Prepared under contract 98-401

REVIEW OF THE UPDATED MAXIMUM INCREMENTAL REACTIVITY SCALE OF DR. WILLIAM CARTER

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Prepared for:
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P.O. Box 2815
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November 29, 1999

DISCLAIMER

ACKNOWLEDGEMENTS

This report was submitted in fulfillment of (ARB contract 98-401, Review of the Updated Maximum Incremental Reactivity Scale of Dr. William Carter) by the Desert Research Institute under the sponsorship of the California Air Resources Board. Work was completed as of November 29, 1999.

ABSTRACT

The objective was to provide a peer review of Dr. William P.L. Carter's detailed chemical mechanism to ensure that the mechanism consists of the best possible atmospheric chemistry. The mechanism was compared with standard evaluated databases and the most recent available literature. The mechanism's documentation was reviewed to ensure that the mechanism, all supporting documents and all computer codes are clearly described. The mechanism was determined to be within the realm of the best available science. The review included an evaluation of the treatment of uncertainty in the mechanism and its impact on MIR values. The method of assessing uncertainty in the mechanism and its effect on MIRs is reasonable. Compounds with relatively well understood mechanisms have MIR values that are uncertain to within a factor of 1.5 and the compounds with less well understood mechanisms have MIR values that are uncertain within a factor of 2. However, the relative ranking of MIR values appears to be much more certain. The relative MIR values of compounds with well known mechanisms require no uncertainty multiplier. For compounds with less well understood mechanisms the multiplier could chosen to be between 1.5 to 2.

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1. Introduction

The California Air Resources Board (CARB) is considering development of volatile organic compound (VOC) control regulations for aerosol coatings based on the maximum incremental reactivity scale (MIR) (Carter, 1994). Regulations based on ozone formation potentials (reactivity) may provide a more cost-effective alternative to purely mass based regulations. The MIRs to be used within this program are based on calculations made with Carter's updated chemical mechanism. Because the detailed updated mechanism consists of hundreds of parameters it must be carefully peer reviewed to be credible.

VOC control strategies aimed at reducing the photochemical formation of ozone have been primarily based on reducing the mass of VOC emitted regardless of the chemical nature of the VOC. However, it is well known that VOCs are oxidized in the atmosphere through very different mechanisms. For example, alkanes and aromatics react only with hydroxyl radicals (HO) in the gas-phase while alkenes react with HO, ozone and nitrate radical (NO_3) (Atkinson, 1994). Oxygenated compounds such as formaldehyde (HCHO) also photolyze to produce radicals in addition to reacting with HO and NO_3 (Atkinson, 1994).

The contribution of each VOC to the formation of ozone is different because each has a different oxidation mechanism in the atmosphere. The ozone formation potential has been characterized by several different measures but the MIR scale (Carter, 1994) is widely used and it has been investigated for potential applications through a number of investigations (Russell et al., 1995; Yang et al. 1995; 1996; Stockwell and Kuhn, 1998).

For a specified scenario of meteorological conditions, emissions and initial concentrations, an incremental reactivity, IR, of an organic compound is the change in the peak ozone concentration, $\Delta[O_3]$ in grams, divided by an incremental change in the initial concentration and emissions of the organic compound, $\Delta[VOC]$ in grams, (Carter, 1994).

$$IR = \Delta[O_3] / \Delta[VOC]$$

MIRs are calculated for reference scenarios consisting of a specified meteorological situation, initial pollutant concentrations and emission rates of NO_x and VOC. If a series of simulations with differing NO_x initial concentrations and emission rates are made, a scenario will be found in the VOC limited region where the aggregate incremental reactivity reaches a maximum and this is defined as the MIR scenario (Carter, 1994). Once the MIR scenario is known incremental reactivities can be calculated through the simulation of cases with small variations in individual organic compounds.

Ozone formation potentials are highly dependent on the chemical mechanisms for VOC oxidation. To consider reactivity as the basis of a VOC control strategy it is necessary that the calculated MIRs be as accurate as possible. The calculation of accurate MIRs requires that the kinetic oxidation mechanism be based on the best possible science. Because detailed chemical mechanisms, such as Carter's updated chemical mechanism, have hundreds of parameters, including rate constants, product yields and for photolysis reactions, quantum yields and absorption cross sections, the mechanism was reviewed. Each individual parameter was checked against standard data bases, such as NASA (DeMore et al., 1997), IUPAC (Atkinson et al., 1997; Atkinson, 1994), and the mechanism's overall structure and approach was checked for consistency with the available data. Kinetic parameters that are not well measured in the laboratory must be considered to be highly uncertain and these parameters were identified. High quality of the documentation of the mechanism and its supporting programs is necessary for the credibility of the mechanism and the acceptance of reactivity as a regulatory tool. Therefore the documentation was critically reviewed as well.

In this work Carter's updated base chemical mechanism, the VOCs represented using the assigned mechanistic parameter method, the use of the "lumped molecule" approach and the handling of uncertainty in both the MIR and the regulation were reviewed. The portions of the mechanism that are highly uncertain, due to the lack of laboratory data and where new data may significantly change the calculated MIRs, were documented. Finally the quality of the documentation of the mechanism was assessed.

2. Evaluation of the Base Mechanism

The base mechanism as received from Dr. Carter on April 19, 1999 and updated on May 5 was evaluated. It consisted of 4 separate spreadsheets, “Species Listing”, “Reaction Listing”, “Base Mech Notes” and “Refs”. The mechanism notes are reprinted here as received from Dr. Carter..

Suggestions Made Regarding the “Species Listings”.

<u>Constant Species</u>
The units for the defaults of the Constant Species should be defined. The units of O_2, M and H_2O appear to be ppm while the unit for light appears to be a multiplier of unity.

HV, light, is listed under Constant Species and characterized as a Type “Con”. Although HV is not a chemical species it is not a constant in the atmosphere. It is suggested that HV be moved to its own category for clarity.

The assignments for the number of carbon atoms (nC), the number of reactive nitrogen atoms (nN) and the radical character (nR) for the constant species are correct for the constant species.

<u>Active Inorganic Species</u>
The active inorganic species list is relatively complete. It could be argued that CO should be listed here but since CO is a very important product of organic reactions it is also understandable that it is placed under Explicit Reactive Organic Product Species.

H_2 should be considered as either a constant species that reacts or as an active inorganic species because the reaction H_2 + HO is a sink for HO that occurs with a rate that is 30% that of the reaction CH_4 + HO for typical atmospheric conditions (Stockwell et al., 1997).

Dr. Carter may want to consider adding SO_2 as an active species. Although SO_2 is not greatly important for incremental reactivity applications the mechanism may be used for other applications, such as aerosol formation studies, where this chemistry can be important. The sulfate produced should be added as a Non-Reacting Species, see below.

It is not clear how “Act^*” differs from “Act”.

Although the name nitrogen pentoxide is commonly used it would be more correct to call it dinitrogen pentoxide.

The assignments for the number of carbon atoms (nC), the number of reactive nitrogen atoms (nN) and the radical character (nR) for the constant species are correct for the active inorganic species.

Active Radical Species and Operators

As mentioned above it is not clear how “Act* differs from “Act”.

The number of active radicals listed appear to be adequate for the base mechanism.

For complete clarity the R2O2. radical could be described as “Peroxy Radical Operator representing NO to NO_2 conversion without HO_2 formation”.

It seems surprising that the radical character (nR) of R2O2 is zero since it is a radical operator.

Other Steady State Radical Species

The category title should be changed because there are no other steady state radical species. It is suggested that the title be changed to Radical Species Treated as in Steady State.

The species treated as steady state are reasonable due to their short lifetime in the atmosphere.

The assignments for nC, nN and nR for the constant species are correct for the radical species treated as in steady state. The oxygen atoms might be labeled as bi-radicals.

PAN and PAN Analogues

The number and nature of the species included in this category are adequate for the base mechanism. The species are clearly named.

The nC given for PBZN is consistent with the BZCO-O2 radical.

The other nC, nN and nR for PAN and PAN Analoges are correct.

Explicit Reactive Organic Product Species

CO could be listed as an active inorganic species because most of CO comes from direct emissions and not the chemical reactions of organic species. However, it is an important product so its inclusion in this category is understandable.

The number and nature of the species included in this category are adequate for the base mechanism. The species are clearly named.

The nC, nN and nR for the explicit reactive organic product species are correct.

Lumped Reactive Organic Product Species

The number, nature and descriptions of the species included in this category are adequate for the base mechanism.

Is there data that suggests that the average carbon number of higher organic peroxides, ROOH, is really as high as 3? I would guess that it is closer to 2.

Non-Reacting Species

Although H2 should be treated as a constant it is not unreactive. It is a sink for HO radicals that should not be ignored.

If SO2 were to be included in the mechanism than sulfate should be included here.

Low Reactivity Compounds or Unknown Products Represented as Unreactive

Treatment of organic acids and methyl nitrate as unreactive is appropriate.

I would expect the stabilizated products from the Crigiee biradicals to be too reactive to be treated in this category. Would it be better to treat them similar to ketones?

Primary Organics Represented Explicitly

I can easily accept that CH4 belongs in this category but given the relative complexity of isoprene chemistry it is not accurate to place it in this category.

Following used in reports

Many of these definitions have been used by Dr. Carter previously and they are reasonable.

Biogenic Compounds in the EKMA Simulations

These are definitions that are reasonable.

Lumped species used to represent the Base ROG mixture in the EKMA model simulations.

These are definitions that are reasonable and within standard practice.

General comments on the Base Mechanism

Representation of Radical Species

Rapidly Reacting Radicals

The treatment of the decomposition of excited Crigiee biradicals is within the present state of knowledge. It is also reasonable to assume that the Crigiee biradicals react with water to produce organic acids. The reaction of Crigiee biradicals with SO_2 could be important only in rare plumes that are relatively dry with high concentrations of SO_2 and alkenes.

Explicitly Represented Organic Radicals

The revision of the mechanism to include representation of a few organic radical species as explicit represents a significant a improvement in the mechanism. Dr. Carter provides good justification for this treatment of methyl peroxy radicals, acyl peroxy radicals t-butoxy radicals, phenoxy radicals, nitro-phenoxy radicals and the formaldehyde + HO_2 intermediate.

There is much uncertainty in the fate of phenoxy radicals and nitro-phenoxy radicals. More research will be required to determine the fate of these radicals produced from aromatic oxidation.

Reactions of Common Products

Explicitly Represented and Lumped Molecule Products

Glyoxal (GLY).
The quantum yields of glyoxal were increased by a factor near 1.4 on the basis of fits to chamber data. These quantum yields are uncertain and Dr. Carter is correct to note that new direct measurements of glyoxal quantum yields as a function of wavelength are required to reduce this uncertainty.

Methyl Glyoxal (MGLY) and Other Higher α-dicarbonyl aldehydes.

Dr. Carter is correct in accepting the revised absorption cross sections of Moortgat for methyl glyoxal.

Phenol (PHEN) and Cresols (CRES).

More data is required for these compounds but given the available data Dr. Carter's treatment of these reactions is reasonable.

Lumped Parameter Products

Derivation of PROD2 and RNO3 Mechanisms.

From the discussion it is not clear why PROD2 which is derived from a set of model species with 7 carbon atoms is represented as having only 6 carbon atoms in the mechanism. This may be correct but the reason for this approach is not clear.

Uncharacterized Aromatic Ring Fragmentation Products

The use of DCB species to represent uncharacterized aromatic ring fragmentation products is a significant advance over the former AFGn treatment. More data will be required to better characterize this aspect of aromatic chemistry.

Unreactive Product Species

The discussion of unreactive product species is reasonable. Although the production of H_2 due to tropospheric reactions is insignificant, the effect of the background concentration of H_2 on HO levels is not. The rate of the HO reaction with H_2 is about 30% of its rate with CH_4. The discussion of H_2 should be revised accordingly.

SUGGESTIONS MADE REGARDING MECHANISM AND DOCUMENTATION NOTES.

Reaction 1

	Notes	
Phot Set= NO2	1,2	NO2 + HV = NO + O3P

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
2	Absorption cross sections and quantum yields from IUPAC recommendation (Atkinson et al, 1997a), except that quantum yields for wl > 410 nm are from NASA (1997), which are consistent with IUPAC (Atkinson et al, 1997a) values except they are more precise. Note that more recent IUPAC recommendations (Atkinson et al, 1997b) gives slightly different absorption cross sections based on data from a more recent study, but the differences are not significant.

Table of absorption cross sections and quantum yields is not yet defined. The recommendations for this reaction are consistent with current knowledge.

Reaction 2

k(300)	A	Ea	B	Notes	
5.91e-34	5.91e-34	0.00	-2.8	3	O3P + O2 + M = O3 + M

Notes

3	Rate constant expression derived from IUPAC (Atkinson et al, 1997b) recommendations for M = 20.9% O2 and 79.1% N2.

The reactants and products formed by Reaction 2 are consistent with current knowledge but the rate constant should be revised.

IUPAC DATA

k(300)	A	B	
5.6e-34	5.6e-34	-2.8	O3P + O2 + N2 = O3 + N2
6.0e-34	6.0e-34	-2.8	O3P + O2 + O2 = O3 + O2

Averaging the two A factors according to the abundances of oxygen and nitrogen.

0.791*5.6e-34 + 0.219*6.0e-34 = 5.74e-34

Recommended Revision to Reaction 2

k(300)	A	B	Notes	
5.74e-34	5.91e-34	-2.8	3	O3P + O2 + M = O3 + M

Reaction 3

k(300)	A	Ea	Notes	
8.34e-15	8.00e-12	4.09	4,5	O3P + O3 = #2 O2

Notes

4	Rate constant is IUPAC, Supplement VI (Atkinson et al, 1997b) and NASA (1997) recommendation.
5	This reaction is probably not important in air, but is included to increase range of applicability.

The reactants and products formed by Reaction 3 are consistent with current knowledge and the rate parameters are those recommended by IUPAC and NASA. The reaction is not important in the lower troposphere under most conditions. However is it a key reaction in the stratosphere and therefore is it not correct to state that it is not important in air.

Recommendation
Note 5 should be revised to read: “This reaction is probably not important in the troposphere, but is included to increase range of applicability.”

Reaction 4

k(300)	A	B	Notes	
1.00e-31	1.00e-31	-1.6	6,7,5	O3P + NO + M = NO2 + M

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
7	Recommended rate constant given for N2 is assumed to be applicable to air.
5	This reaction is probably not important in air, but is included to increase range of applicability.

The reactants and products formed by Reaction 4 are consistent with current knowledge and the rate parameters are those recommended by IUPAC. It should be noted that NASA (1997) treats this reaction as a recombination reaction with a rate parameter described by the Troe expression.

The reaction is not important in the lower troposphere under most conditions. However is it a key reaction in the stratosphere and therefore is it not correct to state that it is not important in air.

Recommendation
Modify Note 5 as suggested under Reaction 3.

Reaction 5

k(300)	A	Ea	Notes	
9.70e-12	6.50e-12	-0.24	4,5	O3P + NO2 = NO + O2

Notes

4	Rate constant is IUPAC, Supplement VI (Atkinson et al, 1997b) and NASA (1997) recommendation.
5	This reaction is probably not important in air, but is included to increase range of applicability.

The reactants and products formed by Reaction 5 are consistent with current knowledge and the rate parameters are those recommended by IUPAC and NASA.

The reaction is not important in the lower troposphere under most conditions. However is it a key reaction in the stratosphere and therefore is it not correct to state that it is not important in air. Recommendation: Modify Note 5 as suggested under Reaction 3.

Reaction 6

k(300)	**Falloff, F**	**Notes**	
1.79e-12	0.80	4,7,5	O3P + NO2 = NO3 + M
	A	**B**	
$\mathbf{k_o}$	9.00e-32	-2.0	
$\mathbf{k_\infty}$	2.20e-11	0.0	

Notes

4	Rate constant is IUPAC, Supplement VI (Atkinson et al, 1997b) and NASA (1997) recommendation.
7	Recommended rate constant given for N2 is assumed to be applicable to air.
5	This reaction is probably not important in air, but is included to increase range of applicability.

The reactants and products formed by Reaction 6 are consistent with current knowledge. The rate parameters for k_o and k_∞ are those recommended by IUPAC and NASA. However NASA recommends 0.6 for all recombination reactions and this leads to a difference in the K(300) that would be calculated from the IUPAC and NASA data. The IUPAC value is 1.79e-12 cm^3 s^{-1} while the NASA calculated value is 1.56e-12 cm^3 s^{-1}.

Recommendations
The differences between the final calculated rate parameters for this reaction between the NASA and IUPAC rate parameters should be noted in the footnotes. Modify Note 5 as suggested under Reaction 3.

Reaction 7
No reaction with that label.

Reaction 8

k(300)	**A**	**Ea**	**Notes**	
1.87e-14	1.80e-12	2.72	6	O3 + NO = NO2 + O2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

The reactants and products formed by Reaction 8 are consistent with current knowledge and the choice of rate parameters by Dr. Carter is acceptable. There is a small difference between the rate parameters recommended by NASA and IUPAC. The NASA recommended values are given below.

k(300)	A	Ea	
1.88e-14	2.00e-12	2.78	O3 + NO = NO2 + O2

The differing sets of rate parameters give almost the same values at 300 K although the A factors differ by 10%. No changes are recommended for this reaction.

Reaction 9

k(300)	A	Ea	B	Notes	
3.72e-17	1.40e-13	4.91		6	O3 + NO2 = O2 + NO3

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

The reactants and products formed by Reaction 9 are consistent with current knowledge and the choice of rate parameters by Dr. Carter is acceptable. Given that there is a change in the two IUPAC recommendations during 1997, and since they differ from NASA, Dr. Carter might want to make a brief note of the reasons for this in his documentation.

Reaction 10

k(300)	A	Ea	Notes	
2.60e-11	1.80e-11	-0.22	6	NO + NO3 = #2 NO2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

The reactants and products formed by Reaction 10 are consistent with current knowledge and the choice of rate parameters by Dr. Carter is acceptable. There is a small difference between the IUPAC and NASA recommendations.

Reaction 11

k(300)	A	Ea	Notes	
1.93e-38	3.30e-39	-1.05	6	NO + NO + O2 = #2 NO2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

The reactants and products formed by Reaction 11 are consistent with current knowledge and the choice of rate parameters by Dr. Carter is in agreement with NASA and IUPAC. It might be noted that this reaction is only important in plumes with very high NO concentrations. There have been no new data on this reaction since 1985.

Reaction 12

k(300)	**Falloff, F**	**Notes**	
1.53e-12	0.45	6,7	NO2 + NO3 = N2O5
	A	**B**	
k_o	2.80e-30	-3.5	
k_∞	2.00e-12	0.2	

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
7	Recommended rate constant given for N2 is assumed to be applicable to air.

N_2O_5 is in equilibrium with NO_3 and NO_2; the reactants and products formed by Reaction 12 are consistent with current knowledge. The rate parameters for k_o and k_∞ are those recommended by IUPAC. Given that there is a change in the two IUPAC recommendations during 1997, and since they differ from NASA, Dr. Carter might want to make a brief note of the reasons for this in his documentation.

Reaction 13

k(300)	**Falloff, F**	**Ea**	**Notes**	
6.74e-2	0.45		6,7	N2O5 = NO2 + NO3
	A		**B**	
k_o	1.00e-3	21.86	-3.5	
k_∞	9.70e+14	22.02	0.1	

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
7	Recommended rate constant given for N2 is assumed to be applicable to air.

N_2O_5 is in equilibrium with NO_3 and NO_2; the reactants and products formed by Reaction 13 are consistent with current knowledge. To understand the form of the rate constant it is necessary to refer to the IUPAC review. It is recommended that formulas to calculate all types of rate constants, Arrhenius, recombination, etc. be given before the mechanism table. There is some difference between the two IUPAC recommendations, especially for the falloff, F_c, that might be noted in the documentation.

Reaction 14

k(300)	A	Ea	Notes	
2.60e-22	2.60e-22	---	8	N2O5 + H2O = #2 HNO3

Notes

8	The data of Mentel et al (1996) indicate that the reaction occurs through pathways which are first order and second order in H2O, where the latter is presumed to be surface-dependent. We assume that the process which is first order in H2O represents a gas-phase reaction, and use the rate expression of Mentel et al (1996) for this process. Note that the IUPAC (Atkinson et al, 1997b) recommendation that the gas-phase rate constant is less than 2 x 10^{-21} cm^{-3} $molec^{-1}$ s^{-1}.

The products and reactants are reasonable but the extent of the occurrence of Reaction 14 as a gas-phase reaction has been a subject of long term debate. The entropy of the supposed transition state is a significant barrier to the occurrence of this reaction. The choice of the Mentel et al (1996) data is very reasonable, especially considering that it is lower than the upper limit of the NASA evaluation.

Reaction 15

k(300)	Notes	
Slow	9	N2O5 + HV = NO3 + NO + O3P

Notes

9	Photolysis of N2O5 is assumed to be negligible compared to decomposition under atmospheric conditions.

Dr. Carter's conclusion regarding Reaction 15 appears to be correct since the NASA evaluation reports that the quantum yield for O^3P is less than 0.1 at 290 nm. In any case there is little N_2O_5 in the polluted troposphere due to the fast photolysis of NO_3. However, the footnote should read: "negligible compared to".

Reaction 16

k(300)	Notes	
Slow	9	N2O5 + HV = NO3 + NO2

Notes

9	Photolysis of N2O5 is assumed to be negligible compare to decomposition under atmospheric conditions.

It is reasonable to exclude Reaction 16 from mechanisms for the lower troposphere due to the low concentrations of N_2O_5 in the polluted troposphere due to the fast photolysis of NO_3. The reaction should also be slow because according to the NASA review the quantum yield for the formation of NO3 is unity at 289 nm but the absorption cross sections are very low at wavelengths above 240 nm. However, the footnote should read: “negligible compared to”.

Reaction 17

k(300)	A	Ea	Notes	
6.75e-16	4.50e-14	2.50	10	NO2 + NO3 = NO + NO2 + O2

Notes

10	The NASA (1997) evaluation states that the existence of this channel has not been firmly established, but results of a number of studies indicate it may occur. Rate constant expression used is that NASA (1997) states gives best fits to the data. Uncertainty is at least a factor of 2. This reaction was not discussed in the recent IUPAC evaluations (Atkinson et al, 1997a,b).

Dr. Carter is correct to write that the occurrence of Reaction 17 and its rate parameters are highly uncertain. The reaction is necessary to explain the results of five laboratory investigations and the values used are consistent with the five experiments according to the NASA evaluations.

Reaction 18

	Notes	
Phot Set= NO3NO	1,11,12	NO3 + HV = NO + O2

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
11	Absorption cross sections from IUPAC (Atkinson et al, 1997a). Values recommended by more recent IUPAC evaluation (Atkinson et al, 1997b) appear to be the same for 298K, though different at lower temperature. Temperature dependence ignored.
12	IUPAC (1997b) and NASA (1997) give no useable recommendations for quantum yields except to recommend that qy(NO2+O)=1 for wl <= 583. Quantum yields of Magnotta and Johnsom (1980), scaled down by a factor of 1.5 to give unit maximum quantum yields, as incorporated in mechanism of Carter (1990) were retained in this mechanism. The calculated rate constant for solar overhead sun is consistent with the recommendations of Magnotta and Johnson (1980), and reasonably consistent with the IUPAC (1997a) recommendation.

The reactants and products of Reaction 18 are in accord with the recommendations. It is well known that the NO_3 absorption cross sections are temperature dependent, therefore it would be desirable if the error made in ignoring the temperature dependence was quantified in the footnote. There may be more data in Wayne et al. (1991) that should be considered.

Reaction 19

	Notes	
Phot Set= NO3NO2	1,11,12	NO3 + HV = NO2 + O3P

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
11	Absorption cross sections from IUPAC (Atkinson et al, 1997a). Values recommended by more recent IUPAC evaluation (Atkinson et al, 1997b) appear to be the same for 298K, though different at lower temperature. Temperature dependence ignored.
12	IUPAC (1997b) and NASA (1997) give no useable recommendations for quantum yields except to recommend that qy(NO2+O)=1 for wl <= 583. Quantum yields of Magnotta and Johnsom (1980), scaled down by a factor of 1.5 to give unit maximum quantum yields, as incorporated in mechanism of Carter (1990) were retained in this mechanism. The calculated rate constant for solar overhead sun is consistent with the recommendations of Magnotta and Johnson (1980), and reasonably consistent with the IUPAC (1997a) recommendation.

The reactants and products of Reaction 19 are in accord with the recommendations. It is well known that the NO_3 absorption cross sections are temperature dependent, therefore it would be desirable if the error made in ignoring the temperature dependence was quantified in the footnote. There may be more data in Wayne et al. (1991) that should be considered.

Reaction 20

	Notes	
Phot Set= O3O3P	1,14,15	O3 + HV = O3P + O2

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
13	Absorption cross sections from IUPAC (Atkinson et al, 1997b). Data are for T=273 K. Temperature dependences for cross section (NASA, 1997) are ignored.
14	Quantum yields for O1D are those tabulated by IUPAC (Atkinson et al, 1997b), which are significantly higher than previous recommendations at wl > 310 nm. Quantum yields for O3P based on assuming total quantum yield of unity, though this was not adequately discussed in the evaluations.

The reactants and products of Reaction 20 are consistent with current knowledge. The increase in the quantum yields is also consistent with the most recent recommendations (see Reaction 21 below).

Reaction 21

	Notes	
Phot Set= O3O1D	1,14,15	O3 + HV = O*1D2 + O2

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
14	Absorption cross sections from IUPAC (Atkinson et al, 1997b). Data are for T=273 K. Temperature dependences for cross section (NASA, 1997) are ignored.
15	Quantum yields for O1D are those tabulated by IUPAC (Atkinson et al, 1997b), which are significantly higher than previous recommendations at wl > 310 nm. Quantum yields for O3P based on assuming total quantum yield of unity, though this was not adequately discussed in the evaluations.

The reactants and products of Reaction 21 are consistent with current knowledge. It seems that a higher base temperature could be chosen for the cross sections this may be important because recent data on the temperature dependence of ozone photolysis (Talukdar et al., 1998) leads to greater $O(^1D)$ formation rates. This could be a problem during the fall and spring because this may lead to more rapid photochemical loss of ozone and greater rates of HO formation.

Reaction 22

k(300)	A	Ea	Notes	
2.20e-10	2.20e-10	---	4	O*1D2 + H2O = #2 HO.

Notes

4	Rate constant is IUPAC, Supplement VI (Atkinson et al, 1997b) and NASA (1997) recommendation.

The reactants, products and rate parameters of Reaction 22 are consistent with current knowledge.

Reaction 23

k(300)	A	Ea	Notes	
2.87e-11	2.09e-11	-0.19	15	O*1D2 + M = O3P + M

Notes

14	Calculated using IUPAC (Atkinson et al, 1997b) recommended rate constants for reaction with O2 and N2, assuming 20.9% O2 and 79.1% N2. Temperature dependence optimized to fit rate constants calculated for T= 270, 300, and 330K.

The reactants, products and rate parameters of Reaction 23 are consistent with current knowledge. It is not clear why it is necessary to fit the rate constant. It would be somewhat more accurate to calculate the rate parameter as:

$$k = 1.80e\text{-}11 * \exp(107/T) * 0.791*[M] + 3.20e\text{-}11 * \exp(67/T) * 0.209*[M]$$

Reaction 24

k(300)	Falloff, F	Notes	
7.31e-12	0.60	16	HO. + NO = HONO
	A	B	
k_o	7.00e-31	-2.6	
k_∞	3.60e-11	-0.1	

Notes

16	Falloff expression recommended by NASA (1997) used because it gives rate constant for 1 atm N2 which is consistent with measurement near those conditions. IUPAC (Atkinson et al, 1997a,b) recommendations are not used because k (1 atm N2) are not consistent with these data, being based on high pressure data in He. This is consistent with current recommendation of Atkinson (private communication, 1997).

The reactants, products and rate parameters of Reaction 24 are consistent with current knowledge. Probably the increase in the rate parameter for the reaction of HO with NO will have little effect on the mechanism's predictions because photolysis will convert all HONO formed through this reaction back to NO and HO.

The signs of the B parameters may be confusing to some readers of the NASA evaluation because the NASA values are given as opposite in sign. It is very important that Dr. Carter provide a table with the equations for all types of rate parameters.

Reaction 25

	Notes	
Phot Set= HONO-NO	1,17,18	HONO + HV = HO. + NO

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
17	The cross sections from Stockwell and Calvert (1978), used in the previous version of the mechanism, are retained because they are higher resolution than the averaged data recommended by IUPAC (1997b), and the areas under the spectra appear to be consistent.
18	Quantum yields are those recommended by IUPAC (Atkinson et al, 1997b).

The IUPAC and the NASA evaluations favor the HONO cross sections given by Bongartz et al. (1991) over the values given by Stockwell and Calvert (1978). Although the IUPAC evaluations report the Bongartz et al. (1991) cross sections with a 5 nm resolution, the NASA evaluation reports them with the same resolution reported by Stockwell and Calvert (1978), 1 nm resolution. The cross sections of Bongartz et al. (1991) should be used because there are significant differences between the values of Stockwell and Calvert and Bongartz et al. (1991); the cross section reported by Stockwell and Calvert are 20% lower than the values of Bongartz et al. at 354 nm.

Reaction 26

	Notes	
Phot Set= HONO-NO2	1,17,18	HONO + HV = HO2. + NO2

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
17	The cross sections from Stockwell and Calvert (1978), used in the previous version of the mechanism, are retained because they are higher resolution than the averaged data recommended by IUPAC (1997b), and the areas under the spectra appear to be consistent.
18	Quantum yields are those recommended by IUPAC (Atkinson et al, 1997b).

The NASA evaluations with the cross sections of Bongartz et al. (1991) should be used rather than the values of Stockwell and Calvert as discussed for Reaction 26. The inclusion of the formation of H atom (as HO_2 in the troposphere) and NO_2 from HONO photolysis is reasonable. This might be expected to improve the model's predictions under high NO_x conditions

Reaction 27

k(300)	A	Ea	Notes	
6.42e-12	2.70e-12	-0.52	6	HO. + HONO = H2O + NO2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

The reactants, products and rate parameters of Reaction 27 are consistent with current knowledge.

