evaluate model predictions of formation of the product in environmental chamber experiments. As indicated above, previous environmental chamber experiments focused on ozone predictions, and comprehensive and high quality measurement data needed to evaluate predictions of most of organic products are highly limited. If impact predictions are desired for products not currently in the mechanism or represented only by lumped species, then modifications to the mechanism are needed, and the product predictions of the modified mechanism may also need to be experimentally evaluated. However, for the major products currently explicitly represented in the mechanism, such as formaldehyde and PAN, the mechanism uncertainties are probably not as important as the other issues, discussed below.

Representativeness of the Model Scenarios

Because of limited resources, the model scenarios used to represent ambient conditions in this project were the same as employed previously when developing the ozone reactivity scales, with the only modification being to update the mixture used to represent VOC emissions from all sources. Although the scenarios employed are highly simplified representations of actual urban conditions, as discussed previously (Carter, 1994a, CARB 1993), using a set of simplified scenarios may not necessarily be inappropriate for developing general reactivity or product impact scales provided that they represent the appropriate range of chemical conditions that will affect the impact of interest. However, the EKMA scenarios used in this and our previous studies are significantly out of date, have predicted ozone levels far higher than currently occur in the urban areas they are intended to represent, are were not designed to represent multi-day effects that characterize many episodes. In addition, these high ozone scenarios may not necessarily represent all the conditions where the highest toxic product concentrations may occur. Indeed, for very rapidly reacting toxic products such as aldehydes, days of lower photochemical activity may give the higher levels of these compounds because of decreased rates of their consumption reactions.

What is needed is a complete update of the scenarios used to develop general reactivity scales, for improving ozone reactivity scales for regulatory applications as well as for improving predictions of product formation potentials such as developed for this work. This needs to be based on an updated assessment of the range of current airshed conditions where potentially unacceptable levels of the pollutant of interest may occur. Probably the best approach is develop a comprehensive set of scenarios that represents all the types of conditions that need to be considered for all types of impacts, which would include episodes of moderate and low as well as high photochemical activity. Ideally comprehensive regional models should be used, since these are considered to give the most realistic representation of actual ambient conditions. However, even with today's faster computers is not really practical to use these highly computationally intensive regional models to calculated incremental impacts for the ~500 types of VOCs that are represented in the current detailed mechanism, especially if a representative distribution of conditions is to be considered. The best approach in the near term is probably to use these regional models to develop a comprehensive set of box or trajectory models that represent chemical conditions and give appropriate predictions of effects of emissions changes on various receptor areas under different meteorological conditions.

Nevertheless, the scenarios employed in this study are probably sufficient for the purpose of obtaining at least approximate indications of the relative impacts of the different VOCs on toxic product

formation at least for days for high ozone and photochemical reactivity. More accurate scenarios probably would not give significantly different results of predictions of which compounds give the highest impacts in days of high photochemical activity. Also there is no clear reason to expect that the ordering of impacts will change significantly if days of lower photochemical activity are considered, at least for compounds or profiles with the highest impacts. Therefore, although the scenarios employed in this study are out-of-date and have other limitations, they use is probably not entirely inappropriate for an initial study such as this.

It should be noted that because of the high sensitivity of ozone formation to NO_x conditions, when developing ozone reactivity scales we used scenarios with NO_x inputs adjusted to represent well-defined conditions of NO_x availability to develop separate scales representing different NO_x conditions. The CARB chose to use the MIR ozone reactivity scale, representing higher NO_x conditions where VOCs have the highest impact on ozone formation, as the preferred scale for regulatory applications. This is because MIR represents conditions where VOC control is the most effective, and because its use in VOC regulations complements the use of NO_x control to reduce ozone in the lower NO_x conditions where VOC control is less effective. However, NO_x conditions are much less important in affecting how VOCs affect formation of their organic oxidation products, and VOC control provides the only means to reduce the formation VOC oxidation products. Therefore, there is no compelling or clearly justifiable policy reason to use adjusted NO_x scenarios when deriving quantifying organic product formation potential scales. For this reason, the results presented in this work use the product formation potentials calculated for the base case scenarios, which, at least to within the limitations discussed above, represent the best available estimate of ambient conditions at the time the scenarios were developed.

The results of this study indicate an approximately 10-15% scenario-to scenario variability on direct VOC impacts on average aldehyde concentrations in the base case scenarios, and approximately 25-35% variability for direct formation of average concentrations of PAN and PAN analogues, at least for those compounds with the highest direct impacts. Much higher variability is obtained if a different product yield quantification method is used besides the average, because of the greater sensitivity of the results on mixing height variations. The total impacts depend on more factors and are therefore somewhat more variable than the direct impacts, though as expected they are highly correlated. The impacts generally are somewhat lower in the relatively high NO_x scenarios where the higher NO_x inhibits radical levels, but tend to be relatively independent of NO_x for scenarios with low or moderate NO_x conditions. However, it should be noted that the scenarios employed were limited to those to represent episodes of highest ozone formation, and more variability might have been obtained had a more comprehensive set of scenarios been employed. Therefore, the scenario-to-scenario variability results obtained in this study must be considered to be lower limits of the likely variability under the full range of atmospheric conditions.

Impact Quantification Methods

Although the chemical mechanism and the scenarios are obviously important, the most important single consideration affecting the result is method chosen to quantify the amount of product formed in the simulation. As indicated above, choices made in this regard will significantly affect not only the magnitudes but also the ordering of the calculated impact factors. The appropriate choice in this regard depends on the intended use of the factors, and on what is considered most important in terms of the health and policy implications of atmospheric formation of the products of interest. Therefore, the choice in impact quantification method is more a policy decision than a scientific one. However, the policy decision needs to be made with an understanding of how the various alternatives will affect the impacts derived, and the various factors involved in how these choices will affect the results.

The first decision that needs to be made is whether impacts should be given in terms of *direct* or *total* effects. The direct impact measures only the product formed directly from the VOC, and does not consider that the VOC may affect the level of the product indirectly by affecting how much of the product is formed from the reactions of other VOCs. Direct impacts are most appropriate when using the data for source attribution studies, while total impacts are most appropriate when we are primarily interested in measuring the effect of the VOC on overall air quality. Since we are uncertain of OEHHA's priorities in this regard, our results tabulations give both direct and total impacts, so the appropriate set can be used depending on the intended application. The practical effect of this choice in terms of which compounds or profiles have the highest impacts is probably not significant, since the compounds or profiles with the highest direct impacts will also have the highest total impacts. However, some compounds with high direct product formation potentials have indirect effects of comparable magnitude, and the indirect effects can be the dominant factor for compounds with low direct impacts.

In terms of affecting ordering of impacts, the most important decision concerns how to quantify the amount of product formed. Possible choices include maximum concentrations, final concentrations, integrated or average concentrations, numbers of moles formed, etc. Significantly different results and orderings can be obtained depending on which is used because the concentration-time profiles of directly formed products can vary significantly depending on the reactivity of the VOC and whether it is formed as a primary or secondary product. This is because the mixing height, which determines product concentrations resulting from formation from a given amount of compound, varies with time in the simulations, and also because if the product is formed early in the simulation it is subsequently consumed by chemical reaction. Quantification by maximum concentration tends to give highest weight to compounds that react rapidly because such compounds form the maximum concentrations of products early in the simulations when the mixing heights tend lowest, and thus concentrations the highest. On the other hand, quantifying by final concentration tends to give low weights to compounds that react rapidly because if the product peaks early in the simulations its final concentrations are relatively low at the end of the simulation because it has had the most time to react. Using the final concentration as the quantification method tends to give the counter-intuitive result that emission of compounds that form the product relatively slowly have higher product formation potentials than emissions of the product itself, because most of the directly emitted product reacts by the end of the simulation. However, this would be the most appropriate quantification method if the purpose of the analysis is to attribute various emissions sources to the observed product concentrations at the end of the day.

For this study we chose the average product concentration as the most appropriate quantification for deriving a general product formation potential scale. The average or integrated concentration is considered to give the most comprehensive measure of the overall exposure to the product, which may be the most appropriate factor to consider for health impact analyses. In addition, because it weighs each time of the simulated day approximately equally, it provides a means to compare impacts of VOCs that form products at different times of the simulated day on an approximately equal basis. It was also the quantification method that was found to be the least dependent on scenario conditions, and thus gives a product impact measure that is least sensitive to specific choice of scenarios employed. This is a significant advantage considering the uncertainty in the representativeness of the scenarios employed in this study.

Compounds with Highest Product Formation Potentials

If the average product yield is used as the impact quantification method, the self-formation potentials for emissions of the products themselves are estimated to be on the order of 0.6-0.8, but these tend to be more sensitive to inversion height variations than calculated formation potentials for reacting

compounds. The highest product formation potentials from reacting compounds tend to be on the order of 0.2-0.3 when quantified on a mass basis, or approximately 1/3 the impact of directly emitting the compound itself. However, these results are highly dependent on the quantification method, and may also depend to some extent on the type of scenario employed.

The compounds found to have the highest impacts on formation of the various products considered were generally those expected based on considerations of known aspects of their mechanisms such as product yields and reaction rates. Alkenes tended to have the highest aldehyde formation potentials because of their rapid rates of reaction and relatively high yields of formation of these products in their initial reactions. Alkenes also had high potentials for forming PAN and higher saturated PAN analogues, though alkyl acetylenes, higher aldehydes, and unsaturated carbonyls that are predicted to directly form PAN precursor appear to have comparable or higher potentials. Styrenes have the highest formation potentials for PBzN, and 1,3-butadiene is the only compound in the current mechanism predicted to form acrolein, and by far has the highest formation potential for this compound (other than acrolein itself). The highest formation potentials for phenols and nitrophenols are calculated to be naphthalenes and isocyanates, but as indicated above the actual compounds represented by these model species are unknown.

Product Formation Potentials for Emissions Profiles

In order to estimate product formation potentials of actual emissions, it is necessary to assign SAPRC-99 detailed model species to the speciation profiles used in the emissions inventories. Such assignments could be made to at least half of the mass for 94% of the 373 profiles used in California, and for >85% of the mass for over 80% of the profiles, allowing product formation potentials for those profiles to be calculated. The results should be as expected based on the types of compounds they contain, but no analysis was carried out other than to tabulate the results by profile. Of the 25 profiles where less than half of the mass was assigned and therefore no estimates were made, 12 are because they contained significant levels of compounds that are not represented in the current mechanism, 7 are because they contain significant levels of poorly defined chemical categories (such as “Fragrances” or “Ingredients < 0.1%”), and 6 because they have both. The chemical mechanism would need to be expanded and the emissions speciation databases would need to be improved if estimates are needed for these profiles. However, these profiles represent a relatively small fraction of the total mass of emissions.

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APPENDIX A.

