



**DOCUMENTATION OF THE SAPRC-99
CHEMICAL MECHANISM FOR
VOC REACTIVITY ASSESSMENT**

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By

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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 comprehensively documented in this report. This can be used in airshed models to determine absolute and relative 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 the SAPRC-90 mechanism of Carter (1990), 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 condensed version was developed for use in regional models. 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 approximately 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. The mechanism was used to update the various ozone reactivity scales developed by Carter (1994a), including the widely used Maximum Incremental Reactivity (MIR) scale. However, the reactivity estimates for many VOC classes are uncertain, which must be taken into account when using these data for regulatory applications. For this reason, uncertainty classifications have been assigned to all VOCs, and upper limit MIRs for VOCs with uncertain mechanisms are presented.

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The opinions and conclusions in this report are entirely those of the author. Mention of trade names and commercial products does not constitute endorsement or recommendation for use.

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I. INTRODUCTION

A. Background

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

One airshed model application where the accuracy of the chemical mechanism is particularly important is the assessment or implementation of control strategies to encourage use of VOCs that have lower impacts on ozone or other secondary pollutant formation than VOCs that are currently emitted. Such strategies require a means to quantify the impacts, or "reactivities" of the VOCs with respect to O_3 or other measures of air quality. There are several examples of control strategies where accurate Q reactivity estimates are important. In the California Air Resources Board (CARB)'s "Low Emissions Vehicle/Clean Fuels" regulations, "reactivity adjustment factors" are used to place exhaust emissions standards for alternatively-fueled vehicles on an equal ozone impact basis as those for vehicles using conventional gasoline (CARB, 1993). These are calculated using the Maximum Incremental Reactivity (MIR) scale (Carter, 1994a), which is a measure of effect of a VOC on O_3 formation in a set of standard airshed scenarios that represent NO_x conditions where ozone formation is most sensitive to VOCs (Carter, 1994a; CARB, 1993). The CARB is now considering using an updated MIR scale for reactivity adjustments in its proposed consumer products regulations (CARB, 1999). In addition, the EPA has used O_3 impacts of VOCs calculated for various environments among the factors they consider when evaluating proposals to exempt various compounds from controls as ozone precursors (Dimitriades, 1999).

The MIR scale adopted in the CARB vehicle regulation was calculated using the SAPRC-90 chemical mechanism (Carter, 1990), which had assigned or estimated mechanisms for over 100 types of VOCs. Although other state-of-the art mechanisms were available for airshed model applications (e.g., Gery et al, 1998, Stockwell et al, 1990), SAPRC-90 used for this purpose because it was the only mechanism that that represented a large number of VOCs that was evaluated against environmental chamber data. 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, with the major documented updates being the "SAPRC-93" (Carter et al, 1993a; Carter, 1995) and the "SAPRC-97" (Carter et al, 1997a) versions. However, the reactions and rate constants for most of the inorganic species and common organic products have not been updated, and the latest documented update (SAPRC-97) does not incorporate important new information concerning mechanisms and reactivities of many classes of VOCs (e.g., Carter et al, 2000a, see also references cited below). This includes particularly improved estimation methods and new reactivity data on many types of

oxygenated VOCs that have not previously been studied but that are or may be important in stationary source emissions, and updated mechanisms for components of mineral spirits and other high molecular weight alkanes.

Because of this, an updated mechanism that represents the current state of the art is needed to calculate an reactivity scale that is appropriate for the CARB's proposed reactivity-based consumer products regulations (CARB, 1999). In addition, the CARB vehicle regulations requires that the MIR scale it uses be updated approximately every three years, and therefore an update of that scale, using an updated and fully documented mechanism, is overdue. To address this need, the CARB contracted the author to develop an updated version of the SAPRC mechanism that represents the state of the art, that can appropriately represent the classes of compounds that need to be considered in VOC regulations, and that is comprehensively documented so that it can undergo peer review. This report documents the updated version of the mechanism, designated SAPRC-99, that represents the results of this effort.

B. Mechanism Overview

The major components of the SAPRC mechanisms are the base mechanism, the assignments and/or estimation procedures used to estimate the reactions of the represented VOCs that are not in the base mechanism, and the lumping procedures used to represent complex mixtures or VOCs for which assignments or estimates are not available. The base mechanism is the portion of the mechanism that represents the reactions of the inorganic species, the common organic products, the intermediate radicals leading to these products, including those formed from the initial reactions of the represented VOCs not in the base mechanism. Most of the VOCs that can be separately represented are not in the base mechanism, but can be added to the mechanism, either as explicit reactions for individual VOCs or as lumped model species whose parameters are derived from the mixture of detailed model species they represent, as needed in the model application. The updates to these various components are briefly summarized below, and are discussed in more detail in the remainder of this report. The remaining areas of uncertainty, and aspects of the mechanism additional work is needed, are also briefly summarized in this section.

1. Updates to the Base Mechanism

This version of the mechanism incorporates the first complete update of the base mechanism since SAPRC-90 was developed. The IUPAC (Atkinson et al, 1997, 1999) and NASA (1997) evaluations, the various reviews by Atkinson (1989, 1991, 1994, 1997a), 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 + NO₂ rate constant based on the new evaluation by NASA (1997)¹. 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 now represented explicitly, without using "operator" approximations or the steady-state approximation that was incorporated in previous mechanisms. This should give somewhat

¹ The high rate constant in the current IUPAC (Atkinson et al, 1997) evaluation is probably inappropriate (Golden, personal communication, 1998).

more accurate predictions of radical fates and C₁ 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 (Stockwell et al, 1990), which was shown to give a good approximation to a version of the mechanism with explicit representation of all peroxy + peroxy reactions (Carter and Lurmann, 1990). 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 C₂₊ organic products may differ under conditions where peroxy + peroxy reactions compete with peroxy + NO reactions. But these approximations have little or no effect on predictions of O₃ formation or O₃ reactivities, especially for the relatively high NO_x scenarios used for calculating the MIR scale (Carter, 1994a), and significantly reduce the number of active species that need to be included in the mechanism.

Although the base mechanism for SAPRC-99 employs a larger number of species than that for SAPRC-90 and as such is more detailed in most respects, a few condensations were employed, relative to the level of detail in the earlier mechanism. The separate model species used to predict formation of low-reactivity C₁-C₃ 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.

Because of the importance of isoprene emissions in many regional model applications, the base mechanism was expanded to include the isoprene photooxidation products used in the "four-product" condensed isoprene mechanism of Carter (1996). Thus, the base mechanism now includes explicit representation of methacrolein, methyl vinyl ketone, lumped C₅ unsaturated aldehyde products (ISOPROD), and the methacrolein PAN analogue (MPAN) formed when they react. Although the more condensed "one product" mechanism gives reasonably good approximations to predictions of effects of isoprene on ozone (Carter, 1996), the four product mechanism is considered to be more accurate, and allows prediction and appropriate representation of the major oxidation products of this important biogenic compound in ambient simulations.

2. Mechanism Generation and Estimation System

Probably the most important single advance in this version of the mechanism is the use of a new mechanism generation and estimation software system to derive fully detailed mechanisms for the atmospheric reactions of many classes of VOCs in the presence of NO_x, which can be used as the basis for deriving an appropriate representation of the VOC in the model. The automated procedure for generated alkane reaction mechanisms for SAPRC-90 (Carter, 1990) was updated based on the results of the evaluation of Atkinson (1997a) and an independent evaluation of alkoxy and peroxy radical reactions, as discussed in this report. More significantly, the software was completely revised and the capabilities of the system 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. 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.

A major effort in developing this system involved incorporating results of various mechanistic, product, and environmental chamber studies that have been carried out in recent years to reduce uncertainties in mechanisms and reactivity predictions for various classes of oxygenated compounds. The branching ratios derived from experimental product studies or adjusted to fit environmental chamber reactivity experiments were used not only as a basis to derive explicit assignments for maximum accuracy of representation and reactivity predictions of the applicable compounds, but also to improve the reliability and scope of the estimation methods when applied to compounds for which data are not available. An important source of the environmental chamber data used for this purpose came from the CARB-funded study of the reactivity of selected consumer products VOCs (Carter et al, 2000a), as well as other recent studies of individual compounds of interest to various private sector groups (see references cited elsewhere in this report)².

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.

The mechanism generation system was also used to generate the reactions of the major reactive oxidation products of the non-aromatic hydrocarbon and oxygenated VOCs. These are used for deriving more accurate representations of the reactions of these products that can be used when assessing the reactivities of the individual VOCs. However, the present version of the software cannot derive adjusted mechanisms for products formed by reactions of VOCs in complex mixtures that are represented by lumped model species.

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 (1996) 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 consistent with the detailed mechanism of Carter and Atkinson (1996) and the condensed mechanisms of Carter (1996) 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.

3. Assigned or Parameterized Mechanisms

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

² Reports on recent environmental chamber studies of various VOCs can be downloaded from <http://cert.ucr.edu/~carter/bycarter.htm>

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 on new data obtained for unsaturated dicarbonyls (e.g., Bierback et al, 1994), and to allow for explicit representation of the α -dicarbonyl products formed from the methylbenzenes. As with SAPRC-97, 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. In addition, this version of the mechanism has parameterized mechanisms for the naphthalenes and tetralin optimized to simulate environmental chamber experiments employing those compounds.

Because the mechanism generation system cannot derive mechanisms for bicyclic compounds, simplified mechanisms for these compounds were derived, based on environmental chamber data for several representative terpenes. Some parameters, such as overall organic nitrate yields and numbers of NO to NO₂ 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.

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 (Carter et al, 1996d, 1997d, 1997h), 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 (Carter et al, 1997h), the few halogenated compounds we have studied [trichloroethylene (Carter et al, 1996d) and alkyl bromides (Carter et al, 1997d)] 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.

4. Mechanism Evaluation

The performance of the mechanism in simulating O₃ 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 481 single VOC - NO_x experiments, 447 incremental reactivity experiments, and 673 experiments with mixtures, though approximately 560 of the mixture runs

were replicate base case reactivity experiments of various types. These include not only experiments in the UCR database through 1993 (Carter et al, 1995d), but also experiments carried out at CE-CERT through mid 1999 for the purpose of developing and evaluating mechanisms for various types of VOCs³.

The results of the evaluation indicated that this version of the mechanism performed approximately as well or better than the previous versions (Carter and Lurmann, 1991; Carter, 1995; Carter et al, 1997a) in simulating experiments with the major hydrocarbon classes found in ambient air and complex or surrogate mixtures. 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 (Carter and Lurmann, 1991; Carter, 1995; Carter et al, 1997a) and other (Carter and Lurmann, 1990, Gery et al, 1988) 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.

For example, the mechanism did not perform particularly well in simulating the experiments with benzene, despite the fact that it generally performed satisfactorily in simulating experiments with most of the alkylbenzenes that were studied. The experiments with the 1-alkenes could only be simulated if it was assumed that the OH yields in the reaction of O₃ with those compounds were lower than indicated by laboratory data. The effects of varying reaction conditions on reactivities of some of the individual VOCs that were studied were not always successfully simulated, despite adjusting uncertain parameters in the mechanisms. These cases are noted in the summaries of the evaluation results for the various compounds. 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 also noted in the summary of the evaluation results.

C. Updated Reactivity Estimates

The updated mechanism was used to calculate updated MIR and other ozone reactivity scales, using the scenarios and methodology developed previously for this purpose (Carter, 1994a,b). Reactivity estimates are given for approximately 560 VOC's, including many that were not in previous tabulations, or whose estimates were based on much more uncertain or approximate mechanisms. The reactivity tabulations include footnotes indicating the type of mechanism or representation employed when calculating the reactivities, the extent to which the reactivity predictions were evaluated against experimental data, and an uncertainty ranking. Upper limit reactivity estimates are also included.

The updated reactivity scale given in this report supercedes those of Carter (1994a) and other interim updates that have been distributed previously. 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 (1994a). Although the estimates for many of the VOCs remain highly uncertain, the present scale provides the best estimates that are currently available. The uncertainty classification given with the scale and the other associated footnotes can be used to indicate the qualitative level of uncertainty for any given VOC. It is recommended that any regulatory application that employs any of the scales given in this report appropriately take uncertainty into account for those VOCs whose reactivities are indicated as having a high level of uncertainty.

³ The experiments used for mechanism evaluation include most of those described in the various reports on CE-CERT chamber studies that can be downloaded from <http://cert.ucr.edu/~carter/bycarter.htm>.

II. BASE MECHANISM

The base mechanism is the portion of the mechanism which must be incorporated when representing the reactions of any generic VOC, and includes the inorganic reactions, the reactions of the common organic products and the reactions of the common radicals formed from these products or any generic VOC. A complete listing of the base mechanism is given in Appendix A on Table A-1 through Table A-5. The species used in the base mechanism listed on Table A-1, their reactions and rate constants listed on Table A-2, the rate constant and mechanism documentation notes referred to there are given in Table A-4, and the absorption cross sections and quantum yields for the photolysis reactions listed on Table A-5. The major features of the mechanisms, and the changes made relative to the previous version (Carter et al, 1997a) are discussed in the following sections.

A. Inorganic Reactions

The inorganic reactions in the mechanism are essentially the same as in the previous versions, except all the rate constants have been updated based on the results of the most recent evaluations (Atkinson et al, 1997, 1999; Atkinson, 1997a; NASA, 1997). This resulted in changes to most of the rate constants, though in most cases the changes were small and probably not of significance to model predictions. In addition, a few reactions that were previously judged to be negligible were added to extend the range of validity of the mechanism. The changes that may not be negligible, and the aspects of the inorganic mechanism that are still considered to be uncertain, are briefly summarized below, in the order that the reactions appear on Table A-2.

- Reactions of O³P with O₃ and NO, which were omitted from the previous mechanism, are now included. These are believed to be negligible under most atmospheric conditions, but may not be in some high concentration experiments.
- The rate constant used for the “homogeneous” portion of the N₂O₅ hydrolysis reaction was decreased from $1 \times 10^{-21} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ to $2.6 \times 10^{-22} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, based on the data of Mentel et al (1996). Note that this reaction may be primarily heterogeneous in nature, and the appropriate rate constant to use in atmospheric simulations is uncertain. However, the rate constant we use is not inconsistent with the IUPAC (Atkinson et al, 1997) recommendation that the gas-phase rate constant is less than $2 \times 10^{-21} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.
- The rate constant for OH + NO for 1 atmosphere and 300K increased by over a factor of 1.5, based on the NASA (1997) recommendation for the high pressure rate constant. The IUPAC (Atkinson et al, 1997) recommendation is to use an even higher high pressure rate constant, but that recommendation is not used because the NASA value is more consistent with measurements made under near-atmospheric conditions.
- There is a significant discrepancy between the NASA (1997) and IUPAC (Atkinson et al, 1997) recommendation concerning the important OH + NO₂ reaction. Again, the NASA recommendation is preferred because it is more consistent with measurements made under near-atmospheric conditions. [The rate parameters actually used are those that will be in the update to the NASA (1977) evaluation (Golden, private communication, 1999).] The high k_{∞} recommended by IUPAC is based on very high pressure data in helium, and there may be artifacts due to the contribution of a second reaction channel, involving HOONO formation, becoming important at higher pressures (Golden, personal communication, 1998). The value used in the current mechanism is about 20% lower than that used in the previous version. Given the importance of

this reaction as a radical termination and NO_x removal process, this change may have a non-negligible effect on model simulations.

- The reaction of OH with HONO, which was omitted in the previous mechanism because of its low importance in ambient simulations, is now included. This reaction can be important in simulations of experiments with HONO added as a radical source, which may be useful for assessing some aspects of VOC reactivity (unpublished results from this laboratory).
- A second photolysis channel for HONO, forming $\text{H} + \text{NO}_2$, was added based on the IUPAC (Atkinson et al, 1997) recommendations. This channel is calculated to occur ~10% of the time under atmospheric conditions.
- The reaction of OH with NO_3 , omitted from the previous mechanism, is now included. The possibility that it may be non-negligible under some nighttime conditions or in some dark experiments has not been ruled out.
- The rate constant for the reaction of HO_2 with NO_3 was increased based on recent laboratory data of Mellouki et al (1993).
- The reaction of NO_3 with itself, which may be non-negligible under some nighttime conditions, (Stockwell et al, 1997) is now included.
- The reaction of OH with hydrogen was added because it may be a non-negligible sink for OH radicals in cleaner or remote atmospheres. The reaction is of negligible importance in urban or environmental chamber simulations, but may be needed in regional models.

The effects of these changes on model simulations have not been evaluated. It is expected the ~20% change in the $\text{OH} + \text{NO}_2$ may be the most important in terms of predictions of ozone formation, and in the model simulations of the environmental chamber experiments used to evaluate the mechanism, as discussed in Section V. However some of the changes concerning NO_3 reactions may have non-negligible effects on nighttime simulations. As indicated above, a number of changes were added that are not expected to influence ambient simulations, but which may be important in simulations of experiments that may be useful for evaluating other aspects of the mechanism. Since including these reactions did not add new species to the model, the impact of these reactions in terms of computational burden in airshed models should be minor.

B. Representation of Radical Species

The approaches used to represent the various types of radical species formed in the atmosphere are discussed in this section. As with the previous mechanism, most of the inorganic and a few of the organic radicals are represented explicitly, but most of the organic radicals are either lumped or not explicitly represented in the model. In particular, rapidly-reacting organic radicals which either react in only one way or whose reactions do not depend on other reacting species are replaced by the set of products they form, and most other radicals are either lumped or represented using a limited number of chemical “operators”. The various approaches employed are discussed in this section.

With regard to computational impacts of radical species incorporated in the model, a distinction is made between *active* species and species where the *steady state* approximation can be employed. Active species are model species whose concentrations need to be calculated by the solver software by integrating their rates of change, and which must be transported in multi-cell model simulations. Steady state species are model species (usually representing rapidly reacting radical or chemical operators representing radicals) for which the steady state approximation can be employed. In that approximation,

the concentration of the species is calculated at each time step assuming that the instantaneous rate of formation is equal to the rate of destruction. This means that the species does not need to be transported or integrated by the model software, saving computer time and memory in multi-cell simulations. This approximation can appropriately be used by species such as alkyl and alkoxy radicals that always react rapidly with O_2 or have rapid unimolecular reactions, and is implicitly used when a radical is removed in the model by replacing it with the compound(s) it forms. However, experience has shown that it cannot be used for peroxy or NO_3 radicals, since their loss processes can become slow compared to their rates of change under low NO_x conditions or at nighttime. In addition because of limitations in the mechanism compiling software used in this work [and also implemented in the FCM version of the UAM (Kumar et al, 1995) and the CALGRID model], the steady state approximation cannot be used for species that react with themselves or other steady state species, or whose instantaneous concentrations cannot be calculated from the active species concentrations in a stepwise manner (Carter, 1988). Because of the latter restriction, the steady state approximation cannot be used for OH radicals when the mechanism is implemented with this software, though probably it is not a bad approximation for this species.

1. Inorganic Radicals

Most of the inorganic radicals in the mechanism are represented explicitly, as shown on Table A-1. The two exceptions are H atoms and $HOSO_2$ radicals, where the latter is formed in the reaction of OH with SO_2 . H atoms are assumed to react exclusively and rapidly with O_2 to form HO_2 , so any reaction that forms H atoms is represented as forming HO_2 instead. Likewise, $HOSO_2$ are assumed to react primarily with O_2 to form HO_2 and SO_3 , so it is replaced by the HO_2 and sulfate (SULF) model species in the OH + SO_2 reaction. Table A-1 indicates those radicals for which the steady state approximation can be used. Note that this approximation should not be used for HO_2 or NO_3 radicals because they may build up significantly in concentration at nighttime or in the absence of NO_x . It probably could be used for OH radicals, but is not because of limitations of software used to implement the mechanism, as indicated above.

2. Rapidly Reacting Radicals.

As with the previous versions of the mechanism, many rapidly reacting radicals are removed from the mechanism by replacing them by the species they are assumed to rapidly form. Note that this can only be done for radicals where (1) the steady state approximation is appropriate, (2) the product(s) they ultimately form do not depend on any other reactants, and (3) the products they form also do not depend on reaction conditions (e.g., temperature) or the variation can be assumed to be insignificant for the conditions of the model application. The specific types of rapidly reacting radical substitution reactions used in this mechanism are as follows. Except as indicated, the substitution is due to an expected rapid reaction of the radical with O_2 .

- HCO is replaced by $HO_2 + CO$.
- Based on product data for reactions of OH radicals with alcohols and other species, α -Hydroxy alkyl radicals are assumed to react with O_2 primarily by abstraction from the α -hydroxy rather than by addition. Therefore, such radicals are replaced by $HO_2 +$ the corresponding carbonyl compound formed when it reacts with O_2 . For example, $CH_3CH(\cdot)OH$ is replaced by $CCHO + HO_2$, where CCHO is the model species for acetaldehyde.
- α -Nitrate alkyl radicals are assumed to decompose unimolecularly to $NO_2 +$ the corresponding carbonyl compound sufficiently rapidly that the decomposition will dominate over reaction with O_2 . Therefore, such radicals are replaced by $NO_2 +$ the corresponding carbonyl compound formed in the decomposition. For example, $CH_3CH(\cdot)NO_2$ is replaced by $CCHO + NO_2$.

- All other carbon-centered radicals, including acyl ($\text{RCO}\cdot$) and alkyl ($\text{R}\cdot$) are assumed to react entirely by O_2 addition. Therefore, these are replaced by the corresponding peroxy radical whenever they are formed.
- With the exception of t-butoxy (model species $\text{TBU-O}\cdot$) and phenoxy (model species $\text{BZ-O}\cdot$) radicals, which are represented explicitly in the mechanism, all alkoxy radicals are replaced by the set of products they are assumed to form when they react under atmospheric conditions. This would include reactions with O_2 and/or unimolecular reactions, as applicable. If the alkoxy radical has more than one reaction pathway that is assumed to be non-negligible, then non-integer stoichiometric coefficients are used for the products, as appropriate. The reactions of alkoxy radicals are discussed in Section III.J.
- The Crigiee biradicals formed in the reactions of O_3 with alkenes are replaced by the set of products they are assumed to form when they react in the atmosphere, which includes stabilization as well as the various decomposition pathways. These reactions are probably temperature and pressure dependent, but since insufficient information is available to estimate these dependences, this is ignored. The reactions of Crigiee biradicals are discussed in the Section III.K.
- Stabilized Crigiee biradicals with α hydrogens are replaced by the corresponding organic acid, on the assumption that their major fate under atmospheric conditions is reaction with H_2O to form the acid. The assumption that reaction with H_2O is the major fate of the biradicals is consistent with the rate constant ratios cited by Atkinson (1997a) for the reactions of HCHO_2 with H_2O , HCHO , CO , and NO_2 . The mechanism for the reactions of stabilized HCHO_2 with water appear to be complex and may involve some formation of H_2O_2 or other peroxides, but based on the discussion of Atkinson (2000) we assume that acid formation is the major fate of the stabilized Crigiee biradicals where this reaction route is possible.

Note that branching ratios for some of the alkoxy radicals and the Crigiee biradicals may be temperature and pressure dependent, and this treatment ignores these dependencies. As discussed in Section III.J, the alkoxy radical branching ratios are estimated for 300°C and 1 atmosphere total pressure, and thus they may not be optimum for simulations of high altitude or extreme temperature conditions. However, it should be pointed out that no other current mechanism represents these temperature and pressure dependences of product branching ratios, and doing so would require a significant increase in the complexity of the mechanism, or would require the model software to support temperature and pressure-varying parameters. Since no information is available concerning the temperature and pressure dependences of Crigiee biradical reactions, any representation of this in the model would be entirely speculative.

3. Explicitly Represented Organic Radicals

Most of the organic radical species are represented either by replacing them with the radicals or products they are expected to exclusively form, or by using the lumped peroxy radical species or “operators” as discussed in the following two sections. However, a few organic radical species are represented explicitly, either because their reactions are sufficiently different that they are not appropriately represented using the other approaches, or because it is believed representing them explicitly will improve the accuracy of the model sufficiently to make the added model species worthwhile. These are briefly discussed below.

Methyl Peroxy Radicals. In the previous mechanism, all peroxy radicals, including methyl peroxy, were represented using the general peroxy radical operators + the products they were expected to

form, as discussed below. In this approach, the same organic products are assumed to be ultimately formed regardless of whether the radical reacts with NO, HO₂, or another peroxy radical. Although, as discussed below, this approach is still used for most of the higher peroxy radicals in this mechanism, in this mechanism methyl peroxy radicals (CH₃OO·) are represented explicitly, using the model species C-O2·. Thus, the appropriate C₁ products are formed when it reacts with HO₂, itself, or other peroxy radicals, which are different than the formaldehyde formed when it reacts with NO. This allows for a more accurate representation of the reactions of at least this peroxy radical and gives this mechanism a level of detail approaching that of the RADM2 (Stockwell et al, 1990) or RACM (Stockwell et al, 1997) mechanisms in the way peroxy radical reactions are treated. As discussed by Carter and Lurmann (1990), the peroxy radical lumping approach used in the RADM2 mechanism appears to be somewhat less approximate than the lumping approach used in the previous SAPRC mechanisms.

Note that the reactions of peroxy radicals with NO₃ were not in the previous version of the mechanism. This reaction, which may be non-negligible at nighttime, was added based on the recommendations of the current evaluations (Atkinson et al, 1997).

Acyl Peroxy Radicals. The previous mechanism used separate steady-state model species to represent acyl peroxy radicals (CCO-O2·), general lumped higher acyl peroxy radicals (C2CO-O2·), and the higher peroxy radicals formed from glyoxal (HCOCO-O2·) and benzaldehyde (BZCO-O2·). In addition, the model species (RCO3·) was used to compute the total concentration without using the steady state approximation, for the purpose of computing peroxy + peroxy reaction rates. The PAN analogues for these radicals (PAN, PPN, GPAN, and BZ-PAN) were also included in the mechanism as active species. In this mechanism, the acyl peroxy radical formed from glyoxal (and its PAN analogue) are removed by lumping them with the other higher general lumped peroxy radicals (or PAN analogues), the acyl peroxy radical (and PAN analogue) formed from methacrolein and other isoprene products are added, and the total acyl peroxy radical model species (RCO3·) is removed. The need for RCO3· is eliminated by treating all the acyl peroxy radical model species as active, and including all their cross reactions. Although this requires more reactions and active species in the mechanism than the approach used previously, it gives a somewhat more accurate representation of the peroxy + peroxy reactions of these species, which can be important at nighttime, and eliminates the need to include a separate total peroxy radical operator as a co-product in every reaction forming such radicals.

t-Butoxy Radicals. As indicated above, most alkoxy radicals are not represented explicitly in the mechanism, but are replaced by the set of species they are assumed to form when they react. In the previous mechanism this was the case for all organic alkoxy radicals except for phenoxy (see below), and in particular t-butoxy radicals were assumed to react exclusively by decomposition to acetone and methyl radicals. However, the decomposition of t-butoxy is believed to be relatively slow (see Table A-2), and if NO₂ levels are sufficiently high then reaction with NO₂ may be non-negligible in high-NO_x scenarios or chamber experiments. The reaction of t-butoxy with NO₂ had to be included for the model to appropriately simulate results of incremental reactivity chamber experiments with isobutane (Carter et al, 1993a). Because the competition between decomposition and NO₂ depends on the NO₂ concentration, this requires that t-butoxy radicals be represented explicitly in the model. This is not necessary for most other alkoxy radicals, which can either react sufficiently rapidly with O₂, or have sufficiently rapid decomposition or isomerization pathways, that reaction with NO₂ can be neglected.

Phenoxy Radicals. Phenoxy radicals are represented explicitly in this and the previous mechanism because they are not expected to react with O₂ and have no known rapid decomposition pathway. In the presence of NO_x, the major fate of phenoxy radicals is believed to be reaction with NO₂, since it has no obvious unimolecular reaction route or mechanism for reaction with O₂. (Reaction with

NO would be expected to form a nitrite that would rapidly photolyze to re-form NO and phenoxy.) Nitrophenol formation has generally been assumed in this reaction (e.g., see Atkinson, 1990; Carter, 1990), presumably via some rearrangement of an initially formed unstable adduct. However, based on lower than expected yields of Nitrophenol in NO_3 + cresol and OH + benzaldehyde systems (Atkinson, 1994), this may be an oversimplification. In the absence of NO_x , the major fate of phenoxy is assumed to be reaction with HO_2 , though the model also includes a slow unimolecular loss to account for situations where NO_2 or HO_2 may be low. Note that the phenoxy radical model species is used as a surrogate for substituted phenoxy radicals as well, except for lumped nitro-substituted phenoxy radicals, discussed below.

Nitro-Phenoxy Radicals. Although their reaction mechanisms are assumed to be the same as phenoxy radicals, the NO_2 -substituted phenoxy radicals assumed to be formed from the reactions of NO_3 with phenols are represented separately. This is done to account for nitrogen balance, and because the dinitroaromatics expected to be formed in the reaction with NO_2 are expected to be either non-volatile or non-reactive, and are thus represented in the model as "lost nitrogen". This is the same representation as used in the previous mechanisms.

Formaldehyde + HO_2 Intermediate. The radical believed to be formed when HO_2 reacts with formaldehyde has to be represented explicitly because its subsequent fate is believed to be affected by NO levels, as shown on Table A-2. The mechanism used is based on the IUPAC (Atkinson et al, 1999) recommendation, and is essentially the same as used in the previous mechanism.

4. Peroxy Radical Operators

Representation of peroxy radical reactions in mechanisms is complicated by the fact that a relatively large number of such radicals are formed even in condensed mechanisms, and they can react to a non-negligible extent with themselves and other peroxy radicals under some conditions. The approach employed in the Carter (1990) mechanism is to represent organic peroxy radicals with the set of products they would ultimately form if they reacted fully in the presence of NO_x and sunlight, together with a set of chemical "operators" that represent their other effects on the system. A total peroxy radical operator ($\text{RO}_2\cdot$) is used to compute the total peroxy radical concentrations for the purpose of computing peroxy + peroxy radical reaction rates; this allows the steady-state approximation to be used for the other peroxy radical operators.

The approach used in this mechanism is similar, except that as indicated above it is not used for methyl peroxy which is now represented explicitly, and also the total peroxy radical species ($\text{RO}_2\cdot$) is eliminated. Instead of the latter, all the peroxy radical operators are treated as active species, and the cross-reactions between the operators are included. The elimination of $\text{RO}_2\cdot$ simplifies the representation of peroxy radical chemistry and reduces the total number of species in the mechanism, though at the expense of having a somewhat larger number of active species and peroxy + peroxy radical cross reactions. The number of peroxy radical operators used to represent organic nitrate formation was reduced to reduce the number of species and cross-reactions. The peroxy radical operators employed in this mechanism are summarized below.

$\text{RO}_2\text{-R}\cdot$. This operator represents the effect of peroxy radical reactions that ultimately cause one NO to NO_2 conversion and formation of HO_2 when they react with NO. It is representing as having zero carbons. When this operator reacts with HO_2 , it is represented as forming ROOH , the lumped higher hydroperoxide species. Unlike the previous mechanism (Carter, 1990), which used a zero-carbon lumped hydroperoxide operator ($-\text{OOH}$) to represent the effect of hydroperoxide photolysis to form radicals, in this mechanism the higher hydroperoxides are represented by a model species whose reactions are based

on those estimated for n-propyl hydroperoxide. In other words, a lumped molecule⁴ approach is used rather than the lumped structure approach. Since the organic portion of the radicals is already represented by the products formed if the radical reacted with NO (which is why the RO₂-R· operators are zero carbon species), formation of the ROOH in the HO₂ reaction does not conserve carbon. To account for this, loss of three “lost carbon” (XC) species are included in this reaction to maintain carbon balance. Although this may appear to be a worse approximation than using a zero-carbon lumped structure species such as the -OOH in the previous mechanism, for most radicals, carbon is lost in the model when the peroxy reacts with NO (because of the use of relatively small products to represent most of the lumped products), so this tends to work towards compensating for that effect. Tracing the “lost carbon” (XC) levels in the model can be used to track the extent to which carbon is lost due to the way the product species are represented.

When this operator reacts with explicitly the represented radical species [i.e., NO₃, methyl peroxy, or any of the acyl peroxy species] the products formed are the same as would be formed if ethyl peroxy (CH₃CH₂OO·) reacted with those species, except that any C₂ organic products (acetaldehyde or ethanol) are removed, and if ethoxy radicals are formed, they are replaced by HO₂ (based on the fact that ethoxy can be represented as rapidly forming acetaldehyde + HO₂, with acetaldehyde removed). In other words, since the RO₂-R· does not represent the organic portions of the peroxy radicals, the organic products formed in its reactions are ignored. Note that it is assumed that in RO₂· + RO₂· reactions that formation of 2 RO· + O₂ and disproportionation to an alcohol + a carbonyl + O₂ occur with equal probability, based on available data for higher peroxy radicals (Atkinson et al, 1999). In the case of reaction of methyl peroxy, it is assumed that the disproportionation forming methanol and that forming formaldehyde occur with equal probability.

R2O2·. This represents the effects of extra NO to NO₂ conversions caused by multi-step reaction mechanisms, as would occur, for example, in mechanisms involving alkoxy radical decompositions or isomerizations. Again, R2O2· is used so the model can account for the formation of RO₂, and [R2O2] is used for the actual reactions of the operator. Unlike the RO₂-R· and the other peroxy operators, this is not strictly speaking a radical species, and it is not represented as having any effect on the system except when it reacts with NO. This is because it does not react to form radical or radical sink species, and is only appropriately used in conjunction with RO₂-R.

RO₂-N·. This represents the reactions of peroxy radicals with NO to form organic nitrates of various types, which are all represented in the model by the 6-carbon lumped alkyl nitrate model species RNO₃ (see Section C.2). Note that in previous versions of the mechanisms two additional operators were used to represent these processes. RO₂-XN· was used to represent peroxy radicals that reacted with NO to form relatively unreactive C₃ nitrates, and RO₂-XN· was used to represent aromatic peroxy radicals that reacted with NO to form aromatic nitrates. In this mechanism RO₂-XN· was removed because the amount of C₃ nitrate formation tends to be extremely small, and RO₂-NP· was removed because nitrate formation is assumed to be relatively minor for most aromatics. In addition, the reactions of the aromatic nitrates formed are so uncertain that representing them separately may not necessarily be any more accurate than lumping them with RNO₃.

Since the RO₂-N· operator is used to represent the organic nitrates formed when the peroxy radicals react with NO, it is represented as having the number of carbons of the nitrate it forms when it reacts with NO, and its reactions with species other than NO are based on this representation. The

⁴ The “lumped molecule” approach refers to representing a compound in the model by another compound, on a mole for mole basis. See Section VI.A.1.

products are derived based on what is considered to be appropriate for a C₆₊ alkyl peroxy radical, since those tend to be the radicals that are the largest precursors to alkyl nitrates in atmospheric simulations. In addition, since primary radicals tend to be formed in lower relative yields from such higher molecular weight compounds than secondary or tertiary radicals (whose C-H bonds tend to be more labile), the carbonyl products are represented by ketone model species (MEK or PROD2), rather than by aldehydes. The specific products used are indicated in the footnotes to Table A-2 for the various reactions.

RO₂ + RO₂ Reactions. Because the rate constants for peroxy + peroxy radical reactions can vary by orders of magnitude depending on the type of radical (e.g., Atkinson, 1997), the rate constant used for the peroxy + peroxy reactions of the peroxy radical operators must necessarily be very approximate. The value used for all these operators is based roughly on the range of rate constants for secondary peroxy radicals given by Atkinson (1997a) and Atkinson et al (1997), and is 30 times higher than the 1×10^{-15} cm³ molec⁻¹ s⁻¹ value used in the previous mechanism (Carter 1990).

C. Reactions of Common Products

A total of 24 model species are used in this mechanism to represent the reactive organic product species, 11 of which are used for organic compounds that are represented explicitly, and 13 of which are used to represent groups of similar products using the "lumped molecule" approach. In most cases, the model species and mechanisms are not significantly different than in previous versions of the mechanisms, except that some of the rate constants were updated as indicated in footnotes to Table A-2. Most of the updates for the C₃ products are based on IUPAC (Atkinson et al, 1997, 1999) recommendations. The species used are summarized below.