Reaction 28

k(300)	**Falloff, F**	**Notes**	
8.81e-12	0.60	19	HO. + NO2 = HNO3
	A	**B**	
$\mathbf{k_o}$	2.43e-30	-3.1	
$\mathbf{k_\infty}$	1.67e-11	-2.1	

Notes

19	NASA (1997) and IUPAC (Atkinson et al, 1997a,b) give significantly different recommendations for rate parameters for this important reaction. The falloff expression used here is based on a re-evaluation of the data by Golden (Personal communication, 1998), and is expected to be the recommendation in the next NASA evaluation. This is essentially the same as the NASA (1997) recommendation except for the temperature dependence, which Golden says was due to improper uncertainty weighting. The data with "weak colliders" (i.e., bath gases other than SF6 or CF4) appear to be well fit by this parameterization, including the data of Donahue et al (1997). The data of Forster et al (1995), which are the basis for the high 1997 IUPAC recommendation, are not used because they may be due to a HOONO-forming channel becoming important at high pressure.

The new rate parameters are about 20% lower than used in many current mechanisms. Dr. Carter's choice of rate parameters appears to be correct based on the current re-evaluations of Dr. Golden that this reviewer has also seen. The 20% decrease in the rate parameter for the reaction of HO with NO_2 is important. It is disturbing that such a "well known reaction" has such these uncertainties in its rate parameter and in the pressure dependence of the rate parameter.

Reaction 29

k(300)	**A**	**Ea**	**Notes**	
2.00e-11	2.00e-11	---	6,20	HO. + NO3 = HO2. + NO2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
20	No recommendation is given concerning the temperature dependence of this rate constant, which is assumed to be small.

The reactants, products and rate parameters of Reaction 291 are consistent with current knowledge.

Reaction 30

k(300)	A	Ea	Notes	
1.44e-13	5.45e-15	-1.95	21,22	HO. + HNO3 = H2O + NO3

Notes

21	The rate parameters were derived to fit the rate constants calculated using the NASA (1997) recommended expression for T 270 - 330 K range and 1 atm. total pressure.
22	This rate constant is strictly valid for 1 atm air only, but the error introduced by neglecting the pressure dependence of this reaction is expected to be small.

Is it necessary to fit the real rate expression for Reaction 30? The error in an Arrhenius expression for the rate parameter derived by assuming 1 atmosphere pressure and then fitting the much more complicated rate constant expression for Reaction 30 may be small but there is little advantage in doing this. It is not difficult to program the full rate expression into air quality models. It is also probable that the mechanism will be used in regional models with upper layers up to 10 km or higher and it that case there may be significant differences.

Reaction 31

	Notes	
Phot Set= HNO3	1,23	HNO3 + HV = HO. + NO2

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
23	Absorption cross-sections from IUPAC (Atkinson et al, 1997b). Recommend quantum yield for the OH + NO2 pathway is "close to unity" for wl > 260 nm, though other pathways become important at lower wavelengths.

The sum of the quantum yield for the HO + NO_2 producing channel and the quantum yield for the HO + NO + O producing channel is greater than 0.97 for wavelengths greater than 260 nm. But the quantum yield for the HO + NO + O producing channel is only 0.13 at 222 nm and that would be expected to decrease at greater wavelengths. Therefore the choice of quantum yields and products for Reaction 31 appears to be correct.

Reaction 32A

k(300)	A	Ea	Notes	
1.30e-13	1.30e-13	---	24	HO. + CO = HO2. + CO2

Notes

24	The rate constants for the OH + CO reactions are based on expression given by IUPAC (Atkinson et al, 1997a). NASA (1997) gives a similar expression, but without temperature dependence.

The reactants and products are consistent with current knowledge. This value is consistent with the NASA recommendation but since the IUPAC evaluation provides a rate parameter with a temperature and pressure dependence it is suggested that the full expression be used.

Reaction 32B

k(300)	A	Ea	Notes	
3.19e-33	3.19e-33	---	24	HO. + CO + M = HO2. + CO2 + M

Notes

24	The rate constants for the OH + CO reactions are based on expression given by IUPAC (Atkinson et al, 1997a). NASA (1997) gives a similar expression, but without temperature dependence.

The reactants and products are consistent with current knowledge. Reaction 33 could be combined with Reaction 32A by making the rate constant for Reaction 32A pressure dependent. This value is consistent with the NASA recommendation but since the IUPAC evaluation provides a rate parameter with a temperature and pressure dependence it is suggested that the full expression be used.

Reaction 33

k(300)	A	Ea	Notes	
6.78e-14	1.90e-12	1.99	6	HO. + O3 = HO2. + O2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

The reactants, products and rate parameters for Reaction 33 are consistent with current knowledge.

Reaction 34

k(300)	A	Ea	Notes	
8.36e-12	3.40e-12	-0.54	6	HO2. + NO = HO. + NO2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

The reactants, products and rate parameters are consistent with current knowledge. It might be noted that the A-factor has been decreased by about 10% from the IUPAC Supplement V evaluation.

Reaction 35

k(300)	**Falloff, F**	**Notes**	
1.36e-12	0.60	6	HO2. + NO2 = HNO4
k_o	1.80e-31	-3.2	
k_∞	4.70e-12	0.0	

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

HO_2NO_2 is in equilibrium with HO_2 and NO_2; the reactants and products formed by Reaction 35 are consistent with current knowledge. To understand the form of the rate constant it is necessary to refer to the IUPAC review. It is recommended that formulas to calculate all types of rate constants, Arrhenius, recombination, etc. be given before the mechanism table.

Reaction 36

k(300)	**Falloff, F**	**Ea**	**Notes**	
9.61e-2	0.50		6	HNO4 = HO2. + NO2
	A		**B**	
k_o	4.10e-5	21.16	0.0	
k_∞	5.70e+15	22.20	0.0	

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

HO_2NO_2 is in equilibrium with HO_2 and NO_2; the reactants and products formed by Reaction 36 are consistent with current knowledge. To understand the form of the rate constant it is necessary to refer to the IUPAC review. It is recommended that formulas to calculate all types of rate constants, Arrhenius, recombination, etc. be given before the mechanism table. There is some difference between the IUPAC Supplement V evaluation that might be noted in the documentation.

Reaction 37

	Notes	
Phot Set= HO2NO2	1,25	HNO4 + HV = #.61 {HO2. + NO2} + #.39 {HO. + NO3}

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
25	Absorption cross sections and quantum yields from IUPAC (Atkinson et al, 1997b). Quantum yields are uncertain and based on data for a single wavelength only.

The reactants, products, quantum yields and cross sections for Reaction 37 are consistent with current knowledge.

Reaction 38

k(300)	A	Ea	Notes	
4.98e-12	1.50e-12	-0.72	6	HNO4 + HO. = H2O + NO2 + O2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

The reactants, products and rate parameters for Reaction 38 are consistent with current knowledge.

Reaction 39

k(300)	A	Ea	Notes	
1.89e-15	1.40e-14	1.19	6	HO2. + O3 = HO. + #2 O2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

The reactants, products and rate parameters for Reaction 39 are consistent with current knowledge.

Reaction 40A

k(300)	A	Ea	Notes	
1.63e-12	2.20e-13	-1.19	26	HO2. + HO2. = HO2H + O2

Notes

26	Reactions and rate constants used for the HO2 + HO2 and HO2 + HO2 + H2O system based on the data of Kircher and Sander (1984) as discussed in the IUPAC (Atkinson et al, 1997b) evaluation.

The reactants, products and rate parameters for Reaction 40A are consistent with current knowledge.

Reaction 40B

k(300)	A	Ea	Notes	
3.48e-30	3.08e-34	-5.56	26	HO2. + HO2. + H2O = HO2H + O2 + H2O

Notes

26	Reactions and rate constants used for the HO2 + HO2 and HO2 + HO2 + H2O system based on the data of Kircher and Sander (1984) as discussed in the IUPAC (Atkinson et al, 1997b) evaluation.

The reactants, products and rate parameters for Reaction 40B are consistent with current knowledge.

Reaction 40C

k(300)	A	Ea	Notes	
4.85e-32	1.85e-33	-1.95	26	HO2. + HO2. + M = HO2H + O2 + M

Notes

26	Reactions and rate constants used for the HO2 + HO2 and HO2 + HO2 + H2O system based on the data of Kircher and Sander (1984) as discussed in the IUPAC (Atkinson et al, 1997b) evaluation.

The reactants, products and rate parameters for Reaction 40C are consistent with current knowledge.

Reaction 40D

k(300)	A	Ea	Notes	
1.04e-49	2.59e-54	-6.32	26	HO2. + HO2. + M + H2O = HO2H + O2 + M + H2O

Notes

26	Reactions and rate constants used for the HO2 + HO2 and HO2 + HO2 + H2O system based on the data of Kircher and Sander (1984) as discussed in the IUPAC (Atkinson et al, 1997b) evaluation.

The reactants, products and rate parameters for Reaction 40D are consistent with current knowledge.

Reaction 41

k(300)	A	Ea	Notes	
4.00e-12	4.00e-12	---	27	NO3 + HO2. = HO. + NO2 + O2

Notes

27	Rate constant recommended by IUPAC (Atkinson et al, 1997b). Mechanism based on data of Mellouki et al (1993) as discussed by IUPAC (Atkinson et al, 1997b).

Although the mechanism is uncertain there probably is a significant radical termination and nitric acid production through the reaction:

$$NO_3 + HO_2 = HNO_3 + O_2$$

this channel should not be ignored. The studies reported in the review by Le Bras (1997) find that the rate of the nitric acid channel is between 20 and 43% of the total reaction rate of NO_3 with HO_2. In fact there is one study by Hjorth that found the reaction channel represented by reaction 41 to be insignificant (Le Bras, 1997). Although that study is probably not correct, it still points to the possible importance of the HNO_3 producing channel.

Reaction 42

k(300)	A	Ea	Notes	
2.41e-16	8.50e-13	4.87	28	NO3 + NO3 = #2 NO2 + O2

Notes

29	Rate expression from NASA (1994) evaluation. More recent evaluations neglect this reaction, though it may be non-negligible under some nighttime conditions (Stockwell et al, 1997).

The reactants, products and rate parameters for Reaction 42 are consistent with current knowledge.

Reaction 43

	Notes	
Phot Set= H2O2	1,29	HO2H + HV = #2 HO.

Notes

1	See Table (number to be determined by Carter) for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
29	Absorption cross sections recommended by IUPAC (Atkinson et al, 1997a,b) used. Quantum yield assumed to be unity.

The reactants, products, quantum yields and cross sections for Reaction 43 are consistent with current knowledge.

Reaction 44

k(300)	**A**	**Ea**	**Notes**	
1.70e-12	2.90e-12	0.32	6	HO2H + HO. = HO2. + H2O

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

The reactants, products and rate parameters for Reaction 44 are consistent with current knowledge.

Reaction 45

k(300)	**A**	**Ea**	**Notes**	
1.10e-10	4.80e-11	-0.50	6	HO. + HO2. = H2O + O2

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.

The reactants, products and rate parameters for Reaction 45 are consistent with current knowledge.

Reaction S2OH

K(300)	**Falloff, F**	**Notes**	
4.00e-31	0.45	6,30	HO. + SO2 = HO2. + SULF
	A	**B**	
k_o	2.00e-12	0.0	
k_∞	4.00e-31	-3.3	

Notes

6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
30	The initially formed HOSO2 is assumed to react primarily with O2, forming HO2 and SO3. The SO3 is assumed to be converted into sulfates, which are represented by the SULF model species.

The reactants, products and rate parameters for Reaction S2OH are consistent with current knowledge. It was first shown by Stockwell and Calvert (1983) that HOSO$_2$ reacts primarily with O$_2$, forming HO$_2$ and SO$_3$. That reference should be cited in the text.

Methyl Peroxy and Methoxy Reactions

Reaction MER1

k(300)	A	Ea	Notes	
7.24e-12	2.80e-12	-0.57	31,32	C-O2. + NO = NO2 + HCHO + HO2.

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
32	The reaction of NO2 is ignored because it is rapidly reversed by the decomposition of the peroxynitrate, resulting in no net reaction. Calculations not neglecting peroxynitrate formation give essentially the same results. However, this may not be valid in low temperature simulations.

The reactants, products and rate parameters for Reaction MER1 are consistent with current knowledge.

Reaction MER3

k(300)	A	Ea	Notes	
1.30e-12	1.30e-12	---	31	C-O2. + NO3 = HCHO + HO2. + NO2

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

The reactants, products and rate parameters for Reaction MER4 are consistent with current knowledge.

Reaction MER4

k(300)	A	Ea	Notes	
5.12e-12	3.80e-13	-1.55	31	C-O2. + HO2. = COOH + O2

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

The reactants, products and rate parameters for Reaction MER4 are consistent with current knowledge.

Reaction MER5

k(300)	A	Ea	Notes	
2.61e-13	2.45e-14	-1.41	33	C-O2. + C-O2. = MEOH + HCHO + O2

Notes

33	Total rate constant and rate constant for methoxy radical formation from IUPAC (Atkinson et al, 1997a, 1999) recommendation. Temperature dependence for rate constant for methanol + HCHO formation derived to be consistent with these.

The total of the overall rate parameter for Reactions MER5 and MER6 is correct. There is some uncertainty in the temperature dependence of the ratio of the rate parameters for Reactions MER5 and MER6 and this affects the derivation of the individual rate parameters for the two reactions. But the fitted rate constant for Reaction MER5 yields a rate constant that is about 6% greater than the value calculated from the simple difference between the IUPAC recommended values for the total rate parameter (MER5 + MER6) and the recommended value for the HCHO + HO_2 forming reaction.

Reaction MER6

k(300)	A	Ea	Notes	
1.08e-13	5.90e-13	1.01	33	C-O2. + C-O2. = #2 {HCHO + HO2.}

Notes

33	Total rate constant and rate constant for methoxy radical formation from IUPAC (Atkinson et al, 1997a, 1999) recommendation. Temperature dependence for rate constant for methanol + HCHO formation derived to be consistent with these.

The rate constant for this channel of the C-O2. + C-O2. is consistent with current knowledge.

Reactions of Peroxy Radical Operators with NO

Reaction RRNO

k(300)	A	Ea	Notes	
8.96E-12	2.70E-12	-0.72	34,35, 32	RO2-R. + NO = NO2 + HO2.

Notes

34	The RO2-R. operator represents the effects of peroxy radicals which react with NO to form NO2 and HO2, and also the effects of peroxy radical reactions on other species. Except as indicated, the organic products from this peroxy radical are not represented.
35	Rate constant recommended by Atkinson (1997a) for general peroxy radicals.
32	The reaction of NO2 is ignored because it is rapidly reversed by the decomposition of the peroxynitrate, resulting in no net reaction. Calculations not neglecting peroxynitrate formation give essentially the same results. However, this may not be valid in low temperature simulations.

This treatment of the generalized peroxy radical, RO2-R, to react with NO to produce NO_2 and an HO_2 is reasonable. The rate constant is consistent with the cited evaluation. The neglect of the formation of RO2NO2 is reasonable because these compounds are believed to be unimportant at most tropospheric temperatures.

Reaction R2NO

k(300)	A	Ea	Notes	
Same as Reaction RRNO			42,43	R2O2. + NO = NO2

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

The rate constant is discussed under Reaction RRNO. This treatment of the generalized peroxy radical, R2NO, to produce only NO_2 is a reasonable compliment to Reaction RRNO.

Reaction RNNO

k(300)	A	Ea	Notes	
Same as Reaction RRNO			42,44	RO2-N. + NO = RNO3

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.

The rate constant is discussed under Reaction RRNO. This treatment of the generalized peroxy radical, RNNO, to produce higher organic nitrates is a reasonable compliment to Reaction RRNO because a fraction of RO_2 radicals react to produce organic nitrates.

Reactions of Peroxy Radical Operators with HO2

Reaction RRH2

k(300)	A	Ea	Notes	
1.45E-11	1.90E-13	-2.58	35,36	RO2-R. + HO2. = ROOH + O2 + #-3 XC

Notes

35	Rate constant recommended by Atkinson (1997a) for general peroxy radicals.
36	The organic products from the HO2 reaction are represented by the lumped higher hydroperoxide species. Negative "lost carbons" are added because this is a zero-carbon operator.

This treatment of the generalized peroxy radical, RO2-R, to react with HO$_2$ to produce a generalized organic peroxide is reasonable. The rate constant is consistent with the cited evaluation. The use of negative carbon atoms for carbon balance is reasonable but may give some numerical chemistry solvers problems.

Reaction R2H2

k(300)	A	Ea	Notes	
Same as Reaction R2H2			42,43	R2O2. + HO2. = HO2.

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

This treatment of the generalized peroxy radical, R2O2. to react with HO$_2$ to consume R2O2 is reasonable. The rate constant is discussed under Reaction RRH2.

Reaction RNH2

k(300)	A	Ea	Notes	
Same as Reaction R2H2			42,44, 45	RO2-N. + HO2. = ROOH + #3 XC

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.
45	The organic products from the HO2 reaction are represented by the lumped higher hydroperoxide species. "Lost carbons" are added because this is a five-carbon operator.

This treatment of the generalized peroxy radical, RO2-R, to react with HO$_2$ to produce a generalized organic peroxide is reasonable. The rate constant is discussed under Reaction RRH2. The addition of extra carbon atoms for carbon balance is probably OK.

Reactions of Peroxy Radical Operators with NO3

Reaction RRN3

k(300)	A	Ea	Notes	
2.30E-12	2.30E-12	---	37,38	RO2-R. + NO3 = NO2 + O2 + HO2.

Notes

37	Rate constant based on that recommenced by IUPAC (Atkinson et al, 1999) for ethyl peroxy + NO3. Formation of alkoxy + NO2 + O2 stated to occur >85% of the time.
38	The reaction is assumed to form the corresponding alkoxy radical. The HO2 represents the radicals regenerated by the alkoxy radical.

This treatment of the generalized peroxy radical, RO2-R, to react with NO_3 to produce NO_2 and a ‘massless’ RO that reacts with O_2 to produce HO_2 is reasonable. The rate constant is consistent with current knowledge.

Reaction R2N3

k(300)	A	Ea	Notes	
Same Reaction as RRN3			42,43	R2O2. + NO3 = NO2

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

This treatment of the generalized peroxy radical, R2O2., to react with NO_3 to produce NO_2 and a ‘massless’ RO that reacts with O_2 to produce HO_2 is reasonable. The rate constant is discussed under Reaction RRN3.

Reaction RNN3

k(300)	A	Ea	Notes	
Same Reaction as RRN3			42,44, 47	RO2-N. + NO3 = NO2 + O2 + HO2. + MEK + #2 XC

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.
47	This reaction is assumed to form the corresponding alkoxy radical, which is assumed to react products represented by MEK + HO2.

This treatment of the generalized peroxy radical, RRN3. appears to be reasonable. The rate constant is discussed under Reaction RRN3.

Reactions of Peroxy Radical Operators with CH3O2

Reaction RRME

k(300)	A	Ea	Notes	
2.00e-13	2.00e-13	---	39,40	RO2-R. + C-O2. = HO2. + #.75 HCHO + #.25 MEOH

Notes

39	Based on rate constant for methyl peroxy + ethyl peroxy rate given by Atkinson (1997a). This is near the middle of the range of rate constants given for other methyl peroxy + higher alkyl peroxy radical reactions given by Atkinson (1997a) or Atkinson et al (1997a).
40	Approximately half of the peroxy + peroxy reaction is assumed to form two O2 + alkoxy radicals. The HO2 represents the radicals regenerated in the fraction of this peroxy radical which reacts in this way.

The rate constant is consistent with the evaluation. The 0.25 yield of MEOH (CH_3OH) is consistent with current knowledge of the rate of the H-atom transfer reaction; this assumption should be added to the footnote.

Reaction R2ME

k(300)	A	Ea	Notes	
Same as Reaction RRME			42,43	R2O2. + C-O2. = C-O2.

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

This treatment of the R2O2. + C-O2. reaction is consistent with the other R2O2. reactions. The rate constant is discussed under Reaction RRME.

Reaction RNME

k(300)	A	Ea	Notes	
Same as Reaction RRME			42,44, 46	RO2-N. + C-O2. = HO2. + #.25 MEOH + #.5 {MEK + PROD2} + #.75 HCHO + XC

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.
46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The MEK + HO2. represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.

The rate constant is discussed under Reaction RRME. The 0.25 yield of MEOH (CH_3OH) is consistent with current knowledge of the rate of the H-atom transfer reaction; this assumption should be added to the footnote.

Reactions of Peroxy Radical Operator Cross Reactions

Reaction RRR2

k(300)	A	Ea	Notes	
3.00E-14	3.00E-14	---	41,40	RO2-R. + RO2-R. = HO2.

Notes

41	The rate constants for peroxy + peroxy radical reactions can vary by orders of magnitude depending on the type of radical (e.g., Atkinson, 1997), so the value used here must be approximate. Value used is based roughly on range of rate constants for secondary peroxy radicals as given by Atkinson (1997a).
40	Approximately half of the peroxy + peroxy reaction is assumed to form two O2 + alkoxy radicals. The HO2 represents the radicals regenerated in the fraction of this peroxy radical which reacts in this way.

The rate constant may be valid but the rational seems weak. Atkinson recommends a rate constant of 5E-15 cm^3 $molecule^{-1}$ s^{-1} for general secondary RO_2 + secondary RO_2 while for the rate parameter for the reaction of general primary is recommended to be 2.5e-13 cm^3 $molecule^{-1}$ s^{-1}. The geometric average of the primary and secondary rate parameters is 3.5E-14 and that may be a bit better to use.

Reaction R2RR

k(300)	A	Ea	Notes	
Same as Reaction RRR2			42,43, 40	R2O2. + RO2-R. = RO2-R.

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.
40	Approximately half of the peroxy + peroxy reaction is assumed to form two O2 + alkoxy radicals. The HO2 represents the radicals regenerated in the fraction of this peroxy radical which reacts in this way.

The rate parameter is discussed under Reaction RRR2. The treatment of this cross reaction is reasonable because its purpose is to consume R2O2. by RO2-R.

Reaction R2R3

k(300)	A	Ea	Notes	
Same as Reaction RRR2			42,43	R2O2. + R2O2. =

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

The rate parameter is discussed under Reaction RRR2. The treatment of this cross reaction is reasonable because its purpose is to consume R2O2. by R2O2.

Reaction RNRR

k(300)	A	Ea	Notes	
Same as Reaction RRR2			42,44, 46	RO2-N. + RO2-R. = HO2. + #.5 {MEK + PROD2} + O2 + XC

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.
46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The MEK + HO2. represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.

The rate parameter is discussed under Reaction RRR2. The treatment of this cross reaction is consistent with the treatment in previous reactions of RO2-N. and RO2-R.

Reaction RNR2

k(300)	A	Ea	Notes	
Same as Reaction RRR2			42,43	RO2-N. + R2O2. = RO2-N.

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

The rate parameter is discussed under Reaction RRR2. The treatment of this cross reaction is consistent with the treatment in previous reactions of RO2-N. and R2O2.

Reaction RNRN

k(300)	A	Ea	Notes	
Same as Reaction RRR2			42,44, 46	RO2-N. + RO2-N. = MEK + HO2. + PROD2 + O2 + #2 XC

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.
46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The MEK + HO2. represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.

The rate parameter is discussed under Reaction RRR2. The treatment of this cross reaction is consistent with the treatment in previous reactions of RO2-N.

Reactions of Acyl Peroxy Radicals, PAN, and PAN Analogues

Reaction APN2

K(300)	Falloff, F	Notes	
1.04E-11	0.30	48	CCO-O2. + NO2 = PAN
	A	**B**	
$\mathbf{k_o}$	2.70E-28	-7.1	
$\mathbf{k_\infty}$	1.20E-11	-0.9	

Notes

48	Falloff expression recommended by IUPAC (Atkinson et al, 1997a, 1999), based on data of Bridier et al (1991).

The reactants, products and rate parameters for Reaction APN2 are consistent with current knowledge. To avoid confusion the rate expression should be given in a separate table.

Reaction DPAN

k(300)	Falloff, F	Ea	Notes	
7.04E-04	0.30		49	PAN = CCO-O2. + NO2
	A		**B**	
k_o	4.90E-03	24.05	0	
k_∞	4.00E+16	27.03	0	

Notes

49	Falloff expression recommended by IUPAC (Atkinson et al, 1992), based on data of Bridier et al (1991). Note: NASA (1997) also recommends using Bridier et al (1991) data, but gives a revised expression which gives a different k at 298K. Based on new data on PAN decomposition which give a factor of ~2 lower rate 298K rate constants, IUPAC (1997a, 1999) recommends a high pressure rate constant expression of 5.4x1016 exp(-13830/T), derived by averaging the data. We are staying with the earlier IUPAC Recommendations based on the data of Bridier et al (1991) because it gives good agreement with the data of Tuazon et al (1991) and is consistent with the NASA (1997) recommended equilibrium constant.

The reactants and products for Reaction DPAN are consistent with current knowledge. The choice of rate constant is reasonable but more research and evaluation is required to improve this highly important rate constant.

Reaction BPN2

k(300)	A	Ea	Notes	
1.37E-11	1.37E-11	---	60	BZCO-O2. + NO2 = PBZN

Notes

60	Rate constant based on k(NO2)/k(NO) ratio measured by Kirchner et al (1992) and the k(NO) used for general higher acyl peroxy radical species.

The rate parameter for Reaction BPN2 is consistent with the product of the k(NO$_2$)/k(NO) ratio (measured by Kirchner as 0.62) and the rate parameter for the reaction of higher acyl radicals with NO (2.18E-11 cm^3 molecule^{-1} s^{-1}).

Reaction BPAN

k(300)	A	Ea	Notes	
4.27E-04	7.90E+16	27.82	61	PBZN = BZCO-O2. + NO2

Notes

61	Rate constant expression based on the data of Kirchner et al (1992).

The reactants, products and rate parameter for Reaction BPAN are consistent with current knowledge.

Reaction PPN2

k(300)	A	B	Notes	
1.20E-11	1.20E-11	-0.9	56,57	RCO-O2. + NO2 = PAN2

Notes

56	The rate parameters are assumed to be approximately the same as those for the reaction of CH3C(O)OO. at the high pressure limit. NASA (1997) and IUPAC (Atkinson et al, 1997a, 1999) give no recommendations for this rate constant for higher acyl peroxy radicals.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

The reactants, products and rate parameters are reasonable for Reaction BPN2. The rate parameter is in agreement with the results of Seefeld (1997). If the rate constant is taken to be the same as $CH_3CH_2CO_3$ + NO_2. Seefeld (1997) the measured k(NO_2)/k(NO) = 0.43±0.07 over the temperature range of 249-302K. This leads to a rate constant of 1.2E-11 cm^3 $molecule^{-1}$ s^{-1} if the rate parameter for the reaction of $CH_3CH_2CO_3$ radicals with NO is assumed to be 2.8E-11 cm^3 $molecule^{-1}$ s^{-1} in agreement with the value chosen by Carter.

Reaction MPN2

k(300)	A	Ea	B	Notes	
Same as PPN2				62,64	MA-RCO3. + NO2 = MA-PAN

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

This treatment of the acyl peroxy radical and PAN analogue formed from any acrolein compound are reasonable for Reaction MPN2.

Reaction PAN2

k(300)	A	Ea	Notes	
5.87E-04	2.00E+15	25.44	57,58	PAN2 = RCO-O2. + NO2

Notes

57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.
58	Rate parameters based on data for PPN. The activation energy is recommended by Atkinson (1994) for thermal decomposition of higher PAN analogues. The A factor is adjusted to yield the average k(298) for PPN as measured by Schurath and Wipprecth (1980) and Mineshos and Glavas (1991). The A factor recommended by Atkinson (1994) not used because it gives k(298) outside the range of both those measurements.

The IUPAC Supplement IV (1999) reports a rate constant of 4.4E-4 (298K) and an expression k = 2E15 * exp(-12800/T) for PPN. Should that value be used for Reaction PAN2?

Reaction MPPN

k(300)	A	Ea	Notes	
4.79E-04	1.60E+16	26.8	65	MA-PAN = MA-RCO3. + NO2

Notes

65	Rate parameters from Roberts and Bertman (1992), as used by Carter and Atkinson (1996).

The rate parameter for Reaction MPPN appears to be consistent with the available laboratory studies.

APNO Reaction and Analogs

Reaction APNO

k(300)	A	Ea	Notes	
2.18E-11	2.18E-11	---	50	CCO-O2. + NO = C-O2. + CO2 + NO2

Notes

50	Rate constant based on the IUPAC (Atkinson et al, 1997a) recommendation is to use k(NO)/K(NO2)=2.1 for atmospheric conditions (298K and 1 atm.), with k(NO) approximately independent of temperature. This is almost the same as the IUPAC(Atkinson et al, 1997a, 1999) recommended value of 2.0x10-11 and the NASA (1997) value of 1.8x10-11.

Although the temperature dependence of this reaction is not great, the temperature dependence as given in IUPAC (Atkinson et al, 1999) evaluation should be included as k = 7.8E-12*EXP(300/T). The reactants and products are consistent with present knowledge.

Reaction PPNO

k(300)	A	Ea	Notes	
Same as Reaction APNO			59,57	RCO-O2. + NO = NO2 + CCHO + RO2-R. + CO2

Notes

59	Assumed to have same rate constant as corresponding reaction of CH3C(O)OO.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

See note for Reaction APNO for comments on rate parameter. The reactants and products are consistent with the assumption that RCO-O2 is $CH_3CH_2CO_3$ and that there is sufficient NO to react with all $CH_3CH_2O_2$ produced to convert it to CH_3CHO.

Reaction BPNO

k(300)	A	Ea	Notes	
Same as Reaction APNO			62,63	BZCO-O2. + NO = NO2 + CO2 + BZ-O. + R2O2.

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See note for Reaction APNO for comments on rate parameter. The reactants and products are consistent with the stated assumptions.

Reaction MPNO

k(300)	A	Ea	Notes	
Same as Reaction APNO			62,64	MA-RCO3. + NO = NO2 + CO2 + HCHO + CCO-O2.

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See note for Reaction APNO for comments on rate parameter. The reactants and products are consistent with present knowledge.

