Development and Evaluation of an Updated Detailed Chemical Mechanism for VOC Reactivity Assessment

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ABSTRACT

A detailed mechanism for the gas-phase atmospheric reactions of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in urban and regional atmospheres is summarized. This can be used in airshed models to determine ozone impacts (reactivities) of the many types of VOCs that can be emitted into the atmosphere, and for other control strategy and research applications. This mechanism, designated SAPRC-99, represents a complete update of previous mechanisms developed by the author, and incorporates recent reactivity data from a wide variety of VOCs. The mechanism has assignments for ~400 types of VOCs, and can be used to estimate reactivities for ~550 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 mechanism was evaluated against the results of almost 1700 environmental chamber experiments, including experiments to test ozone reactivity predictions for over 80 types of VOCs. The mechanism was used to update the various ozone reactivity scales developed previously, including the Maximum Incremental Reactivity (MIR) scale. Uncertainties and areas where additional work is needed are briefly summarized.

INTRODUCTION

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

One example of a chemical mechanism for airshed models is the SAPRC-90 chemical mechanism.[1] Unlike most other chemical mechanisms developed at the time, which were designed for efficient representation of complex ambient mixtures, SAPRC-90 was designed to assess differences in atmospheric impacts of individual VOCs, and had separate representations of over 100 types of VOCs. However, although this mechanism represented the state of the art at the time it was developed, since then there has been

continued progress in basic atmospheric chemistry, and new information has become available concerning the reactions and O_3 impacts of many individual VOCs. This mechanism has been updated several times to incorporate some of the new information that has become available.[2-4] However, until this work the reactions and rate constants for most of the inorganic species and common organic products have not been updated, and important new information concerning mechanisms and reactivities of many classes of VOCs were not incorporated.

To address this, a completely updated version of the SAPRC mechanism, designated SAPRC-99, was developed. This updated mechanism is comprehensively documented in a report to the California Air Resources Board[5] (see also http://cert.ucr.edu/~carter/ reactdat.htm), and its major features are summarized in this paper.

THE BASE MECHANISM

The base mechanism is the portion of the mechanism that represents the reactions of the inorganics and the common organic products. SAPRC-99 incorporates the first complete update of the base mechanism since SAPRC-90 was developed. The IUPAC[6,7] and NASA[8] evaluations, the various reviews by Atkinson,[9-12] and other available information were used to update all the applicable rate constants, absorption cross sections, quantum yields, and reaction mechanisms where appropriate. Although many small changes were made, most are not considered to have obviously important impacts on reactivity predictions. The one possible exception is the ~30% reduction in important $OH + NO_2$ rate constant based on the new evaluation by NASA.[8] However, a complete analysis of the effects of all the changes has not been carried out, so the possibility that other changes to the base mechanism may be important cannot be ruled out.

 The base mechanism was also modified to improve somewhat the accuracy and level of detail in the mechanism in representing no-NO_x or low-NO_x conditions. The methyl peroxy and acetyl peroxy radical model species are not represented explicitly, without using "operator" approximations or the steady-state approximation that was incorporated in previous mechanisms. This should give somewhat more accurate predictions of radical fates and C_1 product formation yields under low NO_x or nighttime conditions when peroxy + peroxy reactions become nonnegligible. The explicit treatment of methyl peroxy is based on the approach used in the RADM-2 mechanism,[13] which was shown to give a good approximation to a version of the mechanism with explicit representation of all peroxy + peroxy reactions.[14] However, "operator" and steady state approximation methods are still employed to represent the higher peroxy radicals, and the current mechanism, like the previous versions, is still not capable of predicting how the C_{2+} organic products may differ under conditions where peroxy + peroxy reactions compete with peroxy + NO reactions. But approximations have little or no effect on predictions of O_3 formation or O_3 reactivities, especially for the relatively high NO_x scenarios used for calculating the MIR scale,[15] and significantly reduce the number of active species that need to be included in the mechanism.

The number of model species used to represent the reactive organic products was increased somewhat in this version of the mechanism. These are listed in Table 1, with

the model species that were not in the SAPRC-90 base mechanism being underlined. The additional species include (1) more species to represent low NO_x reactions of C_1 radicals as indicated above; (2) explicit representation of biacetyl and methyl glyoxal; (3) separate species to represent the various types of uncharacterized aromatic fragmentation products (with the methyl glyoxal model species no longer being used for this purpose); and (4) product species needed to represent the reactions of isoprene, based on the "4-product" mechanism of Carter.[16] The latter was added because of the importance of isoprene in the emissions in many regional models, with the more detailed product representation used for greater accuracy and the ability to test model predictions against ambient data for isoprene's major products.

Table 1. Model species used to represent reactive organic products in the SAPRC-99 mechanism. Model species not in the SAPRC-90 base mechanism are underlined.