MECHANISM LISTING AND RESULTS TABULATIONS

This Appendix contains the complete listings of the portions of the mechanism used in this work that are different from that used by Carter (2000a), and detailed tabulations of input data and results that are too lengthy to be given with the text. Except for Table A-1 and Table A-2, these tabulations are considered to be too long to be appropriate for a printed report. Therefore, distributed with this report is an electronic version of this Appendix, which has all the tables in various sheets in an Excel 97 file. This file can be downloaded from <ftp://ftp.cert.ucr.edu/pub/carter/misc/oeaha/appndx.xls>.

Table A-1 through Table A-4 give a complete listing of the version of the SAPRC-99 mechanism employed in this study. Table A-1 lists the model species employed and describes the types of compounds they represent. Table A-2 lists all the reactions in the mechanism except for the reactions of the VOCs represented using the generalized model species with assigned parameters. The reactions of the VOCs represented using the generalized model species are given in Table A-3. Note that for many of these VOCs, the reactive products formed in sufficiently high yield that are not explicitly represented in the mechanism are represented using adjusted parameter product species as discussed by Carter (2000a). The reactions used for these product species (PRD1, etc.) are included in the listing on Table A-3 immediately after the reactions of the parent VOC. Note that the reactions of these adjusted parameter product species are different for each VOC, and if no reactions of such species are shown following the initial reactions of the VOC then all its products are represented by explicit model species. The absorption cross-sections and quantum yields used in this mechanism are given in Table A-4.

Table A-5 and Table A-6 contain emissions inventory speciation data that were used as inputs to the model simulations discussed in this report. Table A-5 contains the compounds in the SCOS-97 emissions inventory that was used to derive the base ROG surrogate employed in this study, and the assignments of the compounds to SAPRC-99 model species. Table A-6 contains the compositions of all the profiles in the current CARB database (as of 11/29/2000), and the assignments of the compounds in the profiles to SAPRC-99 model species. These assignments were used as the basis for the calculated product formation potentials of these profiles.

The major results of this project are given in Table A-7 and Table A-8, which give the direct and total product formation potentials for all the SAPRC-97 compounds and mixtures (in Table A-7) and for all the CARB emissions profiles (in Table A-8) where they could be calculated. The tabulated data are averages and standard deviations of the impacts on hourly average concentrations in the 39 base case EKMA scenarios, quantified on a mass basis. Data for the individual scenarios (in 12 Excel files of approximately 11 MB each) are available on request.

Table A-1. Listing of model species used in the mechanism employed in this study. Except as indicated, the reactions of these species are given in Table A-2.

Type and Name	Description
<u>Inorganic and Non-Reacting Organic Species</u>	
<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 Inorganic Radical Species and Operators.</u>	
HO.	Hydroxyl Radicals
HO2.	Hydroperoxide Radicals
RO2-R.	Peroxy Radical Operator representing NO to NO ₂ conversion with HO ₂ formation.
R2O2.	Peroxy Radical Operator representing NO to NO ₂ conversion without HO ₂ formation.
<u>Steady State Radical Species</u>	
O3P	Ground State Oxygen Atoms
O*1D2	Excited Oxygen Atoms
<u>Non-Reacting Species (No reactions given)</u>	
CO2	Carbon Dioxide
XC	Lost Carbon
XN	Lost Nitrogen
SULF	Sulfates (SO ₃ or H ₂ SO ₄)
<u>Low Reactivity Compounds or Unknown Products Represented as Unreactive (No reactions given)</u>	
H2	Hydrogen
HCOOH	Formic Acid
CCO-OH	Acetic Acid
RCO-OH	Higher organic acids
CCO-OOH	Peroxy Acetic Acid
RCO-OOH	Higher organic peroxy acids
NROG	Unspecified Unreactive Carbon

Table A-1 (continued)

Type and Name	Description
<u>Organic Species used to Represent Base Case VOCs and their Intermediates and Products</u>	
<u>Active Organic Radical Species and Operators.</u>	
C-O2.	Methyl Peroxy Radicals
RO2-N.	Peroxy Radical Operator representing NO consumption with organic nitrate formation.
CCO-O2.	Acetyl Peroxy Radicals
RCO-O2.	Peroxy Propionyl and higher peroxy acyl Radicals
BZCO-O2.	Peroxyacyl radical formed from Aromatic Aldehydes
MA-RCO3.	Peroxyacyl radicals formed from methacrolein and other acroleins.
<u>Steady State Organic Radical Species</u>	
TBU-O.	t-Butoxy Radicals
BZ-O.	Phenoxy Radicals
BZ(NO2)-O.	Nitro-substituted Phenoxy Radical
HOCOO.	Radical formed when Formaldehyde reacts with HO2
<u>Reactive Organic Product Species</u>	
HCHO	Formaldehyde
CCHO	Acetaldehyde
RCHO	Lumped C3+ Aldehydes
ACET	Acetone
MEK	Ketones and other non-aldehyde oxygenated products which react with OH radicals slower than $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-2} \text{ sec}^{-1}$.
MEOH	Methanol
COOH	Methyl Hydroperoxide
ROOH	Lumped higher organic hydroperoxides
GLY	Glyoxal
MGLY	Methyl Glyoxal
BACL	Biacetyl
PHEN	Phenol
CRES	Cresols
NPHE	Nitrophenols
BALD	Aromatic aldehydes (e.g., benzaldehyde)
ACRO	Acrolein (Not in standard mechanism. Added as an explicit species for this study.)
MACR	Methacrolein
MVK	Methyl Vinyl Ketone
IPRD	Lumped isoprene product species
PRDX	Ketones and other non-aldehyde oxygenated products which react with OH radicals faster than $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-2} \text{ sec}^{-1}$.
RNO3	Lumped Organic Nitrates
DCB1	Reactive Aromatic Fragmentation Products that do not undergo significant photodecomposition to radicals.
DCB2	Reactive Aromatic Fragmentation Products which photolyze with alpha-dicarbonyl-like action spectrum.
DCB3	Reactive Aromatic Fragmentation Products which photolyze with acrolein action spectrum.
PAN	Peroxy Acetyl Nitrate

Table A-1 (continued)

Type and Name	Description
PAN2	PPN and other higher alkyl PAN analogues
PBZN	PAN analogues formed from Aromatic Aldehydes
MPAN	PAN analogue formed from Methacrolein

Species used in Lumped Mechanisms for Base Case ROG

Primary Organics Represented explicitly

CH4	Methane
ETHENE	Ethene
ISOPRENE	Isoprene

Lumped Parameter Species

ALK1	Alkanes and other non-aromatic compounds that react only with OH, and have $k_{OH} < 5 \times 10^2 \text{ ppm}^{-1} \text{ min}^{-1}$. (Primarily ethane)
ALK2	Alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} between 5×10^2 and $2.5 \times 10^3 \text{ ppm}^{-1} \text{ min}^{-1}$. (Primarily propane and acetylene)
ALK3	Alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} between 2.5×10^3 and $5 \times 10^3 \text{ ppm}^{-1} \text{ min}^{-1}$.
ALK4	Alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} between 5×10^3 and $1 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$.
ALK5	Alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} greater than $1 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$.
ARO1	Aromatics with $k_{OH} < 2 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$.
ARO2	Aromatics with $k_{OH} > 2 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$.
OLE1	Alkenes (other than ethene) with $k_{OH} < 7 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$.
OLE2	Alkenes with $k_{OH} > 7 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$.
TERP	Terpenes

Duplicate species for product formation effects study

Radical Species formed from Test VOCs

pC-O2.	Methyl Peroxy Radicals
pRO2-N.	Peroxy Radical Operator representing NO consumption with organic nitrate formation.
pCCO-O2.	Acetyl Peroxy Radicals
pRCO-O2.	Peroxy Propionyl and higher peroxy acyl Radicals
pBZCO-O2.	Peroxyacyl radical formed from Aromatic Aldehydes
pMA-RCO3.	Peroxyacyl radicals formed from methacrolein and other acroleins.
pTBU-O.	t-Butoxy Radicals
pBZ-O.	Phenoxy Radicals
pBZ(NO2)-O.	Nitro-substituted Phenoxy Radical
pHOCOO.	Radical formed when Formaldehyde reacts with HO_2
pHCHO	Formaldehyde
pCCHO	Acetaldehyde
pRCHO	Lumped C3+ Aldehydes
pACET	Acetone
pMEK	Ketones and other non-aldehyde oxygenated products that react with OH radicals slower than $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-2} \text{ sec}^{-1}$.
pMEOH	Methanol

Table A-1 (continued)

Type and Name	Description
pCOOH	Methyl Hydroperoxide
pROOH	Lumped higher organic hydroperoxides
pGLY	Glyoxal
pMGLY	Methyl Glyoxal
pBACL	Biacetyl
pPHEN	Phenol
pCRES	Cresols
pNPHE	Nitrophenols
pBALD	Aromatic aldehydes (e.g., benzaldehyde)
pACRO	Acrolein
pMACR	Methacrolein
pMVK	Methyl Vinyl Ketone
pIPRD	Lumped isoprene product species
pPRDX	Ketones and other non-aldehyde oxygenated products which react with OH radicals faster than $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-2} \text{ sec}^{-1}$.
pRNO3	Lumped Organic Nitrates
pDCB1	Reactive Aromatic Fragmentation Products that do not undergo significant photodecomposition to radicals.
pDCB2	Reactive Aromatic Fragmentation Products which photolyze with alpha-dicarbonyl-like action spectrum.
pDCB3	Reactive Aromatic Fragmentation Products which photolyze with acrolein action spectrum.
pPAN	Peroxy Acetyl Nitrate
pPAN2	PPN and other higher alkyl PAN analogues
pPBZN	PAN analogues formed from Aromatic Aldehydes
pMPAN	PAN analogue formed from Methacrolein
PRD1 ... PRD6	Adjusted parameter product species used to represent reactive products of assigned parameter test VOCs as discussed by Carter (2000a). The reactions of these products are given in Table A-3 immediately following the reactions of the VOCs forming them.
<u>Explicitly Represented as Test VOCs</u>	
pCH4	Methane
pETHE	Ethene
pISOP	Isoprene
(various)	Test VOC represented generalized model species with assigned parameters. The reactions of these VOCs are given in Table A-3.

Table A-2. Listing of the reactions of the inorganic, base case organic, and test compound product species in the mechanism used in this project.