APH2 Reaction and Analogs

Reaction APH2

k(300)	A	Ea	Notes	
1.38E-11	4.30E-13	-2.07	51	CCO-O2. + HO2. = #.75 {CCO-OOH +O2} + #.25 {CCO-OH + O3}

Notes

51	Branching ratio and rate constant expression recommended by IUPAC (Atkinson et al, 1997a, 1999).

The branching ratio and the rate parameter are consistent with Atkinson et al. (1999).

Reaction PPH2

k(300)	A	Ea	Notes	
Same as Reaction APH2			59,57	RCO-O2. + HO2. = RCO-OOH + O2

Notes

59	Assumed to have same rate constant as corresponding reaction of CH3C(O)OO.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

See note for Reaction APH2 for comments on rate parameter. The treatment of this reaction is consistent with present knowledge. Note 57 is not exactly correct because while 25% of the acetyl peroxy radicals react with HO_2 to produce O_3 while, in contrast, 100% of the peroxy propionyl and higher peroxy acyl radicals are assumed to react with HO_2 to produce higher peroxy organic acids.

Reaction BPH2

k(300)	A	Ea	Notes	
Same as Reaction APH2			62,63	BZCO-O2. + HO2. = RCO-OOH + O2 + #4 XC

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See note for Reaction APH2 for comments on rate parameter. The treatment of this reaction is consistent with present knowledge. On Note 63 the comments given for Note 57 under Reaction PPH2 apply here too.

Reaction MPH2

k(300)	A	Ea	Notes	
Same as Reaction APH2			62,64	MA-RCO3. + HO2. = RCO-OOH + O2 + XC

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See note for Reaction APH2 for comments on rate parameter. The treatment of this reaction is consistent with present knowledge. On Note 64 the comments given for Note 57 under Reaction PPH2 apply here too.

APN3 Reaction and Analogs

Reaction APN3

k(300)	A	Ea	Notes	
4.00E-12	4.00E-12	---	52	CCO-O2. + NO3 = C-O2. + CO2 + NO2 + O2

Notes

52	Rate constant from Canosa-Mass et al (1996).

The reactants, products and rate parameter are consistent with present knowledge.

Reaction PPN3

k(300)	A	Ea	Notes	
Same as Reaction APN3			59,57	RCO-O2. + NO3 = NO2 + CCHO + RO2-R. + CO2 + O2

Notes

59	Assumed to have same rate constant as corresponding reaction of CH3C(O)OO.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

The rate parameter is consistent with Reaction APN3. The reactants and products are consistent with the assumption that RCO-O2 is $CH_3CH_2CO_3$ and that there is sufficient NO to react with all $CH_3CH_2O_2$ produced to convert it to CH_3CHO.

Reaction BPN3

k(300)	A	Ea	Notes	
Same as Reaction APN3			62,63	BZCO-O2. + NO3 = NO2 + CO2 + BZ-O. + R2O2. + O2

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

The rate parameter is consistent with Reaction APN3. The reactants and products are consistent with present knowledge.

Reaction MPN3

k(300)	A	Ea	Notes	
Same as Reaction APN3			62,64	MA-RCO3. + NO3 = NO2 + CO2 + HCHO + CCO-O2. + O2

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

The rate parameter is consistent with Reaction APN3. The reactants and products are consistent with present knowledge.

APME Reaction and Analogs

Reaction APME

k(300)	A	Ea	Notes	
9.53E-12	1.80E-12	-0.99	53	CCO-O2. + C-O2. = CCO-OH + HCHO + O2

Notes

53	Rate constant expression recommended by IUPAC (Atkinson et al, 1999) evaluation. As discussed there, the data are inconclusive as to the importance of the competing reaction forming CH3O + CH3CO2 + O2, but the study which indicate that it occurs, which was used in the previous IUPAC (Atkinson et al, 1997a) evaluation, indicates that it occurs less than ~15% under atmospheric conditions. Therefore, the reaction is assumed to involve disproportionation 100% of the time.

The rate parameter is consistent with the IUPAC (Atkinson et al, 1999) evaluation. Although this choice is reasonable it must be noted that at 50 ˚F the yield of CH_3OOH may be near 25% if Horie and Moortgat (1992) as quoted in Atkinson et al. (1999) are correct. The uncertainty in the branching ratio represents a major uncertainty in this reaction.

Reaction PPME

k(300)	A	Ea	Notes	
Same Reaction as AMPE			59,57	RCO-O2. + C-O2. = RCO-OH + HCHO + O2

Notes

59	Assumed to have same rate constant as corresponding reaction of CH3C(O)OO.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

See comments for Reaction APME. The reaction is consistent with the stated assumptions.

Reaction BPME

k(300)	A	Ea	Notes	
Same Reaction as AMPE			62,63	BZCO-O2. + C-O2. = RCO-OH + HCHO + O2 + #4 XC

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See comments for Reaction APME. The reaction is consistent with the stated assumptions.

Reaction MPME

k(300)	A	Ea	Notes	
Same Reaction as AMPE			62,64	MA-RCO3. + C-O2. = RCO-OH + HCHO + XC + O2

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See comments for Reaction APME. The reaction is consistent with the stated assumptions.

APRR Reaction and Analogs

Reaction APRR

k(300)	A	Ea	Notes	
1.00E-11	1.00E-11	---	54,55	CCO-O2. + RO2-R. = CCO-OH

Notes

54	Rate constant based on values for rate constants for acetyl peroxy + methyl peroxy and CH3C(O)CH2OO. given by Atkinson et al (1997a).
55	This reaction is assumed to proceed primarily by disproportionation to form the organic acid and a carbonyl compound, based on data for the acetyl peroxy + methyl peroxy reaction.

The rate parameter is much closer to the IUPAC value for acetyl peroxy + methyl peroxy radical than for methyl peroxy + $CH_3C(O)CH_2OO$. The basis for the averaging should be given in Note 54. Given that these reactions involve operator radicals it is probably best to assume that the reactions proceed by disproportionation for simplicity. However, it is not clear that this choice is supported by the data for the acetyl peroxy + methyl peroxy reaction, see comments about Reaction APME.

Reaction APR2

k(300)	A	Ea	Notes	
Same as Reaction APRR			42,43	CCO-O2. + R2O2. = CCO-O2.

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

See comment for Reaction APRR.

Reaction APRN

k(300)	A	Ea	Notes	
Same as Reaction APRR			42,55, 46	CCO-O2. + RO2-N. = CCO-OH + PROD2

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
55	This reaction is assumed to proceed primarily by disproportionation to form the organic acid and a carbonyl compound, based on data for the acetyl peroxy + methyl peroxy reaction.
46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The MEK + HO2. represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.

See comment for Reaction APRR. The treatment of the RO2-N. radical appears to be reasonable.

Reaction BPRR

k(300)	A	Ea	Notes	
Same as Reaction APRR			62,63	BZCO-O2. + RO2-R. = RCO-OH + O2 + #4 XC

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See comment for Reaction APRR.

Reaction BPR2

k(300)	A	Ea	Notes	
Same as Reaction APRR			43,62	BZCO-O2. + R2O2. = BZCO-O2.

Notes

43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.
62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.

See comment for Reaction APRR.

Reaction BPRN

k(300)	A	Ea	Notes	
Same as Reaction APRR			46,62, 63	BZCO-O2. + RO2-N. = RCO-OH + PROD2 + O2 + #4 XC

Notes

46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The MEK + HO2. represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.
62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See comment for Reaction APRR. The treatment of the RO2-N. radical appears to be reasonable and consistent with Reaction APRN.

Reaction PPRR

k(300)	A	Ea	Notes	
Same as Reaction APRR			59,57	RCO-O2. + RO2-R. = RCO-OH + O2

Notes

59	Assumed to have same rate constant as corresponding reaction of CH3C(O)OO.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

See comment for Reaction APRR.

Reaction PPR2

k(300)	A	Ea	Notes	
Same as Reaction APRR			59,43	RCO-O2. + R2O2. = RCO-O2.

Notes

59	Assumed to have same rate constant as corresponding reaction of CH3C(O)OO.
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

See comment for Reaction APRR.

Reaction PPRN

k(300)	A	Ea	Notes	
Same as Reaction APRR			59,46, 57	RCO-O2. + RO2-N. = RCO-OH + PROD2 + O2

Notes

59	Assumed to have same rate constant as corresponding reaction of CH3C(O)OO.
46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The MEK + HO2. represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

See comment for Reaction APRR.

Reaction MPRR

k(300)	A	Ea	Notes	
Same as Reaction APRR			62,64	MA-RCO3. + RO2-R. = RCO-OH + XC

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. and MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See comment for Reaction APRR.

Reaction MPR2

k(300)	A	Ea	Notes	
Same as Reaction APRR			43,62	MA-RCO3. + R2O2. = MA-RCO3.

Notes

43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.
62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.

See comment for Reaction APRR.

Reaction MPRN

k(300)	A	Ea	Notes	
Same as Reaction APRR			62,64	MA-RCO3. + RO2-N. = #2 RCO-OH + O2 + #4 XC

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. and MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See comment for Reaction APRR.

Reaction APAP and Analogs

Reaction APAP

k(300)	A	Ea	Notes	
1.54E-11	2.90E-12	-0.99	31	CCO-O2. + CCO-O2. = #2 {C-O2. + CO2} + O2

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

Reactants, products and rate parameter are consistent with present knowledge.

Reaction PPAP

k(300)	A	Ea	Notes	
Same as Reaction APAP			59,57	RCO-O2. + CCO-O2. = #2 CO2 + C-O2. + CCHO + RO2-R. + O2

Notes

59	Assumed to have same rate constant as corresponding reaction of CH3C(O)OO.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

Reactants, products and rate parameter are consistent with present knowledge. However it must be noted that acetaldehyde is formed only if there is sufficient NO_x to convert the produced $CH_3CH_2O_2$ to CH_3CHO.

Reaction PPPP

k(300)	A	Ea	Notes	
Same as Reaction APAP			59,57	RCO-O2. + RCO-O2. = #2 {CCHO + RO2-R. + CO2}

Notes

59	Assumed to have same rate constant as corresponding reaction of CH3C(O)OO.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

Reactants, products and rate parameter are consistent with present knowledge. See comment about Reaction PPAP.

Reaction BPAP

k(300)	A	Ea	Notes	
Same as Reaction APAP			62,63	BZCO-O2. + CCO-O2. = #2 CO2 + C-O2. + BZ-O. + R2O2.

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Reaction BPPP

k(300)	A	Ea	Notes	
Same as Reaction APAP			62,57, 63	BZCO-O2. + RCO-O2. = #2 CO2 + CCHO + RO2-R. + BZ-O. + R2O2.

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Reaction BPBP

k(300)	A	Ea	Notes	
Same as Reaction APAP			62,63	BZCO-O2. + BZCO-O2. = #2 {BZ-O. + R2O2. + CO2}

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Reaction MPAP

k(300)	A	Ea	Notes	
Same as Reaction APAP			62,64	MA-RCO3. + CCO-O2. = #2 CO2 + C-O2. + HCHO + CCO-O2. + O2

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Reaction MPPP

k(300)	A	Ea	Notes	
Same as Reaction APAP			62,64	MA-RCO3. + RCO-O2. = HCHO + CCO-O2. + CCHO + RO2-R. + #2 CO2

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Reaction MPBP

k(300)	A	Ea	Notes	
Same as Reaction APAP			62,64	MA-RCO3. + BZCO-O2. = HCHO + CCO-O2. + BZ-O. + R2O2. + #2 CO2

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Reaction MPMP

k(300)	A	Ea	Notes	
Same as Reaction APAP			62,64	MA-RCO3. + MA-RCO3. = #2 {HCHO + CCO-O2. + CO2}

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Other Organic Radical Species

Reaction TBON

k(300)	A	Ea	Notes	
2.40e-11	2.40e-11	--	66,67	TBU-O. + NO2 = RNO3 + #-2 XC

Notes

66	The rate expression recommended by Atkinson (1997) for general alkoxy + NO2 reactions is 2.3x10-11 exp(+150/T). This is reduced by a factor of 1.58 to be consistent with environmental chamber data, as discussed in a separate note.
67	The effects of isobutane and t-butyl alcohol on ozone formation and radical levels in environmental chamber experiments are not consistent with predictions of models which assume the recommended rate constant ratios for the decomposition of t-butoxy radicals relative to reaction with NO2. The data are better fit if the ratio is increased by a factor of 2.5. The error is assumed to be equally distributed in each rate constant, so they are both adjusted by the a factor of 1.58, which is the square root of 2.5.

The reactants, products and rate parameter are consistent with the Atkinson (1997) recommendations. However the need to adjust the rate parameter to fit environmental chamber data raises concerns about the uncertainty of the rate parameter. Also since Atkinson (1997) recommends an Ea of -0.30 kcal mole^{-1} it should be included in the rate parameter expression.

Reaction TBOD

k(300)	A	Ea	Notes	
1.18e+3	7.50e+14	16.20	68,67	TBU-O. = ACET + C-O2.

Notes

68	Atkinson (1997b) recommends the high-pressure rate expression of 6.0x10+14 exp(-16.2/RT). Batt and Robinson (1987) calculate that at one atmosphere the rate constant is 79% the high pressure limit, giving an estimated rate expression of 4.74x10-14 exp(-16.2/RT). This is increased by a factor of 1.58 to be consistent with environmental chamber data, as discussed in a separate note.
67	The effects of isobutane and t-butyl alcohol on ozone formation and radical levels in environmental chamber experiments are not consistent with predictions of models which assume the recommended rate constant ratios for the decomposition of t-butoxy radicals relative to reaction with NO2. The data are better fit if the ratio is increased by a factor of 2.5. The error is assumed to be equally distributed in each rate constant, so they are both adjusted by the a factor of 1.58, which is the square root of 2.5.

The reactants, products and rate parameter are consistent with present knowledge but the need to adjust the rate parameter to fit environmental chamber data raises concerns about the uncertainty of the rate parameter.

Reaction BRN2

k(300)	A	Ea	Notes	
3.79e-11	2.30e-11	-0.30	69	BZ-O. + NO2 = NPHE

Notes

69	The rate constant is based on the general recommendation of Atkinson (1994) for alkoxy + NO2 reactions at the high pressure limit. 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 nitrophenols in NO3 + cresol and OH + benzaldehyde systems (Atkinson, 1994), this may be an oversimplification.

The reactants and rate parameter are consistent with the Atkinson (1997) recommendations. The products are very uncertain.

Reaction BRH2

k(300)	A	Ea	Notes	
Same k as rxn RRH2			70	BZ-O. + HO2. = PHEN

Notes

70	Assumed to have the same rate constant as the reaction of HO2 with peroxy radicals. This may underestimate the actual rate constant.

The rate parameter is highly uncertain but this approach is reasonable given the lack of measurements. It is not clear that the chosen rate parameter must be less than the actual rate parameter.

Reaction BRXX

k(300)	A	Ea	Notes	
1.00e-3	1.00e-3	--	71	BZ-O. = PHEN

Notes

71	This is included to avoid problems if these radicals are ever formed under conditions where both HO2 and NO2 are very low (which is considered to be unlikely under most ambient conditions), and can be considered to represent its reaction with organics present. The rate constant is arbitrary, and is such that this process becomes significant only if [NO2] < ~3x10-6 ppm and [HO2] < 1x10-5 ppm.

This reaction is completely arbitrary and has been inserted to avoid potential numerical problems. It seems unlikely that the [NO_2] could become less than ~3E-6 ppm and [HO_2] become less than 1E-5 ppm while [BZ-O.]. is significant.

Reaction BNN2

k(300)	A	Ea	Notes	
Same k as rxn BRN2			72	BZ(NO2)-O. + NO2 = #2 XN + #6 XC

Notes

72	The rate constant is based on the general recommendation of Atkinson (1994) for alkoxy + NO2 reactions at the high pressure limit. The products of this reaction (presumed to be aromatic dinitro compounds) are expected to have very low vapor pressures and are represented as unreactive nitrogen and carbon.

The reactants and rate parameter are consistent with the Atkinson (1997) recommendations. The products are very uncertain and it could be that compounds more reactive dinitro aromatics are formed but given the lack of data this treatment is reasonable.

Reaction BNH2

k(300)	A	Ea	Notes	
Same k as rxn RRH2			70	BZ(NO2)-O. + HO2. = NPHE

Notes

70	Assumed to have the same rate constant as the reaction of HO2 with peroxy radicals. This may underestimate the actual rate constant.

The rate parameter is highly uncertain but this approach is reasonable given the lack of measurements. It is not clear that the chosen rate parameter must be less than the actual rate parameter.

Reaction BNXX

k(300)	A	Ea	Notes	
Same k as rxn BRXX			71	BZ(NO2)-O. = NPHE

Notes

71	This is included to avoid problems if these radicals are ever formed under conditions where both HO2 and NO2 are very low (which is considered to be unlikely under most ambient conditions), and can be considered to represent its reaction with organics present. The rate constant is arbitrary, and is such that this process becomes significant only if [NO2] < ~3x10-6 ppm and [HO2] < 1x10-5 ppm.

This treatment is reasonable and may avoid numerical problems.

Explicit and Lumped Molecule Organic Products

Reaction FAHV

	Notes	
Phot Set= HCHO_R	73	HCHO + HV = #2 HO2. + CO

Notes

73	Absorption cross sections and quantum yields recommended by IUPAC (Atkinson et al, 1997a) used. Absorption cross sections used are those given for T = 285K.

This treatment of the radical product producing channel for HCHO photolysis is consistent with present knowledge.

Reaction FAVS

	Notes	
Phot Set= HCHO_M	73	HCHO + HV = H2 + CO

Notes

73	Absorption cross sections and quantum yields recommended by IUPAC (Atkinson et al, 1997a) used. Absorption cross sections used are those given for T = 285K.

This treatment of the molecular product producing channel for HCHO photolysis is consistent with present knowledge.

Reaction FAOH

k(300)	A	Ea	Notes	
9.19e-12	8.60e-12	-0.04	31	HCHO + HO. = HO2. + CO + H2O

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

The reactants, products and rate parameter are consistent with present knowledge.

Reaction FAH2

k(300)	A	Ea	Notes	
7.79e-14	9.70e-15	-1.24	31	HCHO + HO2. = HOCOO.

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

The reactants, products and rate parameter are consistent with present knowledge.

Reaction FAHR

k(300)	A	Ea	Notes	
1.76e+2	2.40e+12	13.91	31	HOCOO. = HO2. + HCHO

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

The reactants, products and rate parameter are consistent with present knowledge.

Reaction FAHN

k(300)	A	Ea	Notes	
Same k as rxn MER1			74	HOCOO. + NO = HCOOH + NO2 + HO2.

Notes

74	Rate constant assumed to be the same as used for methylperoxy + NO.

The reactants and products are consistent with present knowledge. The rate parameter is consistent with the rate parameter used for CH_3O_2 + NO.

Reaction FAN3

k(300)	A	Ea	Notes	
6.06e-16	2.00e-12	4.83	75	HCHO + NO3 = HNO3 + HO2. + CO

Notes

75	T=298K Rate constant recommended by IUPAC (Atkinson et al, 1979a). Temperature dependence is as estimated by IUPAC (Atkinson et al, 1979a).

The reactants, products and rate parameter are consistent with present knowledge. But the rate parameter is known only within a factor of 2. The rate parameter used is consistent with the more recent recommendation of Atkinson et al. (1999).

Reaction AAOH

k(300)	A	Ea	Notes	
1.57e-11	5.60e-12	-0.62	31	CCHO + HO. = CCO-O2. + H2O

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

The reactants, products and rate parameter are consistent with present knowledge.

Reaction AAHV

	Notes	
Phot Set= CCHO_R	76	CCHO + HV = CO + HO2. + C-O2.

Notes

76	Absorption cross sections and quantum yields recommended by IUPAC (Atkinson et al, 1997a, 1999) used. Reaction assumed to occur primarily by breaking the C-CHO bond. Pathway forming molecular products from acetaldehyde is calculated to be negligible under atmospheric conditions, and is not included in the model.

This treatment of the radical product producing channel for acetaldehyde photolysis is consistent with present knowledge. Neglect of the molecular product channel is acceptable.

Reaction AAN3

k(300)	A	Ea	Notes	
2.84e-15	1.40e-12	3.70	77	CCHO + NO3 = HNO3 + CCO-O2.

Notes

77	Rate constant expression recommended by IUPAC, Supplement V (Atkinson et al, 1997a).

The reactants, products and rate parameter are consistent with present knowledge. The rate parameter used is consistent with the more recent recommendation of Atkinson et al. (1999).

Reaction PAOH

k(300)	A	Ea	Notes	
2.00e-11	2.00e-11	---	78,31, 79, 80	RCHO + HO. = #.034 RO2-R. + #.001 RO2-N. + #.965 RCO-O2. + #.034 CO + #.034 CCHO + #-0.003 XC

Notes

78	The mechanism for RCHO is based on reactions estimated for propionaldehyde.
31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
79	OH reactions at various positions in the molecule estimated using the group-additivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996).
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).

The reactants, products and rate parameter are consistent with present knowledge. and the assumptions as stated in the notes.

Reaction PAHV

	Notes	
Phot Set= C2CHO	78,76	RCHO + HV = CCHO + RO2-R. + CO + HO2.

Notes

78	The mechanism for RCHO is based on reactions estimated for propionaldehyde.
76	Absorption cross sections and quantum yields recommended by IUPAC (Atkinson et al, 1997a, 1999) used. Reaction assumed to occur primarily by breaking the C-CHO bond. Pathway forming molecular products from acetaldehyde is calculated to be negligible under atmospheric conditions, and is not included in the model.

Note 76 is not correct for Reaction PAHV because it discusses acetaldehyde and not propionaldehyde. Otherwise the reaction appears to be consistent with present knowledge.

Reaction PAN3

k(300)	A	Ea	Notes	
Same k as rxn AAN3			78,81	RCHO + NO3 = HNO3 + RCO-O2.

Notes

78	The mechanism for RCHO is based on reactions estimated for propionaldehyde.
81	Assumed to have same rate constant and analogous mechanism as reaction of acetaldehyde.

This procedure may underestimate the rate parameter for this reaction. There is a roughly log-linear relationship between k_{HO} and k_{NO3} for HCHO and CH_3CHO. If the most recent values for k_{HO} and k_{NO3} for HCHO and CH3CHO are fit we get $k_{NO3} = 2.78*k_{HO} + 15.44$. This yields a k_{NO3} of 5.0E-15 for propionaldehyde if a k_{HO} of 2.0E-11for propionaldehyde is assumed.

Reaction K3OH

k(300)	A	Ea	Notes	
1.94e-13	1.10e-12	1.03	31,82	ACET + HO. = HCHO + CCO-O2. + R2O2.

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
82	Reaction in the presence of NOx is assumed to involve formation of CH3C(O)CH2O., after one NO to NO2 conversion. Based on the data of Jenkin et al (1993), this radical is believed to rapidly decompose to HCHO + CH3CO.

The reactants, products and rate parameter are consistent with present knowledge.

Reaction K3HV

	Notes	
Phot Set= ACETONE	83	ACET + HV = CCO-O2. + C-O2.

Notes

83	Absorption cross sections and quantum yields used are those recommended by IUPAC (Atkinson et al, 1997a) except as noted. The reported quantum yields at 230 and 330 are expected to be high and an estimated correction was made as discussed by Carter et al (1993b). The corrected quantum yield data for wavelengths less than 290 nm were then fit to a smooth curve to estimate the quantum yields for higher wavelengths, with no weight being given to the highly uncertain 330 nm point. As discussed by Carter et al (1993b), using these corrections results in better fits of model calculations to environmental chamber experiments involving acetone.

The reactants and products are consistent with present knowledge. This approach to the treatment of the photolysis rates appears to be reasonable.

Reaction K4OH

k(300)	A	Ea	B	Notes	
1.20e-12	1.30e-12	0.05	2.0	31, 79, 80	MEK + HO. = #.37 RO2-R. + #.042 RO2-N. + #.616 R2O2. + #.492 CCO-O2. + #.096 RCO-O2. + #.115 HCHO + #.482 CCHO + #.37 RCHO + #.287 XC

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
79	OH reactions at various positions in the molecule estimated using the group-additivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996).
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).

The rate parameter is in agreement with the recommendations of Atkinson et al. (1999). The estimation procedure used is reasonable and the sum of the rate parameters for the HO reactions at various positions in the molecule sum to within 13% of the measured rate parameter.

Reaction K4HV

	Notes	
Phot Set= KETONE qy= 1.0e-1	84	MEK + HV = CCO-O2. + CCHO + RO2-R.

Notes

84	The absorption coefficients used for MEK are from Moortgat (Private communication, 1996). The overall MEK quantum yield of 0.1 was derived from fits to UNC chamber data as determined by Carter et al (1986), and is consistent with results of MEK reactivity experiments carried out in our laboratories (Carter et al, 1999a). The reaction is assumed to proceed primarily by breaking the weakest CO-C bond.

The absorption coefficients for MEK from Moortgat are the best available. The quantum yield must be regarded as uncertain since it is derived from environmental chamber data and is not the result of a direct measurement. The assumed mechanism is reasonable.

Reaction MeOH

k(300)	A	Ea	B	Notes	
9.34e-13	3.10e-12	0.72	2.0	85	MEOH + HO. = HCHO + HO2.

Notes

85	The mechanism and rate constants are as recommended by IUPAC (Atkinson et al, 1997a, 1999). The branching ratio is for T=298K only. The overall reaction assumes the major fate of the alpha hydorxy radical is reaction with O2 to form HO2 and HCHO.

The reactants and the rate parameter are in agreement with the Atkinson et al. (1999) recommendations. The CH_2OH reaction channel does represent 85% of the overall reaction at 298K. The products are reasonable if the CH_2OH produced mainly reacts through abstraction of the H atom attached to the OH group. The CH_3O reaction channel would be expected to produce almost all HCHO and HO_2.

Reaction MER9

k(300)	A	Ea	Notes	
5.46e-12	2.90e-12	-0.38	86	COOH + HO. = H2O + #.35 {HCHO + HO.} + #.65 C-O2.

Notes

86	Rate constant and branching ratio for initial OH reaction based on IUPAC (Atkinson et al, 1997a, 1999) recommendation. The .CH2OOH radical is assumed to rapidly decompose to HCHO + OH, based on its high estimated exothermicity.

The reactants, products and rate parameters are consistent with the recommendations of Atkinson et al. (1999).

Reaction MERA

	Notes	
Phot Set= COOH	87	COOH + HV = HCHO + HO2. + HO.

Notes

87	Absorption cross sections from IUPAC (Atkinson et al, 1997a, 1999), which also recommends assuming unit total quantum yield, but gives no recommendation as to the exact mechanism. Breaking the O-O bond assumed to be the major pathway.

The reactants, products, quantum yields and absorption cross sections are consistent with current knowledge.

Reaction LPR9

k(300)	A	Ea	Notes	
1.10e-11	1.10e-11	--	88,89	ROOH + HO. = H2O + RCHO + #.34 RO2-R. + #.66 HO.

Notes

88	The mechanism for ROOH is based on reactions estimated for n-propyl hydroperoxide.
89	Reaction at the OOH position is assumed to be as fast as in CH3OOH. Reaction at the 1-position is estimated to be ~7x10-12 (i.e., ~2/3 of the time) based on comparing rates of analogous reactions for methanol, ethanol, and CH3OOH (IUPAC, 1997a, 1999). The alpha-hydroperoxy radicals are assumed to decompose rapidly to OH and the carbonyl on the basis of estimated high exothermicity. Reaction at the 2- or 3-positions are estimated to occur no more than ~10% of the time and are neglected.

The basis of this reaction appears to be highly uncertain but the estimation procedures used for the products and rate parameter are reasonable.

Reaction LPRA

	Notes	
Phot Set= COOH	90	ROOH + HV = RCHO + HO2. + HO.

Notes

90	Reaction assumed to occur with the same rate and analogous mechanism as methyl hydroperoxide.

The reactants, products, quantum yields and absorption cross sections are consistent with current knowledge but the reaction is uncertain due to that fact that it is derived through analogy.

Reaction GLHV

	Notes	
Phot Set= GLY_R	91,92	GLY + HV = #2 {CO + HO2.}

Notes

91	Absorption cross sections from Plum et al (1983), as recommended by IUPAC (Atkinson et al, 1997a, 1999) in the case of glyoxal.
92	For the low wavelength band, a constant quantum yield of 0.4 is assumed, based on data of Langford and Moore (1984). For the high wavelength band, quantum yield is assumed to decrease linearly to zero at the threshold wavelength of 418 nm, starting at a "falloff" wavelength, which is adjusted to yield fits to chamber data for acetylene - NOx and acetylene reactivity experiments, as discussed by Carter et al (1997c). "Best fit" falloff wavelength of 380 nm used. Note that this gives overall quantum yields which are ~1.4 times higher than overall quantum yield reported by Plum et al (1983) for conditions of those experiments. Although use of acetylene reactivity data is a highly indirect way to obtain glyoxal quantum yields, it is considered to be a less uncertain way to estimate radical quantum yields then the data of Plum et al (1993), which uses a UV-poor light source and only measures rates of glyoxal decay.

The reactants, products, quantum yields and absorption cross sections are consistent with present knowledge but derived photolysis frequencies are uncertain due to the fitting of environmental chamber data.

Reaction GLVM

	Notes	
Phot Set= GLY_ABS qy= 6.0e-3	91,93	GLY + HV = HCHO + CO

Notes

91	Absorption cross sections from Plum et al (1983), as recommended by IUPAC (Atkinson et al, 1997a, 1999) in the case of glyoxal.
93	Plum et al (1983) observed 13% formaldehyde yield in photodecomposition, so overall quantum yield adjusted to give this yield relative to the radical forming process for the spectral distribution of those experiments. A wavelength-independent quantum yield is used because of lack of information on wavelength dependence.

The reactants, products, quantum yields and absorption cross sections are consistent with present knowledge. The use of a wavelength-independent quantum yield contributes to the uncertainty in the derived photolysis frequencies.