Formaldehyde	Acetaldehyde
Lumped C3+ Aldehydes	Acetone
Ketones, etc with kOH $< 5 \times 10^{-12}$ cm^3 molec^{-1} sec^{-1}	Ketones, etc with kOH $> 5 \times 10^{-12}$ cm^3 molec^{-2} sec^{-1}
Methanol	Methyl Hydroperoxide
Higher Organic Hydroperoxides	
Lumped Organic Nitrates	Peroxy Acetyl Nitrate
PPN And Other Higher Alkyl PAN Analogues	PAN Analogues Formed From Aromatic Aldehydes
Methacrolein	Methyl Vinyl Ketone
Other Isoprene Products	Methacrolein PAN Analogue
Glyoxal	Methyl Glyoxal
Biacetyl	Non-Photoreactive Aromatic Fragmentation Products
Photoreactive Aromatic Fragmentation Products (α-Dicarbonyl Spectrum)	Photoreactive Aromatic Fragmentation Products (Acrolein Spectrum)
Phenol	Cresols
Nitrophenols	Aromatic Aldehydes

Although the base mechanism for SAPRC-99 is more detailed than previous versions in most respects, a few condensations were employed. The separate model species used to predict formation of low-reactivity C_1-C_3 organic nitrates in the reactions of peroxy radicals with NO was lumped with the model species used to predict the formation of higher nitrates in these reactions because of the low total yield of the low reactivity

nitrates. The PAN analogue formed from glyoxal, GPAN, is now lumped with the rest of the higher PAN analogues because of the relatively low amounts of GPAN predicted to be formed in atmospheric simulations. The effects of these approximations, which resulted in fewer species and significantly fewer reactions in the base mechanism, was shown to be small even in simulations of VOCs where these model species are predicted to be formed.

MECHANISM GENERATION AND ESTIMATION SYSTEM

Probably the most important single advance in this version of the mechanism is the use of a computerized mechanism generation and estimation system to derive explicit mechanisms for the atmospheric reactions of many classes of VOCs in the presence of NO_x. These are then used as the basis for deriving an appropriate representation of the VOC in the model. The automated procedure for generated alkane reaction mechanisms that was incorporated in SAPRC-90[1] was updated based on the results of the evaluation of Atkinson[12] and an independent evaluation of alkoxy and peroxy radical reactions. More significantly, the software was completely revised and its capabilities were extended to include not only alkanes, but also alkenes (with no more than one double bond), and many classes of oxygenates including alcohols, ethers, glycols, esters, aldehydes, ketones, glycol ethers, carbonates, etc. The types of compounds and reactions the system can process are summarized on Table 2.

Table 2. Summary of compounds and reactions that can be processed using the SAPRC-99 mechanism generation system.

Generates mechanisms for VOCs containing following groups:

CH_3-, -CH_2-, >CH-, >CH<, -O-, -OH, -CHO, -CO-, -ONO_2, =CH_2, =CH-, =C<
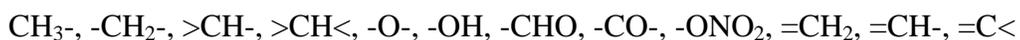
Currently cannot process reactions of following types of VOCs:

- VOCs with more than one double bond
- VOCs with more than one ring
- VOCs that form radicals whose ΔH_F's cannot be estimated

Generates reactions and estimates branching ratios for following types of reactions:

- VOC + OH
- Alkene + O_3, NO_3 and O^3P
- Aldehyde + NO_3
- Aldehyde + hν $\rightarrow$ R· + HCO·
- Ketone + hν $\rightarrow$ R· + R'CO·
- $RONO_2$ + hν $\rightarrow$ RO· + NO2
- R· + O_2
- RO_2 + NO $\rightarrow$ y_N $RONO_2$ + (1-y_N) RO· + NO_2
- Alkoxy + O_2
- Alkoxy radical decompositions (β-scission and "ester rearrangements")
- Alkoxy radical isomerizations
- Crigiee biradical reactions

Although many of the estimated rate constants and rate constant ratios are highly uncertain, this procedure provides a consistent basis for deriving "best estimate" mechanisms for chemical systems which are too complex to be examined in detail in a reasonable amount of time. The system allows for assigning or adjusting rate constants or branching ratios in cases where data are available, or where adjustments are necessary for model simulations to fit chamber data. Therefore, it could be used for deriving fully detailed mechanisms for VOCs that fully incorporate whatever relevant data are available, relying on various estimation methods only when information is not otherwise available. The program also outputs documentation for the generated mechanism, indicating the source of the estimates or assumptions or explicit assignments that were used.

The various types of estimation methods employed in the current mechanism generation system are summarized in the following section. A detailed discussion of these methods is given elsewhere.[5]

Summary of Estimation Methods

VOC + OH Rate Constants and Branching Ratios

The rate constants for the reactions of OH radicals at various positions of the molecule are estimated using the structure-reactivity estimation methods of Kwok and Atkinson[17] as updated by Kwok et al.[18] These include both OH abstraction from C-H bonds and OH addition to double bonds. The total rate constant is derived from summing up the estimated rate constants for reactions at various positions in the molecule, and the branching ratios are estimated by the ratio of the estimated rate constant for reaction at each position to the estimated total rate constant. If the total rate constant is known, then estimates are used for the branching ratios only. If product data are available, these are used to derive assigned branching ratios, and estimates are not used.

For higher molecular weight alkenes such as 1-butene, etc, reactions can occur both by addition to the double bond and abstraction from non-vinylic C-H bonds. However, the current system assumes that the only significant mode of reaction of OH to alkenes is by addition to the double bond. This is because the thermochemical estimates needed to estimate mechanisms for the unsaturated radicals formed following OH abstractions from alkenes are insufficient to estimate the possible branching ratios for the radicals predicted to be formed. In addition, the unsaturated radicals have possible modes of reactions for which estimates have not been developed. Fortunately, OH addition to the double bond is estimated to be the major reaction route for most alkenes that are considered.

Alkene + O_3 Rate Constants and Branching Ratios

Reactions of O_3 with alkenes are assumed to occur entirely by addition to the double bond forming a primary ozonide, which then decomposes to a carbonyl compound and an excited Crigiee biradical. Total rate constants and branching ratios (i.e., relative yields of the two possible sets of carbonyl and Crigiee products for unsymmetrical compounds) can be estimated by assuming that reactions at $CH_2=CH-$, $CH_2=C<$, $-CH=CH-$, $-CH=C<$, and $>C=C<$ all have the same rate constants and branching ratios. Thus averages of rate constants and branching ratios of compounds where these are known can be used for

general estimates when measured rate constant data are not available. Note that this method performs relatively poorly in estimating total rate constants for O_3 reactions,[19] but fortunately the O_3 rate constants have been measured for most VOCs of interest.