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
<u>Inorganic Reactions</u>					
1		Phot Set= NO2			NO2 + HV = NO + O3P
2	5.79e-34	5.68e-34	0.00	-2.8	O3P + O2 + M = O3 + M
3	7.96e-15	8.00e-12	4.09		O3P + O3 = #2 O2
4	1.01e-31	1.00e-31	0.00	-1.6	O3P + NO + M = NO2 + M
5	9.72e-12	6.50e-12	-0.24		O3P + NO2 = NO + O2
6	1.82e-12	Falloff, F=0.80			O3P + NO2 = NO3 + M
		0:	9.00e-32	0.00	-2.0
		inf:	2.20e-11	0.00	0.0
8	1.81e-14	1.80e-12	2.72		O3 + NO = NO2 + O2
9	3.52e-17	1.40e-13	4.91		O3 + NO2 = O2 + NO3
10	2.60e-11	1.80e-11	-0.22		NO + NO3 = #2 NO2
11	1.95e-38	3.30e-39	-1.05		NO + NO + O2 = #2 NO2
12	1.54e-12	Falloff, F=0.45			NO2 + NO3 = N2O5
		0:	2.80e-30	0.00	-3.5
		inf:	2.00e-12	0.00	0.2
13	5.28e-2	Falloff, F=0.45			N2O5 = NO2 + NO3
		0:	1.00e-3	21.86	-3.5
		inf:	9.70e+14	22.02	0.1
14	2.60e-22	2.60e-22			N2O5 + H2O = #2 HNO3
15		(Slow)			N2O5 + HV = NO3 + NO + O3P
16		(Slow)			N2O5 + HV = NO3 + NO2
17	6.56e-16	4.50e-14	2.50		NO2 + NO3 = NO + NO2 + O2
18		Phot Set= NO3NO			NO3 + HV = NO + O2
19		Phot Set= NO3NO2			NO3 + HV = NO2 + O3P
20		Phot Set= O3O3P			O3 + HV = O3P + O2
21		Phot Set= O3O1D			O3 + HV = O*1D2 + O2
22	2.20e-10	2.20e-10			O*1D2 + H2O = #2 HO.
23	2.87e-11	2.09e-11	-0.19		O*1D2 + M = O3P + M
24	7.41e-12	Falloff, F=0.60			HO. + NO = HONO
		0:	7.00e-31	0.00	-2.6
		inf:	3.60e-11	0.00	-0.1
25		Phot Set= HONO-NO			HONO + HV = HO. + NO
26		Phot Set= HONO-NO2			HONO + HV = HO2. + NO2
27	6.46e-12	2.70e-12	-0.52		HO. + HONO = H2O + NO2
28	8.98e-12	Falloff, F=0.60			HO. + NO2 = HNO3
		0:	2.43e-30	0.00	-3.1
		inf:	1.67e-11	0.00	-2.1
29	2.00e-11	2.00e-11			HO. + NO3 = HO2. + NO2
30	1.47e-13	k = k0+k3M/(1+k3M/k2)			HO. + HNO3 = H2O + NO3
		k0:	7.20e-15	-1.56	0.0
		k2:	4.10e-16	-2.86	0.0
		k3:	1.90e-33	-1.44	0.0
31		Phot Set= HNO3			HNO3 + HV = HO. + NO2
32	2.09e-13	k = k1 + k2 [M]			HO. + CO = HO2. + CO2

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
		k1: 1.30e-13	0.00	0.0	
		k2: 3.19e-33	0.00	0.0	
33	6.63e-14	1.90e-12	1.99		HO. + O3 = HO2. + O2
34	8.41e-12	3.40e-12	-0.54		HO2. + NO = HO. + NO2
35	1.38e-12	Falloff, F=0.60			HO2. + NO2 = HNO4
		0: 1.80e-31	0.00	-3.2	
		inf: 4.70e-12	0.00	0.0	
36	7.55e-2	Falloff, F=0.50			HNO4 = HO2. + NO2
		0: 4.10e-5	21.16	0.0	
		inf: 5.70e+15	22.20	0.0	
37		Phot Set= HO2NO2			HNO4 + HV = #.61 {HO2. + NO2} + #.39 {HO. + NO3}
38	5.02e-12	1.50e-12	-0.72		HNO4 + HO. = H2O + NO2 + O2
39	1.87e-15	1.40e-14	1.19		HO2. + O3 = HO. + #2 O2
40A	2.87e-12	k = k1 + k2 [M]			HO2. + HO2. = HO2H + O2
		k1: 2.20e-13	-1.19	0.0	
		k2: 1.85e-33	-1.95	0.0	
40B	6.46e-30	k = k1 + k2 [M]			HO2. + HO2. + H2O = HO2H + O2 + H2O
		k1: 3.08e-34	-5.56	0.0	
		k2: 2.59e-54	-6.32	0.0	
41	4.00e-12	4.00e-12			NO3 + HO2. = #.8 {HO. + NO2 + O2} + #.2 {HNO3 + O2}
42	2.28e-16	8.50e-13	4.87		NO3 + NO3 = #2 NO2 + O2
43		Phot Set= H2O2			HO2H + HV = #2 HO.
44	1.70e-12	2.90e-12	0.32		HO2H + HO. = HO2. + H2O
45	1.11e-10	4.80e-11	-0.50		HO. + HO2. = H2O + O2
S2OH	9.77e-13	Falloff, F=0.45			HO. + SO2 = HO2. + SULF
		0: 4.00e-31	0.00	-3.3	
		inf: 2.00e-12	0.00	0.0	
H2OH	6.70e-15	7.70e-12	4.17		HO. + H2 = HO2. + H2O
<u>Methyl peroxy and methoxy reactions</u>					
MER1	7.29e-12	2.80e-12	-0.57		C-O2. + NO = NO2 + HCHO + HO2.
MER4	5.21e-12	3.80e-13	-1.55		C-O2. + HO2. = COOH + O2
MEN3	1.30e-12	1.30e-12			C-O2. + NO3 = HCHO + HO2. + NO2
MER5	2.65e-13	2.45e-14	-1.41		C-O2. + C-O2. = MEOH + HCHO + O2
MER6	1.07e-13	5.90e-13	1.01		C-O2. + C-O2. = #2 {HCHO + HO2.}
<u>Peroxy Radical Operators</u>					
RRNO	9.04e-12	2.70e-12	-0.72		RO2-R. + NO = NO2 + HO2.
RRH2	1.49e-11	1.90e-13	-2.58		RO2-R. + HO2. = ROOH + O2 + #-3 XC
RRN3	2.30e-12	2.30e-12			RO2-R. + NO3 = NO2 + O2 + HO2.
RRME	2.00e-13	2.00e-13			RO2-R. + C-O2. = HO2. + #.75 HCHO + #.25 MEOH
RRR2	3.50e-14	3.50e-14			RO2-R. + RO2-R. = HO2.
R2NO		Same k as rxn RRNO			R2O2. + NO = NO2
R2H2		Same k as rxn RRH2			R2O2. + HO2. = HO2.
R2N3		Same k as rxn RRN3			R2O2. + NO3 = NO2
R2ME		Same k as rxn RRME			R2O2. + C-O2. = C-O2.
R2RR		Same k as rxn RRR2			R2O2. + RO2-R. = RO2-R.

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
R2R3	Same k as rxn RRR2				R2O2. + R2O2. =
RNNO	Same k as rxn RRNO				RO2-N. + NO = RNO3
RNH2	Same k as rxn RRH2				RO2-N. + HO2. = ROOH + #3 XC
RNME	Same k as rxn RRME				RO2-N. + C-O2. = HO2. + #.25 MEOH + #.5 {MEK + PRDX} + #.75 HCHO + XC
RNN3	Same k as rxn RRN3				RO2-N. + NO3 = NO2 + O2 + HO2. + MEK + #2 XC
RNRR	Same k as rxn RRR2				RO2-N. + RO2-R. = HO2. + #.5 {MEK + PRDX} + O2 + XC
RNR2	Same k as rxn RRR2				RO2-N. + R2O2. = RO2-N.
RNRN	Same k as rxn RRR2				RO2-N. + RO2-N. = MEK + HO2. + PRDX + O2 + #2 XC
<u>Reactions of Acyl Peroxy Radicals, PAN, and PAN analogues</u>					
APN2	1.05e-11	Falloff, F=0.30			CCO-O2. + NO2 = PAN
		0:	2.70e-28	0.00	-7.1
		inf:	1.20e-11	0.00	-0.9
DPAN	5.21e-4	Falloff, F=0.30			PAN = CCO-O2. + NO2
		0:	4.90e-3	24.05	0.0
		inf:	4.00e+16	27.03	0.0
APNO	2.13e-11	7.80e-12	-0.60		CCO-O2. + NO = C-O2. + CO2 + NO2
APH2	1.41e-11	4.30e-13	-2.07		CCO-O2. + HO2. = #.75 {CCO-OOH + O2} + #.25 {CCO-OH + O3}
APN3	4.00e-12	4.00e-12			CCO-O2. + NO3 = C-O2. + CO2 + NO2 + O2
APME	9.64e-12	1.80e-12	-0.99		CCO-O2. + C-O2. = CCO-OH + HCHO + O2
APRR	7.50e-12	7.50e-12			CCO-O2. + RO2-R. = CCO-OH
APR2		Same k as rxn APRR			CCO-O2. + R2O2. = CCO-O2.
APRN		Same k as rxn APRR			CCO-O2. + RO2-N. = CCO-OH + PRDX
APAP	1.55e-11	2.90e-12	-0.99		CCO-O2. + CCO-O2. = #2 {C-O2. + CO2} + O2
PPN2	1.21e-11	1.20e-11	0.00	-0.9	RCO-O2. + NO2 = PAN2
PAN2	4.43e-4	2.00e+15	25.44		PAN2 = RCO-O2. + NO2
PPNO	2.80e-11	1.25e-11	-0.48		RCO-O2. + NO = NO2 + CCHO + RO2-R. + CO2
PPH2		Same k as rxn APH2			RCO-O2. + HO2. = #.75 {RCO-OOH + O2} + #.25 {RCO-OH + O3}
PPN3		Same k as rxn APN3			RCO-O2. + NO3 = NO2 + CCHO + RO2-R. + CO2 + O2
PPME		Same k as rxn APME			RCO-O2. + C-O2. = RCO-OH + HCHO + O2
PPRR		Same k as rxn APRR			RCO-O2. + RO2-R. = RCO-OH + O2
PPR2		Same k as rxn APRR			RCO-O2. + R2O2. = RCO-O2.
PPRN		Same k as rxn APRR			RCO-O2. + RO2-N. = RCO-OH + PRDX + O2
PPAP		Same k as rxn APAP			RCO-O2. + CCO-O2. = #2 CO2 + C-O2. + CCHO + RO2-R. + O2
PPPP		Same k as rxn APAP			RCO-O2. + RCO-O2. = #2 {CCHO + RO2-R. + CO2}
BPN2	1.37e-11	1.37e-11			BZCO-O2. + NO2 = PBZN
BPAN	3.12e-4	7.90e+16	27.82		PBZN = BZCO-O2. + NO2
BPNO		Same k as rxn PPNO			BZCO-O2. + NO = NO2 + CO2 + BZ-O. + R2O2.
BPH2		Same k as rxn APH2			BZCO-O2. + HO2. = #.75 {RCO-OOH + O2} + #.25 {RCO-OH + O3} + #4 XC
BPN3		Same k as rxn APN3			BZCO-O2. + NO3 = NO2 + CO2 + BZ-O. + R2O2. + O2
BPME		Same k as rxn APME			BZCO-O2. + C-O2. = RCO-OH + HCHO + O2 + #4 XC