Reaction GLOH

k(300)	A	Ea	Notes	
1.10e-11	1.10e-11		31,94, 95	GLY + HO. = #.63 HO2. + #1.26 CO + #.37 RCO-O2. + #-.37 XC

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
94	Product distribution based on the data of Niki et al (1985), as discussed by IUPAC (Atkinson et al, 1997a). Product distribution is calculated for 1 atm air at 298K.
95	HCO(CO)OO. is represented by the lumped higher acyl peroxy species RCO-OO.

The reactants, products and rate parameters are consistent with the recommendations of Atkinson et al. (1999).

Reaction GLN3

k(300)	A	Ea	Notes	
Same k as rxn AAN3			95,96	GLY + NO3 = HNO3 + #.63 HO2. + #1.26 CO + #.37 RCO-O2. + #-.37 XC

Notes

95	HCO(CO)OO. is represented by the lumped higher acyl peroxy species RCO-OO.
96	Assumed to have the same rate constant and mechanism as the analogous reaction with acetaldehyde.

The products are consistent with the treatment of the HO reaction, Reaction GLOH. The rate parameter is uncertain due to its derivation by analogy.

Reaction MGHV

	Notes	
Phot Set= MGLY_ADJ	97	MGLY + HV = HO2. + CO + CCO-O2.

Notes

97	Absorption cross sections obtained from Moortgat (personal communication, 1996). These are essentially the same as those recommended by IUPAC (Atkinson et al, 1997a, 1999), except slightly better resolution. Photolysis at the low wavelength band is assumed to have unit quantum yields, based on data for biacetyl. Photolysis above the cutoff wavelength of 421 nm (Atkinson et al, 1977a) is assumed to have zero quantum yields. For the rest of the high wavelength region, the wavelength dependence was derived by assuming the quantum yields decline linearly from 1 at 344 nm to 0 at a wavelength (407 nm) which was adjusted to be such that the calculated overall quantum yields for the conditions of the experiments of Plum et al (1983) agreed with the overall quantum yield they observed experimentally. The quantum yields recommended by IUPAC (Atkinson et al, 1999) lack sufficient wavelength resolution to be useful for modeling.

The absorption coefficients for MEK from Moortgat are the best available. The procedure used to derive the quantum yields from the experimental data is to be reasonable.

Reaction MGOH

k(300)	A	Ea	Notes	
1.50e-11	1.50e-11	--	31	MGLY + HO. = CO + CCO-O2.

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

The reactants, products and rate parameters are consistent with current knowledge.

Reaction MGN3

k(300)	A	Ea	Notes	
Same k as rxn AAN3			96	MGLY + NO3 = HNO3 + CO + CCO-O2.

Notes

96	Assumed to have the same rate constant and mechanism as the analogous reaction with acetaldehyde.

The products are consistent with the treatment of the HO reaction, Reaction MGOH. The rate parameter is uncertain due to its derivation by analogy.

Reaction BAHV

	Notes	
Phot Set= BACL_ADJ	91,98	BACL + HV = #2 CCO-O2.

Notes

91	Absorption cross sections from Plum et al (1983), as recommended by IUPAC (Atkinson et al, 1997a, 1999) in the case of glyoxal.
98	Assumed to have unit quantum yield at low wavelength band based on data cited by Atkinson (1994). For the high wavelength band, the quantum yields were assumed to decline linearly from 1 at 350 nm to 0 at a wavelength (420 nm) which was adjusted to be such that the calculated overall quantum yields for the conditions of the experiments of Plum et al (1983) agreed with the overall quantum yield they observed experimentally.

The absorption coefficients for biacetyl are based on glyoxal while the quantum yields are estimated. Given the lack of measurements the procedure is reasonable but the uncertainty in the photolysis frequencies derived from the absorption coefficients and quantum yields are high.

Reaction PHOH

k(300)	A	Ea	Notes	
2.63e-11	2.63e-11	--	99,100	PHEN + HO. = #.24 BZ-O. + #.76 RO2-R. + #.23 GLY + #4.1 XC

Notes

99	Rate constant recommended by Atkinson (1994).
100	The parameterized mechanism is estimated by analogy to the parameterized mechanism derived for cresols (see footnotes for OH + cresol reaction).

The rate parameter is consistent with the recommendations of Atkinson (1994). The uncertainty in the products is relatively high due to the need to fit environmental chamber data.

Reaction PHN3

k(300)	A	Ea	Notes	
3.78e-12	3.78e-12	--	99,101	PHEN + NO3 = HNO3 + BZ-O.

Notes

99	Rate constant recommended by Atkinson (1994).
101	In absence of definitive data concerning this reaction, the same mechanism is used as assumed by Carter (1990). However, see footnotes concerning phenoxy reactions.

The rate parameter is consistent with the recommendations of Atkinson (1994). The reactants and products are consistent with the stated assumptions in the footnotes concerning phenoxy reactions.

Reaction CROH

k(300)	A	Ea	Notes	
4.20e-11	4.20e-11	--	99,102	CRES + HO. = #.24 BZ-O. + #.76 RO2-R. + #.23 MGLY + #4.87 XC

Notes

99	Rate constant recommended by Atkinson (1994).
102	The parameterized mechanism is based on that used by Carter (1990), but was reoptimized to fit the NO, ozone, PAN, and cresol data in the o-cresol - NOx experiment EC281.

The rate parameter is consistent with the recommendations of Atkinson (1994) but it should be noted that o-cresol is assumed here. The uncertainty in the products is relatively high due to the need to fit environmental chamber data.

Reaction CRN3

k(300)	A	Ea	Notes	
1.37e-11	1.37e-11		99,101	CRES + NO3 = HNO3 + BZ-O. + XC

Notes

99 101	Rate constant recommended by Atkinson (1994). In absence of definitive data concerning this reaction, the same mechanism is used as assumed by Carter (1990). However, see footnotes concerning phenoxy reactions.

The rate parameter is consistent with the recommendations of Atkinson (1994) but it should be noted that o-cresol is assumed here. The reactants and products are consistent with the stated assumptions in the footnotes concerning phenoxy reactions.

Reaction NPN3

k(300)	A	Ea	Notes	
Same k as rxn PHN3			103	NPHE + NO3 = HNO3 + BZ(NO2)-O.

Notes

103	Assumed to have the same rate constant as the reaction of NO3 with phenol. Reaction with NO3 is assumed to dominate over reaction with OH radicals and other loss processes.

The assumed rate parameter and products are reasonable although the uncertainty is high due to the lack of measurements.

Reaction BZOH

k(300)	A	Ea	Notes	
1.29e-11	1.29e-11		99	BALD + HO. = BZCO-O2.

Notes

99	Rate constant recommended by Atkinson (1994).

The rate parameter is consistent with the recommendations of Atkinson (1994).

Reaction BZHV

	Notes	
Phot Set= BZCHO qy= 5.0e-2	104	BALD + HV = #7 XC

Notes

104	Absorption coefficients are from Majer et al (1969). The overall quantum yield derived by Carter (1990), which are based on model simulations of benzaldehyde decay rates in SAPRC evacuable chamber experiments, is used. Because of lack of data, the quantum yield is assumed to be independent of wavelength. The products formed from benzaldehyde photolysis are unknown, except that both radical formation and benzene formation appear to be minor (Carter, 1990). This benzaldehyde photolysis mechanism gives reasonably good model simulations of benzaldehyde - NOx experiments recently carried out in the CE-CERT xenon Teflon chamber (Carter et al, 1998a).

This treatment is reasonable given the lack of direct measurements.

Reaction BZNT

k(300)	A	Ea	Notes	
2.73e-15	1.40e-12	3.72	105	BALD + NO3 = HNO3 + BZCO-O2.

Notes

105	T=298K rate constant recommended by Atkinson (1994). Temperature dependence estimated by assuming the reaction has the same A factor as the reaction of NO3 with acetaldehyde.

The rate parameter for 298K recommended by Atkinson, 2.6e-15 cm^3 molecule^{-1} s^{-1}, is consistent with this assignment. The temperature dependence used is highly uncertain due to its reliance on the highly uncertain temperature dependence of the NO3 + NO2 = N2O5 equilibrium constant.

Reaction MAOH

k(300)	A	Ea	Notes	
3.35e-11	1.86e-11	-0.35	106, 80,107	METHACRO + HO. = #.5 RO2-R. + #.416 CO + #.084 HCHO + #.416 MEK + #.084 MGLY + #.5 MA-RCO3. + #-0.416 XC

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).
107	MEK is used to represent hydroxyacetone.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction MAO3

k(300)	A	Ea	Notes	
1.19e-18	1.36e-15	4.20	106, 108, 109, 110	METHACRO + O3 = #.008 HO2. + #.1 RO2-R. + #.208 HO. + #.1 RCO-O2. + #.45 CO + #.117 CO2 + #.2 HCHO + #.9 MGLY + #.333 HCOOH + #-0.1 XC

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
108	The excited HCHO2 biradical is assumed to react as recommended by Atkinson (1997) based on data for the O3 + ethene system, i.e., 37% stabilization, 12% decomposition to HCO + OH, 13% decomposition to CO2 + H2, and 38% decomposition to CO + H2O. Note that this is different than used for this species when formed in the isoprene products mechanisms of Carter and Atkinson (1996) and Carter (1996).
109	The vibrationally excited HCOC(CH3)CO2 biradicals are assumed to rearrange and decompose to HCOC(O)CH2. + OH, where the former forms HCOC(O). + HCHO after O2 addition and NO to NO2 conversion. RCO-O2. is used to represent HCOC(O)OO. in this reaction. Vibrationally excited CH3C(O)CHO2 is assumed to rapidly convert to HCOC(CH3)CO2 as discussed by Carter and Atkinson (1996).
110	The organic acid(s) formed in this reaction represent the formation of stabilized Crigiee biradicals, which are assumed to be consumed primarily by reaction with H2O forming the corresponding acid.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction MAN3

k(300)	A	Ea	Notes	
4.76e-15	1.50e-12	3.43	106, 111, 80,112	METHACRO + NO3 = #.5 {HNO3 + RO2-R. + CO +MA-RCO3.} + #1.5 XC + #.5 XN

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
111	NO3 radical addition assumed to occur primarily at the least substituted position.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).
112	The product CH3C(O)CH2ONO2 is expected to be relatively unreactive and is represented as "lost nitrogen" + 3 "lost carbons".

The reactants, products and rate parameter are consistent with current knowledge.

Reaction MAOP

k(300)	A	Ea	Notes	
6.34e-12	6.34e-12	--	113,5	METHACRO + O3P = RCHO + XC

Notes

113	Rate constant estimated from linear correlation between log k for OH and O3P reaction. Chamber data for C3+ alkenes are better fit by models assuming O3P reactions with C3+ species do not form radicals. Stable products represented by the lumped higher aldehyde or ketone, depending on type of product(s) expected to be formed.
5	This reaction is probably not important in air, but is included to increase range of applicability.

The reactants, products and rate parameter are estimated and therefore have a high degree of uncertainty. The reaction is probably not important in air under most conditions.

Reaction MAHV

	Notes	
Phot Set= ACROLEIN, qy= 4.1e-3	106,114	METHACRO + HV = #.34 HO2. + #.33 RO2-R. + #.33 HO. + #.67 CCO-O2. + #.67 CO + #.67 HCHO + #.33 MA-RCO3. + #-0 XC

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
114	The overall quantum yield was reoptomized to fit the same data as discussed by Carter and Atkinson (1996). In the case of methacrolein, he changes to the other portion of the mechanism resulted in an ~14% increase in the best fit overall quantum yield compared to that derived by Carter and Atkinson (1996). In the case of MVK, the best fit overall quantum yield decreased by a factor of 5.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction MVOH

k(300)	A	Ea	Notes	
1.87e-11	4.14e-12	-0.90	106,80	MVK + HO. = #.3 RO2-R. + #.025 RO2-N. + #.675 R2O2. + #.675 CCO-O2. + #.3 HCHO + #.675 RCHO + #.3 MGLY + #-0.725 XC

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction MVO3

k(300)	A	Ea	Notes	
4.74e-18	7.51e-16	3.02	106, 108, 109, 80, 110	MVK + O3 = #.064 HO2. + #.05 RO2-R. + #.164 HO. + #.05 RCO-O2. + #.475 CO + #.124 CO2 + #.1 HCHO + #.95 MGLY + #.351 HCOOH + #-0.05 XC

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
108	The excited HCHO2 biradical is assumed to react as recommended by Atkinson (1997) based on data for the O3 + ethene system, i.e., 37% stabilization, 12% decomposition to HCO + OH, 13% decomposition to CO2 + H2, and 38% decomposition to CO + H2O. Note that this is different than used for this species when formed in the isoprene products mechanisms of Carter and Atkinson (1996) and Carter (1996).
109	The vibrationally excited HCOC(CH3)CO2 biradicals are assumed to rearrange and decompose to HCOC(O)CH2. + OH, where the former forms HCOC(O). + HCHO after O2 addition and NO to NO2 conversion. RCO-O2. is used to represent HCOC(O)OO. in this reaction. Vibrationally excited CH3C(O)CHO2 is assumed to rapidly convert to HCOC(CH3)CO2 as discussed by Carter and Atkinson (1996).
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).
110	The organic acid(s) formed in this reaction represent the formation of stabilized Crigiee biradicals, which are assumed to be consumed primarily by reaction with H2O forming the

	corresponding acid.

The reactants, products and rate parameter are consistent with current knowledge but there is considerable uncertainty regarding the any potential reaction of Crigiee intermediates with H_2O.

Reaction MVN3

k(300)	A	Ea	Notes	
(Slow)			106	MVK + NO3 = #4 XC + XN

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.

It seems surprising that the rate parameter for the reaction of MVK with NO_3 is negligible.

Reaction MVOP

k(300)	A	Ea	Notes	
4.32e-12	4.32e-12		113,5	MVK + O3P = #.45 RCHO + #.55 MEK + #.45 XC

Notes

113	Rate constant estimated from linear correlation between log k for OH and O3P reaction. Chamber data for C3+ alkenes are better fit by models assuming O3P reactions with C3+ species do not form radicals. Stable products represented by the lumped higher aldehyde or ketone, depending on type of product(s) expected to be formed.
5	This reaction is probably not important in air, but is included to increase range of applicability.

The reactants, products and rate parameter are estimated and therefore have a high degree of uncertainty. The reaction is probably not important in air under most conditions.

Reaction MVHV

	Notes	
Phot Set= ACROLEIN qy= 2.1e-3	106,114, 115	MVK + HV = #.3 C-O2. + #.7 CO + #.7 PROD2 + #.3 MA-RCO3. + #-2.4 XC

Notes

106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
114	The overall quantum yield was reoptomized to fit the same data as discussed by Carter and Atkinson (1996). In the case of methacrolein, he changes to the other portion of the mechanism resulted in an ~14% increase in the best fit overall quantum yield compared to that derived by Carter and Atkinson (1996). In the case of MVK, the best fit overall quantum yield decreased by a factor of 5.
115	CH2=CHC(O)OO. Is represented by MA-RCO3.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction IPOH

k(300)	A	Ea	Notes	
6.19e-11	6.19e-11		116, 106, 80	ISOPROD + HO. = #.705 RO2-R. + #.006 RO2-N. + #.0 R2O2. + #.289 MA-RCO3. + #.357 CO + #.056 HCHO + #.134 CCHO + #.015 RCHO + #.158 MEK + #.352 PROD2 + #.158 GLY + #.179 MGLY + #-0.514 XC

Notes

116	As discussed by Carter (1996), isoprod is the "four product" lumped isoprene product species whose mechanism is derived by lumping rate constant and product parameters for a mixture of 30% hydroxymethacrolein, and 70% equal amounts of cis and trans HCOC(CH3)=CHCH2OH and HCOCH=C(CH3)CH2OH. These proportions are based on the estimated yields of these products in the reactions of OH with isoprene (Carter and Atkinson, 1996), which are represented by ISOPROD in the four product condensed mechanism (Carter, 1996). The other footnotes refer to the estimated mechanisms for these four individual compounds which were used to derive the lumped ISOPROD mechanism. RCHO, PROD2, MA-RCO3, etc. are used to represent various compounds as indicated in the descriptions of these lumped model species. See Carter and Atkinson (1996) for the specific compounds which can be formed in the various reactions of these species.
106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.

80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction IPO3

k(300)	A	Ea	Notes	
4.18e-18	4.18e-18		116, 106, 80, 117, 109, 118, 110	ISOPROD + O3 = #.4 HO2. + #.048 RO2-R. + #.048 RCO-O2. + #.285 HO. + #.498 CO + #.14 CO2 + #.125 HCHO + #.047 CCHO + #.21 MEK + #.023 GLY + #.742 MGLY + #.1 HCOOH + #.372 RCO-OH + #-.33 XC

Notes

116	As discussed by Carter (1996), isoprod is the "four product" lumped isoprene product species whose mechanism is derived by lumping rate constant and product parameters for a mixture of 30% hydroxymethacrolein, and 70% equal amounts of cis and trans HCOC(CH3)=CHCH2OH and HCOCH=C(CH3)CH2OH. These proportions are based on the estimated yields of these products in the reactions of OH with isoprene (Carter and Atkinson, 1996), which are represented by ISOPROD in the four product condensed mechanism (Carter, 1996). The other footnotes refer to the estimated mechanisms for these four individual compounds which were used to derive the lumped ISOPROD mechanism. RCHO, PROD2, MA-RCO3, etc. are used to represent various compounds as indicated in the descriptions of these lumped model species. See Carter and Atkinson (1996) for the specific compounds which can be formed in the various reactions of these species.
106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).
117	The HC(O)CHO2 biradical can decopose either to OH + HCO + CO via an internal H abstraction from HCO, or to HCO + HCO2 via rearrangement to HCOCH(O.)O. and decomposition. (The HCO would form HO2 + CO and the HCO2 would form HO2 + CO2 after reaction with O2.) These two pathways are assumed to have equal probability. Note that decomposition for these biradicals is assumed to be faster than for biradicals such as CH3CHO2 because of the weaker H-CO and C-CO bonds.

109	The vibrationally excited HCOC(CH3)CO2 biradicals are assumed to rearrange and decompose to HCOC(O)CH2. + OH, where the former forms HCOC(O). + HCHO after O2 addition and NO to NO2 conversion. RCO-O2. is used to represent HCOC(O)OO. in this reaction. Vibrationally excited CH3C(O)CHO2 is assumed to rapidly convert to HCOC(CH3)CO2 as discussed by Carter and Atkinson (1996).
118	The excited CH3C(O2)CH2OH biradical is assumed to react primarily via rearrangement to the unsaturated hydroperoxide followed by decomposition to OH radicals and the corresponding carbonyl compound, as is assumed in the general alkene mechanism (Carter, 1999b). Two possible such rearrangements can occur in the case of this biradical, one to CH2=C(OOH)CH2OH, which decomposes to OH + HOCH2C(O)CH2., and the other to HOCH=C(OOH)CH3, which decomposes to OH + CH3C(O)CH(.)OH. The relative importances of the competing rearrangements in such cases is estimated by assuming they are approximately proportional to the estimated OH abstracting rate constant from the H-donating group (Carter, 1999b). Based on this, the overall reaction is estimated to be OH + 0.04 HOCH2C(O)CH2. + 0.96 CH3C(O)CH(.)OH, with the subsequent reactions of these radicals being derived by the general estimation methods (Carter, 1999a).
110	The organic acid(s) formed in this reaction represent the formation of stabilizied Crigiee biradicals, which are assumed to be consumed primairly by reaction with H2O forming the corresponding acid.

The reactants, products and rate parameter are consistent with current knowledge but there is considerable uncertainty regarding the any potential reaction of Crigiee intermediates with H_2O.

Reaction IPN3

k(300)	A	Ea	Notes	
1.00e-13	1.00e-13		116, 106, 80	ISOPROD + NO3 = #.85 RO2-R. + #.15 MA-RCO3. + #.609 CO + #.15 HNO3 + #.241 HCHO + #.233 RCHO + #.008 MGLY + #.609 RNO3 + #.241 XN + #-.827 XC

Notes

116	As discussed by Carter (1996), isoprod is the "four product" lumped isoprene product species whose mechanism is derived by lumping rate constant and product parameters for a mixture of 30% hydroxymethacrolein, and 70% equal amounts of cis and trans HCOC(CH3)=CHCH2OH and HCOCH=C(CH3)CH2OH. These proportions are based on the estimated yields of these products in the reactions of OH with isoprene (Carter and Atkinson, 1996), which are represented by ISOPROD in the four product condensed mechanism (Carter, 1996). The other footnotes refer to the estimated mechanisms for these four individual compounds which were used to derive the lumped ISOPROD

	mechanism. RCHO, PROD2, MA-RCO3, etc. are used to represent various compounds as indicated in the descriptions of these lumped model species. See Carter and Atkinson (1996) for the specific compounds which can be formed in the various reactions of these species.
106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction IPHV

	Notes	
Phot Set= ACROLEIN qy= 4.1e-3	116,106, 80,119	ISOPROD + HV = #1.233 HO2. + #.467 CCO-O2. + #.3 RCO-O2. + #1.233 CO + #.3 HCHO + #.467 CCHO + #.233 MEK + #-.233 XC

Notes

116	As discussed by Carter (1996), isoprod is the "four product" lumped isoprene product species whose mechanism is derived by lumping rate constant and product parameters for a mixture of 30% hydroxymethacrolein, and 70% equal amounts of cis and trans HCOC(CH3)=CHCH2OH and HCOCH=C(CH3)CH2OH. These proportions are based on the estimated yields of these products in the reactions of OH with isoprene (Carter and Atkinson, 1996), which are represented by ISOPROD in the four product condensed mechanism (Carter, 1996). The other footnotes refer to the estimated mechanisms for these four individual compounds which were used to derive the lumped ISOPROD mechanism. RCHO, PROD2, MA-RCO3, etc. are used to represent various compounds as indicated in the descriptions of these lumped model species. See Carter and Atkinson (1996) for the specific compounds which can be formed in the various reactions of these species.
106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and

	alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).
119	All the species represented by ISOPROD are assumed to have the same overall photolysis rate as used for methacrolein.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction K6OH

k(300)	A	Ea	Notes	
1.60e-11	1.60e-11	--	120	PROD2 + HO. = #.373 HO2. + #.479 RO2-R. + #.068 RO2-N. + #.028 CCO-O2. + #.052 RCO-O2. + #.218 HCHO + #.083 CCHO + #.555 RCHO + #.122 MEK + #.329 PROD2 + #.872 XC

Notes

120	The PROD2 mechanism was derived by averaging mechanisms for CH3C(O)CH2CH2CH2OH, CH3C(O)CH2CH(CH3)CH2OH, CH3CH(OH)CH2CH2C(O)CH2CH3, CH3CH2CH(OH)CH2CH2C(O)CH2CH3, and CH3CH2CH2CH(OH)CH2CH2C(O)CH2CH3, which were taken as representative of the products formed from VOCs measured in ambient air that are represented by PROD2 in the model (Carter, 1999). The mechanisms for these five representative PROD2 compounds were derived using the mechanism generation and estimation methods discussed by Carter (1999).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction K6HV

	Notes	
Phot Set= KETONE qy= 1.0e-1	120,121	PROD2 + HV = #.968 RO2-R. + #.032 RO2-N. + #.708 R2O2. + #.4 CCO-O2. + #.6 RCO-O2. + #.331 HCHO + #.233 CCHO + #.878 RCHO + #-.221 XC

Notes

120	The PROD2 mechanism was derived by averaging mechanisms for CH3C(O)CH2CH2CH2OH, CH3C(O)CH2CH(CH3)CH2OH, CH3CH(OH)CH2CH2C(O)CH2CH3, CH3CH2CH(OH)CH2CH2C(O)CH2CH3, and CH3CH2CH2CH(OH)CH2CH2C(O)CH2CH3, which were taken as representative of the products formed from VOCs measured in ambient air that are represented by PROD2 in the model (Carter, 1999). The mechanisms for these five representative PROD2 compounds were derived using the mechanism generation and estimation methods discussed by Carter (1999).

121	Assumed to photolyze with the same rate absorption cross section and quantum yields as used for MEK.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction RNOH

k(300)	A	Ea	Notes	
8.50e-12	8.50e-12		122	RNO3 + HO. = #.309 NO2 + #.076 HO2. + #.426 RO2-R. + #.19 RO2-N. + #.639 R2O2. + #.026 HCHO + #.146 CCHO + #.393 RCHO + #.032 ACET + #.143 MEK + #.138 PROD2 + #.218 RNO3 + #.473 XN + #.559 XC

Notes

122	The RNO3 mechanism was derived by averaging mechanisms for CH3CH2CH2CH2CH(ONO2)CH2OH, CH3CH(CH3)CH2C(CH3)(ONO2)CH2CH3, and CH3CH2CH(ONO2)CH2CH2CH2CH3, which were taken as representative of the products formed from VOCs measured in ambient air that are represented by RNO3 in the model (Carter, 1999). The mechanisms for these three representative RNO3 compounds were derived using the mechanism generation and estimation methods discussed by Carter (1999).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction RNHV

	Notes	
Phot Set= IC3ONO2	122,123	RNO3 + HV = NO2 + #.263 HO2. + #.641 RO2-R. + #.096 RO2-N. + #.192 R2O2. + #.392 HCHO + #.085 CCHO + #.403 RCHO + #.052 ACET + #.143 MEK + #.445 PROD2 + #.251 XC

Notes

122	The RNO3 mechanism was derived by averaging mechanisms for CH3CH2CH2CH2CH(ONO2)CH2OH, CH3CH(CH3)CH2C(CH3)(ONO2)CH2CH3, and CH3CH2CH(ONO2)CH2CH2CH2CH3, which were taken as representative of the products formed from VOCs measured in ambient air that are represented by RNO3 in the model (Carter, 1999). The mechanisms for these three representative RNO3 compounds were derived using the mechanism generation and estimation methods discussed by Carter (1999).

123	Absorption cross sections given by IUPAC (Atkinson et al, 1997a, 1999) for isopropyl nitrate are used. As discussed by IUPAC (Atkinson et al, 1999), the quantum yield is expected to be near unity for formation of NO2.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction D1OH

k(300)	A	Ea	Notes	
5.00e-11	5.00e-11	--	124, 125	DCB1 + HO. = RCHO + RO2-R. + CO

Notes

124	DCB1 is used to represent aromatic ring fragmentation products that do not undergo significant photodecomposition to radicals. Its mechanism is largely parameterized, but it is based roughly on that expected for unsaturated dicarbonys such as 2-butene-1,3-dial.
125	The rate constant is based on data of Bierbach et al (1994). The reaction is assumed to proceed via addition of OH to double bond, followed by decomposition of the alkoxy radical to HCO and HC(O)CH(OH)CHO, where the latter is represented by RCHO. Although this mechanism may not be what one would estimate for the non-photoreactive unsaturated diketones (Bierback et al, 1994; Tuazon et al, ??) expected to be formed from o-substitued aromatics, best fits to the o-xylene and 1,2,4-trimethylbenzene chamber data are obtained if this mechanism is used.

The rate parameter of Bierbach et al (1994) does include a temperature dependence of k = 2.8e-11*exp(175/T). This might be included in the mechanism.

Reaction D1HV

k(300)	A	Ea	Notes	
(Slow)		--	124, 126	DCB1 + HV = HO2. + #2 CO + RO2-R. + GLY + R2O2.

Notes

124	DCB1 is used to represent aromatic ring fragmentation products that do not undergo signficant photodecomposition to radicals. Its mechanism is largely parameterized, but it is based roughly on that expected for unsaturated dicarbonys such as 2-butene-1,3-dial.
126	The photolysis action spectra of these products are assumed to be similar to that for acrolein, so the absorption cross sections of acrolein are used, with a wavelength-independent overall quantum yield. The overall quantum yield is adjusted to optimize fits of model simulations to the benzene - NOx experiments used in the optimization of the previous version of the mechanism by Carter et al (1997a), The photolyisis mechanism is represented as being similar to that used for DCB2 and DCB3. However, best fits to benzene - NOx experiments are obtained if this photolysis is assumed to be slow, so the reaction is not included in the mechanism.

The reactants, products and rate parameter are consistent with current knowledge but the reaction is uncertain due to the fitting of environmental chamber data.

Reaction D1O3

k(300)	A	Ea	Notes	
2.00e-18	2.00e-18	--	124, 127, 117	DCB1 + O3 = #1.5 HO2. + #.5 HO. + #1.5 CO + #.5 CO2 + GLY

Notes

124	DCB1 is used to represent aromatic ring fragmentation products that do not undergo signficant photodecomposition to radicals. Its mechanism is largely parameterized, but it is based roughly on that expected for unsaturated dicarbonys such as 2-butene-1,3-dial.
127	The rate constant is based on the data of Bierbach et al (1994). The reaction is assumed to involve initial formation of glyoxal and HC(O)CHO2.
117	The HC(O)CHO2 biradical can decopose either to OH + HCO + CO via an internal H abstraction from HCO, or to HCO + HCO2 via rearrangement to HCOCH(O.)O. and decomposition. (The HCO would form HO2 + CO and the HCO2 would form HO2 + CO2 after reaction with O2.) These two pathways are assumed to have equal probability. Note that decomposition for these biradicals is assumed to be faster than for biradicals such as CH3CHO2 because of the weaker H-CO and C-CO bonds.

The reactants, products and rate parameter are consistent with current knowledge.

Reaction D2OH

k(300)	A	Ea	Notes	
5.00e-11	5.00e-11	--	128, 129	DCB2 + HO. = R2O2. + RCHO + CCO-O2.

Notes

128	DCB2 and DCB3 represent the highly photoreactive unsaturated dicarbonyl product formed from the ring-opening reactions of the alkylbenzenes. To fit chamber data using differing light sources, they are represented by two species, which differ only in their action spectra and overall quantum yields, with the action spectrum of DCB2 being like methyl glyoxal, and that of DCB3 being like acrolein, and with the overall quantum yields adjusted separately to fit chamber data. Its reactions are based roughly on estimated reactions of a 5-carbon compound with general structure XC(O)CX=CXC(O)X, where X can be H or alkyl.
129	Assumed to have the same rate constant as used for DCB1. Mechanism represented as OH adding to double bond in XC(O)CX=CXC(O)X, with alkoxy radical decomposing to CH3CO. and XCO-CH(OH)-CXO, the latter being represented by RCHO. Note that the general alkoxy radical estimation method (Carter, 1999) predicts that alkoxy radicals like RCH(OH)CH(O.)C(O)R' will decompose primarily to RCH(OH)CHO + RC(O).