VOC + NO$_3$ Rate Constants and Branching Ratios

Reactions of NO_3 with VOCs by C-H abstraction forming nitric acid and the corresponding alkyl radical are assumed to be relatively unimportant for all VOCs except for aldehydes, and thus are neglected. (The reactions of NO_3 with phenolic compounds are included in the base mechanism, but the mechanism generation system is not used for aromatics.) For aldehydes, the abstraction rate constants are estimated based on measured rate constants for NO_3 + acetaldehyde, the correlation between kNO_3 and kOH given by Atkinson,[10] and measured or estimated OH rate constants.

Reaction of NO_3 with alkenes are assumed to occur entirely by addition to the double bond, with all the addition assumed to occur at the least substituted end for unsymmetrical molecules. Total rate constants are estimated by assuming that reactions at $CH_2=CH-$, $CH_2=C<$, $-CH=CH-$, $-CH=C<$, and $>C=C<$ all have the same rate constants, and using averaged measured rate constants for compounds where data are available.

Aldehyde Photolysis Rates and Initial Reactions

With lack of available data at the time the mechanism was developed, it is assumed that all saturated C_{3+} aldehydes photolyze at the same rate. Thus the absorption cross sections and quantum yields used in the base mechanism for propionaldehyde is used for all such aldehydes. The products are assumed to be exclusively $R·$ + $HCO·$. However, the recent data of Wirtz[20] indicate that this is an oversimplification, and that this aspect of the estimation method would have to be refined in future versions of the mechanism.

### *Ketone Photolysis Rates and Initial Reactions*

In the previous versions of the mechanism, it has been assumed that all higher saturated ketones photolyze with the same rate and overall quantum yields as methyl ethyl ketone, whose overall quantum yield was adjusted to fit results of a limited number of outdoor chamber runs with that compound. Since then, environmental chamber data obtained under more controlled lighting conditions have become available not only for methyl ethyl ketone, but also several higher aldehydes. These data could be used to derive overall quantum yields for the photodecompositions of these ketones, and the resulting values indicated that, contrary to the assumption in the earlier mechanisms, the overall quantum yield declines with carbon number. Therefore, for general estimation purposes, the overall quantum yields for ketones are estimated to depend on the number of carbons in the molecule, ranging from 0.15 to C_4 ketones to 0 for ketones with more than 8 carbons. The mechanism for ketone photodecomposition is assumed to be scission of the weakest C-CO bond in the molecule, forming the corresponding $R·$ + $R'CO·$ radicals.

Nitrate Yields from Peroxy + NO

The formation of alkyl nitrates from the reaction of peroxy radicals with NO can be a significant radical and NO_x termination process, and the importance of this process

assumed in the model can significantly affect reactivity predictions for higher molecular weight VOCs. The previous mechanism used estimates given by Carter and Atkinson[21], based on available data on nitrate yields for normal and a limited number of branched alkanes. Recently, Atkinson and co-workers[22] remeasured the nitrate yields from the C_{5+} n-alkanes, and obtained significantly lower yields than were previously estimated. Atkinson (private communication) considers the new data to supercede the older measurements, and thus the nitrate yield estimates of Carter and Atkinson[21] were re-derived to be consistent with the new data. The new and old data and estimates of nitrate yields for reactions of secondary peroxy radicals with NO are shown on Figure 1.

Figure 1. Measured and estimated organic nitrate yields for the reactions of NO with secondary alkyl peroxy radicals, as a function of carbon number.
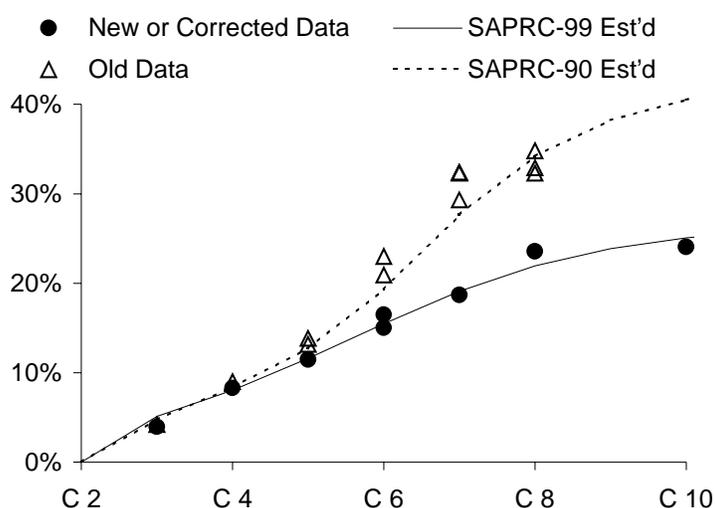

Note that the new data indicate that nitrate yields in the reactions of the initially formed peroxy radicals in the reactions of NO with the C_{8+} n-alkanes are about ~50% lower than previously assumed. In the previous versions of the SAPRC mechanism it was found that the C_{8+} n-alkane chamber data could be fit by model simulations only if it was assumed that all the nitrate formation came from the initially formed peroxy radicals, and that nitrate formation from the reaction of the δ-hydroxy peroxy radicals formed following alkoxy radical isomerizations was negligible. This is not chemically reasonable because reactions involving formation of these radicals are expected to be important in the C_{8+} alkane photooxidation mechanisms, and nitrate formation from the reactions of NO from the non-substituted analogues is significant. However, with the lower nitrate yields indicated by the new data, it is no longer to make this chemically unreasonable assumption for the model to fit the C_{8+} n-alkane reactivity data.