1. Explicitly Represented and Lumped Molecule Products

Formaldehyde (HCHO) and Acetaldehyde (CCHO). The mechanisms for these two compounds are essentially the same as in the previous mechanism, except that some of the rate constants and absorption cross sections have been updated as recommended by IUPAC (Atkinson et al, 1997, 1999). Note that this mechanism differs from most condensed mechanisms in that acetaldehyde is represented explicitly, with most higher aldehydes lumped with propionaldehyde, as discussed below. The one exception is glycolaldehyde (HOCH₂CHO), which is expected to have a reactivity closer to acetaldehyde than propionaldehyde, and therefore is represented by acetaldehyde in this mechanism.

Propionaldehyde and Lumped Higher Aldehydes (RCHO). The reactions of the model species RCHO, which represents all C₃₊ aldehydes except α -dicarbonyls, aromatic aldehydes, and acroleins, is based on the expected mechanism for propionaldehyde. Note that, based on structure-reactivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996), approximately 4% of the reaction with OH radicals is estimated to occur by abstraction from the CH₂ group and ~1% at the methyl. The reactions of the radicals subsequently formed are derived using the general mechanism estimation methods, as discussed below. However, most of the OH reaction is analogous to the reaction of OH with acetaldehyde, forming RCO-O₂·, the lumped higher acyl peroxy radical. The NO₃ and photolysis reactions are also assumed to be analogous to those for acetaldehyde, though a slightly higher NO₃ radical rate constant is assumed (based on the somewhat higher OH rate constant), and absorption cross sections and quantum yields specific to propionaldehyde are used.

Acetone (ACET). Acetone is represented explicitly because its reactivity is significantly lower than that for other ketones, yet is sufficiently reactive that its reactions are probably not negligible in long-range transport scenarios. Its mechanism is based on that discussed by Carter et al (1993b). Based on

the data of Jenkin et al (1993), the $\text{CH}_3\text{COCH}_2\text{O}\cdot$ radical is believed to primarily decompose to formaldehyde and $\text{CH}_3\text{CO}\cdot$. The absorption cross sections and quantum yields are based on the IUPAC (Atkinson et al, 1997), except that the reported quantum yields at 230 and 330 nm are believed to be high, and were corrected as discussed by Carter et al (1993b) and the footnotes to the acetone photolysis reaction on Table A-2.

Methyl Ethyl Ketone and Lumped Lower Reactivity Ketones (MEK). This model species is used to represent ketones and other reactive oxygenated product species whose OH radical rate constant is between 5×10^{-13} and $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. Note that this is different from previous versions of the SAPRC mechanism, where MEK was used for all higher non-aldehyde, non-aromatic oxygenated products that were more reactive than acetone. The MEK mechanism is based on that derived for methyl ethyl ketone using the general mechanism estimation methods discussed below, the IUPAC recommended OH rate constant (Atkinson et al, 1999) and absorption cross sections provided by Moortgat (private communication, 1996). The overall photolysis quantum yield of 15% was derived by fits to MEK - NO_x and MEK incremental reactivity environmental chamber experiments carried out in our laboratories (see Section V and Carter et al, 2000a), and is somewhat higher than the ~10% overall quantum yield derived previously based on fits to a few UNC outdoor chamber experiments (Carter, 1990; Carter and Lurmann, 1991).

Methanol (MEOH). In previous SAPRC mechanisms methanol in emissions was represented as an assigned parameter detailed model species, which permitted it to be represented explicitly or lumped with other compounds, depending on the model application. However, this approach does not permit representing formation of methanol as a reaction product. In this mechanism methanol is assigned an explicit model species in order to permit its formation of a product in no- NO_x reactions of methyl peroxy reaction. These reactions, and the subsequent reactions of methanol so formed, may be non-negligible in some long-range transport scenarios. Since methanol is potentially important in emissions, many model applications would probably use a separate model species for it in any case. Indeed, methanol is now represented explicitly even in some condensed models such as expanded Carbon Bond IV (e.g., Carter, 1994b and references therein). The mechanism is based on IUPAC (Atkinson et al, 1997, 1999) recommendations.

Methyl Hydroperoxide (COOH) and Lumped Higher Peroxides (ROOH). In previous SAPRC mechanisms, the hydroperoxide species formed in peroxy + HO_2 reactions were represented by a single "lumped structure" model species "-OOH", combined with the organic products formed in the peroxy + NO reactions. In this mechanism, for more accurate representation of low- NO_x chemistry, for regional or long-range transport simulations, methyl hydroperoxide is represented explicitly, and the other hydroperoxides are represented using a separate model species (ROOH) using the "lumped molecule" approach. In the case of methyl hydroperoxide, the OH reaction is assumed to occur at both the methyl and OOH positions as recommended by IUPAC (Atkinson et al, 1997, 1999), with the $\cdot\text{CH}_2\text{OOH}$ radical formed in the former reaction being assumed to rapidly decompose to formaldehyde + OH. The absorption cross sections are also based on IUPAC recommendations, with unit quantum yields assumed, and with the reaction assuming to proceed entirely by breaking the weak O-O bond.

The reactions of the lumped higher hydroperoxide (ROOH) are based on the estimated mechanism for n-propyl hydroperoxide. As discussed in footnotes to Table A-2 in Table A-4, the OH reaction is estimated to occur at the OOH group ~2/3 of the time, based on assuming the same rate constant as the same reaction of methyl hydroperoxide. Most of the remainder of the reaction is assumed to occur at the 1-position, yielding an α -hydroperoxy radical which is assumed to rapidly decompose to

propionaldehyde (RCHO) and OH. The photolysis is assumed to have the same rate and an analogous mechanism as methyl hydroperoxide.

Glyoxal (GLY). Glyoxal, which is formed in the reactions of most aromatics, acetylene, and some other species [including some isoprene oxidation products (Carter and Atkinson, 1996)], continues to be represented explicitly in this mechanism. Since it is less reactive than some other aromatic products it is often not represented in condensed mechanisms, but it is known to make an important contribution to the reactivity of acetylene (Carter et al, 1997c) and benzene (see Section IV.A.1) and its reactivity is not well approximated by other model species. On the hand, this mechanism is somewhat more condensed than previous detailed SAPRC mechanisms in that the acyl peroxy radical and PAN analogue predicted to be formed from the OH + glyoxal reaction [$\text{HCO}(\text{CO})\text{OO}\cdot$ and $\text{HCO}(\text{CO})\text{OONO}_2$] are not represented explicitly, but are lumped with RCO-O \cdot and PAN2 (see below). The mechanism for the OH reaction is based on the data of Niki et al (1985) as discussed by IUPAC (Atkinson et al, 1997).

The glyoxal absorption cross sections were the same as used previously (Plum et al, 1983), as recommended by the IUPAC evaluation (Atkinson et al, 1997). However, the quantum yields were significantly revised based modeling of acetylene - NO $_x$ and acetylene reactivity environmental chamber data (Carter et al, 1997c), as discussed in the footnotes to Table A-2 in Table A-4. The model simulations of those chamber experiments were found to be highly sensitive to glyoxal absorption cross sections used in the mechanism, and no other reasonable adjustments to the mechanism would yield acceptable fits to the data (Carter et al, 1997c). Note that to fit the data quantum yields which are ~1.4 times higher than overall quantum yield reported by Plum et al (1983) for conditions of those experiments must be used. Although use of acetylene reactivity data is a highly indirect way to obtain glyoxal quantum yields, we consider it to be a less uncertain way to estimate radical quantum yields than the data of Plum et al (1993), which uses a UV-poor light source, and only measures rates of glyoxal decay. Clearly this is uncertain and direct measurements of glyoxal quantum yields as a function of wavelength are needed.

Methyl Glyoxal (MGLY) and Other Higher α -dicarbonyl aldehydes. Methyl glyoxal is formed in the reactions of methylbenzenes and from some carbonyl compounds. Because of its high reactivity, its formation can significantly affect the reactivity of compounds that form it. The MGLY model species is also used to represent other α -dicarbonyl aldehydes, such as ethylglyoxal, etc. However, unlike the SAPRC-97 mechanism of Carter et al (1997a), but like earlier versions of the mechanism (Carter, 1990, 1995; Carter et al, 1993b), it is not used in this version of the mechanism to represent any of the uncharacterized aromatic ring fragmentation products (see discussion of unknown aromatic fragmentation products, below). The mechanism for the OH and NO $_3$ reactions are similar to those in the previous mechanism, with the latter reaction assumed to have the same rate constant and analogous mechanism as for acetaldehyde.

The IUPAC recommended (Atkinson et al, 1997, 1999) absorption cross sections for methyl glyoxal are approximately a factor of 2 higher than the Plum et al (1983) values used in the previous mechanism. The current mechanism uses cross sections obtained from Moortgat (personal communication, 1996), which are consistent with the IUPAC recommendations but have higher resolution. Unit quantum yields were assumed in the low wavelength band ($\lambda \leq 340$ nm) and zero quantum yields were assumed for wavelengths above the cutoff of 421 nm, as determined by the thermochemistry. For the rest of the high wavelength regime, the quantum yield was assumed to decline linearly from unity at 344 nm to zero at a wavelength (407 nm) that was adjusted such that the calculated overall photolysis rates under the conditions of the experiments of Plum et al (1983) agreed with the experimentally measured values. (An analogous treatment was used in when deriving the quantum yields for glyoxal and biacetyl, though in the glyoxal case the adjustment was to fit the acetylene chamber data,

as indicated above.) Note that this gives a different wavelength dependence than assumed in the previous mechanism, where a wavelength-dependent overall quantum yield was assumed for the entire high-wavelength band, including wavelengths above the high wavelength cutoff.

Biacetyl (BACL) and Other α -Dicarbonyl Ketones. Biacetyl or other α -dicarbonyl ketones are formed in significant yields from p-xylene, 1,2,4-trimethylbenzene and other o-dimethyl aromatics, and might be formed from the reactions of some carbonyl compounds. Biacetyl was not represented in previous versions of the mechanism, being in effect represented by methyl glyoxal. However, because its chemistry is in some ways quite different from methyl glyoxal (it reacts only slowly with OH, and its photolysis forms only PAN precursors), it was decided to represent it explicitly in this mechanism. The BACL model species is also used for other α -dicarbonyl ketones.

The reaction of biacetyl with OH radicals is ignored because the OH + biacetyl rate constant is probably not much different than that for acetone, making it a negligible loss process compared to photolysis. The photolysis is assumed to proceed via breaking the weak CO-CO bond, as shown on Table A-2. The absorption cross sections used were those from Plum et al (1983), and the wavelength-dependence of the quantum yields were derived from the data of Plum et al (1983) in a manner exactly analogous to that discussed above for methyl glyoxal (see footnotes to Table A-2 in Table A-4).

Phenol (PHEN) and Cresols (CRES). Cresols are formed in the reactions of the substituted aromatics, and phenol is formed from the reactions of benzene. In addition, phenol is represented as being formed in the subsequent reactions of aromatic ring-retaining products such as cresols or benzaldehydes. Cresol is used to represent phenolic products formed from all alkyl-substituted benzenes, while phenol is used to represent such products formed from benzene and naphthalene, as well as phenolic products formed in secondary reactions of cresols. The relatively rapid reactions of these compounds with NO_3 represents a NO_x sink in the aromatic mechanisms that largely explains their predicted tendency to inhibit O_3 under low NO_x conditions. Therefore, it is important that these model species be in the mechanism. They are kept as separate model species because the reactions of cresols are assumed to involve some PAN (or PAN analogue) formation, while this is assumed not to be the case for phenol.

There are still inadequate data concerning the atmospheric reactions of these compounds and the products they form, and the highly parameterized mechanisms used in the previous versions of the SAPRC mechanisms are essentially unchanged in this version. The main consumption reactions are with OH and NO_3 , and the rate constants used are those recommended by Atkinson (1994). The OH + cresol mechanism is based on the highly parameterized mechanism derived by Carter (1990), but the version for this mechanism was reoptimized to fit the data from the single o-cresol - NO_x chamber experiment EC281 (Pitts et al, 1979; Carter et al, 1995d). The OH + phenol mechanism was derived by analogy with the resulting cresol mechanism. The NO_3 reactions are assumed to proceed via the formation of phenoxy radicals + HNO_3 , with the BZ-O \cdot model species used for substituted as well as unsubstituted radicals. The BZ-O \cdot then reacts as discussed above in Section B.3. Note that although the mechanism for the NO_3 reaction (like that for the reaction with OH) is highly uncertain, it clearly must involve some sort of NO_x sink process in order for model simulations to fit chamber data for aromatics.

Nitrophenols (NPHE). The "nitrophenol" model species is used to represent whatever products are formed when phenoxy reacts with NO_2 , which as indicated above is uncertain. It is assumed that the NO_2 -substitution slows down the rate of reaction with OH radicals, and that its only significant consumption process is reaction with NO_3 , for which it is assumed to have the same rate constant as phenol. This representation is unchanged from previous versions of the mechanism. Obviously this aspect of the mechanism is uncertain, but this representation appears to perform reasonably well in simulating

effects of aromatics on peak O₃ yields, which are determined by NO_x-sink processes that are represented by the formation and reactions of NPHE.

Benzaldehyde (BALD) and Other Aromatic Aldehydes. Benzaldehyde, tolualdehydes and other aromatic aldehydes that are formed in a minor but non-negligible route in the reactions of OH with methylbenzenes are represented by the benzaldehyde (BALD) model species. Its OH and NO₃ reactions are assumed to be analogous to other aldehydes, except that separate model species (BZCO-O₂· and BZ-PAN) are used to represent the acyl peroxy radical and PAN analogue formed. This is necessary because the reaction of the benzoyl peroxy radical with NO forms phenoxy radicals, and the subsequent reactions of phenoxy radicals are not believed to regenerate radicals, unlike the subsequent reactions of the radicals formed when the other acyl peroxy radicals react with NO.

The absorption cross sections for benzaldehyde (Majer et al, 1969) indicate that its photolysis can be significant if the quantum yield is sufficiently high. The quantum yields are unknown, but chamber data indicates that it is probably consumed to a non-negligible by photolysis, though the overall quantum yield is relatively low and the photolysis apparently does not involve significant radical formation. The overall quantum yield derived by Carter (1990) to fit SAPRC evacuable chamber data (Pitts et al, 1979) is retained in this mechanism. It was found to give reasonably good model simulations of benzaldehyde - NO_x experiments carried out in the CE-CERT Xenon Teflon Chamber (Carter et al, 1998a).

Methacrolein (METHACRO) and Methyl Vinyl Ketone (MVK). This version of the mechanism incorporates the “four product” isoprene mechanism (Carter, 1996) as part of the base mechanism, so it includes model species for methacrolein, MVK, and the lumped other isoprene products (ISOPROD). The mechanisms used for methacrolein and MVK are essentially the same as derived by Carter and Atkinson (1996), with some minor updates as indicated in footnotes to Table A-2 in Table A-4. The mechanisms were generated using the mechanism generation system discussed in Section III, which incorporated most of the estimates and assignments of Carter and Atkinson (1996) for the reactions specific to the isoprene and isoprene product system. The use of the mechanism generation system resulted in some minor changes to yields of minor product in some reactions. In addition, because of these changes and changes to the overall base mechanism, the overall quantum yields for the methacrolein MVK photolysis were reoptimized, using the same procedures and data as discussed by Carter and Atkinson (1996). This resulted the overall quantum yield for methacrolein being increased by ~14%, while that for MVK was reduced by over a factor of ~5. The reason for this large change in the optimized MVK quantum yield is not clear, but it may be due to a relatively low sensitivity of model simulation results to large changes in this parameter. (See Section V and Appendix B for results of model simulations of the methacrolein and MVK experiments.)

Methacrolein is also used to represent acrolein in reactions where acrolein is predicted to be formed as a product. This is to avoid adding a new model species to represent a relatively minor product in most ambient mixtures. However, as discussed later and shown on Table A-6, acrolein can be represented explicitly for the purpose of assessing the reactivities of acrolein or VOCs that form acrolein as a major product.

Lumped Isoprene Products (ISOPROD). The ISOPROD model species is used to represent reactive isoprene products other than methacrolein and MVK, and also to represent other unsaturated ketones or aldehydes (other than acrolein itself, which is represented by methacrolein) when formed in reactions of other VOCs. Its mechanism is based on the ISOPROD model species in the “four product” isoprene mechanism of Carter (1996), with some minor modifications as indicated in footnotes to Table A-2 in Table A-4. Its mechanism is derived from weighted averages of rate constants and parameters for a

mixture of 30% hydroxymethacrolein and 23% each cis-HCOC(CH₃)-CHCH₂OH, trans-HCOC(CH₃)-CHCH₂OH, and HCOCH=C(CH₃)CH₂OH. As with methacrolein and MVK, the mechanisms for these species were derived using the mechanism generation system discussed in Section III, incorporating estimates and assignments of Carter and Atkinson (1996) where applicable.

2. Lumped Parameter Products

“Lumped parameter” species refer to model species whose mechanisms are derived by averaging rate constants and product yield parameters from a representative mixture of compounds that they are designed to represent. Although the previous versions of the SAPRC mechanism used this approach only for model species representing emitted VOCs, this mechanism also uses this approach for two of the lumped organic product species, as discussed below.

Lumped Higher Reactivity Non-Aldehyde Oxygenates (PROD2). This model species, which is new to this version of the mechanism, is used to represent ketones, alcohols, and other reactive non-aromatic and non-double-bond-containing oxygenated products whose rate constants are greater than $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. This was added because it was judged that many of the bi- or polyfunctional product species that were previously represented by MEK when they were formed as products are in fact much more reactive than MEK, at least in terms of their reaction rate with OH radicals. The reaction mechanism of PROD2 is based on averaging mechanisms derived for a representative set of product species as discussed below.

Lumped Organic Nitrate Products (RNO3). This model species is used to represent various organic nitrates (other than PAN or PAN analogues), primarily those formed in the reactions of peroxy radicals from NO. This is consumed primarily by reaction with OH radicals, but a slow photolysis, which may be non-negligible in long-range transport simulations, is also included in the mechanism. Unlike previous SAPRC mechanisms, RNO3 is also used to represent those species formed from aromatic peroxy radicals with NO; previously the nitrophenol (NPHE) model species was used for this purpose. As indicated above, this change was made to avoid having to add the separate peroxy radical “operator” needed to support separate representation of aromatic nitrates, which are formed in relatively low yields and for which the appropriateness of the NPHE vs the RNO3 representation is unknown. The reaction mechanism of RNO3 is based on averaging mechanisms derived for a representative set of product species as discussed below.

Derivation of PROD2 and RNO3 Mechanisms. Although in principle the mechanisms for the lumped parameter product species can be derived for each emissions inventory in the manner used for the lumped parameter model species used for emitted VOCs (see Section III.A), the necessary software to do this has not yet been developed. Instead, in this version of the mechanism the parameters are derived from sets of representative species representing products predicted to be formed from the reactions of the mixture of VOCs used as the “Base ROG” mixture in the atmospheric reactivity calculations (Carter, 1994a; see also Section VII.A.1), and are held fixed in the model simulations. The Base ROG mixture is used to represent reactive VOCs from all sources, and is derived from the “all city average” mixture derived by Jeffries et al (1989) from analysis of air quality data, with minor modifications as discussed by Carter (1994a,b)⁵. For the purpose of determining the contributions of the reactions of the compounds in the mixture to the formation of a lumped product, the contribution of each emitted VOC is weighed by the amount of each VOC that is estimated to react in a one-day scenario, multiplied by the yield of the

⁵ The complete mixture, indicating the specific detailed model species used to represent it in the model, is given in Table 50. See also Carter (1994b).

lumped product used in the model for the reactions of the VOC. The amount reacted is obtained from the amount emitted multiplied by the “mechanistic reactivity” (Carter and Atkinson, 1989a; Carter, 1994a), which is the fraction of the VOC estimated to react. The latter is obtained from mechanistic reactivities in the “averaged conditions” scenario where the NO_x inputs are adjusted to yield maximum peak ozone concentrations (the “MOIR” scenario)⁶ (Carter, 1994a). Table 1 and Table 2 show the contributions of the reactions of various types of VOCs in the base ROG mixture to the formation of the RNO3 and PROD2 model species.

The set of compound that are represented by various model species can be calculated for those model species whose mechanisms can be derived using the mechanism generation/estimation system that is discussed in Section III. For each of these compounds, the system generates the set of products that are predicted to be formed using a fully explicit mechanism for the reactions in the presence of NO_x, which are then used, together with the “lumping rules” discussed in Section III.K.5, to determine the lumped product yields for the model. From this, the distribution of individual product VOCs represented by each lumped product model species can be determined, at least for the reactions of the VOCs whose mechanisms can be generated using this system. Although this system cannot generate mechanisms for aromatic compounds and terpenes, for which parameterized mechanisms must still be used, Table 1 and Table 2 show that their contributions to PROD2 or RNO3 formation from the base ROG mixture are minor. In particular, reactions of aromatics and terpenes account for less than 6% of the PROD2 formation, and for less than 5% of the formation of RNO3 in one-day scenarios.

Table 3 and Table 4 show the 35 most important products predicted to be formed from the reactions of the VOCs in the base ROG mixture that are represented by PROD2 (Table 3) or RNO3 (Table 4). The tables also show the contribution of each product to the total of all products represented by PROD2 or RNO3, their OH radical rate constant and carbon numbers, and the average OH rate constant and carbon number for all the products, weighed by their molar contribution to the total. Note that no single compound dominates the lists, and in the case of the organic nitrates the top 35 compounds account for less than half of the products formed that are represented by RNO3. Therefore, in both cases there is no obvious choice of a single “representative” or “typical” compound to use for lumped molecule representations.

In the case of PROD2, the average OH radical rate constant is $1.5 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, and the average carbon number is slightly over 7. For the purpose of deriving a PROD2 mechanism in the model, five individual compounds, indicated by being underlined on Table 3, were chosen as being representative of the entire set. The choice was largely subjective, but was made such that the average OH rate constant and the average number of carbons was approximately the same as the average, and so they included examples of different types of compounds on the list. For each of these five compounds the reaction mechanism with ·OH and photolysis was generated using the mechanism estimation/generation procedure discussed in Section III, and the PROD2 parameters were derived by averaging the values obtained, weighing each of the five compounds equally⁷. Since most of these compounds are ketones, the ketone absorption cross sections and the quantum yields assumed to be appropriate for ketones with 7 carbons

⁶ The MOIR mechanistic reactivities are used because they are typical mechanistic reactivities in a wide range of scenarios. MIR mechanistic reactivities tend to be lower than in other scenarios because the relatively high NO_x levels tend to suppress radical levels.

⁷ The mechanisms derived for these representative individual compounds are included with the mechanism listings for the detailed model species, given in Section VI. The detailed model species names assigned to them are indicated on Table 3 or Table 4.

(see Section III.G.1) were used for the photolysis reactions. The mechanisms derived for these representative individual compounds are included with the mechanism listings for the detailed model

Table 1. Contributions of various types of model species in the base ROG mixture to the formation of the PROD2 lumped product species.

VOC	Cont'n	VOC	Cont'n	VOC	Cont'n	VOC	Cont'n
N-C5	14.5%	4-ME-C7	2.9%	1-C9E	1.0%	3-ME-C11	0.3%
N-C10	8.1%	1-HEPTEN	2.7%	24-DM-C5	0.9%	26DM-C9	0.2%
N-C6	6.2%	24-DM-C7	2.5%	3-ME-C6	0.9%	ME-CYCC6	0.2%
N-C7	5.8%	3-ME-C6	2.2%	1-HEXENE	0.8%	1-C10E	0.2%
<u>Aromatics</u>	<u>5.2%</u>	2-ME-C6	1.9%	N-C11	0.7%	4-ME-C10	0.2%
1-HEXENE	5.0%	4-ME-C8	1.9%	3-ME-C5	0.6%	3-ME-C10	0.2%
24-DM-C6	4.5%	2-ME-C8	1.8%	36DM-C10	0.6%	1-PENTEN	0.1%
2-ME-C7	4.2%	26DM-C8	1.7%	24-DM-C5	0.5%	23-DM-C5	0.1%
2-ME-C5	3.6%	4-ME-C9	1.6%	1-OCTENE	0.5%	1-PENTEN	0.1%
N-C8	3.5%	2-ME-C9	1.6%	ET-CYCC6	0.4%	N-C13	0.1%
N-C9	3.4%	N-C12	1.4%	1-C11E	0.3%	2-ME-C5	0.1%
CYCC6	3.0%	ME-CYCC6	1.1%	5-ME-C11	0.3%	3M-1-BUT	0.0%

Table 2. Contributions of various types of model species in the base ROG mixture to the formation of the RNO3 lumped product species.

VOC	Cont'n	VOC	Cont'n	VOC	Cont'n	VOC	Cont'n
2-ME-C4	7.7%	23-DM-C5	1.6%	N-C11	0.6%	C-2-BUTE	0.2%
N-C4	5.9%	<u>Terpenes</u>	<u>1.4%</u>	1-C11E	0.5%	1-PENTEN	0.2%
N-C10	5.8%	24-DM-C5	1.3%	ET-CYCC6	0.5%	1-C10E	0.2%
24-DM-C6	4.9%	2-ME-C3	1.3%	2M-1-BUT	0.5%	1-BUTENE	0.2%
N-C5	4.9%	2-ME-C9	1.3%	1-OCTENE	0.5%	1C6RCHO	0.2%
2-ME-C5	4.0%	2-ME-C8	1.3%	T-3-C7E	0.5%	T-2-C7E	0.2%
ME-CYCC5	3.1%	4-ME-C9	1.2%	1-PENTEN	0.4%	13-BUTDE	0.2%
Aromatics	2.7%	4-ME-C8	1.2%	PROPENE	0.4%	3M-1-BUT	0.2%
24-DM-C7	2.5%	1-C9E	1.2%	T-4-C9E	0.4%	T-4-C10E	0.2%
26DM-C8	2.5%	PROPANE	1.2%	T-2-C6E	0.4%	3-ME-C10	0.1%
3-ME-C5	2.4%	N-C12	1.1%	C-2-C6E	0.4%	1C5RCHO	0.1%
2-ME-C7	2.4%	CYCC5	1.0%	T-5-C11E	0.4%	4-ME-C10	0.1%
N-C7	2.4%	2-ME-C6	0.9%	22-DM-C4	0.3%	CYC-HEXE	0.1%
4-ME-C7	2.3%	CYCC6	0.9%	T-2-BUTE	0.3%	MEK	0.1%
3-ME-C6	2.1%	ISOBUTEN	0.9%	ME-CYCC6	0.3%	23-DM-C4	0.1%
N-C9	2.1%	3-ME-C6	0.9%	3-ME-C11	0.3%	2-ME-C5	0.1%
N-C8	1.9%	23-DM-C4	0.9%	5-ME-C11	0.3%	3-ME-C5	0.1%
N-C6	1.8%	C-2-PENT	0.8%	26DM-C9	0.3%	N-C13	0.1%
1-HEPTEN	1.8%	T-2-PENT	0.8%	T-4-C8E	0.3%	36DM-C11	0.0%
ME-CYCC6	1.7%	24-DM-C5	0.7%	2M-2-BUT	0.3%		
1-HEXENE	1.7%	36DM-C10	0.6%	1-HEXENE	0.2%		

Table 3. Product compounds predicted to be formed in the atmospheric reactions of compounds in the base ROG mixture that are represented by the PROD2 model species.

Cont'n [a]	kOH [b]	nC [c]	Model Species [d]	Product Structure [e]
	<u>1.5e-11</u>	<u>7.19</u>		<u>Average of all Products</u>
16.4%	9.6e-12	5	PROD2-1	<u>CH3-CO-CH2-CH2-CH2-OH</u>
6.1%	1.7e-11	6		CH3-CH(OH)-CH2-CH2-CO-CH2-OH
3.8%	1.5e-11	6	PROD2-2	<u>CH3-CO-CH2-CH(CH3)-CH2-OH</u>
3.4%	6.4e-12	6		*CH2-CH2-CH2-CH2-CH2-CO-*
3.1%	1.4e-11	6		CH3-CH(OH)-CH2-CH2-CO-CH3
2.9%	1.1e-11	6		CH3-CH2-CO-CH2-CH2-CH2-OH
2.9%	2.0e-11	7		CH3-CH2-CH(OH)-CH2-CH2-CO-CH2-OH
2.7%	5.5e-12	6		CH3-CO-CH2-C(CH3)(OH)-CH2-OH
2.7%	1.5e-11	7	PROD2-3	<u>CH3-CH(OH)-CH2-CH2-CO-CH2-CH3</u>
2.3%	2.7e-11	5		CH3-CH(OH)-CH2-CO-CH3
2.2%	1.7e-11	7		CH3-CH2-CH(OH)-CH2-CH2-CO-CH3
2.2%	2.3e-11	10		CH3-CH2-CH2-CH(OH)-CH2-CH2-CO-CH2-CH2-CH3
2.1%	2.1e-11	10		CH3-CH2-CH2-CH2-CH(OH)-CH2-CH2-CO-CH2-CH3
2.0%	7.1e-12	8		CH3-C(CH3)(OH)-CH2-CH2-CO-CH2-CH3
1.7%	2.1e-11	10		CH3-CH2-CH2-CH2-CH2-CH(OH)-CH2-CH2-CO-CH3
1.5%	1.9e-11	7		CH3-CH(OH)-CH(CH3)-CH2-CO-CH3
1.3%	2.2e-11	8		CH3-CH2-CH(OH)-CH(CH3)-CH2-CO-CH3
1.3%	1.8e-11	8	PROD2-4	<u>CH3-CH2-CH(OH)-CH2-CH2-CO-CH2-CH3</u>
1.3%	6.0e-12	7		CH3-C(CH3)(OH)-CH2-CH2-CO-CH3
1.3%	2.4e-11	10		CH3-CH2-CH(OH)-CH2-CH2-CO-CH2-CH2-CH2-CH3
1.3%	1.9e-11	8		CH3-CH(OH)-CH2-CH2-CO-CH2-CH2-CH3
1.2%	7.4e-12	8		CH3-C(CH3)(OH)-CH2-CH(CH3)-CO-CH3
1.2%	1.7e-11	8		CH3-CH(OH)-CH2-CH(CH3)-CO-CH2-CH3
1.2%	1.4e-11	7		CH3-CH2-CH2-CO-CH2-CH2-CH2-OH
1.1%	1.6e-11	7		CH3-CH(OH)-CH2-CH(CH3)-CO-CH3
1.1%	1.9e-11	8		CH3-CH2-CH2-CH(OH)-CH2-CH2-CO-CH3
1.1%	2.0e-11	9	PROD2-5	<u>CH3-CH2-CH2-CH(OH)-CH2-CH2-CO-CH2-CH3</u>
1.1%	2.2e-11	9		CH3-CH2-CH(OH)-CH2-CH2-CO-CH2-CH2-CH3
1.0%	1.4e-11	6		CH3-CH(CH3)-CH2-CO-CH3
1.0%	2.3e-11	9		CH3-CH2-CH2-CH2-CH(OH)-CH2-CH2-CO-CH2-OH
1.0%	2.2e-11	10		CH3-CH(OH)-CH2-CH2-CO-CH2-CH2-CH2-CH2-CH3
0.8%	2.0e-11	9		CH3-CH2-CH2-CH2-CH(OH)-CH2-CH2-CO-CH3
0.8%	1.9e-11	8		CH3-CH(CH3)-CH(OH)-CH2-CH2-CO-CH3
0.8%	1.7e-11	7		*CH(CH3)-CH2-CH2-CH2-CO-CH2-*
0.8%	1.7e-11	8		CH3-CH(OH)-CH2-CH2-CO-CH(CH3)-CH3
21.6%				All Others

- [a] Amount of formation of this compound relative to all products represented as PROD2, on a molar basis.
- [b] OH radical rate constant estimated using structure-reactivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996), in units of $\text{cm}^3 \text{molec}^{-1} \text{sec}^{-1}$.
- [c] Number of carbons.
- [d] Detailed model species name used when computing mechanism for compound that was used for deriving PROD2 mechanism for the model.
- [e] Product structure as used in the mechanism generation system. The "*" symbol is used to indicate groups that are bonded in cyclic compounds. Underlined structures are those used to derive the PROD2 mechanism.

Table 4. Product compounds predicted to be formed in the atmospheric reactions of compounds in the base ROG mixture that are represented by the RNO3 model species.

Cont'n [a]	kOH [b]	nC [c]	Model Species [d]	Product Structure [e]
	<u>7.8e-12</u>	<u>6.58</u>		Average of all Products
6.5%	1.6e-12	4	RNO3-1	<u>CH3-CH(ONO2)-CH2-CH3</u>
3.6%	3.0e-12	5		CH3-CH(CH3)-CH(ONO2)-CH3
2.8%	4.2e-13	3		CH3-CH(ONO2)-CH3
2.6%	1.7e-12	5		CH3-C(CH3)(ONO2)-CH2-CH3
2.5%	3.0e-12	5		CH3-CH(ONO2)-CH2-CH2-CH3
1.4%	2.8e-12	5		CH3-CH2-CH(ONO2)-CH2-CH3
1.0%	4.7e-12	6	RNO3-3	<u>CH3-CH(ONO2)-CH(CH3)-CH2-CH3</u>
1.0%	1.2e-11	5	RNO3-2	<u>CH3-CH(OH)-CH2-CH2-CH2-ONO2</u>
1.0%	5.1e-13	4		CH3-C(CH3)(ONO2)-CH3
1.0%	3.1e-12	6		CH3-C(CH3)(ONO2)-CH2-CH2-CH3
0.9%	4.5e-12	4		CH3-C(CH3)(ONO2)-CH2-OH
0.9%	4.2e-12	6		CH3-CH(CH3)-CH(ONO2)-CH2-CH3
0.9%	9.9e-12	10	RNO3-6	<u>CH3-CH2-CH(ONO2)-CH2-CH2-CH2-CH2-CH2-CH3</u>
0.9%	9.9e-12	10		CH3-CH2-CH2-CH(ONO2)-CH2-CH2-CH2-CH2-CH2-CH3
0.9%	9.9e-12	10		CH3-CH2-CH2-CH2-CH(ONO2)-CH2-CH2-CH2-CH2-CH3
0.9%	5.6e-12	8	RNO3-5	<u>CH3-CH(CH3)-CH2-C(CH3)(ONO2)-CH2-CH3</u>
0.8%	9.9e-12	7	RNO3-4	<u>CH3-CH2-CH2-CH2-CH2-CH(ONO2)-CH2-OH</u>
0.8%	2.8e-12	6		CH3-CH2-C(CH3)(ONO2)-CH2-CH3
0.8%	1.0e-11	5		CH3-CH(OH)-CH(ONO2)-CH2-CH3
0.8%	1.2e-11	5		CH3-CH(ONO2)-CH(OH)-CH2-CH3
0.8%	4.4e-12	6		CH3-CH(CH3)-CH2-CH(ONO2)-CH3
0.8%	7.2e-12	6		*CH(ONO2)-CH2-CH2-CH2-CH2-CH2-*
0.7%	1.0e-11	10		CH3-CH(ONO2)-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3
0.7%	6.2e-12	8		CH3-C(CH3)(ONO2)-CH2-CH(CH3)-CH2-CH3
0.7%	4.2e-12	7		CH3-CH2-C(CH3)(ONO2)-CH2-CH2-CH3
0.7%	4.2e-12	6		CH3-CH2-CH(ONO2)-CH2-CH2-CH3
0.7%	5.6e-12	7		CH3-CH2-CH(ONO2)-CH2-CH2-CH2-CH3
0.7%	8.5e-12	6		CH3-CH2-CH2-CH2-CH(ONO2)-CH2-OH
0.6%	8.9e-12	4		CH3-CH(OH)-CH(ONO2)-CH3
0.6%	1.9e-11	10		CH3-CH2-CH(OH)-CH2-CH2-CH(ONO2)-CH2-CH2-CH2-CH3
0.6%	1.9e-11	10		CH3-CH2-CH2-CH(OH)-CH2-CH2-CH(ONO2)-CH2-CH2-CH3
0.6%	3.1e-12	6		CH3-C(CH3)(ONO2)-CH(CH3)-CH3
0.6%	1.8e-11	6		CH3-CH(ONO2)-CH2-CH2-CH(OH)-CH2-OH
0.6%	3.4e-12	6		CH3-C(CH3)(OH)-CH2-CH2-CH2-ONO2
0.6%	4.4e-12	6		CH3-CH(ONO2)-CH2-CH2-CH2-CH3
58.0%				All Others

[a] Amount of formation of this compound relative to all products represented as RNO3, on a molar basis.

