

**DOCUMENTATION OF THE SAPRC99
CHEMICAL MECHANISM FOR
VOC REACTIVITY ASSESSMENT**

DRAFT

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By

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**OVERVIEW OF
MECHANISM
GENERATION SYSTEM
AND DISCUSSION OF
INITIAL
REACTIONS ONLY**

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C. Generated and Estimated Mechanisms

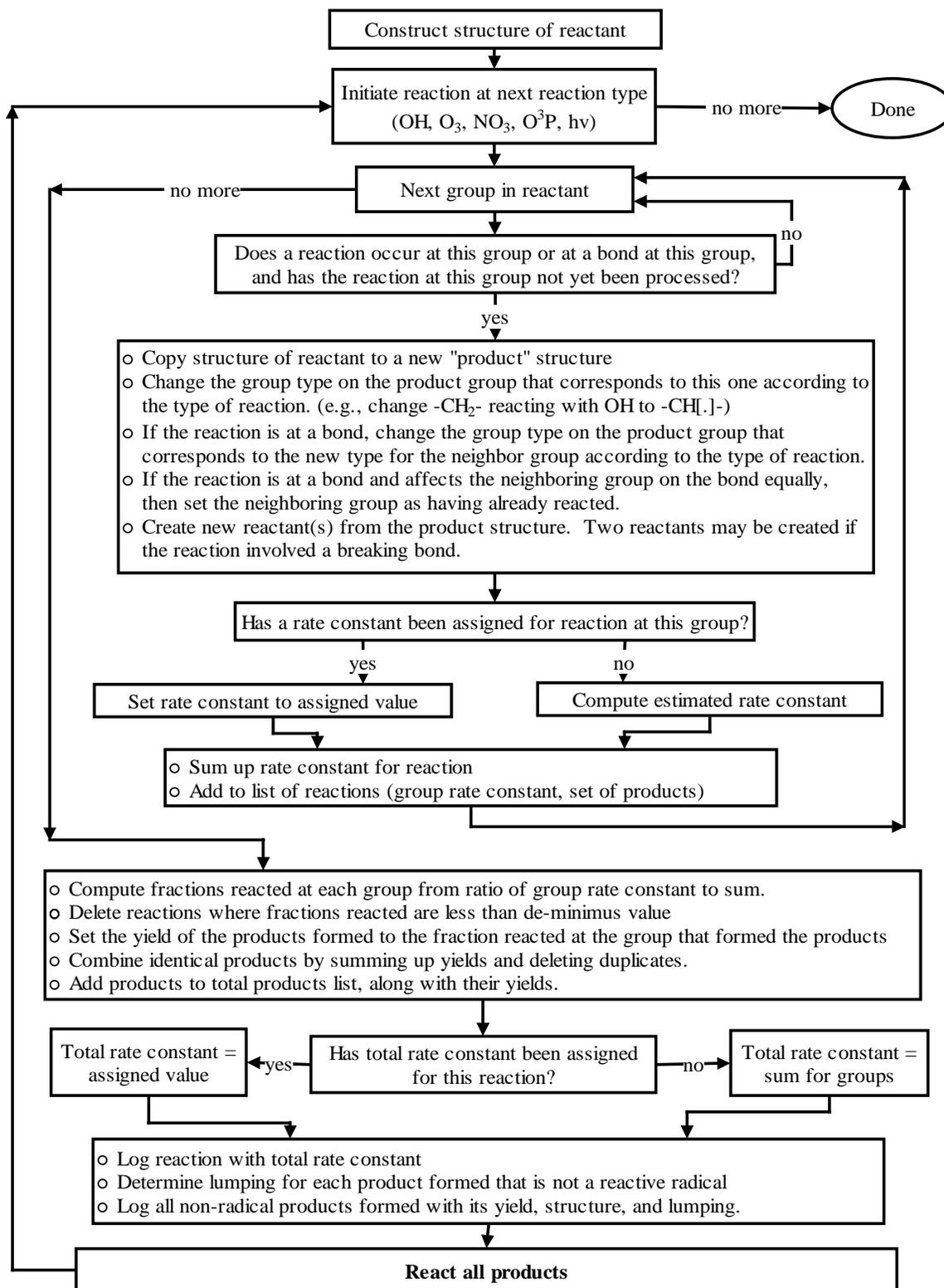
The atmospheric reaction mechanisms for most of the organic compounds that are represented by this mechanism are complex, can involve a large number of reactive intermediates (particularly for larger molecules), and in almost all cases involve reactions whose rate constants are unknown and have to be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

1. Mechanism Generation Procedure Overview

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

- The user inputs the structure of the compound. The structure is specified in terms of “groups” such as $-\text{CH}_2-$, $-\text{CO}-$, $-\text{OH}$, etc., which are similar to those used in the group additivity thermochemical estimation methods of Benson (1976) or the structure-reactivity kinetic estimate methods of Atkinson (1987). The specific groups used are summarized in Section II.C.2.
- The initial reactions of the compound with OH, O_3 , NO_3 , O^3P or photolysis are processed as shown schematically on Figure II-1. The rates of reactions at competing positions are estimated as discussed in Sections II.C.3 through 0, and the products and radicals formed, together with their yields, are logged. Documentation text is generated and logged, as appropriate.
- For each reactive organic radical formed, either in the initial reaction with OH, etc., or through the reactions of a previously formed radical, the system generates the all the reactions that are believed to be potentially important for the radical in the presence of NO_x in air. The radicals and products formed, and their yields (obtained by multiplying the yield of the starting radical times the branching ratios for the reactions forming them) are logged for further processing. Documentation text is also generated and logged for those reactions where estimates are involved. The types of radicals involved, and the reactions the system considers, are as follows:
 - Carbon centered (e.g. alkyl) radicals: Reaction with O_2 . In most cases this involves formation of the corresponding peroxy radical, but in a few cases (e.g. α -hydroxy alkyl radicals) other reactions can occur. In all cases, only a single reaction pathway is assumed, so the yield of the product(s) are assigned the yield of the starting radical. These reactions are discussed in Section II.C.8.

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



- Peroxy radicals (other than acetyl peroxy): Reaction with NO. This can involve formation of the corresponding alkyl nitrate (RONO₂) or formation of NO₂ and the corresponding alkoxy (RO·) radical. The conversion of NO to NO₂ in the latter reaction is logged as the formation of the “NO to NO₂ conversion product”. Nitrate yield estimates, discussed in Section II.C.9, are used to determine the yields of the nitrate, alkoxy radical, and NO to NO₂ conversion products relative to the starting radical.
- Alkoxy radicals: Reaction with O₂; β-scission decomposition; 1,4-H shift isomerization; or α-ester rearrangement (Tuazon et al, 1998b), when possible. The O₂ reaction involves the formation of HO₂ and a stable product, while the other reactions can involve formation of various carbon-centered radicals, in some cases with stable co-products. Various estimation methods or assignments, discussed in Section II.C.10 are used to derive the relevant rate constants or branching ratios.

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

- For each “product” species formed, which includes acetyl peroxy radicals, HO₂ and the NO to NO₂ conversion product as well as stable organic products, the yield, structure, and generation (number of NO to NO₂ conversions involved before it is formed) is logged. The lumping assignment for the product (the way it is represented in the base mechanism) is also determined and logged. Lumping assignments are discussed in Section II.C.11.
- Processing is completed once all the reactive radicals have been converted to stable products or radicals whose reactions are not generated (e.g., HO₂ or acyl peroxy radicals). The generated reaction list, product log (list of all products giving yields, structure and lumping), is saved for output or processing.
- Once all the relevant reactions for a VOC have been generated, the overall reactions or mechanistic parameters for the species can be derived, for use in model simulations. The sum of the yields of HO₂ and the NO to NO₂ conversion product in the product log are used to derive the corresponding HO₂, RO₂-R· and/or R₂O₂· yields. The yields of the lumped species representing the various organic products are summed to determine their total yields in the overall reaction. Loss or gain of carbon and nitrogens are tracked, and if necessary yields of “lost carbon” or “lost nitrogen” model species are determined to maintain balance.

Note that the system does not generate complete mechanisms for the VOCs, since peroxy + peroxy and peroxy + NO₂ reactions are ignored, and as indicated above acetyl peroxy radical reactions are not generated. However, even if the system generated all the peroxy + peroxy reactions, the current mechanism is not set up to use this information, because of the way the reactions of peroxy radicals are represented (see Section II.A.2.d). The present mechanism neglects the formation and decompositions of most peroxy nitrates because their rapid decompositions at ambient temperatures result in no net reaction, so information on the formation and generation of these species would also be ignored. The current mechanism is also not set up to take advantage of any detailed product information concerning the reactions of individual acyl peroxy radicals and their corresponding PAN analogues. Therefore the present system is sufficient to provide all the information that the current version of the mechanism can use. Expanded capabilities can be added in the future as mechanisms and models that can use them are developed.