The rate parameter of Bierbach et al (1994) does include a temperature dependence of k = 2.8e-11*exp(175/T). This might be included in the mechanism.

Reaction D2HV

	Notes	
Phot Set= MGLY_ABS qy= 3.7e-1	128,130	DCB2 + HV = RO2-R. + #.5 {CCO-O2. + HO2.} + CO + R2O2. + #.5 {GLY + MGLY + XC}

Notes

128	DCB2 and DCB3 represent the highly photoreactive unsaturated dicarbonyl product formed from the ring-opening reactions of the alkylbenzenes. To fit chamber data using differing light sources, they are represented by two species, which differ only in their action spectra and overall quantum yields, with the action spectrum of DCB2 being like methyl glyoxal, and that of DCB3 being like acrolein, and with the overall quantum yields adjusted separately to fit chamber data. Its reactions are based roughly on estimated reactions of a 5-carbon compound with general structure XC(O)CX=CXC(O)X, where X can be H or alkyl.
130	The overall quantum yields for DCB2 and DCB3 were optimized to give best fits of model simulations of NO oxidation, O3 formation and xylene consumption in m-xylene - NOx chamber runs with various light sources, and also to mini-surrogate - NOx runs. The DCB2 and DCB3 quantum yields had to be adjusted as well as the yields of these products from m-xylene to best fit the data for the various light sources, and also to fit the results of the mini-surrogate as well as the m-xylene only runs. (For the other aromatics, only the DCB2 and DCB3 yields are optimized.) The photolysis mechanisms are unknown, and probably highly variable depending on the species involved. For an RC(O)CH=CHC(O)H structure, the most energetically favored initial reaction is formation of R. + HCOCH=CHCO., but assuming that mechanism results in a model that consistently under predicts PAN yields in alkylbenzene - NOx chamber experiments. Therefore, a set of products is assumed to be formed that may result from various different reactions, and give predictions of PAN yields that are more consistent with available chamber data.

The reactants, products and rate parameter are consistent with current knowledge but the reaction is uncertain due to the fitting of environmental chamber data.

Reaction D3OH

k(300)	A	Ea	Notes	
5.00e-11	5.00e-11		128, 129	DCB3 + HO. = R2O2. + RCHO + CCO-O2.

Notes

128	DCB2 and DCB3 represent the highly photoreactive unsaturated dicarbonyl product formed from the ring-opening reactions of the alkylbenzenes. To fit chamber data using differing light sources, they are represented by two species, which differ only in their

	action spectra and overall quantum yields, with the action spectrum of DCB2 being like methyl glyoxal, and that of DCB3 being like acrolein, and with the overall quantum yields adjusted separately to fit chamber data. Its reactions are based roughly on estimated reactions of a 5-carbon compound with general structure XC(O)CX=CXC(O)X, where X can be H or alkyl.
129	Assumed to have the same rate constant as used for DCB1. Mechanism represented as OH adding to double bond in XC(O)CX=CXC(O)X, with alkoxy radical decomposing to CH3CO. and XCO-CH(OH)-CXO, the latter being represented by RCHO. Note that the general alkoxy radical estimation method (Carter, 1999) predicts that alkoxy radicals like RCH(OH)CH(O.)C(O)R' will decompose primarily to RCH(OH)CHO + RC(O).

The rate parameter of Bierbach et al (1994) does include a temperature dependence of k = 2.8e-11*exp(175/T). This might be included in the mechanism.

Reaction D3HV

	Notes	
Phot Set= ACROLEIN qy= 7.3e+0	128,130	DCB3 + HV = RO2-R. + #.5 {CCO-O2. + HO2.} + CO + R2O2. + #.5 {GLY + MGLY + XC}

Notes

128	DCB2 and DCB3 represent the highly photoreactive unsaturated dicarbonyl product formed from the ring-opening reactions of the alkylbenzenes. To fit chamber data using differing light sources, they are represented by two species, which differ only in their action spectra and overall quantum yields, with the action spectrum of DCB2 being like methyl glyoxal, and that of DCB3 being like acrolein, and with the overall quantum yields adjusted separately to fit chamber data. Its reactions are based roughly on estimated reactions of a 5-carbon compound with general structure XC(O)CX=CXC(O)X, where X can be H or alkyl.
130	The overall quantum yields for DCB2 and DCB3 were optimized to give best fits of model simulations of NO oxidation, O3 formation and xylene consumption in m-xylene - NOx chamber runs with various light sources, and also to mini-surrogate - NOx runs. The DCB2 and DCB3 quantum yields had to be adjusted as well as the yields of these products from m-xylene to best fit the data for the various light sources, and also to fit the results of the mini-surrogate as well as the m-xylene only runs. (For the other aromatics, only the DCB2 and DCB3 yields are optimized.) The photolysis mechanisms are unknown, and probably highly variable depending on the species involved. For an RC(O)CH=CHC(O)H structure, the most energetically favored initial reaction is formation of R. + HCOCH=CHCO., but assuming that mechanism results in a model that consistently underpredicts PAN yields in alkylbenzene - NOx chamber experiments. Therefore, a set of products is assumed to be formed that may result from various different reactions, and give predictions of PAN yields that are more consistent with available chamber data.

The reactants, products and rate parameter are consistent with current knowledge but the reaction is uncertain due to the fitting of environmental chamber data.

Reaction c1OH

k(300)	A	Ea	Notes	
6.62e-15	2.15e-12	3.45	31	CH4 + HO. = H2O + C-O2.

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction ISOH

k(300)	A	Ea	Notes	
9.73e-11	2.50e-11	-0.81	131, 132	ISOPRENE + HO. = #.909 RO2-R. + #.091 RO2-N. + #.079 R2O2. + #.626 HCHO + #.23 METHACRO + #.32 MVK + #.359 ISOPROD + #-.167 XC

Notes

131	Isoprene mechanism used is based on the "four product" condensed isoprene mechanism of Carter (1996) which in turn is based on the detailed isoprene mechanism of Carter and Atkinson (1996). The rate constants and the major initial reaction pathways are the same as used in those mechanisms. Some minor changes in product yields resulted in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction schemes, or as indicated in other footnotes.
132	The overall nitrate yield is slightly higher than the adjusted nitrate yields in the Carter and Atkinson (1996) mechanism because the mechanism generation system included some nitrate formation from peroxy radicals formed in secondary reactions. Although the yields were not readjusted, the mechanism still gives satisfactory fits to the isoprene chamber data used in the nitrate yield adjustments by Carter and Atkinson (1996).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction ISO3

k(300)	A	Ea	Notes	
1.34e-17	7.86e-15	3.80	131, 108, 133, 110	ISOPRENE + O3 = #.066 RO2-R. + #.134 R2O2. + #.266 HO. + #.275 CO + #.122 CO2 + #.6 HCHO + #.1 PROD2 + #.39 METHACRO + #.16 MVK + #.2 MA-RCO3. + #.204 HCOOH + #.15 RCO-OH + #-.251 XC

Notes

131	Isoprene mechanism used is based on the "four product" condensed isoprene mechanism of Carter (1996) which in turn is based on the detailed isoprene mechanism of Carter and Atkinson (1996). The rate constants and the major initial reaction pathways are the same as used in those mechanisms. Some minor changes in product yields resulted in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction schemes, or as indicated in other footnotes.
108	The excited HCHO2 biradical is assumed to react as recommended by Atkinson (1997) based on data for the O3 + ethene system, i.e., 37% stabilization, 12% decomposition to HCO + OH, 13% decomposition to CO2 + H2, and 38% decomposition to CO + H2O. Note that this is different than used for this species when formed in the isoprene products mechanisms of Carter and Atkinson (1996) and Carter (1996).
133	The excited CH2=CHC(O2)CH3 and CH2=C(CH3)CHO2. biradical reactions are the same as given by Carter and Atkinson (1996), except that the CH2=CHC(O)O2. formed from the former is represented by MA-RCO3, and the propene formed from the latter is represented by PROD2.
110	The organic acid(s) formed in this reaction represent the formation of stabilized Crigiee biradicals, which are assumed to be consumed primarily by reaction with H2O forming the corresponding acid.

The reactants, products and rate parameter are consistent with current knowledge. The reaction of stabilized Crigiee with H_2O is highly uncertain.

Reaction ISN3

k(300)	A	Ea	Notes	
6.81e-13	3.03e-12	0.89	131, 134	ISOPRENE + NO3 = #.19 NO2 + #.76 RO2-R. + #.05 RO2-N. + #.19 R2O2. + #.95 ISOPROD + #-.05 XC + #.81 XN

Notes

131	Isoprene mechanism used is based on the "four product" condensed isoprene mechanism of Carter (1996) which in turn is based on the detailed isoprene mechanism of Carter and Atkinson (1996). The rate constants and the major initial reaction pathways are the same as used in those mechanisms. Some minor changes in product yields resulted in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction schemes, or as indicated in other footnotes.
134	All the organic products formed in this reaction are represented by ISOPROD. A small amount of nitrate formation is estimated to occur from the reactions of the substituted peroxy radicals with NO (Carter, 1999a).

The reactants, products and rate parameter are consistent with current knowledge.

Reaction ISOP

k(300)	A	Ea	Notes	
3.60e-11	3.60e-11		131, 135	ISOPRENE + O3P = #.25 RO2-R. + #.25 R2O2. + #.5 HCHO + #.75 PROD2 + #.25 MA-RCO3. + #-1 XC

Notes

131	Isoprene mechanism used is based on the "four product" condensed isoprene mechanism of Carter (1996) which in turn is based on the detailed isoprene mechanism of Carter and Atkinson (1996). The rate constants and the major initial reaction pathways are the same as used in those mechanisms. Some minor changes in product yields resulted in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction schemes, or as indicated in other footnotes.
135	PROD2 is used to represent the various isoprene oxide products. And MA-RCO3 us used to represent CH2=CHC(O)OO. Note that this mechanism, which is based on that of Carter and Atkinson (1996) is inconsistent with the mechanisms for the reactions of O3P with the other higher alkenes, which are assumed not to form radical products. However, assuming no radical formation in the reaction of O3P with isoprene results in somewhat degraded model performance in simulations of the results of the isoprene experiments discussed by Carter and Atkinson (1996).

The reactants, products and rate parameter are estimated and therefore have a high degree of uncertainty. The reaction is probably not important in air under most conditions.

3. Evaluation of the VOCs Represented Using the Assigned Mechanistic Parameter Method

Atmospheric chemical mechanisms can be generated through the use of computer based methods. These automatic procedures should allow mechanisms to be generated more objectively and with fewer typographical errors than manual molecule-by-molecule assignments. In the new version of the SAPRC mechanism, Dr. Carter has expanded the use of objective measures to include almost all organic compounds except for the chemistry of aromatics and terpenes.

The SAPRC automatic mechanism generation procedure treats the reaction of HO with all organic compounds of atmospheric interest. The group additivity methods for the reactions of HO with organic compounds as developed by Kwok and Atkinson (1995) and Kwok et al. (1996) are well established. The SAPRC automatic mechanism generation procedure treats the reaction of alkenes and selected dialkenes with O_2, O^3P and NO_3; and it treats the photolysis of carbonyls and organic nitrates. The range of organic species treated by this software is adequate for most VOCs that are now emitted into the atmosphere. But the range of reactions might require expansion to treat new low reactive organic compounds that may be emitted due to the effects of reactivity based emission regulations. The treatment of reduced sulfur containing compounds might be useful for certain applications.

The mechanism generation program on the web was examined. The system was relatively easy to use and the online documentation although brief was clear. The method of specifying the structures of organic compounds is logical and it should be possible to specify the organic compounds treatable by the program. It would be helpful if more detailed instructions were provided for first-time users.

HO REACTIONS

The approach to estimating the HO rate constants for the rate parameters, excluding propene from the calculation of group rate constants for monosubstituted alkenes, is valid since the estimates will be made for the higher molecular weight compounds. The exclusion of abstraction reactions from alkenes also seems to be a valid simplification due to the lack of estimation methods for unsaturated radicals.

The methods for estimating the products for the reactions of HO with alkenes depend upon data with some significant uncertainties. In contrast to the rate constants the fraction of HO radicals that react with the least substituted end of a double bond is very poorly known. The only available experimental data are available for terminal alkenes, CH2=CH-. The only available data (Cvetanovic, 1976) was only published as a conference proceeding. For all other alkenes the fraction of HO radicals that react with the least substituted end of a double bond are estimated on the basis of little data. New measurements are required to determine the site of HO addition to alkenes.

One concern is that the HO rate parameters for compounds containing oxygen tend to be the most inaccurate. The difference between the estimated and measured values for some oxygenated compounds is greater than 400% (Table II-8 in the mechanism documentation). Since many of the proposed substitute low reactivity organic compounds are highly oxygenated compounds this may represent a significant source of uncertainty in the calculations.

NO_3 REACTIONS

The discussion on the treatment of NO_3 radical reactions by the SAPRC automatic mechanism generation procedure needs to be clarified in places. The following needs to be said more clearly. The program considers only the abstraction of hydrogen atoms by NO_3 from aldehydes and the addition of NO_3 to alkenes. If rate constants for the abstraction of hydrogen atoms by NO_3 from aldehydes are estimated then the same rate parameter for the reaction of NO_3 from acetaldehyde is used. If the compound is a acid R-(CO)OH or a formate $X^+H(CO)O^-$ than the rate parameter is assumed to be zero.

These assumptions are reasonable but as noted for Reaction PAN3 this procedure may underestimate the rate parameter for this reaction. Figure 2 in Atkinson (1991) suggests that there is a roughly log-linear relationship between k_{HO} and k_{NO3} for HCHO and CH3CHO that may extend to higher aldehydes. For example, if the most recent values for k_{HO} and k_{NO3} for HCHO and CH_3CHO are fit, extrapolation yields a k_{NO3} of 5.0E-15 for propionaldehyde if a k_{HO} of 2.0E-11for propionaldehyde is assumed.

The addition of NO_3 primarily to the least substituted end of a molecule is a reasonable assumption but there are much less data available to support this assumption than available for the addition reactions of HO with alkenes.

Assigned NO_3 Radical Rate Constants

It should be stressed that there is very limited data available for the abstraction of hydrogen atoms from -CHO groups. Data is available for only HCHO and CH_3CHO.

Estimated NO_3 Radical Rate Constants

Dr. Carter's discussion is a significant improvement over previous treatments. In comparison with hydroxyl radical reactions there is little data available for NO_3 that can be used to estimate trends. More data is required to reduce the uncertainties in NO_3 radical rate parameters.

Assigned Mechanisms for Initial NO_3 Reactions

There is very little data available on these mechanisms. The uncertainty in the mechanisms for the reactions of NO_3 is extremely high.

O_3 REACTIONS

There are much more data available for the reactions of ozone with alkenes and measured rate parameters are used for most of the O_3 - VOC reactions in the mechanism. The use of average rate parameters for alkenes according to the number of substitutents on the double bond is the best that can be done now but this procedure is highly uncertain. From the trends in the rate parameters it appears that steric effects compete with electron donating effects in the determination of the rate parameters. The treatment of the branching ratios for biradical formation are consistent with the available data.

Assigned O_3 Rate constants

There is much data available for the alkenes in the emission inventories and Dr. Carter's choices are reasonable.

Estimated Total Rate Constants

Dr. Carter shows that there is considerable variation in the rate parameters for the O_3 + alkene reactions for alkenes with the same configurations of constituents attached to the double bond. This high variability in the rate parameters makes estimation very difficult. Dr. Carter's approach is reasonable but new methods for estimating the impact of steric effects on the O_3 + alkene rate parameters need to be developed.

Branching Ratios for Biradical Formation

Dr. Carter's approach is reasonable given the available data.

Assigned Mechanisms for Initial O_3 Reactions

Dr. Carter's approach is reasonable given the available data.

In Table 21 the "excited" label seems redundant and misplaced. The "excited" label is always on the -OO- although the entire reactive intermediate is excited.

O^3P REACTIONS

It is valid to include these reactions in the mechanism due to the possibility of it being used to describe the chemistry of plumes with relatively high pollutant concentrations or for the mechanism's evaluation by environmental chamber data. The rate parameters for these reactions are relatively well known but the mechanisms of these reactions are poorly known. Environmental chamber data are not fit well by mechanisms that incorporate recently measured branching ratios. Given the importance of chamber data in the evaluation of mechanisms this introduces some uncertainty in their evaluation and could involve compensating errors. Further research is required to evaluate the mechanisms of O^3P reactions.

The treatment of these reactions is reasonable but the most of the data are old from Atkinson and Lloyd (1984). The reactions of O^3P are not very important for most atmospheric conditions. These reactions may be important when chamber experiments are used to evaluate the mechanism due to the high VOC concentrations used in chamber experiments.

Assigned O^3P Rate Constants

Dr. Carter's approach is reasonable given the available data.

Estimated O^3P Rate Constants

Dr. Carter's approach is reasonable given the available data.

Estimated Mechanisms for O^3P Reactions

These mechanisms appear to be uncertain because the best available data does not give simulations that test well against chamber data. This may represent an important uncertainty if these reactions affected the evaluation of the mechanism when it was tested against chamber data.

Assigned Mechanisms for Dialkenes

Dr. Carter's approach is reasonable given the available data.

Photolysis Reactions

In this section the term "photolysis rate" is misleading. It would be much better to replace "photolysis rate" with the term "photolysis rate parameter" or "photolysis frequency". A photolysis rate is the product of a photolysis rate parameter and the concentration of the chemical species that is undergoing photolysis.

It is not completely clear how "groups" are counted in Table 26. For example, is CH_3-CH_2-CO-CH_2-CH_2-CH_3 a molecule with 6 groups?

The cross sections and quantum yields of higher carbonyl compounds are assumed to be the same as those for lower molecular weight carbonyl compounds. The most chemically similar compound is chosen from those available. The same procedure is applied for organic nitrates. This is a reasonable procedure and an advance over the previous mechanism.

The assumption that the carbonyl compounds break along the -CHO bond is consistent with acetaldehyde photolysis and the assumption that ketones break along the bond with the lowest estimated heat of reaction is consistent with the photolysis of methyl ethyl ketone. These are reasonable assumptions to apply to estimate the photolysis mechanisms of other aldehydes and ketones. The use of specific mechanisms for the photolysis of unsaturated aldehydes is reasonable.

The assumptions regarding the cross sections and that the quantum yield for the formation of NO_2 from organic nitrate photolysis appear to be valid.

Default Carbonyl Unsaturated Carbonyl and Organic Nitrate Photolysis Photolysis Mechanisms

The treatment of these reactions is reasonable.

Reactions of Carbon Centered Radicals

Dr. Carter's approach is reasonable given the available data. There are significant uncertainties in the treatment of allylic radicals. As Dr. Carter points out the treatment of allylic radicals is not always consistent. The inconsistencies in the treatment of allylic radicals are due to need to be consistent with product data.

Reactions of Peroxy Radicals

The fraction of peroxy radicals that react to produce organic nitrate is an important sink of NO_x. From the discussion given on page 89 it appears that earlier measurements of the organic nitrate yield were too high. Lower yields of organic nitrates lead to better fits of chamber experiments. However, Dr. Carter states at the end of the first paragraph: "Therefore, the earlier nitrate yields of Atkinson et al (1982b, 1983b, 1984), which are all based on similar analytical methods, appear to be low." Does he not mean high?

The data set is not extensive enough to allow trends to be estimated accurately. For example, the data in Figures 5 and 6, pages 99 and 100 respectively, show no trends if each class of organic compound is examined individually.

Reactions of Alkoxy Radicals

H-Shift Isomerizations

Dr. Carter's approach is reasonable given the available data.
The acronym BDE (bond dissociation energy) should be defined at the top of page when it is first used.

Beta Scission Decomposition

For Table 34 the criteria for judging the quality of the agreement between estimation and experimental are not clear. What level of agreement is "ok"? It is more important to have good agreement with the minimum, "Exp'd" or maximum values? Is "Exp'd" the best experimental value?

Isomerization Corrections, Ester Rearrangement, Acyloxy Radicals, Explicit Alkoxy Reaction Assignments

Dr. Carter's approach is reasonable given the available data.

Thermochemical Assignments Used in Estimates

Dr. Carter's approach is reasonable but it appears that the more recent data needs to be incorporated in to the database in the future.

Reactions of Crigiee Biradicals

Dr. Carter's approach is reasonable given the available data.

$HCHO_2$ Biradicals, $RCHO_2$ Biradicals and R_2COO Biradicals

Dr. Carter's approach is reasonable given the available data.

Page 152 is the "size" of a substituent is much more clearly defined here than the number of "groups" in Table 26.

Assigned Reactions of α-Carbonyl or Unsaturated Crigiee Biradicals

Dr. Carter's approach is reasonable given the available data.

Lumping Assignments

Dr. Carter's approach is reasonable and the description is clear.

Representation of Aromatics

Aromatics, Benzene, Terpenes and Other Compounds

Dr. Carter's approach is reasonable given the available data. It is important to stress that these mechanisms are based on fits to chamber data and that there is uncertainty in extrapolating these results to the real atmosphere.

Detailed Model Species

The choice of the acronym DMS is unfortunate because it often means dimethyl sulfide. I suggest avoiding this acronym in this report.

4. Evaluation of the Use of the "Lumped Molecule" Approach

It is not possible to represent all possible chemical reactions explicitly in the mechanism because of unknowns in the chemistry and also because of the potentially excessive demands on computational resources. It is currently not possible to run a complex 3-d air quality model with a mechanism with thousands of chemical species and reactions. Current detailed chemical mechanisms do contain over 10,000 reactions and species to describe the chemistry of about 100 emitted organic species.

The “lumped molecule” approach refers to model species that react with average rate parameters and average product yields. But it must be recognized that it is unavoidable that information must be lost when different real species are grouped or "lumped" together into model species.

The lumped molecule approach is applied to the chemistry of some of the higher ketones, alcohols and other highly reactive saturated oxygenated compounds that are not aromatics or aldehydes. These compounds represent product species that are more reactive than methyl ethyl ketone. The model PROD2 is used to represent these species. The approach is also applied to the chemistry of various organic nitrates and these are represented as RNO3.

The procedure used to derive the rate parameters and product yields for the model species is valid. Tables 4 and 5 in the mechanism documentation that describe the contributions of various types of model species in the base ROG mixture to the formation of the PROD2 and RNO3 lumped product species, respectively, were examined and appear to be reasonable. The range of compounds represented by PROD2 and NO_3 as given in Tables 6 and 7, respectively, of the mechanism documentation are also reasonable. Given the large number of compounds that could be in the mechanism if they were all explicitly included in the mechanism and the uncertainties in their individual chemistries this lumped approach is both necessary and reasonable.

The lumped molecule approach is applied very heavily to uncharacterized aromatic ring products. There is not yet sufficient understanding to treat the aromatic reaction mechanism from a fundamental and explicit point of view. The model species DCB1, DCB2 and DCB3 are used to characterize the reactivity of uncharacterized ring-fragmentation products. The names are appropriate because these compounds are probably dicarbonyls. DCB1 reacts with HO and ozone but it does not undergo significant photolysis. DCB2 and DCB3 photolyize rapidly enough that the ozone reaction is assumed to be negligible. The reactions of HO with DCB2 and DCB3 are included.

The reactions of the lumped aromatic species are based on fits of environmental chamber data as all other atmospheric chemistry mechanisms for air quality modeling. This does introduce significant uncertainty into the mechanism when it is applied to aromatic species. However mechanisms are improving due to the studies cited by Carter in the documentation.

There are several “unreactive species” that are within the category of lumped molecule species. These are treated sufficiently well within the mechanism

5. Evaluation of the Handling of Uncertainty in both the MIR and the Regulation

Sources of Mechanistic Uncertainty

There are many sources of uncertainty in current atmospheric chemistry mechanisms for air quality modeling. These are described relatively well in the mechanism documentation. Dr. Carter is to be commended for developing a high quality mechanism that is within the state of the science for air quality modeling. The mechanism makes full use of the available kinetic data and reflects the considerable progress that has been made in improving our understanding of atmospheric chemistry. However there remain several important outstanding issues to be resolved by further experimental studies.

Better mechanistic data for most higher molecular weight organic compounds and their photooxidation products are needed. Most of the mechanism for compounds with carbon numbers greater than 3 or 4 are based on analogy with the reactions and rate parameters of lower molecular weight compounds. While the rate parameters for the reactions of HO with a wide range for parameters are relatively well known, in contrast, much more data are needed for the rate parameters for the reactions of NO_3 and O_3. It is surprising that rate constants for the reactions of NO_3 with many higher aldehydes are not available. The quantum yields, absorption cross sections and product yields for photolysis reactions for most higher aldehydes, ketones, alcohols, dicarbonyls and similar compounds are not well known.

More data are required for the product yield for the reactions of HO, NO_3 and O_3 with alkenes. HO and NO_3 add to the double bonds of alkenes but the site is relatively unknown. There is a little data available for the site of the HO addition but almost no available information available for NO_3. For some alkenes this uncertainty may affect the estimated organic product yields. Given the relatively high reactivity of alkenes this may be significant.

The product yields for the reactions of ozone with alkenes are in relatively better condition than they are for either the HO or NO_3 reactions. But product yields for the reactions of ozone with alkenes could be better characterized especially for any Criegee biradicals beyond those produced from ethene and propene. The required data include the nature and yield of radicals and organic acids.

Better data are required for the reactions of peroxy radicals with NO_3 and for their reactions with other RO_2. The reactions of NO_3 with RO_2 are important during the night when NO_3 concentrations may be high (Stockwell et al., 1995). The reactions of RO_2 with RO_2 may be important under some nighttime conditions and when there are low concentrations of nitric oxide (Stockwell et al., 1995).

The mechanism for aromatic species is not known in explicit detail and therefore the uncertainties are very high. There has been much progress during recent years but the nature of many products remains unknown. Especially the nature of the ring fragmentation products has not been determined. All aromatic chemistry mechanisms for air quality models are based upon parameterizations from environmental chamber experiments. It is possible that the parameterizations are not always applicable to the real atmosphere.

The mechanism is clearly within the realm of the best available science. Air quality models that make use of previous versions of Dr. Carter's mechanism should update to this new version. But are the uncertainties low enough that the mechanism can be used to reliably estimate the incremental reactivity of VOCs for regulatory purposes? Russell et al. (1995) examined this question for a previous version of Dr. Carter's mechanism. They found that although there was significant uncertainty in the calculated MIR and MOIR values that the relative relationships between the incremental reactivities were relatively robust. This would be expected to be true of the MIR and MOIR values calculated using the present mechanism with significantly reduced uncertainty.

Treatment of Mechanistic Uncertainties in the Regulation

Evaluation of Dr. Carter's Scheme for Classifying Mechanistic Uncertainties

In this section Dr. Carter's uncertainty scheme and its application to MIR value uncertainties is evaluated. Dr. Carter defines 6 categories or "bins" to describe the "certainty" of the chemical mechanism used to determine MIR values. There are 5 additional footnotes that can be applied to the categories. The uncertainty scale, Table 5-1, is subjective but it is Dr. Carter's best judgment of a chemical mechanism's certainty for an organic compound and its effect on a compound's estimated MIR value.

The uncertainty scheme must be understandable to the stakeholders and the general public so it must be relatively simple. It is proposed for the regulation that these 6 bins should be used as a basis for estimating an uncertainty in an organic compound's MIR. For regulatory uses Dr. Carter suggests that compounds in uncertainty bins 1 through 3 have no adjustments to their MIR values because their MIRs would be expected to change by no more than a factor of two. Dr. Carter suggests that compounds in bins 4 through 6 should have an uncertainty adjustment factor because of their MIRs' greater potential for change.

Some measure of the uncertainty in a MIR is required to account for the possibility that a MIR value could change due to new mechanistic data. If a MIR increases in the future due to new data, an air quality disbenefit could result unless the reactivity based regulation makes some allowance for present uncertainty. Consideration of uncertainty in the regulation is required because both regulators and other stakeholder need to account for the "stability" of the MIR value.

Table 5-1. Dr. W.P.L. Carter's "certainty" scale for MIR values.

Certainty Code	Description
-	No representation of this compound has been developed for this version of the mechanism.
0	Compound believed to be unreactive.
1	Considered to be relatively certain, or some uncertainties but reactivity is not expected to change significantly.
2	Uncertain mechanism may change somewhat if refined, but change is expected to be less than a factor of two. If the compound is predicted to inhibit O_3, changes are not expected to affect predicted inhibition, but may affect magnitude of inhibition. This code is also used for (1) compounds whose reactivities are expected to be sensitive to the representation of the reactive products, whose accuracy is difficult to test experimentally and (2) compounds whose reactivities are expected to be highly sensitive to ambient conditions or to changes in the base mechanism.
3	Uncertain and may change if compound is studied (or studied further) or estimation methods are updated. Change in MIR could be as much as a factor of two. This code is also used for (1) compounds whose reactivities are expected to be sensitive to the representation of the reactive products, whose accuracy is difficult to test experimentally and (2) compounds whose reactivities are expected to be highly sensitive to ambient conditions or to changes in the base mechanism.
4	Uncertain and is expected to change if compound is studied or estimation methods are updated. It is recommended that uncertainty adjustments be employed in regulatory applications.
5	Non-negligible chance of the estimate being incorrect in significant respects. It is recommended that uncertainty adjustments be employed in regulatory applications.
6	Current mechanism is probably incorrect, but biases in atmospheric reactivity predictions are uncertain. It is recommended that uncertainty adjustments be employed in regulatory applications.

Table 5-1, continued. Dr. W.P.L. Carter's "certainty" scale for MIR values.

Certainty Code Footnotes	Description
a	The reactivity of this compound is expected to be sensitive to ambient conditions and/or changes in the base mechanism.
b	Some uncertainty due to differences in reactivities of compounds represented by this class. Look at differences among compounds in this class for the magnitude of this uncertainty.
c	Parameterized mechanism used, with uncertain portions adjusted to fit chamber data for representative compounds.
d	Highly simplified "Placeholder" mechanism used to represent the approximate range of reactivity of this compound. Mechanism does not represent an estimate of the actual mechanism of the compound.
e	The current version of this mechanism does not represent these compounds, but based on previous studies they are expected to be O_3 inhibitors under all conditions.