[b] OH radical rate constant estimated using structure-reactivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996), in units of $\text{cm}^3 \text{molec}^{-1} \text{sec}^{-1}$.

[c] Number of carbons.

[d] Detailed model species name used when computing mechanism for compound that was used for deriving the RNO3 mechanism for the model.

[e] Product structure as used in the mechanism generation system. See Section III.B. The "*" symbol is used to indicate groups that are bonded in cyclic compounds. Underlined structures are those used to derive the RNO3 mechanism.

species, given in Table A-6. Note that although the PROD2 mechanism is derived based on a set of model species with average carbon numbers of 7, this is represented as having 6 carbons in the mechanism for the purpose of computing carbon balance.

In the case of RNO3, the average OH radical rate constant is $7.8 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, and the average carbon number is around 6.5. The RNO3 mechanism in the model is derived by choosing one representative compound each for carbon numbers of 4-8 and 10, such that the average OH rate constant is close to the average for the mixture. These six compounds are indicated by being underlined on Table 4. The mechanisms for these compounds were generated and the product yield parameters obtained⁷ were averaged (weighing each equally) to obtain the product yields for the reactions of RNO3. The rate of photolysis is estimated by using the absorption cross sections given by IUPAC (Atkinson et al, 1997, 1999) for isopropyl nitrate, assuming unit quantum yield for production for NO₂.

3. Uncharacterized Aromatic Ring Fragmentation Products

Despite considerable progress in recent years towards understanding aromatic reaction mechanism (e.g., see Atkinson, 2000, and references therein), there is still insufficient information about the ring-opening products formed when OH radicals react with aromatic compounds to determine the appropriate mechanism for atmospheric modeling. In particular, the observed α -dicarbonyl and ring-retaining products from the aromatics are insufficient to account for the observed reactivity of aromatics in environmental chamber experiments, and it is necessary to assume formation of products that photolyze relatively rapidly to form radicals for model simulations to fit the environmental chamber data (e.g. Carter, 1990). To fit the data, the Carter (1990) mechanism included model species AFG1 and AFG2 to represent the contribution to reactivity of these uncharacterized ring-fragmentation products, with their yields and approximate photolysis rates adjusted to fit chamber data. Their mechanisms were based roughly on those for glyoxal and methyl glyoxal, respectively, although their action spectrum had a greater short wavelength contribution [eventually being based on that for acrolein (Carter et al, 1993b; Carter, 1995)] in order to fit reactivity data using differing types of light sources. More recently, to fit new aromatics environmental chamber data obtained using Teflon chambers with a xenon arc light source, it was found that it was also necessary to represent at least portion of the uncharacterized ring-opening products by model species with α -dicarbonyl action spectra (Carter et al, 1997a). These were represented in the model by methyl glyoxal – i.e., by increasing the methyl glyoxal yield by an adjustable amount in order to fit the chamber data (Carter et al, 1997a).

In this version of the mechanism, the general approach of using photoreactive model species with yields adjusted to fit the chamber data to represent the effects of unknown reactive aromatic ring fragmentation products is retained. However, the number of model species used for this purpose was increased to three, and their mechanisms were derived to be somewhat more consistent with the actual types of species expected to be involved. Their mechanisms were changed to be more consistent with the actual types of unsaturated dicarbonyl species expected to be involved, and their names were changed from AFGn to DCBn. A third model species (DCB3) was added to allow for separate representation of products with action spectra like α -dicarbonyls, and thus end the use the methyl glyoxal model species (MGLY) for this purpose. This was done so that the mechanism used may be more appropriate for an unsaturated carbonyl, and so model predictions of MGLY will actually represent methyl glyoxal and similar species. These are discussed in more detail below⁸.

⁸ See also Section IV.A for a discussion of the derivations of the yields and photolysis rates of these species based on model simulations of the aromatic - NO_x chamber experiments.

DCB1 is used to represent the uncharacterized ring-opening products that do not undergo significant photodecomposition to form radicals. This includes not only the ring fragmentation formed from benzene and naphthalene, but also unsaturated diketones such as 3-hexene-2,5-dione, which the data of Bierbach et al (1994) and Tuazon et al (1985) show do not undergo significant radical-forming photodecomposition. This non-photoreactive model species replaces the AFG1 used in the previous versions of the mechanism to represent the uncharacterized ring-fragmentation products from benzene because fits to the benzene - NO_x chamber data are not significantly improved if it is assumed that there are other photoreactive ring-opening products besides glyoxal. This is in contrast with the previous version of the mechanism, where significant photolysis of AFG1 to radicals had to be assumed to fit these data. This change is because benzene also forms glyoxal, whose photolysis to radicals was increased significantly in this version of the mechanism in order to be consistent with new chamber data on the reactivity of acetylene (Carter et al, 1997c). Also, the reaction of this species with O₃ is an additional radical source that was not in the previous mechanism.

This species is also used in the mechanisms of the alkylbenzenes because at least some of the ring-opening products are expected to have low photoreactivity, yet are expected to react rapidly by other means, particularly with OH. In particular, o-substituted aromatics such as o-xylene and 1,2,4-trimethylbenzene are expected to form higher yields of unsaturated diketones, which as indicated above do not seem to be highly photoreactive (Bierbach et al, 1994; Tuazon et al, (1985). The fact that these o-substituted aromatics have relatively low reactivity in environmental chamber experiments, and that lower yields of photoreactive products give the best fits to these data (Carter et al, 1997a), is consistent with the expected lower photoreactivity of these compounds. As discussed in Section IV.A, the yield of DCB1 is determined by assuming that the sum of all the DCBs (DCB1 + DCB2 + DCB3) is equal to the total ring fragmentation route, where the yields of the photoreactive DCB1 and DCB2 being determined by optimization. Note that this means the DCBs are used represent co-products formed with the measured α -dicarbonyls, as well as products formed in non- α -dicarbonyl-forming fragmentation routes.

The DCB1 reactions are based roughly on those estimated for HCOCH=CHCHO, with OH and O₃ rate constants based on the data of Bierbach et al (1994), and the mechanisms derived as discussed in Footnotes to Table A-2 in Table A-4. Although an OH reaction mechanism for an unsaturated diketone product such as might be formed from o-substituted aromatics may be somewhat different than that expected for 2-butene 1,4-dial, best fits to the p-xylene and 1,2,4-trimethylbenzene chamber data are obtained if the present DCB1 + OH mechanism is used.

DCB2 and DCB3 are used to represent the highly photoreactive ring-opening products formed from alkylbenzenes. As discussed by Carter et al (1997a), to fit chamber data using various light sources, it is necessary to assume two separate model species for this purpose, one with an action spectrum like acrolein, and the other with an action spectrum like an α -dicarbonyl. DCB2 is used to represent those compounds with action spectra like α -dicarbonyls, and thus uses absorption cross sections of methyl glyoxal, with a wavelength-independent overall quantum yield adjusted to give best fits to the chamber data as discussed in Section IV.A. Likewise, DCB3 uses the absorption cross sections of acrolein, with the overall quantum yield adjusted to fit the same chamber data. Note that the overall "quantum yield" used in the model for DCB3 is greater than unity, indicating that the absorption cross sections of the actual compounds being represented must be significantly greater than those for acrolein. However, in view of lack of information concerning the nature of these compounds and their photolysis reactions, it is assumed that the wavelength dependences of the action spectra are approximately the same as that for acrolein.

Other than the photolysis rates, the reactions of DCB2 and DCB3 are the same. They are based roughly on estimated mechanisms for $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CHCHO}$. The rate constant for the OH reaction was assumed to be the same as that used for DCB1, with the mechanism estimated as indicated in footnotes to Table A-2 in Table A-4. Because of the rapid photolysis, it is assumed that consumption of these species by reaction with O_3 is negligible. The photolysis mechanisms are unknown, and are probably highly variable depending on the individual species involved. In this mechanism, these are very approximately represented by an estimated set of products which gives reasonably good performance in model simulations of available chamber data (see Section IV.A).

4. Unreactive Product Species

The mechanism has several model species whose subsequent reactions are ignored, either because they are unreactive or because the effects of their gas-phase reactions are expected to be small. These also include “counter species” for the purpose of tracking carbon and nitrogen balance. Since their computed concentrations do not effect transformations of any of the other gas-phase species, they could be eliminated from the model if their concentrations, or tracking carbon or nitrogen balance, are not of interest.

Formic Acid (HCOOH), Acetic Acid (CCO-OH), Lumped Higher Organic Acids (RCO-OH), Peroxy Acetic Acid (CCO-OOH), and Lumped Higher Organic Peroxy Acids (RCO-OOH). Formic acid is predicted to be formed in the reactions of formaldehyde with HO_2 , acetic and higher organic acids are predicted to be formed from the reactions of acyl peroxy radicals with other peroxy radicals, and peroxy acetic and higher peroxy acids are predicted to be formed when acyl peroxy radicals react with HO_2 . In addition, formation of formic and higher organic acids are assumed to be the major fate of stabilized Crigee biradicals (Atkinson, 1997a, 2000). Their subsequent reactions with OH radicals is assumed to be negligible compared to other loss processes such as deposition, though the reaction with OH may in fact be non-negligible for the higher acids or peroxy acids. Formation of these acids is included in the model because of their potential involvement in acid deposition. Depending on the model application, it may be appropriate to remove them from the model or lump them into a single organic acid species.

Carbon Dioxide (CO₂). Since CO_2 does not undergo gas-phase reactions and its formation is not expected to have any other effects on the environment (since background CO_2 concentrations are much higher), the only reason for having this species in the model is carbon balance.

Unreactive Carbon (NROG). This model species is used to represent emitted VOCs whose subsequent reactions are assumed to be negligible, and which are not otherwise represented in the model. It can be removed from the model if carbon balance is not of interest. It is represented as having one carbon, with the other carbons in the unreactive VOC or product being represented by the “lost carbon” species.

Lost Carbon (XC). The lost carbon model species is used to account for carbons that are lost (or gained) if the model species has a different number of carbons than the VOC or VOC products being represented. Note that this is different from the “unreactive carbon” (NROG) model species in that the former is used to represent *molecules* that are treated as unreactive, while the latter represents *parts of molecules* that are not being represented (i.e., that are “lost”) as a result of the mechanism condensation processes. This model species can be removed in model applications where carbon balance is not of interest.

Lost Nitrogen (XN). This model species is analogous to the lost carbon (XC) species except that in this case it is used for nitrogen balance. It is not recommended that this be removed from the

mechanism, so that nitrogen balance can always be verified in any model simulation. Because of the importance of nitrogen species in affecting not only O_3 formation but also radical cycles and chain lengths, any modeling system that does not maintain proper nitrogen balance must be considered to be unreliable.

Sulfates (SULF). The SULF model species is used to represent the formation of SO_3 from the reactions of SO_2 with OH. It is assumed that the fate of SO_3 in the atmosphere would be formation of sulfate aerosol. This model species would be important in models for secondary aerosol formation in scenarios where SO_2 is emitted, but could be removed if aerosols are not represented in the model application.

III. GENERATED AND ESTIMATED MECHANISMS

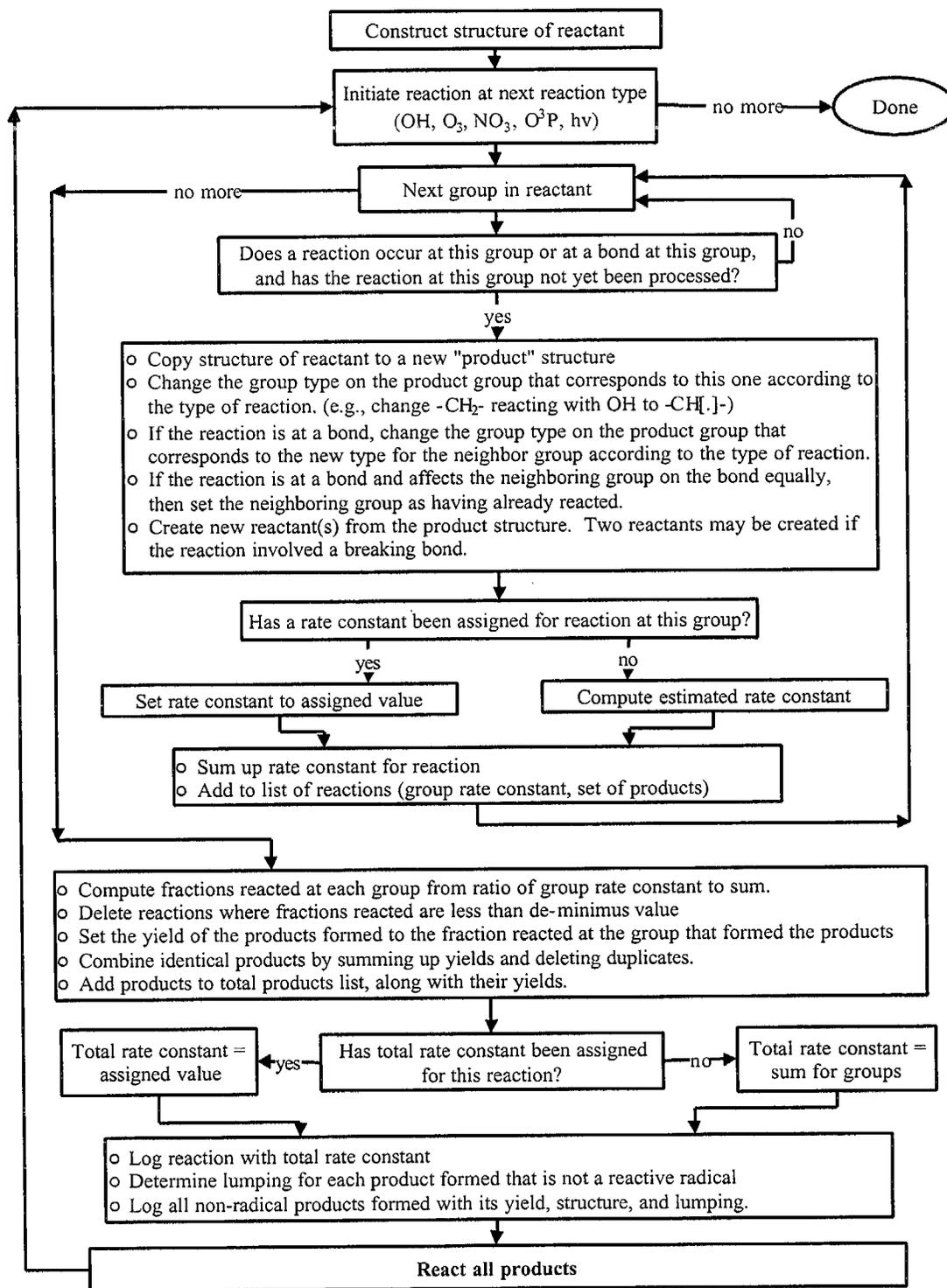
The atmospheric reaction mechanisms for most of the organic compounds that are represented by this mechanism are complex, can involve a large number of reactive intermediates (particularly for larger molecules), and in almost all cases involve reactions whose rate constants are unknown and have to be estimated. Because of the complexity, for practical reasons it is necessary either to greatly simplify the mechanisms for most VOCs, use extensive lumping or condensations in VOC representations, or use an automated procedure to generate the mechanisms. In the previous versions of the SAPRC mechanism, an automated procedure was used to derive mechanisms for the alkanes, but molecule-by-molecule assignments or various lumping or condensation approaches were used for all the other VOCs. In this version, an automated procedure is now used to derive the mechanisms for a much wider variety of compounds, which includes almost all compounds for which mechanistic assignments have been made except for the aromatics and terpenes. This procedure, and the estimation methods and assignments that it employs, are discussed in this section.

A. Mechanism Generation Procedure Overview

The mechanism generation is carried out using a set of object-oriented computer programs that derives explicit mechanisms for the major atmospherically-relevant reactions of a VOC in the presence of NO_x , given the structure of the VOC. The results are then used to determine the representation of these reactions in terms of the model species in the base mechanism. The current system can generate the atmospherically-relevant reactions of alkanes, monoalkenes, a variety of oxygenates, and selected dialkenes and alkynes with OH, reactions of monoalkenes and selected dialkenes with O_3 , NO_3 , and O^3P , and photolysis reactions of carbonyls and organic nitrates. The overall operation of the system involves the following steps:

- The user inputs the structure of the compound. The structure is specified in terms of "groups" such as $-\text{CH}_2-$, $-\text{CO}-$, $-\text{OH}$, etc., which are similar to those used in the group additivity thermochemical estimation methods of Benson (1976) or the structure-reactivity kinetic estimate methods of Atkinson (1987). The specific groups used are summarized in Section III.B.
- The initial reactions of the compound with OH, O_3 , NO_3 , O^3P or photolysis are processed as shown schematically on Figure 1. The rates of reactions at competing positions are estimated as discussed in Sections III.C through III.G, and the products and radicals formed, together with their yields, are logged. Documentation text is generated and logged, as appropriate.
- For each reactive organic radical formed, either in the initial reaction with OH, etc., or through the reactions of a previously formed radical, the system generates all the reactions that are believed to be potentially important for the radical in the presence of NO_x in air. The radicals and products formed, and their yields (obtained by multiplying the yield of the starting radical times the branching ratios for the reactions forming them) are logged for further processing. Documentation text is also generated and logged for those reactions where estimates are involved. The types of radicals involved, and the reactions the system considers, are as follows:

Figure 1. Flow diagram for the initial reactions of a VOC in the mechanism generation process.



- Carbon centered (e.g, alkyl) radicals: Reaction with O₂. In most cases this involves formation of the corresponding peroxy radical, but in a few cases (e.g, α-hydroxy alkyl radicals) other reactions can occur. In all cases, only a single reaction pathway is assumed, so the yield of the product(s) are assigned the yield of the starting radical. These reactions are discussed in Section III.H.
- Peroxy radicals (other than acetyl peroxy): Reaction with NO. This can involve formation of the corresponding alkyl nitrate (RONO₂) or formation of NO₂ and the corresponding alkoxy (RO·) radical. The conversion of NO to NO₂ in the latter reaction is logged as the formation of the “NO to NO₂ conversion product”. Nitrate yield estimates, discussed in Section III.I, are used to determine the yields of the nitrate, alkoxy radical, and NO to NO₂ conversion products relative to the starting radical.
- Alkoxy radicals: Reaction with O₂; β-scission decomposition; 1,4-H shift isomerization; or α-ester rearrangement (Tuazon et al, 1998b), when possible. The O₂ reaction involves the formation of HO₂ and a stable product, while the other reactions can involve formation of various carbon-centered radicals, in some cases with stable co-products. Various estimation methods or assignments, discussed in Section III.J are used to derive the relevant rate constants or branching ratios.

Note that acetyl peroxy radicals (e.g. RC(O)O₂·) are treated as product species and their reactions are not generated. This is because they are lumped with generic acyl peroxy radical species in the model (e.g., CCO-O₂· or RCO-O₂·), so the information obtained by generating their reactions is not used. Note that their ultimate products they form (PAN or RC(O)O· decomposition products) depend on environmental conditions and thus cannot be uniquely determined.

- For each “product” species formed, which includes acetyl peroxy radicals, HO₂ and the NO to NO₂ conversion product as well as stable organic products, the yield, structure, and generation (number of NO to NO₂ conversions involved before it is formed) is logged. The lumping assignment for the product (the way it is represented in the base mechanism) is also determined and logged. Lumping assignments are discussed in Section III.K.5.
- Processing is completed once all the reactive radicals have been converted to stable products or radicals whose reactions are not generated (e.g., HO₂ or acyl peroxy radicals). The generated reaction list, product log (list of all products giving yields, structure and lumping), is saved for output or processing.
- Once all the relevant reactions for a VOC have been generated, the overall reactions or mechanistic parameters for the species can be derived for use in model simulations. The sum of the yields of HO₂ and the NO to NO₂ conversion product in the product log are used to derive the corresponding HO₂, RO₂-R· and/or R₂O₂· yields. The yields of the lumped species representing the various organic products are summed to determine their total yields in the overall reaction. Loss or gain of carbon and nitrogens are tracked, and if necessary yields of “lost carbon” or “lost nitrogen” model species are determined to maintain balance.
- The system can also be used to generate mechanisms for the major reactive products formed from the reactions of the VOC, for more accurate representation of these products when calculating reactivities of the individual VOCs. The system uses the procedures discussed above to generate mechanisms for each of the VOC’s reaction products that are formed in yields greater than 2.5% and that would otherwise be represented by relatively reactive organic product species (such as PROD2 or RCHO). These VOC product mechanisms are then used to derive lumped mechanisms for the major type of product species tailored to represent the specific set of product species the VOC is predicted to form.

This procedure is discussed in more detail in Section III.M. Note that these "explicit product" mechanisms with VOC-specific product model species can only be used when representing the VOCs explicitly, not when they are lumped with other VOCs in complex mixtures. Therefore, both explicit product and standard lumped product mechanisms are derived for each VOC where such mechanisms can be generated.

Note that the system does not generate complete mechanisms for the VOCs, since peroxy + peroxy and peroxy + NO₂ reactions are ignored, and as indicated above acetyl peroxy radical reactions are not generated. However, even if the system generated all the peroxy + peroxy reactions, the current mechanism is not set up to use this information, because of the way the reactions of peroxy radicals are represented (see Section II.B.4). The present mechanism neglects the formation and decompositions of most peroxy nitrates because their rapid decompositions at ambient temperatures result in no net reaction, so information on the formation and generation of these species would also be ignored. The current mechanism is also not set up to take advantage of any detailed product information concerning the reactions of individual acyl peroxy radicals and their corresponding PAN analogues. Therefore the present system is sufficient to provide all the information that the current version of the mechanism can use. Expanded capabilities can be added in the future as mechanisms and models that can use them are developed.

B. Specification of Reactants and Summary of Groups

In this section, the method used to specify structures of reactions, and the types of structures that can be represented, are discussed. A knowledge of this is necessary not only for those who wish to use the system, but also because some of the tables given in this report use this method to identify reactants and radicals.

The structure of a reactant VOC or radical is specified by giving the "groups" in the molecule, and indicating which groups they are bonded to. Groups are parts of the molecule that are treated as a unit by the system, and as indicated above are generally the same as the groups used in the structure-reactivity kinetic estimation method of Atkinson and co-workers (Atkinson, 1987; Kwok and Atkinson, 1995; Atkinson, 1997a). The list of groups that can be supported by the present system is given in Table 5 and Table 6. Table 5 shows the groups that can be used for constructing VOC structures to be reacted with OH, etc, and Table 6 shows the groups that can appear in reactive radical and product species that are formed.

If the molecule or radical contains atoms not shown on Table 5 or Table 6, then the reactions of that species cannot be generated by the current system. In addition, there are some groups for which there are insufficient thermochemical group additivity data in the system's thermochemical database to support the data requirements of the estimation methods, which means that reactions of molecules containing those groups usually cannot be generated. Those cases are indicated on Table 5.

The structures of the molecules are specified as follows. Straight chain structures are given by groups separated by "-" or "=". For example:

Propane:	CH3-CH2-CH3
Propene:	CH3-CH=CH2
Propionic acid:	CH3-CH2-CO-OH
Ethyl acetate:	CH3-CH2-O-CO-CH3
ethoxyethanol:	HO-CH2-CH2-O-CH2-CH2-O-CH2-CH2-OH

Table 5. Listing of groups for stable molecules that can be supported by the present mechanism generation system.

Group	Reactions at Group
<u>Groups for which mechanisms can usually be generated</u>	
-CH3	OH (H- Abstraction)
-CH2-	OH (H- Abstraction)
>CH-	OH (H- Abstraction)
>C<	none
-O-	none
-OH	OH (H- Abstraction)
-CHO	OH, NO ₃ (H- Abstraction), hv (HCO.- Bond Scission)
-CO-	hv (CO.- Bond scission)
=CH2	OH, O ₃ , O ³ P, NO ₃ (Double Bond Addition)
=CH	OH, O ₃ , O ³ P, NO ₃ (Double Bond Addition)
=C<	OH, O ₃ , O ³ P, NO ₃ (Double Bond Addition)
<u>Groups for which mechanisms can be generated in some cases</u>	
-ONO2	hv (-O. + NO ₂ formation)
<u>Groups for which mechanisms usually cannot be generated</u>	
-F	none
-Cl	none
-Br	none
-I	none
-NO2	none

Branched structures are indicated by using ()'s to show groups off to the side. For example:

Isobutane: CH₃-CH(CH₃)-CH₃
 3,3-diethyl pentan-2-ol: CH₃-CH(OH)-C(CH₂-CH₃)(CH₂-CH₃)-CH₂-CH₃
 4-isopropyl heptane: CH₃-CH₂-CH₂-CH(CH(CH₃)-CH₃)-CH₂-CH₂-CH₃

Cyclic structures are indicated by using a "*" character to mark the group which is used to close the ring. Note that the present system does not support specification of compounds with more than one ring, since no way of indicating such structures is presently defined.

3-methyl furan: *O-CH₂-CH(CH₃)-CH₂-CH₂-*

The system presently supports structures with single double bonds between carbon-centered groups only, and may not successfully generate reactions for non-hydrocarbon species with double bonds because of insufficient thermochemical group data in the present database. Double bonds are indicated using a "=" symbol in place of a "-", and *cis* and *trans* configurations are indicated using parentheses, as follows:

cis-2-butene: CH₃-CH=CH-CH₃
trans-2-Hexene: CH₃-CH=CH(CH₂-CH₂-CH₃)

Although one can often enter structures in more than one way (for example, both CH₃-CH(CH₃)-CH₂-CH₃ and CH₃-CH₂-CH(CH₃)-CH₃ are acceptable ways to enter 2-methyl butane), the system uses an algorithm to generate a (usually) unique structure definition string for each structure. This is done so that the structure definition string can be used to determine if two products or intermediate species generated by the system are the same compound. Therefore, the structure specification generated by the

Table 6. Listing of radical center groups and non-reactive product groups that can be supported by the present mechanism generation system.

Group	Reactions at Group
<u>Carbon-Centered Radical centers</u>	
CH3.	O2 -> CH3OO.
-CH2.	O2 -> -CH2OO.
-CH[.]-	O2 -> -CH[OO.]
>C[.]-	O2 -> >C[OO.]
HCO.	O2 -> HO2. + CO
-CO.	O2 -> -CO[OO.]
<u>Vinyl Radical centers</u>	
=CH.	X=CH2 + O2 -> X=O + HCO., where X is =CH2, =CH-, or =C<
=C[.]	X=CH[.] + O2 -> X=O + -C[OO.], where X is =CH2, =CH-, or =C<
<u>Peroxy Radical Centers</u>	
CH3OO.	NO -> CH3O.
-CH2OO.	NO -> -CH2O. + [NO conv NO2], NO -> -CH2-ONO2
-CH[OO.]	NO -> -CH[O.] + [NO conv NO2], NO -> -CH(ONO2)-
>C[OO.]	NO -> >C[O.] + [NO conv NO2], NO -> >C(ONO2)-
<u>Acyl Peroxy Radical Centers</u>	
-CO[OO.]	Not reacted
<u>Alkoxy radical Centers</u>	
CH3O.	O2 -> HO2 + HCHO
-CH2O.	O2 -> HO2 + -CHO, Decomposition, 1,4-H-shift isom, Ester rearrangement
-CH[O.]	O2 -> HO2 + -CO-, Decomposition, 1,4-H shift isom, Ester rearrangement
>C[O.]	Decomposition, 1,4-H shift isom.
HCO2.	O2 -> HO2 + CO2
-CO2.	Decomposition to R. + CO2
<u>Carbene Radical Centers</u>	
CH2:	O2 -> CH2OO[excited]
-CH:	O2 -> -CHOO[excited]
-C[.]-	O2 -> COO[excited]
<u>Excited Crigiee Biradical Centers</u>	
CH2OO[excited]	Various unimolecular reactions -- see text
-CHOO[excited]	Various unimolecular reactions -- see text
-COO[excited]-	Various unimolecular reactions -- see text
<u>Stabilized Crigiee Biradical Centers</u>	
CH2OO[stab]	-> HCO-OH + H2O
-CHOO[stab]	-> -CO-OH + H2O
-COO[stab]-	No reaction (usually not formed -- see text)
<u>Elementary Product Groups</u>	
CH4	Not reacted (elementary product)
HCHO	Not reacted (elementary product)
CO	Not reacted (elementary product)
CO2	Not reacted (elementary product)
NO2	Not reacted (elementary product)
[NO conv NO2]	Used for Mechanism Processing

system when a new molecule is specified may be slightly different than the one input by the user, though they would refer to the same compound. Note that the current version of the software is not completely finished in this regard, since unique structure definition strings are not always produced for some cyclic compounds. However, this only causes inefficiency in the mechanism generation algorithm, not errors in the generation of the overall mechanisms.

In order for the system to be useful for generating mechanisms for a wider variety of compounds, it is also possible to specify *special reactants* whose structures cannot be specified explicitly. Although the system cannot automatically generate reactions for these special reactants, it will accept assignments for their reactions. If these assigned reactions form products that can be specified with known groups, the system then automatically generate the reactions of these products, thus generating the overall reaction mechanism of the special reactant. The special reactants that are supported in the present system are listed in Table 7

Table 7. Special reactants that are presently supported as reactants or products in the mechanism generation system

Reactant	Designation	Reactions Supported
1,3-Butadiene	CH ₂ =CH-CH=CH ₂	OH, O ₃ , O ³ P, NO ₃ (Double Bond Addition)
Isoprene	CH ₂ =CH-C(CH ₃)=CH ₂	OH, O ₃ , O ³ P, NO ₃ (Double Bond Addition)
Acetylene	HC::CH	OH, O ₃
Methyl Acetylene	HC::C-CH ₃	OH, O ₃
1-Butyne	HC::C-CH ₂ -CH ₃	OH, O ₃
2-Butyne	CH ₃ -C::C-CH ₃	OH, O ₃
3-Methyl Furan	*O-CH=C(CH ₃)-CH=CH-*	Product only (formed from isoprene)

C. Reactions with OH Radicals

Reactions with OH radicals can occur by two mechanisms, depending on whether the group has a double bond or an abstractable hydrogen. If the group has an abstractable hydrogen, the reaction is



where XH is any H-containing group and X· is the corresponding radical formed when the H atom is removed. If the compound has a double bond, the reaction is



Note that two reactions are generated for each double bond, one where the OH adds to each side of the bond. (If the reactions are equivalent, as would be the case for symmetrical molecules, they are combined after they are generated – the system uses the products formed to determine equivalency.) For each molecule that reacts with OH, one reaction is generated for each group in the molecule that can react in this way. The fractions reacted at the various group are determined from the ratio of the estimated rate

constant at each group, divided by the total of the estimated rate constants for all groups. The group rate constants are estimated as discussed below.

1. Assigned Total OH Radical Rate Constants

Total OH radical rate constants have been measured for many (indeed most) of the VOCs in the current mechanism, and in those cases assigned rate constants are used when generating the mechanisms rather than estimated values. Table 8 gives the OH radical rate constants assigned to all VOCs in the current mechanism, along with references and notes indicating the basis for the assignment. Most of the rate constants are based on recommendations by Atkinson (1989, 1994, 1997a). For completeness, this table has the rate constants for all VOCs in the current mechanism for which such assignments have been made, including those (e.g., aromatics and terpenes) whose mechanisms cannot be generated by the current system. For VOCs whose OH reactions can be automatically generated by the system, the table also shows the estimated T=300K rate constants, which were derived as discussed in the following section. The percentage differences between the assigned and estimated values are also shown (unless the differences are greater than 100%).

2. Estimation of OH Abstraction Rate Constants

Group rate constants for OH abstraction reactions are estimated using the group additivity method developed by Atkinson (1987), as updated by Kwok and Atkinson (1995), Kwok et al (1996) and in this work. The rate constant for the reaction of OH at any group is a function of the group and the groups bonded to it (the "neighbor groups"), and is derived from the equation

$$k(\text{OH} + \text{group}) = k(\text{group}) \prod_{\text{neighbor groups}} F(\text{neighbor group}) \quad (1)$$

where "k(group)" is the rate constant for OH reaction at the group if it were only bonded to methyl radicals, and "F(neighbor group)" is the substituent correction factor for a neighbor group. The group rate constants as currently implemented in the mechanism estimation system are given in Table 9. As indicated in the footnotes to the table, most of the group rate constants and correction factors were obtained from Kwok and Atkinson (1995), with one updated value from Kwok et al (1996) and with a few gaps filled in this work. Note that in some cases, the correction factor depends not only on the neighbor group but also the next nearest neighbor; these modified groups are referred to as "subgroups" on the table. Note also that formate -CHO groups are treated as separate groups than aldehyde -CHO groups for the purpose of OH rate constant estimates. This is because OH abstraction reaction appears to be essentially negligible for the former, but very rapid for the latter.

If the compound has a C=C double bond anywhere in the molecule, at present the system assumes the abstraction reactions from any H-containing group are all negligible compared to the addition to the C=C double bond, and the abstraction rate constant is set at zero. Although methods exist for estimating these abstraction rate constants (Kwok and Atkinson, 1997), it is currently necessary to make this approximation because general methods for generating and estimating the rates of all the possible reactions of the unsaturated radicals formed in these reactions have not yet been developed. Ignoring these abstraction reactions from unsaturated compounds is not a bad approximation for smaller molecules such as propene and the butenes, and all known mechanisms currently used in atmospheric models incorporate this approximation. However, abstraction at groups away from the double bonds can become non-negligible for the larger alkenes (see Atkinson, 1997a and references therein), so this approximation

Table 8. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with OH radicals in the present mechanism.