There are limited data on nitrate yields from the reactions of NO with non-secondary alkyl peroxy radicals or with peroxy radicals with -OH, -CO-, or other substituents. In most cases, the only "data" available comes from adjusting nitrate yields so model simulations can fit environmental chamber reactivity data. Environmental chamber experiments are sensitive to this parameter, but other uncertainties in the estimated or

assumed VOC oxidation mechanisms can affect the results. Therefore these data are uncertain.

The limited data on measured or estimated nitrate yields from non-secondary or substituted peroxy radicals indicate that nitrate yields from such radicals tend to be lower than those from secondary alkyl peroxy radicals, but the dependence on structure is unclear. Because of lack of information on structural dependences, the same estimates are used for all such radicals. In particular, nitrate yields from the reaction of NO with substituted or non-secondary are assumed to be those estimated for secondary alkyl peroxy radicals with the carbon number reduced by 1.5. The 1.5 reduction was derived to minimize the least squares error between estimated and measured or adjusted nitrate yields for compounds forming such radicals. The performance of this estimation method for these radicals is shown on Figure 2, which shows a plot of estimated vs. experimentally determined overall nitrate for various VOCs forming such radicals. It can be seen that there are several VOCs where the overall nitrate yields are not well predicted, but for most others the overall nitrate yields are predicted to within ±60%.

Figure 2. Plots of estimated overall nitrate yields formed in the photooxidations of various VOCs forming substituted or non-secondary peroxy radicals against experimentally determined values or values adjusted to fit environmental chamber data.
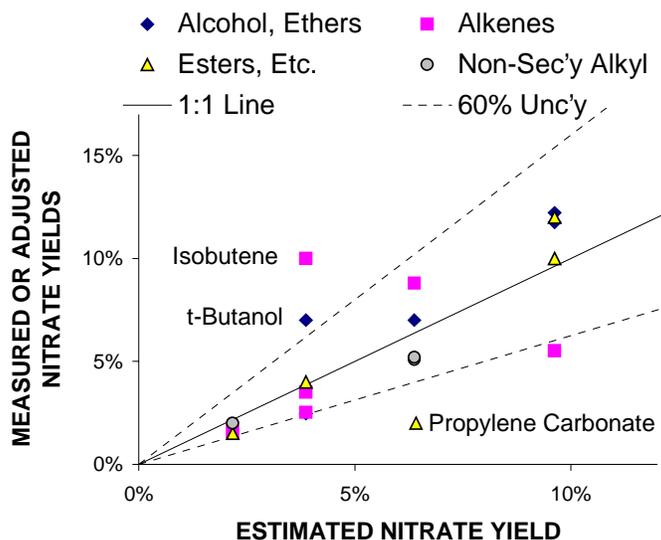
Estimation of Alkoxy Radical Rate Constants

Alkoxy radicals can react by a number of competing processes, and the variety of reactions the higher molecular weight alkoxy radicals can undergo accounts for much of the complexity of the VOC photooxidation mechanisms. The branching ratios for these competing reactions can affect not only the number of NO to NO_2 conversions involved in a VOCs photooxidation mechanism, but also the nature (and thus the reactivity) of the organic products formed.

Atkinson[12, 23] developed estimation methods for the reactions of the alkoxy radicals formed in the photooxidations of the alkanes and alkenes that was reasonably successful in estimating the rate constants involved. However, these estimates were found to perform poorly when extended to the substituted alkoxy radicals involved in the photooxidations of ethers, esters, and other substituted organics. Therefore, although the alkoxy radical estimation methods of Atkinson[12, 23] served as a useful starting point, they needed to be revised and extended to be useful for general mechanism estimation purposes.

The alkoxy radical reactions for which estimates were derived included reaction with O_2, β-scission decomposition, 1,4-H shift isomerization, and the "ester rearrangement" reaction undergone by radicals with the structure -CH[O·]-O-C(O)-[24]. In each case, rate constants were estimated by making separate estimates of the Arrhenius A factors and activation energies. The A-factors estimates adopted by Atkinson[12, 23] and Baldwin et al[25] were retained for this work, with the "ester rearrangement" A factor being assumed to be the same as for the 1,4-H shift isomerization, based on expected similarities in the structure of the transition state. Various approaches were used to estimate the activation energy depending on the type of reaction, as discussed below.

Reaction with O_2. The few measured alkoxy + O_2 rate constants were found to give reasonably good correlation between the estimated heat of reaction and the activation energy derived using the estimated A factor. This correlation was then used to estimate the activation energies for the reactions of other alkoxy radicals with O_2. This is considered to give more reasonable estimates than the approach adopted by Atkinson,[12, 23] which is to use a correlation between the rate constant and the heat of reaction. The problem with that approach is that it estimates rate constants for some of the highly exothermic O_2 reactions which are greater than the A factors for the reactions whose rate constants have been measured.

1,4-H Shift Isomerizations. The activation energies for these reactions are estimated based on thinking of them as an H-atom abstraction by an alkoxy radical. The correlation between C-H bond energies and activation energies for various bimolecular H-atom abstractions by methoxy radicals are used to estimate activation energies for abstractions from various groups. Substituent correction factors are derived by analogy with those used in the structure-reactivity method s of Atkinson[26] and Kwok and Atkinson[17] for estimating OH radical rate constants. A comparison of the activation energies derived based on the methoxy radical reactions with the activation energies derived for the few 1,4-H shift isomerizations for which there are data (based on the rate constant and the estimated A factors) indicate that it is appropriate to add a ~1.6 kcal/mole "strain" term when estimating the isomerization activation energies from those estimated for bimolecular reactions of methoxy radicals.