2. Specification of Reactants and Summary of Groups

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

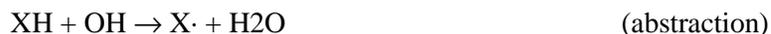
Group	Reactions at Group
<u>Carbon-Centered Radical centers</u>	
CH3.	O2 -> CH3OO.
-CH2.	O2 -> -CH2OO.
-CH[.]	O2 -> -CH[OO.]
>C[.]	O2 -> >C[OO.]
HCO.	O2 -> HO2. + CO
-CO.	O2 -> -CO[OO.]
<u>Vinyllic Radical centers</u>	
=CH.	X=CH2 + O2 -> X=O + HCO., where X is =CH2, =CH-, or =C<
=C[.]	X=CH[.] + O2 -> X=O + -C[OO.], where X is =CH2, =CH-, or =C<
<u>Peroxy Radical Centers</u>	
CH3OO.	NO -> CH3O.
-CH2OO.	NO -> -CH2O. + [NO conv NO2], NO -> -CH2-ONO2
-CH[OO.]	NO -> -CH[O.] + [NO conv NO2], NO -> -CH(ONO2)-
>C[OO.]	NO -> >C[O.] + [NO conv NO2], NO -> >C(ONO2)-
<u>Acyl Peroxy Radical Centers</u>	
-CO[OO.]	Not reacted
<u>Alkoxy radical Centers</u>	
CH3O.	O2 -> HO2 + HCHO
-CH2O.	O2 -> HO2 + -CHO, Decomposition, 1,5-H-shift isom, Ester rearrangement
-CH[O.]	O2 -> HO2 + -CO-, Decomposition, 1,5-H shift isom, Ester rearrangement
>C[O.]	Decomposition, 1,5-H shift isom.
HCO2.	O2 -> HO2 + CO2
-CO2.	Decomposition to R. + CO2
<u>Carbene Radical Centers</u>	
CH2:	O2 -> CH2OO[excited]
-CH:	O2 -> -CHOO[excited]
-C[:]	O2 -> COO[excited]
<u>Excited Crigiee Biradical Centers</u>	
CH2OO[excited]	Various unimolecular reactions -- see text
-CHOO[excited]	Various unimolecular reactions -- see text
-COO[excited]	Various unimolecular reactions -- see text
<u>Stabilized Crigiee Biradical Centers</u>	
CH2OO[stab]	Not reacted
-CHOO[stab]	Not reacted
-COO[stab]	Not reacted
<u>Elementary Product Groups</u>	
CH4	Not reacted (elementary product)
HCHO	Not reacted (elementary product)
CO	Not reacted (elementary product)
CO2	Not reacted (elementary product)
NO2	Not reacted (elementary product)
[NO conv NO2]	Used for Mechanism Processing

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

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

3. Reactions with OH Radicals

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



where XH is any H-containing group and X· is the corresponding depending on whether the compound. If the group has a double bond, the reaction is



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

a. Assigned Total OH Radical Rate Constants

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

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

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

Table II-8 (continued)

Compound	DMS name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
<u>Alkenes</u>								
Ethene	ETHENE	8.43e-12	1.96e-12		-0.870	1	8.44e-12	0%
Propene	PROPENE	2.60e-11	4.85e-12		-1.002	1	3.16e-11	21%
1-Butene	1-BUTENE	3.11e-11	6.55e-12		-0.928	1	3.16e-11	2%
3-Methyl-1-Butene	3M-1-BUT	3.14e-11	5.32e-12		-1.059	1	3.16e-11	1%
1-Pentene	1-PENTEN	3.11e-11	5.86e-12		-0.994	13	3.16e-11	2%
1-Hexene	1-HEXENE	3.66e-11	6.91e-12		-0.994	13	3.16e-11	-14%
3,3-Dimethyl-1-Butene	33M1-BUT	2.77e-11	5.23e-12		-0.994	13	3.16e-11	14%
1-Heptene	1-HEPTEN	3.96e-11	7.47e-12		-0.994	13	3.16e-11	-20%
Isobutene	ISOBUTEN	5.09e-11	9.47e-12		-1.002	1	5.79e-11	14%
2-Methyl-1-Butene	2M-1-BUT	6.04e-11	1.14e-11		-0.994	13	5.79e-11	-4%
2-Methyl-1-Pentene	2M1-C5E	6.23e-11	1.18e-11		-0.994	13	5.79e-11	-7%
trans-2-Butene	T-2-BUTE	6.32e-11	1.01e-11		-1.093	1	6.34e-11	0%
cis-2-Butene	C-2-BUTE	5.58e-11	1.10e-11		-0.968	1	6.34e-11	14%
2-Methyl-2-Butene	2M-2-BUT	8.60e-11	1.92e-11		-0.894	1	8.71e-11	1%
trans-2-Pentene	T-2-PENT	6.63e-11	1.25e-11		-0.994	13	6.34e-11	-4%
cis-2-Pentene	C-2-PENT	6.43e-11	1.21e-11		-0.994	13	6.34e-11	-1%
2,3-Dimethyl-2-Butene	23M2-BUT	1.09e-10	2.05e-11		-0.994	13	1.05e-10	-4%
Trans 4-Methyl-2-Hexene	T4M2-C5E	6.04e-11	1.14e-11		-0.994	13	6.34e-11	5%
2-Methyl-2-Pentene	2M-2-C5E	8.81e-11	1.66e-11		-0.994	13	8.71e-11	-1%
2,3-Dimethyl-2-Hexene	23M2-C5E	1.02e-10	1.92e-11		-0.994	13	1.05e-10	3%
Trans 4,4-dimethyl-2-Hexene	T44M2C5E	5.44e-11	1.03e-11		-0.994	13	6.34e-11	16%
Trans-2-Heptene	T-2-C7E	6.73e-11	1.27e-11		-0.994	13	6.34e-11	-6%
Trans-4-Octene	T-4-C8E	6.83e-11	1.29e-11		-0.994	13	6.34e-11	-7%
Cyclopentene	CYC-PNTE	6.63e-11	1.25e-11		-0.994	13	6.34e-11	-4%
Cyclohexene	CYC-HEXE	6.70e-11	1.26e-11		-0.994	13	6.34e-11	-5%
1,3-Butadiene	13-BUTDE	6.59e-11	1.48e-11		-0.890	1		
Isoprene	ISOPRENE	1.00e-10	2.55e-11		-0.815	1		
3-Carene	3-CARENE	8.71e-11	1.64e-11		-0.994	13	8.71e-11	0%
Sabinene	SABINENE	1.16e-10	2.19e-11		-0.994	13	5.79e-11	-50%
b-Pinene	B-PINENE	7.82e-11	2.38e-11		-0.709	1	5.79e-11	-26%
d-Limonene	D-LIMONE	1.69e-10	3.19e-11		-0.994	13	8.71e-11	-49%
a-Pinene	A-PINENE	5.31e-11	1.21e-11		-0.882	1	8.71e-11	64%
Styrene	STYRENE	5.80e-11				1		
2-(Cl-methyl)-3-Cl-Propene	CL2IBUTE	3.16e-11				1	5.79e-11	83%
<u>Aromatics</u>								
Benzene	BENZENE	1.24e-12	2.47e-12		0.411	3		
Toluene	TOLUENE	5.91e-12	1.81e-12		-0.705	3		
Ethyl Benzene	C2-BENZ	7.10e-12				3		
n-Propyl Benzene	N-C3-BEN	6.00e-12				3		
Isopropyl Benzene (cumene)	I-C3-BEN	6.50e-12				3		
s-Butyl Benzene	S-C4-BEN	6.00e-12				10		
m-Xylene	M-XYLENE	2.36e-11	2.36e-11		0.000	3		
o-Xylene	O-XYLENE	1.37e-11	1.37e-11		0.000	3		
p-Xylene	P-XYLENE	1.43e-11	1.43e-11		0.000	3		
1,2,4-Trimethyl Benzene	124-TMB	3.25e-11	3.25e-11		0.000	3		

Table II-8 (continued)

Compound	DMS name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
1,3,5-Trimethyl Benzene	135-TMB	5.75e-11	5.75e-11		0.000	3		
1,2,3-Trimethyl Benzene	123-TMB	3.27e-11	3.27e-11		0.000	3		
Indan	INDAN	9.20e-12				12		
Naphthalene	NAPHTHAL	2.12e-11	1.07e-12		-1.779	3		
Tetralin	TETRALIN	3.43e-11				6		
1-Methyl Naphthalene	1ME-NAPH	5.30e-11				11		
2-Methyl Naphthalene	2ME-NAPH	5.23e-11				5		
Methyl Naphthalenes	ME-NAPH	5.20e-11				4		
2,3-Dimethyl Naphth.	23-DMN	7.68e-11				5		
Phenol	PHENOL	2.63e-11				3		
o-Cresol	O-CRESOL	4.20e-11				3		
m-Cresol	M-CRESOL	6.40e-11				3		
p-Cresol	P-CRESOL	4.70e-11				3		
Nitrobenzene	NO2-BENZ	1.50e-13				8		
Monochlorobenzene	CL-BEN	7.70e-13				3		
p-Dichlorobenzene	CL2-BEN	5.55e-13				7		
Benzotrifluoride	CF3-BEN	4.60e-13				9		
p-Trifluoromethyl-Cl-Benzene	PCBTF	2.40e-13				9		
<u>Alkynes</u>								
Acetylene	ACETYLEN	9.12e-13	9.40e-12		1.391	14		
Methyl Acetylene	ME-ACTYL	5.90e-12				14		
Ethyl Acetylene	ET-ACTYL	8.00e-12				14		
2-Butyne	2-BUTYNE	2.72e-11	1.00e-11		-0.596	14		
<u>Alcohols and Glycols</u>								
Methanol	MEOH	9.34e-13	3.10e-12		0.715	17	6.25e-13	-33%
Ethanol	ETOH	3.28e-12	5.56e-13		-1.057	17	3.61e-12	10%
Isopropyl Alcohol	I-C3-OH	5.32e-12	6.49e-13		-1.254	14	7.26e-12	37%
n-Propyl Alcohol	N-C3-OH	5.53e-12				14	5.51e-12	0%
t-Butyl Alcohol	T-C4-OH	1.13e-12	3.86e-13		-0.640	21	6.87e-13	-39%
n-Butyl Alcohol	N-C4-OH	8.57e-12				14	6.93e-12	-19%
Cyclopentanol	CC5-OH	1.07e-11				22	1.03e-11	-4%
Pentyl Alcohol	C5OH	1.11e-11				14	8.35e-12	-25%
2-Pentanol	2-C5OH	1.18e-11				22	1.14e-11	-3%
3-Pentanol	3-C5OH	1.22e-11				22	1.30e-11	7%
2-Hexanol	2-C6OH	1.21e-11				22	1.28e-11	6%
1-Hexanol	1-C6OH	1.25e-11				14	9.78e-12	-22%
1-Heptanol	1-C7OH	1.37e-11				14	1.12e-11	-18%
1-Octanol	1-C8-OH	2.02e-11				23	1.26e-11	-38%
2-Octanol	2-C8-OH	2.52e-11				23	1.56e-11	-38%
3-Octanol	3-C8-OH	3.14e-11				23	1.73e-11	-45%
4-Octanol	4-C8-OH	2.87e-11				23	1.73e-11	-40%
Ethylene Glycol	ET-GLYCL	1.47e-11				24	8.38e-12	-43%
Propylene Glycol	PR-GLYCL	2.15e-11				24	1.28e-11	-40%