Compound	Model Name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Refs	Est'd k(300) k	(diff)
<u>Alkanes</u>								
Ethane	ETHANE	2.60e-13	1.37e-12	2.0	0.990	1	2.78e-13	7%
Propane	PROPANE	1.14e-12	1.40e-12	2.0	0.121	1	1.28e-12	12%
n-Butane	N-C4	2.47e-12	1.52e-12	2.0	-0.288	1	2.65e-12	7%
n-Pentane	N-C5	4.04e-12	2.20e-12	2.0	-0.364	1	4.07e-12	1%
n-Hexane	N-C6	5.47e-12	1.38e-12	2.0	-0.823	1	5.49e-12	0%
n-Heptane	N-C7	7.04e-12	1.43e-12	2.0	-0.950	1	6.91e-12	-2%
n-Octane	N-C8	8.76e-12	2.48e-12	2.0	-0.751	1	8.33e-12	-5%
n-Nonane	N-C9	1.00e-11	2.26e-12	2.0	-0.888	1	9.75e-12	-3%
n-Decane	N-C10	1.13e-11	2.82e-12	2.0	-0.827	1	1.12e-11	-1%
n-Undecane	N-C11	1.29e-11				1	1.26e-11	-2%
n-Dodecane	N-C12	1.39e-11				1	1.40e-11	1%
n-Tridecane	N-C13	1.60e-11				1	1.54e-11	-4%
n-Tetradecane	N-C14	1.80e-11				1	1.69e-11	-6%
n-Pentadecane	N-C15	2.10e-11				1	1.83e-11	-13%
n-C16	N-C16	2.30e-11				1	1.97e-11	-14%
Isobutane	2-ME-C3	2.21e-12	1.04e-12	2.0	-0.447	1	2.45e-12	11%
Neopentane	22-DM-C3	8.63e-13	1.62e-12	2.0	0.376	1	6.83e-13	-21%
Iso-Pentane	2-ME-C4	3.70e-12				1	4.05e-12	9%
2,2-Dimethyl Butane	22-DM-C4	2.38e-12	3.22e-11		1.552	1	1.84e-12	-23%
2,3-Dimethyl Butane	23-DM-C4	5.79e-12	1.12e-12	2.0	-0.982	1	5.45e-12	-6%
2-Methyl Pentane	2-ME-C5	5.30e-12				1	5.47e-12	3%
3-Methylpentane	3-ME-C5	5.40e-12				1	5.75e-12	6%
2,2,3-Trimethyl Butane	223TM-C4	4.25e-12	7.61e-13	2.0	-1.025	1	3.24e-12	-24%
2,2-Dimethyl Pentane	22-DM-C5	3.40e-12				1	3.26e-12	-4%
2,4-Dimethyl Pentane	24-DM-C5	5.00e-12				1	6.87e-12	37%
2,2,3,3-Tetramethyl Butane	2233M-C4	1.06e-12	1.72e-12	2.0	0.286	1	1.02e-12	-4%
2,2,4-Trimethyl Pentane	224TM-C5	3.60e-12	1.87e-12	2.0	-0.389	1	4.66e-12	30%
2,2-Dimethyl Hexane	22-DM-C6	4.80e-12				1	4.68e-12	-2%
2,3,4-Trimethyl Pentane	234TM-C5	7.10e-12				1	8.55e-12	20%
2,3,5-Trimethyl Hexane	235TM-C6	7.90e-12				1	9.97e-12	26%
2-Methyl Octane	2-ME-C8	1.01e-11				1	9.73e-12	-4%
3,3-Diethyl Pentane	33-DE-C5	4.90e-12				1	5.31e-12	8%
4-Methyl Octane	4-ME-C8	9.70e-12				1	1.00e-11	3%
2,6-Dimethyl Octane	26DM-C8	1.29e-11				2	1.14e-11	-12%
2-Methyl Nonane	2-ME-C9	1.28e-11				2	1.12e-11	-12%
3,4-Diethyl Hexane	34-DE-C6	7.40e-12				3	1.25e-11	69%
Cyclopropane	CYCC3	8.40e-14				1	8.52e-14	1%
Cyclobutane	CYCC4	1.50e-12				1	1.59e-12	6%
Cyclopentane	CYCC5	5.06e-12	2.31e-12	2.0	-0.467	1	4.54e-12	-10%
Cyclohexane	CYCC6	7.26e-12	2.59e-12	2.0	-0.614	1	8.52e-12	17%
Isopropyl Cyclopropane	IPR-CC3	2.70e-12				1	2.86e-12	6%
Cycloheptane	CYCC7	1.30e-11				1	9.94e-12	-24%
Methylcyclohexane	ME-CYCC6	1.00e-11				1	1.02e-11	2%
Cyclooctane	CYCC8	1.40e-11				1	1.14e-11	-19%
1,1,3-Trimethyl Cyclohex.	113MCYC6	8.70e-12				1	9.12e-12	5%
Hexyl Cyclohexane	C6-CYCC6	1.78e-11				4	1.77e-11	-1%

Table 8 (Continued)

Compound	Model Name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Refs	Est'd k(300) k	(diff)
<u>Alkenes</u>								
Ethene	ETHENE	8.43e-12	1.96e-12		-0.870	1	8.44e-12	0%
Propene	PROPENE	2.60e-11	4.85e-12		-1.002	1	3.16e-11	21%
1-Butene	1-BUTENE	3.11e-11	6.55e-12		-0.928	1	3.16e-11	2%
1-Pentene	1-PENTEN	3.11e-11	5.86e-12		-0.994	5	3.16e-11	2%
3-Methyl-1-Butene	3M-1-BUT	3.14e-11	5.32e-12		-1.059	1	3.16e-11	1%
1-Hexene	1-HEXENE	3.66e-11	6.91e-12		-0.994	5	3.16e-11	-14%
3,3-Dimethyl-1-Butene	33M1-BUT	2.77e-11	5.23e-12		-0.994	5	3.16e-11	14%
1-Heptene	1-HEPTEN	3.96e-11	7.47e-12		-0.994	5	3.16e-11	-20%
Isobutene	ISOBUTEN	5.09e-11	9.47e-12		-1.002	1	5.79e-11	14%
2-Methyl-1-Butene	2M-1-BUT	6.04e-11	1.14e-11		-0.994	5	5.79e-11	-4%
2-Methyl-1-Pentene	2M1-C5E	6.23e-11	1.18e-11		-0.994	5	5.79e-11	-7%
cis-2-Butene	C-2-BUTE	5.58e-11	1.10e-11		-0.968	1	6.34e-11	14%
trans-2-Butene	T-2-BUTE	6.32e-11	1.01e-11		-1.093	1	6.34e-11	0%
2-Methyl-2-Butene	2M-2-BUT	8.60e-11	1.92e-11		-0.894	1	8.71e-11	1%
cis-2-Pentene	C-2-PENT	6.43e-11	1.21e-11		-0.994	5	6.34e-11	-1%
trans-2-Pentene	T-2-PENT	6.63e-11	1.25e-11		-0.994	5	6.34e-11	-4%
2,3-Dimethyl-2-Butene	23M2-BUT	1.09e-10	2.05e-11		-0.994	5	1.05e-10	-4%
2-Methyl-2-Pentene	2M-2-C5E	8.81e-11	1.66e-11		-0.994	5	8.71e-11	-1%
Trans 4-Methyl-2-Hexene	T4M2-C5E	6.04e-11	1.14e-11		-0.994	5	6.34e-11	5%
2,3-Dimethyl-2-Hexene	23M2-C5E	1.02e-10	1.92e-11		-0.994	5	1.05e-10	3%
Trans-2-Heptene	T-2-C7E	6.73e-11	1.27e-11		-0.994	5	6.34e-11	-6%
Trans 4,4-dimethyl-2-Hexene	T44M2C5E	5.44e-11	1.03e-11		-0.994	5	6.34e-11	16%
Trans-4-Octene	T-4-C8E	6.83e-11	1.29e-11		-0.994	5	6.34e-11	-7%
Cyclopentene	CYC-PNTE	6.63e-11	1.25e-11		-0.994	5	6.34e-11	-4%
Cyclohexene	CYC-HEXE	6.70e-11	1.26e-11		-0.994	5	6.34e-11	-5%
1,3-Butadiene	13-BUTDE	6.59e-11	1.48e-11		-0.890	1		
Isoprene	ISOPRENE	1.00e-10	2.55e-11		-0.815	1		
3-Carene	3-CARENE	8.71e-11	1.64e-11		-0.994	5		
a-Pinene	A-PINENE	5.31e-11	1.21e-11		-0.882	1		
b-Pinene	B-PINENE	7.82e-11	2.38e-11		-0.709	1		
d-Limonene	D-LIMONE	1.69e-10	3.19e-11		-0.994	5		
Sabinene	SABINENE	1.16e-10	2.19e-11		-0.994	5		
Styrene	STYRENE	5.80e-11				1		
2-(Cl-methyl)-3-Cl-Propene	CL2IBUTE	3.16e-11				1	5.79e-11	83%
<u>Aromatics</u>								
Benzene	BENZENE	1.24e-12	2.47e-12		0.411	6		
Toluene	TOLUENE	5.91e-12	1.81e-12		-0.705	6		
Ethyl Benzene	C2-BENZ	7.10e-12				6		
Isopropyl Benzene (cumene)	I-C3-BEN	6.50e-12				6		
n-Propyl Benzene	N-C3-BEN	6.00e-12				6		
s-Butyl Benzene	S-C4-BEN	6.00e-12				7		
m-Xylene	M-XYLENE	2.36e-11	2.36e-11		0.000	6		
o-Xylene	O-XYLENE	1.37e-11	1.37e-11		0.000	6		
p-Xylene	P-XYLENE	1.43e-11	1.43e-11		0.000	6		
1,2,3-Trimethyl Benzene	123-TMB	3.27e-11	3.27e-11		0.000	6		
1,2,4-Trimethyl Benzene	124-TMB	3.25e-11	3.25e-11		0.000	6		
1,3,5-Trimethyl Benzene	135-TMB	5.75e-11	5.75e-11		0.000	6		
Indan	INDAN	9.20e-12				8		

Table 8 (Continued)

Compound	Model Name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Refs	Est'd k(300) k	(diff)
Naphthalene	NAPHTHAL	2.12e-11	1.07e-12		-1.779	6		
Tetralin	TETRALIN	3.43e-11				9		
1-Methyl Naphthalene	1ME-NAPH	5.30e-11				10		
2-Methyl Naphthalene	2ME-NAPH	5.23e-11				11		
Methyl Naphthalenes	ME-NAPH	5.20e-11				12		
2,3-Dimethyl Naphth.	23-DMN	7.68e-11				11		
Phenol	PHENOL	2.63e-11				6		
m-Cresol	M-CRESOL	6.40e-11				6		
o-Cresol	O-CRESOL	4.20e-11				6		
p-Cresol	P-CRESOL	4.70e-11				6		
Nitrobenzene	NO2-BENZ	1.50e-13				13		
Monochlorobenzene	CL-BEN	7.70e-13				6		
Benzotrifluoride	CF3-BEN	4.60e-13				14		
p-Dichlorobenzene	CL2-BEN	5.55e-13				15		
p-Trifluoromethyl-Cl-Benzene	PCBTF	2.40e-13				14		
<u>Alkynes</u>								
Acetylene	ACETYLEN	9.12e-13	9.40e-12		1.391	16		
Methyl Acetylene	ME-ACTYL	5.90e-12				16		
2-Butyne	2-BUTYNE	2.72e-11	1.00e-11		-0.596	16		
Ethyl Acetylene	ET-ACTYL	8.00e-12				16		
<u>Alcohols and Glycols</u>								
Methanol	MEOH	9.34e-13	3.10e-12		0.715	17	6.25e-13	-33%
Ethanol	ETOH	3.28e-12	5.56e-13		-1.057	17	3.61e-12	10%
Isopropyl Alcohol	I-C3-OH	5.32e-12	6.49e-13		-1.254	16	7.26e-12	37%
n-Propyl Alcohol	N-C3-OH	5.53e-12				16	5.51e-12	0%
n-Butyl Alcohol	N-C4-OH	8.57e-12				16	6.93e-12	-19%
t-Butyl Alcohol	T-C4-OH	1.13e-12	3.86e-13		-0.640	18	6.87e-13	-39%
Cyclopentanol	CC5-OH	1.07e-11				19	1.03e-11	-4%
2-Pentanol	2-C5OH	1.18e-11				19	1.14e-11	-3%
3-Pentanol	3-C5OH	1.22e-11				19	1.30e-11	7%
Pentyl Alcohol	C5OH	1.11e-11				16	8.35e-12	-25%
1-Hexanol	1-C6OH	1.25e-11				16	9.78e-12	-22%
2-Hexanol	2-C6OH	1.21e-11				19	1.28e-11	6%
1-Heptanol	1-C7OH	1.37e-11				16	1.12e-11	-18%
1-Octanol	1-C8-OH	2.02e-11				20	1.26e-11	-38%
2-Octanol	2-C8-OH	2.52e-11				20	1.56e-11	-38%
3-Octanol	3-C8-OH	3.14e-11				20	1.73e-11	-45%
4-Octanol	4-C8-OH	2.87e-11				20	1.73e-11	-40%
Ethylene Glycol	ET-GLYCL	1.47e-11				21	8.38e-12	-43%
Propylene Glycol	PR-GLYCL	2.15e-11				21	1.28e-11	-40%
<u>Ethers and Glycol Ethers</u>								
Dimethyl Ether	ME-O-ME	3.01e-12	1.04e-11		0.739	16	2.30e-12	-24%
Trimethylene Oxide	TME-OX	1.03e-11				22	5.76e-12	-44%
Tetrahydrofuran	THF	1.61e-11				16	1.41e-11	-12%
Dimethoxy methane	METHYLAL	4.90e-12				23	6.69e-11	>100%
Diethyl Ether	ET-O-ET	1.31e-11	8.02e-13		-1.663	16	1.59e-11	22%
Alpha-Methyltetrahydrofuran	AM-THF	2.20e-11	2.52e-12		-1.292	24	2.08e-11	-5%
Tetrahydropyran	THP	1.38e-11				22	2.34e-11	70%

Table 8 (Continued)

Compound	Model Name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Refs	Est'd k(300) k	(diff)
Methyl n-Butyl Ether	MNBE	1.48e-11				16	1.35e-11	-9%
Methyl t-Butyl Ether	MTBE	2.94e-12	5.89e-13	2.0	-0.960	16	1.66e-12	-44%
Ethyl n-Butyl Ether	ENBE	2.13e-11				16	2.03e-11	-5%
Ethyl t-Butyl Ether	ETBE	8.84e-12				16	8.48e-12	-4%
Methyl t-Amyl Ether	MTAE	7.91e-12				19	2.82e-12	-64%
Di n-Propyl Ether	PR-O-PR	1.84e-11	1.18e-12		-1.639	16	2.18e-11	18%
Di-n-butyl Ether	BU-O-BU	2.88e-11				16	2.46e-11	-15%
Di-Isobutyl Ether	IBU2-O	2.60e-11				25	2.46e-11	-5%
Di-n-Pentyl Ether	C5-O-C5	3.47e-11				26	2.75e-11	-21%
2-Methoxy-Ethanol	MEO-ETOH	1.33e-11	4.50e-12		-0.646	22	1.49e-11	12%
2-Ethoxy-Ethanol	ETO-ETOH	1.87e-11				27	2.17e-11	16%
1-Methoxy-2-Propanol	MEOC3OH	2.00e-11				28	1.93e-11	-3%
3-Ethoxy-1-Propanol	3ETOC3OH	2.20e-11				22	2.31e-11	5%
3-Methoxy-1-Butanol	3MEOC4OH	2.36e-11				22	2.67e-11	13%
2-Butoxy-Ethanol	BUO-ETOH	2.57e-11				29	2.61e-11	2%
2-(2-Ethoxyethoxy) EtOH	CARBITOL	5.08e-11				30	4.09e-11	-19%
<u>Esters</u>								
Methyl Formate	ME-FORM	2.27e-13				31	1.25e-13	-45%
Ethyl Formate	ET-FORM	1.02e-12				31	1.02e-12	0%
Methyl Acetate	ME-ACET	3.49e-13	8.30e-13		0.517	31	2.65e-13	-24%
n-Propyl Formate	C3-FORM	2.38e-12				31	2.37e-12	0%
Ethyl Acetate	ET-ACET	1.60e-12				6	1.72e-12	7%
Methyl Propionate	ME-PRAT	1.03e-12				31	6.87e-13	-33%
n-Butyl Formate	C4-FORM	3.12e-12				31	3.79e-12	21%
Ethyl Propionate	ET-PRAT	2.14e-12				31	2.14e-12	0%
Isopropyl Acetate	IPR-ACET	3.40e-12				6	3.48e-12	2%
Methyl Butyrate	ME-BUAT	3.04e-12				31	1.91e-12	-37%
Methyl Isobutyrate	ME-IBUAT	1.73e-12				32	1.17e-12	-32%
Propyl Acetate	PR-ACET	3.40e-12				6	3.21e-12	-6%
n-Butyl Acetate	BU-ACET	4.20e-12				6	4.63e-12	10%
Ethyl Butyrate	ET-BUAT	4.94e-12				31	3.36e-12	-32%
Methyl Pivalate	ME-PVAT	1.27e-12				33	7.34e-13	-42%
n-Propyl Propionate	PR-PRAT	4.02e-12				31	3.64e-12	-9%
s-Butyl Acetate	SBU-ACET	5.50e-12				6	5.34e-12	-3%
t-Butyl Acetate	TBU-ACET	4.25e-13				34	5.56e-13	31%
n-Propyl Butyrate	PR-BUAT	7.41e-12				31	4.86e-12	-34%
n-Butyl Butyrate	BU-BUAT	1.06e-11				31	6.28e-12	-41%
Dimethyl Carbonate	DMC	3.30e-13				23	4.44e-13	35%
Propylene Carbonate	PC	6.90e-13				35	3.79e-12	>100%
Methyl Lactate	ME-LACT	2.76e-12				36	2.67e-12	-3%
Ethyl Lactate	ET-LACT	3.91e-12				36	4.12e-12	5%
Methyl Isopropyl Carbonate	MIPR-CB	2.55e-12				37	3.66e-12	44%
Pr. Glycol Methyl Ether Acetate	PGME-ACT	1.44e-11				20	1.47e-11	2%
Dimethyl Succinate	DBE-4	1.50e-12				38	1.17e-12	-22%
Dimethyl Glutarate	DBE-5	3.50e-12				38	2.59e-12	-26%
Dimethyl Adipate	DBE-6	8.80e-12				38	4.01e-12	-54%
<u>Oxides</u>								
Ethylene Oxide	ETOX	7.60e-14				6	3.83e-13	>100%

Table 8 (Continued)

Compound	Model Name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Refs	Est'd k(300) k	(diff)
Propylene Oxide	PROX	5.20e-13				6	7.57e-13	46%
1,2-Epoxybutane	12BUOX	1.91e-12				39	2.00e-12	5%
<u>Acids</u>								
Formic Acid	FORMACID	4.50e-13	4.50e-13		0.000	6	5.44e-11	>100%
Acetic Acid	ACETACID	8.00e-13				16	2.10e-13	-74%
Propionic Acid	PROPACID	1.16e-12				16	1.34e-12	16%
<u>Misc. Unsaturated Oxygenates</u>								
2-Methyl-2-Butene-3-ol	MBUTENOL	6.26e-11	8.20e-12		-1.212	40	3.16e-11	-50%
<u>Aldehydes</u>								
Acetaldehyde	ACETALD	1.57e-11	5.60e-12		-0.616	41	1.58e-11	0%
Propionaldehyde	PROPALD	2.00e-11				41	2.01e-11	1%
Butanal	1C4RCHO	2.33e-11	5.26e-12		-0.886	6	2.14e-11	-8%
2-Methylpropanal	2MEC3AL	2.60e-11	6.61e-12		-0.817	6	2.10e-11	-19%
Pentanal	1C5RCHO	2.82e-11	6.34e-12		-0.890	6	2.28e-11	-19%
2,2-Dimethylpropanal (pivaldehyde)	22DMC3AL	2.63e-11	6.82e-12		-0.805	6	1.97e-11	-25%
3-Methylbutanal	3MC4RCHO	2.74e-11				6	2.28e-11	-17%
Acrolein	ACROLEIN	1.99e-11				6	1.07e-11	-46%
Crotonaldehyde	CROTALD	3.64e-11				42	2.16e-11	-41%
Methacrolein	METHACRO	3.33e-11	1.86e-11		-0.348	43	1.97e-11	-41%
Hydroxy Methacrolein	HOMACR	4.30e-11				44	1.97e-11	-54%
Isoprene Product #1	IP-MHY1	7.00e-11				44	2.96e-11	-58%
Isoprene Product #2	IP-MHY2	7.00e-11				44	2.96e-11	-58%
Isoprene Product #3	IP-HMY	7.00e-11				44	2.96e-11	-58%
<u>Ketones</u>								
Acetone	ACETONE	2.22e-13	2.80e-12		1.510	41	2.09e-13	-6%
Cyclobutanone	CC4-KET	8.70e-13				45	4.42e-12	>100%
Methyl Ethyl Ketone	MEK	1.20e-12	1.30e-12		0.050	17	1.35e-12	13%
Cyclopentanone	CC5-KET	2.94e-12				45	6.83e-12	>100%
3-Pentanone	DEK	2.00e-12				6	2.49e-12	25%
2-Pentanone	MPK	4.56e-12				46	4.78e-12	5%
Cyclohexanone	CC6-KET	6.39e-12				45	1.21e-11	89%
4-Methyl-2-Pentanone	MIBK	1.41e-11				6	8.82e-12	-37%
Methyl n-Butyl Ketone	MNBK	9.10e-12				6	6.77e-12	-26%
Methyl t-Butyl Ketone	MTBK	1.21e-12				47	1.72e-12	42%
2-Heptanone	C7-KET-2	1.17e-11				46	8.19e-12	-30%
Di-Isopropyl Ketone	DIPK	5.38e-12				48	5.07e-12	-6%
2-Octanone	C8-KET-2	1.10e-11				47	9.61e-12	-13%
2-Nonanone	C9-KET-2	1.22e-11				47	1.10e-11	-10%
Di-isobutyl ketone (2,6- dimethyl-4-heptanone)	DIBK	2.75e-11				6	1.74e-11	-37%
2-Decanone	C10-K-2	1.32e-11				47	1.24e-11	-6%
Methylvinyl ketone	MVK	1.87e-11	4.14e-12		-0.900	6	2.84e-11	52%
Hydroxy Acetone	HOACET	3.02e-12				22	3.11e-12	3%
Methoxy Acetone	MEOACET	6.77e-12				22	7.11e-12	5%
<u>Nitrogen-Containing Compounds</u>								
Para Toluene Isocyanate	P-TI	5.90e-12				49		
Toluene Diisocyanate	TDI	7.40e-12				50		

Table 8 (Continued)

Compound	Model Name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Refs	Est'd k(300) k (diff)
Methylene Diphenylene Diisocyanate	MDI	1.18e-11				51	
Dimethyl Amine	DM-AMINE	6.58e-11	2.89e-11		-0.491	6	
Ethyl Amine	ET-AMINE	2.76e-11	1.47e-11		-0.376	6	
Trimethyl Amine	TM-AMINE	6.07e-11	2.62e-11		-0.501	6	
Methyl Nitrite	ME-NITRT	2.20e-13				16	
Ethanolamine	ETOH-NH2	3.15e-11				52	
Dimethylaminoethanol	DMAE	9.00e-11	9.00e-11		0.000	53	
Diethanol Amine	ETOH2-NH	9.37e-11				54	
Triethanolamine	ETOH3-N	1.16e-10				55	
N-Methyl-2-Pyrrolidone	NMP	2.15e-11				35	
<u>Halogen-Containing Compounds</u>							
Methyl Chloride	CH3-CL	4.48e-14	3.15e-13	2.0	1.163	16	
Vinyl Chloride	CL-ETHE	6.90e-12	1.69e-12		-0.839	16	
Ethyl Chloride	C2-CL	4.18e-13	6.94e-13	2.0	0.302	16	
Dichloromethane	CL2-ME	1.45e-13	7.69e-13	2.0	0.994	6	
Methyl Bromide	ME-BR	4.12e-14	2.34e-13	2.0	1.035	6	
1,1-Dichloroethane	11CL2-C2	2.60e-13				6	
Ethylene Dichloride	12CL2-C2	2.53e-13	9.90e-13	2.0	0.813	16	
Ethyl Bromide	C2-BR	3.08e-13	2.72e-11		2.671	6	
Chloroform	CHCL3	1.06e-13	5.67e-13	2.0	1.002	6	
n-Propyl Bromide	C3-BR	1.18e-12				56	
1,1,1-Trichloroethane	111-TCE	1.24e-14	5.33e-13	2.0	2.244	6	
1,1,2-Trichloroethane	112CL3C2	2.00e-13	4.00e-13	2.0	0.413	16	
n-Butyl Bromide	C4-BR	2.46e-12				56	
Ethylene Dibromide	11BR2-C2	2.27e-13	9.27e-13	2.0	0.839	16	
Trans-1,2-Dichloroethene	T-12-DCE	2.32e-12	1.01e-12		-0.497	16	
Trichloroethylene	CL3-ETHE	2.34e-12	5.63e-13		-0.849	16	
Perchloroethylene	CL4-ETHE	1.71e-13	9.64e-12		2.403	16	
<u>Sulfur-Containing Compounds</u>							
Dimethyl Sulfide	DMS	4.85e-12	1.13e-11		0.505	16	
Dimethyl Sulfoxide	DMSO	6.20e-11				6	
<u>Silicon-Containing Compounds</u>							
Hexamethyldisiloxane	SI2OME6	1.38e-12				6	
Hydroxymethyldisiloxane'	SI2OMEOH	1.89e-12				6	
D4 Cyclosiloxane	(SIOME)4	1.00e-12				6	
D5 Cyclosiloxane	(SIOME)5	1.55e-12				6	

References

- 1 Rate constant expression recommended by Atkinson (1997a)
- 2 Carter et al (2000b)
- 3 Atkinson et al. (2000a)
- 4 Room temperature rate constant from Carter et al (2000c).
- 5 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated based on data for similar alkenes.
- 6 Rate constant expression recommended by Atkinson (1989). Recommendation not changed in evaluation update by Atkinson (1994).

Table 8 (Continued)

- 7 Assumed to have same rate constant as n-propyl benzene
- 8 Rate constant from Baulch et al (1989).
- 9 Rate constant from Atkinson and Aschmann (1988a)
- 10 Rate constant from Atkinson and Aschmann (1987).
- 11 Rate constant from Atkinson and Aschmann (1986).
- 12 Rate constant based on average of values for 1- and 2- isomers tabulated by Atkinson (1989).
- 13 Rate constant based on data tabulated by Atkinson (1989) and consistent with more recent measurement given by Atkinson (1994).
- 14 Rate constant from Atkinson et al (1985).
- 15 Rate constant from average of values for o-, m- and p- isomers tabulated by Atkinson (1989).
- 16 Rate constant expression recommended by Atkinson (1994)
- 17 Rate expression recommended by IUPAC panel (Atkinson et al, 1999).
- 18 Rate constant used is Atkinson (1989) recommendation. $k=8.1e-13$ from Saunders et al (1994) not used because problems reported. $k=1.43e-12$ from Tuazon and co-workers (Carter et al, 1986c) does not fit chamber results (Carter et al, 1986c).
- 19 Rate constant from Wallington et al (1988a).
- 20 Rate constant from Carter et al (2000a).
- 21 Rate constant from Aschmann and Atkinson (1998).
- 22 Rate constant from Dagaut et al (1988a).
- 23 Rate constant used is average of various measurements tabulated by Sidebottom et al (1997).
- 24 Rate constant from Wallington et al (1990).
- 25 Rate constant from Bennett and Kerr (1989).
- 26 Rate constant from Wallington et al (1988b).
- 27 Rate constant of Dagaut et al (1988a) used. Value of Hartmann et al (1986) not consistent with chamber data (Carter et al, 1993a)
- 28 Average of values of Porter et al (1995) and Aschmann and Atkinson (1998)
- 29 Average of values of Dagaut et al (1988a), Stemmler et al (1996) and Aschmann and Atkinson (1998), as tabulated by Aschmann and Atkinson (1997).
- 30 Rate constant from Carter et al (1993a).
- 31 Rate constant from Wallington et al (1988d).
- 32 Rate constant from Wells et al. (1999).
- 33 Absolute rate constant determined by Orkin (NIST unpublished results, 1999) is used. This value is in good agreement with a more imprecise relative determination of Carter et al (2000d)
- 34 Rate constant from Smith et al (1992). Average of values relative to propane and n-butane
- 35 Rate constant from Carter et al (1996c).
- 36 Rate constant from Atkinson and Carter (1995).
- 37 Carter et al (unpublished results, 2000d)
- 38 Rate constant from Carter et al (1997e).
- 39 Rate constant from Wallington et al (1988c).
- 40 Rudich et al (1995), as recommended by Atkinson (personal communication, 2000). Good agreement with data of Ferronato et al (1998).
- 41 Rate expression recommended by IUPAC panel (Atkinson et al, 1997a).
- 42 Rate constant from Atkinson et al (1983).
- 43 See Carter and Atkinson (1996) and references therein.
- 44 Rate constant estimated by Carter and Atkinson (1996).

Table 8 (Continued)

- 45 Rate constant from Daguat et al (1988b).
- 46 Atkinson et al, (2000b)
- 47 Rate constant from Wallington and Kurylo (1987).
- 48 Rate constant from Atkinson et al (1982).
- 49 Carter et al (1999a)
- 50 Becker et al (1988)
- 51 Estimated to have a rate constant that is twice that of *para*-toluene isocyanate, based on the structure of the molecule (Carter et al, 1999a).
- 52 Rate constant estimated from the 298K rate constant for ethylamine and the difference between estimated rates of reaction at -CH₃ or -CH₂OH derived using the group-additivity methods of Kwok and Atkinson (1995).
- 53 Anderson and Stephens (1988), as recommended by Atkinson (1989)
- 54 Rate constant estimated by adding 2 times the difference between the rate constant for ethylene glycol and ethanol to the rate constant for dimethylamine.
- 55 Rate constant estimated by adding 3 times the difference between the rate constant for ethylene glycol and ethanol to the rate constant for trimethylamine.
- 56 Donaghy et al. (1993)

should be removed once methods to generate and estimate reactions of unsaturated radicals are developed.

3. Estimation of OH Addition Rate Constants

Rate constant estimates for additions to double bonds are made by estimating total rate constants for reaction at a double bond with a given number and configuration of substituents, and then, for unsymmetrical molecules, estimating the fraction that reacts at the each end. These estimates are shown in Table 10, along with an indication of the derivation of the values used. The total rate constant estimates are based on measured rate constants for representative molecules, but only limited information is available upon which to base the branching ratio estimates, which are therefore more uncertain. These estimates are then used to derive a group rate constant for each of the two groups around the double bond. Note that since the present system does not support generating mechanisms with more than one C=C double bond (except for "special reactants", as discussed later), the estimates on this table are only applicable to monoalkenes.

The group rate constant estimates on Table 10 are somewhat different than those given by Kwok and Atkinson (1997) for several reasons. Propene is not used when deriving the group rate constants for monosubstituted alkenes because its OH rate constant is known and kinetic data for the higher 1-alkenes, which are expected to be more similar to the types of compounds for which estimates may be needed, are better fit by slightly higher values. The estimates of Kwok and Atkinson (1997) also take into account the possibility that some of the reaction may be occurring by abstraction from other groups, which is ignored in our estimates (see below). Kwok and Atkinson (1997) give correction factors for oxygenated substituents, but these are also not fully implemented in the present system because in this work estimates are mainly needed only for hydrocarbon species. The few unsaturated oxygenated species that are handled by the system (primarily acrolein and isoprene products) already have measured or assigned total OH rate constants (e.g., see Carter and Atkinson, 1996). However, correction factors from Kwok and Atkinson

Table 9. Group rate constants and substituent factors used to estimate OH radical abstraction rate constants.

Group	k(group) = A T ^B e ^{-D/T} (cm ³ molec ⁻¹ s ⁻¹)					F(group)		F(subgroup)		
	k(298)	A	B	D	Ref	F	Ref	Subgroup	F	Ref
-CH ₃	1.36e-13	4.49e-18	2	320	a	1.00	a			
-CH ₂ -	9.34e-13	4.50e-18	2	-253	a	1.23	a	-CH ₂ (CO-)	3.90	a
								-CH ₂ (CO-O-)	1.23	a
								-CH ₂ (F)	0.61	a
								-CH ₂ (Cl)	0.36	a
								-CH ₂ (Br)	0.46	a
>CH-	1.95e-12	2.12e-18	2	-696	a	1.23	a	-CH(CO-)	3.90	a
								-CH(CO-O-)	1.23	a
								-CH(F)-	0.21	a
								-CH(Cl)-	0.36	a
								-CH(Br)-	0.46	a
>C<						1.23		>C(CO-)	3.90	a
								>C(CO-O-)	1.23	a
								>C(F)-	0.21	a
								>C(Cl)-	0.36	a
								>C(Br)-	0.46	a
-O-						8.40	a	-O(CO-)	1.60	a
								-O(CHO)-	0.90	e
								-O(NO ₂)-	0.04	a
-OH	1.40e-13	2.10e-18	2	85	a	3.50	a			
-CHO	1.58e-11	5.55e-12	0	-311	b	0.75	a			
HCO(O)-	0.00e+00				c	-				
-CO-						0.75	a	-CO(O-)	0.31	d
-ONO ₂						0.04	a			
-F						0.09	a			
-Cl						0.38	a			
-Br						0.28	a			
-I						0.53	a			
-NO ₂						0.00	a			

References

- a Kwok and Atkinson (1995)
- b Based on kOH for acetaldehyde (Atkinson et al, 1997a, 1999)
- c Reaction at formate group assumed to be negligible based on low OH + formate rate constants (Atkinson, 1989)
- d Updated value from Kwok et al (1996)
- e Adjusted to fit experimental kOH's for ethyl and methyl formate. (Does not work well for methyl formate, but assigned kOH is used for that compound.)

Table 10. Group rate constants used for estimating rates of OH addition reactions.

Group	Estimated Total Rate Constant (300K) ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)	Fraction reacting at least substituted end
CH ₂ =CH-	3.16e-11 Total rate constant based on average for 300K rate constants for 1-butene, 3-methyl-1-butene, 1-pentene, 1-hexene and 3-3-dimethyl-1-butene (Atkinson, 1997a).	0.65 Terminal bond addition fraction from Cvetanovic (1976).
CH ₂ =C<	5.79e-11 Total rate constant based on average for 300K rate constants for isobutene, 2-methyl-1-butene and 2-methyl-1-pentene (Atkinson, 1997a).	1.00 100% addition at terminal end assumed.
-CH=CH-	6.33e-11 Total rate constant based on average for 300K rate constants for the 2-butenes, the 2-pentenenes, trans-4-methyl-2-pentene, trans-4,4-dimethyl-2-pentene, trans-2-heptene, trans-4-octene, cyclopentene, and cyclohexene (Atkinson, 1997a).	0.50 Equal addition at each position assumed.
-CH=C<	8.70e-11 Total rate constant based on average for 300K rate constants for 2-methyl-2-butene and 2-methyl-2-pentene (Atkinson, 1997a).	0.75 No information available concerning relative addition rates at the different positions. Roughly estimate 75% addition at the least substituted position.
>C=C<	1.05e-10 Total rate constant based on average for 300K rate constants for 2,3-dimethyl-2-butene and 2,3-dimethyl-2-pentene (Atkinson, 1997a).	0.50 Equal addition at each position assumed.

Table 11. Summary of average biases and errors in estimates of OH radical rate constants from data given on Table 8.

Class	Count	Average	
		Bias	Error
Alkanes	46	2%	11%
Alkenes	26	4%	10%
Alcohols and Glycols	41	-11%	22%
Esters	27	-9%	21%
Saturated Aldehydes	7	-13%	13%
Acyclic Ketones	16	9%	9%

Notes:

Bias is average of percentage differences between experimental and estimated values

Error is average of absolute value of percentage differences.

(1997) for -CHO and -CO- substituents, of 0.35 and 0.9, respectively, have been incorporated on a preliminary basis.

4. Comparison of Estimated and Assigned Rate Constants

Table 8, above, shows a comparison of the estimated and assigned OH radical rate constants, from which one can obtain an indication of the overall performance of the estimation methods for the various types of VOCs. Table 11 shows a summary of average percentage errors (biases) and average absolute percentage errors (errors) for OH radical rate constant estimates for various classes of VOCs. It can be seen that the estimation method performs reasonably well for alkanes and alkenes, having biases of less than 5% and an average error of less than 12%. The estimates do not perform as well for the oxygenated compounds, with average errors on the order of 15-25%. Refinements to the estimation method may improve the performance for these oxygenates, but updating the work of Kwok and Atkinson (1995) was beyond the scope of this report.

5. Assigned Mechanisms for Initial OH Reactions

Because estimation methods for the branching ratios for the reactions of OH radicals at different positions of the molecule have some uncertainty, branching ratios are explicitly assigned for those compounds where experimental data are available, and indicate that the estimates may not be appropriate. In addition, as indicated in Table 7, several alkynes and dialkenes have also been incorporated into the mechanism generation system as "special reactants", whose reactions cannot be estimated and therefore need to be specified explicitly. The explicitly assigned branching ratios for initial OH radical reactions that are currently incorporated in the system are summarized on Table 12, along with the basis for the various assignments that are used.

Table 12. Assigned mechanisms for the initial reactions of OH radicals with compounds for which estimates could not be made, or where experimental data indicate that the estimates may not be appropriate.