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
BPRR		Same k as rxn APRR			BZCO-O2. + RO2-R. = RCO-OH + O2 + #4 XC
BPR2		Same k as rxn APRR			BZCO-O2. + R2O2. = BZCO-O2.
BPRN		Same k as rxn APRR			BZCO-O2. + RO2-N. = RCO-OH + PRDX + O2 + #4 XC
BPAP		Same k as rxn APAP			BZCO-O2. + CCO-O2. = #2 CO2 + C-O2. + BZ-O. + R2O2.
BPPP		Same k as rxn APAP			BZCO-O2. + RCO-O2. = #2 CO2 + CCHO + RO2-R. + BZ-O. + R2O2.
BPBP		Same k as rxn APAP			BZCO-O2. + BZCO-O2. = #2 {BZ-O. + R2O2. + CO2}
MPN2		Same k as rxn PPN2			MA-RCO3. + NO2 = MPAN
MPPN	3.55e-4	1.60e+16	26.80		MPAN = MA-RCO3. + NO2
MPNO		Same k as rxn PPNO			MA-RCO3. + NO = NO2 + CO2 + HCHO + CCO-O2.
MPH2		Same k as rxn APH2			MA-RCO3. + HO2. = #.75 {RCO-OOH + O2} + #.25 {RCO-OH + O3} + XC
MPN3		Same k as rxn APN3			MA-RCO3. + NO3 = NO2 + CO2 + HCHO + CCO-O2. + O2
MPME		Same k as rxn APME			MA-RCO3. + C-O2. = RCO-OH + HCHO + XC + O2
MPRR		Same k as rxn APRR			MA-RCO3. + RO2-R. = RCO-OH + XC
MPR2		Same k as rxn APRR			MA-RCO3. + R2O2. = MA-RCO3.
MPRN		Same k as rxn APRR			MA-RCO3. + RO2-N. = #2 RCO-OH + O2 + #4 XC
MPAP		Same k as rxn APAP			MA-RCO3. + CCO-O2. = #2 CO2 + C-O2. + HCHO + CCO-O2. + O2
MPPP		Same k as rxn APAP			MA-RCO3. + RCO-O2. = HCHO + CCO-O2. + CCHO + RO2-R. + #2 CO2
MPBP		Same k as rxn APAP			MA-RCO3. + BZCO-O2. = HCHO + CCO-O2. + BZ-O. + R2O2. + #2 CO2
MPMP		Same k as rxn APAP			MA-RCO3. + MA-RCO3. = #2 {HCHO + CCO-O2. + CO2}
<u>Other Organic Radical Species</u>					
TBON	2.40e-11	2.40e-11			TBU-O. + NO2 = RNO3 + #-2 XC
TBOD	9.87e+2	7.50e+14	16.20		TBU-O. = ACET + C-O2.
BRN2	3.80e-11	2.30e-11	-0.30		BZ-O. + NO2 = NPHE
BRH2		Same k as rxn RRH2			BZ-O. + HO2. = PHEN
BRXX	1.00e-3	1.00e-3			BZ-O. = PHEN
BNN2		Same k as rxn BRN2			BZ(NO2)-O. + NO2 = #2 XN + #6 XC
BNH2		Same k as rxn RRH2			BZ(NO2)-O. + HO2. = NPHE
BNXX		Same k as rxn BRXX			BZ(NO2)-O. = NPHE
<u>Explicit and Lumped Molecule Organic Products for Base Case Species</u>					
FAHV		Phot Set= HCHO_R			HCHO + HV = #2 HO2. + CO
FAVS		Phot Set= HCHO_M			HCHO + HV = H2 + CO
FAOH	9.20e-12	8.60e-12	-0.04		HCHO + HO. = HO2. + CO + H2O
FAH2	7.90e-14	9.70e-15	-1.24		HCHO + HO2. = HOCOO.
FAHR	1.51e+2	2.40e+12	13.91		HOCOO. = HO2. + HCHO
FAHN		Same k as rxn MER1			HOCOO. + NO = HCOOH + NO2 + HO2.
FAN3	5.74e-16	2.00e-12	4.83		HCHO + NO3 = HNO3 + HO2. + CO
AAOH	1.58e-11	5.60e-12	-0.62		CCHO + HO. = CCO-O2. + H2O

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
AAHV		Phot Set= CCHO_R			CCHO + HV = CO + HO2. + C-O2.
AAN3	2.73e-15	1.40e-12	3.70		CCHO + NO3 = HNO3 + CCO-O2.
PAOH	2.00e-11	2.00e-11			RCHO + HO. = #.034 RO2-R. + #.001 RO2-N. + #.965 RCO-O2. + #.034 CO + #.034 CCHO + #-0.003 XC
PAHV		Phot Set= C2CHO			RCHO + HV = CCHO + RO2-R. + CO + HO2.
PAN3	3.67e-15	1.40e-12	3.52		RCHO + NO3 = HNO3 + RCO-O2.
K3OH	1.92e-13	1.10e-12	1.03		ACET + HO. = HCHO + CCO-O2. + R2O2.
K3HV		Phot Set= ACETONE			ACET + HV = CCO-O2. + C-O2.
K4OH	1.18e-12	1.30e-12	0.05	2.0	MEK + HO. = #.37 RO2-R. + #.042 RO2-N. + #.616 R2O2. + #.492 CCO-O2. + #.096 RCO-O2. + #.115 HCHO + #.482 CCHO + #.37 RCHO + #.287 XC
K4HV		Phot Set= KETONE, qy= 1.5e-1			MEK + HV = CCO-O2. + CCHO + RO2-R.
MeOH	9.14e-13	3.10e-12	0.72	2.0	MEOH + HO. = HCHO + HO2.
MER9	5.49e-12	2.90e-12	-0.38		COOH + HO. = H2O + #.35 {HCHO + HO.} + #.65 C-O2.
MERA		Phot Set= COOH			COOH + HV = HCHO + HO2. + HO.
LPR9	1.10e-11	1.10e-11			ROOH + HO. = H2O + RCHO + #.34 RO2-R. + #.66 HO.
LPRA		Phot Set= COOH			ROOH + HV = RCHO + HO2. + HO.
GLHV		Phot Set= GLY_R			GLY + HV = #2 {CO + HO2.}
GLVM		Phot Set= GLY_ABS, qy= 6.0e-3			GLY + HV = HCHO + CO
GLOH	1.10e-11	1.10e-11			GLY + HO. = #.63 HO2. + #1.26 CO + #.37 RCO-O2. + #-0.37 XC
GLN3	9.63e-16	2.80e-12	4.72		GLY + NO3 = HNO3 + #.63 HO2. + #1.26 CO + #.37 RCO-O2. + #-.37 XC
MGHV		Phot Set= MGLY_ADJ			MGLY + HV = HO2. + CO + CCO-O2.
MGOH	1.50e-11	1.50e-11			MGLY + HO. = CO + CCO-O2.
MGN3	2.43e-15	1.40e-12	3.77		MGLY + NO3 = HNO3 + CO + CCO-O2.
BAHV		Phot Set= BACL_ADJ			BACL + HV = #2 CCO-O2.
PHOH	2.63e-11	2.63e-11			PHEN + HO. = #.24 BZ-O. + #.76 RO2-R. + #.23 GLY + #4.1 XC
PHN3	3.78e-12	3.78e-12			PHEN + NO3 = HNO3 + BZ-O.
CROH	4.20e-11	4.20e-11			CRES + HO. = #.24 BZ-O. + #.76 RO2-R. + #.23 MGLY + #4.87 XC
CRN3	1.37e-11	1.37e-11			CRES + NO3 = HNO3 + BZ-O. + XC
NPN3		Same k as rxn PHN3			NPHE + NO3 = HNO3 + BZ(NO2)-O.
BZOH	1.29e-11	1.29e-11			BALD + HO. = BZCO-O2.
BZHV		Phot Set= BZCHO, qy= 5.0e-2			BALD + HV = #7 XC
BZNT	2.62e-15	1.40e-12	3.72		BALD + NO3 = HNO3 + BZCO-O2.

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
MAOH	3.36e-11	1.86e-11	-0.35		MACR + HO. = #.5 RO2-R. + #.416 CO + #.084 HCHO + #.416 MEK + #.084 MGLY + #.5 MA-RCO3. + #-0.416 XC
MAO3	1.13e-18	1.36e-15	4.20		MACR + O3 = #.008 HO2. + #.1 RO2-R. + #.208 HO. + #.1 RCO-O2. + #.45 CO + #.117 CO2 + #.2 HCHO + #.9 MGLY + #.333 HCOOH + #-0.1 XC
MAN3	4.58e-15	1.50e-12	3.43		MACR + NO3 = #.5 {HNO3 + RO2-R. + CO + MA-RCO3.} + #1.5 XC + #.5 XN
MAOP	6.34e-12	6.34e-12			MACR + O3P = RCHO + XC
MAHV	Phot Set= ACROLEIN,	qy= 4.1e-3			MACR + HV = #.34 HO2. + #.33 RO2-R. + #.33 HO. + #.67 CCO-O2. + #.67 CO + #.67 HCHO + #.33 MA-RCO3. + #-0 XC
MVOH	1.89e-11	4.14e-12	-0.90		MVK + HO. = #.3 RO2-R. + #.025 RO2-N. + #.675 R2O2. + #.675 CCO-O2. + #.3 HCHO + #.675 RCHO + #.3 MGLY + #-0.725 XC
MVO3	4.58e-18	7.51e-16	3.02		MVK + O3 = #.064 HO2. + #.05 RO2-R. + #.164 HO. + #.05 RCO-O2. + #.475 CO + #.124 CO2 + #.1 HCHO + #.95 MGLY + #.351 HCOOH + #-0.05 XC
MVN3		(Slow)			MVK + NO3 = #4 XC + XN
MVOP	4.32e-12	4.32e-12			MVK + O3P = #.45 RCHO + #.55 MEK + #.45 XC
MVHV	Phot Set= ACROLEIN,	qy= 2.1e-3			MVK + HV = #.3 C-O2. + #.7 CO + #.7 PRDX + #.3 MA-RCO3. + #-2.4 XC
IPOH	6.19e-11	6.19e-11			IPRD + HO. = #.67 RO2-R. + #.041 RO2-N. + #.289 MA-RCO3. + #.336 CO + #.055 HCHO + #.129 CCHO + #.013 RCHO + #.15 MEK + #.332 PRDX + #.15 GLY + #.174 MGLY + #-0.504 XC
IPO3	4.18e-18	4.18e-18			IPRD + O3 = #.4 HO2. + #.048 RO2-R. + #.048 RCO-O2. + #.285 HO. + #.498 CO + #.14 CO2 + #.125 HCHO + #.047 CCHO + #.21 MEK + #.023 GLY + #.742 MGLY + #.1 HCOOH + #.372 RCO-OH + #-0.33 XC
IPN3	1.00e-13	1.00e-13			IPRD + NO3 = #.799 RO2-R. + #.051 RO2-N. + #.15 MA-RCO3. + #.572 CO + #.15 HNO3 + #.227 HCHO + #.218 RCHO + #.008 MGLY + #.572 RNO3 + #.28 XN + #-0.815 XC
IPHV	Phot Set= ACROLEIN,	qy= 4.1e-3			IPRD + HV = #1.233 HO2. + #.467 CCO-O2. + #.3 RCO-O2. + #1.233 CO + #.3 HCHO + #.467 CCHO + #.233 MEK + #-0.233 XC
K6OH	1.50e-11	1.50e-11			PRDX + HO. = #.379 HO2. + #.473 RO2-R. + #.07 RO2-N. + #.029 CCO-O2. + #.049 RCO-O2. + #.213 HCHO + #.084 CCHO + #.558 RCHO + #.115 MEK + #.329 PRDX + #.886 XC
K6HV	Phot Set= KETONE,	qy= 2.0e-2			PRDX + HV = #.96 RO2-R. + #.04 RO2-N. + #.515 R2O2. + #.667 CCO-O2. + #.333 RCO-O2. + #.506 HCHO + #.246 CCHO + #.71 RCHO + #.299 XC
RNOH	7.80e-12	7.80e-12			RNO3 + HO. = #.338 NO2 + #.113 HO2. + #.376 RO2-R. + #.173 RO2-N. + #.596 R2O2. + #.01 HCHO + #.439 CCHO + #.213 RCHO + #.006 ACET + #.177 MEK + #.048 PRDX + #.31 RNO3 + #.351 XN + #.56 XC
RNHV	Phot Set= IC3ONO2				RNO3 + HV = NO2 + #.341 HO2. + #.564 RO2-R. + #.095 RO2-N. + #.152 R2O2. + #.134 HCHO + #.431 CCHO + #.147 RCHO + #.02 ACET + #.243 MEK + #.435 PRDX + #.35 XC