Table II-8 (continued)

Compound	DMS name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
<u>Ethers and Glycol Ethers</u>								
Dimethyl Ether	ME-O-ME	3.01e-12	1.04e-11		0.739	14	2.30e-12	-24%
Trimethylene Oxide	TME-OX	1.03e-11				16	5.76e-12	-44%
Tetrahydrofuran	THF	1.61e-11				14	1.41e-11	-12%
Diethyl Ether	ET-O-ET	1.31e-11	8.02e-13		-1.663	14	1.59e-11	22%
Alpha-Methyltetrahydrofuran	AM-THF	2.20e-11	2.52e-12		-1.292	25	2.08e-11	-5%
Tetrahydropyran	THP	1.38e-11				16	2.34e-11	70%
Methyl n-Butyl Ether	MNBE	1.48e-11				14	1.35e-11	-9%
Methyl t-Butyl Ether	MTBE	2.94e-12	5.89e-13		-0.960	14	1.66e-12	-44%
Ethyl t-Butyl Ether	ETBE	8.84e-12				14	8.48e-12	-4%
Di n-Propyl Ether	PR-O-PR	1.84e-11	1.18e-12		-1.639	14	2.18e-11	18%
Ethyl n-Butyl Ether	ENBE	2.13e-11				14	2.03e-11	-5%
Methyl t-Amyl Ether	MTAE	7.91e-12				22	2.82e-12	-64%
Di-n-butyl Ether	BU-O-BU	2.88e-11				14	2.46e-11	-15%
Di-Isobutyl Ether	IBU2-O	2.60e-11				26	2.46e-11	-5%
Di-n-Pentyl Ether	C5-O-C5	3.47e-11				27	2.75e-11	-21%
2-Methoxy-Ethanol	MEO-ETOH	1.33e-11	4.50e-12		-0.646	16	1.49e-11	12%
1-Methoxy-2-Propanol	MEOC3OH	2.00e-11				29	1.93e-11	-3%
2-Ethoxy-Ethanol	ETO-ETOH	1.87e-11				28	2.17e-11	16%
3-Ethoxy-1-Propanol	3ETOC3OH	2.20e-11				16	2.31e-11	5%
3-Methoxy-1-Butanol	3MEOC4OH	2.36e-11				16	2.67e-11	13%
2-Butoxy-Ethanol	BUO-ETOH	2.57e-11				30	2.61e-11	2%
2-(2-Ethoxyethoxy) EtOH	CARBITOL	5.08e-11				31	4.09e-11	-19%
<u>Esters</u>								
Methyl Formate	ME-FORM	2.27e-13				32	1.25e-13	-45%
Ethyl Formate	ET-FORM	1.02e-12				32	1.02e-12	0%
Methyl Acetate	ME-ACET	3.49e-13	8.30e-13		0.517	32	2.65e-13	-24%
Methyl Propionate	ME-PRAT	1.03e-12				32	6.87e-13	-33%
n-Propyl Formate	C3-FORM	2.38e-12				32	2.37e-12	0%
Ethyl Acetate	ET-ACET	1.60e-12				3	1.72e-12	7%
Ethyl Propionate	ET-PRAT	2.14e-12				32	2.14e-12	0%
n-Butyl Formate	C4-FORM	3.12e-12				32	3.79e-12	21%
Methyl Butyrate	ME-BUAT	3.04e-12				32	1.91e-12	-37%
Propyl Acetate	PR-ACET	3.40e-12				3	3.21e-12	-6%
Isopropyl Acetate	IPR-ACET	3.40e-12				3	3.48e-12	2%
Methyl Isobutyrate	ME-IBUAT	1.73e-12				33	1.17e-12	-32%
t-Butyl Acetate	TBU-ACET	4.25e-13				34	5.56e-13	31%
s-Butyl Acetate	SBU-ACET	5.50e-12				3	5.34e-12	-3%
n-Propyl Propionate	PR-PRAT	4.02e-12				32	3.64e-12	-9%
Ethyl Butyrate	ET-BUAT	4.94e-12				32	3.36e-12	-32%
n-Butyl Acetate	BU-ACET	4.20e-12				3	4.63e-12	10%
n-Propyl Butyrate	PR-BUAT	7.41e-12				32	4.86e-12	-34%
n-Butyl Butyrate	BU-BUAT	1.06e-11				32	6.28e-12	-41%

Table II-8 (continued)

Compound	DMS name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
Propylene Carbonate	PC	6.90e-13				36	3.79e-12	449%
Methyl Lactate	ME-LACT	2.76e-12				37	2.67e-12	-3%
Ethyl Lactate	ET-LACT	3.91e-12				37	4.12e-12	5%
Pr. Glycol Methyl Ether Acetate	PGME-ACT	1.44e-11				23	2.30e-11	59%
Dimethyl Succinate	DBE-4	1.50e-12				38	1.17e-12	-22%
Dimethyl Glutarate	DBE-5	3.50e-12				38	2.59e-12	-26%
Dimethyl Adipate	DBE-6	8.80e-12				38	4.01e-12	-54%
<u>Oxides</u>								
Ethylene Oxide	ETOX	7.60e-14				3	3.83e-13	404%
Propylene Oxide	PROX	5.20e-13				3	7.57e-13	46%
1,2-Epoxybutane	12BUOX	1.91e-12				39	2.00e-12	5%
<u>Acids</u>								
Formic Acid	FORMACID	4.50e-13	4.50e-13		0.000	3		
Acetic Acid	ACETACID	8.00e-13				14	2.10e-13	-74%
Propionic Acid	PROPACID	1.16e-12				14	1.34e-12	16%
<u>Aldehydes</u>								
Acetaldehyde	ACETALD	1.57e-11	5.60e-12		-0.616	15	1.58e-11	0%
Propionaldehyde	PROPALD	2.00e-11				15	2.01e-11	1%
2-Methylpropanal	2MEC3AL	2.60e-11	6.61e-12		-0.817	3	2.10e-11	-19%
Butanal	1C4RCHO	2.33e-11	5.26e-12		-0.886	3	2.14e-11	-8%
Pentanal	1C5RCHO	2.82e-11	6.34e-12		-0.890	3	2.28e-11	-19%
2,2-Dimethylpropanal (pivaldehyde)	22DMC3AL	2.63e-11	6.82e-12		-0.805	3	1.97e-11	-25%
3-Methylbutanal	3MC4RCHO	2.74e-11				3	2.28e-11	-17%
Acrolein	ACROLEIN	1.99e-11				3	3.16e-11	59%
Crotonaldehyde	CROTALD	3.64e-11				42	6.34e-11	74%
Methacrolein	METHACRO	3.33e-11	1.86e-11		-0.348	40	5.79e-11	74%
Hydroxy Methacrolein	HOMACR	4.30e-11				41	5.79e-11	35%
Isoprene Product #1	IP-MHY1	7.00e-11				41	8.71e-11	24%
Isoprene Product #2	IP-MHY2	7.00e-11				41	8.71e-11	24%
Isoprene Product #3	IP-HMY	7.00e-11				41	8.71e-11	24%
<u>Ketones</u>								
Acetone	ACETONE	2.22e-13	2.80e-12		1.510	15	2.09e-13	-6%
Cyclobutanone	CC4-KET	8.70e-13				18	4.42e-12	408%
Methyl Ethyl Ketone	MEK	1.20e-12	1.30e-12		0.050	17	1.35e-12	13%
Cyclopentanone	CC5-KET	2.94e-12				18	6.83e-12	132%
3-Pentanone	DEK	2.00e-12				3	2.49e-12	25%
2-Pentanone	MPK	4.90e-12				3	4.78e-12	-2%
Cyclohexanone	CC6-KET	6.39e-12				18	1.21e-11	89%
Methyl t-Butyl Ketone	MTBK	1.21e-12				19	1.72e-12	42%
4-Methyl-2-Pentanone	MIBK	1.41e-11				3	8.82e-12	-37%
Methyl n-Butyl Ketone	MNBK	9.10e-12				3	6.77e-12	-26%
Di-Isopropyl Ketone	DIPK	5.38e-12				20	5.07e-12	-6%
2-Heptanone	C7-KET-2	8.67e-12				19	8.19e-12	-6%

Table II-8 (continued)

Compound	DMS name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
2-Octanone	C8-KET-2	1.10e-11				19	9.61e-12	-13%
2-Nonanone	C9-KET-2	1.22e-11				19	1.10e-11	-10%
Di-isobutyl ketone (2,6-dimethyl 4-heptanone)	DIBK	2.75e-11				3	1.74e-11	-37%
2-Decanone	C10-K-2	1.32e-11				19	1.24e-11	-6%
Methylvinyl ketone	MVK	1.87e-11	4.14e-12		-0.900	3	3.16e-11	69%
<u>Other Oxygenates</u>								
Hydroxy Acetone	HOACET	3.02e-12				16	3.11e-12	3%
Methoxy Acetone	MEOACET	6.77e-12				16	7.11e-12	5%
Dimethyl Carbonate	DMC	3.30e-13				35	4.44e-13	35%