Reactant and Products [a]	Factor	Documentation
<u>1,3-Butadiene</u> [CH ₂ =CH-CH=CH ₂] CH ₂ =CH-CH[.] -CH ₂ -OH	100.0%	Terminal addition assumed to dominate because of formation of resonance-stabilized radical.
<u>Isoprene</u> [CH ₂ =CH-C(CH ₃)=CH ₂] CH ₂ =CH-C[.](CH ₃)-CH ₂ -OH	52.4%	Mechanism assumed to be as discussed by Carter and Atkinson (1996).
CH ₂ =C(CH ₃)-CH[.] -CH ₂ -OH	42.6%	See above.
CH ₂ =CH-C(OH)(CH ₂ .)-CH ₃	2.5%	Based on observed 3-methyl furan yields as discussed by Carter and Atkinson (1996).
CH ₂ =C(CH ₃)-CH(CH ₂ .)-OH	2.5%	See above.
<u>Acetylene</u> [HC::CH] HO-CH=CH.	90.0%	Estimated mechanism is based on the data of Hatakeyama et al (1986) and modeling acetylene environmental chamber runs Carter et al (1997c).
HCO-CH ₂ .	10.0%	See above. Adjusted to fit chamber data.
<u>Methyl Acetylene</u> [HC::C-CH ₃] CH ₃ -C[.] =CH-OH	100.0%	Estimated to be the major reaction pathway.
<u>Ethyl Acetylene</u> [HC::C-CH ₂ -CH ₃] CH ₃ -CH ₂ -C[.] =CH-OH	100.0%	Estimated to be the major reaction pathway.
<u>2-Butyne</u> [CH ₃ -C::C-CH ₃] CH ₃ -C(OH)=C[.] -CH ₃	100.0%	Estimated to be the major reaction pathway.
<u>Methanol</u> [CH ₃ -OH] HO-CH ₂ .	85.0%	Branching ratios recommended by IUPAC (Atkinson et al, 1997, 1999).
CH ₃ O.	15.0%	See above.
<u>Ethanol</u> [CH ₃ -CH ₂ -OH] CH ₃ -CH[.] -OH	90.0%	Branching ratios recommended by IUPAC (Atkinson et al, 1997, 1999).
CH ₃ -CH ₂ O.	5.0%	See above
HO-CH ₂ -CH ₂ .	5.0%	See Above
<u>1-Octanol</u> [CH ₃ -CH ₂ -OH] CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH[.] -OH	19.2%	Based on yields of octanal from 1-octanol (Carter et al, 2000a).
HO-CH ₂ -CH ₂ .	1.5%	Relative branching ratios of other routes estimated using method of Kwok and Atkinson (1995).
CH ₃ -CH[.] -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -OH	10.8%	See above.
CH ₃ -CH ₂ -CH[.] -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -OH	13.3%	See above.
CH ₃ -CH ₂ -CH ₂ -CH[.] -CH ₂ -CH ₂ -CH ₂ -CH ₂ -OH	13.3%	See above.
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH[.] -CH ₂ -CH ₂ -CH ₂ -OH	13.3%	See above.

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH[.] -CH ₂ -CH ₂ -OH	13.3%	See above.
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH[.] -CH ₂ -OH	13.3%	See above.
CH ₃ -CH ₂ O.	1.7%	See above.
<u>2-Octanol [CH₃-CH(OH)-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃]</u>		
CH ₃ -C[.](OH)-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	36.5%	Based on yield of 2-octanone from 2-octanol (Carter et al, 2000a)
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH(CH ₂ .)-OH	1.5%	Relative branching ratios of other routes estimated using method of Kwok and Atkinson (1995).
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH[O.] -CH ₃	1.5%	See above.
CH ₃ -CH(OH)-CH[.] -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	12.3%	See above.
CH ₃ -CH(OH)-CH ₂ -CH[.] -CH ₂ -CH ₂ -CH ₂ -CH ₃	12.3%	See above.
CH ₃ -CH(OH)-CH ₂ -CH ₂ -CH[.] -CH ₂ -CH ₂ -CH ₃	12.3%	See above.
CH ₃ -CH(OH)-CH ₂ -CH ₂ -CH ₂ -CH[.] -CH ₂ -CH ₃	9.9%	See above.
CH ₃ -CH(OH)-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ .	1.5%	See above.
<u>3-Octanol [CH₃-CH₂-CH(OH)-CH₂-CH₂-CH₂-CH₂-CH₃]</u>		
CH ₃ -CH ₂ -C[.](OH)-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	42.4%	Based on yield of 3-octanone from 3-octanol (Carter et al, 2000a)
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH(OH)-CH ₂ -CH ₂ .	1.4%	Relative branching ratios of other routes estimated using method of Kwok and Atkinson (1995).
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH(OH)-CH[.] -CH ₃	9.4%	See above.
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH[O.] -CH ₂ -CH ₃	1.4%	See above.
CH ₃ -CH ₂ -CH(OH)-CH[.] -CH ₂ -CH ₂ -CH ₂ -CH ₃	11.5%	See above.
CH ₃ -CH ₂ -CH(OH)-CH ₂ -CH[.] -CH ₂ -CH ₂ -CH ₃	11.5%	See above.
CH ₃ -CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH[.] -CH ₂ -CH ₃	11.5%	See above.
CH ₃ -CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH ₂ -CH[.] -CH ₃	9.4%	See above.
CH ₃ -CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ .	1.4%	See above.
<u>4-Octanol [CH₃-CH₂-CH₂-CH(OH)-CH₂-CH₂-CH₂-CH₃]</u>		
CH ₃ -CH ₂ -CH ₂ -C[.](OH)-CH ₂ -CH ₂ -CH ₂ -CH ₃	36.6%	Based on yield of 4-octanone from 4-octanol (Carter et al, 2000a)
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH ₂ .	1.6%	Relative branching ratios of other routes estimated using method of Kwok and Atkinson (1995).
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH(OH)-CH ₂ -CH[.] -CH ₃	10.3%	See above.

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH(OH)-CH[.] -CH ₂ -CH ₃	12.7%	See above.
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH[O.] -CH ₂ -CH ₂ -CH ₃	1.6%	See above.
CH ₃ -CH ₂ -CH ₂ -CH(OH)-CH[.] -CH ₂ -CH ₂ -CH ₃	12.7%	See above.
CH ₃ -CH ₂ -CH ₂ -CH(OH)-CH ₂ -CH[.] -CH ₂ -CH ₃	12.7%	See above.
CH ₃ -CH ₂ -CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH[.] -CH ₃	10.3%	See above.
CH ₃ -CH ₂ -CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH ₂ -CH ₂ .	1.6%	See above.
<u>Methyl t-Butyl Ether [CH₃-C(CH₃)(CH₃)-O-CH₃]</u>		
CH ₃ -C(CH ₃)(CH ₃)-O-CH ₂ .	80.0%	Branching ratios based on product studies of Tuazon et al, (1991b); and Smith et al (1991), with overall yields increased to account for 100% reaction.
CH ₃ -C(CH ₃)(CH ₂ .)-O-CH ₃	20.0%	See Above
<u>1-Methoxy-2-Propanol [CH₃-CH(OH)-CH₂-O-CH₃]</u>		
CH ₃ -O-CH ₂ -CH(CH ₂ .)-OH	0.0%	Estimated to be minor
CH ₃ -C[.](OH)-CH ₂ -O-CH ₃	39.0%	Based on observed methoxyacetone yields (Tuazon et al, 1998a).
CH ₃ -O-CH ₂ -CH[O.] -CH ₃	0.0%	Estimated to be minor
CH ₃ -CH(OH)-CH[.] -O-CH ₃	58.0%	Based on observed methyl formate and acetaldehyde yields, the expected products from this route (Tuazon et al, 1998a)
CH ₃ -CH(OH)-CH ₂ -O-CH ₂ .	3.0%	Estimated to occur ~6% of the time. 3% yield assumed to account for 100% reaction.
<u>2-Butoxy-Ethanol [CH₃-CH₂-CH₂-CH₂-O-CH₂-CH₂-OH]</u>		
CH ₃ -CH ₂ -CH ₂ -CH ₂ -O-CH[.] -CH ₂ -OH	57.0%	Branching ratio based on observed yield of n-butyl formate, which is the expected major product from this route (Tuazon et al, 1998a).
CH ₃ -CH ₂ -CH ₂ -CH[.] -O-CH ₂ -CH ₂ -OH	22.0%	Branching ratio based on observed yields of 2-hydroxyethyl formate and propanal, the expected major products from this route (Tuazon et al, 1998a).
HO-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -CH ₂ -CH ₂ .	0.5%	Relative branching ratios for this and the other routes estimated using method of Kwok and Atkinson (1996).
CH ₃ -CH[.] -CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -OH	3.5%	See above.
CH ₃ -CH ₂ -CH[.] -CH ₂ -O-CH ₂ -CH ₂ -OH	4.3%	See above.
CH ₃ -CH ₂ -CH ₂ -CH ₂ -O-CH ₂ -CH[.] -OH	12.2%	See above.
CH ₃ -CH ₂ -CH ₂ -CH ₂ -O-CH ₂ -CH ₂ O.	0.6%	See above.
<u>Methyl Acetate [CH₃-O-CO-CH₃]</u>		
CH ₃ -CO-O-CH ₂ .	100.0%	Environmental chamber reactivity data fit somewhat better if reaction at the CH ₃ -CO end is assumed to be negligible.
CH ₃ -O-CO-CH ₂ .	0.0%	See above

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
<u>Propylene Carbonate [*CH(CH3)-CH2-O-CO-O-*</u>		
CH(CH2.)-CH2-O-CO-O-	25.0%	Branching ratio estimated from ratio of estimate for reaction at this position using method of Kwok and Atkinson (1996) to measured total rate constant Carter et al, 1996c).
C[.](CH3)-CH2-O-CO-O-	37.5%	Model simulations are somewhat more consistent with environmental chamber reactivity data if the other two reaction routes are assumed to occur with approximately equal probability.
*CH(CH3)-O-CO-O-CH[.]	37.5%	See above
<u>Methyl Isobutyrate [CH3-CH(CH3)-CO-O-CH3]</u>		
CH3-C[.](CH3)-CO-O-CH3	67.0%	Branching ratio derived from total rate constant and estimated rate constants for the competing reaction routes. This results in higher predicted yields for acetone, which is more consistent with the product data of Wells et al (1999).
CH3-CH(CH2.)-CO-O-CH3	20.0%	Branching ratio derived from ratio of rate constant for this route estimated using the method of Kwok and Atkinson (1995), relative to the total rate constant.
CH3-CH(CH3)-CO-O-CH2.	13.0%	See above.
<u>Propylene Glycol Methyl Ether Acetate [CH3-O-CH(CH3)-CH2-O-CO-CH3]</u>		
CH3-CO-O-CH2-CH(CH3)-O-CH2.	7.9%	Group rate constant estimated using method of Kwok and Atkinson (1995)
CH3-O-C[.](CH3)-CH2-O-CO-CH3	45.3%	Group rate constant adjusted to fit environmental chamber reactivity data, and to be consistent with measured total rate constant.
CH3-O-CH(CH2.)-CH2-O-CO-CH3	1.2%	Group rate constant estimated using method of Kwok and Atkinson (1995)
CH3-O-CH(CH3)-CH[.]O-CO-CH3	45.3%	Group rate constant adjusted to fit environmental chamber reactivity data, and to be consistent with measured total rate constant.
CH3-O-CH(CH3)-CH2-O-CO-CH2.	0.3%	Group rate constant estimated using method of Kwok and Atkinson (1995)
<u>Dimethyl Succinate (DBE-4) [CH3-O-CO-CH2-CH2-CO-O-CH3]</u>		
CH3-O-CO-CH2-CH2-CO-O-CH3 + OH -> H2O + CH3-O-CO-CH2-CH2-CO-O- CH2.	90.0%	Branching ratio derived from the ratio of the rate constant for the analogous reaction for dimethyl adipate (DBE-5) to the total rate constant. The former was derived from the DBE-5 yield data of Tuazon et al (1999) and total DBE-5 rate constant of Carter et al (1997e). Assuming that this reaction dominates also gives better results of model simulations of DBE-4 reactivity environmental chamber experiments.
CH3-O-CO-CH2-CH2-CO-O-CH3 + OH -> H2O + CH3-O-CO-CH2-CH[.]CO-O- CH3	10.0%	Branching ratio derived from branching ratio estimated for competing reaction.
<u>Dimethyl Adipate (DBE-5) [CH3-O-CO-CH2-CH2-CH2-CO-O-CH3]</u>		
CH3-O-CO-CH2-CH2-CH2-CO-O-CH2.	39.0%	Based on yield of CH3-O-CO-CH2-CH2-CH2-CO-OH observed by Tuazon et al (1999)

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
CH ₃ -O-CO-CH ₂ -CH[.]-CH ₂ -CO-O-CH ₃	41.0%	Yield of CH ₃ -O-CO-CH ₂ -CO-CH ₂ -CO-O-CH ₃ observed by Tuazon et al (1999) corresponds to this route occurring 33% of the time. However, model simulations fit chamber data somewhat better if this route is assumed to be relatively more important; so the fraction reacted at in this position is estimated from the ratio of the rate constant derived using estimates of Kwok and Atkinson (1985) as updated by Kwok et al (1996) to the measured total rate constant. This is within the uncertainty of the yield measurement.
CH ₃ -O-CO-CH ₂ -CH ₂ -CH[.]-CO-O-CH ₃	20.0%	See above
<u>Dimethoxy Methane [CH₃-O-CH₂-O-CH₃]</u> CH ₃ -O-CH ₂ -O-CH ₂ .	67.0%	Based on ratio of yields of CH ₃ -O-CH ₂ -O-CHO relative to CH ₃ -O-CO-O-CH ₃ + CH ₃ -O-CHO given by Sidebottom et al (1997), which is consistent with product data of Wallington et al (1997).
CH ₃ -O-CH[.]-O-CH ₃	33.0%	See above.
<u>2-Methyl-3-Buten-2-ol [CH₂=CH-C(CH₃)(OH)-CH₃]</u> CH ₃ -C(CH ₃)(OH)-CH[.]-CH ₂ -OH	66.7%	Based on product data reported by Alvarado et al (1999). The corresponding alkoxy radical is estimated to decompose form glycolaldehyde and the precursor to acetone, both observed products.
CH ₃ -C(CH ₃)(OH)-CH(OH)-CH ₂ .	33.3%	See above. Reaction at this position is assumed to be the only source of the observed formation of formaldehyde and 2-hydroxy-2-methylpropanal.
<u>Acrolein [CH₂=CH-CHO]</u> CH ₂ =CH-CO.	75.0%	Estimated rate constant for reaction at this position is intermediate between the estimate based on the analogous reaction of methacrolein and estimation using method of Atkinson (1987).
HCO-CH[.]-CH ₂ -OH	17.0%	Addition to double bond assumed to occur 25% of the time, based on total rate constant and estimate for reaction at the CHO position. Terminal/internal ratio based on the ratio determined for OH + propene.
HCO-CH(CH ₂ .)-OH	8.0%	See above.
<u>Crotonaldehyde [CH₃-CH=CH(CHO)]</u> CH ₃ -CH=CH(CO.)	45.0%	Assumed to occur with the same rate constant as the analogous reaction for methacrolein.
CH ₃ -CH[.]-CH(OH)-CHO	27.5%	Fraction reacted based on total rate constant, estimated rate for abstraction from -CHO, and assumption that addition at each side of the double bond is equal.
CH ₃ -CH(OH)-CH[.]-CHO	27.5%	See above.
<u>Methacrolein [CH₂=C(CHO)-CH₃]</u> CH ₃ -C[.](CHO)-CH ₂ -OH	44.0%	Adjusted to give same product distribution as used by Carter and Atkinson (1996), and to be consistent with available product data.
CH ₃ -C(OH)(CH ₂ .)-CHO	6.0%	See above.
CH ₂ =C(CO.)-CH ₃	50.0%	See above.

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
<u>Hydroxy Methacrolein [CH₂=C(CHO)-CH₂-OH]</u>		
CH ₂ =C(CO.)-CH ₂ -OH	38.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HO-CH ₂ -C[.](CHO)-CH ₂ -OH	52.0%	See above.
HCO-C(OH)(CH ₂ .)-CH ₂ -OH	10.0%	See above.
<u>Isoprene Product #1 [CH₃-C(CHO)=CH(CH₂-OH)]</u>		
CH ₃ -C(CO.)=CH(CH ₂ -OH)	25.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH ₃ -C[.](CHO)-CH(OH)-CH ₂ -OH	50.0%	See above.
CH ₃ -C(CHO)(OH)-CH[.]-CH ₂ -OH	25.0%	See above.
<u>Isoprene Product #2 [CH₃-C(CHO)=CH-CH₂-OH]</u>		
CH ₃ -C(CO.)=CH-CH ₂ -OH	25.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH ₃ -C[.](CHO)-CH(OH)-CH ₂ -OH	50.0%	See above.
CH ₃ -C(CHO)(OH)-CH[.]-CH ₂ -OH	25.0%	See above.
<u>Isoprene Product #3 [HCO-CH=C(CH₃)-CH₂-OH]</u>		
HO-CH ₂ -C(CH ₃)=CH-CO.	25.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCO-CH(OH)-C[.](CH ₃)-CH ₂ -OH	50.0%	See above.
HCO-CH[.]-C(CH ₃)(OH)-CH ₂ -OH	25.0%	See above.
<u>Cyclohexanone [*CH₂-CH₂-CH₂-CH₂-CH₂-CO-*]</u>		
CH ₂ -CH ₂ -CH ₂ -CH ₂ -CO-CH[.]-	44.0%	Better fits of model simulations to results of environmental chamber reactivity experiments are obtained if equal probability of reaction at alpha and beta positions (Carter et al, 2000a).
CH ₂ -CH ₂ -CH ₂ -CO-CH ₂ -CH[.]-	44.0%	See above.
CH ₂ -CH ₂ -CO-CH ₂ -CH ₂ -CH[.]-	12.0%	Approximately the fraction reacted at this position estimated by method of Kwok and Atkinson (1995)
<u>Methylvinyl ketone [CH₂=CH-CO-CH₃]</u>		
CH ₃ -CO-CH[.]-CH ₂ -OH	70.0%	Based on product distribution of Tuazon and Atkinson (1989), as discussed by Carter and Atkinson (1996)
CH ₃ -CO-CH(CH ₂ .)-OH	30.0%	See above.
<u>Formic Acid [HCO-OH]</u>		
HCO ₂ .	100.0%	Believed to be the major reaction route.

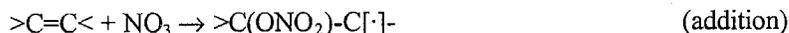
[a] Formation of H₂O, where applicable, is not shown.

D. Reactions with NO₃ Radicals

Reactions with NO₃ radicals can be a non-negligible fate for alkenes and aldehydes under some conditions, and therefore are included in the mechanism. These reactions are considered in essentially the same way as reaction with OH radicals, except that HNO₃ or ONO₂-substituted products are formed. Thus, if the group has an abstractable hydrogen, the reaction is



And if the molecule has a double bond, the reaction is



However, the current system assumes that rate constants for all abstraction reactions are negligible except for reaction at aldehyde -CHO groups. Therefore, only H abstraction reactions of NO₃ with aldehydes or additions to alkenes are considered in the current mechanism.

1. Assigned NO₃ Radical Rate Constants

NO₃ radical rate constants have been measured for a number of VOCs in the current mechanism, though the coverage is nowhere near as complete as is the case for the OH radical reaction. Table 13 gives the NO₃ radical rate constants assigned to all VOCs in the current mechanism for which the reaction with NO₃ radicals is represented. Note that the table does not include measured NO₃ radical rate constants for alkanes and other species that the current mechanism neglects as being of negligible importance. Footnotes indicate the basis for the rate parameter assignments, most of which are based on Atkinson (1991, 1994, 1997a) recommendations.

2. Estimated NO₃ Radical Rate Constants

Reaction of NO₃ with aldehyde groups are based on the measured rate constant for the reaction of NO₃ with acetaldehyde, which is (Atkinson et al, 1997, 1999),

$$k(\text{NO}_3 + \text{X-CHO}) = 1.40 \times 10^{-12} e^{-3.696/RT} \cdot F(\text{X}) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.$$

where F(X) is the substituent factor for groups other than -CH₃ bonded to the -CHO. The correlation between NO₃ and OH radical abstraction rate constants given by Atkinson (1991)⁹ is used to estimate these group substituent correction factors, F(X), which are as follows:

- F(-CH₂-) = F(-CH-) = F(>C<) = 1.34 is derived from the correlation of Atkinson (1991) and the rate constant for OH abstraction from -CHO groups derived by the group-additivity method of Kwok and Atkinson (1995).
- F(-CHO) = 0.18 is derived from the correlation and the OH rate constant for glyoxal.
- F(-CO-) = 0.89 is derived from the correlation and the OH rate constant for methyl glyoxal.

Note that rate constants for NO₃ abstraction from -CHO groups bonded to an oxygen (e.g., formates) are estimated to be zero, so such reactions are not generated.

The group rate constants used for estimating NO₃ addition rate constants is given on Table 14, along with the documentation for the rate constant assignments. Note that in the case of NO₃ reactions we assume that addition always occurs to the least substituted position around the bond, based on the assumption that since NO₃ addition rate constants are lower than those for OH addition, they will tend to be more selective. Rate constant data are available for only a few compounds of each type, so the estimates are necessarily more uncertain than those for OH radical reactions. As with the OH addition estimates, the rate constant for propene is not used for making the estimates for general 1-alkenes because 1-butene is considered to be more representative of the types of the higher monoalkenes for which rate constant estimates would be needed.

⁹ Atkinson (1993) noted a good correlation between OH and NO₃ abstraction rate constants per abstractable hydrogen, with the data being fit by $\ln k_{\text{NO}_3} = 6.498 + 1.611 \ln k_{\text{OH}}$.

Table 13. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with NO₃ radicals in the present mechanism.

Compound	Model Name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
Propene	PROPENE	9.73e-15	4.59e-13		2.297	1	1.38e-14	42%
1-Butene	1-BUTENE	1.38e-14	3.14e-13		1.864	1	1.38e-14	0%
Isobutene	ISOBUTEN	3.32e-13	3.32e-13		0.000	2	3.32e-13	0%
cis-2-Butene	C-2-BUTE	3.47e-13	1.10e-13		-0.687	3	3.70e-13	7%
trans-2-Butene	T-2-BUTE	3.92e-13	1.10e-13	2.0	-0.759	1	3.70e-13	-6%
2-Methyl-2-Butene	2M-2-BUT	9.37e-12	9.37e-12		0.000	2	9.37e-12	0%
2,3-Dimethyl-2-Butene	23M2-BUT	5.72e-11	5.72e-11		0.000	2	5.72e-11	0%
Cyclopentene	CYC-PNTE	5.30e-13	5.30e-13		0.000	2	3.70e-13	-30%
Cyclohexene	CYC-HEXE	5.88e-13	1.05e-12		0.346	1	3.70e-13	-37%
1,3-Butadiene	13-BUTDE	1.00e-13	1.00e-13		0.000	2		
Isoprene	ISOPRENE	6.85e-13	3.03e-12		0.886	1		
a-Pinene	A-PINENE	6.09e-12	1.19e-12		-0.974	1		
3-Carene	3-CARENE	9.10e-12	9.10e-12		0.000	2		
b-Pinene	B-PINENE	2.51e-12	2.51e-12		0.000	2		
Sabinene	SABINENE	1.00e-11	1.00e-11		0.000	2		
d-Limonene	D-LIMONE	1.22e-11	1.22e-11		0.000	2		
2-Methyl-2-Butene-3-ol	MBUTENOL	1.21e-14	4.60e-14		0.795	13	1.38e-14	14%
2-(Cl-methyl)-3-Cl-Propene	CL2IBUTE	1.00e-15				4		
Styrene	STYRENE	1.51e-13				5		
Acetaldehyde	ACETALD	2.84e-15	1.40e-12		3.696	6	2.84e-15	0%
Methylvinyl ketone	MVK	0.00e+00				7	2.76e-18	
Methacrolein	METHACRO	4.76e-15	1.50e-12		3.430	8		
Isoprene Product #1	IP-MHY1	1.00e-13				9		
Isoprene Product #2	IP-MHY2	1.00e-13				9		
Isoprene Product #3	IP-HMY	1.00e-13				9		
Hydroxy Methacrolein	HOMACR	4.76e-15	1.50e-12		3.430	10		
Crotonaldehyde	CROTALD	5.12e-15				11		

References

- 1 Rate constant expression recommended by Atkinson (1997a)
- 2 Rate constant from Atkinson (1997a). Temperature dependence is assumed to be small.
- 3 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for trans-2-butene.
- 4 This rate constant estimated by Atkinson (private communication, 1997) based on the rate constant for NO₃ + Allyl chloride (Atkinson, 1991)
- 5 Rate constant from Atkinson and Aschmann (1988a).
- 6 Rate constant expression recommended by IUPAC, Supplement V (Atkinson et al, 1997).
- 7 Data of Kwok et al (1997) indicate that the total rate constant is less than 6e-18 cm³ molec⁻¹ s⁻¹, which make it unimportant under atmospheric conditions.
- 8 Total rate constant from Kwok et al (1996). Temperature dependence estimated by Carter and Atkinson (1996)
- 9 Rate constant estimated by Carter and Atkinson (1996).
- 10 Rate constant assumed to be the same as for methacrolein (Carter and Atkinson, 1996)
- 11 Atkinson et al (1987)
- 12 Rate constant from Carter et al (1996c).

Table 14. Group rate constants and group substituent correction factors used for estimating rates of NO₃ addition reactions.

Groups	Estimated Total Rate Constant (300K) (cm ³ molec ⁻¹ s ⁻¹)	Fraction reacting at least substituted end
CH ₂ =CH-	1.38e-14 Total rate constant based on 300K value for 1-butene (Atkinson, 1997a).	1.0 100% addition at terminal end assumed.
CH ₂ =C<	3.32e-13 Total rate constant based on 300K value for isobutene (Atkinson, 1997a)	1.0 100% addition at terminal end assumed.
-CH=CH-	1.85e-13 Total rate constant based on averaging the 300K values for cis and trans 2-butene (Atkinson, 1997a).	0.5 Equal addition at each position assumed.
-CH=C<	3.32e-13 Total rate constant based on 300K value for 2-methyl-2-butene (Atkinson, 1997a).	1.0 100% addition at the least substituted end is assumed.
>C=C<	2.86e-11 Total rate constant based on the 300K value for 2,3-dimethyl-2-butene (Atkinson, 1997a).	0.5 Equal addition at each position assumed.

The group rate constants shown on Table 14 are strictly speaking applicable only for estimating rate constants for unsaturated hydrocarbons. Group correction factors, which are multiplied by the group rate constants shown on Table 14, are used for estimating rate constants for NO₃ to double bonds in unsaturated carbonyls. These are as follows:

- A factor of 0.007 is used if the double bond has a -CHO substituent, based on the ratio of the estimated rate constant for NO₃ addition to methacrolein (Carter and Atkinson, 1996) to the group rate constant for CH₂=C<.
- A factor of 2×10^{-4} is used if the double bond has a -CO- substituent, based on the upper limit rate constant for the reaction of NO₃ with methyl vinyl ketone (Carter and Atkinson, 1996). The actual upper limit rate constant of 6×10^{-18} cm³ molec⁻¹ s⁻¹ corresponds to a factor of $\sim 4 \times 10^{-4}$, but we arbitrarily use a factor which is half that. This is sufficiently small to make reactions of NO₃ with such compounds to be of negligible importance.

The performance of the estimation method in predicting the measured NO₃ radical rate constants is indicated on Table 13. Except for propene (for which estimates are not needed) and the halogenated alkene on the list (whose subsequent reactions are not currently supported by the system), the estimates generally perform reasonably well. Of course, in most cases this is because the estimates are based on these data. There does seem to be a bias towards underpredicting the rate constants for the cycloalkenes, and it may be appropriate to add a ring correction term for such compounds.

3. Assigned Mechanisms for Initial NO₃ Reactions

As with OH reactions discussed above, explicit assignments are used for the initial reactions for those VOCs where estimates cannot be made, where available experimental data indicate the estimates are inappropriate, or where alternative estimates are used. The explicitly assigned branching ratios for the

initial NO₃ radical reactions that are currently incorporated in the system are summarized on Table 15, along with the basis for the various assignments that are used.

E. Reactions with O₃

Reactions with O₃ are assumed to occur only at carbon-carbon double bonds¹⁰, and the reactions are assumed to involve ultimately breaking the bond and forming a carbonyl and an excited Crigiee biradical, i.e.



Two reactions are generated for each C=C bond, involving formation of the biradical from each of the two groups around the bond. Therefore, it is necessary to know both the total rate constant and the fraction of biradical formation at each of the groups around the bond.

1. Assigned O₃ Rate constants

Rate constants for reaction with O₃ have been measured for most of the VOCs in the current mechanism for which O₃ reactions are assumed to be non-negligible. Table 16 lists the rate parameter assignments for all VOCs for which this is the case, and indicates the source of the assignments. Again, this includes all VOCs in the current mechanism, not just those whose reactions can be processed by the mechanism generation system. As with the other reactions, almost all of the assignments are based on recommendations from various Atkinson reviews (Atkinson and Carter, 1984; Atkinson, 1994, 1997a).

2. Estimated Total Rate Constants

As discussed by Atkinson and Carter (1984), ozone + alkene rate constants tend to be quite variable depending on the structure of the compound, even if grouped according to the number of substituents on each side of the double bond. This is shown on Figure 2, which shows a comparison of the T=300K rate constants for the various monoalkenes tabulated by Atkinson (1997a), with a separate plot for each type of double bond structure. Note that cyclohexenes (which tend to have higher O₃ rate constants) and terpenes (whose structures the mechanism generation system cannot presently handle) are not shown. It can be seen that there is variability in the rate constants, particularly for the 1,1-disubstituted compounds. It is interesting to note that the more highly branched compounds tend to have the lowest rate constants, suggesting that steric effects may be important.

Fortunately, measured O₃ rate constants are available for most of the alkenes that are important in current emissions, which tend to be the lower molecular weight compounds. However, it is still necessary to have a method to estimate rate constants for those compounds where no data are available, even if it is uncertain. For this purpose, we use the average of the rate constants for the reactions at the various types of double bonds, as shown on Figure 2, and as summarized on Table 17. Table 16, shows the discrepancies between the experimental and estimated values for all the alkenes in the current mechanism. The anomalously low value for 3,4-dietlyl-2-hexene (which may be low because of steric hindrance) was not used when computing the average for -CH=C<. Although there is variability, the averages are probably appropriate as best estimates for compounds whose rate constants are not known, at least for use by the mechanism generation system at its current state of development. Obviously, compounds with large steric effects need to be estimated on a case-by-case basis.

¹⁰ Reactions of O₃ with alkynes are included as assigned reactions for special reactants (see Section III.E.4), but are not automatically generated by the system.

Table 15. Assigned mechanisms for the reactions of NO₃ radicals with compounds for which estimates could not be made, or where experimental data or other considerations indicate that the general estimates may not be appropriate.

Reactant and Products	Factor	Documentation
<u>1,3-Butadiene [CH₂=CH-CH=CH₂]</u> CH ₂ =CH-CH[.] -CH ₂ -ONO ₂	100.0%	Terminal addition assumed to dominate because of formation of resonance-stabilized radical.
<u>Isoprene [CH₂=CH-C(CH₃)=CH₂]</u> CH ₂ =CH-C[.](CH ₃)-CH ₂ -ONO ₂	100.0%	Mechanism of Carter and Atkinson (1996) is assumed.
<u>Crotonaldehyde [CH₃-CH=CH(CHO)]</u> CH ₃ -CH=CH(CO.)	45.0%	Assumed to occur with the same rate constant as the analogous reaction for methacrolein.
CH ₃ -CH[.] -CH(ONO ₂)-CHO	27.5%	Fraction reacted based on total rate constant, estimated rate for abstraction from -CHO, and assumption that addition at each side of the double bond is equal.
CH ₃ -CH(ONO ₂)-CH[.] -CHO	27.5%	See above.
<u>Methacrolein [CH₂=C(CHO)-CH₃]</u> HNO ₃ + CH ₂ =C(CO.)-CH ₃	50.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH ₃ -C[.](CHO)-CH ₂ -ONO ₂	50.0%	See above.
<u>Hydroxy Methacrolein [CH₂=C(CHO)-CH₂-OH]</u> HNO ₃ + CH ₂ =C(CO.)-CH ₂ -OH	50.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HO-CH ₂ -C[.](CHO)-CH ₂ -ONO ₂	50.0%	See above.
<u>Isoprene Product #1 [CH₃-C(CHO)=CH(CH₂-OH)]</u> CH ₃ -C[.](CHO)-CH(ONO ₂)-CH ₂ -OH	100.0%	Mechanism of Carter and Atkinson (1996) is assumed. Abstraction from -CHO is estimated to occur only ~4% of the time.
<u>Isoprene Product #2 [CH₃-C(CHO)=CH-CH₂-OH]</u> CH ₃ -C[.](CHO)-CH(ONO ₂)-CH ₂ -OH	100.0%	Mechanism of Carter and Atkinson (1996) is assumed. Abstraction from -CHO is estimated to occur only ~4% of the time.
<u>Isoprene Product #3 [HCO-CH=C(CH₃)-CH₂-OH]</u> HCO-CH(ONO ₂)-C[.](CH ₃)-CH ₂ -OH	100.0%	Mechanism of Carter and Atkinson (1996) is assumed. Abstraction from -CHO is estimated to occur only ~4% of the time.

Table 16. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with O₃ in the present mechanism.