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
D1OH	5.00e-11	5.00e-11			DCB1 + HO. = RCHO + RO2-R. + CO
D1HV		(Slow)			DCB1 + HV = HO2. + #2 CO + RO2-R. + GLY + R2O2.
D1O3	2.00e-18	2.00e-18			DCB1 + O3 = #1.5 HO2. + #.5 HO. + #1.5 CO + #.5 CO2 + GLY
D2OH	5.00e-11	5.00e-11			DCB2 + HO. = R2O2. + RCHO + CCO-O2.
D2HV	Phot Set= MGLY_ABS,	qy= 3.7e-1			DCB2 + HV = RO2-R. + #.5 {CCO-O2. + HO2.} + CO + R2O2. + #.5 {GLY + MGLY + XC}
D3OH	5.00e-11	5.00e-11			DCB3 + HO. = R2O2. + RCHO + CCO-O2.
D3HV	Phot Set= ACROLEIN,	qy= 7.3e+0			DCB3 + HV = RO2-R. + #.5 {CCO-O2. + HO2.} + CO + R2O2. + #.5 {GLY + MGLY + XC}
<u>Base Case Product Species Added for Aldehyde Potential Study</u>					
ACOH	1.99e-11	1.99e-11	0.00		ACRO + HO. = #.25 RO2-R. + #.75 MA-RCO3. + #.167 CO + #.083 HCHO + #.167 CCHO + #.083 GLY + #-0.75 XC
ACO3	2.90e-19	1.36e-15	5.01		ACRO + O3 = #.31 HO. + #.81 HO2. + CO + #.315 CO2 + #.5 HCHO + #.5 GLY + #.185 HCOOH
ACN3	2.94e-15	2.94e-15	0.00		ACRO + NO3 = #.031 RO2-R. + #.002 RO2-N. + #.967 MA-RCO3. + #.031 CO + #.031 RCHO + #-1.003 XC + XN
ACOP	2.37e-12	2.37e-12			ACRO + O3P = RCHO
ACHV	Phot Set= ACROLEIN,	qy= 2.0e-3			ACRO + HV = #.172 HO. + #1.01 HO2. + #.172 C-O2. + #.33 MA-RCO3. + #1.182 CO + #.046 CO2 + #.34 HCHO + #.112 CCO-OH + #-0.284 XC
<u>Explicitly Represented Primary Organics</u>					
c1OH	6.37e-15	2.15e-12	3.45		CH4 + HO. = H2O + C-O2.
etOH	8.52e-12	1.96e-12	-0.87		ETHENE + HO. = RO2-R. + #1.61 HCHO + #.195 CCHO
etO3	1.59e-18	9.14e-15	5.13		ETHENE + O3 = #.12 HO. + #.12 HO2. + #.5 CO + #.13 CO2 + HCHO + #.37 HCOOH
etN3	2.05e-16	4.39e-13	4.53	2.0	ETHENE + NO3 = RO2-R. + RCHO + #-1 XC + XN
etOA	7.29e-13	1.04e-11	1.57		ETHENE + O3P = #.5 HO2. + #.2 RO2-R. + #.3 C-O2. + #.491 CO + #.191 HCHO + #.25 CCHO + #.009 GLY + #.5 XC
isOH	9.82e-11	2.50e-11	-0.81		ISOPRENE + HO. = #.907 RO2-R. + #.093 RO2-N. + #.079 R2O2. + #.624 HCHO + #.23 MACR + #.32 MVK + #.357 IPRD + #-0.167 XC
isO3	1.28e-17	7.86e-15	3.80		ISOPRENE + O3 = #.266 HO. + #.066 RO2-R. + #.008 RO2-N. + #.126 R2O2. + #.192 MA-RCO3. + #.275 CO + #.122 CO2 + #.592 HCHO + #.1 PRDX + #.39 MACR + #.16 MVK + #.204 HCOOH + #.15 RCO-OH + #-0.259 XC
isN3	6.74e-13	3.03e-12	0.89		ISOPRENE + NO3 = #.187 NO2 + #.749 RO2-R. + #.064 RO2-N. + #.187 R2O2. + #.936 IPRD + #-0.064 XC + #.813 XN
isOP	3.60e-11	3.60e-11			ISOPRENE + O3P = #.01 RO2-N. + #.24 R2O2. + #.25 C-O2. + #.24 MA-RCO3. + #.24 HCHO + #.75 PRDX + #-1.01 XC

Lumped Terpenes (Based on estimated North America annual emissions rate of top 5 terpenes.)

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
t1OH	8.27e-11	1.83e-11	-0.89		TERP + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.276 HCHO + #.474 RCHO + #.276 PRDX + #5.146 XC
t1O3	6.88e-17	1.08e-15	1.63		TERP + O3 = #.567 HO. + #.033 HO2. + #.031 RO2-R. + #.18 RO2-N. + #.729 R2O2. + #.123 CCO-O2. + #.201 RCO-O2. + #.157 CO + #.037 CO2 + #.235 HCHO + #.205 RCHO + #.13 ACET + #.276 PRDX + #.001 GLY + #.031 BACL + #.103 HCOOH + #.189 RCO-OH + #4.183 XC
t1N3	6.57e-12	3.66e-12	-0.35		TERP + NO3 = #.474 NO2 + #.276 RO2-R. + #.25 RO2-N. + #.75 R2O2. + #.474 RCHO + #.276 RNO3 + #5.421 XC + #.25 XN
t1OP	3.27e-11	3.27e-11			TERP + O3P = #.147 RCHO + #.853 PRDX + #4.441 XC
<u>Lumped Primary Organics (Based on base SCOS-97 BASE ROG mixture used in reactivity scenarios)</u>					
a1OH	2.54e-13	9.98e-12	2.17		ALK1 + HO. = RO2-R. + #.008 HCHO + #.983 CCHO + #.008 RCHO
a2OH	9.14e-13	9.35e-12	1.38		ALK2 + HO. = #.563 HO. + #.277 HO2. + #.155 RO2-R. + #.002 RO2-N. + #.002 R2O2. + #.002 CCO-O2. + #.367 CO + #.09 HCHO + #.017 RCHO + #.044 ACET + #.567 GLY + #.277 HCOOH + #.002 CCO-OH + #.93 XC
a3OH	2.80e-12	2.94e-12	0.03		ALK3 + HO. = #.273 HO2. + #.542 RO2-R. + #.05 RO2-N. + #.343 R2O2. + #.029 C-O2. + #.007 RCO-O2. + #.099 TBU-O. + #.091 HCHO + #.512 CCHO + #.073 RCHO + #.016 ACET + #.303 MEK + #.001 PRDX + #.007 CCO-OH + #.037 NROG + #.6 XC
a4OH	4.67e-12	4.83e-12	0.02		ALK4 + HO. = #.062 HO. + #.09 HO2. + #.655 RO2-R. + #.124 RO2-N. + #.807 R2O2. + #.008 C-O2. + #.043 CCO-O2. + #.003 RCO-O2. + #.015 TBU-O. + #.003 CO + #.048 HCHO + #.299 CCHO + #.211 RCHO + #.482 ACET + #.06 MEK + #.109 PRDX + #.062 MGLY + #.031 HCOOH + #.003 CCO-OH + #.001 NROG + #.245 XC
a5OH	1.26e-11	1.23e-11	-0.01		ALK5 + HO. = #.07 HO2. + #.632 RO2-R. + #.295 RO2-N. + #.834 R2O2. + #.001 C-O2. + #.001 CCO-O2. + #.066 HCHO + #.107 CCHO + #.261 RCHO + #.066 ACET + #.109 MEK + #.329 PRDX + #.001 CCO-OH + #.003 NROG + #1.548 XC
b1OH	5.91e-12	5.91e-12	0.00		ARO1 + HO. = #.229 HO2. + #.761 RO2-R. + #.009 RO2-N. + #.027 PRDX + #.118 GLY + #.125 MGLY + #.012 PHEN + #.217 CRES + #.071 BALD + #.479 DCB1 + #.131 DCB2 + #.053 DCB3 + #1.25 XC
b2OH	2.43e-11	2.37e-11	-0.02		ARO2 + HO. = #.201 HO2. + #.777 RO2-R. + #.012 RO2-N. + #.01 RCO-O2. + #.095 GLY + #.296 MGLY + #.056 BACL + #.016 PHEN + #.185 CRES + #.044 BALD + #.481 DCB1 + #.153 DCB2 + #.099 DCB3 + #1.711 XC
o1OH	2.72e-11	5.11e-12	-0.99		OLE1 + HO. = #.978 RO2-R. + #.02 RO2-N. + #.011 R2O2. + #.002 TBU-O. + #.971 HCHO + #.831 CCHO + #.146 RCHO + #.004 ACET + #.002 PRDX + #.002 NROG + #0.225 XC
o1O3	1.01e-17	5.02e-15	3.68		OLE1 + O3 = #.286 HO. + #.06 HO2. + #.008 RO2-R. + #.218 C-O2. + #.476 CO + #.124 CO2 + #.5 HCHO + #.426 CCHO + #.08 RCHO + #.001 ACET + #.002 PRDX + #.185 HCOOH + #.143 CCO-OH + #.069 RCO-OH + #.06 NROG + #0.165 XC