In order to fit the available product data for oxygenated VOCs which form alkoxy radicals where 1,4-H shift isomerizations compete with β-scission decompositions, and to be consistent with β-scission decomposition rate constant estimates derived for other radicals, it is necessary to assume that isomerizations involving -CO- or -O- groups in the ring in the transition state have higher activation energies than isomerizations of

unsubstituted alkoxy radicals. The data are best fit by an additional strain energy of 3.5 kcal/mole for isomerizations involving intermediates with such groups.

β-Scission Decompositions. By far the most difficult problem in developing estimation procedures for alkoxy radical reactions was deriving general estimation methods for the various types of β-scission decompositions. Direct measurements of β-scission decomposition rate constants are available only for a few relatively simple radicals, but estimates of rate constants for a wide variety of other radicals could be derived by analysis of product yield data for a variety of VOCs. In many cases, relative yields of various products can be used to estimate rate constant ratios for decompositions relative to competing reactions of the alkoxy radicals with O_2 or by 1,4-H shift isomerization. From O_2 or isomerization rate constants estimated as discussed above, these product yield ratios can then be used to obtain estimates of β-scission decomposition rate constants for a wide variety of compounds. These estimated rate constants can then be used as a basis for deriving general estimation methods for alkoxy radical decomposition reactions. Although uncertain, they provide the only available data base that can be used for this purpose.

Based on the approach of Atkinson,[12, 23] activation energies for β-scission decompositions, Ea, are estimated based on the assumption that Ea ≈ EaA + EaB · ΔH_R, where ΔH_R is the heat of reaction of the decomposition reaction, EaA is a parameter that is assumed to depend only on the nature of the radical *formed* in the decomposition, and EaB is assumed to be the same for all alkoxy radical decompositions. A value of EaB ≈ 0.44 was derived from data for alkoxy radical reactions forming CH_3· radicals, and is assumed to be applicable to all β-scission decomposition reactions.

The values of EaA were derived based on available measured or estimated alkoxy radical decomposition rate constants, or from various other estimates in cases where rate constant data or estimates were not available. Atkinson[12, 23] noted a correlation between the EaA parameter and the ionization potential of the radical form, and that correlation was used for estimating certain EaA parameters for which data were not available. However, this correlation was not found to be useful only for estimating EaA parameters for reactions forming radicals of the same type.

The decomposition activation energy and rate constant estimates are considered to be highly uncertain in many (if not most) cases, being based in many cases on very uncertain alkoxy + O_2 or isomerization rate constants, employing many highly uncertain and untested assumptions, and not giving satisfactory predictions in all cases. Clearly, additional data are needed, particularly for reactions of oxygen-containing alkoxy radicals, to test, refine, and improve these estimates and the many assumptions they incorporate. Indeed, it may not be possible to develop a totally satisfactory estimation method that can accurately predict rate constants for the full variety of these reactions, without carrying out detailed theoretical calculations for each system. Thus, rate constants or branching ratios derived from experimental data are used whenever possible when developing reaction mechanisms for atmospheric reactivity predictions. However,

when no data are available, we have no choice but to use estimates such as those developed in this work.

Ester Rearrangements. There are no data available concerning the rate constant for these reactions. However, this reaction clearly is the dominant pathway in the reactions of the $CH_3CH[O\cdot]OC(O)CH_3$ radical formed in the ethyl acetate system,[24] and model simulations of n-butyl acetate reactivity experiments can only fit the data if it is assumed that 1,4-isomerization dominates over the ester rearrangement in the reactions of $CH_3CH_2CH_2CH(O\cdot)O\text{-}CO\text{-}CH_3$ radicals. This information, together with estimates of the rate constants for the competing reactions of these radicals, and estimates for the A factor as discussed above, are then used to derive an approximate estimate of ~7.4 kcal/mole for the activation energy of this reaction. This is clearly highly uncertain.

Crigiee Biradical Reactions

Excited Crigiee biradicals are assumed to be formed in the reactions of O_3 with alkenes and alkynes, and the subsequent reactions of these species are incorporated in the mechanism generation system. Four types of Crigiee biradicals are considered, as discussed below. Note that it is assumed that the biradical reactions are assumed not to depend on the reaction forming them. The validity of this assumption is subject to question, since the reaction forming them would be expected to affect the distribution of excitation energy in the biradical, and the excitation energy would be expected to affect the mechanism of reaction in some if not all cases.

CH_2OO Biradicals. The recommendations of Atkinson[11, 12] concerning branching ratios for stabilization and the various decomposition routes are used without modification.

RCHOO Biradicals. The recommendations of Atkinson[12] for CH_3CHOO biradicals and an analysis of OH measurements from the reactions of O_3 with various 1-alkenes in the absence of NO_x can be used to derive a general set of estimates for the various competing reactions for these biradicals. These estimates involve predictions of OH yields of ~55%, independent of the size of the biradical. However, results of 1-butene - NO_x and 1-hexene - NO_x environmental chamber data can only be successfully simulated if it is assumed that the OH yields from the biradical formed in these systems are only ~5% and less than 1%, respectively. It is also necessary to assume that the OH yields from the CH_3CHOO biradicals are lower than recommended by Atkinson[12] in order to obtain nonbiased simulations of the large body of propene - NO_x environmental chamber data. Therefore, the SAPRC-99 mechanism assumes that OH yields from RCHOO biradicals decrease with the size of the molecule, to be consistent with the chamber data.