The scheme in Table 5-1 is reasonable way to assign uncertainties to an overall mechanism and Dr. Carter has made reasonable assignments of uncertainty to the compounds in his new mechanism. This scheme is an advance over the scheme presented in Carter (1994) as discussed below.

Evaluation of the Stability of MIR Values and Uncertainty Multipliers from Monte Carlo Analysis

It is difficult to estimate what effect new data will have on any compound's MIR. The uncertainty scale developed by Carter (1994) was somewhat different from his 1999 scale but bin 1 represents the most certain mechanism and bin 9 represents the least certain mechanism, Table 5-2. Both scales are an acceptable measure of uncertainty in Dr. Carter's mechanisms.

Table 5-2. Dr. W.P.L. Carter's "certainty" scale for MIR values from Carter (1994).

Certainty	Description
1	Least uncertain mechanism, and tested against chamber data.
2	Mechanism probably not uncertain, but was not tested.
3	Laboratory data are available for the major reactions in the mechanism, but the mechanism was not tested.
4	Uncertain portions of the mechanism are adjusted or parameterized to fit chamber data.
5	The mechanism is uncertain, and only limited or uncertain data were available to test it.
6	The mechanism was not optimized to fit existing chamber data.
7	The mechanism was estimated and was not tested.
8	The mechanism was estimated and was not tested, and must be considered to be highly uncertain.
9	The mechanism was estimated and was not tested, and is likely to be incorrect. Suitable only for estimating reactivities of mixtures where this is a component.

A concern is that, since MIRs are calculated for mixtures of organic compounds, the MIR for even a compound with a relatively certain mechanism might still have an uncertain MIR because of the interactions between all of the oxidation mechanisms. Thus it is difficult to assign MIR multiplication factors to account for the uncertainty in the mechanisms of individual compounds. To examine this question we examined coefficients of variation for the MIRs calculated by Yang (1995), these are given in Table 5-3 along with the assigned uncertainties from Carter (1994).

Yang (1995) performed Monte Carlo calculations based on mechanistic uncertainties in rate parameters and product yields. The analysis of mechanistic uncertainties in rate parameters and product yields was based on a detailed analysis of the uncertainties in each reaction (Yang et al., 1995). The coefficient of variation for a compound as determined from the Monte Carlo calculations is the standard deviation of its MIR divided by its mean value (Yang, 1995). The average coefficient of variation in Table 5-3 is 0.42 and Figure 5-1 shows that there is no correlation between the coefficients of variation and the assigned mechanistic uncertainty values.

The work of Yang (1995) has been updated recently (L. Wang and J.B. Milford, private communication). Table 5-4 gives new coefficients of variation for the 1997 version of the SAPRC mechanism and Carter's mechanistic uncertainty assignments for 1999. The coefficients of variation are lower with an average coefficient of variation of 0.29. Figure 5-1 shows a plot of the new coefficients of variation as a function of the mechanistic uncertainty assignments. The updated coefficients of variation do not correlate well with assigned mechanistic uncertainty values.

On the basis of these two studies the average coefficient of variation has decreased from 0.42 to 0.29. These studies also show that the coefficient of variation is not very dependent on the assigned mechanistic uncertainty. On this basis it would be better to assume that the one-sigma uncertainties are at least ±30% and that a multiplier of 1.3 would be more realistic. However, the historical record supports a somewhat higher multiplier to the absolute MIRs.

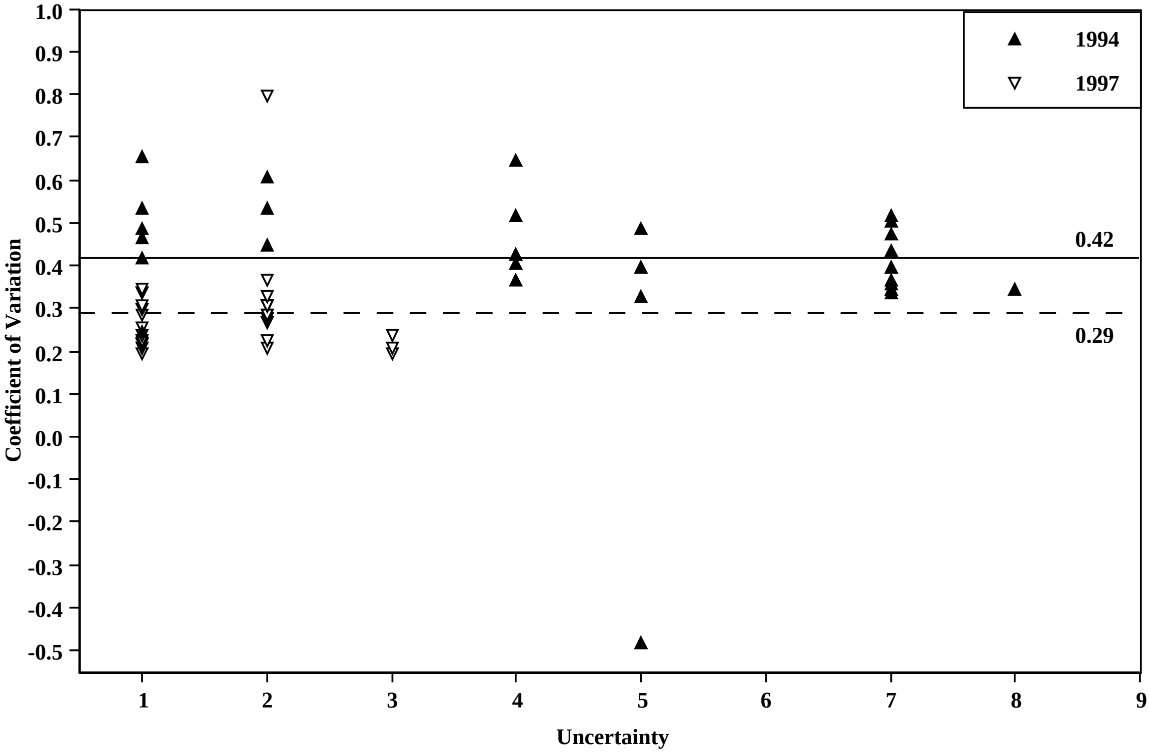
Table 5-3. Coefficients of variation from (Yang, 1995) and mechanistic uncertainties from Carter (1994).

Compound	Coefficients of Variation	1994 Mechanistic Uncertainty
Formaldehyde	0.25	1
Ethene	0.42	1
Ethanol	0.66	1
Methanol	0.47	1
Butane	0.54	1
MTBE	0.49	1
Propane	0.54	2
Ethane	0.61	2
Methane	0.45	2
Propene	0.37	4
Acetaldehyde	0.41	4
m,p Xylene	0.43	4
Toluene	0.52	4
Benzene	0.65	4
Propionaldehyde	0.40	5
Methylethylketone	0.49	5
Acetone	0.33	5
Benzaldehyde	-0.48	5
124-trimethylbenzene	0.37	7
3-m-Cyclopentene	0.35	7
2-m-2-Butene	0.34	7
2-m-1-Butene	0.36	7
m-cyclopentane	0.44	7
Ethylbenzene	0.52	7
ETBE	0.40	7
2-m-Pentane	0.48	7
224-tri-m-Pentane	0.51	7
1,3-Butadiene	0.35	8

Table 5-4. Coefficients of variation from (L. Wang and J.B. Milford, private communication) and mechanistic uncertainties from Carter (1999).

Compound	1997 Coefficients of Variation	1999 Mechanistic Uncertainty	Compound	Coefficients of Variation	1999 Mechanistic Uncertainty
Isoprene	0.20	1	Methylcyclopentane	0.29	2
Acetaldehyde	0.21	1	2-Methyl-2-Butene	0.29	2
Propene	0.21	1	n-Hexane	0.31	2
trans-2 Butene	0.22	1	1,3,5-Trimethyl Benzene	0.31	2
Acetone	0.23	1	1,2,3-Trimethyl Benzene	0.31	2
Ethene	0.24	1	Benzene	0.31	2
2-Butoxy Ethanol	0.24	1	2-Methyl Pentane	0.31	2
C4 Ketones	0.26	1	1,2,4-Trimethyl Benzene	0.33	2
Methane	0.29	1	n-Butyl Acetate	0.37	2
Methyl t-Butyl Ether	0.30	1	Benzaldehyde	0.80	2
Propane	0.31	1	2-Methyl-1-Butene	0.20	3
Ethane	0.34	1	1,3-Butadiene	0.21	3
Ethanol	0.34	1	Ethyl t-Butyl Ether	0.24	3
Methanol	0.34	1			
n-Butane	0.35	1			
a-Pinene	0.21	2			
C3 Aldehydes	0.23	2			
Formaldehyde	0.27	2			
o-Xylene	0.27	2			
Toluene	0.27	2			
p-Xylene	0.28	2			
Ethyl Benzene	0.28	2			
m-Xylene	0.29	2			

Figure 5-1. The filled triangles, labeled 1994, represent coefficients of variation for 1994 version of the SAPRC mechanism (Yang, 1995) as a function of the assigned mechanistic uncertainties from Carter (1994). The open triangles, labeled 1997, represent coefficients of variation for 1997 version of the SAPRC mechanism (L. Wang and J.B. Milford, private communication) and their assigned mechanistic uncertainties by Carter in 1999. The solid line represents the mean of the coefficients of variation for 1994 version of the SAPRC mechanism while the dashed line represents the mean of the coefficients of variation for 1997 version of the SAPRC mechanism.



Evaluation of the Stability of MIR Values and Uncertainty Multipliers from Experience

Since Dr. Carter provided MIR values and estimates of their uncertainty in Carter (1994), it is possible to evaluate how these have changed between 1994 and the currently available values. Comparison of the percent change in MIR values between 1994 and 1999 is an estimate of the stability of MIR values. When the changes in MIR values between 1994 and 1999 are compared with the assigned uncertainties from 1994 the effect of uncertainty can be estimated. However, in 1999 there is much more data available than in 1994 and Dr. Carter has incorporated this new data into his mechanism so it would be expected that this approach might yield an overestimate of the instability of MIR values and of the uncertainty multipliers that should be assigned to the MIRs.

The compounds with the greatest percent change in their MIRs are listed in Table 5-5. These compounds include aromatic species and their products, higher molecular weight alkanes, acetylenes and 2-methyl-2-butene. The high percent changes in the MIRs of the acetylenes, aromatic species and glyoxal (a product of aromatic oxidation) is understandable due to the fact that the mechanisms of these species is derived to a great extent from environmental chamber fitting. The percent change in the MIRs of higher molecular weight alkanes and 2-methyl-2-butene may be due to uncertainties in the yields of organic nitrates for higher molecular weight organic compounds. In any case Dr. Carter should explain the large differences in the MIRs of these compounds in the final version of his mechanism documentation.

In Table 5-6 the mechanistic uncertainty, MIRs, relative MIRs, the percent change in the MIRs and relative MIRs, the rank of the MIRs and the difference in the rank of the MIRs between Carter (1994) and SAPRC 1999 are shown for the compounds that were common to both assessments. The most reactive compound has a rank equal to 1 and the least has a rank of 116. The compounds with the greatest percent change in their MIRs, listed in Table 5-5, are shown in bold font in Table 5-6.

Figures 5-2 and 5-3 show a comparison of the ranks of the MIR values determined in 1994 with those determined in 1999. In these figures the rank of the 1999 MIR is plotted as a function of the rank of the 1994 MIR. The diagonal line represents the line of perfect agreement between the two rankings. The assigned uncertainty (Carter, 1994) is given in the center of each data point. Figure 5-2 is the same as Figure 5-3 except only the ranks of the 50 most reactive compounds are plotted.

Figures 5-2 and 5-3 show that the relative ranking of the MIR values was remarkably stable between 1994 and 1999. The greatest changes in the ranking of the MIRs have occurred for compounds with assigned uncertainties greater than 5 except for one point with an uncertainty of 3. A large changed occurred for glyoxal which was assigned to bin 3 but its MIR changed by 573%. Overall, this stability is surprising because of the relatively high uncertainty in the mechanisms assigned in 1994. This result supports the hypothesis that MIRs can be used in a relative fashion and this result is in accord with Russell et al. (1995).

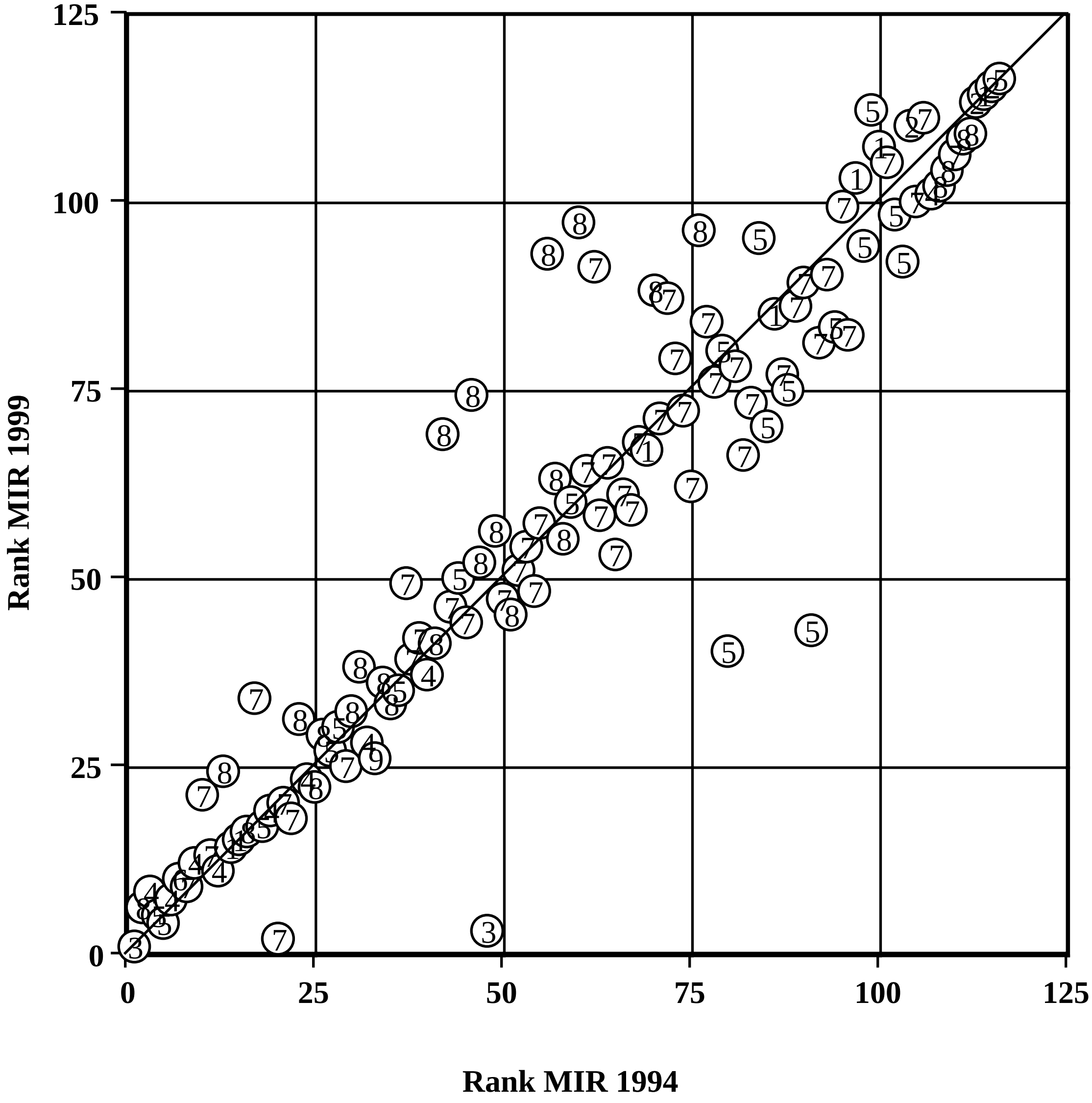
The percent change in the MIR values between 1994 and 1999 as a function of the assigned uncertainty (Carter, 1994) is plotted in Figure 5-4. The 1999 MIR values are an average of 43% greater than the values estimated by Carter (1994). This suggests that a multiplier of 1.5 would be more realistic. Also, Figure 5-4 shows that in general the greater the assigned mechanistic uncertainty the greater the percent change between 1994 and 1999. Since compounds with greater uncertainties may have greater changes in their MIR values the values should be multiplied by a greater uncertainty factor.

Figure 5-5 shows a plot of the percent change in the relative MIR values between 1994 and 1999 as a function of the assigned uncertainty (Carter, 1994). The percent change in the relative MIR values shows the same trends as the percent change in the MIR values but the average relative MIR increased by only 13%. The relative MIR values are more robust than the absolute MIRs and this result is in agreement with the results plotted in Figures 5-2 and 5-3.

Table 5-5. The compounds with a percent change greater than 50% in their MIRs between Carter (1994) and SAPRC 1999.

Compound	Change in MIR (Percent)	Compound	Change in MIR (Percent)
Glyoxal	573.09	n-Heptane	82.73
Tetralin	219.73	2,2-Dimethylbutane	77.22
Naphthalene	198.21	n-Hexane	74.55
Acetylene	161.17	2,2,4-Trimethylpentane	70.41
2-Methyl-2-Butene	133.87	n-Pentane	70.30
n-Tetradecane	127.17	Phenol	68.75
n-Tridecane	118.73	3-Methylheptane	67.12
Benzene	116.88	Methylacetylene	63.53
n-Octane	113.14	2-Methylhexane	60.85
3,3-Dimethylpentane	112.60	Cyclohexane	57.64
n-Dodecane	111.87	Toluene	57.02
n-Undecane	110.32	3-Methylpentane	54.97
n-Decane	110.11	2-Methylheptane	52.32
Neopentane	107.56	2,2,5-Trimethylhexane	51.32
n-Nonane	103.28		

Figures 5-2. A comparison of the rankings of the MIR values determined in 1994 with those determined in 1999. The rank of the 1999 MIR is plotted as a function of the rank of the 1994 MIR. The most reactive compound was assigned a rank of 1 and the least reactive compound was assigned the highest rank, 116. The diagonal line represents the line of perfect agreement between the two rankings. The assigned uncertainty (Carter, 1994) is given in the center of each data point.



Figures 5-3. A comparison of the ranks of the MIR values determined in 1994 with those determined in 1999 for the 50 most reactive compounds. The rank of the 1999 MIR is plotted as a function of the rank of the 1994 MIR. The most reactive compound was assigned a rank of 1 and the least reactive compound in this plot was assigned the highest rank, 50. The diagonal line represents the line of perfect agreement between the two rankings. The assigned uncertainty (Carter, 1994) is given in the center of each data point.

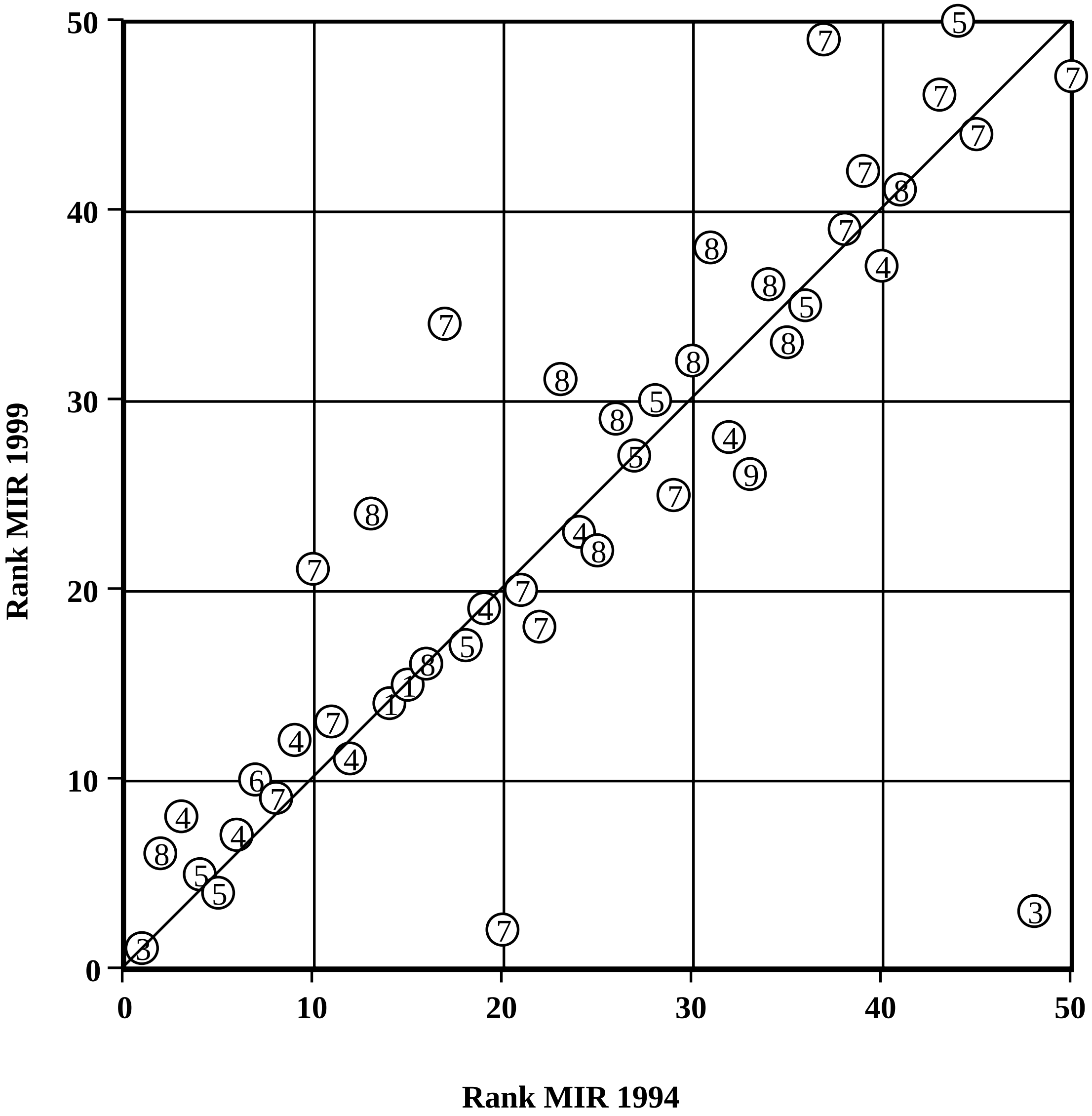


Figure 5-4. The percent change in the MIR values between 1994 and 1999 plotted as a function of the assigned uncertainty (Carter, 1994).

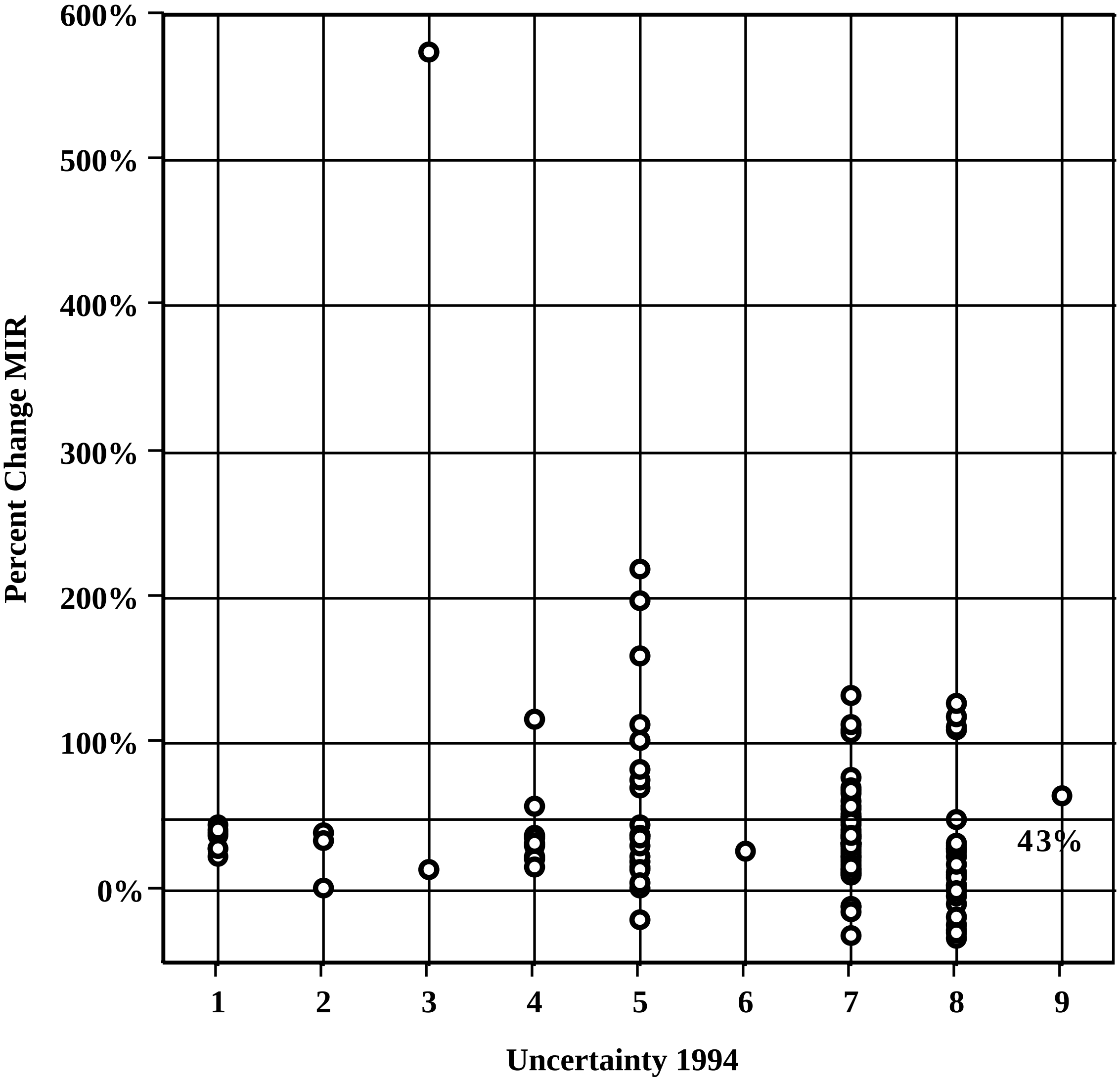


Figure 5-5. The percent change in the relative MIR values between 1994 and 1999 plotted as a function of the assigned uncertainty (Carter, 1994).

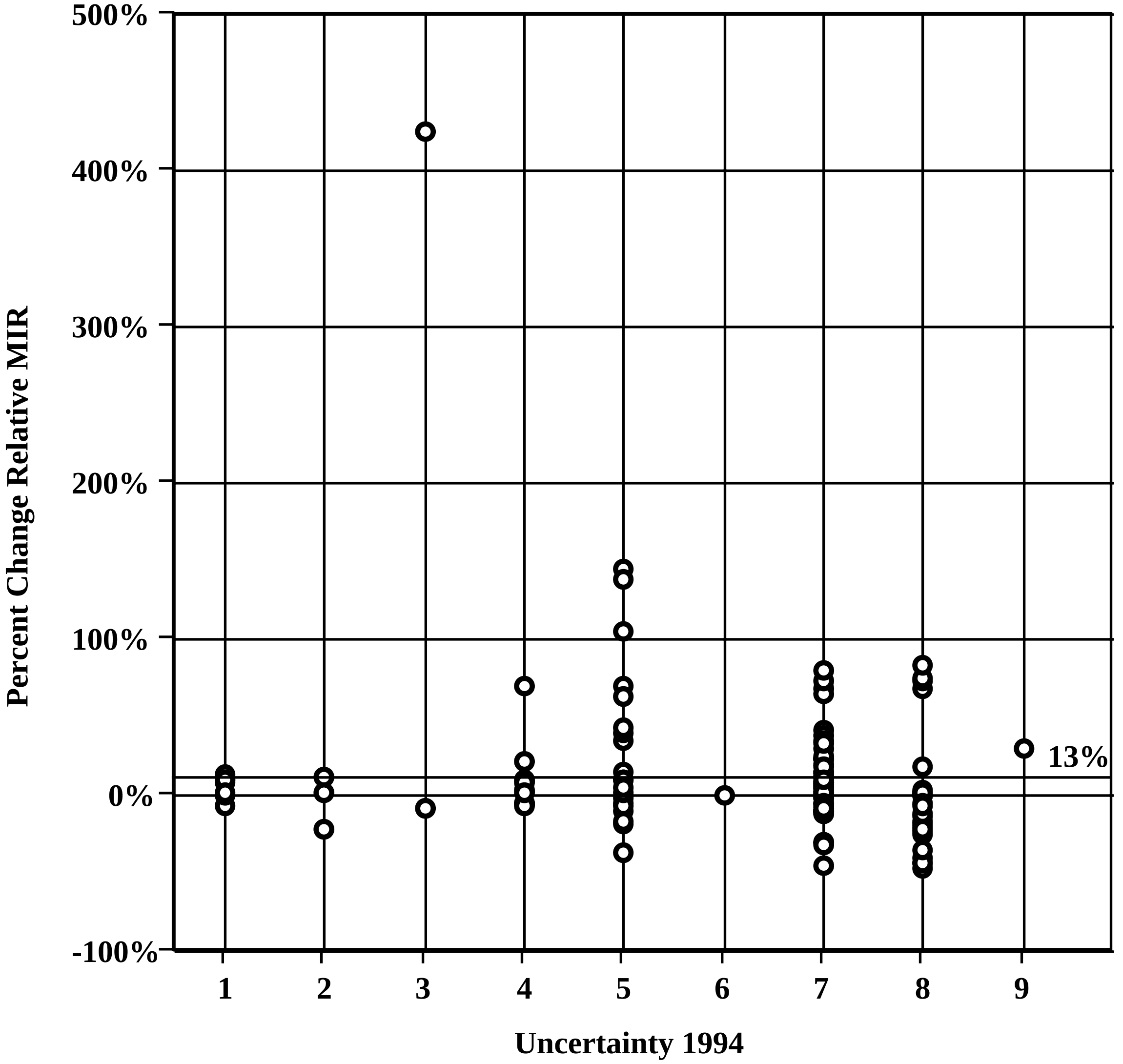


Figure 5-6 shows a plot of the absolute and relative MIRs for the 1994 and 1999 versions of the SAPRC mechanism and the assigned uncertainty values from 1994 for each compound. Figure 5-7 shows a plot of the percent change in the absolute and relative MIRs between 1994 and 1999 and the assigned uncertainty values from 1994. Figures 5-6 and 5-7 show that the compounds in the higher uncertainty bins had a greater change in the MIRs as also seen in Figure 5-4 and 5-5. However there was not a sharp cutoff point where a higher assigned uncertainty was associated with a large percent change in the MIR values. Figure 5-7 shows that change in the relative MIRs was less than absolute MIRs.