Compound	Model Name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	Ea kcal/mole	Ref	Est'd	
						k(300)	(diff)
Ethene	ETHENE	1.68e-18	9.14e-15	5.127	1	1.68e-18	0%
Propene	PROPENE	1.05e-17	5.51e-15	3.732	1	1.01e-17	-4%
1-Butene	1-BUTENE	1.00e-17	3.36e-15	3.466	1	1.01e-17	1%
Isobutene	ISOBUTEN	1.17e-17	2.70e-15	3.243	1	1.18e-17	1%
cis-2-Butene	C-2-BUTE	1.28e-16	3.22e-15	1.924	1	1.15e-16	-10%
trans-2-Butene	T-2-BUTE	1.95e-16	6.64e-15	2.104	1	1.15e-16	-41%
1-Pentene	1-PENTEN	1.04e-17	3.36e-15	3.445	2	1.01e-17	-3%
2-Methyl-1-Butene	2M-1-BUT	1.66e-17	2.70e-15	3.037	3	1.18e-17	-29%
2-Methyl-2-Butene	2M-2-BUT	4.08e-16	2.87e-15	1.162	4	3.48e-16	-15%
3-Methyl-1-Butene	3M-1-BUT	1.14e-17	3.36e-15	3.388	2	1.01e-17	-12%
1-Hexene	1-HEXENE	1.14e-17	3.36e-15	3.388	2	1.01e-17	-12%
Cis-3-Hexene	C-3-C6E	1.53e-16	3.22e-15	1.816	5	1.15e-16	-25%
Trans-3-Hexene	T-3-C6E	1.74e-16	6.64e-15	2.170	6	1.15e-16	-34%
2-Methyl-1-Pentene	2M1-C5E	1.55e-17	2.70e-15	3.075	3	1.18e-17	-24%
3-Methyl-1-Pentene	3M1-C5E	5.12e-18	3.36e-15	3.867	2	1.01e-17	97%
4-Methyl-1-Pentene	4M1-C5E	9.57e-18	3.36e-15	3.494	2	1.01e-17	6%
Cis-3-Methyl-2-Hexene	C3M2-C5E	4.56e-16	2.87e-15	1.096	4	3.48e-16	-24%
Trans 3-Methyl-2-Hexene	T3M2-C5E	5.66e-16	2.87e-15	0.967	4	3.48e-16	-39%
2,3-Dimethyl-1-Butene	23M1-BUT	1.35e-17	2.70e-15	3.160	3	1.18e-17	-12%
3,3-Dimethyl-1-Butene	33M1-BUT	5.43e-18	3.36e-15	3.832	2	1.01e-17	86%
2,3-Dimethyl-2-Butene	23M2-BUT	1.14e-15	3.03e-15	0.584	1	6.74e-16	-41%
2-Ethyl-1-Butene	2E1-BUT	1.35e-17	2.70e-15	3.160	3	1.18e-17	-12%
1-Heptene	1-HEPTEN	1.25e-17	3.36e-15	3.337	2	1.01e-17	-19%
2,3,3-trimethyl-1-Butene	233M1BUT	8.63e-18	2.70e-15	3.426	3	1.18e-17	37%
1-Octene	1-OCTENE	1.45e-17	3.36e-15	3.246	2	1.01e-17	-30%
Cis-4-Octene	C-4-C8E	9.73e-17	3.22e-15	2.086	5	1.15e-16	18%
Trans-4-Octene	T-4-C8E	1.44e-16	6.64e-15	2.285	6	1.15e-16	-20%
Trans 2,5-Dimethyl 3-Hexene	T25M3C6E	4.24e-17	6.64e-15	3.013	6	1.15e-16	>100%
Trans 2,2-Dimethyl 3-Hexene	T22M3C6E	4.34e-17	6.64e-15	2.998	6	1.15e-16	>100%
2,4,4-trimethyl-2-Pentene	244M2C5E	1.43e-16	2.87e-15	1.788	4	3.48e-16	>100%
3-Methyl-2-Isopropyl-1-Butene	3M2I1C4E	3.45e-18	2.70e-15	3.972	3	1.18e-17	>100%
1-Decene	1-C10E	9.67e-18	3.36e-15	3.488	2	1.01e-17	4%
Cis-5-Decene	C-5-C10E	1.23e-16	3.22e-15	1.948	5	1.15e-16	-6%
3,4-Diethyl-2-Hexene	34E2-C6E	4.39e-18	2.87e-15	3.864	4	3.48e-16	>100%
Cyclopentene	CYC-PNTE	5.61e-16	1.80e-15	0.696	1	1.15e-16	-79%
1-Methyl cyclohexene	1M-CC5E	6.76e-16	2.70e-15	0.825	3	3.48e-16	-49%
Cyclohexene	CYC-HEXE	8.33e-17	2.88e-15	2.112	1	1.15e-16	38%
1-Methyl Cyclohexene	1M-CC6E	1.68e-16	2.87e-15	1.690	4	3.48e-16	>100%
4-Methyl Cyclohexene	4M-CC6E	8.40e-17	2.88e-15	2.107	7	1.15e-16	37%
1,2-Dimethyl Cyclohexene	12M-CC6E	2.11e-16	3.03e-15	1.589	8	6.74e-16	>100%
1,3-Butadiene	13-BUTDE	6.64e-18	1.34e-14	4.537	1		
Isoprene	ISOPRENE	1.34e-17	7.86e-15	3.802	1		
a-Pinene	A-PINENE	8.80e-17	1.01e-15	1.455	1		
3-Carene	3-CARENE	3.78e-17	1.01e-15	1.958	9		
b-Pinene	B-PINENE	1.54e-17	1.01e-15	2.493	9		
Sabinene	SABINENE	8.74e-17	1.01e-15	1.459	9		
d-Limonene	D-LIMONE	2.04e-16	3.71e-15	1.729	10		
2-Methyl-2-Butene-3-ol	MBUTENOL	9.30e-18			18	1.01e-17	9%

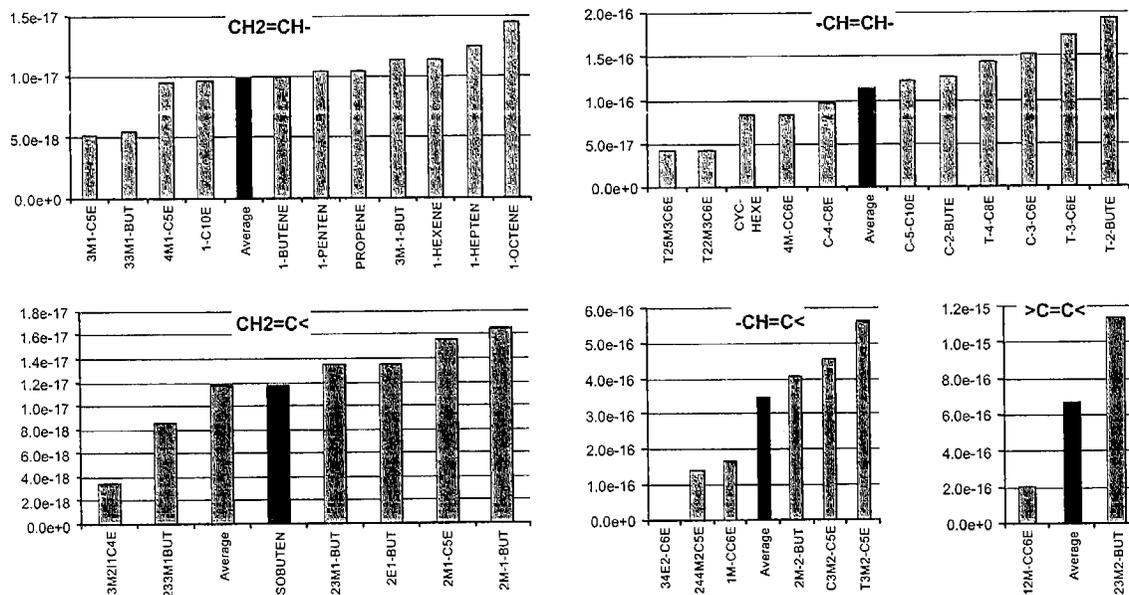
Table 16 (continued)

Compound	Model Name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	Ea kcal/mole	Ref	Est'd k(300) (diff)
2-(Cl-methyl)-3-Cl-Propene	CL2IBUTE	3.90e-19			11	
Styrene	STYRENE	1.71e-17			12	
Acetylene	ACETYLEN	8.61e-21	2.00e-14	8.739	13	
Methyl Acetylene	ME-ACTYL	1.56e-20	1.00e-14	7.970	14	
Ethyl Acetylene	ET-ACTYL	2.15e-20	1.00e-14	7.780	14	
2-Butyne	2-BUTYNE	2.15e-20	1.00e-14	7.780	15	
Methylvinyl ketone	MVK	4.74e-18	7.51e-16	3.020	12	
Methacrolein	METHACRO	1.19e-18	1.36e-15	4.200	12	
Isoprene Product #1	IP-MHY1	1.00e-17			16	
Isoprene Product #2	IP-MHY2	1.00e-17			16	
Isoprene Product #3	IP-HMY	1.00e-17			16	
Hydroxy Methacrolein	HOMACR	1.19e-18	1.36e-15	4.200	17	
Crotonaldehyde	CROTALD	9.00e-19			11	
Acrolein	ACROLEIN	3.07e-19	1.36e-15	5.006	19	

References

- 1 Rate constant expression recommended by Atkinson (1997a)
- 2 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for 1-butene.
- 3 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for isobutene.
- 4 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as the average of those for isobutene and 2,3-dimethyl-2-butene.
- 5 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for cis-2-butene.
- 6 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for trans-2-butene.
- 7 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for cyclohexene.
- 8 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for 2,3-dimethyl-2-butene.
- 9 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for a-pinene.
- 10 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the sum of those for a-pinene and isobutene.
- 11 Rate constant recommended by Atkinson and Carter (1984)
- 12 Rate constant recommended by Atkinson (1994).
- 13 T=298K rate constant is from Atkinson and Aschmann (1984), as recommended by IUPAC (Atkinson et al, 1999). The temperature dependence is estimated based on assuming the A factor is roughly twice that for O₃ + ethylene.
- 14 T=298K rate constant is from Atkinson and Aschmann (1984). The temperature dependence is estimated based on assuming the A factor is roughly twice that for O₃ + propene.
- 15 Assumed to have approximately the same rate constant as 1-butyne, based on data given by Atkinson and Carter (1984).
- 16 Rate constant estimated by Carter and Atkinson (1996)
- 17 Estimated to have the same rate constant as methacrolein (Carter and Atkinson, 1996)
- 18 Average of 291K rate constant of Grosjean and Grosjean (1994) and the 298K rate constant of Fantechi et al (1998).
- 19 Rate constant at 298K of 2.9e-19 recommended by Atkinson (1994). Activation energy assumed to be the same as used for methacrolein.

Figure 2. Comparison of O_3 + alkene rate constants for alkenes with the same configurations of constituents about the double bond.



3. Branching Ratios for Biradical Formation

Since the biradical and carbonyl formation in the initial O_3 reaction can occur on two different positions in unsymmetrical molecules, it is necessary to specify their relative importances. Information concerning this can be obtained from the measured yields of the primary carbonyl products, which are summarized by Atkinson (1997a). The averages of the primary yield data given by Atkinson (1997a) are summarized on Table 18 through Table 20 for the olefins with the various types of unsymmetrical groups where such data are available. In most cases the sum of these primary product yields are within experimental uncertainty of unity, indicating that these products account for the total O_3 + alkene reactions. (The main exceptions are propene [Table 18] and isobutene [Table 19], where higher than unit yields can be attributed to formaldehyde formation from the secondary reactions of the excited biradical.) Atkinson (1997a) also summarizes carbonyl yield data for symmetrical alkenes (not shown here), and in most of those cases near-unit yields of the expected single carbonyl product are observed.

For alkenes with $CH_2=CH-$ groups, Table 18 indicates that the data for most alkenes are consistent with assuming equal probability for each of the two possible reaction modes. This is therefore assumed when generating O_3 reaction mechanisms for all alkenes of this type. The major exception appears to be highly branched compounds such as 3,3-dimethyl-1-butene, where steric effects may tend to reduce biradical formation on the most substituted side. Since the current mechanism generation system is not capable of assessing steric effects, such compounds need to be handled on a case-by-case basis. However, present assignments are not made for such compounds because they are not important in current emissions inventories. The average error in assuming equal splits for the compounds where data are available is less than 10%, and the absolute value of the percentage error is less than 15%.

Table 17. Summary of rate constant estimates for reactions of O₃ at alkene groups.

Groups	Estimated Total Rate Constant (300K) (cm ³ molec ⁻¹ s ⁻¹)	
CH ₂ =CH-	1.01e-17	Average of 300K values for propene, 1-butene, 3-methyl-1-butene, 1-pentene, 1-hexene, 3-methyl-1-pentene, 3,3-dimethyl-1-butene, 4-methyl-1-pentene, 1-heptene, 1-octene, and 1-decene (Atkinson, 1997a).
CH ₂ =C<	1.18e-17	Average of 300K values for isobutene, 2-methyl-1-butene, 2,3-dimethyl-1-butene, 2-ethyl-1-butene, 2-methyl-1-pentene, 2,3,3-trimethyl-1-butene, 3-methyl-2-isopropyl-1-butene, and 3,4-diethyl-2-hexene (Atkinson, 1997a).
-CH=CH-	1.15e-16	Average of 300K values for trans-2-butene, cis-2-butene, trans-3-hexene, cis-3-hexene, cis-4-octene, trans-4-octene, trans 2,5-dimethyl 3-hexene, trans 2,2-dimethyl 3-hexene, cis-5-decene, cyclohexene, and 4-methyl cyclohexene (Atkinson, 1997a).
-CH=C<	3.48e-16	Average of 300K values for 2-methyl-2-butene, cis-3-methyl-2-hexene, trans 3-methyl-2-hexene, 2,4,4-trimethyl-2-pentene, and 1-methyl cyclohexene (Atkinson, 1997a).
>C=C<	6.74e-16	Average of 300K values for 2,3-dimethyl-2-butene and 1,2-dimethyl cyclohexene (Atkinson, 1997a).

For alkenes with CH₂=C< groups, Table 19 indicates that the data are more consistent with assuming that fragmentation to formaldehyde + the disubstituted is essentially twice as probable as fragmentation to the ketone + HCHO₂ in essentially all cases. Steric effects appear to be less important in affecting this generalization, as suggested by the data for 2,3,3-trimethyl-1-butene. Therefore, the O₃ reactions of alkenes of this type are generated based on assuming that ketone + HCHO₂ formation occurs 33.3% of the time, as indicated on the table. This gives an average error of less than 5% and an average absolute percentage error of less than 15%.

For alkenes with -CH=C< groups, Table 20 indicates that aldehyde + disubstituted biradical formation occurs a larger fraction of the time than formation of the ketone + the monosubstituted biradical, but the limited data indicate somewhat variable ratios. For mechanism estimation and generation purposes, we assume that ketone + monosubstituted biradical formation occurs 30% of the time, as indicated on the table. This gives an average error of 10% and an average absolute percentage error of slightly less than 20% for the three compounds that were studied.

Atkinson (1997a) gives no information concerning primary carbonyl yields from unsymmetrical molecules with -CH=CH- or >C=C< groups – only data for symmetrical molecules are tabulated. For estimation and mechanism generation purposes, we assume equal probability for the two modes of reaction in such cases. The data for the other unsymmetrical molecules indicate that this is probably a good approximation, with the possible exception of molecules that are highly branched on one side where steric effects may come into play.

Table 18. Experimental and estimated yields of primary carbonyl products and OH radicals from the reactions of O₃ with alkenes with CH₂=CH- groups.

	Experimental			Estimated		OH Yield		
	HCHO	RCHO	Sum	RCHO	Error	Expt.	Est'd.	Error
<u>CH₂=CH- Average</u>		<u>0.54</u>		<u>0.50</u>	<u>-8%</u>			<u>-6%</u>
Propene	0.71	0.48	1.20	0.50	3%	0.33	0.32	-3%
1-Butene	0.63	0.35	0.98	0.50	30%	0.41	0.32	-22%
1-Pentene	0.55	0.52	1.07	0.50	-4%	0.37	0.32	-14%
1-Hexene	0.54	0.53	1.07	0.50	-5%	0.32	0.32	0%
1-Heptene	0.52	0.55	1.07	0.50	-9%	0.27	0.32	19%
1-Octene	0.50	0.51	1.01	0.50	-2%	0.32	0.32	0%
1-Decene	0.53	0.49	1.02	0.50	2%			
3-Methyl-1-Butene	0.50	0.51	1.01	0.50	-2%			
3-Methyl-1-Pentene	0.39	0.63	1.03	0.50	-26%			
4-Methyl-1-Pentene	0.44	0.71	1.15	0.50	-41%			
3,3-Dimethyl-1-Butene	0.32	0.67	0.99	0.50	-34%			
Cyclohexene						0.68	0.52	-24%

Table 19. Experimental and estimated yields of primary carbonyl products and OH radicals from the reactions of O₃ with alkenes with CH₂=C< groups.

	Experimental			Estimated		OH Yield		
	HCHO	R-CO-R'	Sum	R-CO-R'	Error	Expt.	Calc	Error
<u>CH₂=C< Average</u>		<u>0.34</u>		<u>0.33</u>	<u>-2%</u>			<u>4%</u>
Isobutene	0.98	0.32	1.29	0.33	4%	0.84	0.71	-16%
2-Methyl-1-Butene	0.64	0.28	0.92	0.33	16%	0.83	0.71	-15%
2-Methyl-1-Pentene	0.62	0.32	0.94	0.33	3%			
2-Ethyl-1-Butene	0.49	0.30	0.80	0.33	9%			
2,3-Dimethyl-1-Butene	0.72	0.38	1.10	0.33	-14%	0.5	0.71	41%
2,3,3-trimethyl-1-Butene	0.64	0.35	0.99	0.33	-6%			
3-Methyl-2-Isopropyl-1-Butene	0.61	0.43	1.03	0.33	-28%			

Table 20. Experimental and estimated yields of primary carbonyl products and OH radicals from the reactions of O₃ with alkenes with -CH=C< groups.

	Experimental			Estimated		Expt.	OH Yield	
	RCHO	R-CO-R'	Sum	R-CO-R'	Error		Calc	Error
<u>-CH=C< Average</u>		<u>0.27</u>		<u>0.30</u>	<u>10%</u>			<u>-8%</u>
2-Methyl-2-Butene	0.72	0.34	1.05	0.30	-13%	0.91	0.84	-8%
2,4,4-Trimethyl-2-Pentene	0.84	0.19	1.03	0.30	38%			
3,4-Diethyl-2-Hexene	0.71	0.29	0.99	0.30	4%			
1-Methyl Cyclohexene						0.90	0.84	-7%

Table 18 through Table 20 also show measured yields of OH radicals, which are believed to be formed from secondary radicals of the biradical intermediates (see Section III.K). If it is assumed that the OH yields from the excited HCHO₂, RCHO₂, and RR'CO₂ biradicals are independent of the molecule from which they are formed, then these OH yields should be consistent with the assumed branching ratios and the OH yields assumed for the various types of biradicals. As discussed in Section III.K, the current mechanism assumes that OH yields from excited HCHO₂, CH₃CHO₂, and RR'CO₂ biradicals are respectively 12%, 52%, and 100%, based primarily on recommendations and data discussed by Atkinson (1997a). The "Calc'd" OH yields on Table 18 through Table 20 show the yields for the various molecules derived based on these assumptions, where they can be compared with the experimental data. In most cases these are consistent with the experimental data, with the percentage errors being no greater than those for the estimated carbonyl yields. Therefore, the estimates based on carbonyl yields and OH yields are self-consistent. However, as discussed in Section III.K, the experimental and estimated OH yields for the C₄₊ 1-alkenes are not consistent with the environmental chamber reactivity data for these compounds, and lower adjusted OH yields have to be used for the purpose of reactivity predictions. However, these adjustments do not affect the assumed branching ratios for the initial O₃ + alkene reactions.

4. Assigned Mechanisms for Initial O₃ Reactions

As with the other reactions discussed above, explicit assignments are used for the initial reactions for those VOCs where estimates cannot be made, where available experimental data indicate the estimates are inappropriate, or where alternative estimates are used. The explicitly assigned branching ratios for the initial O₃ reactions that are currently incorporated in the system are summarized on Table 21, along with the basis for the various assignments that are used.

F. Reactions with O³P

O³P atoms can react with compounds with C=C double bonds, forming an excited adduct that may decompose in various ways or undergo collisional stabilization. Although these reactions are generally of negligible importance under most ambient atmospheric conditions, they have been found to be non-negligible in some of the environmental chamber experiments used for mechanism evaluation,

Table 21. Assigned mechanisms for the reactions of O₃ with compounds for which estimates could not be made, or where experimental data or other considerations indicate that the general estimates may not be appropriate.

Reactant and Products	Factor	Documentation
<u>2-Methyl-3-Buten-2-ol [CH₂=CH-C(CH₃)(OH)-CH₃]</u>		
CH ₃ -C(OH)(CHOO[excited])-CH ₃ + HCHO	30.0%	Based on product data of Alvarado et al (1999).
CH ₂ OO[excited] + CH ₃ -C(CHO)(OH)-CH ₃	70.0%	See above.
<u>1,3-Butadiene [CH₂=CH-CH=CH₂]</u>		
HCHO + CH ₂ =CH-CHOO[excited]	50.0%	Estimated mechanism.
CH ₂ =CH-CHO + CH ₂ OO[excited]	50.0%	Estimated mechanism.
<u>Isoprene [CH₂=CH-C(CH₃)=CH₂]</u>		
HCHO + CH ₂ =CH-COO[excited]-CH ₃	20.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCHO + CH ₂ =C(CHOO[excited])-CH ₃	20.0%	See above.
CH ₂ =C(CHO)-CH ₃ + CH ₂ OO[excited]	39.0%	See above.
CH ₂ =CH-CO-CH ₃ + CH ₂ OO[excited]	16.0%	See above.
O ₂ + *C(CH=CH ₂)(CH ₃)-CH ₂ -O-*	2.5%	See above.
O ₂ + *CH(C(CH ₃)=CH ₂)-CH ₂ -O-*	2.5%	See above.
<u>Acetylene [HC::CH]</u>		
HCO-CHOO[excited]	100.0%	The initially formed primary ozonide is assumed to rearrange to the Crigiee biradical via an O-O bond scission. [a]
<u>Methyl Acetylene [HC::C-CH₃]</u>		
CH ₃ -COO[excited]-CHO	50.0%	The initially formed primary ozonide is assumed to rearrange to the Crigiee biradical via an O-O bond scission. Equal probability of formation of each possible isomer is assumed. [a]
CH ₃ -CO-CHOO[excited]	50.0%	See above.
<u>Ethyl Acetylene [HC::C-CH₂-CH₃]</u>		
CH ₃ -CH ₂ -COO[excited]-CHO	50.0%	The initially formed primary ozonide is assumed to rearrange to the Crigiee biradical via an O-O bond scission. Equal probability of formation of each possible isomer is assumed. [a]
CH ₃ -CH ₂ -CO-CHOO[excited]	50.0%	See above.
<u>2-Butyne [CH₃-C::C-CH₃]</u>		
CH ₃ -CO-CHOO[excited]-CH ₃	100.0%	The initially formed primary ozonide is assumed to rearrange to the Crigiee biradical via an O-O bond scission. [a]
<u>Methacrolein [CH₂=C(CHO)-CH₃]</u>		
HCHO + CH ₃ -COO[excited]-CHO	10.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH ₃ -CO-CHO + CH ₂ OO[excited]	90.0%	See above
<u>Hydroxy Methacrolein [CH₂=C(CHO)-CH₂-OH]</u>		
HCO-CO-CH ₂ -OH + CH ₂ OO[excited]	90.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCHO + HCO-COO[excited]-CH ₂ -OH	10.0%	See above
<u>Isoprene Product #1 [CH₃-C(CHO)=CH(CH₂-OH)]</u>		
CH ₃ -CO-CHO + HO-CH ₂ -CHOO[excited]	90.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCO-CH ₂ -OH + CH ₃ -COO[excited]-CHO	10.0%	See above

Table 21 (continued)

Reactant and Products	Factor	Documentation
CH ₃ -CO-CHO + HO-CH ₂ -CHOO[excited]	90.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCO-CH ₂ -OH + CH ₃ -COO[excited]-CHO	10.0%	See above
<u>Isoprene Product #3 [HCO-CH=C(CH₃)-CH₂-OH]</u>		
CH ₃ -CO-CH ₂ -OH + HCO-CHOO[excited]	90.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCO-CHO + CH ₃ -COO[excited]-CH ₂ -OH	10.0%	See above
<u>Methylvinyl ketone [CH₂=CH-CO-CH₃]</u>		
HCHO + CH ₃ -CO-CHOO[excited]	5.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH ₃ -CO-CHO + CH ₂ OO[excited]	95.0%	See above

[a] Although the biradical excitation energies are almost certainly different from those formed in the reactions of O₃ with acroleins, because of lack of available information it is assumed to react to form the same products, and thus is represented by the same species.

where NO₂ concentrations tend to be higher under ambient conditions¹¹. They may also be non-negligible in plumes that have higher NO_x concentrations than ambient. For these reasons, O³P + alkene reactions are included in the current mechanism and are supported by the mechanism generation system.

1. Assigned O³P Rate Constants

The rate constant assignments used for the O³P reactions that are incorporated in the present mechanism are given on Table 22, where they are compared for the estimated values for those VOCs for which estimates can be made. The table also indicates the source of the rate constant assignments, which in most cases are from Atkinson (1997a).

2. Estimated O³P Rate Constants

Since the reactions of alkenes with O³P and OH radicals are both believed to involve primarily addition to the double bond, one might expect the rate constants for these reactions to be correlated. This is indeed the case for most of the alkenes where both rate constants have been measured, as is shown on Figure 3, which gives a log-log plot of O³P and OH radical rate constants for the alkenes listed on Table 22. The line shows the least squares fit for the log-log plot for the monoalkenes, which was used for the purpose of estimating O³P rate constants for those alkenes for which data are not available. This is given by:

$$\ln(kO^3P) = 19.160 + 1.864 k(OH) \quad (II)$$

where kO^3P and kOH are the O³P and OH radical rate constants in $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$. (Note that the third digits are significant since they are being used to compute logarithms.) Although the dialkenes and the terpenes were not used when deriving this fit, Table 22 and Figure 3 show that the above equation performs reasonably well in predicting their rate constants in most cases. Including the terpenes and

¹¹ Reactions with O₃P increase in importance as NO₂ concentrations increase because NO₂ photolysis is the primary source of O³P.

Table 22. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with O³P atoms in the present mechanism.

Compound	Model Name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
Ethene	ETHENE	7.42e-13	1.04e-11	1.574	1		
Propene	PROPENE	4.01e-12	1.18e-11	0.644	1	3.91e-12	-2%
1-Butene	1-BUTENE	4.22e-12	1.25e-11	0.648	1	5.43e-12	29%
Isobutene	ISOBUTEN	1.69e-11			2	1.36e-11	-20%
cis-2-Butene	C-2-BUTE	1.76e-11			2	1.62e-11	-8%
trans-2-Butene	T-2-BUTE	2.18e-11			2	2.04e-11	-6%
1-Pentene	1-PENTEN	4.69e-12	1.48e-11	0.686	3	5.42e-12	16%
cis-2-Pentene	C-2-PENT	1.70e-11			2	2.09e-11	23%
3-Methyl-1-Butene	3M-1-BUT	4.18e-12	1.32e-11	0.686	3	5.55e-12	33%
2-Methyl-2-Butene	2M-2-BUT	5.10e-11			2	3.62e-11	-29%
1-Hexene	1-HEXENE	4.69e-12	1.48e-11	0.686	3	7.37e-12	57%
2,3-Dimethyl-2-Butene	23M2-BUT	7.64e-11			2	5.60e-11	-27%
Cyclopentene	CYC-PNTE	2.10e-11			2	2.23e-11	6%
Cyclohexene	CYC-HEXE	2.00e-11			2	2.26e-11	13%
1-Methyl Cyclohexene	1M-CC6E	9.00e-11			2	3.71e-11	-59%
1,3-Butadiene	13-BUTDE	1.98e-11			2		
Isoprene	ISOPRENE	3.60e-11			4		
a-Pinene	A-PINENE	3.20e-11			2		
3-Carene	3-CARENE	3.20e-11			2		
b-Pinene	B-PINENE	2.70e-11			2		
d-Limonene	D-LIMONE	7.20e-11			2		

References

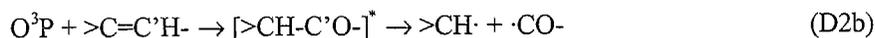
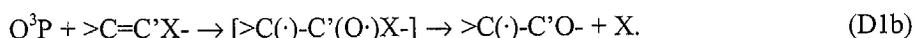
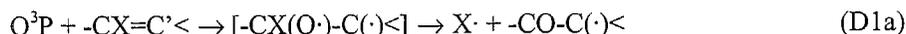
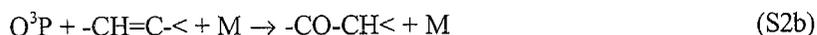
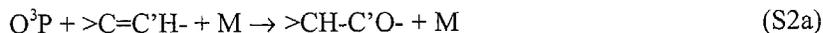
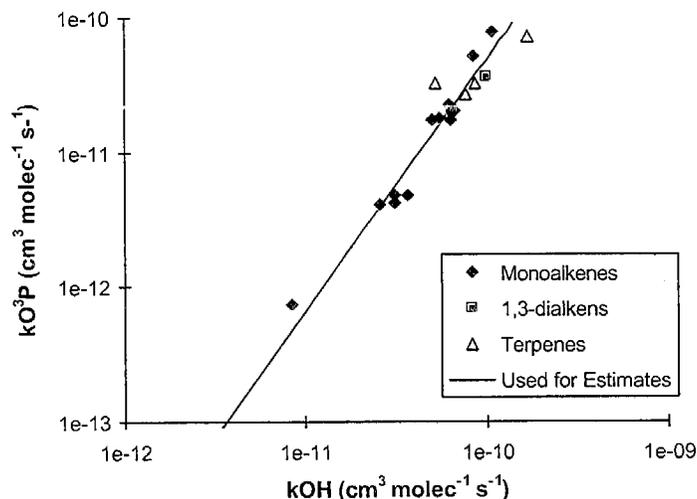
- 1 Rate constant expression from Atkinson and Lloyd (1984). T=298K value is consistent with recommendation of Atkinson (1997a).
- 2 Rate constant from Atkinson (1997a). Temperature dependence is expected to be small.
- 3 T=298K rate constant from Atkinson (1997a). Activation energy estimated from propene and 1-butene, as given by Atkinson and Lloyd (1984).
- 4 Rate constant from Paulson et al (1995).

dialkenes, the average discrepancy is around 25%, and all the discrepancies in all cases except for d-limonene are less than 60%.

3. Estimated Mechanisms for O³P Reactions

The mechanisms for the reactions of O³P with the simpler alkenes have been recently reviewed by Atkinson (1997a), though the discussion there is based primarily on the earlier review of Atkinson and Lloyd (1984). The reaction presumably proceeds by O adding to the double bond forming an excited oxide, which can either be collisionally stabilized, undergo a 1,2-H shift to a carbonyl compound and then be stabilized, or decompose in various ways. Neglecting reactions requiring pentavalent transition states that are chemically unreasonable (e.g., formation of isobutyraldehyde from O³P + 2-butenes), the alternative reaction routes given by Atkinson and Lloyd (1984) and Atkinson (1997a) can be classified as follows:

Figure 3. Plot of OH radical vs. O³P rate constants for VOCs in the mechanism where both rate constants are available. Rate constants are for T=300K.



Where, for unsymmetrical molecules, C' refers to the carbon that has the greater number of substituents.

Branching ratios estimated or interpolated based on these data are given in Table 23, where the branching ratio designations used are as indicated above, and footnotes indicate the source of the estimated mechanisms. Note that these ratios are applicable to one atmosphere total pressure only – the mechanism generation system currently does not support predicting the effects of total pressure on these yields¹². Atkinson (1997a) and Atkinson and Lloyd (1994) gave no recommendations for compounds of with CH₂=C<, -CH=C<, or >C=C<, and highly approximate estimates are made based on considerations

¹² Ignoring these pressure dependences is unlikely to introduce significant errors in tropospheric simulations because NO₂ concentrations are expected to be sufficiently low at higher altitudes that reactions of O³P with alkenes is expected to be negligible.

Table 23. Estimated branching ratios for the reactions of O³P with alkenes, based on the recommendations of Atkinson (1997a) and Atkinson and Lloyd (1984). Note that these ratios are not used in the final mechanism because of unsatisfactory results when simulating environmental chamber experiments.

Compound	Branching Ratio							Notes
	S1	S2a	S2b	D1a	D1b	D2a	D2b	
<u>CH₂=CH₂</u>								
Ethene	0%	0%		60%		40%		1
<u>CH₂=CH-</u>								
Propene	30%	30%	0%	20%	0%	20%	0%	2
1-Butene	45%	40%	0%	15%	0%	0%	0%	2
C5 Alkenes	50%	45%	0%	5%	0%	0%	0%	3
C6+ Alkenes	55%	45%	0%	0%	0%	0%	0%	3
<u>CH₂=C<</u>								
Isobutene	40%	-	30%	0%	15%	15%	-	4
C5 Alkenes	50%	-	38%	0%	6%	6%	-	3
C6 Alkenes	56%	-	40%	0%	2%	2%	-	3
C7+ Alkenes	60%	-	40%	0%	0%	0%	-	3
<u>-CH=CH-</u>								
2-Butenes	50%	20%		30%		0%		5
C5 Alkenes	64%	24%		12%		0%		3
C6 Alkenes	72%	24%		4%		0%		3
C7+ Alkenes	76%	24%		0%		0%		3
<u>-CH=C<</u>								
2-Methyl-2-Butene	50%	-	38%	6%	6%	0%	-	4
C6 Alkenes	56%	-	40%	2%	2%	0%	-	3
C7+ Alkenes	60%	-	40%	0%	0%	0%	-	3
<u>>C=C<</u>								
2,3-Dimethyl-2-Butene	96%	-		2%	2%			4
C7+ Alkenes	100%	-		0%	0%			3

Notes

- 1 Based on Atkinson (1997a) recommendation, ignoring ketene formation, which is lumped with the D2 decomposition route
- 2 Based on Atkinson (1997a) and Atkinson and Lloyd (1984) recommendation. Numbers rounded to nearest 5%
- 3 Based on extrapolating from data for lower molecular weight alkenes, assuming that stabilization will increase with the size of the molecule increases.
- 4 Estimated based on recommended mechanisms given by Atkinson and Lloyd (1994) for other alkenes.
- 5 Based on the Atkinson (1997a) and Atkinson and Lloyd (1984) recommendation, with the chemically unreasonable 20% CH₃ shift represented by increasing oxide formation and decomposition eacy by 10%.

of data given by Atkinson and Lloyd (1994) for other compounds¹³. As indicated on the table, stabilization is assumed to become increasingly important for higher molecular weight compounds, and to dominate for C₇₊ alkenes.

Although the branching ratios shown on Table 23 represent our current best estimates based on available product data (Atkinson, 1997a), it was found that using these branching ratios gave unsatisfactory results when conducting model simulations of the available chamber database. This was found to be the case even after reasonable adjustment of the other uncertain parameters in the mechanism that affect radical initiation or termination processes. In order to fit the data, it was necessary to assume much lower radical yields from these O³P reactions, i.e., that stabilization is much more important than indicated by the available product data. In particular, the model significantly overpredicts the reactivity of 1-butene and 1-hexene if any radical formation in the O³P reaction is assumed, and consistent fits to the chamber data cannot be obtained unless it is assumed that radical formation from O³P + propene is also negligible. In addition, assuming only 50% fragmentation in the O³P + ethene rather than the recommended 100% removes biases in the simulation of the large database of ethene experiments.

The reason for this apparent inconsistency between the chamber data and the O³P branching ratios indicated by the available product data is unknown, and needs to be investigated. Although O³P reactions are not important under most atmospheric conditions, they are non-negligible in many of the chamber experiments used for mechanism evaluation, and using incorrect O³P + alkene mechanisms may compensate for other errors in the mechanism. However, no reasonable adjustments of the other uncertainties in the alkene mechanisms that involve radical initiation/termination processes (such as nitrate yields from the peroxy radicals formed in the OH reaction, radical yields from the biradicals formed in the O₃ reaction, or radical generation in the alkene + NO₃ reactions) could be found to give satisfactory fits to the chamber data using the recommended O³P branching ratios. Therefore, adjusted branching ratios, assuming no radical formation from C₃₊ alkenes and assuming only 50% fragmentation from ethene, are used in the current version of the mechanism that is developed in this work. These adjusted yields are given on Table 24.

4. Assigned Mechanisms for Dialkenes

Although it is expected that the reactions of O³P with alkynes are unimportant and therefore are ignored in the mechanism, their reactions with isoprene and 1,3-butadiene may be non-negligible under some conditions, and need to be specified explicitly. The assigned O³P mechanisms for these compounds are shown on Table 25. The O³P + isoprene mechanism is based on that of Carter and Atkinson (1996), and the mechanism for 1,3-butadiene is assumed to be analogous. The current system does not have assigned mechanisms for any other VOCs.

G. Photolysis Reactions

The previous mechanism represented all photoreactive VOCs (e.g., aldehydes, ketones, and organic nitrates) either explicitly or using the lumped molecule approach, so mechanisms for photolysis reactions were all derived on a case-by-base basis. However, the lumped molecule approach has proven to

¹³ It is probable that improved estimates could be made for some of these compounds by reviewing the product data literature. This review was not carried out because of the relatively low importance of these O³P reactions in most atmospheric simulations, and because in any case the branching ratios had to be revised to fit the chamber data.

Table 24. Adjusted branching ratios for the reactions of O³P with alkenes that are found to give best fits to the available chamber database and are used in the final version of the mechanism developed in this work.

Groups	Branching Ratio				
	S1	S2a	S2b	D1a+D1b	D2a+D2b
CH ₂ =CH ₂	25%	25%		20%	30%
CH ₂ =CH-	55%	45%	0%	0%	0%
CH ₂ =C>	60%	-	40%	0%	0%
-CH=CH-	76%	24%		0%	0%
-CH=C<	60%	-	40%	0%	0%
>C=C<	100%	-		0%	-

Table 25. Assigned mechanisms for the reactions of O³P atoms with the dialkenes in the current mechanism.