The discrepancy between laboratory measurements of OH yields from 1-alkenes and the lower OH yields needed to fit chamber data for such compounds is clearly a concern, and additional work is needed to resolve this discrepancy. It might be due to the interaction of these biradicals with NO_x, which is present in the environmental chamber experiments but not in the laboratory systems where OH yields are measured. However, the SAPRC-99 Crigiee biradical mechanisms do not include any biradical + NO_x reactions; all their reactions are treated as unimolecular processes. Note that this includes

stabilization – pressure effects of Crigiee biradical reactions are not represented in the current version of the mechanism.

RR'COO Biradicals with α Hydrogens. These biradicals are assumed to exclusively rearrange to the unsaturated hydroperoxide intermediate, which then decomposes to form OH radicals in 100% yield, i.e.,

$$>CHC(OO)- \rightarrow >C=C(OOH)- \rightarrow >C=C(O\cdot) + OH \rightarrow >C[\cdot]-C(O)- + OH$$

This is consistent with the relatively high OH yields observed in the reactions of O_3 with internal alkenes, and in this case the model assuming these high OH yields gives reasonably good simulations of the available environmental chamber data.

Other RR'COO Biradicals. The above mechanism cannot occur for those disubstituted Crigiee biradicals that do not have substituents with α hydrogens. It is also considered to be unlikely if the only substituent(s) with α hydrogens are -CHO groups, since it is expected that formation of a ketene hydroperoxide intermediate would involve a strained transition state. In the cases of biradicals with carbonyl groups, the mechanisms assumed are based on those derived by Carter and Atkinson[27] for reactions of O_3 with isoprene products. In the other cases, which do not occur in many cases for the VOCs currently considered in the mechanism, we arbitrarily assume that 90% is stabilized and 10% decomposes to CO_2 + 2 R·.

Mechanism Generation

This mechanism generation system is used as the primary means of deriving SAPRC-99 mechanistic parameters for all the classes of VOCs that it can handle, including alkanes, alkenes, and the variety of oxygenated species as indicated above. Although the program outputs mechanisms that can (for larger molecules) involve hundreds or even thousands of reactions or products, various "lumping rules" are used to convert the detailed generated mechanisms and product distributions into the lumped reactions incorporating the appropriate model species used in the base mechanism. The use of this program has permitted estimation of detailed mechanisms for a much larger number of compounds than otherwise would be possible without incorporating approximations that might significantly compromise the accuracy of reactivity predictions.

Although the mechanism generation system currently cannot be used to derive mechanisms for dialkenes and unsaturated aldehydes and ketones, the estimates in the detailed mechanism of Carter and Atkinson[27] for isoprene and its major products were incorporated explicitly in the mechanism generation system, allowing full mechanisms for these species to be generated. The results are therefore are consistent with the detailed mechanism of Carter and Atkinson[27] and the condensed mechanisms of Carter[16] for these compounds. A similar approach was used so the system could be used to generate reactions of 1,3-butadiene acrolein, and various alkynes.

ASSIGNED OR PARAMETERIZED MECHANISMS

Aromatics

Despite progress in recent years, there are still too many uncertainties concerning the details of the photooxidation mechanisms of aromatics and the reactive products they form to allow for explicit mechanisms to be derived or estimated. Therefore, simplified and parameterized mechanisms, with uncertain parameters adjusted to fit environmental chamber data, are still employed. However, the representation of the uncharacterized aromatic ring fragmentation products was revised somewhat based new data obtained for unsaturated dicarbonyls (e.g., Bierback et al[28]), and to allow for explicit representation of the α-dicarbonyl products formed from the methylbenzenes. As with SAPRC-97,[4] this version of the mechanisms appropriately represents reactivity differences among various xylene and trimethylbenzene isomers, and is able to correctly simulate how aromatic reactivities vary with differing light sources.

This mechanism also uses parameterized representations for naphthalenes and tetralin, with parameters adjusted to fit the limited chamber data for naphthalene, 2,3-dimethyl naphthalene, and tetralin. These compounds tended to have much lower mechanistic reactivities than the alkylbenzenes, and thus their mechanisms use lower yields of the model species that represent photoreactive ring fragmentation products. In addition, to fit the chamber data, it is necessary for the model to assume that these compounds form radicals that react like PAN precursors. The actual mechanistic implications of this parameterizations is unknown, and the reliability of model predictions for these compounds is uncertain.

Terpenes

Because the mechanism generation system cannot derive mechanisms for bicyclic compounds, simplified mechanisms were derived for the terpenes, based on environmental chamber data for several representative terpenes. Some parameters, such as overall organic nitrate yields and numbers of NO to NO_2 conversions in the OH reaction, were adjusted based on the chamber data, and the mechanism generation system for compounds with similar structures was employed to derive estimated mechanisms for their reactions with ozone. The mechanism correctly predicts observed reactivity differences among various terpene isomers, though some experiments, particularly with β-pinene, are not well simulated in some respects.

Other Compounds

Assigned mechanisms were also derived for styrene, N-methyl-2-pyrroladone, toluene diisocyanate, and diphenylene diisocyanate, based on available kinetic and mechanistic data, estimated or parameterized mechanisms, and results of environmental chamber experiments employing those or related compounds.