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
o1N3	1.02e-14	3.55e-13	2.10		OLE1 + NO3 = #.936 RO2-R. + #.059 RO2-N. + #.043 R2O2. + #.002 RCO-O2. + #.003 TBU-O. + #.009 CCHO + #.031 RCHO + #.018 ACET + #.113 RNO3 + #.002 CCO-OH + #1.78 XC + #.887 XN
o1OP	4.02e-12	1.18e-11	0.64		OLE1 + O3P = #.45 RCHO + #.549 MEK + #-0.551 XC
o2OH	6.23e-11	1.15e-11	-1.00		OLE2 + HO. = #.941 RO2-R. + #.059 RO2-N. + #.32 HCHO + #.79 CCHO + #.148 RCHO + #.313 ACET + #.012 MEK + #.015 BALD + #.091 ACRO + #.091 IPRD + #.482 XC
o2O3	7.59e-17	1.22e-15	1.64		OLE2 + O3 = #.335 HO. + #.037 HO2. + #.009 RO2-R. + #.116 R2O2. + #.167 C-O2. + #.12 CCO-O2. + #.002 RCO-O2. + #.337 CO + #.111 CO2 + #.392 HCHO + #.342 CCHO + #.225 RCHO + #.059 ACET + #.004 MEK + #.025 PRDX + #.011 BALD + #.095 ACRO + #.071 MVK + #.131 HCOOH + #.109 CCO-OH + #.109 RCO-OH + #.045 NROG + #.676 XC
o2N3	5.18e-13	5.06e-13	-0.01		OLE2 + NO3 = #.348 NO2 + #.532 RO2-R. + #.078 RO2-N. + #.43 R2O2. + #.042 C-O2. + #.091 HCHO + #.468 CCHO + #.267 RCHO + #.357 ACET + #.001 MGLY + #.004 BALD + #.175 MVK + #.101 RNO3 + #.254 XC + #.551 XN
o2OP	2.04e-11	2.04e-11			OLE2 + O3P = #.048 HO2. + #.044 RO2-R. + #.004 RO2-N. + #.044 CO + #.175 RCHO + #.595 MEK + #.182 PRDX + #.044 ACRO + #.803 XC

Duplicate Reactions of Product Species: Product Species Formed from Test VOCs

dup1	7.29e-12	2.80e-12	-0.57		pC-O2. + NO = NO2 + pHCHO + HO2.
dup2	5.21e-12	3.80e-13	-1.55		pC-O2. + HO2. = pCOOH + O2
dup3	1.30e-12	1.30e-12			pC-O2. + NO3 = pHCHO + HO2. + NO2
dup4	2.65e-13	2.45e-14	-1.41		pC-O2. + pC-O2. = pMEOH + pHCHO + O2
dup5	1.07e-13	5.90e-13	1.01		pC-O2. + pC-O2. = #2 {pHCHO + HO2.}
dup6		Same k as rxn RRNO			pRO2-N. + NO = pRNO3
dup7		Same k as rxn RRH2			pRO2-N. + HO2. = pROOH + #3 XC
dup8		Same k as rxn RRME			pRO2-N. + pC-O2. = HO2. + #.25 pMEOH + #.5 {pMEK + pPRDX} + #.75 pHCHO + XC
dup9		Same k as rxn RRN3			pRO2-N. + NO3 = NO2 + O2 + HO2. + pMEK + #2 XC
dp10		Same k as rxn RRR2			pRO2-N. + RO2-R. = HO2. + #.5 {pMEK + pPRDX} + O2 + XC
dp11		Same k as rxn RRR2			pRO2-N. + R2O2. = pRO2-N.
dp12		Same k as rxn RRR2			pRO2-N. + pRO2-N. = pMEK + HO2. + pPRDX + O2 + #2 XC
dp13	1.05e-11	Falloff, F=0.30			pCCO-O2. + NO2 = pPAN
		0:	2.70e-28	0.00	-7.1
		inf:	1.20e-11	0.00	-0.9
dp14	5.21e-4	Falloff, F=0.30			pPAN = pCCO-O2. + NO2
		0:	4.90e-3	24.05	0.0
		inf:	4.00e+16	27.03	0.0
dp15	2.13e-11	7.80e-12	-0.60		pCCO-O2. + NO = pC-O2. + CO2 + NO2
dp16	1.41e-11	4.30e-13	-2.07		pCCO-O2. + HO2. = #.75 {CCO-OOH + O2} + #.25 {CCO-OH + O3}
dp17	4.00e-12	4.00e-12			pCCO-O2. + NO3 = pC-O2. + CO2 + NO2 + O2

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
dp18	9.64e-12	1.80e-12	-0.99		pCCO-O2. + pC-O2. = CCO-OH + pHCHO + O2
dp19	7.50e-12	7.50e-12			pCCO-O2. + RO2-R. = CCO-OH
dp20	Same k as rxn APRR				pCCO-O2. + R2O2. = pCCO-O2.
dp21	Same k as rxn APRR				pCCO-O2. + pRO2-N. = CCO-OH + pPRDX
dp22	1.55e-11	2.90e-12	-0.99		pCCO-O2. + pCCO-O2. = #2 {pC-O2. + CO2} + O2
dp23	1.21e-11	1.20e-11	0.00	-0.9	pRCO-O2. + NO2 = pPAN2
dp24	4.43e-4	2.00e+15	25.44		pPAN2 = pRCO-O2. + NO2
dp25	2.80e-11	1.25e-11	-0.48		pRCO-O2. + NO = NO2 + pCCHO + RO2-R. + CO2
dp26	Same k as rxn APH2				pRCO-O2. + HO2. = #.75 {RCO-OOH + O2} + #.25 {RCO-OH + O3}
dp27	Same k as rxn APN3				pRCO-O2. + NO3 = NO2 + pCCHO + RO2-R. + CO2 + O2
dp28	Same k as rxn APME				pRCO-O2. + pC-O2. = RCO-OH + pHCHO + O2
dp29	Same k as rxn APRR				pRCO-O2. + RO2-R. = RCO-OH + O2
dp30	Same k as rxn APRR				pRCO-O2. + R2O2. = pRCO-O2.
dp31	Same k as rxn APRR				pRCO-O2. + pRO2-N. = RCO-OH + pPRDX + O2
dp32	Same k as rxn APAP				pRCO-O2. + pCCO-O2. = #2 CO2 + pC-O2. + pCCHO + RO2-R. + O2
dp33	Same k as rxn APAP				pRCO-O2. + pRCO-O2. = #2 {pCCHO + RO2-R. + CO2}
dp34	1.37e-11	1.37e-11			pBZCO-O2. + NO2 = pPBZN
dp35	3.12e-4	7.90e+16	27.82		pPBZN = pBZCO-O2. + NO2
dp36	Same k as rxn PPNO				pBZCO-O2. + NO = NO2 + CO2 + pBZ-O. + R2O2.
dp37	Same k as rxn APH2				pBZCO-O2. + HO2. = #.75 {RCO-OOH + O2} + #.25 {RCO-OH + O3} + #4 XC
dp38	Same k as rxn APN3				pBZCO-O2. + NO3 = NO2 + CO2 + pBZ-O. + R2O2. + O2
dp39	Same k as rxn APME				pBZCO-O2. + pC-O2. = RCO-OH + pHCHO + O2 + #4 XC
dp40	Same k as rxn APRR				pBZCO-O2. + RO2-R. = RCO-OH + O2 + #4 XC
dp41	Same k as rxn APRR				pBZCO-O2. + R2O2. = pBZCO-O2.
dp42	Same k as rxn APRR				pBZCO-O2. + pRO2-N. = RCO-OH + pPRDX + O2 + #4 XC
dp43	Same k as rxn APAP				pBZCO-O2. + pCCO-O2. = #2 CO2 + pC-O2. + pBZ-O. + R2O2.
dp44	Same k as rxn APAP				pBZCO-O2. + pRCO-O2. = #2 CO2 + pCCHO + RO2-R. + pBZ-O. + R2O2.
dp45	Same k as rxn APAP				pBZCO-O2. + pBZCO-O2. = #2 {pBZ-O. + R2O2. + CO2}
dp46	Same k as rxn PPN2				pMA-RCO3. + NO2 = pMPAN
dp47	3.55e-4	1.60e+16	26.80		pMPAN = pMA-RCO3. + NO2
dp48	Same k as rxn PPNO				pMA-RCO3. + NO = NO2 + CO2 + pHCHO + pCCO-O2.
dp49	Same k as rxn APH2				pMA-RCO3. + HO2. = #.75 {RCO-OOH + O2} + #.25 {RCO-OH + O3} + XC
dp50	Same k as rxn APN3				pMA-RCO3. + NO3 = NO2 + CO2 + pHCHO + pCCO-O2. + O2
dp51	Same k as rxn APME				pMA-RCO3. + pC-O2. = RCO-OH + pHCHO + XC + O2
dp52	Same k as rxn APRR				pMA-RCO3. + RO2-R. = RCO-OH + XC
dp53	Same k as rxn APRR				pMA-RCO3. + R2O2. = pMA-RCO3.
dp54	Same k as rxn APRR				pMA-RCO3. + pRO2-N. = #2 RCO-OH + O2 + #4 XC
dp55	Same k as rxn APAP				pMA-RCO3. + pCCO-O2. = #2 CO2 + pC-O2. + pHCHO + pCCO-O2. + O2