References

- 1 Rate constant expression recommended by Atkinson (1997a)
- 2 Room temperature rate constant from Carter et al (1999b).
- 3 Rate constant expression recommended by Atkinson (1989). Recommendation not changed in evaluation update by
- 4 Rate constant based on average of values for 1- and 2- isomers tabulated by Atkinson (1989).
- 5 Rate constant from Atkinson and Aschmann (1986).
- 6 Rate constant from Atkinson and Aschmann (1988a)
- 7 Rate constant from average of values for o-, m- and p- isomers tabulated by Atkinson (1989).
- 8 Rate constant based on data tabulated by Atkinson (1989) and consistent with more recent measurement given by Atkinson (1994).
- 9 Rate constant from Atkinson et al (1985).
- 10 Assumed to have same rate constant as n-propyl benzene
- 11 Rate constant from Atkinson and Aschmann (1987).
- 12 Rate constant from Baulch et al (1989).
- 13 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated based on data for similar alkenes.
- 14 Rate constant expression recommended by Atkinson (1994)
- 15 Rate expression recommended by IUPAC panel (Atkinson et al, 1997a).
- 16 Rate constant from Dagaut et al (1988a).
- 17 Rate expression recommended by IUPAC panel (Atkinson et al, 1999).
- 18 Rate constant from Dagaut et al (1988b).
- 19 Rate constant from Wallington and Kurylo (1987).
- 20 Rate constant from Atkinson et al (1982).
- 21 Rate constant used is Atkinson (1989) recommendation. k=8.1e-13 from Saunders et al (1994) not used because problems reported. k=1.43e-12 from Tuazon and co-workers (Carter et al, 1986c) does not fit chamber results (Carter et al, 1986c).
- 22 Rate constant from Wallington et al (1988a).
- 23 Rate constant from Carter et al (1999a).
- 24 Rate constant from Aschmann and Atkinson (1998).
- 25 Rate constant from Wallington et al (1990).
- 26 Rate constant from Bennett and Kerr (1989).
- 27 Rate constant from Wallington et al (1988b).
- 28 Rate constant of Dagaut et al (1988a) used. Value of Hartmann et al (1986) not consistent with chamber data (Carter

Table II-8 (continued)

References (continued)

- 29 Average of values of Porter et al (1995) and Aschmann and Atkinson (1998)
- 30 Average of values of Dagaut et al (1988a), Stemmler et al (1996) and Aschmann and Atkinson (1998), as tabulated by Aschmann and Atkinson (1997).
- 31 Rate constant from Carter et al (1993a).
- 32 Rate constant from Wallington et al (1988d).
- 33 Rate constant from Wells et al. (1999).
- 34 Rate constant from Smith et al (1992). Average of values relative to propane and n-butane
- 35 Rate constant used is average of various measurements tabulated by Sidebottom et al (1997).
- 36 Rate constant from Carter et al (1996c).
- 37 Rate constant from Atkinson and Carter (1995).
- 38 Rate constant from Carter et al (1997e).
- 39 Rate constant from Wallington et al (1988c).
- 40 See Carter and Atkinson (1996) and references therein.
- 41 Rate constant estimated by Carter and Atkinson (1996).
- 42 Rate constant from Atkinson et al (1983).

b. Estimation of OH Abstraction Rate Constants

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

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

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

If the compound has a C=C double bond anywhere in the molecule, at present the system assumes the abstraction reactions from any H-containing group are all negligible compared to the addition to the C=C double bond, and the abstraction rate constant is set at zero. Although methods exist for estimating these abstraction rate constants (Kwok and Atkinson, 1997), it is currently necessary to make

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

Group	k(group) = A T ^B e ^{-D/T} (cm ³ molec ⁻¹ s ⁻¹)					F(group)		F(subgroup)		
	k(298)	A	B	D	Ref	F	Ref	Subgroup	F	Ref
-CH3	1.36e-13	4.49e-18	2	320	a	1.00	a			
-CH2-	9.34e-13	4.50e-18	2	-253	a	1.23	a	-CH2(CO-)	3.90	a
								-CH2(CO-O-)	1.23	a
								-CH2(F)	0.61	a
								-CH2(Cl)	0.36	a
								-CH2(Br)	0.46	a
>CH-	1.95e-12	2.12e-18	2	-696	a	1.23	a	-CH(CO-)-	3.90	a
								-CH(CO-O-)-	1.23	a
								-CH(F)-	0.21	a
								-CH(Cl)-	0.36	a
								-CH(Br)-	0.46	a
>C<						1.23		>C(CO-)-	3.90	a
								>C(CO-O-)-	1.23	a
								>C(F)-	0.21	a
								>C(Cl)-	0.36	a
								>C(Br)-	0.46	a
-O-						8.40	a	-O(CO-)	1.60	a
								-O(CHO)-	0.90	e
								-O(NO2)-	0.04	a
-OH	1.40e-13	2.10e-18	2	85	a	3.50	a			
-CHO	1.58e-11	5.55e-12	0	-311	b	0.75	a			
HCO(O)-	0.00e+00				c	-				
-CO-						0.75	a	-CO(O-)	0.31	d
-ONO2						0.04	a			
-F						0.09	a			
-Cl						0.38	a			
-Br						0.28	a			
-I						0.53	a			
-NO2						0.00	a			

References

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

this approximation because general methods for generating and estimating the rates of all the possible reactions of the unsaturated radicals formed in these reactions have not yet been developed. Ignoring these abstraction reactions from unsaturated compounds is not a bad approximation for smaller molecules such as propene and the butenes, and all known mechanisms currently used in atmospheric models incorporate this approximation. However, abstraction at groups away from the double bonds can become non-negligible for the larger alkenes (see Atkinson, 1997a and references therein), so this approximation should be removed once methods to generate and estimate reactions of unsaturated radicals are developed.

c. Estimation of OH Addition Rate Constants

Rate constant estimates for additions to double bonds are made by estimating total rate constants for reaction at a double bond with a given number and configuration of substituents, and then, for unsymmetrical molecules, estimating the fraction that reacts at the each end. These estimates are shown on Table II-10, along with an indication of the derivation of the values used. The total rate constant estimates are based on measured rate constants for representative molecules, but only limited information is available upon which to base the branching ratio estimates,

These estimates are then used to derive a group rate constant for each of the two groups around the double bond. Note that since the present system does not support generating mechanisms with more than one C=C double bond (except for “special reactants”, as discussed later), the estimates on this table are only applicable to monoalkenes.

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

d. Comparison of Estimated and Assigned Rate Constants

Table II-8, above, shows a comparison of the estimated and assigned OH radical rate constants, from which one can obtain an indication of the overall performance of the estimation methods for the various types of VOCs. Table II-11 shows a summary of average percentage errors (biases) and average absolute percentage errors (errors) for OH radical rate constant estimates for various classes of VOCs. It can be seen that the estimation method performs reasonably well for alkanes and alkenes, having essentially no bias and an average error of less than 15%. The estimates do not perform as well for the oxygenated compounds, and appears to be biased high in the case of aldehydes and ketones. Refinements to the estimation method may improve the performance for these oxygenates, but updating the work of Kwok and Atkinson (1995) was beyond the scope of this report.

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

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

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

Class	Count	Average	
		Bias	Error
Alkanes	43	1%	10%
Alkenes	31	1%	14%
Alcohols and Glycols	41	-11%	22%
Esters	26	7%	38%
Aldehydes	14	16%	29%
Ketones	34	37%	54%
Others	3	14%	14%

Notes:

Bias is average of percentage differences between experimental and estimated values

Error is average of absolute value of percentage differences.

e. Assigned Mechanisms for Alkynes and Dialkenes

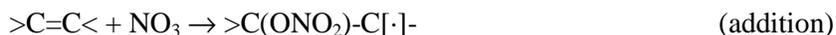
As indicated in Table II-7, mechanistic assignments for the reactions of several alkynes and dialkenes have also been incorporated into the mechanism generation system. Because these are “special reactants” containing groups that are currently not recognized by the system, all their reactions need to be explicitly. The rate constants for their reactions with OH radicals have been measured, and are included in Table II-8, above, and the mechanisms for these reactions are summarized on Table II-12. Footnotes to the table indicate the basis for the assigned mechanisms and branching ratios.

4. Reactions with NO₃ Radicals

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



And if it has a double bond, the reaction is



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

Table II-12. Assigned mechanisms for the reactions of OH radicals with the alkynes and dialkenes in the current mechanism.

Compound	Reaction	Factor	Ref
Acetylene	HC::CH + OH -> HO-CH=CH.	90%	1
	HC::CH + OH -> HCO-CH2.	10%	
Methyl Acetylene	HC::C-CH3 + OH -> CH3-C[.] =CH(OH)	100%	2
1-Butyne	HC::C-CH2-CH3 + OH -> CH3-CH2-C[.] =CH(OH)	100%	2
2-Butyne	CH3-C::C-CH3 + OH -> CH3-C(OH)=C[.] -CH3	100%	2
Isoprene	CH2=CH-C(CH3)=CH2 + OH -> HO-CH2-C[.](CH3)-CH=CH2	52.4%	3,4
	CH2=CH-C(CH3)=CH2 + OH -> CH2=C(CH3)-CH[.] -CH2-OH	42.6%	
	CH2=CH-C(CH3)=CH2 + OH -> CH2=CH-C(OH)(CH3)-CH2.	2.5%	
	CH2=CH-C(CH3)=CH2 + OH -> CH2=C(CH3)-CH(OH)-CH2.	2.5%	
1,3-Butadiene	CH2=CH-CH=CH2 + OH -> CH2=CH-CH[.] -CH2-OH	100%	2,4

References

- 1 The OH + acetylene mechanism is estimated based on the data of Hatakeyama et al (1986) and modeling acetylene environmental chamber runs (Carter et al, 1997c).
- 2 Addition to the terminal position is assumed to be the major reaction route
- 3 Mechanism of Carter and Atkinson (1996).
- 4 See the assigned reactions for carbon-centered radicals for the assumed relative rates of addition at the various radical centers of the allylic radicals.