Reactant and Products	Factor	Documentation
<u>Isoprene [CH₂=CH-C(CH₃)=CH₂]</u>		
C(CH=CH ₂)(CH ₃)-CH ₂ -O-	50.0%	As assumed by Carter and Atkinson (1996). Products represented by epoxides. Most of the reaction is assumed to occur at the more substituted position.
CH(C(CH ₃)=CH ₂)-CH ₂ -O-	25.0%	See above.
CH ₂ =CH-CO-CH ₂ . + CH ₃ .	25.0%	Fragmentation mechanism and yield as assumed by Carter and Atkinson (19896). Approximately 25% radical yield also necessary to obtain satisfactory fit to data with updated mechanism.
<u>1,3-Butadiene [CH₂=CH-CH=CH₂]</u>		
CH(CH=CH ₂)-CH ₂ -O-	75.0%	Assumed to be analogous to the isoprene mechanism of Carter and Atkinson (1996). Products represented by epoxides.
CH ₂ =CH-CH[.]CHO + H.	25.0%	Analogous to the fragmentation mechanism in the isoprene system as assumed by Carter and Atkinson (1996).

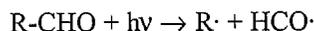
be unsatisfactory for the higher ketones (Carter et al, 2000a) and is therefore not used in this mechanism for the higher aldehydes, ketones, and nitrates. Instead, specific mechanistic assignments are made for these compounds, based on generated mechanisms for their reactions with OH radicals, NO₃ (for aldehydes), and photolyses. Specific mechanistic assignments are also made for the OH radical and photolysis reactions of organic nitrates, which were used for determining the lumped organic nitrate mechanism as discussed in Section II.C.2. The estimation and generation of their initial reactions with OH radicals and NO₃ were discussed above. This section discusses the estimation and generation of their initial photolysis reactions

Photolysis rates for the aldehydes, α -dicarbonyls, vinyl ketones and organic nitrates are estimated by assuming that they have the same absorption cross sections and quantum yields as the most chemically similar lower molecular weight analogue that is in the base mechanism. In the case of the simple ketones, it is assumed that the overall quantum yield decreases with the size of the molecule, based on overall quantum yields which give best fits of model simulations to environmental chamber data for methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, and methyl amyl ketone (see Section V and Appendix B). The specific assignments are as summarized on Table 26, along with footnotes indicating the derivations of the assignments and the groups used by the mechanism generation system to classify compounds according to photolysis type.

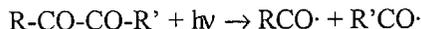
Note that if the molecule has groups bonded to the carbonyl or nitrate groups that are different than those indicated on the table, then the system cannot currently generate photolysis reactions for compounds with that structure. If the molecule has more than one photoreactive center (e.g., $\text{CH}_3\text{-CO-CH}_2\text{CHO}$), then the photolysis reaction is assumed to occur only at the most reactive center, based on an assumed reactivity ordering of α -dicarbonyls > unsaturated aldehydes or ketones > aldehydes > ketones > nitrates. This obviously is an approximation and it would be much better if such multifunctional molecules could be handled on a case-by-case basis if information were available.

1. Default Carbonyl Photolysis Mechanisms

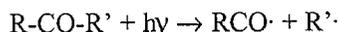
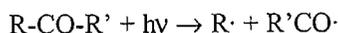
Although the actual mechanisms for the photolysis reactions of the higher molecular weight carbonyl compounds may well be more complex (Calvert and Pitts, 1966), unless information is available otherwise, it is assumed that all photolyses of carbonyls proceed by breaking the weakest CO-C bond. In the case of aldehydes (including glyoxals) this means the reaction is assumed to always proceed via



(where "R" would be $\text{R}'\text{CO}$ in the case of glyoxals) and in the case of α -dicarbonyl ketones it is assumed always to proceed via



In the case of unsymmetrical ketones, two possible reactions are considered:



In this case, the pathway with the lowest estimated heat of reaction is assumed to 100% of the time, regardless of the differences between them. This gives a prediction that is consistent with the assumed photolysis mechanism for methyl ethyl ketone in the base mechanism.

2. Unsaturated Carbonyl Photolysis

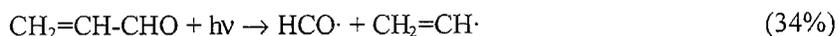
Somewhat different photolysis mechanisms are assigned for acrolein, methacrolein and methyl vinyl ketone, based on the mechanisms for the latter two given by Carter and Atkinson (1996). The base mechanism listing gives the assignments and documentation in the cases of methacrolein and MVK. In the case of acrolein, the following initial photolysis mechanism is used, which is derived by analogy to the Carter and Atkinson (1996) mechanism for methacrolein.

Table 26. Summary of assignments of absorption cross sections and quantum yields for carbonyl and organic nitrate photolysis reactions.

Compound Type	Phot. Set	Q.Yield	Notes	Group Definition used to Determine Type
Aldehydes	C2CHO	-	1,2	-CHO groups bonded to -CH ₃ , -CH ₂ -, -CH< or -C<
Ketones (4 groups)	KETONE	0.15	3,4	-CO- groups bonded to -CH ₃ , -CH ₂ -, -CH< or -C<, with a total of 4 groups in the molecule.
Ketones (5 groups.)	KETONE	0.10	3,5	As above, but 5 groups in the molecule
Ketones (6 groups.)	KETONE	0.05	3,6	As above, but 6 groups in the molecule
Ketones (7 groups.)	KETONE	0.02	3,7	As above, but 7 groups in the molecule
Ketones (8 groups.)	KETONE	0.01	3,8	As above, but 8 groups in the molecule
Ketones (9+ groups.)	No photolysis		3,9	As above, but more than 8 groups in the molecule
Alkyl Glyoxal	MGLY_ADJ	-	1,4	-CHO- groups bonded to -CO-
Dialkyl Glyoxyl	BACL_ADJ	-	1,5	-CO- groups bonded to -CO-
Acrolein	ACROLEIN	2.0e-3	3,6	CH ₂ =CH-CHO only.
Other Acroleins	ACROLEIN	4.1e-3	3,7	-CHO groups bonded to -CH= or >C=
Vinyl Ketone	ACROLEIN	2.1e-3	3,8	-CO- groups bonded to -CH= or >C=
Ester or Acid	No photolysis		9	-CO- or -CHO- groups bonded to -O- or -OH
Organic Nitrates	IC3ONO2	1.0	10	-ONO ₂ groups bonded to -CH ₃ , -CH ₂ - -CH< or -C<

Notes

- 1 The wavelength dependent quantum yields are given with the absorption cross sections in the photolysis set. See base mechanism documentation and mechanism listing.
- 2 Assumed to have same photolysis rate as propionaldehyde.
- 3 The photolysis set gives the absorption cross sections only, which are given with the base mechanism listing. The wavelength-independent quantum yield is shown on the table.
- 4 Overall quantum yield adjusted based on model simulations of environmental chamber experiments with methyl ethyl ketone (Carter et al, 2000a).
- 5 Overall quantum yield adjusted based on model simulations of environmental chamber experiments with methyl propyl ketone (Carter et al, 2000e).
- 6 Overall quantum yield adjusted based on model simulations of environmental chamber experiments with methyl isobutyl ketone (Carter et al, 2000a).
- 7 Overall quantum yield adjusted based on model simulations of environmental chamber experiments with 2-heptanone (Carter et al, 2000e).
- 8 Estimated to have an overall quantum yield which is half that estimated for ketones with seven groups.
- 9 Photodecomposition is estimated to be unimportant for ketones with nine or more groups.
- 4 Assumed to have the same photolysis rate as methyl glyoxal.
- 5 Assumed to have the same photolysis rate as biacetyl.
- 6 Overall quantum yield adjusted to fit model simulations of O₃, NO, acrolein, and formaldehyde in acrolein - NO_x chamber runs ITC941, 943, and 944.
- 7 Assumed to have same photolysis rate as methacrolein. See base mechanism documentation.
- 8 Assumed to have same photolysis rate as methyl vinyl ketone. See base mechanism documentation.
- 9 Photolysis assumed to be negligible, based on absorption cross section data given by Calvert and Pitts (1966).
- 10 All alkyl nitrates are assumed to photolyze at the same rate and with a unit quantum yield. Absorption cross sections used are those recommended by IUPAC (Atkinson et al, 1997, 1999) for isopropyl nitrate.

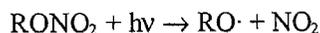


The subsequent reactions of the radicals or carbenes formed are discussed in the following sections.

For the other unsaturated aldehydes, including specifically those used to derive the mechanism for the ISOPROD model species, the default mechanism, based on assuming 100% HCO \cdot formation is used. The current mechanism has no mechanistic assignments for unsaturated ketones other than MVK, and in general specific assignments would need to be given for the individual compounds.

3. Organic Nitrate Photolysis

As discussed in Section II.C.2, although organic nitrate products are represented using the lumped molecule approach, the mechanism for the generic organic nitrate model species used for this purpose is derived based on generated mechanisms for individual organic nitrate compounds. The rates of their photolysis reactions are determined as shown on Table 26, which indicates that all organic nitrates are assumed to photolyze using the absorption cross sections recommended by IUPAC (Atkinson et al, 1997, 1999) for isopropyl nitrate. As discussed there, the quantum yield for NO $_2$ formation is assumed to be unity. In view of this, all organic nitrate photolysis reactions are represented by the general mechanism

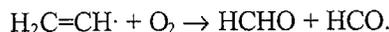


The subsequent reactions of the alkoxy radicals are then derived using the general methods discussed in Section III.J.

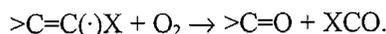
H. Reactions of Carbon Centered Radicals

Carbon-centered radicals are any radicals containing the groups CH $_3\cdot$, -CH $_2\cdot$, -CH[\cdot], >C[\cdot], HCO \cdot , -CO \cdot , =CH \cdot , or =C[\cdot]. Except as indicated below or in Table 27, these are assumed to react exclusively by O $_2$ addition, forming the corresponding peroxy group. The general exceptions are as follows:

- Vinylic radicals are assumed to react via the mechanism



based on the data of Slagle et al (1984). Except as indicated below, substituted vinylic radicals are assumed to react analogously, e.g.,



Where -X is -H or any non-radical group. The exceptions are radicals of the type HO-C=C \cdot formed in the reactions of OH with acetylenes, where specific mechanistic assignments are made as indicated below in Table 27.

- α -Hydroxy alkyl radicals are assumed to react by O $_2$ abstraction from the -OH, forming HO $_2$ and the corresponding carbonyl compound, e.g.,

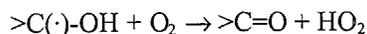


Table 27. Mechanistic assignments for carbon-centered radicals that are assumed not to react as estimated for general carbon-centered radicals.

Reactant	Product(s)	Yield	Notes
<u>OH-Substituted Vinylic Radicals (from OH + Acetylenes)</u>			
HO-CH=CH.	HCO-OH + HCO. HCO-CHO + OH	33% 67%	1
CH ₃ -C[.] = CH(OH)	HCO-OH + CH ₃ -CO. CH ₃ -CO-CHO + OH	33% 67%	2
CH ₃ -C[.] = CH-OH	HCO-OH + CH ₃ -CO. CH ₃ -CO-CHO + OH	33% 67%	2
CH ₃ -C(OH) = C[.] - CH ₃	CH ₃ -CO-OH + CH ₃ -CO. CH ₃ -CO-CO-CH ₃ + OH	33% 67%	2
CH ₃ -CH ₂ -C[.] = CH-OH	HCO-OH + CH ₃ -CH ₂ -CO. CH ₃ -CH ₂ -CO-CHO + OH	33% 67%	2
<u>Allylic Radicals</u>			
CH ₂ =CH-C[.](CH ₃)-CH ₂ -OH	CH ₂ =CH-C[OO.](CH ₃)-CH ₂ -OH HO-CH ₂ -C(CH ₃)=CH-CH ₂ OO. HO-CH ₂ -C(CH ₃)=CH(CH ₂ OO.)	67% 16.5% 16.5%	3,4
CH ₂ =C(CH ₃)-CH[.] - CH ₂ -OH	CH ₂ =C(CH ₃)-CH[OO.] - CH ₂ -OH CH ₃ -C(CH ₂ OO.)=CH(CH ₂ -OH) CH ₃ -C(CH ₂ OO.)=CH-CH ₂ -OH	59.2% 20.4% 20.4%	3,5
HO-CH ₂ -C(CH ₂ .)=CH(CH ₂ -OH)	CH ₂ =C(CH ₂ -OH)-CH[OO.] - CH ₂ -OH	100%	3,6
*C(CH ₃)=CH-O-CH ₂ -CH[.] - *	*O-CH=C(CH ₃)-CH=CH-* + HO ₂ .	100%	3,7
C[.](CH ₃)-CH=CH-O-CH ₂ -	*O-CH=C(CH ₃)-CH=CH-* + HO ₂ .	100%	3,7
CH ₂ =CH-C[.](CH ₃)-CH ₂ -ONO ₂	.OOCH ₂ -CH=C(CH ₃)-CH ₂ -ONO ₂	100%	3,8
CH ₂ =CH-CH[.] - CH ₂ -OH	CH ₂ =CH-CH[OO.] - CH ₂ -OH HO-CH ₂ -CH=CH-CH ₂ OO. HO-CH ₂ -CH=CH(CH ₂ OO.)	50% 25% 25%	9
CH ₂ =CH-CH[.] - CH ₂ -ONO ₂	.OOCH ₂ -CH=CH-CH ₂ -ONO ₂ .OOCH ₂ -CH=CH(CH ₂ -ONO ₂)	50% 50%	3,10
<u>Allylic Radical Precursors</u>			
*C(CH ₃)(OH)-CH ₂ -O-CH ₂ -CH[.] - *	H ₂ O + *C(CH ₃)=CH-O-CH ₂ -CH[.] - *	100%	3,7
CH(OH)-C[.](CH ₃)-CH ₂ -O-CH ₂ -	H ₂ O + *C[.](CH ₃)-CH=CH-O-CH ₂ -*	100%	3,7

Notes

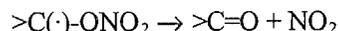
- 1 Estimated mechanism is based on the data of Hatakeyama et al (1986) and modeling acetylene environmental chamber runs Carter et al (1997c).
- 2 Estimated by analogy with assumed reactions of HO-CH=CH. from acetylene.
- 3 Ratios of reaction of O₂ at different positions of the allylic radical is assumed to be as discussed by Carter and Atkinson (1996).
- 4 The relative importance of this reaction is based on observed yields of methyl vinyl ketone in the reactions of OH radicals with isoprene.

Table 27 (continued)

- 5 The relative importance of this reaction is based on observed yields of methyl vinyl ketone in the reactions of OH radicals with methacrolein.
- 6 This reaction is assumed to dominate to be consistent with results of API-MS isoprene + OH product studies of Kwok et al (1995), which indicate that C5-dihydroxycarbonyls, the predicted products of the competing reactions, are not formed.
- 7 It is necessary to assume this radical reacts as shown in order to explain the observed formation of 3-methyl furan from the reaction of OH radicals with isoprene (Carter and Atkinson, 1996).
- 8 Assumed to dominate over addition at the least substituted end of the allylic radical to be consistent with product data, as discussed by Carter and Atkinson (1996). Formation of only one of the two possible cis-trans isomers is shown because the reactions of the other isomer are expected to give the same products.
- 9 Equal probability of addition at either radical center of the allylic radical is assumed.
- 10 100% terminal addition to allylic radical is assumed, to be consistent with mechanism assumed for isoprene (Carter and Atkinson, 1996). Equal probability of cis and trans formation is assumed.

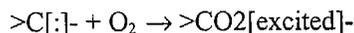
The assumption that this reaction dominates for α -hydroxy radicals is based on results of product studies of reactions of alcohols and other OH-substituted compounds in the presence of O₂.

- α -Nitroxy alkyl radicals, which can be formed in the reactions of NO₃ radicals with alkenes, are assumed to undergo rapid unimolecular decomposition to NO₂ and the corresponding carbonyl compound, e.g.,



This is assumed to be an extremely rapid decomposition based on its high estimated exothermicity, combined with the expectation that the decomposition should not have a large activation energy. However, experimental (and theoretical) verification of this assumption would be useful.

- Carbenes are assumed to react with O₂, forming an excited Crigiee biradical, e.g.,



Although the excitation energy is almost certainly different than those formed in O₃ + alkene reactions, since information to the contrary is not available, the excited Crigiee biradicals are assumed to react with the same mechanism, and are therefore represented by the same species in the mechanism generation system. The reactions of Crigiee biradicals are discussed in Section III.K.

In addition to the above general exceptions, specific mechanistic assignments are made for some of the unsaturated carbon-centered radicals formed in the reactions of the special reactants that are currently supported by the system. These assignments are indicated on Table 27, along with footnotes documenting the reasons for the assignments. As shown there, there are three types of radicals that are considered, as follows:

- 1) OH-substituted vinylic radicals formed by OH addition to acetylenes whose mechanisms are assigned based on the assumed mechanism for acetylene (Carter et al, 1997c);

- 2) various allylic radicals where O₂ can add at more than one radical center, where the branching ratio assignments are based primarily on data from isoprene product studies (Carter and Atkinson, 1996); and
- 3) precursors to allylic radicals that are assumed to react with O₂ by abstraction forming HO₂ and allylic radicals, in order to account for the formation of 3-methyl furan from the reactions of OH with isoprene (Carter and Atkinson, 1996).

Note that the assignments for the allylic radicals that are based on product data are not always consistent with each other [e.g., addition of O₂ to the least substituted position is assumed for the nitrate-substituted radicals, while the opposite assumption is made for HO-CH₂-C(CH₂)=CH(CH₂-OH) to be consistent with product data]. Thus, these must be considered to be highly uncertain.

Although one might expect radicals of the type R-O-C(O)· to rapidly decompose to R· + CO₂, Kirchner et al (1997) and Christensen et al (1999) reported synthesizing CH₃OC(O)OONO₂ from the reaction of C₂ with methyl formate, which is only possible if CH₃OC(O)· lasts long enough to react with O₂ to form CH₃OC(O)OO·. In addition, model simulations of reactivity experiments with methyl isobutyrate, which is predicted to form CH₃OC(O)· radicals in high yields, cannot fit the data if this decomposition is assumed (Carter et al, 2000a). Therefore, we assume that these radicals do not decompose, but instead add O₂ to form radicals of the type ROC(O)OO·, which can react with NO₂ to form PAN analogues of the type ROC(O)OONO₂, as observed by Kirchner et al (1997) and Christensen et al (1999).

I. Reactions of Peroxy Radicals

Peroxy radicals are critical intermediates in almost all the generated mechanisms. Although under atmospheric conditions they can react with NO₂, NO₃, HO₂, and other peroxy radicals, the current version of the system only generates their reactions with NO. This is because reaction with NO is the major fate of peroxy radicals under conditions where reactions of VOCs contribute to tropospheric ozone, and the current base mechanism uses condensed approaches to represent the effects of the other reactions (see Section II.B.4). The reactions of non-acyl peroxy radicals with NO₂ are ignored because they are assumed to be rapidly reversed by the thermal decomposition of the peroxy nitrate formed. The reactions of acyl peroxy radicals with NO₂ are not considered because acyl peroxy radicals are represented by lumped species so their reactions do not need to be generated. The products of peroxy + NO₃ and peroxy + peroxy reactions are represented by lumped species, so they are not considered in the mechanism generation system.

The main factor that needs to be determined when generating reactions of peroxy radicals with NO is the branching ratio between formation of NO₂ and the corresponding alkoxy radical, or addition and rearrangement forming the organic nitrate, e.g.



The rate constant ratio $k_N/(k_A+k_N)$ is referred to as the “nitrate yield” in the subsequent discussion. This is a potentially important factor affecting a VOC’s atmospheric impact because nitrate formation (process “N”) is a radical termination process and can significantly inhibit radical levels if it is sufficiently important compared to propagation (process “A”). Unfortunately, except for secondary peroxy radicals formed from the C₃-C₁₀ n-alkanes, direct information concerning nitrate yields is extremely limited, and

nitrate yields have to be either estimated or (for those few cases where this is possible) adjusted to fit overall reactivity observed in environmental chamber experiments.

For the peroxy radicals formed from alkane photooxidations, the previous version of the mechanisms used yields estimated by Carter and Atkinson (1989b). These are based on data for nitrate yields from reactions of OH with C₃-C₈ n-alkanes and several C₅ and C₆ branched alkanes at ambient temperature and pressure, and on nitrate yields at different temperatures and pressures from OH reactions of several C₅ and C₇ alkanes. The data indicate that nitrate yields from alkyl peroxy radicals increase with the size of the molecule from less than 5% for C₃ to ~33% for C₈ (with an apparent upper limit of 40-50% for larger molecules), and also increase with decreasing temperature and decrease with decreasing pressure. This suggests that the rate of the nitrate formation reaction is governed by similar factors affecting other three-body reactions, whose temperature and pressure dependences can be parameterized using a modified version of the "Troe" falloff expression that is currently used in the evaluations. Based on this, Carter and Atkinson (1989b) used the following parameterization to fit the nitrate yield data for the secondary alkyl peroxy radicals:

$$Y_{\text{sec}}(n_C, T, M) = (k_N/k_R) / [1 + (k_N/k_R)] \quad (\text{III})$$

where Y_{sec} is the nitrate yield for secondary alkyl radicals with n_C carbons at temperature T (in °K) and total pressure M (in molecules cm⁻³), and the rate constant ratio k_N/k_R is derived from

$$k_N/k_R = \{R_0(T, n_C) \cdot M / [1 + R_0(T, n_C) \cdot M / R_\infty(T)]\} \cdot F^Z \quad (\text{IV})$$

where

$$R_0(T, n_C) = \alpha \cdot e^{\beta \cdot n_C} \cdot (T/300)^{-m_0}$$

$$R_\infty(T) = R_\infty^{300} \cdot (T/300)^{-m_\infty}$$

$$Z = \{1 + [\log_{10}\{R_0(T, n_C) \cdot M / R_\infty(T)\}]^2\}^{-1}$$

and α , β , R_∞^{300} , m_0 , m_∞ , and F are empirical parameters that are optimized to fit the data. Based on the data available at the time, Carter and Atkinson (1989b) derived $\alpha = 1.94 \times 10^{-22}$ cm³ molecule⁻¹, $\beta = 0.97$, $R_\infty^{300} = 0.826$, $m_0 = 0$, $m_\infty = 8.1$, and $F = 0.411$. The limited (and somewhat inconsistent) data for primary and tertiary peroxy radicals indicate that lower nitrate yields are formed from these radicals, and Carter and Atkinson (1989b) recommended using scaling factors of 0.4 ± 0.05 and 0.3 ± 0.15 for secondary and tertiary peroxy radicals, respectively.

Most of the data concerning the effects of nitrate yields on carbon number come from the measurements of Atkinson et al (1982b, 1984), and the temperature and pressure effects data come from Atkinson et al (1983b). More recently, using improved chromatographic methods, Arey et al (2000) remeasured the nitrate yields from the C3-C8 n-alkanes. They obtained significantly lower nitrate yields for the C5+ radicals, and Atkinson and co-workers (unpublished results, 1999) also obtained lower nitrate yields from n-decane than estimated using the parameterization of Carter and Atkinson (1989b). For example, the new data indicate a nitrate yield of 24% for the C₈ secondary peroxy radicals, compared to the previous measurement of ~33%. As discussed below, these lower nitrate yields resulted in the model being able to fit chamber data without having to make the chemically unreasonable assumption that hydroxy-substituted C₆₊ peroxy radicals formed after alkoxy radical isomerizations did not form nitrates when they reacted with NO, as had to be made in previous versions of the mechanism (Carter, 1990; Carter and Atkinson, 1985). Therefore, the earlier nitrate yields of Atkinson et al (1982b, 1983b, 1984), which are all based on similar analytical methods, appear to be high.

Because of this, the parameter values of Carter and Atkinson (1989b) are no longer appropriate for general estimation purposes and need to be re-derived to be consistent with the new data. To determine temperature and pressure effects, we assume that the data of Atkinson et al (1983b) are valid in a relative sense (i.e., the errors are in the nitrate calibrations), so relative changes with temperature and pressure are still correct, and based on this corrected the earlier data to be consistent with the remeasured yields at atmospheric temperature and pressure. Table 28 gives the nitrate yield data that were used to re-derive the parameterization, along with footnotes giving the source of the data or how they were derived. These include all the new data currently available from Atkinson's laboratory, together with the pentyl and heptyl nitrate yields at varying temperatures and pressures from Atkinson et al (1983b), corrected to be consistent with the new data. The temperature and pressure effects data for the branched secondary alkyl nitrate data from Atkinson et al (1983b) (see also Carter and Atkinson, 1989b) were not used because there are no more recent data available to correct the yields, and because the pentyl and heptyl nitrate data should be a sufficient basis for the optimization.

The new parameter values were derived using a non-linear optimization procedure to minimize the quantity

$$\text{Fit Error} = \sum_{\text{Measurement Data}} \text{Weight} \left(\frac{(\text{Estimated Nitrate Yield}) - (\text{Corrected Measured Nitrate Yield})}{\text{Maximum}(0.1, \text{Corrected Measured Nitrate Yield})} \right)^2$$

where "Weight" is the relative weight given to the measurement in determining the total error, as shown on Table 28. The expression in the denominator was used to weight the points because minimizing absolute errors resulted in giving undue weight to the somewhat uncertain data obtained at the lowest temperature causing the derivation of unreasonable optimized parameters. Minimizing simply relative errors put undue weight on the lowest nitrate yields, which have the highest experimental uncertainty and are least important in affecting reactivity predictions. The parameter obtained in the optimization were as follows:

$$\begin{aligned} \alpha &= 3.94 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \\ \beta &= 0.705 \\ R_{\infty}^{300} &= 0.380 \\ m_0 &= 2.15 \\ m_{\infty} &= 6.36 \\ F &= 0.745 \end{aligned}$$

Note that the above value of R_{∞}^{300} , which is essentially the upper limit nitrate yield for high molecular weight compounds at ambient temperatures, is a factor of 1.6 lower than the upper limit derived from the previous parameterization. On the other hand, nitrate yield predictions for lower molecular weight compounds under ambient conditions are not as significantly affected.

Table 28 shows the nitrate yields estimated using these reoptimized parameters. These are used as the basis for the secondary nitrate yields estimates in the current mechanism, except as indicated below. A comparison for the experimental and calculated values for these data is also shown on Figure 4. It can be seen that reasonably good fits are obtained, though there may be a slight tendency for the parameterization to underpredict the yields at the lowest temperature and highest pressure.

Table 28. Alkyl nitrate yield data from the reactions of NO with secondary alkyl radicals that were used to derive the parameters to estimate secondary alkyl nitrate yields as a function of temperature, pressure, and carbon number.

Compound or Radical	nC	T (K)	P (molec cm ³)	Yield			Fit		
				Uncor	Corr	Notes	Calc	Weight	Error
<u>Total nitrate yield from compound</u>									
Propane	3	300	2.37e+19		4.0%	1,2	5.0%	100%	11%
n-Butane	4	300	2.37e+19		8.3%	1,2	7.9%	100%	-4%
n-Pentane	5	300	2.37e+19	13.4%	11.5%	1,2	11.4%	100%	0%
n-Hexane	6	300	2.37e+19		15.0%	1,2	15.3%	100%	2%
n-Heptane	7	300	2.37e+19	29.1%	18.7%	1,2	18.9%	100%	1%
n-Octane	8	300	2.37e+19		23.6%	1,2	21.8%	100%	-7%
n-Decane	10	300	2.37e+19		24.1%	2,3	25.0%	100%	4%
Cyclohexane	6	300	2.37e+19		16.5%	4	15.3%	100%	-7%
<u>Yield of specific radicals at varying T and P</u>									
2-Pentyl from n-pentane	5	284	2.52e+19	15.8%	13.5%	5	14.3%	5%	6%
	5	284	1.21e+19	10.6%	9.1%		9.7%	5%	6%
	5	284	5.27e+18	6.8%	5.8%		5.5%	5%	-3%
	5	300	1.63e+19	9.9%	8.5%		9.5%	5%	10%
	5	300	1.13e+19	9.5%	8.1%		7.7%	5%	-4%
	5	300	4.96e+18	6.0%	5.1%		4.5%	5%	-7%
	5	300	1.82e+18	3.1%	2.7%		2.0%	5%	-7%
	5	328	2.18e+19	8.2%	7.0%		7.8%	5%	8%
	5	326	1.19e+19	6.4%	5.5%		5.9%	5%	5%
	5	327	4.46e+18	3.9%	3.3%		3.2%	5%	-2%
3-Pentyl from n-pentane	5	337	2.12e+19	7.9%	6.8%		6.9%	5%	2%
	5	284	2.52e+19	17.4%	14.9%	3,4	14.3%	5%	-4%
	5	284	1.21e+19	12.0%	10.3%		9.7%	5%	-6%
	5	284	5.27e+18	7.5%	6.4%		5.5%	5%	-9%
	5	300	1.63e+19	10.7%	9.2%		9.5%	5%	3%
	5	300	1.13e+19	10.3%	8.8%		7.7%	5%	-11%
	5	300	4.96e+18	5.9%	5.0%		4.5%	5%	-6%
	5	300	1.82e+18	3.1%	2.7%		2.0%	5%	-7%
	5	328	2.18e+19	8.4%	7.2%		7.8%	5%	6%
	5	326	1.19e+19	6.6%	5.6%		5.9%	5%	3%
2-Heptyl from n-heptane	5	327	4.46e+18	4.4%	3.8%		3.2%	5%	-6%
	5	337	2.12e+19	8.1%	6.9%		6.9%	5%	0%
	7	284	2.52e+19	29.8%	19.1%		23.9%	2.5%	25%
	7	285	1.18e+19	24.9%	16.0%		18.6%	2.5%	16%
	7	283	5.43e+18	16.3%	10.5%		13.6%	2.5%	30%
	7	284	1.97e+18	11.5%	7.4%		7.4%	2.5%	1%
	7	300	1.14e+19	23.1%	14.8%		15.1%	2.5%	2%
	7	300	5.15e+18	14.6%	9.4%		10.8%	2.5%	14%
	7	300	1.80e+18	10.1%	6.5%		5.9%	2.5%	-6%
	7	323	2.21e+19	20.4%	13.1%		13.5%	2.5%	3%
7	323	1.06e+19	16.3%	10.5%		10.9%	2.5%	4%	

Table 28 (continued)

Compound or Radical	nC	T (K)	P (molec cm ³)	Yield			Fit		
				Uncor	Corr	Notes	Calc	Weight	Error
3-Heptyl from n-heptane	7	324	4.65e+18	10.4%	6.7%		7.7%	2.5%	10%
	7	321	1.79e+18	7.1%	4.6%		4.7%	2.5%	2%
	7	339	2.11e+19	15.9%	10.2%		10.7%	2.5%	5%
	7	342	4.52e+18	8.9%	5.7%		6.1%	2.5%	4%
	7	284	2.52e+19	35.2%	22.6%		23.9%	2.5%	6%
	7	285	1.18e+19	29.1%	18.7%		18.6%	2.5%	-1%
	7	283	5.43e+18	19.6%	12.6%		13.6%	2.5%	8%
	7	284	1.97e+18	14.1%	9.1%		7.4%	2.5%	-16%
	7	300	1.14e+19	29.3%	18.8%		15.1%	2.5%	-20%
	7	300	5.15e+18	17.7%	11.4%		10.8%	2.5%	-5%
	7	300	1.80e+18	12.2%	7.8%		5.9%	2.5%	-19%
	7	323	2.21e+19	22.6%	14.5%		13.5%	2.5%	-7%
	7	323	1.06e+19	17.9%	11.5%		10.9%	2.5%	-5%
	7	324	4.65e+18	12.2%	7.8%		7.7%	2.5%	-1%
4-Heptyl from n-heptane	7	321	1.79e+18	8.8%	5.7%		4.7%	2.5%	-9%
	7	339	2.11e+19	17.2%	11.1%		10.7%	2.5%	-3%
	7	342	4.52e+18	9.6%	6.2%		6.1%	2.5%	0%
	7	284	2.52e+19	31.4%	20.2%		23.9%	2.5%	18%
	7	285	1.18e+19	26.5%	17.0%		18.6%	2.5%	9%
	7	283	5.43e+18	17.6%	11.3%		13.6%	2.5%	20%
	7	284	1.97e+18	12.1%	7.8%		7.4%	2.5%	-3%
	7	300	1.14e+19	23.6%	15.2%		15.1%	2.5%	0%
	7	300	5.15e+18	15.3%	9.8%		10.8%	2.5%	10%
	7	300	1.80e+18	10.5%	6.7%		5.9%	2.5%	-8%
	7	323	2.21e+19	20.0%	12.9%		13.5%	2.5%	5%
	7	323	1.06e+19	16.0%	10.3%		10.9%	2.5%	6%
	7	324	4.65e+18	10.2%	6.6%		7.7%	2.5%	11%
	7	321	1.79e+18	7.3%	4.7%		4.7%	2.5%	0%
7	339	2.11e+19	15.3%	9.8%		10.7%	2.5%	9%	
7	342	4.52e+18	8.4%	5.4%		6.1%	2.5%	7%	

Notes

- 1 Nitrate yields for secondary radicals derived from total secondary nitrate yield from reactions of the n-alkane, divided by the fraction of formation of secondary radicals, as estimated using the method of Kwok and Atkinson (1995).
- 2 Total secondary nitrate yields from Arey et al (2000).
- 3 Total secondary nitrate yield from Atkinson (unpublished data, 1999).
- 4 Aschmann et al. (1997).
- 5 Nitrate yields relative to nitrate yields at ~300K and 1 atm total pressure from Atkinson et al (1983), as tabulated by Carter and Atkinson (1989). Data placed on an absolute basis using the ~300K, 1 atm total secondary nitrate yield data from Arey et al (2000), divided by the fraction of formation of secondary radicals as estimated by the method of Kwok and Atkinson (1995).

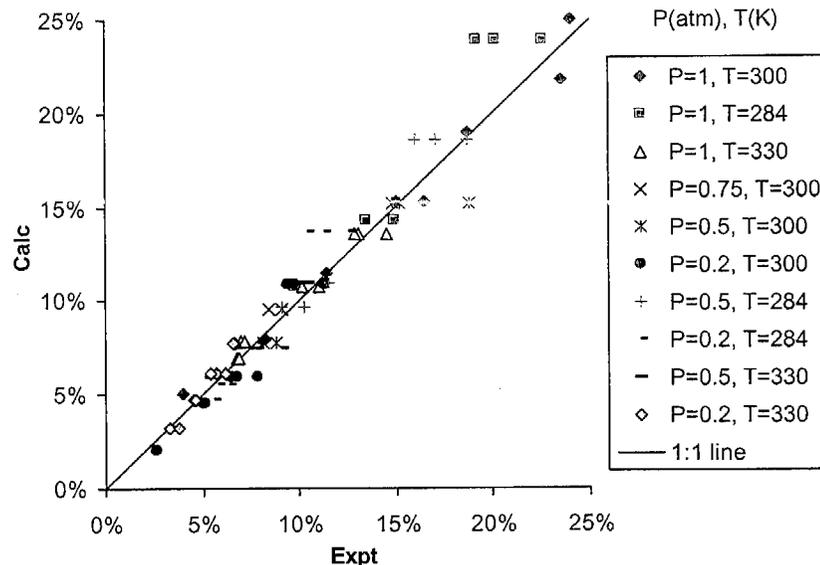


Figure 4. Plots of experimental vs calculated secondary alkyl nitrate yields that were used to optimize the parameters for estimation purposes.

The data summarized by Carter and Atkinson (1989b) indicate that the parameterization that fits the data for secondary alkyl nitrates does not perform well in predicting the limited nitrate yield data for primary and tertiary peroxy radicals. In addition, the presence of -OH, -O-, -CO-, ester, or other groups may also affect nitrate yields. Available information concerning nitrate yields that can serve as a basis for deriving estimates for substituted and non-secondary peroxy radicals is given in Table 29. As indicated on the table, most of these "nitrate yields" are not results of direct measurements, but results of optimizations of nitrate yield parameters in order to fit environmental chamber data. Although these chamber data are highly sensitive to this parameter, this is obviously a highly uncertain "measurement" because the results can be affected by other uncertainties in the VOCs' mechanisms, as well in the ability of the model to simulate the conditions of the experiment (see Section V). Nevertheless, for most types of radicals this provides the only information available from which general estimates can be derived.