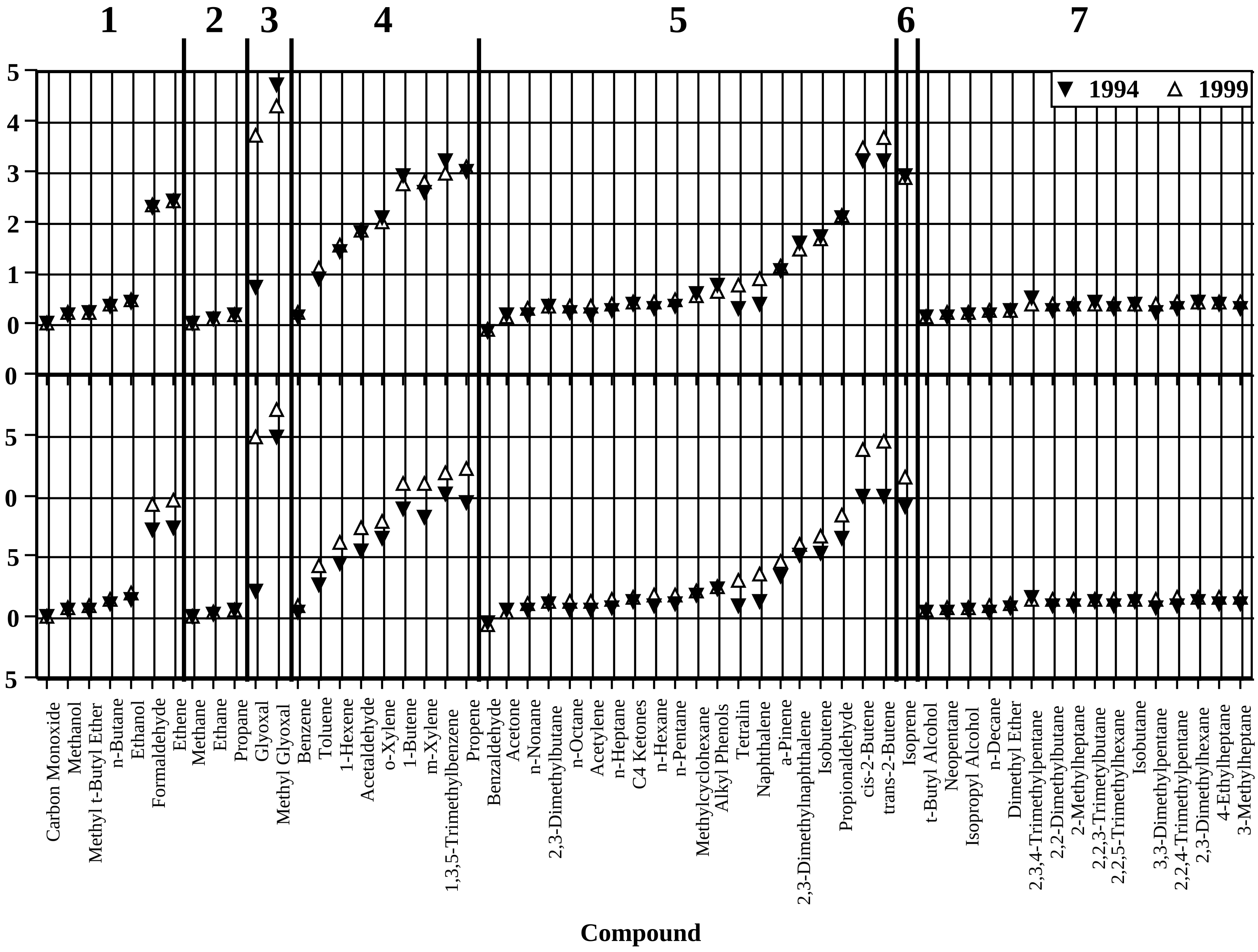
Conclusions

Carter's scheme of assigning organic compounds to 6 bins based on the compound’s mechanistic uncertainty is reasonable. The assignments made by him appear to be reasonable in view of the current state of chemical knowledge.

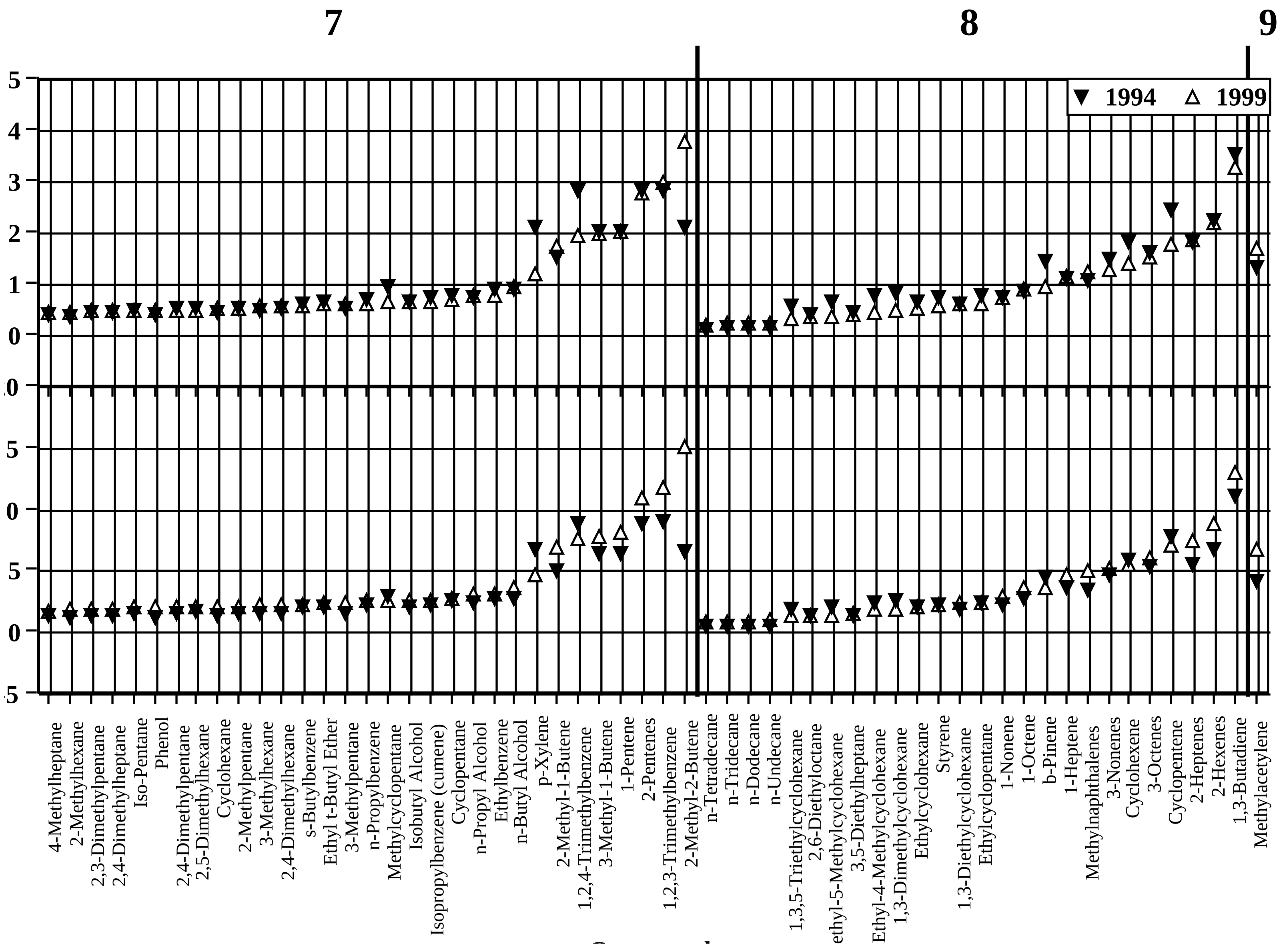
A minimum multiplier of 1.5 should be used to estimate the uncertainty in all absolute MIRs. This is recommended because the average coefficient of variation was 0.29 for SAPRC 1997 and because the average MIRs increased by 43% between 1994 and 1999. Based on the past changes it is conservative to assume that any MIR might vary by 50% in future calculations and therefore bins 1 and 2 should be adjusted by a factor of 1.5. Based on this analysis a factor of 2 is a large enough adjustment for bin 3 and the higher bins. It is suggested that these new factors are a more reasonable method of handling uncertainty in MIRs while minimizing the possibility of underestimating a product's reactivity. Use of these proposed higher factors is a reasonable method of handling uncertainty in MIRs while minimizing the possibility of underestimating a product's reactivity.

The use of relative MIRs accounts for changes in the MIR of the total VOC mixture due to changes in the overall mechanism or due to changes in the MIR calculation procedure. This means that multipliers could be smaller for a regulation based on relative MIRs. Between 1994 and 1999 the average relative MIR increased by 13% compared to a 43% increase in the average absolute MIR. On this basis no multiplier would need to be applied relative MIRs for compounds in bins 1 and 2. For bin 3 and higher bins Figure 5.7 suggests that a factor of 1.5 to 2.0 would be adequate to capture almost all of the uncertainty in the relative MIRs.

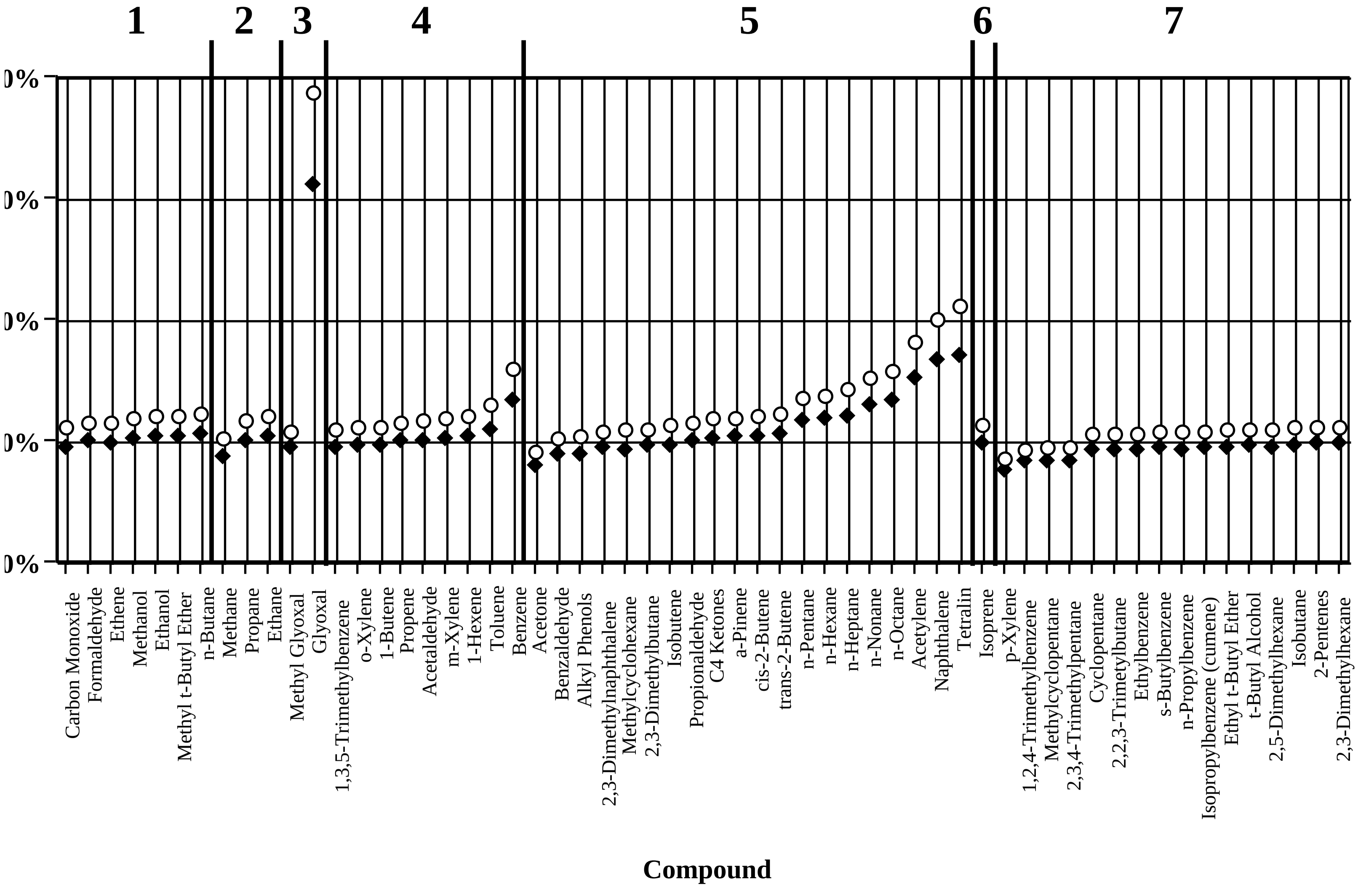
ngles, labeled 1994, represent the absolute and relative MIR for the 1994 version of the SAPRC mechanism (Carter, 1994). The open triangles, represent the absolute and relative MIR for the 1999 version of the SAPRC mechanism. The large numbers at the top of the graph are the assigned for the 1994 version of the SAPRC mechanism.



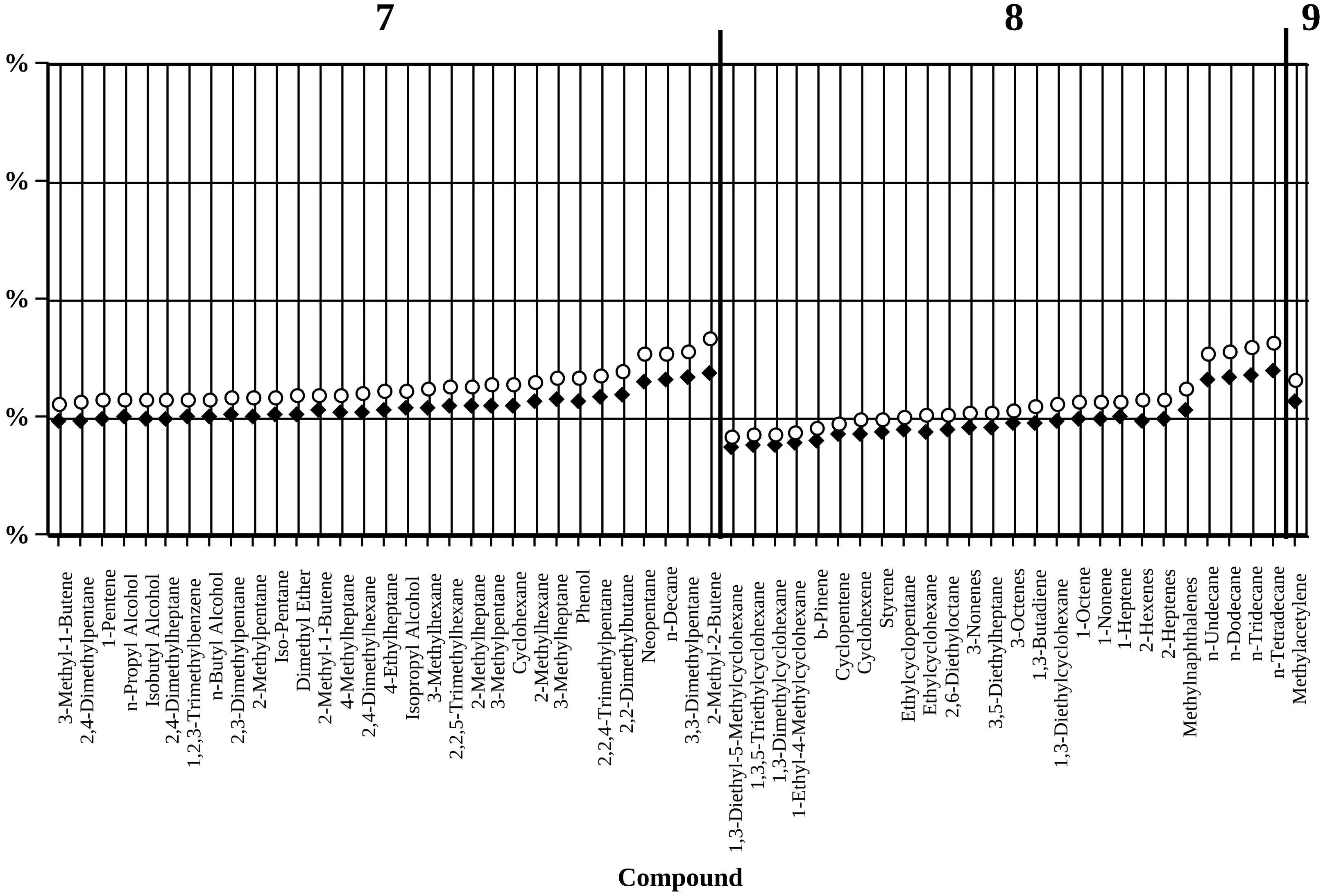
The filled triangles, labeled 1994, represent the absolute and relative MIR for the 1994 version of the SAPRC mechanism (Carter, 1994). The open triangles, labeled 1999, represent the absolute and relative MIR for the 1999 version of the SAPRC mechanism. The large numbers at the top of the graph are the assigned uncertainties for the 1994 version of the SAPRC mechanism.



ge in absolute and relative MIR between the 1994 (Carter, 1994) and the 1999 version of the SAPRC mechanism. The open circles represent the ge in the MIR values between the two versions of the SAPRC mechanism and the filled diamonds represent the percent change in the relative MIR en the two versions. The large numbers at the top of the graph are the assigned uncertainties for the 1994 version of the SAPRC mechanism.



Percent change in absolute and relative MIR between the 1994 (Carter, 1994) and the 1999 version of the SAPRC mechanism. The open circles represent the percent change in the MIR values between the two versions of the SAPRC mechanism and the filled diamonds represent the percent change in the relative MIR values between the two versions. The large numbers at the top of the graph are the assigned uncertainties for the 1994 version of the SAPRC mechanism.



c uncertainty, MIRs, relative MIRs, the percent change in the MIRs and relative MIRs, the rank of the MIRs and the difference in the rank of the Carter (1994) and SAPRC 1999 are shown for the compounds that were common to both assessments. The most reactive compound has a rank e least has a rank of 116. Compounds with a percent change in their MIRs greater than 50% are shown in bold font.

1994 Mechanistic Uncertainty	1994 MIR (O_3 g / VOC g)	1999 MIR (O_3 g / VOC g)	1994 Relative MIR	1999 Relative MIR	Change in MIR (Percent)	Change in Relative MIR (Percent)	1994 Rank by MIR	1999 Rank by MIR	Difference in Rank (1999 - 1994)
1	0.05	0.07	0.018	0.017	23.20	-7.02	114	114	0
1	0.56	0.77	0.180	0.193	36.96	7.20	100	107	7
1	0.62	0.88	0.200	0.220	41.33	10.22	97	103	6
1	1.02	1.48	0.330	0.372	44.80	12.60	86	85	-1
1	1.34	1.88	0.430	0.474	40.47	10.12	69	67	-2
1	7.20	9.27	2.300	2.333	28.81	1.44	15	15	0
1	7.40	9.53	2.400	2.398	28.83	-0.06	14	14	0
2	0.02	0.02	0.005	0.004	2.40	-22.71	115	115	0
2	0.25	0.35	0.079	0.088	39.43	11.00	113	113	0
2	0.48	0.64	0.160	0.161	33.68	0.89	104	110	6
3	**2.20**	**14.81**	**0.710**	**3.725**	**573.09**	**424.70**	**48**	**3**	**-45**
3	14.80	16.99	4.700	4.274	14.78	-9.07	1	1	0
4	**0.42**	**0.91**	**0.135**	**0.229**	**116.88**	**69.75**	**107**	**101**	**-6**
4	**2.70**	**4.24**	**0.880**	**1.067**	**57.02**	**21.20**	**40**	**37**	**-3**
4	4.40	6.09	1.400	1.533	38.46	9.47	32	28	-4
4	5.50	7.25	1.800	1.825	31.89	1.39	24	23	-1
4	6.50	7.87	2.100	1.980	21.09	-5.71	19	19	0
4	8.20	11.04	2.600	2.779	34.69	6.87	12	11	-1
4	8.90	10.91	2.900	2.745	22.58	-5.35	9	12	3
4	9.40	12.19	3.000	3.066	29.66	2.21	6	7	1

The mechanistic uncertainty, MIRs, relative MIRs, the percent change in the MIRs and relative MIRs, the rank of the MIRs and the difference in he rank of the MIRs between Carter (1994) and SAPRC 1999 are shown for the compounds that were common to both assessments. The most eactive compound has a rank equal to 1 and the least has a rank of 116. Compounds with a percent change in their MIRs greater than 50% are hown in bold font.

1994 Mechanistic Uncertainty	1994 MIR (O_3 g / VOC g)	1999 MIR (O_3 g / VOC g)	1994 Relative MIR	1999 Relative MIR	Change in MIR (Percent)	Change in Relative MIR (Percent)	1994 Rank by MIR	1999 Rank by MIR	Difference in Rank (1999 - 1994)
4	10.10	11.76	3.200	2.959	16.46	-7.53	3	8	5
5	-0.57	-0.58	-0.180	-0.145	1.41	-19.21	116	116	0
5	**0.50**	**1.31**	**0.160**	**0.329**	**161.17**	**105.33**	**103**	**92**	**-11**
5	**0.54**	**1.10**	**0.170**	**0.276**	**103.28**	**62.45**	**102**	**98**	**-4**
5	0.56	0.45	0.180	0.113	-19.93	-37.33	99	112	13
5	**0.60**	**1.28**	**0.190**	**0.322**	**113.14**	**69.34**	**98**	**94**	**-4**
5	**0.81**	**1.48**	**0.260**	**0.372**	**82.73**	**43.22**	**94**	**83**	**-11**
5	**0.94**	**3.01**	**0.310**	**0.756**	**219.73**	**143.91**	**91**	**43**	**-48**
5	**0.98**	**1.71**	**0.310**	**0.430**	**74.55**	**38.82**	**88**	**75**	**-13**
5	**1.04**	**1.77**	**0.330**	**0.446**	**70.30**	**35.02**	**85**	**70**	**-15**
5	1.07	1.28	0.340	0.321	19.17	-5.65	84	95	11
5	**1.17**	**3.49**	**0.370**	**0.878**	**198.21**	**137.24**	**80**	**40**	**-40**
5	1.18	1.59	0.380	0.400	34.63	5.17	79	80	1
5	1.80	2.08	0.590	0.525	15.83	-11.10	59	60	1
5	2.30	2.41	0.740	0.605	4.64	-18.18	44	50	6
5	3.30	4.51	1.040	1.134	36.62	9.06	36	35	-1
5	5.10	5.85	1.600	1.472	14.74	-7.99	28	30	2
5	5.30	6.59	1.700	1.657	24.29	-2.51	27	27	0
5	6.50	8.43	2.100	2.120	29.65	0.96	18	17	-1
5	10.00	13.81	3.200	3.474	38.08	8.56	4	5	1

The mechanistic uncertainty, MIRs, relative MIRs, the percent change in the MIRs and relative MIRs, the rank of the MIRs and the difference in he rank of the MIRs between Carter (1994) and SAPRC 1999 are shown for the compounds that were common to both assessments. The most eactive compound has a rank equal to 1 and the least has a rank of 116. Compounds with a percent change in their MIRs greater than 50% are hown in bold font.

1994 Mechanistic Uncertainty	1994 MIR (O_3 g / VOC g)	1999 MIR (O_3 g / VOC g)	1994 Relative MIR	1999 Relative MIR	Change in MIR (Percent)	Change in Relative MIR (Percent)	1994 Rank by MIR	1999 Rank by MIR	Difference in Rank (1999 - 1994)
5	10.00	14.51	3.200	3.650	45.10	14.07	5	4	-1
6	9.10	11.48	2.900	2.889	26.17	-0.39	7	10	3
7	**0.37**	**0.77**	**0.117**	**0.193**	**107.56**	**65.13**	**110**	**106**	**-4**
7	0.42	0.50	0.132	0.125	18.16	-5.41	106	111	5
7	**0.46**	**0.97**	**0.146**	**0.243**	**110.11**	**66.55**	**105**	**100**	**-5**
7	0.54	0.80	0.170	0.200	47.37	17.77	101	105	4
7	**0.71**	**1.51**	**0.220**	**0.380**	**112.60**	**72.61**	**96**	**82**	**-14**
7	0.77	1.05	0.240	0.265	36.67	10.31	95	99	4
7	**0.82**	**1.45**	**0.260**	**0.366**	**77.22**	**40.61**	**93**	**90**	**-3**
7	**0.93**	**1.58**	**0.290**	**0.399**	**70.41**	**37.49**	**92**	**81**	**-11**
7	**0.96**	**1.46**	**0.300**	**0.368**	**52.32**	**22.63**	**90**	**89**	**-1**
7	**0.97**	**1.47**	**0.300**	**0.369**	**51.32**	**23.09**	**89**	**86**	**-3**
7	**0.99**	**1.65**	**0.310**	**0.416**	**67.12**	**34.27**	**87**	**77**	**-10**
7	**1.08**	**1.74**	**0.340**	**0.437**	**60.85**	**28.54**	**83**	**73**	**-10**
7	**1.12**	**1.89**	**0.360**	**0.475**	**68.75**	**32.08**	**82**	**66**	**-16**
7	1.13	1.63	0.360	0.411	44.48	14.10	81	78	-3
7	1.20	1.67	0.380	0.420	39.18	10.57	78	76	-2
7	1.21	1.48	0.390	0.372	22.11	-4.69	77	84	7
7	**1.28**	**2.02**	**0.410**	**0.508**	**57.64**	**23.81**	**75**	**62**	**-13**
7	1.31	1.62	0.410	0.407	23.46	-0.76	73	79	6

The mechanistic uncertainty, MIRs, relative MIRs, the percent change in the MIRs and relative MIRs, the rank of the MIRs and the difference in he rank of the MIRs between Carter (1994) and SAPRC 1999 are shown for the compounds that were common to both assessments. The most eactive compound has a rank equal to 1 and the least has a rank of 116. Compounds with a percent change in their MIRs greater than 50% are hown in bold font.

1994 Mechanistic Uncertainty	1994 MIR (O_3 g / VOC g)	1999 MIR (O_3 g / VOC g)	1994 Relative MIR	1999 Relative MIR	Change in MIR (Percent)	Change in Relative MIR (Percent)	1994 Rank by MIR	1999 Rank by MIR	Difference in Rank (1999 - 1994)
7	1.31	1.75	0.410	0.440	33.43	7.26	74	72	-2
7	1.32	1.47	0.420	0.369	11.13	-12.13	72	87	15
7	1.33	1.75	0.430	0.441	31.72	2.49	71	71	0
7	1.38	1.87	0.440	0.471	35.65	7.04	68	68	0
7	1.40	2.10	0.440	0.528	49.85	19.95	67	59	-8
7	1.50	1.90	0.480	0.477	26.50	-0.55	64	65	1
7	1.50	2.02	0.480	0.509	34.86	6.03	66	61	-5
7	1.50	2.13	0.480	0.536	41.98	11.62	63	58	-5
7	**1.50**	**2.32**	**0.480**	**0.585**	**54.97**	**21.84**	**65**	**53**	**-12**
7	1.60	1.42	0.510	0.358	-11.00	-29.75	62	91	29
7	1.60	1.90	0.520	0.478	18.86	-7.99	61	64	3
7	1.90	2.15	0.600	0.540	12.91	-10.05	55	57	2
7	1.90	2.49	0.620	0.628	31.30	1.23	54	48	-6
7	2.00	2.32	0.640	0.583	15.89	-8.89	53	54	1
7	2.10	2.40	0.680	0.603	14.09	-11.36	52	51	-1
7	2.20	2.53	0.710	0.636	14.94	-10.40	50	47	-3
7	2.30	3.00	0.720	0.755	30.52	4.90	45	44	-1
7	2.40	2.65	0.760	0.666	10.22	-12.43	43	46	3
7	2.70	3.03	0.860	0.763	12.36	-11.26	39	42	3
7	2.70	3.57	0.860	0.897	32.08	4.32	38	39	1

The mechanistic uncertainty, MIRs, relative MIRs, the percent change in the MIRs and relative MIRs, the rank of the MIRs and the difference in he rank of the MIRs between Carter (1994) and SAPRC 1999 are shown for the compounds that were common to both assessments. The most eactive compound has a rank equal to 1 and the least has a rank of 116. Compounds with a percent change in their MIRs greater than 50% are hown in bold font.