a. Assigned NO₃ Radical Rate Constants

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

b. Estimated NO₃ Radical Rate Constants

Reaction of NO₃ with aldehyde groups are assumed to occur with the same rate constant as the used in the base mechanism for the reaction of NO₃ with acetaldehyde, which is (Atkinson et al, 1997a, 1999)

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

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

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

Compound	DMS name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
<u>Alkanes</u>								
Ethene	ETHENE	2.18e-16	4.39e-13	2.0	4.535	1	2.18e-16	0%
Propene	PROPENE	9.73e-15	4.59e-13		2.297	1	1.38e-14	42%
1-Butene	1-BUTENE	1.38e-14	3.14e-13		1.864	1	1.38e-14	0%
Isobutene	ISOBUTEN	3.32e-13	3.32e-13		0.000	2	3.32e-13	0%
cis-2-Butene	C-2-BUTE	3.47e-13	1.10e-13		-0.687	3	3.70e-13	7%
trans-2-Butene	T-2-BUTE	3.92e-13	1.10e-13	2.0	-0.759	1	3.70e-13	-6%
2-Methyl-2-Butene	2M-2-BUT	9.37e-12	9.37e-12		0.000	2	9.37e-12	0%
2,3-Dimethyl-2-Butene	23M2-BUT	5.72e-11	5.72e-11		0.000	2	5.72e-11	0%
Cyclopentene	CYC-PNTE	5.30e-13	5.30e-13		0.000	2	3.70e-13	-30%
Cyclohexene	CYC-HEXE	5.88e-13	1.05e-12		0.346	1	3.70e-13	-37%
1,3-Butadiene	13-BUTDE	1.00e-13	1.00e-13		0.000	2		
Isoprene	ISOPRENE	6.85e-13	3.03e-12		0.886	1		
a-Pinene	A-PINENE	6.09e-12	1.19e-12		-0.974	1		
3-Carene	3-CARENE	9.10e-12	9.10e-12		0.000	2		
b-Pinene	B-PINENE	2.51e-12	2.51e-12		0.000	2		
Sabinene	SABINENE	1.00e-11	1.00e-11		0.000	2		
d-Limonene	D-LIMONE	1.22e-11	1.22e-11		0.000	2		
2-(Cl-methyl)-3-Cl-Propene	CL2IBUTE	1.00e-15				4	3.32e-13	(large)
Styrene	STYRENE	1.51e-13				5		

References

- 1 Rate constant expression recommended by Atkinson (1997a)
- 2 Rate constant from Atkinson (1997a). Temperature dependence is assumed to be small.
- 3 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for trans-2-butene.
- 4 This rate constant estimated by Atkinson (private communication, 1997) based on the rate constant for NO₃ + Allyl chloride (Atkinson, 1991)
- 5 Rate constant from Atkinson and Aschmann (1988a).

The group rate constants used for estimating NO₃ addition rate constants is given on

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

The performance of the estimation method in predicting the measured NO₃ radical rate constants is indicated on Table II-13. Except for propene (for which estimates are not needed) and the halogenated alkene on the list (whose subsequent reactions are not currently supported by the system), the estimates generally perform reasonably well. Of course, in most cases this is because the estimates are

Table II-14. Group rate constants used for estimating rates of NO₃ addition reactions.

Groups	Estimated Total Rate Constant (300K) (cm ³ molec ⁻¹ s ⁻¹)	Fraction reacting at least substituted end
CH ₂ =CH-	1.38e-14 Total rate constant based on 300K value for 1-butene (Atkinson, 1997a).	1.0 100% addition at terminal end assumed.
CH ₂ =C<	3.32e-13 Total rate constant based on 300K value for isobutene (Atkinson, 1997a)	1.0 100% addition at terminal end assumed.
-CH=CH-	1.85e-13 Total rate constant based on averaging the 300K values for cis and trans 2-butene (Atkinson, 1997a).	0.5 Equal addition at each position assumed.
-CH=C<	9.37e-12 Total rate constant based on 300K value for 2-methyl-2-butene (Atkinson, 1997a).	1.0 100% Addition at the least substituted end is assumed.
>C=C<	2.86e-11 Total rate constant based on the 300K value for 2,3-dimethyl-2-butene (Atkinson, 1997a).	0.5 Equal addition at each position assumed.

based on these data. There does seem to be a bias towards underpredicting the rate constants for the cycloalkenes, and it may be appropriate to add a ring correction term for such compounds.

c. Assigned Mechanisms for Alkynes and Dialkenes

As discussed above, mechanistic assignments for the reactions of several alkynes and dialkenes have also been incorporated into the mechanism generation system, but their initial reactions need to be specified explicitly. Although reactions of NO₃ radicals with alkynes are assumed to be negligible the reactions of NO₃ with dialkenes isoprene and 1,3-butadiene may be nonnegligible. The mechanisms assigned to these reactions are given on Table II-15. Note that terminal addition is assumed to dominate in both cases, and in the case of isoprene the addition is assumed to occur primarily to the 1-position, based on the mechanism of Carter and Atkinson (1996).

5. Reactions with O₃

Reactions with O₃ are assumed to occur only at carbon-carbon double bonds⁵, and the reactions are assumed to involve ultimately breaking the bond and forming a carbonyl and an excited Crigee biradical, i.e.



⁵ Reactions of O₃ with alkynes are included as assigned reactions for special reactants (see Section II.C.5.d), but are not automatically generated by the system.

Table II-15. Assigned mechanisms for the reactions of NO₃ radicals with the dialkenes in the current mechanism.

Compound	Reaction	Ref
Isoprene	CH ₂ =CH-C(CH ₃)=CH ₂ + NO ₃ -> CH ₂ =CH-C[.](CH ₃)-CH ₂ -ONO ₂	1,2
1,3-Butadiene	CH ₂ =CH-CH=CH ₂ + NO ₃ -> CH ₂ =CH-CH[.]-CH ₂ -ONO ₂	3,2

References

- 1 Mechanism of Carter and Atkinson (1996) assumes that addition at this end of the molecule dominates.
- 2 See the assigned reactions for carbon-centered radicals for the assumed relative rates of addition at the various radical centers of the allylic radicals.
- 3 Estimated to be the major reaction route

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

a. Assigned O₃ Rate constants

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

b. Estimated Total Rate Constants

As discussed by Atkinson and Carter (1984), ozone + alkene rate constants tend to be quite variable depending on the structure of the compound, even if grouped according to the number of substituents on each side of the double bond. This is shown on

Figure II-2, which shows a comparison of the T=300K rate constants for the various monoalkenes tabulated by Atkinson (1997a), with a separate plot for each type of double bond structure. Note that cyclohexenes (which tend to have higher O₃ rate constants) and terpenes (whose structures the mechanism generation system cannot presently handle) are not shown. It can be seen that there is variability in the rate constants, particularly for the 1,1-disubstituted compounds. It is interesting to note that the more highly branched compounds tend to have the lowest rate constants, suggesting that steric effects may be important.

Fortunately, measured O₃ rate constants are available for most of the alkenes that are important in current emissions, which tend to be the lower molecular weight compounds. However, it is still necessary to have a method to estimate rate constants for those compounds where no data are available, even if it is uncertain. For this purpose, we use the average of the rate constants for the

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

Compound	DMS name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
<u>Alkanes</u>							
Ethene	ETHENE	1.68e-18	9.14e-15	5.127	1	1.68e-18	0%
Propene	PROPENE	1.05e-17	5.51e-15	3.732	1	1.01e-17	-4%
1-Butene	1-BUTENE	1.00e-17	3.36e-15	3.466	1	1.01e-17	1%
Isobutene	ISOBUTEN	1.17e-17	2.70e-15	3.243	1	1.18e-17	1%
cis-2-Butene	C-2-BUTE	1.28e-16	3.22e-15	1.924	1	1.15e-16	-10%
trans-2-Butene	T-2-BUTE	1.95e-16	6.64e-15	2.104	1	1.15e-16	-41%
1-Pentene	1-PENTEN	1.04e-17	3.36e-15	3.445	2	1.01e-17	-3%
2-Methyl-1-Butene	2M-1-BUT	1.66e-17	2.70e-15	3.037	3	1.18e-17	-29%
2-Methyl-2-Butene	2M-2-BUT	4.08e-16	2.87e-15	1.162	4	3.48e-16	-15%
3-Methyl-1-Butene	3M-1-BUT	1.14e-17	3.36e-15	3.388	2	1.01e-17	-12%
1-Hexene	1-HEXENE	1.14e-17	3.36e-15	3.388	2	1.01e-17	-12%
Cis-3-Hexene	C-3-C6E	1.53e-16	3.22e-15	1.816	5	1.15e-16	-25%
Trans-3-Hexene	T-3-C6E	1.74e-16	6.64e-15	2.170	6	1.15e-16	-34%
2-Methyl-1-Pentene	2M1-C5E	1.55e-17	2.70e-15	3.075	3	1.18e-17	-24%
3-Methyl-1-Pentene	3M1-C5E	5.12e-18	3.36e-15	3.867	2	1.01e-17	97%
4-Methyl-1-Pentene	4M1-C5E	9.57e-18	3.36e-15	3.494	2	1.01e-17	6%
Cis-3-Methyl-2-Hexene	C3M2-C5E	4.56e-16	2.87e-15	1.096	4	3.48e-16	-24%
Trans 3-Methyl-2-Hexene	T3M2-C5E	5.66e-16	2.87e-15	0.967	4	3.48e-16	-39%
2,3-Dimethyl-1-Butene	23M1-BUT	1.35e-17	2.70e-15	3.160	3	1.18e-17	-12%
3,3-Dimethyl-1-Butene	33M1-BUT	5.43e-18	3.36e-15	3.832	2	1.01e-17	86%
2,3-Dimethyl-2-Butene	23M2-BUT	1.14e-15	3.03e-15	0.584	1	6.74e-16	-41%
2-Ethyl-1-Butene	2E1-BUT	1.35e-17	2.70e-15	3.160	3	1.18e-17	-12%
1-Heptene	1-HEPTEN	1.25e-17	3.36e-15	3.337	2	1.01e-17	-19%
2,3,3-trimethyl-1-Butene	233M1BUT	8.63e-18	2.70e-15	3.426	3	1.18e-17	37%
1-Octene	1-OCTENE	1.45e-17	3.36e-15	3.246	2	1.01e-17	-30%
Cis-4-Octene	C-4-C8E	9.73e-17	3.22e-15	2.086	5	1.15e-16	18%
Trans-4-Octene	T-4-C8E	1.44e-16	6.64e-15	2.285	6	1.15e-16	-20%
Trans 2,5-Dimethyl 3-Hexene	T25M3C6E	4.24e-17	6.64e-15	3.013	6	1.15e-16	171%
Trans 2,2-Dimethyl 3-Hexene	T22M3C6E	4.34e-17	6.64e-15	2.998	6	1.15e-16	165%
2,4,4-trimethyl-2-Pentene	244M2C5E	1.43e-16	2.87e-15	1.788	4	3.48e-16	144%
3-Methyl-2-Isopropyl-1-Butene	3M2I1C4E	3.45e-18	2.70e-15	3.972	3	1.18e-17	242%
1-Decene	1-C10E	9.67e-18	3.36e-15	3.488	2	1.01e-17	4%
Cis-5-Decene	C-5-C10E	1.23e-16	3.22e-15	1.948	5	1.15e-16	-6%
3,4-Diethyl-2-Hexene	34E2-C6E	4.39e-18	2.87e-15	3.864	4	3.48e-16	(large)
Cyclopentene	CYC-PNTE	5.61e-16	1.80e-15	0.696	1	1.15e-16	-79%
1-Methyl cyclohexene	1M-CC5E	6.76e-16	2.70e-15	0.825	3	3.48e-16	-49%
Cyclohexene	CYC-HEXE	8.33e-17	2.88e-15	2.112	1	1.15e-16	38%
1-Methyl Cyclohexene	1M-CC6E	1.68e-16	2.87e-15	1.690	4	3.48e-16	107%
4-Methyl Cyclohexene	4M-CC6E	8.40e-17	2.88e-15	2.107	7	1.15e-16	37%
1,2-Dimethyl Cyclohexene	12M-CC6E	2.11e-16	3.03e-15	1.589	8	6.74e-16	220%
1,3-Butadiene	13-BUTDE	6.64e-18	1.34e-14	4.537	1		
Isoprene	ISOPRENE	1.34e-17	7.86e-15	3.802	1		
a-Pinene	A-PINENE	8.80e-17	1.01e-15	1.455	1		