Table 29 shows that the estimates for secondary alkyl peroxy radicals (shown in the Y_{sec} column on the table) generally perform very poorly in fitting the data for these substituted or other radicals, in most cases overpredicting the observed or adjusted yields. This means that some correction is needed when estimating nitrate yields for substituted or non-secondary peroxy radicals. Carter and Atkinson (1989b) recommended using a correction factor for the purpose of estimating primary and tertiary nitrate yields. This is equivalent to assuming that

$$Y_i(n_C, T, M) = Y_{\text{sec}}(n_C, T, M) \cdot f_i \quad (\text{V})$$

where Y_i is the yield computed for radicals of type i , Y_{sec} is the yield for secondary alkyl radicals computed as shown above, and f_i is a correction factor for this type of radical. This method, if generally applied, would mean that substitution or radical structure affects nitrate yields in a way that does not

Table 29. Alkyl nitrate yield assignments used in the current mechanism, including data used to derive general estimation methods for primary, tertiary, and substituted peroxy radicals.

Compound and Radical	Nitrate Yield			Ref.
	Value Used	Estimated Y_{sec}	Estimated Y_{corr}	
<u>Propane</u>				
CH ₃ -CH ₂ -CH ₂ OO.	2.0%	5.0%	0.0%	1
CH ₃ -CH[OO.]-CH ₃	4.0%	5.0%	5.0%	2
<u>Neopentane</u>				
CH ₃ -C(CH ₃)(CH ₂ OO.)-CH ₃	5.1%	11.4%	6.4%	1
<u>2,2,4-Trimethyl Pentane [b]</u>				
CH ₃ -C(CH ₃)(CH ₃)-CH ₂ -C[OO.](CH ₃)-CH ₃	10.2%	21.8%	17.2%	3
CH ₃ -C(CH ₃)(CH ₂ OO.)-CH ₂ -C(CH ₃)(OH)-CH ₃	10.2%	21.8%	17.2%	3
CH ₃ -C(CH ₃)(CH ₃)-CH[OO.]-CH(CH ₃)-CH ₃	12.9%	21.8%	21.9%	3
CH ₃ -C(CH ₃)(CH ₂ OO.)-CH ₂ -CH(CH ₃)-CH ₃	10.2%	21.8%	17.2%	3
CH ₃ -C(CH ₃)(CH ₃)-CH ₂ -CH(CH ₂ OO.)-CH ₃	10.2%	21.8%	17.2%	3
CH ₃ -C[OO.](CH ₃)-CH ₂ -C(CH ₃)(CH ₃)-CH ₂ -OH	10.2%	21.8%	17.2%	3
CH ₃ -C(CH ₃)(OH)-CH ₂ -C(CH ₃)(CH ₂ OO.)-CH ₂ -OH	10.2%	21.8%	17.2%	3
CH ₃ -C(CH ₃)(OH)-CH ₂ -C[OO.](CH ₃)-CH ₃	7.9%	19.0%	13.4%	3
CH ₃ -C(OH)(CH ₂ OO.)-CH ₂ -C(CH ₃)(OH)-CH ₃	7.9%	19.0%	13.4%	3
CH ₃ -CH(CH ₃)-CH ₂ -C[OO.](CH ₃)-CH ₃	7.9%	19.0%	13.4%	3
CH ₃ -C(CH ₃)(CH ₃)-CH ₂ -CH[OO.]-CH ₃	11.2%	19.0%	19.0%	3
CH ₃ -C(CH ₃)(CH ₂ OO.)-CH ₂ -CH(OH)-CH ₃	7.9%	19.0%	13.4%	3
CH ₃ -C(CH ₃)(OH)-CH ₂ -CH(CH ₂ OO.)-CH ₃	7.9%	19.0%	13.4%	3
<u>2-Methyl Butane</u>				
CH ₃ -C[OO.](CH ₃)-CH ₂ -CH ₃	5.2%	11.4%	6.4%	1
CH ₃ -CH(CH ₃)-CH[OO.]-CH ₃ [a]	14.1%	11.4%	11.4%	1
<u>Propene</u>				
CH ₃ -CH[OO.]-CH ₂ -OH	1.5%	5.0%	0.0%	4
CH ₃ -CH(CH ₂ OO.)-OH	1.8%	5.0%	0.0%	4
<u>1-Butene</u>				
CH ₃ -CH ₂ -CH(CH ₂ OO.)-OH	3.1%	7.9%	3.9%	5
CH ₃ -CH ₂ -CH[OO.]-CH ₂ -OH	2.2%	7.9%	3.9%	5
<u>1-Hexene</u>				
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH(CH ₂ OO.)-OH	6.6%	15.3%	9.6%	6
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH[OO.]-CH ₂ -OH	4.9%	15.3%	9.6%	6
<u>Cis-2-Butene</u>				
CH ₃ -CH(OH)-CH[OO.]-CH ₃	3.5%	7.9%	3.9%	7
<u>Isoprene</u>				
HO-CH ₂ -C(CH ₃)=CH-CH ₂ OO.	8.8%	11.4%	6.4%	8
HO-CH ₂ -C(CH ₃)=CH(CH ₂ OO.)	8.8%	11.4%	6.4%	8
CH ₂ =CH-C[OO.](CH ₃)-CH ₂ -OH	8.8%	11.4%	6.4%	8
CH ₃ -C(CH ₂ OO.)=CH(CH ₂ -OH)	8.8%	11.4%	6.4%	8

Table 29 (continued)

Compound and Radical	Nitrate Yield			Ref.
	Value Used	Estimated Y _{sec}	Estimated Y _{corr}	
CH ₃ -C(CH ₂ OO.)=CH-CH ₂ -OH	8.8%	11.4%	6.4%	8
CH ₂ =C(CH ₃)-CH[OO.] -CH ₂ -OH	8.8%	11.4%	6.4%	8
CH ₂ =CH-C(OH)(CH ₂ OO.)-CH ₃	8.8%	11.4%	6.4%	8
CH ₂ =C(CH ₃)-CH(CH ₂ OO.)-OH	8.8%	11.4%	6.4%	8
<u>T-Butyl Alcohol</u>				
CH ₃ -C(OH)(CH ₂ OO.)-CH ₃	7.0%	7.9%	3.9%	9
<u>MTBE</u>				
CH ₃ -C(CH ₃)(CH ₃)-O-CH ₂ OO.	7.0%	11.4%	6.4%	10
CH ₃ -C(CH ₃)(CH ₂ OO.)-O-CH ₃	7.0%	11.4%	6.4%	10
<u>Ethoxy Ethanol</u>				
CH ₃ -CH[OO.] -O-CH ₂ -CH ₂ -OH	2.5%	7.9%	3.9%	11
CH ₃ -CH ₂ -O-CH[OO.] -CH ₂ -OH	2.5%	7.9%	3.9%	11
HO-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ OO.	2.5%	7.9%	3.9%	11
<u>Carbitol</u>				
HO-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ OO.	12.2%	15.3%	9.6%	12
CH ₃ -CH[OO.] -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -OH	12.2%	15.3%	9.6%	12
CH ₃ -CH ₂ -O-CH[OO.] -CH ₂ -O-CH ₂ -CH ₂ -OH	12.2%	15.3%	9.6%	12
CH ₃ -CH ₂ -O-CH ₂ -CH[OO.] -O-CH ₂ -CH ₂ -OH	12.2%	15.3%	9.6%	12
CH ₃ -CH ₂ -O-CH ₂ -CH ₂ -O-CH[OO.] -CH ₂ -OH	12.2%	15.3%	9.6%	12
<u>Methyl Acetate</u>				
CH ₃ -CO-O-CH ₂ OO.	1.5%	5.0%	0.0%	13
<u>2-Butoxyethanol</u>				
HO-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -CH ₂ -CH ₂ OO.	11.8%	15.3%	9.6%	14
CH ₃ -CH[OO.] -CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -OH	11.8%	15.3%	9.6%	14
CH ₃ -CH ₂ -CH[OO.] -CH ₂ -O-CH ₂ -CH ₂ -OH	11.8%	15.3%	9.6%	14
CH ₃ -CH ₂ -CH ₂ -CH[OO.] -O-CH ₂ -CH ₂ -OH	11.8%	15.3%	9.6%	14
CH ₃ -CH ₂ -CH ₂ -CH ₂ -O-CH[OO.] -CH ₂ -OH	11.8%	15.3%	9.6%	14
<u>Ethyl Acetate</u>				
CH ₃ -CO-O-CH ₂ -CH ₂ OO.	4.0%	7.9%	3.9%	15
CH ₃ -CO-O-CH[OO.] -CH ₃	4.0%	7.9%	3.9%	15
CH ₃ -CH ₂ -O-CO-CH ₂ OO.	4.0%	7.9%	3.9%	15
<u>Dimethyl Succinate (DBE-4)</u>				
CH ₃ -O-CO-CH ₂ -CH ₂ -CO-O-CH ₂ OO.	8.0%	15.3%	9.6%	16
CH ₃ -O-CO-CH ₂ -CH[OO.] -CO-O-CH ₃	8.0%	15.3%	9.6%	16
CH ₃ -O-CO-CH ₂ -CH(OH)-CO-O-CH ₂ OO.	8.0%	15.3%	9.6%	16
<u>Dimethyl Gluturate (DBE-5)</u>				
CH ₃ -O-CO-CH ₂ -CH ₂ -CH ₂ -CO-O-CH ₂ OO.	14.8%	19.0%	13.4%	17
CH ₃ -O-CO-CH ₂ -CH ₂ -CH[OO.] -CO-O-CH ₃	14.8%	19.0%	13.4%	17
CH ₃ -O-CO-CH ₂ -CH[OO.] -CH ₂ -CO-O-CH ₃	14.8%	19.0%	13.4%	17
CH ₃ -O-CO-CH ₂ -CH ₂ -CH(OH)-CO-O-CH ₂ OO.	14.8%	19.0%	13.4%	17

Table 29 (continued)

Compound and Radical	Nitrate Yield			Ref.
	Value Used	Estimated Y _{sec}	Estimated Y _{corr}	
<u>Methyl Isobutyrate</u>				
CH ₃ -CH(CH ₂ OO.)-CO-O-CH ₃	6.4%	11.4%	6.4%	18
CH ₃ -C[OO.](CH ₃)-CO-O-CH ₃	6.4%	11.4%	6.4%	18
CH ₃ -CH(CH ₃)-CO-O-CH ₂ OO.	6.4%	11.4%	6.4%	18
<u>t-Butyl Acetate</u>				
CH ₃ -C(CH ₃)(CH ₂ OO.)-O-CO-CH ₃	12.0%	15.3%	9.6%	19
CH ₃ -C(CH ₃)(CH ₃)-O-CO-CH ₂ OO.	12.0%	15.3%	9.6%	19
<u>Propylene Carbonate [b]</u>				
CH(CH ₃)-O-CO-O-CH[OO.]-	1.2%	7.9%	3.9%	20
C[OO.](CH ₃)-CH ₂ -O-CO-O-	1.2%	7.9%	3.9%	20
CH(CH ₂ OO.)-CH ₂ -O-CO-O-	1.2%	7.9%	3.9%	20
CH ₃ -CO-O-CO-O-CH ₂ OO.	1.2%	7.9%	3.9%	20
CH ₃ -CH[OO.]-O-CO-O-CHO	1.2%	7.9%	3.9%	20
<u>Isobutene</u>				
CH ₃ -C[OO.](CH ₃)-CH ₂ -OH	10.0%	7.9%	3.9%	21
<u>n-Butyl Acetate</u>				
CH ₃ -CO-O-CH ₂ -CH ₂ -CH ₂ -CH ₂ OO.	10.0%	15.3%	9.6%	22
CH ₃ -CO-O-CH ₂ -CH ₂ -CH[OO.]-CH ₃	10.0%	15.3%	9.6%	22
CH ₃ -CH ₂ -CH[OO.]-CH ₂ -O-CO-CH ₃	10.0%	15.3%	9.6%	22
CH ₃ -CH ₂ -CH ₂ -CH[OO.]-O-CO-CH ₃	10.0%	15.3%	9.6%	22
CH ₃ -CH ₂ -CH ₂ -CH ₂ -O-CO-CH ₂ OO.	10.0%	15.3%	9.6%	22
<u>Methyl Pivalate</u>				
CH ₃ -C(CH ₃)(CH ₂ OO.)-CO-O-CH ₃	13.0%	15.3%	9.8%	23
CH ₃ -C(CH ₃)(CH ₃)-CO-O-CH ₂ OO.	13.0%	15.3%	9.8%	23
<u>Methyl Isopropyl Carbonate</u>				
CH ₃ -CH(CH ₂ OO.)-O-CO-O-CH ₃	4.5%	11.4%	6.5%	24
CH ₃ -C[OO.](CH ₃)-O-CO-O-CH ₃	4.5%	11.4%	6.5%	24
CH ₃ -CH(CH ₃)-O-CO-O-CH ₂ OO.	4.5%	11.4%	6.5%	24
<u>Cyclohexanone</u>				
CH ₂ -CH ₂ -CH ₂ -CH ₂ -CO-CH[OO.]-	15.0%	15.3%	9.6%	25
CH ₂ -CH ₂ -CH ₂ -CO-CH ₂ -CH[OO.]-	15.0%	15.3%	9.6%	25
CH ₂ -CH ₂ -CO-CH ₂ -CH ₂ -CH[OO.]-	15.0%	15.3%	9.6%	25
<u>1-Methoxy-2-Propanol</u>				
CH ₃ -CH(OH)-CH[OO.]-O-CH ₃	1.6%	7.9%	3.9%	26
CH ₃ -CH(OH)-CH ₂ -O-CH ₂ OO.	1.6%	7.9%	3.9%	26

[a] Experimental value is probably high. Not used for determining best fit parameters.

[b] Other uncertainties in the mechanism affect the nitrate yield that gives the best fits to the mechanism to such an extent that the adjusted yield for this compound was not used to determine the best fit parameters.

Table 29 (continued)

References

- 1 Based on nitrate yield data tabulated by Carter and Atkinson (1989).
- 2 Based on 2-propyl nitrate yields from propane from Arey et al (2000), corrected fraction of 2-propyl formation estimated using the method of Kwok and Atkinson (1995).
- 3 Nitrate yields from C₇ and C₈ peroxy radicals formed from 2,2,4-trimethyl pentane reduced by a factor of 1.7 to fit results of environmental chamber reactivity experiments.
- 4 Based on nitrate yield data from propene from Shepson et al (1985) and O'Brien et al (1998), corrected for estimated fraction of reaction from terminal position based on data of Cvetanovic (1976).
- 5 Based on nitrate yield data from 1-butene from O'Brien et al (1998), corrected for estimated fraction of reaction from terminal position based on data of Cvetanovic (1976) for propene.
- 6 Based on nitrate yield data from 1-hexene from O'Brien et al (1998), corrected for estimated fraction of reaction from terminal position based on data of Cvetanovic (1976) for propene.
- 7 Based on nitrate yield data from cis-2-butene from Muthuramu et al (1993) and O'Brien et al (1998).
- 8 Adjusted to fit environmental chamber reactivity data for isoprene.
- 9 Adjusted to fit environmental chamber reactivity data for t-butanol..
- 10 Adjusted to fit environmental chamber reactivity data for MTBE.
- 11 Adjusted to fit environmental chamber reactivity data for ethoxy ethanol.
- 12 Adjusted to fit environmental chamber reactivity data for carbitol.
- 13 Adjusted to fit environmental chamber reactivity data for methyl acetate.
- 14 Adjusted to fit environmental chamber reactivity data for 2-butoxyethanol.
- 15 Adjusted to fit environmental chamber reactivity data for ethyl acetate.
- 16 Adjusted to fit environmental chamber reactivity data for DBE-4.
- 17 Adjusted to fit environmental chamber reactivity data for DBE-5.
- 18 Adjusted to fit environmental chamber reactivity data for methyl isobutyrate.
- 19 Adjusted to fit environmental chamber reactivity data for t-butyl acetate.
- 20 Adjusted to fit environmental chamber reactivity data for propylene carbonate.
- 21 Adjusted to fit environmental chamber data for isobutene.
- 22 Adjusted to fit environmental chamber reactivity data for n-butyl acetate.
- 23 Adjusted to fit environmental chamber reactivity data for methyl pivalate.
- 24 Adjusted to fit environmental chamber reactivity data for methyl isopropyl carbonate.
- 25 Adjusted to fit environmental chamber reactivity data for cyclohexanone.
- 26 Adjusted to fit environmental chamber reactivity data for 1-Methoxy-2-Propanol.

depend on the size of the radical. An alternative approach is to adjust the carbon number used to estimate the yields, i.e.,

$$Y_i(n_c, T, M) = Y_{sec}(n_c - n_i, T, M) \quad (VI)$$

where n_i is a correction term used to derive an “effective carbon number” for radicals of type i . This would predict that the effects of substitution or structure tend to become less important as the size of the radical increases, since the parameterization predicts that the nitrate yield becomes less dependent on n_c as n_c increases.

Figure 5 shows plots of the observed or adjusted overall nitrate yields derived for compounds forming non-secondary or substituted peroxy radicals against secondary nitrate yields (Y_{sec}) calculated for the same number of carbons using Equations (III and IV)¹⁴. It can be seen that in most cases the ratio of the observed or adjusted yields to Y_{sec} range from ~0.4 to 1, with no apparent dependence of the ratio on the nature of the radical or its substituents. The best fit line for all the data corresponds to a correction factor of ~0.65, if the constant correction factor method (Equation V) is employed, with an uncertainty of approximately a factor of 1.6. Because of the lack of a clear dependence of the correction on the type of radical, the most appropriate approach is probably to use this factor for all substituted or non-secondary radicals.

However, if the constant correction factor method (Equation V) is employed, then the model tends to overpredict the ozone reactivities of high molecular weight alkanes (e.g., n-octane and n-dodecane) in environmental chamber reactivity experiments. Better fits are obtained if higher nitrate yields from the C_{8+} OH-substituted peroxy radicals formed in the oxidations of these compounds (following 1,4-H shift isomerizations, as discussed in Section III.J.2) are assumed than predicted using Equation (V) and $f=0.65$. This suggests that the effects of substitution may decrease as the size of the radical increases, as is predicted by the “effective carbon number” adjustment approach (Equation VI). Therefore, “effective carbon number” adjustment this approach is adopted in this work.

The best fits to the available experimental or adjusted nitrate yield data for are obtained by using Equation (VI) with the carbon numbers reduced by ~1.5 for non-secondary or substituted peroxy radicals, with no apparent dependence of the reduction on the type of radical or its substituents. Figure 6 shows the performance of this method in estimating overall nitrate yields for compounds forming substituted or non-secondary peroxy radicals that are used as the basis for deriving our estimates. The 1:1 line and lines showing a factor of 1.6 uncertainty range are also shown. A comparison of Figure 5 and Figure 6 shows that the carbon number adjustment method performs about as well (or poorly) as the factor adjustment method, with the data being an insufficient basis for choosing between them. However, the use of Equation (VI) with a carbon number reduction of 1.5 for all non-secondary or substituted radicals is preferred because of its superior performance in simulating the overall reactivities of the higher n-alkanes.

There are several cases where the observed or adjusted nitrate yields are not well fit by either method. These include $CH_3C(OH)(CH_3)CH_2OO\cdot$ from t-butanol, $CH_3C(OO\cdot)(CH_3)CH_2OH$ from isobutene, and $CH_3C(O)OC(CH_3)(CH_3)CH_2OO\cdot$ from t-butyl acetate, where the estimated yields are considerably lower than those that must be assumed for model simulations to fit the chamber data. On the other hand, the estimates tend to underpredict nitrate yields that were measured in the reactions of OH radicals with 1-butene and 1-hexene (O’Brein et al, 1998). It is interesting to note that the cases where the nitrate yields are higher than estimated all have the radical center is at or near a quaternary carbon.

¹⁴ The adjusted nitrate yield for methyl isobutyrate, whose mechanism is highly uncertain, is not shown.

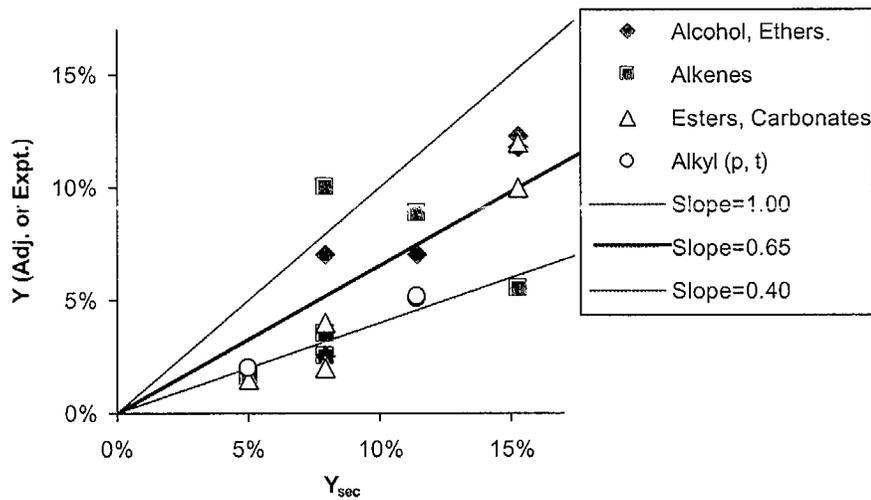


Figure 5. Plots of observed or adjusted overall nitrate yields against Y_{sec} values derived using Equations (III and IV) for compounds forming non-secondary and substituted peroxy radicals.

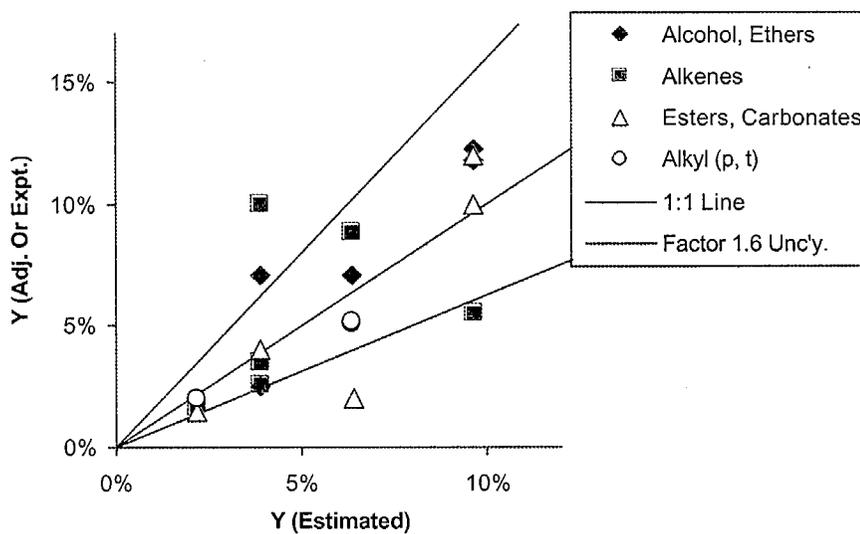


Figure 6. Plots of observed or adjusted overall nitrate yields for compounds forming non-secondary and substituted peroxy radicals against overall nitrate yields estimated using Equation (VI) and a carbon number reduction of 1.5.

However, the alkyl nitrate yield data for neopentyl, 2-methyl-2-butyl and 2-methyl-2-pentyl (Carter and Atkinson, 1989b) are reasonably consistent with the predictions using the estimated corrections discussed above, so no general conclusions can be made for radicals with this structure. The reason why the nitrate yields from radicals formed from 1-butene and 1-hexene are too low is unclear, and the possibility of experimental problems cannot necessarily be ruled out.

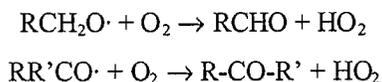
The approach adopted in this work to use Equation (VII) with a carbon number reduction of 1.5 to derive the correction factors for estimating nitrate yields in cases of non-secondary or substituted radicals where no data are available, and to use explicit assignments for those radicals (including the outliers discussed above) for which available data indicate the estimates are not appropriate. These assignments are indicated on the “value used” column on Table 29.

J. Reactions of Alkoxy Radicals

Alkoxy radicals are also critical intermediates in the photooxidation mechanisms of most VOCs, and the variety of possible reactions that higher molecular weight alkoxy radicals can undergo is a major source of the complexity (and uncertainty) in the generated photooxidation mechanisms for most VOCs. Primary and secondary alkoxy radicals can react with O₂, C₂₊ alkoxy radicals can react via β-scission forming smaller molecules and radicals, long chain alkoxy radicals can undergo H-shift isomerizations ultimately forming disubstituted radicals, and certain substituted alkoxy radicals can undergo other reactions. Knowledge of the rate constants or branching ratios for all these processes need to be specified to generate the mechanisms. Unfortunately, relevant information concerning these processes is highly limited, and estimates are usually necessary. The methods used to estimate the various rate constants or branching ratios, and the specific assignments that are used in those cases where data are available, are discussed in this section.

1. Reaction with O₂

Primary and secondary alkoxy radicals can react with O₂, forming HO₂ and the corresponding carbonyl compound.



Absolute rate constants for these reactions are available only for methoxy, ethoxy, and isopropoxy radicals, and the IUPAC recommended rate parameters (Atkinson et al, 1998) are given on Table 30. Non-Arrhenius temperature dependences are observed and the A factors are much lower than expected for an abstraction reaction, possibly indicating a complex mechanism. However, the A factors are reasonably consistent for the reactions of the different radicals, increasing as expected with the number of abstractable hydrogens, though the A factor per hydrogen for isopropoxy is approximately half that of ethoxy ($3.0 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$).

For estimation purposes, we assume that all primary alkoxy radicals react with O₂ with the same A factor as does ethoxy, and that all secondary alkoxy + O₂ A factors are the same as for isopropoxy radicals:

$$\begin{aligned} A(\text{O}_2, \text{primary RO}\cdot) &= 6.0 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \\ A(\text{O}_2, \text{secondary RO}\cdot) &= 1.5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \end{aligned}$$

Table 30. Recommended kinetic parameters for reactions of alkoxy radicals with O₂.

Radical	n	A	A/n	K(298)	ΔH _r	E _a
		(cm ³ molec ⁻¹ s ⁻¹)			(kcal/mol)	
CH ₃ O.	3	7.20e-14	2.40e-14	1.92e-15	-26.28	2.15
CH ₃ -CH ₂ O.	2	6.00e-14	3.00e-14	9.48e-15	-32.03	1.09
CH ₃ -CH[O.] -CH ₃	1	1.50e-14	1.50e-14	7.67e-15	-35.82	0.40

From Atkinson (1997a), Table 9

Because the low A factors and non-Arrhenius behavior these estimates must be considered to be uncertain, and quantitative data are clearly needed for other alkoxy radicals.

Table 30 shows that the apparent activation energies for the alkoxy + O₂ reaction appear to be correlated with the heat of reaction. In fact, a plot of the activation energy vs. ΔH_r (not shown) indicates that X perhaps by coincidence X the data for these three radicals fall almost exactly on a straight line, which is given by:

$$E_a(O_2) = 6.96 + 0.183 \Delta H_r(O_2) \quad (\text{VIII})$$

where E_a(O₂) is the activation energy and ΔH_r(O₂) is the heat of reaction¹⁵ This therefore can be used to estimate activation energies, and therefore rate constants, for any alkoxy + O₂ reaction.

However, the above equation cannot be used for estimating activation energies for reactions of O₂ with alkoxy radicals such as CH₃OCH₂O≡, whose reaction with O₂ are sufficiently exothermic that Equation (VIII) predicts a negative activation energy. In those cases, we assume for estimation purposes that no alkoxy + O₂ reaction has an activation energy that is less than the a certain minimum value, which should be somewhere between 0 and 0.4 kcal/mole. We assume that the actual minimum is near the high end of this range, or 0.4 kcal/mole. Therefore, for estimation purposes we use:

$$E_a(O_2) = \max [0.4, 6.96 + 0.183 \Delta H_r(O_2)] \quad (\text{IX})$$

Note that the 0 to 0.4 kcal/mole range for the minimum activation energy amounts to an uncertainty in the rate constant of a factor of ~2 for highly exothermic alkoxy + O₂ reactions. This is not a large uncertainty given the uncertainty in assuming that the A factors for the O₂ reactions are the same for all primary or all secondary alkoxy radicals.

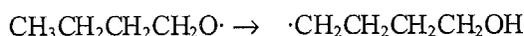
The estimates for the reactions of O₂ with the saturated hydrocarbon alkoxy radicals (i.e, alkoxy radicals containing only -CH₃, -CH₂-, >CH-, or >C< groups) are probably the least uncertain because they are the most similar to the simple alkoxy radicals used as the basis for the estimate. These estimates become increasingly uncertain for the oxygenated radicals with significantly higher reaction exothermicities (i.e., the reaction of O₂ with CH₃OCH₂O≡ has an estimated ΔH_r of -46.6 kcal/mole, compared to -35.8 for isopropoxy). The estimates used here predict that these highly exothermic alkoxy + O₂ reactions have 298K rate constants of ~3 x 10⁻¹⁴ cm³ molec⁻¹ s⁻¹ for primary radicals and ~8 x 10⁻¹⁵ cm³

¹⁵ Heats of reaction are estimated by group additivity as discussed in Section IV.A.5, based primarily on the thermochemical groups in the NIST (1994) database. Some reactants or products had groups that are not in the NIST (1994) database, and the thermochemical contributions of these groups had to be estimated. Tabulated heats of reaction may be uncertain by at least 2 kcal/mole.

molec⁻¹ s⁻¹ for secondary radicals. However, the possibility that these rate constants may be orders of magnitude higher cannot be ruled out. For example, if the approach of Atkinson (1997a), which uses a relationship between the rate constant (not the activation energy) and the heat of reaction, estimates the rate constant for the reaction of O₂ with, for example, CH₃OCH₂O≡, to be ~3.7 x 10⁻¹³ cm³ molec⁻¹ s⁻¹, which is a factor of ~12 higher than the estimation approach discussed above. This, of course, would imply that the effective A factors for these highly exothermic reactions are significantly higher than for those radicals whose rate constants have been measured – which we assume is not the case.

2. H-Shift Isomerizations

Long chain alkoxy radicals can react unimolecularly by abstraction by the alkoxy center from a C-H bond elsewhere in the radical, via a cyclic transition state, forming a hydroxy-substituted carbon-centered radical, e.g.,



Rate constants for these reactions can be estimated based on activation energies for bimolecular H-atom abstractions by alkoxy radicals plus ring strain energies for the cyclic transition states, and estimates of A factors (Carter et al, 1976; Baldwin et al, 1977; Carter and Atkinson, 1985; Atkinson, 1994). The results indicate that 1,4-H shift reactions (such as shown above), involving a relatively unstrained 6-member ring transition state, will be relatively rapid and should dominate over competing processes, at least for the hydrocarbon alkoxy radicals formed in alkane photooxidation systems. On the other hand, the estimates indicate that hydrogen shifts involving strained transition states, such as 1,3-H shifts involving a 5 member ring, as well as those involving more strained rings, are not likely to be sufficiently rapid to be important. Therefore except for the “ester rearrangement” reaction discussed below, only 1,4 H shift isomerizations are considered when the estimated mechanisms are generated.

The only data available concerning rates of 1,4-H shift isomerizations of alkoxy radicals are rate constants relative to competing alkoxy + O₂ or decomposition reactions. Although the rate constants for the competing reactions have also not been measured, they can be estimated in the case of the O₂ reactions as discussed above. Table 31 lists the isomerization reactions whose rate have been determined relative to the competing O₂ reaction, together with the rate constant ratios as summarized by Atkinson (1997a). Table 31 also shows the A factors estimated by Atkinson (1997a) and the corresponding activation energies, which are based on assuming

$$A(\text{isom}) = 8.0 \times 10^{10} \times (\text{number of abstractable hydrogens}) \text{ sec}^{-1}.$$

This is based on the previous estimates of Baldwin et al (1977), and is incorporated in the 1,4-H shift estimates used in this work.

The limited number of species for which isomerization rate constants have been measured and the relative imprecision of the data for 2-hexoxy provide an inadequate data base from which to derive a general estimation method for the activation energies. It is reasonable to assume that the activation energy will be correlated with the C-H bond dissociation energy for the bond that is being attacked by the alkoxy center. To provide a somewhat larger database in this regard, it is useful to look at available kinetic information for a bimolecular analogue for this reaction, namely the H-atom abstraction reactions of methoxy radicals. Table 31 lists the rate constants or Arrhenius parameters found for such reactions in the NIST kinetics database (NIST, 1989). The Arrhenius parameters have been estimated for those species where temperature dependence information was not given by using the average of those determined for

Table 31. Rate constants for H abstraction reactions by alkoxy radicals.

Reaction	BDE [a] (kcal)	A [b]	Ea (kcal)	T (K)	k(T)	Refs [c]
<u>Alkoxy Isomerizations (sec⁻¹)</u>						
1-Butoxy [d]	101.4	2.4e+11	8.42	<u>298</u>	<u>1.60e+5</u>	1,2
2-Pentoxy [d]	101.4	2.4e+11	8.16	<u>298</u>	<u>2.50e+5</u>	1,2
3-Hexoxy	101.4	2.4e+11	8.04	<u>298</u>	<u>3.05e+5</u>	2,3
2-Hexoxy	98.1	1.6e+11	6.44	<u>298</u>	<u>3.05e+6</u>	2,4
<u>Methoxy + RH Reactions (cm³ molec⁻¹ sec⁻¹)</u>						
CH ₄	104.9	<u>2.6e-13</u>	8.84			5
C ₂ H ₆ -> i-C ₂ H ₅	101.2	<u>4.0e-13</u>	7.09			5
C ₃ H ₈ -> i-C ₃ H ₇	98.6	<u>2.4e-13</u>	4.57			6
(CH ₃) ₂ CHCH(CH ₃) ₂	96.8	1.7e-13	4.11	<u>373</u>	<u>6.64e-16</u>	7,8
CH ₃ OH -> CH ₂ OH	98.1	<u>5.0e-13</u>	<u>4.07</u>			9
CH ₃ CHO	85.9	8.4e-14	0.63	<u>298</u>	<u>2.88e-14</u>	8,10
<u>Alkoxy Isomerization Group Rate Constants for estimations (sec⁻¹)</u>						
-CH ₃	101.4	2.4e+11	8.49	298	1.44e+5	2,11
-CH ₂ -	98.1	1.6e+11	6.33	298	3.63e+6	2,11
-CH<	96.8	8.0e+10	5.51	298	7.29e+6	2,11
-CHO	85.9	8.0e+10	5.75	299	5.02e+6	2,12

[a] Bond dissociation energies are derived from the NIST (1994) thermochemical database or from heats of formation given in the IUPAC evaluation (Atkinson et al, 1997).

[b] Underlined A, Ea, T, or k data are experimental measurements. Data not underlined are estimates.

[c] Notes and references:

- 1 Rate constant recommended by Atkinson (1997a)
- 2 A factors estimated for general alkoxy radical isomerizations by Atkinson (1997a), based on earlier estimates of Baldwin et al (1977)
- 3 Use middle value of range given by Eberhard et a. (1995). Varies from 1.8 - 4.3 x 10⁵ sec⁻¹.
- 4 Use middle value of range given by Eberhard et a. (1995). Varies from 1.4 - 4.7 x 10⁶ sec⁻¹.
- 5 Tsang and Hampson (1986)
- 6 Tsang (1988)
- 7 Alcock and Mile (1975)
- 8 A factor per abstracted hydrogen is assumed to be the average of that for the methoxy + ethane, propane and propane (to isopropyl) reactions.
- 9 Tsang (1987)
- 10 Weaver et al, (1975), Kelly and Keicklen (1978). These report rate constant ratios relative to methoxy + O₂ of 14-15. Placed on an absolute basis using the methoxy + O₂ rate constant.
- 11 Activation energy derived from correlation between methoxy + RH rate constants and BDE, with an added 1.6 kcal/mole "strain" correction for consistency with data for isomerization reactions, as discussed in the text.
- 12 Activation energy estimated from that estimated for the methoxy + acetaldehyde reaction, plus the 1.6 kcal/mole "strain" correction used for the other groups, plus an additional 3.5 kcal/mole "strain" correction for reactions with -CO- groups in the transition state, derived as discussed in the text.