Although ClO_x or BrO_x chemistries have been incorporated as extensions to the SAPRC-97 mechanism,[29-31] this is not yet incorporated in the current version of this updated mechanism. With the exception of chloropicrin, which appears to have relatively

simple and unique chemistry,[31] the few halogenated compounds we have studied (trichloroethylene[29] and alkyl bromides[30]) indicate that we cannot account for the reactivities of those compounds with explicit mechanisms. Therefore, the current version of the mechanisms uses a highly simplified and parameterized "placeholder" mechanism to provide very rough estimates of the approximate range of reactivities of halogenated compounds under MIR conditions, given their OH radical rate constants. The predictions of these mechanisms must be considered to be highly uncertain, and the available chamber data indicate they are almost certainly not valid under low NO_x conditions.

A parameterized "placeholder" mechanism is also used to estimate the approximate reactivity ranges of amines, given their measured or estimated OH radical rate constants. The predictions of this mechanism for those compounds must also be considered to be highly uncertain, especially since they have not been evaluated using environmental chamber data. However, use of this mechanism allows at least approximate estimates to be made.

MECHANISM EVALUATION

The performance of the mechanism in simulating O_3 formation, rates of NO oxidation, and other measures of reactivity was evaluated by conducting model simulations of over 1600 environmental chamber experiments carried out the Statewide Air Pollution Research Center (SAPRC) and the College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California at Riverside (UCR). These include not only experiments in the UCR database through 1993,[32] but also experiments carried out at CE-CERT through mid 1999 for the purpose of developing and evaluating mechanisms for various types of VOCs. The types of experiments and number of VOCs in the chamber data base used in the evaluation are summarized on Table 3, and the types of chambers employed are summarized on Table 4.

Table 3. Environmental chamber data base used for evaluating the SAPRC-99 mechanism.

| Type of experiment	Runs	VOCs
Characterization runs	76	
VOC - NO_x runs	484	37
Incremental reactivity runs	447	80
Miscellaneous mixture - NO_x	95	
"Base case" surrogate - NO_x mixtures with reactivity runs	561	

Table 4. Summary of major characteristics of the environmental chambers used in the mechanism evaluation.

Walls	Lights	RH	Vol (L)	Runs
Teflon Film	Blacklight	50%	6000	139
Teflon Film	Blacklight	Dry	3000-6000	1066
Teflon Film	Xenon Arc	Dry	2500-5000	323
Teflon Coated Al, Quartz	Xenon Arc	50%	6400	107
Teflon Film	Sunlight	Dry	20,000	42

The results of the evaluation indicated that this version of the mechanism performed slightly, though not dramatically, better than the previous versions[3, 4, 33] in simulating experiments with the major hydrocarbon classes found in ambient air and complex or surrogate mixtures. The overall performance in the mechanism in simulating the amount of O_3 formed + NO oxidized for all the environmental chamber runs modeled is shown on Figure 3. It can be seen that for most experiments the model was able to simulate this to within ±20%, which is slightly better than the ±30% performance obtained previously. Of course, this could in part be due to the fact that the current data set included much fewer of the more difficult-to-characterize outdoor experiments, and includes a much larger number of very recent experiments carried out under more reproducible conditions.

Figure 3. Distribution plot of model performance in simulating the amount of NO oxidized + NO formed, $\Delta([O3]-[NO])$, for all environmental chamber runs modeled.
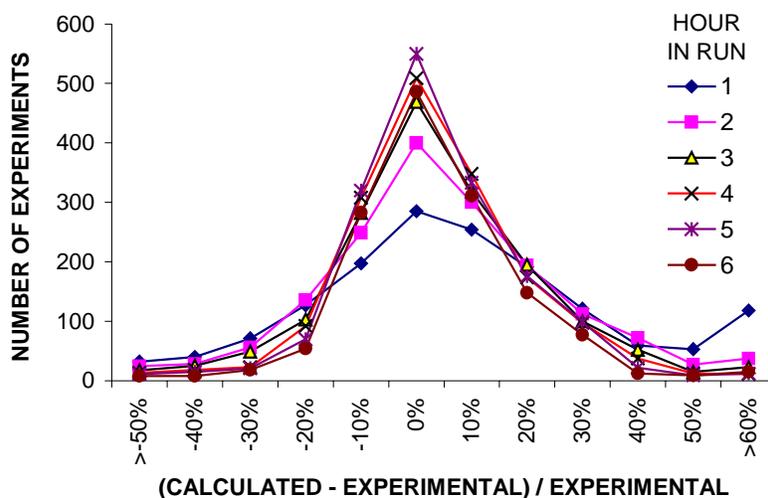
In addition, this version of the mechanism generally gave satisfactory fits to the reactivity data for most of the experiments using the various compounds that were studied more recently, which were either not represented or poorly represented in the previous versions. However, as with previous evaluations of this[3, 4, 33] and other[14, 34] mechanisms, there were cases where satisfactory simulations were not obtained. Many of these cases of poor performance in simulating the data can be attributed to problems with the mechanism, but this is probably not true in all cases. However, reactivities of most VOCs were reasonably well simulated, though in many cases adjustments to uncertain portions were made to achieve the fits. These cases are noted in the detailed summary of the evaluation results.[5]

UPDATED REACTIVITY SCALES

The updated mechanism was used to calculate updated MIR and other ozone reactivity scales, using the scenarios and methodology developed previously for this purpose.[15] Reactivity estimates were derived for a total of 557 VOC's, including many that were not in previous tabulations, or whose estimates were based on much more uncertain or approximate mechanisms. It is therefore recommended that these be used in any application that calls for use of the MIR scale or any of the other scales given by Carter.[15] Although the estimates for many of the VOCs remain highly uncertain, the present scale provides the best estimates that are currently available.