Table II-16 (continued)

Compound	DMS name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	Ea kcal/mole	Ref	Est'd k(300) k (diff)
3-Carene	3-CARENE	3.78e-17	1.01e-15	1.958	9	3.48e-16
b-Pinene	B-PINENE	1.54e-17	1.01e-15	2.493	9	1.18e-17
Sabinene	SABINENE	8.74e-17	1.01e-15	1.459	9	1.18e-17
d-Limonene	D-LIMONE	2.04e-16	3.71e-15	1.729	10	3.48e-16
2-(1-methyl)-3-Cl-Propene	CL2IBUTE	3.90e-19			11	1.18e-17
Styrene	STYRENE	1.71e-17			12	
<u>Alkynes</u>						
Acetylene	ACETYLEN	8.61e-21	2.00e-14	8.739	13	
Methyl Acetylene	ME-ACTYL	1.56e-20	1.00e-14	7.970	14	
Ethyl Acetylene	ET-ACTYL	2.15e-20	1.00e-14	7.780	14	
2-Butyne	2-BUTYNE	2.15e-20	1.00e-14	7.780	15	

References

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

Figure II-2. Comparison of O₃ + alkene rate constants for alkenes with the same configurations of constituents about the double bond.

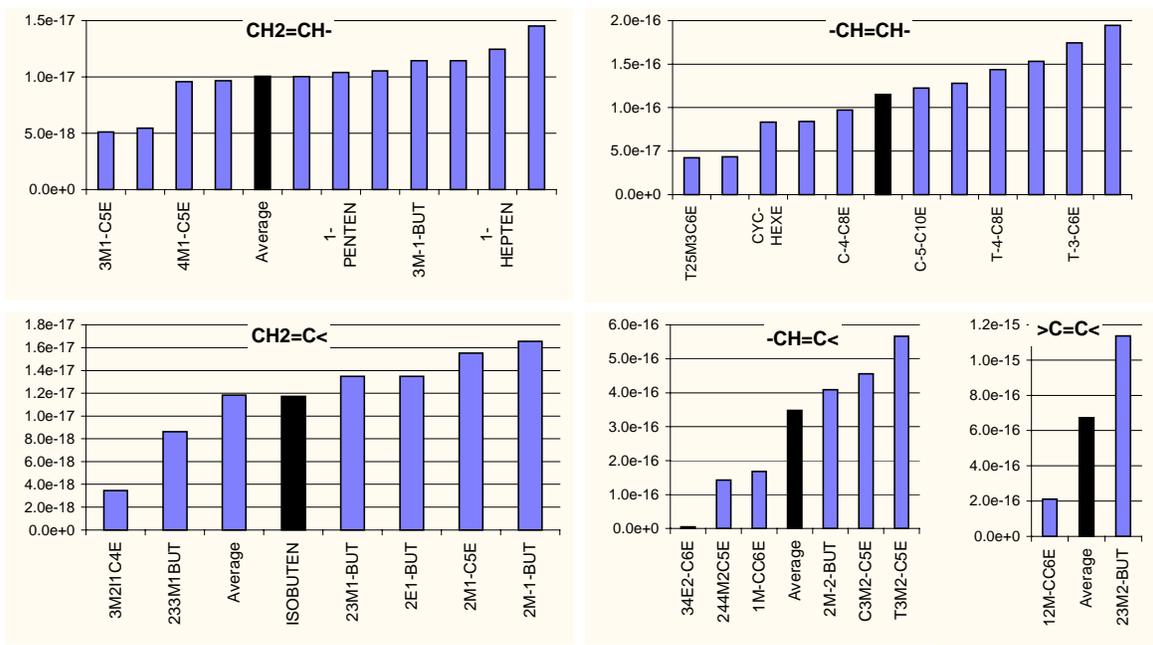


Table II-17. Summary of rate constant estimates for reactions of O₃ at alkene groups.

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

reactions at the various types of double bonds, as shown on Figure II-2, and as summarized on Table II-17. Table II-16, above, shows the discrepancies between the experimental and estimated values for all the alkenes in the current mechanism. The anomalously low value for 3,4-dietyl-2-hexene (which may be low because of steric hindrance) was not used when computing the average for $-\text{CH}=\text{C}<$. Although there is variability, the averages are probably appropriate as best estimates for compounds whose rate constants are not known, at least for use by the mechanism generation system at its current state of development. Obviously, compounds with large steric effects need to be estimated on a case-by-case basis.

c. Branching Ratios for Biradical Formation

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

For alkenes with $\text{CH}_2=\text{CH}-$ groups, Table II-18 indicates that the data for most alkenes are consistent with assuming equal probability for each of the two possible reaction modes. This is therefore assumed when generating O_3 reaction mechanisms for all alkenes of this type. The major exception appears to be highly branched compounds such as 3,3-dimethyl-1-butene, where steric effects may tend to reduce biradical formation on the most substituted side. Since the current mechanism generation system is not capable of assessing steric effects, such compounds need to be handled on a case-by-case basis. However, present assignments are not made for such compounds because they are not important in current emissions inventories. The average error in assuming equal splits for the compounds where data are available is less than 10%, and the absolute value of the percentage error is less than 15%.

For alkenes with $\text{CH}_2=\text{C}<$ groups, Table II-19 indicates that the data are more consistent with assuming that fragmentation to formaldehyde + the disubstituted is essentially twice as probable as fragmentation to the ketone + HCHO_2 in essentially all cases. Steric effects appear to be less important in affecting this generalization, as suggested by the data for 2,3,3-trimethyl-1-butene. Therefore, the O_3 reactions of alkenes of this type are generated based on assuming that ketone + HCHO_2 formation occurs 33.3% of the time, as indicated on the table. This gives an average error of less than 5% and an average absolute percentage error of less than 15%.