1994 Mechanistic Uncertainty	1994 MIR (O_3 g / VOC g)	1999 MIR (O_3 g / VOC g)	1994 Relative MIR	1999 Relative MIR	Change in MIR (Percent)	Change in Relative MIR (Percent)	1994 Rank by MIR	1999 Rank by MIR	Difference in Rank (1999 - 1994)
7	2.80	2.46	0.900	0.619	-12.17	-31.26	37	49	12
7	4.90	6.78	1.500	1.706	38.43	13.76	29	25	-4
7	6.20	7.72	2.000	1.943	24.57	-2.85	21	20	-1
7	6.20	8.00	2.000	2.013	29.09	0.67	22	18	-4
7	**6.40**	**14.97**	**2.100**	**3.766**	**133.87**	**79.31**	**20**	**2**	**-18**
7	6.60	4.56	2.100	1.147	-30.95	-45.40	17	34	17
7	8.80	7.57	2.800	1.904	-13.98	-31.99	10	21	11
7	8.80	10.86	2.800	2.732	23.39	-2.44	11	13	2
7	8.90	11.74	2.800	2.955	31.95	5.52	8	9	1
8	**0.32**	**0.73**	**0.100**	**0.183**	**127.17**	**82.88**	**112**	**109**	**-3**
8	**0.35**	**0.77**	**0.110**	**0.193**	**118.73**	**75.09**	**111**	**108**	**-3**
8	**0.38**	**0.81**	**0.118**	**0.203**	**111.87**	**71.66**	**109**	**104**	**-5**
8	**0.42**	**0.88**	**0.132**	**0.222**	**110.32**	**68.36**	**108**	**102**	**-6**
8	1.23	1.27	0.390	0.321	3.64	-17.76	76	96	20
8	1.33	1.46	0.430	0.368	10.01	-14.40	70	88	18
8	1.70	1.20	0.540	0.302	-29.31	-44.01	60	97	37
8	1.80	2.24	0.570	0.563	24.35	-1.21	58	55	-3
8	1.90	1.28	0.610	0.323	-32.49	-47.10	56	93	37
8	1.90	1.95	0.620	0.490	2.59	-20.91	57	63	6
8	2.20	2.17	0.710	0.545	-1.46	-23.18	49	56	7

he mechanistic uncertainty, MIRs, relative MIRs, the percent change in the MIRs and relative MIRs, the rank of the MIRs and the difference in he rank of the MIRs between Carter (1994) and SAPRC 1999 are shown for the compounds that were common to both assessments. The most eactive compound has a rank equal to 1 and the least has a rank of 116. Compounds with a percent change in their MIRs greater than 50% are hown in bold font.

1994 Mechanistic Uncertainty	1994 MIR (O_3 g / VOC g)	1999 MIR (O_3 g / VOC g)	1994 Relative MIR	1999 Relative MIR	Change in MIR (Percent)	Change in Relative MIR (Percent)	1994 Rank by MIR	1999 Rank by MIR	Difference in Rank (1999 - 1994)
8	2.20	2.82	0.710	0.710	28.22	-0.05	51	45	-6
8	2.30	1.74	0.730	0.437	-24.48	-40.14	46	74	28
8	2.30	2.36	0.730	0.593	2.41	-18.82	47	52	5
8	2.50	1.82	0.810	0.457	-27.27	-43.53	42	69	27
8	2.70	3.42	0.850	0.861	26.69	1.24	41	41	0
8	3.30	4.89	1.050	1.229	48.07	17.07	35	33	-2
8	3.50	4.49	1.100	1.130	28.34	2.73	34	36	2
8	4.40	3.58	1.400	0.902	-18.54	-35.59	31	38	7
8	4.60	5.04	1.460	1.267	9.49	-13.21	30	32	2
8	5.30	5.97	1.600	1.502	12.68	-6.10	26	29	3
8	5.50	7.26	1.800	1.826	31.98	1.45	25	22	-3
8	5.70	5.47	1.800	1.375	-4.09	-23.59	23	31	8
8	6.70	8.68	2.200	2.185	29.63	-0.68	16	16	0
8	7.70	7.04	2.400	1.770	-8.63	-26.25	13	24	11
8	10.90	12.88	3.500	3.240	18.16	-7.42	2	6	4
9	**4.10**	**6.70**	**1.310**	**1.687**	**63.53**	**28.76**	**33**	**26**	**-7**

6. Evaluation of the Mechanism Documentation

The available documentation was examined. In general the documentation was adequate and reasonably well written. There were several places where it would be highly desirable for Dr. Carter to provide more detailed information in the documentation and these have been noted in the comments given above.

7. Conclusions

The purpose of this report was to provide the California Air Resources Board with a peer review of Dr. William P.L. Carter's detailed chemical mechanism. Carter's mechanism is being proposed as a basis for VOC control regulations based on reactivity calculations. We have performed a peer review of Carter's detailed chemical mechanism, its documentation and supporting databases. The chemical kinetic data in the mechanism and its supporting material were compared with data from standard kinetic databases, such as DeMore et al. (1997), Atkinson et al. (1997) and Atkinson (1994) and the most recent available literature. The kinetic parameters checked included the reactions, rate constants, product yields and lumping methods. Finally all documentation was reviewed to ensure that the mechanism, all supporting documents and all computer codes are clearly described. The objective of our peer review was to ensure that the Carter's detailed mechanism consists of the best possible atmospheric chemistry that is now available and that it is well documented.

Dr. Carter is to be commended for developing a high quality mechanism that is state of the science for air quality modeling. The mechanism is clearly within the realm of the best available science. Air quality models that make use of previous versions of Dr. Carter's mechanism should update to this new version. But the rate parameters of the mechanism should include correct temperature and pressure dependencies rather than any "fits" for surface temperature and pressure. Although the simplified expressions might be adequate for reactivity calculations, they are not acceptable if the mechanism is to be implemented in regional scale air quality models such as EPA's Models3.

The mechanism makes full use of the available kinetic data and reflects the considerable progress that has been made in improving our understanding of atmospheric chemistry. However there remain several important outstanding issues to be resolved by further experimental studies including: better mechanistic data for most higher molecular weight organic compounds; more data on the product yields for the reactions of HO, NO_3 and O_3 with alkenes; and fundamental data on aromatic reaction mechanisms.

Carter's scheme of assigning organic compounds to 6 bins based on the compound's mechanistic uncertainty is reasonable. The assignments made by him appear to be reasonable in view of the current state of chemical knowledge.

A minimum multiplier of 1.5 should be used to estimate the uncertainty in all absolute MIRs. This is recommended because the average coefficient of variation was 0.29 for SAPRC 1997 and because the average MIRs increased by 43% between 1994 and 1999. Based on the past changes it is conservative to assume that any MIR might vary by 50% in future calculations and therefore bins 1 and 2 should be adjusted by a factor of 1.5. Based on this analysis a factor of 2 is a large enough adjustment for bin 3 and the higher bins. It is suggested that these new factors are a more reasonable method of handling uncertainty in MIRs while minimizing the possibility of underestimating a product's reactivity.

The use of relative MIRs accounts for changes in the MIR of the total VOC mixture due to changes in the overall mechanism or due to changes in the MIR calculation procedure. This means that multipliers could be smaller for a regulation based on relative MIRs. Between 1994 and 1999 the average relative MIR increased by 13% compared to a 43% increase in the average absolute MIR. On this basis no multiplier would need to be applied to relative MIRs for compounds in bins 1 and 2. For bin 3 and higher bins Figure 5.7 suggests that a factor of 1.5 to 2.0 would be adequate to capture almost all of the uncertainty in the relative MIRs.

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Glossary of Acronyms

A	Arrhenius parameter, also called the pre-exponential factor. It is found in the Arrhenius equation for kinetic rate parameters: $k=A*\exp(E_a/T)$, where k is the rate parameter, E_a is the activation energy and T is the temperature
B	Exponent for the rate parameters of "third order reactions" and for the rate parameters of the high pressure limits of these reactions. For third order reactions: $k_0(T) = k_0^{300}(T/300)^{-B}$ and for their high pressure limits: $k_\infty(T) = k_\infty^{300}(T/300)^{-B}$
E_a	Activation energy, see definition of A, Arrhenius parameter, given above.
Falloff, F	A parameter used to interpolate between third order rate parameters (low pressure limit) and high pressure rate parameters to estimate reaction rate parameters at atmospheric pressure. See also the definition for "B".
Falloff Expression	Equation used to interpolate between third order rate parameters (low pressure limit) and high pressure rate parameters to estimate reaction rate parameters at atmospheric pressure. See also the definition for "B".
IR	Incremental reactivity, the change in the grams of ozone formed per change in grams of volatile organic compound present in the polluted atmosphere.
IUPAC	International Union of Pure and Applied Chemistry.
k_0	Third order reaction rate parameter. See also the definition for "B" and Falloff Expression.
k_∞	High pressure rate parameter. See also the definition for "B" and Falloff Expression.
k(300)	Rate parameter at 300 K for "third order reactions" and for the high pressure limits of these reactions. See also the definition for "B".
MIR	Maximum incremental reactivity. An incremental reactivity calculated for a volatile organic mixture where the emissions of NO_x ($NO + NO_2$) have been adjusted to maximize the calculated MIR.

NASA	National Aeronautics and Space Administration.
Radical	A reactive chemical intermediate with an unpaired electron.
Rate Parameter	A parameter used to calculate the rate of a chemical reaction from the concentrations of the reactants. For example, the rate of a bimolecular reaction is: $R = k[A][B]$, where R is the rate, k is the rate parameter, $[A]$ is the concentration of a reactant and $[B]$ is the concentration of the second reactant.
Reactant	Chemical species lost in a chemical reaction.
Product	Chemical species formed by a chemical reaction.
VOC	Volatile Organic Compound.

Appendix A: Drafts of Dr. William P.L. Carter's Mechanism Used for this Review

1. SAPRC-99 Base Mechanism as of January 9, 1999 (Base mechanism).

2. Documentation of the SAPRC99 Chemical Mechanism for VOC Reactivity Assessment, April 27, 1999 (Base mechanism).

3. Documentation of the SAPRC99 Chemical Mechanism for VOC Reactivity Assessment, May 27, 1999 (Overview of mechanism generation system and discussion of initial reactions only).

4. Documentation of the SAPRC99 Chemical Mechanism for VOC Reactivity Assessment, July 3, 1999 (Lumped Molecule Approach and Parameterized Method).

5. Documentation of the SAPRC99 Chemical Mechanism for VOC Reactivity Assessment, August 4, 1999 (Lumped Molecule Approach and Parameterized Method).

6. SAPRC 1999 Spreadsheet of MIR values and Uncertainty Assignments, September 1999.

Appendix B: Dr. William P.L. Carter's Response to Comments Received from this Review

by

William P. L. Carter

August 3, 1999

The California Air Resources Board (CARB) has contracted Dr. William R. Stockwell to carry out a peer review of the updated SAPRC mechanism and its documentation, being prepared by the author under separate CARB contracts. As part of his efforts for this project, Dr Stockwell has prepared a draft final report, in which he gave some comments and recommendations concerning primarily the base mechanism and some of its current documentation. Since that time, some modifications have been made to the base mechanism and its documentation, in part as a response Dr. Stockwell's comments, and in part for other reasons.

Given below are summaries of various comments given in those reports that might be interpreted as criticisms or suggestions for change, and the authors responses to those comments. Note that in a number of cases the author agreed with the comments and has changed the mechanism accordingly, though there are some cases where the author does not completely agree with the comments or where changes could not be made.

Species Listing Format

Comment: The units for the defaults of the Constant Species should be defined. The units of O2, M and H2O appear to be ppm while the unit for light appears to be a multiplier of unity. HV, light, is listed under Constant Species and characterized as a Type "Con". Although HV is not a chemical species it is not a constant in the atmosphere. It is suggested that HV be moved to its own category for clarity. It is not clear how "Act*" differs from "Act"

Response: The tabulation that appears in the documentation report will not have default concentrations for constant species, since this is a function of the model scenario and not the mechanism. HV will be kept in the "constant" category because this is the way it is treated by the software, though it is recognized that it is not a chemical species. The model user should know the difference between HV and a chemical species. The "type" column, which contains the notation "Act*", etc., is used only by the macro producing the preparation input from the reaction listing spreadsheet, and will not be included in the documentation.

Comment: For complete clarity the R2O2. radical could be described as "Peroxy Radical Operator representing NO to NO2 conversion without HO2 formation". It seems surprising that the radical character (nR) of R2O2 is zero since it is a radical operator.

Response: As discussed in the report text, R2O2 isn't strictly speaking a radical. But this is a minor point because the "nR" assignments are used for internal checking only, and will not be in the documentation report.

Species Scope

Comment: H2 should be considered as either a constant species that reacts or as an active inorganic species because the reaction H2 + HO is a sink for HO that occurs with a rate that is 30% that of the reaction CH4 + HO for typical atmospheric conditions (Stockwell et al., 1997). Although H2 should be treated as a constant it is not unreactive. It is a sink for HO radicals that should not be ignored.

Response: Although the reaction of OH with H_2 may occur at a comparable rate as its reaction with methane, it is my understanding that the amount of H_2 in the atmosphere is much lower than the amount of methane, such that its reaction with OH is of no importance. Therefore, the effect of the OH + H_2 reaction is ignored, so H2 can either be included as a buildup species if there is any need to track H_2, or it can be removed from the mechanism otherwise.

Comment: Dr. Carter may want to consider adding SO2 as an active species. Although SO2 is not greatly important for incremental reactivity applications the mechanism may be used for other applications, such as aerosol formation studies, where this chemistry can be important. The sulfate produced should be added as a Non-Reacting Species.

Response: This point is well taken. SO_2 and SULF have been added to the mechanism, as active and buildup species, respectively. The reaction of SO_2 with OH has been added, but its reactions with stabilized Crigiee biradicals are assumed to be negligible.

Comment: Are there data that suggest that the average carbon number of higher organic peroxides, ROOH, is really as high as 3? I would guess that it is closer to 2.

Response: The model species is given the carbon number of 3 because its reactions are based on those estimated for a propyl hydroperoxide. It is being used to represent the hydroperoxides formed from all organic radicals, which in general would have a much higher carbon number. In the remote atmosphere methyl hydroperoxide may dominate, but there is already a separate model species for it.

Comment: I would expect the stabilized products from the Crigiee biradicals to be too reactive to be treated as unreactive products. Would it be better to treat them as something at least like ketones?

Response: Stabilized Crigiee biradicals are now assumed to be consumed primarily by reaction with H_2O to form the corresponding carboxylic acid. They are therefore removed from this version of the mechanism, and represented by the carboxylic acids themselves. These acids are represented as unreactive because they react relatively slowly, and it is expected that their loss by deposition would be more important than their loss by gas-phase reaction.

Comment: I can easily accept that CH4 belongs in the category “Primary Organics Represented Explicitly” but given the relative complexity of isoprene chemistry it is not accurate to place it in this category.

Response: The complexity of the chemistry is not really relevant to the categorization. However, the reviewer has a point that it seems sort of strange to categorize isoprene with methane in this context. For organizational purposes isoprene itself (but not its unique products – which must be retained to allow isoprene to be accurately represented) has been removed from the base mechanism, being represented by a detailed model species like the other alkenes. The issue of whether it is represented explicitly will depend on the model application, but the recommendation concerning model implementation will be to represent isoprene explicitly. This will be discussed in a separate section which will concern lumping recommendations.

Comment: The definitions in “Biogenic Compounds in the EKMA Simulations” and “Lumped species used to represent the Base ROG mixture in the EKMA model simulations” are reasonable and within standard practice.

Response: These species are not part of the base mechanism, but will be given in a separate section on recommended lumped mechanisms for modeling.

Responses to comments on Reactions in Base Mechanism

Reaction 2: O3P + O2 + M = O3 + M

Comment: The rate constant parameters are not computed correctly for the abundance of O_2 and N_2 in air. They should be: A = 5.61e-34, B=-2.8

Response: The rate constant in the original version was computed with O_2 and N_2 concentrations interchanged. This has been corrected. The corrected parameters are A=5.68e-34 and B=-2.8. The reviewer made a slight miscalculation for the recommended A factor.

Reaction 21: O3 + HV = O*1D2 + O2

Comment: It seems that a higher base temperature could be chosen for the cross sections this may be important because recent data on the temperature dependence of ozone photolysis (Talukdar et al., 1998) leads to greater $O(^1D)$ formation rates. This could be a problem during the fall and spring because this may lead to more rapid photochemical loss of ozone and greater rates of HO formation.

Response: The reviewer has a good point, but I presently I do not have access to absorption cross section data at a higher temperature. Data are only given for $T=273^oK$ in the evaluations.

Reaction 23: O*1D2 + M = O3P + M

Comment: It would be somewhat more accurate to calculate the rate parameter as: k = 1.80e-11* exp (107/T)* 0.791*[M] + 3.20e-11 * exp(67/T) *0.209*[M]

Response: The difference between what the reviewer recommends and what is in the mechanism is insignificant and not worth the overhead of using a more complex expression in the mechanism.

Reaction 25: HONO + HV = HO. + NO

Comment: The IUPAC and the NASA evaluations favor the HONO cross sections given by Bongartz et al. (1991) over the values given by Stockwell and Calvert (1978). Although the IUPAC evaluations report the Bongartz et al. (1991) cross sections with a 5 nm resolution, the NASA evaluation reports them with the same resolution reported by Stockwell and Calvert (1978), 1 nm resolution The cross sections of Bongartz et al. (1991) should be used because there are significant differences between the values of Stockwell and Calvert and Bongartz et al. (1991); the cross section reported by Stockwell and Calvert are 20% lower than the values of Bongartz et al. at 354 nm.

Response: The HONO absorption cross section data have been replaced by those in the NASA evaluation, as the reviewer recommended. The change in the calculated photolysis rate is non-negligible, though the impact on actual ambient simulations will probably be minor.

Reaction 32A: HO. + CO = HO2. + CO2

Reaction 32B: HO. + CO + M = HO2. + CO2 + M

Comment: The rate constant expression is consistent with the NASA recommendation but since the IUPAC evaluation provides a rate parameter with a temperature and pressure dependence it is suggested that the full expression be used.

Response: Although the form used in the mechanism (with the reaction split up into Reactions 32A and 32B) is no approximation, the expression has been re-formatted to the form used in the IUPAC evaluation as recommended by the reviewer. Thus, 32A and 32B have been combined into one reaction with the appropriate pressure and temperature dependence parameterization. The mechanism preparation program had to be modified to implement this. Note that this means that FCM and CALGRID mechanism preparation software will need to be updated to implement this mechanism.

Reaction 41: NO3 + HO2. = HO. + NO2 + O2

Comment: Although the mechanism is uncertain there probably is a significant radical termination and nitric acid production through the reaction: $NO_3 + HO_2 = HNO_3 + O_2$ that channel should not be ignored. The studies reported in the review by Le Bras (1997) find that the rate of the nitric acid channel is between 20 and 43% of the total reaction rate of NO3 with HO2. In fact there is one study by Hjorth that found the reaction channel represented by reaction 41 to be insignificant (Le Bras, 1997) although that study is probably not correct it still points to the possible importance of the HNO3 producing channel.

Response: The reviewer's recommendation to incorporate that channel is reasonable. The reaction has been changed to:
NO3 + HO2. = #.8 {HO. + NO2 + O2} + #.2 {HNO3 + O2}
And the footnote documentation has been changed to:
Rate constant recommended by IUPAC (Atkinson et al, 1997b). Measurement of the branching ratios vary, so the mechanism is uncertain. The branching ratio assumed is approximately in the middle of the range given by IUPAC (Atkinson et al, 1997b) and NASA (1997) evaluations, which is 0.6 - 1.0 for the OH-forming channel.
Reaction S2OH: SO2 + OH = HO2. + SULF

Comment: The conclusion of note 30 was first proved by Stockwell and Calvert (1983:Stockwell, W.R. and J.G. Calvert, The Mechanism of the HO-SO2 Reaction, Atmos. Envir., 17, 2231 - 2235, 1983. That paper should be cited in Note 30 and the references.

Response: The existing draft documentation already incorporates this reference.

Reaction MER5: C-O2. + C-O2. = MEOH + HCHO + O2

Comment: There is some uncertainty in the temperature dependence of the ratio of the rate parameters for Reactions MER5 and MER6 and this affects the derivation of the individual rate parameters for the two reactions. But the fitted rate constant for Reaction MER5 yields a rate constant that is about 6% greater than the value calculated from the simple difference between the IUPAC recommended values for the total rate parameter (MER5 + MER6) and the recommended value for the HCHO + HO2 forming reaction.

Response: No change was made because the difference is not considered to be significant.

Reaction RRME: RO2-R. + C-O2. = HO2. + #.75 HCHO + #.25 MEOH
Comment: The 0.25 yield of MEOH (CH3OH) is consistent with current knowledge of the rate of the H-atom transfer reaction; this assumption should be added to the footnote.

Response: A somewhat more complete discussion of how the 0.25 yield was derived was added to the footnote.

Reaction RNME: RO2-N. + C-O2. = HO2. + #.25 MEOH + #.5 {MEK + PROD2} + #.75 HCHO + XC
Comment: The 0.25 yield of MEOH (CH3OH) is consistent with current knowledge of the rate of the H-atom transfer reaction; this assumption should be added to the footnote.

Response: The added discussion given in the footnote for RRME is considered to be sufficient, so no change was made to the footnote for this reaction.

Reaction RRR2: RO2-R. + RO2-R. = HO2.

Comment: The rate constant may be valid but the rational seems weak. Atkinson recommends a rate constant of 5E-15 cm3 molecule-1 s-1 for general secondary RO2 + secondary RO2 while for the rate parameter for the reaction of general primary is recommended to be 2.5e-13 cm3 molecule-1 s-1. The geometric average of the primary and secondary rate parameters is 3.5E-14 and that may be a bit better to use.

Response: The rate constant was changed to be the geometric average as recommended by the reviewer.

Reaction APNO: CCO-O2. + NO = C-O2. + CO2 + NO2

Comment: Although the temperature dependence of this reaction is not great the temperature dependence as given in IUPAC (Atkinson et al, 1999) evaluation should be included as k = 7.8E-12*EXP(300/T).

Response: The rate parameters in the mechanism were modified to be exactly the same as the IUPAC (1999) recommendation, though the effect of the change is small.
Reaction PPN2: RCO-O2. + NO2 = PAN2
Reaction PPNO: RCO-O2. + NO = NO2 + CCHO + RO2-R. + CO2

Comment: The reactants, products and rate parameters are reasonable for Reaction BPN2. The rate parameter is in agreement with the results of Seefeld (1997). If the rate constant is taken to be the same as CH3CH2CO3 + NO2. Seefeld (1997) the measured k(NO2)/k(NO) = 0.43±0.07 over the temperature range of 249-302K. This leads to a rate constant of 1.2E-11 cm^3 $molecule^{-1}$ s^{-1} if the rate parameter for the reaction of CH3CH2CO3 radicals with NO is assumed to be 2.8E-11 cm^3 $molecule^{-1}$ s^{-1} in agreement with the value chosen by Carter.

Response: Although this was not noted by the reviewer, the rate constants used in the mechanism for PPN2 and PPNO are in fact not consistent with the data of Seefeld and Kerr (1997). The documentation for PPN2 was changed to note that the assumption that the rate constant was the same as the high pressure limit for the CCO-O2 + NO2 reaction was implicitly incorporated in the 1999 IUPAC evaluation when they gave their recommendation for the $CH_3CH_2CO_3$ + NO rate constant. The rate constant for PPNO was changed to be consistent with this recommendation, which is based on the data of Seefeld and Kerr (1997). This is a 30% increase, and may result in a nonnegligible change in model predictions.

Reaction PAN2: PAN2 = RCO-O2. + NO2

Comment: The IUPAC Supplement IV (1999) reports a rate constant of 4.4E-4 (298K) and an expression k = 2E15 * exp(-12800/T) for PPN. Should that value be used for Reaction PAN2?

Response: The rate parameters in the mechanism are in fact exactly the same as the IUPAC (1999) recommendation. The footnote was changed to state simply that this IUPAC recommendation was used.

Reaction PPH2: RCO-O2. + HO2. = RCO-OOH + O2
Reaction BPH2: BZCO-O2. + HO2. = RCO-OOH + O2 + #4 XC
Reaction MPH2: MA-RCO3. + HO2. = RCO-OOH + O2 + XC

Comment: Note 57 is not exactly correct because while 25% of the acetyl peroxy radicals react with HO2 to produce O3 while, in contrast, 100% of the peroxy propionyl and higher peroxy acyl radicals are assumed to react with HO2 to produce higher peroxy organic acids.

Response: The mechanisms for these reactions were changed to be consistent with the mechanism used for acetyl peroxy radicals, i.e., to form 75% RCO-OOH + O_2 and 25% RCO-OH + O_3.

Reaction APME: CCO-O2. + C-O2. = CCO-OH + HCHO + O2

Comment: Although this choice is reasonable it must be noted that at 50 ˚F the yield of CH3OOH may be near 25% if Horie and Moortgat (1992) as quoted in Atkinson et al. (1999) are correct. The uncertainty in the branching ratio represents a major uncertainty in this reaction.

Response: The discussion already notes that there is an inconsistency in the data, indicating that there is an uncertainty. No modifications were made.

Reaction APRR: CCO-O2. + RO2-R. = CCO-OH

Comment: The rate parameter is much closer to the IUPAC value for acetyl peroxy + methyl peroxy radical than for methyl peroxy + CH3C(O)CH2OO. The basis for the averaging should be given in Note 54. Given that these reactions involve operator radicals it is probably best to assume that the reactions proceed by disproportionation for simplicity. However, it is not clear that this choice is supported by the data for the acetyl peroxy + methyl peroxy reaction, see comments about Reaction APME

Response: The rate constant was changed to be the average of that for acetyl peroxy + ethyl peroxy and acetyl peroxy + $CH_3C(O)CH_2OO\cdot$. Although this is within the uncertainty of the value used, it is justification is more clear. The mechanism used is consistent with the assumptions used for APME.

Reaction TBON: TBU-O. + NO2 = RNO3 + #-2 XC

Comment: However the need to adjust the rate parameter to fit environmental chamber data raises concerns about the uncertainty of the rate parameter. Also since Atkinson

(1997) recommends an Ea of -0.30 kcal mole-1 it should be included in the rate parameter expression

Response: The temperature dependence is small compared to the uncertainty, so is not included. The comment that the rate constant “must be considered to be uncertain by at least this amount” was added to the footnote for this and the other adjusted rate constant.
Reaction BRH2: BZ-O. + HO2. = PHEN
Reaction BNH2: BZCO-O2. + HO2. = RCO-OOH + O2 + #4 XC

Comment: It is not clear that the chosen rate parameter must be less than the actual rate parameter [as stated in the footnote documenting the estimated rate constant].

Response: The footnote was modified slightly to indicate why I suspected this to be the case. The footnote now reads: “Assumed to have the same rate constant as the reaction of HO2 with peroxy radicals. This may underestimate the actual rate constant because alkoxy radicals tend to be more reactive than peroxy radicals.”
Reaction PAHV: RCHO + HV = CCHO + RO2-R. + CO + HO2

Comment: Note 76 is not correct for Reaction PAHV because it discusses acetaldehyde and not propionaldehyde. Otherwise the reaction appears to be consistent with present knowledge.

Response: The note was changed to “Pathway forming molecular products is assumed to be negligible under atmospheric conditions, based on calculated rate for analogous reaction of acetaldehyde.”

Reaction PAN3: RCHO + NO3 = HNO3 + RCO-O2.
Reaction GLN3: GLY + NO3 = HNO3 + #.63 HO2. + #1.26 CO + #.37 RCO-O2. + #-.37 XC
Reaction MGN3: MGLY + NO3 = HNO3 + CO + CCO-O2.
Comment: This procedure [assuming the rate constant is the same as for acetaldehyde] may underestimate the rate parameter for this reaction. Figure 2 [of the Atkinson (1991) NO_3 review] suggests that there is a roughly log-linear relationship between kHO and kNO3 for HCHO and CH3CHO. If the most recent values for kHO and kNO3 for HCHO and CH3CHO are fit we get kNO3 = 2.78*kHO + 15.44. This yields a kNO3 of 5.0E-15 for propionaldehyde if a kHO of 2.0E-11for propionaldehyde is assumed.

Response: The estimated rate constants were changed according to the procedure suggested by the reviewer. Note that the estimated value we obtained for propionaldehyde is somewhat lower than that suggested by the reviewer, because we used only the OH rate constant for reaction at the -CHO group, which is slightly lower than the total rate constant. The footnotes were modified accordingly.

Reaction MeOH: MEOH + HO. = HCHO + HO2
Comment: The reactants and the rate parameter are in agreement with the Atkinson et al. (1999) recommendations. The CH2OH reaction channel does represent 85% of the overall reaction at 298K. The products are reasonable if the CH2OH produced mainly reacts through abstraction of the H atom attached to the OH group. The CH3O reaction channel would be expected to produce almost all HCHO and HO2.

Response: The footnote with the reaction needed to be modified because it appropriate for an earlier version of the mechanism, which represented methoxy radicals explicitly. In the present version of the mechanism, the value used for the branching ratio is irrelevant because the overall process after the reaction of the radicals with O_2 is the same. The footnote was modified to note the recommended branching ratios, but to point out that the overall mechanism is the same regardless.

Reaction BAHV: BACL + HV = #2 CCO-O2.
Comment: The absorption coefficients for biacetyl are based on glyoxal while the quantum yields are estimated.

Response: The footnote for this reaction mislead the reviewer, since in fact the absorption coefficients used are those measured for biacetyl. The footnotes were modified to clarify this.

Reaction CROH: CRES + HO. = #.24 BZ-O. + #.76 RO2-R. + #.23 MGLY + #4.87 XC

Comment: The rate parameter is consistent with the recommendations of Atkinson (1994) but it should be noted that o-cresol is assumed here.

Response: The footnote was changed to indicate that the rate constant is based on that for o-cresol..

Reaction D1OH: DCB1 + HO. = RCHO + RO2-R. + CO
Reaction D2OH: DCB2 + HO. = R2O2. + RCHO + CCO-O2.
Reaction D3OH: DCB3 + HO. = R2O2. + RCHO + CCO-O2.

Comment: The rate parameter of Bierbach et al (1994) does include a temperature dependence of k = 2.8e-11*exp(175/T). This might be included in the mechanism.

Response: No change was made because the temperature dependence is negligible compared to the uncertainties involved.

Discussion of Mechanism Generation of NO_3 Radical Reactions

Comment: The discussion on the treatment of NO_3 radical reactions by the SAPRC automatic mechanism generation procedure needs to be clarified in places. The following needs to be said more clearly. The program considers only the abstraction of hydrogen atoms by NO_3 from aldehydes and the addition of NO_3 to alkenes. If rate constants for the abstraction of hydrogen atoms by NO_3 from aldehydes are estimated then the same rate parameter for the reaction of NO_3 from acetaldehyde is used. If the compound is a acid R-(CO)OH or a formate $X^+H(CO)O^-$ than the rate parameter is assumed to be zero.

Response: The discussion in the introductory paragraph in this section was modified slightly to hopefully clarify the matter. It now reads: “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.”