The effects of the updates in the mechanism on calculated reactivities in the Maximum Incremental Reactivity (MIR) scale are shown on Table 5. This compares incremental reactivities of the ambient mixture and relative reactivities of selected VOCs in this version of the mechanism and the SAPRC-97 mechanism.[3, 4] It can be seen that there is almost no change in the ambient mixture incremental reactivity, but the relative reactivities (i.e., incremental reactivities of the VOCs divided by the incremental reactivity of the ambient mixture) changed by 15-50% for many VOCs, and by larger factors for a few others. The large change for high molecular weight alkanes is due in part to the use of a more reactive model species to represent alkane photooxidation products, and also to the fact that the reactivities of these compounds, whose net reactivities are differences in large positive and negative factors, are highly sensitive to changes in the base mechanism. The large change for acetylene is due to the higher reactivity for its major product, glyoxal, used in the current mechanism, which was made for the model to fit results of new experiments with acetylene.[35] The large change for ethylene glycol is due to a new value for its OH radical rate constant. Reactivities of a number of other individual VOCs changed due to new information on their mechanism, or the availability of new environmental chamber data that indicate needs for modifications for their mechanisms.

The California Air Resources Board (CARB)'s vehicle emissions regulations[36] use "Reactivity Adjustment Factors" (RAFs) in emissions standards for alternatively fueled vehicles, where the RAFs are calculated from the ratio of MIR reactivities of the exhaust divided by that of a standard gasoline. The current regulations uses RAFs derived from the MIR scale calculated using the SAPRC-90 mechanism.[15] Table 6 shows effects of the subsequent updates to the SAPRC mechanism on the calculated RAF values for

transitional low emissions vehicle (TLEV) exhausts of interests to the CARB. It can be seen that the mechanism updates had relatively small effects on these RAFs, with the update from SAPRC-97 to SAPRC-99 tending to counteract the changes caused when SAPRC-90 was updated to SAPRC-97.

Table 5. Effects of mechanism updates on Maximum Incremental Reactivities.

VOC or Mixture	SAPRC-97	SAPRC-99	Δ%
Incremental Reactivities (gm O3 / gm VOC)			
Ambient Mixture	4.06	3.98	-2%
Relative Reactivities (mass basis)			
Ethane	0.08	0.09	12%
n-Decane	0.13	0.24	91%
1-Hexene	1.40	1.53	9%
Isoprene	2.30	2.89	25%
a-Pinene	0.96	1.13	19%
Toluene	1.26	1.07	-15%
m-Xylene	3.49	2.78	-20%
p-Xylene	0.71	1.15	61%
Acetylene	0.09	0.33	276%
Ethanol	0.42	0.47	13%
Ethylene Glycol	0.56	0.92	63%
Methyl t-Butyl Ether	0.18	0.22	25%
2-Butoxyethanol	0.57	0.84	47%
Formaldehyde	1.62	2.33	44%
Methyl Ethyl Ketone	0.35	0.40	14%
Mineral Spirits "B" (Type II-C)	0.35	0.24	-29%

Table 6. Effects of mechanism updates on TLEV exhaust reactivity adjustment factors (RAFs) calculated using the MIR scale.

Exhaust Type	SAPRC-99		SAPRC-97		SAPRC-90
	RAF	Change	RAF	Change	RAF
RFA	1.00	-	1.00	-	1.00
M85	0.38	14%	0.34	-10%	0.37
E85	0.67	11%	0.61	-4%	0.63
CNG	0.19	16%	0.16	-9%	0.18
LPG	0.52	12%	0.46	-8%	0.50
Phase 2	0.99	1%	0.98	0%	0.98

CONCLUSIONS

The mechanism described in this work supercedes the previous versions of the SAPRC mechanism, and it is recommended that this be used in airshed model applications where a detailed representation of the atmospheric reactions of VOCs is required. It has been designed particularly for developing ozone reactivity scales, and the VOC reactivity scale developed in this work supercedes the previously published values.[15] It has been comprehensively evaluated using the currently available relevant environmental chamber data, and has been shown to perform reasonably well in simulating O_3 impacts and other measures of reactivity for most VOCs that have been studied.

Although the current mechanism represents the state of the art, significant areas of uncertainty remain, which result in corresponding uncertainties in atmospheric reactivity predictions. The aromatics, terpenes, and other important classes of VOCs are still represented by highly parameterized mechanisms because of lack of information concerning the major reactions and products formed. Although fully explicit mechanisms can be generated for many other classes of VOCs, estimation methods for many important reactions are highly uncertain, and in some cases predictions are made that are known to be inconsistent with available data. Therefore, research into the atmospheric reaction mechanisms of VOCs, and in particular development of improved methods for estimating the reactions and branching ratios for the many types of radicals that can be formed, is still needed.

The SAPRC-99 mechanism represents a greater level of chemical detail than most mechanisms currently used in airshed models (especially in the United States), and in fact may be more detailed than appropriate for some airshed model applications. Development of condensed versions of this mechanism for such applications, to replace outdated condensed mechanisms such as Carbon Bond IV.[34] may be appropriate. On the other hand, this mechanism still uses a relatively condensed representation of the peroxy radical reactions that are important under low NO_x conditions, and the reactions of the many types of organic photooxidation products that can be formed. The effects of using more chemically detailed representations of these reactions and products on airshed model predictions have not been adequately assessed.

Nevertheless the SAPRC-99 mechanism represents the current state of the art, and, because of its chemical detail and its extensive evaluation against chamber data, is probably most appropriate for airshed model applications where chemical detail is important. Although uncertainties remain and further research is needed, it represents our current best estimates concerning how to estimate and represent the atmospheric reactions of VOCs in urban and regional models.

ACKNOWLEDGEMENTS

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