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

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

	Experimental			Estimated		OH Yield		
	HCHO	RCHO	Sum	RCHO	Error	Expt.	Est'd.	Error
<u>CH₂=CH- Average</u>		<u>0.54</u>		<u>0.5</u>	<u>-8%</u>			<u>-6%</u>
Propene	0.71	0.48	1.20	0.5	3%	0.33	0.32	-3%
1-Butene	0.63	0.35	0.98	0.5	30%	0.41	0.32	-22%
1-Pentene	0.55	0.52	1.07	0.5	-4%	0.37	0.32	-14%
1-Hexene	0.54	0.53	1.07	0.5	-5%	0.32	0.32	0%
1-Heptene	0.52	0.55	1.07	0.5	-9%	0.27	0.32	19%
1-Octene	0.50	0.51	1.01	0.5	-2%	0.32	0.32	0%
1-Decene	0.53	0.49	1.02	0.5	2%			
3-Methyl-1-Butene	0.50	0.51	1.01	0.5	-2%			
3-Methyl-1-Pentene	0.39	0.63	1.03	0.5	-26%			
4-Methyl-1-Pentene	0.44	0.71	1.15	0.5	-41%			
3,3-Dimethyl-1-Butene	0.32	0.67	0.99	0.5	-34%			
Cyclohexene						0.68	0.52	-24%

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

	Experimental			Estimated		OH Yield		
	HCHO	R-CO-R'	Sum	R-CO-R'	Error	Expt.	Calc	Error
<u>CH₂=C< Average</u>		<u>0.34</u>		<u>0.333</u>	<u>-2%</u>			<u>4%</u>
Isobutene	0.98	0.32	1.29	0.333	4%	0.84	0.71	-16%
2-Methyl-1-Butene	0.64	0.28	0.92	0.333	16%	0.83	0.71	-15%
2-Methyl-1-Pentene	0.62	0.32	0.94	0.333	3%			
2-Ethyl-1-Butene	0.49	0.30	0.80	0.333	9%			
2,3-Dimethyl-1-Butene	0.72	0.38	1.10	0.333	-14%	0.5	0.71	41%
2,3,3-trimethyl-1-Butene	0.64	0.35	0.99	0.333	-6%			
3-Methyl-2-Isopropyl-1-Butene	0.61	0.43	1.03	0.333	-28%			

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

	Experimental			Estimated		OH Yield		
	RCHO	R-CO-R'	Sum	R-CO-R'	Error	Expt.	Calc	Error
<u>-CH=C< Average</u>		<u>0.27</u>		<u>0.3</u>	<u>10%</u>			<u>-8%</u>
2-Methyl-2-Butene	0.72	0.34	1.05	0.3	-13%	0.91	0.84	-8%
2,4,4-Trimethyl-2-Pentene	0.84	0.19	1.03	0.3	38%			
3,4-Diethyl-2-Hexene	0.71	0.29	0.99	0.3	4%			
1-Methyl Cyclohexene						0.90	0.84	-7%

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

Table II-18 through Table II-20 also show measured yields of OH radicals, which are believed to be formed from secondary radicals of the biradical intermediates (see Section ??). If it is assumed that the OH yields from the excited HCHO_2 , RCHO_2 , and $\text{RR}'\text{CO}_2$ biradicals are independent of the molecule from which they are formed and on the nature of the “R” or “R'” substituents, then these OH yields should be consistent with the assumed branching ratios and the OH yields assumed for the various types of biradicals. As discussed in Section ??, the current mechanism assumes that OH yields from excited HCHO_2 , CH_3CHO_2 , are respectively 12%, 52%, and 100%, based primarily on recommendations and data discussed by Atkinson (1997a). The “Calc'd” OH yields on Table II-18 through Table II-20 show the yields for the various molecules derived based on these assumptions, where they can be compared with the experimental data. In most cases these are consistent with the experimental data, with the percentage errors being no greater than those for the estimated carbonyl yields. Therefore, the estimates based on carbonyl yields and OH yields are self-consistent. However, as discussed in Section ??, the experimental and estimated OH yields for the C_{4+} 1-alkenes are not consistent with the environmental chamber reactivity data for these compounds, and lower adjusted OH yields have to be used for the purpose of reactivity predictions. However, these adjustments do not affect the assumed branching ratios for the initial $\text{O}_3 + \text{alkene}$ reactions.

d. Assigned Mechanisms for Alkynes and Dialkenes

As discussed above, the mechanisms for the initial reactions of alkynes and dialkenes need to be specified explicitly. The mechanisms used for the reactions of ozone with these compounds are given in Table II-21, along with footnotes indicating the sources of the mechanisms that are used. Note that the mechanisms for the reactions of O_3 with acetylenes are largely speculative, and are based on the assumption that they are analogous to the reactions of O_3 with alkenes, which may not in fact be the case. It is also assumed that the excited biradicals predicted to be formed in the $\text{O}_3 + \text{alkyne}$ reactions will react in the same way as the when those biradicals are formed from, for example, $\text{O}_3 + \text{acrolein}$, even though they almost certainly will have different excitation energy.

The isoprene + NO_3 mechanism is based on that of Carter and Atkinson (1996). The reactions of 1,3-butadiene are expected to be similar, though in this case the formation of the oxide is ignored.

6. Reactions with O^3P

O^3P atoms can react with compounds with $\text{C}=\text{C}$ double bonds, forming an excited adduct that may decompose in various ways or undergo collisional stabilization. Although these reactions are generally of negligible importance under most ambient atmospheric conditions, they have been found to

Table II-21. Assigned mechanisms for the reactions of NO₃ radicals with the acetylenes and dialkenes in the current mechanism.

Compound	Reaction	Factor	Ref
Acetylene	HC::CH + O ₃ -> HCO-CHOO[excited]	100%	1
Methyl Acetylene	HC::C-CH ₃ + O ₃ -> CH ₃ -COO[excited]-CHO	50%	2
	HC::C-CH ₃ + O ₃ -> CH ₃ -CO-CHOO[excited]	50%	
1-Butyne	HC::C-CH ₂ -CH ₃ + O ₃ -> CH ₃ -CH ₂ -COO[excited]-CHO	50%	2
	HC::C-CH ₂ -CH ₃ + O ₃ -> CH ₃ -CH ₂ -CO-CHOO[excited]	50%	
2-Butyne	CH ₃ -C::C-CH ₃ + O ₃ -> CH ₃ -CO-COO[excited]-CH ₃	100%	2
	CH ₂ =CH-C(CH ₃)=CH ₂ + O ₃ -> HCHO + CH ₂ =CH-COO[excited]-CH ₃	20%	
	CH ₂ =CH-C(CH ₃)=CH ₂ + O ₃ -> HCHO + CH ₂ =C(CHOO[excited])-CH ₃	20%	
Isoprene	CH ₂ =CH-C(CH ₃)=CH ₂ + O ₃ -> CH ₂ =C(CHO)-CH ₃ + CH ₂ OO[excited]	39%	3,4
	CH ₂ =CH-C(CH ₃)=CH ₂ + O ₃ -> CH ₂ =CH-CO-CH ₃ + CH ₂ OO[excited]	16%	
	CH ₂ =CH-C(CH ₃)=CH ₂ + O ₃ -> O ₂ + CH ₂ =CH-C(CH ₃)(O*)-CH ₂ -*	2.5%	
	CH ₂ =CH-C(CH ₃)=CH ₂ + O ₃ -> O ₂ + CH ₂ =C(CH ₃)-CH(O*)-CH ₂ -*	2.5%	
1,3-Butadiene	CH ₂ =CH-CH=CH ₂ + O ₃ -> HCHO + CH ₂ =CH-CHOO[excited]	50%	2,4
	CH ₂ =CH-CH=CH ₂ + O ₃ -> CH ₂ =CH-CHO + CH ₂ OO[excited]	50%	

References

- 1 The reaction is assumed to proceed via initial formation of a primary ozonide, followed by an O-O bond scission forming the excited biradical structure formed. Although the biradical excitation energy is expected to be different from the biradical that might be formed from the reaction of O₃ with an acrolein, it is assumed to have the same subsequent reactions, and is therefore shown as the same species.
- 2 Mechanism assumed to be analogous to the mechanism shown for acetylene, above. Equal probability of breaking the two O-O bonds in the primary ozonide is assumed.
- 3 Mechanism of Carter and Atkinson (1996).
- 4 Equal probability assumed for the two possible decompositions for the primary ozone, as assumed for the reactions of O₃ with monoalkenes such as 1-butene. Although some oxide formation may also occur, it is expected to be relatively minor and is ignored.

be non-negligible in some of the environmental chamber experiments used for mechanism evaluation, where NO₂ concentrations tend to be higher under ambient conditions⁶. They may also be non-negligible in plumes that have higher NO_x concentrations than ambient. For these reasons, O³P + alkene reactions are included in the current mechanism and are supported by the mechanism generation system.

a. Assigned O³P Rate Constants

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

b. Estimated O³P Rate Constants

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

$$\ln(k\text{O}^3\text{P}) = 19.160 + 1.864 k(\text{OH}) \quad (\text{II})$$

where $k\text{O}^3\text{P}$ and $k\text{OH}$ are the O³P and OH radical rate constants in cm³ molec⁻¹ s⁻¹. (Note that the third digits are significant since they are being used to compute logarithms.) Although the dialkenes and the terpenes are not used when deriving this fit, Table II-22 and Figure II-3 show that Equation (II) performs reasonably well in predicting their rate constants in most cases. Including the terpenes and dialkenes, the average discrepancy is around 25%, and all the discrepancies in all cases except for d-limonene are less than 60%.

c. Estimated Mechanisms for O³P Reactions

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

⁶ Reactions with O₃P increase in importance as NO₂ concentrations increase because NO₂ photolysis is the primary source of O³P.

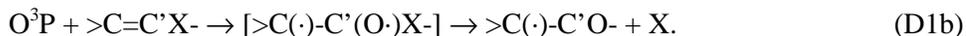
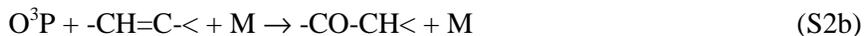
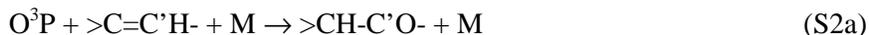
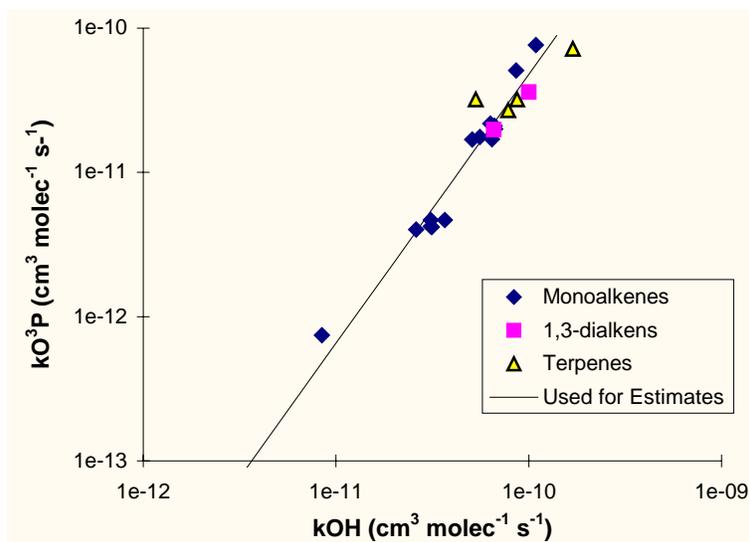
Table II-22. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with O³P atoms in the present mechanism.