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
dp56		Same k as rxn APAP			pMA-RCO3. + pRCO-O2. = pHCHO + pCCO-O2. + pCCHO + RO2-R. + #2 CO2
dp57		Same k as rxn APAP			pMA-RCO3. + pBZCO-O2. = pHCHO + pCCO-O2. + pBZ-O. + R2O2. + #2 CO2
dp58		Same k as rxn APAP			pMA-RCO3. + pMA-RCO3. = #2 {pHCHO + pCCO-O2. + CO2}
dp59	2.40e-11	2.40e-11			pTBU-O. + NO2 = pRNO3 + #-2 XC
dp60	9.87e+2	7.50e+14	16.20		pTBU-O. = pACET + pC-O2.
dp61	3.80e-11	2.30e-11	-0.30		pBZ-O. + NO2 = pNPHE
dp62		Same k as rxn RRH2			pBZ-O. + HO2. = pPHEN
dp63	1.00e-3	1.00e-3			pBZ-O. = pPHEN
dp64		Same k as rxn BRN2			pBZ(NO2)-O. + NO2 = #2 XN + #6 XC
dp65		Same k as rxn RRH2			pBZ(NO2)-O. + HO2. = pNPHE
dp66		Same k as rxn BRXX			pBZ(NO2)-O. = pNPHE
dp67		Phot Set= HCHO_R			pHCHO + HV = #2 HO2. + CO
dp68		Phot Set= HCHO_M			pHCHO + HV = H2 + CO
dp69	9.20e-12	8.60e-12	-0.04		pHCHO + HO. = HO2. + CO + H2O
dp70	7.90e-14	9.70e-15	-1.24		pHCHO + HO2. = pHOCOO.
dp71	1.51e+2	2.40e+12	13.91		pHOCOO. = HO2. + pHCHO
dp72		Same k as rxn MER1			pHOCOO. + NO = HCOOH + NO2 + HO2.
dp73	5.74e-16	2.00e-12	4.83		pHCHO + NO3 = HNO3 + HO2. + CO
dp74	1.58e-11	5.60e-12	-0.62		pCCHO + HO. = pCCO-O2. + H2O
dp75		Phot Set= CCHO_R			pCCHO + HV = CO + HO2. + pC-O2.
dp76	2.73e-15	1.40e-12	3.70		pCCHO + NO3 = HNO3 + pCCO-O2.
dp77	2.00e-11	2.00e-11			pRCHO + HO. = #.034 RO2-R. + #.001 pRO2-N. + #.965 pRCO-O2. + #.034 CO + #.034 pCCHO + #-0.003 XC
dp78		Phot Set= C2CHO			pRCHO + HV = pCCHO + RO2-R. + CO + HO2.
dp79	3.67e-15	1.40e-12	3.52		pRCHO + NO3 = HNO3 + pRCO-O2.
dp80	1.92e-13	1.10e-12	1.03		pACET + HO. = pHCHO + pCCO-O2. + R2O2.
dp81		Phot Set= ACETONE			pACET + HV = pCCO-O2. + pC-O2.
dp82	1.18e-12	1.30e-12	0.05	2.0	pMEK + HO. = #.37 RO2-R. + #.042 pRO2-N. + #.616 R2O2. + #.492 pCCO-O2. + #.096 pRCO-O2. + #.115 pHCHO + #.482 pCCHO + #.37 pRCHO + #.287 XC
dp83		Phot Set= KETONE, qy= 1.5e-1			pMEK + HV = pCCO-O2. + pCCHO + RO2-R.
dp84	9.14e-13	3.10e-12	0.72	2.0	pMEOH + HO. = pHCHO + HO2.
dp85	5.49e-12	2.90e-12	-0.38		pCOOH + HO. = H2O + #.35 {pHCHO + HO.} + #.65 pC-O2.
dp86		Phot Set= COOH			pCOOH + HV = pHCHO + HO2. + HO.
dp87	1.10e-11	1.10e-11			pROOH + HO. = H2O + pRCHO + #.34 RO2-R. + #.66 HO.

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
dp88		Phot Set= COOH			pROOH + HV = pRCHO + HO2. + HO.
dp89		Phot Set= GLY_R			pGLY + HV = #2 {CO + HO2.}
dp90		Phot Set= GLY_ABS, qy= 6.0e-3			pGLY + HV = pHCHO + CO
dp91	1.10e-11	1.10e-11			pGLY + HO. = #.63 HO2. + #1.26 CO + #.37 pRCO-O2. + #-0.37 XC
dp92	9.63e-16	2.80e-12	4.72		pGLY + NO3 = HNO3 + #.63 HO2. + #1.26 CO + #.37 pRCO-O2. + #-0.37 XC
dp93		Phot Set= MGLY_ADJ			pMGLY + HV = HO2. + CO + pCCO-O2.
dp94	1.50e-11	1.50e-11			pMGLY + HO. = CO + pCCO-O2.
dp95	2.43e-15	1.40e-12	3.77		pMGLY + NO3 = HNO3 + CO + pCCO-O2.
dp96		Phot Set= BACL_ADJ			pBACL + HV = #2 pCCO-O2.
dp97	2.63e-11	2.63e-11			pPHEN + HO. = #.24 pBZ-O. + #.76 RO2-R. + #.23 pGLY + #4.1 XC
dp98	3.78e-12	3.78e-12			pPHEN + NO3 = HNO3 + pBZ-O.
dp99	4.20e-11	4.20e-11			pCRES + HO. = #.24 pBZ-O. + #.76 RO2-R. + #.23 pMGLY + #4.87 XC
d100	1.37e-11	1.37e-11			pCRES + NO3 = HNO3 + pBZ-O. + XC
d101		Same k as rxn PHN3			pNPHE + NO3 = HNO3 + pBZ(NO2)-O.
d102	1.29e-11	1.29e-11			pBALD + HO. = pBZCO-O2.
d103		Phot Set= BZCHO, qy= 5.0e-2			pBALD + HV = #7 XC
d104	2.62e-15	1.40e-12	3.72		pBALD + NO3 = HNO3 + pBZCO-O2.
d105	3.36e-11	1.86e-11	-0.35		pMACR + HO. = #.5 RO2-R. + #.416 CO + #.084 pHCHO + #.416 pMEK + #.084 pMGLY + #.5 pMA-RCO3. + #-0.416 XC
d106	1.13e-18	1.36e-15	4.20		pMACR + O3 = #.008 HO2. + #.1 RO2-R. + #.208 HO. + #.1 pRCO-O2. + #.45 CO + #.117 CO2 + #.2 pHCHO + #.9 pMGLY + #.333 HCOOH + #-0.1 XC
d107	4.58e-15	1.50e-12	3.43		pMACR + NO3 = #.5 {HNO3 + RO2-R. + CO + MA-RCO3.} + #1.5 XC + #.5 XN
d108	6.34e-12	6.34e-12			pMACR + O3P = pRCHO + XC
d109		Phot Set= ACROLEIN, qy= 4.1e-3			pMACR + HV = #.34 HO2. + #.33 RO2-R. + #.33 HO. + #.67 pCCO-O2. + #.67 CO + #.67 pHCHO + #.33 pMA-RCO3. + #-0 XC
d110	1.89e-11	4.14e-12	-0.90		pMVK + HO. = #.3 RO2-R. + #.025 pRO2-N. + #.675 R2O2. + #.675 pCCO-O2. + #.3 pHCHO + #.675 pRCHO + #.3 pMGLY + #-0.725 XC
d111	4.58e-18	7.51e-16	3.02		pMVK + O3 = #.064 HO2. + #.05 RO2-R. + #.164 HO. + #.05 pRCO-O2. + #.475 CO + #.124 CO2 + #.1 pHCHO + #.95 pMGLY + #.351 HCOOH + #-0.05 XC
d112		(Slow)			pMVK + NO3 = #4 XC + XN
d113	4.32e-12	4.32e-12			pMVK + O3P = #.45 pRCHO + #.55 pMEK + #.45 XC

Table A-2 (continued)

Label	Rate Parameters [a]			Reaction and Products [b]
	k(298)	A	Ea B	
d114	Phot Set= ACROLEIN, qy= 2.1e-3			pMVK + HV = #.3 pC-O2. + #.7 CO + #.7 pPRDX + #.3 pMA-RCO3. + #-2.4 XC
d115	6.19e-11	6.19e-11		pIPRD + HO. = #.67 RO2-R. + #.041 pRO2-N. + #.289 pMA-RCO3. + #.336 CO + #.055 pHCHO + #.129 pCCHO + #.013 pRCHO + #.15 pMEK + #.332 pPRDX + #.15 pGLY + #.174 pMGLY + #-0.504 XC
d116	4.18e-18	4.18e-18		pIPRD + O3 = #.4 HO2. + #.048 RO2-R. + #.048 pRCO-O2. + #.285 HO. + #.498 CO + #.14 CO2 + #.125 pHCHO + #.047 pCCHO + #.21 pMEK + #.023 pGLY + #.742 pMGLY + #.1 HCOOH + #.372 RCO-OH + #-0.33 XC
d117	1.00e-13	1.00e-13		pIPRD + NO3 = #.799 RO2-R. + #.051 pRO2-N. + #.15 pMA-RCO3. + #.572 CO + #.15 HNO3 + #.227 pHCHO + #.218 pRCHO + #.008 pMGLY + #.572 pRNO3 + #.28 XN + #-0.815 XC
d118	Phot Set= ACROLEIN, qy= 4.1e-3			pIPRD + HV = #1.233 HO2. + #.467 pCCO-O2. + #.3 pRCO-O2. + #1.233 CO + #.3 pHCHO + #.467 pCCHO + #.233 pMEK + #-0.233 XC
d119	1.50e-11	1.50e-11		pPRDX + HO. = #.379 HO2. + #.473 RO2-R. + #.07 pRO2-N. + #.029 pCCO-O2. + #.049 pRCO-O2. + #.213 pHCHO + #.084 pCCHO + #.558 pRCHO + #.115 pMEK + #.329 pPRDX + #.886 XC
d120	Phot Set= KETONE, qy= 2.0e-2			pPRDX + HV = #.96 RO2-R. + #.04 pRO2-N. + #.515 R2O2. + #.667 pCCO-O2. + #.333 pRCO-O2. + #.506 pHCHO + #.246 pCCHO + #.71 pRCHO + #.299 XC
d121	7.80e-12	7.80e-12		pRNO3 + HO. = #.338 NO2 + #.113 HO2. + #.376 RO2-R. + #.173 pRO2-N. + #.596 R2O2. + #.01 pHCHO + #.439 pCCHO + #.213 pRCHO + #.006 pACET + #.177 pMEK + #.048 pPRDX + #.31 pRNO3 + #.351 XN + #.56 XC
d122	Phot Set= IC3ONNO2			pRNO3 + HV = NO2 + #.341 HO2. + #.564 RO2-R. + #.095 pRO2-N. + #.152 R2O2. + #.134 pHCHO + #.431 pCCHO + #.147 pRCHO + #.02 pACET + #.243 pMEK + #.435 pPRDX + #.35 XC
d123	5.00e-11	5.00e-11		pDCB1 + HO. = pRCHO + RO2-R. + CO
d124		(Slow)		pDCB1 + HV = HO2. + #2 CO + RO2-R. + pGLY + R2O2.
d125	2.00e-18	2.00e-18		pDCB1 + O3 = #1.5 HO2. + #.5 HO. + #1.5 CO + #.5 CO2 + pGLY
d126	5.00e-11	5.00e-11		pDCB2 + HO. = R2O2. + pRCHO + pCCO-O2.
d127	Phot Set= MGLY_ABS, qy= 3.7e-1			pDCB2 + HV = RO2-R. + #.5 {pCCO-O2. + HO2.} + CO + R2O2. + #.5 {pGLY + pMGLY + XC}
d128	5.00e-11	5.00e-11		pDCB3 + HO. = R2O2. + pRCHO + pCCO-O2.
d129	Phot Set= ACROLEIN, qy= 7.3e+0			pDCB3 + HV = RO2-R. + #.5 {pCCO-O2. + HO2.} + CO + R2O2. + #.5 {pGLY + pMGLY + XC}
d130	1.99e-11	1.99e-11	0.00	pACRO + HO. = #.25 RO2-R. + #.75 pMA-RCO3. + #.167 CO + #.083 pHCHO + #.167 pCCHO + #.083 pGLY + #-0.75 XC

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
d131	2.90e-19	1.36e-15	5.01		pACRO + O3 = #.31 HO. + #.81 HO2. + CO + #.315 CO2 + #.5 pHCHO + #.5 pGLY + #.185 HCOOH
d132	2.94e-15	2.94e-15	0.00		pACRO + NO3 = #.031 RO2-R. + #.002 pRO2-N. + #.967 pMA-RCO3. + #.031 CO + #.031 pRCHO + #-1.003 XC + XN
d133	2.37e-12	2.37e-12			pACRO + O3P = pRCHO
d134	Phot Set= ACROLEIN, qy= 2.0e-3				pACRO + HV = #.172 HO. + #.101 HO2. + #.172 pC-O2. + #.33 pMA-RCO3. + #.1.182 CO + #.046 CO2 + #.34 pHCHO + #.112 CCO-OH + #-0.284 XC

Duplicate Reactions of Explicitly Represented Emitted VOCs When Used for Test VOCs

dl35	6.37e-15	2.15e-12	3.45		pCH4 + HO. = H2O + pC-O2.
dl36	8.52e-12	1.96e-12	-0.87		pETHE + HO. = RO2-R. + #1.61 pHCHO + #.195 pCCHO
dl37	1.59e-18	9.14e-15	5.13		pETHE + O3 = #.12 HO. + #.12 HO2. + #.5 CO + #.13 CO2 + pHCHO + #.37 HCOOH
dl38	2.05e-16	4.39e-13	4.53	2.0	pETHE + NO3 = RO2-R. + pRCHO + #-1 XC + XN
dl39	7.29e-13	1.04e-11	1.57		pETHE + O3P = #.5 HO2. + #.2 RO2-R. + #.3 pC-O2. + #.491 CO + #.191 pHCHO + #.25 pCCHO + #.009 pGLY + #.5 XC
dl40	9.82e-11	2.50e-11	-0.81		pISOP + HO. = #.907 RO2-R. + #.093 pRO2-N. + #.079 R2O2. + #.624 pHCHO + #.23 pMACR + #.32 pMVK + #.357 pIPRD + #-0.167 XC
dl41	1.28e-17	7.86e-15	3.80		pISOP + O3 = #.266 HO. + #.066 RO2-R. + #.008 pRO2-N. + #.126 R2O2. + #.192 pMA-RCO3. + #.275 CO + #.122 CO2 + #.592 pHCHO + #.1 pPRDX + #.39 pMACR + #.16 pMVK + #.204 HCOOH + #.15 RCO-OH + #-0.259 XC
dl42	6.74e-13	3.03e-12	0.89		pISOP + NO3 = #.187 NO2 + #.749 RO2-R. + #.064 pRO2-N. + #.187 R2O2. + #.936 pIPRD + #-0.064 XC + #.813 XN
dl43	3.60e-11	3.60e-11			pISOP + O3P = #.01 pRO2-N. + #.24 R2O2. + #.25 pC-O2. + #.24 pMA-RCO3. + #.24 pHCHO + #.75 pPRDX + #-1.01 XC

Cross Reactions of Product and Base Radical Species

xr01	2.65e-13	2.45e-14	-1.41		C-O2. + pC-O2. = #.5 {MEOH + HCHO + pMEOH + pHCHO} + O2
xr02	1.07e-13	5.90e-13	1.01		C-O2. + pC-O2. = HCHO + pHCHO + #2 HO2.
xr03	Same k as rxn RRME				RO2-N. + pC-O2. = HO2. + #.25 pMEOH + #.5 {MEK + PRDX} + #.75 pHCHO + XC
xr04	Same k as rxn RRME				pRO2-N. + C-O2. = HO2. + #.25 MEOH + #.5 {pMEK + pPRDX} + #.75 HCHO + XC
xr05	Same k as rxn RRR2				RO2-N. + pRO2-N. = #.5 {MEK + PRDX + pMEK + pPRDX} + HO2. + O2 + #2 XC
xr06	9.64e-12	1.80e-12	-0.99		CCO-O2. + pC-O2. = CCO-OH + pHCHO + O2
xr07	9.64e-12	1.80e-12	-0.99		pCCO-O2. + C-O2. = CCO-OH + HCHO + O2
xr08	Same k as rxn APRR				CCO-O2. + pRO2-N. = CCO-OH + pPRDX
xr09	Same k as rxn APRR				pCCO-O2. + RO2-N. = CCO-OH + PRDX
xr10	1.55e-11	2.90e-12	-0.99		CCO-O2. + pCCO-O2. = C-O2. + pC-O2. + #2 CO2 + O2
xr11	Same k as rxn APME				RCO-O2. + pC-O2. = RCO-OH + pHCHO + O2
xr12	Same k as rxn APME				pRCO-O2. + C-O2. = RCO-OH + HCHO + O2
xr13	Same k as rxn APRR				RCO-O2. + pRO2-N. = RCO-OH + pPRDX + O2

Table A-2 (continued)

Label	Rate Parameters [a]			B	Reaction and Products [b]
	k(298)	A	Ea		
xr14					pRCO-O2. + RO2-N. = RCO-OH + PRDX + O2
xr15					RCO-O2. + pCCO-O2. = #2 CO2 + pC-O2. + CCHO + RO2-R. + O2
xr16					pRCO-O2. + CCO-O2. = #2 CO2 + C-O2. + pCCHO + RO2-R. + O2
xr17					RCO-O2. + pRCO-O2. = CCHO + pCCHO + #2 {RO2-R. + CO2}
xr18					BZCO-O2. + pC-O2. = RCO-OH + pHCHO + O2 + #4 XC
xr19					pBZCO-O2. + C-O2. = RCO-OH + HCHO + O2 + #4 XC
xr20					BZCO-O2. + pRO2-N. = RCO-OH + pPRDX + O2 + #4 XC
xr21					pBZCO-O2. + RO2-N. = RCO-OH + PRDX + O2 + #4 XC
xr22					BZCO-O2. + pCCO-O2. = #2 CO2 + pC-O2. + BZ-O. + R2O2.
xr23					pBZCO-O2. + CCO-O2. = #2 CO2 + C-O2. + pBZ-O. + R2O2.
xr24					BZCO-O2. + pRCO-O2. = #2 CO2 + pCCHO + RO2-R. + BZ-O. + R2O2.
xr25					pBZCO-O2. + RCO-O2. = #2 CO2 + CCHO + RO2-R. + pBZ-O. + R2O2.
xr26					BZCO-O2. + pBZCO-O2. = BZ-O. + pBZ-O. + #2 {R2O2. + CO2}
xr27					MA-RCO3. + pC-O2. = RCO-OH + pHCHO + XC + O2
xr28					pMA-RCO3. + C-O2. = RCO-OH + HCHO + XC + O2
xr29					MA-RCO3. + pRO2-N. = #2 RCO-OH + O2 + #4 XC
xr30					pMA-RCO3. + RO2-N. = #2 RCO-OH + O2 + #4 XC
xr31					MA-RCO3. + pCCO-O2. = #2 CO2 + pC-O2. + HCHO + CCO-O2. + O2
xr32					pMA-RCO3. + CCO-O2. = #2 CO2 + C-O2. + pHCHO + pCCO-O2. + O2
xr33					MA-RCO3. + pRCO-O2. = HCHO + CCO-O2. + pCCHO + RO2-R. + #2 CO2
xr34					pMA-RCO3. + RCO-O2. = pHCHO + pCCO-O2. + CCHO + RO2-R. + #2 CO2
xr35					MA-RCO3. + pBZCO-O2. = HCHO + CCO-O2. + pBZ-O. + R2O2. + #2 CO2
xr36					pMA-RCO3. + BZCO-O2. = pHCHO + pCCO-O2. + BZ-O. + R2O2. + #2 CO2
xr37					MA-RCO3. + pMA-RCO3. = HCHO + CCO-O2. + pHCHO + pCCO-O2. + #2 CO2

[a] Except as indicated, the rate constants are given by $k(T) = A \cdot (T/300)^B \cdot e^{-E_a/RT}$, where the units of k and A are $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$, E_a are kcal mol^{-1} , T is $^\circ\text{K}$, and $R=0.0019872 \text{ kcal mol}^{-1} \text{ deg}^{-1}$. The following special rate constant expressions are used:

Phot Set = name: The absorption cross sections and quantum yields for the photolysis reaction are given in Table A-5 in Carter (2000a), 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 $k(T,M) = \{k_0(T) \cdot [M] / [1 + k_0(T) \cdot [M] / \text{kinf}(T)]\} \cdot F^Z$, where $Z = \{1 + [\log_{10}\{k_0(T) \cdot [M] / \text{kinf}(T)\}]^2\}^{-1}$, [M] is the total pressure in molecules cm^{-3} , F is as indicated on the table, and the temperature dependences of k_0 and kinf are as indicated on the table.

(Slow): The reaction is assumed to be negligible and is not included in the mechanism. It is shown on the listing for documentation purposes only.

Table A-2 (continued)

$k = k_0 + k_3 M / (1 + k_3 M / k_2)$: The rate constant as a function of temperature and pressure is calculated using $k(T, M) = k_0(T) + k_3(T) \cdot [M] \cdot (1 + k_3(T) \cdot [M] / k_2(T))$, where $[M]$ is the total bath gas (air) concentration in molecules cm^{-3} , and the temperature dependences for k_0 , k_2 and k_3 are as indicated on the table.

$k = k_1 + k_2 [M]$: The rate constant as a function of temperature and pressure is calculated using $k(T, M) = k_1(T) + k_2(T) \cdot [M]$, where $[M]$ is the total bath gas (air) concentration in molecules cm^{-3} , and the temperature dependences for k_1 , and k_2 are as indicated on the table.

Same k as Rxn label: The rate constant is the same as the reaction with the indicated label.

- [b] 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. See Table A-1 for a listing of the model species used.

The data in the following tables are available in an Excel 97 file that is distributed with this report. This file can be downloaded from <ftp://ftp.cert.ucr.edu/pub/carter/misc/oehha/appendx.xls>

Table	Caption
Table A-3.	Listing of reactions used to represent the individual VOC species that were represented using generalized model species with assigned parameters.
Table A-4.	Listing of the absorption cross-sections and quantum yields for the photolysis reactions.
Table A-5.	Compounds in the SCOS-97 emissions inventory used to derive the base ROG mixture used in this study.
Table A-6.	Compositions of emissions profiles used in the CARB database, and assignments of SAPRC-99 model species to these profiles.
Table A-7.	Average and standard deviations of product mass-based formation potentials of all individual VOC classes in the base case scenarios, quantified as effects on average product concentrations.
Table A-8.	Average and standard deviations of product mass-based formation potentials of the CARB emissions profiles in the base case scenarios that had more than 50% of their mass assigned to SAPRC model species, quantified as effects on average product concentrations.