Compound	DMS name	k(300) (cm ³ molec ⁻¹ s ⁻¹)	A	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
<u>Alkanes</u>							
Ethene	ETHENE	7.42e-13	1.04e-11	1.574	1		
Propene	PROPENE	4.01e-12	1.18e-11	0.644	1	3.91e-12	-2%
1-Butene	1-BUTENE	4.22e-12	1.25e-11	0.648	1	5.43e-12	29%
Isobutene	ISOBUTEN	1.69e-11			2	1.36e-11	-20%
cis-2-Butene	C-2-BUTE	1.76e-11			2	1.62e-11	-8%
trans-2-Butene	T-2-BUTE	2.18e-11			2	2.04e-11	-6%
1-Pentene	1-PENTEN	4.69e-12	1.48e-11	0.686	3	5.42e-12	16%
cis-2-Pentene	C-2-PENT	1.70e-11			2	2.09e-11	23%
3-Methyl-1-Butene	3M-1-BUT	4.18e-12	1.32e-11	0.686	3	5.55e-12	33%
2-Methyl-2-Butene	2M-2-BUT	5.10e-11			2	3.62e-11	-29%
1-Hexene	1-HEXENE	4.69e-12	1.48e-11	0.686	3	7.37e-12	57%
2,3-Dimethyl-2-Butene	23M2-BUT	7.64e-11			2	5.60e-11	-27%
Cyclopentene	CYC-PNTE	2.10e-11			2	2.23e-11	6%
Cyclohexene	CYC-HEXE	2.00e-11			2	2.26e-11	13%
1-Methyl Cyclohexene	1M-CC6E	9.00e-11			2	3.71e-11	-59%
1,3-Butadiene	13-BUTDE	1.98e-11			2		
Isoprene	ISOPRENE	3.60e-11			4		
a-Pinene	A-PINENE	3.20e-11			2	1.48e-11	-54%
3-Carene	3-CARENE	3.20e-11			2	3.69e-11	15%
b-Pinene	B-PINENE	2.70e-11			2	3.03e-11	12%
d-Limonene	D-LIMONE	7.20e-11			2	1.28e-10	78%

References

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

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



Where, for unsymmetrical molecules, C' refers to the carbon that has the greater number of substituents. Branching ratios estimated or interpolated based on these data are given in Table II-23, where the branching ratio designations used are as indicated above, and footnotes indicate the source of the estimated mechanisms. Note that these ratios are applicable to one atmosphere total pressure only – the mechanism generation system currently does not support predicting the effects of total pressure on these yields⁷. Atkinson (1997a) and Atkinson and Lloyd (1994) gave no recommendations for compounds of with CH₂=C<, -CH=C<, or >C=C<, and highly approximate estimates are made based on

⁷ Ignoring these pressure dependences is unlikely to introduce significant errors in tropospheric simulations because NO₂ concentrations are expected to be sufficiently low at higher altitudes that reactions of O³P with alkenes is expected to be negligible.

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

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

1 Based on Atkinson (1997a) recommendation, ignoring ketene formation, which is lumped with the D2 decomposition route

2 Based on Atkinson (1997a) and Atkinson and Lloyd (1984) recommendation. Numbers rounded to nearest 5%

3 Based on extrapolating from data for lower molecular weight alkenes, assuming that stabilization will increase with the size of the molecule increases.

4 Estimated based on recommended mechanisms given by Atkinson and Lloyd (1994) for other alkenes.

5 Based on the Atkinson (1997a) and Atkinson and Lloyd (1984) recommendation, with the chemically unreasonable 20% CH₃ shift represented by increasing oxide formation and

considerations of data given by Atkinson and Lloyd (1994) for other compounds⁸. As indicated on the table, stabilization is assumed to become increasingly important for higher molecular weight compounds, and to dominate for C₇₊ alkenes.

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

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

d. Assigned Mechanisms for Dialkenes

Although it is expected that the reactions of O³P with alkynes are unimportant and therefore are ignored in the mechanism, their reactions with isoprene and 1,3-butadiene may be non-negligible under some conditions, and need to be specified explicitly. The assigned O³P mechanisms for these compounds are shown on Table II-25. The O³P + isoprene mechanism is based on that of Carter and Atkinson (1996), and the mechanism for 1,3-butadiene is assumed to be analogous.

7. Photolysis Reactions

Although the previous mechanism represented all aldehydes and ketones using the lumped molecule approach, this approach has proven to be unsatisfactory for the higher ketones (Carter et al, 1999a) and is therefore not used in this mechanism. Instead, specific mechanistic assignments are made for these compounds, based on generated mechanisms for their reactions with OH radicals, NO₃ (for

⁸ It is probable that improved estimates could be made for some of these compounds by reviewing the product data literature. This review was not carried out because of the relatively low importance of these O³P reactions in most atmospheric simulations, and because in any case the branching ratios had to be revised to fit the chamber data.

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

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

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

Compound	Reaction	Ref
Isoprene	CH ₂ =CH-C(CH ₃)=CH ₂ + O ₃ P -> CH ₂ =CH-C(CH ₃)(O*)-CH ₂ -*	50%
	CH ₂ =CH-C(CH ₃)=CH ₂ + O ₃ P -> CH ₂ =C(CH ₃)-CH(O*)-CH ₂ -*	25%
	CH ₂ =CH-C(CH ₃)=CH ₂ + O ₃ P -> CH ₂ =CH-CO-CH ₂ . + CH ₃ .	25%
1,3-Butadiene	CH ₂ =CH-CH=CH ₂ + O ₃ P -> CH ₂ =CH-CH(O*)-CH ₂ -*	75%
	CH ₂ =CH-CH=CH ₂ + O ₃ P -> CH ₂ =CH-CH[.]CHO + H.	25%

References

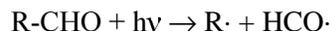
- 1 Mechanism of Carter and Atkinson (1996). Most of the O addition is assumed to occur at the most substituted end of the molecule, so a higher yield is assumed for the corresponding oxide.
- 2 Assumed to be analogous to the mechanism used for isoprene (Carter and Atkinson, 1996).

aldehydes), and photolyses. Specific mechanistic assignments are also made for the OH radical and photolysis reactions of organic nitrates, which were used for determining the lumped organic nitrate mechanism as discussed in Section II.A.3.b. The estimation and generation of their initial reactions with OH radicals and NO₃ were discussed above. This section discusses the estimation and generation of their initial photolysis reactions.

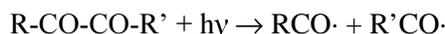
Photolysis rates for carbonyl compounds and organic nitrates are estimated by assuming that they have the same absorption cross sections and quantum yields as the most chemically similar lower molecular weight analogue that is in the base mechanism. The specific assignments are as summarized on Table II-26, along with the groups used by the mechanism generation system to classify compounds according to photolysis type, and footnotes indicating the derivation of the assignments. Note that if the molecule has groups bonded to the carbonyl or nitrate groups that are different than those indicated on the table, then the system cannot currently generate photolysis reactions for compounds with that structure.

a. Default Carbonyl Photolysis Mechanisms

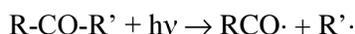
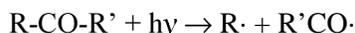
Although the actual mechanisms for the photolysis reactions of the higher molecular weight carbonyl compounds may well be more complex (Calvert and Pitts, 1966), unless information is available otherwise is assumed that all photolyses of carbonyls proceed by breaking the weakest CO-C bond. In the case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



(where “R” would be R’CO in the case of glyoxals) and in the case of α -dicarbonyl ketones it is assumed always to proceed via



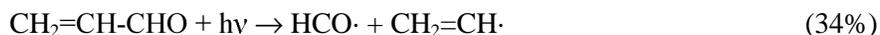
In the case of unsymmetrical ketones, two possible reactions are considered:



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

b. Unsaturated Carbonyl Photolysis

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



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

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

c. Organic Nitrate Photolysis

As discussed in Section II.A.3.b, although organic nitrate products are represented using the lumped molecule approach, the mechanism for the generic organic nitrate model species used for this purpose is derived based on generated mechanisms for individual organic nitrate compounds. The rates

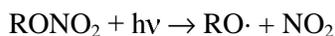
Table II-26. Summary of assignments of absorption cross sections and quantum yields for carbonyl and organic nitrate photolysis reactions.

Compound Type	Phot. Set	Q.Yield	Ref	Group Definition used to Determine Type
Aldehydes	C2CHO	-	1,2	-CHO groups bonded to -CH ₃ , -CH ₂ -, -CH< or -C<
Ketone	KETONE	0.10	3	-CO- groups bonded to -CH ₃ , -CH ₂ -, -CH< or -C<
Alkyl Glyoxal	MGLY_ADJ	-	1,4	-CHO- broups bonded to -CO-
Dialkyl Glyoxyl	BACL_ADJ	-	1,5	-CO- groups bonded to -CO-
Acrolein	ACROLEIN	3.3e-3	3,6	CH ₂ =CH-CHO only.
Other Acroleins	ACROLEIN	4.1e-3	3,7	-CHO groups bonded to -CH= or >C=
Vinyl Ketone	ACROLEIN	2.1e-3	3,8	-CO- groups bonded to -CH= or >C=
Ester or Acid	No photolysis		9	-CO- or -CHO- groups bonded to -O- or -OH
Organic Nitrates	IC3ONO2	1.0	10	-ONO ₂ groups bonded to -CH ₃ , -CH ₂ - -CH< or -C<

References

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

of their photolysis reactions are determined as shown on Table II-26, which indicates that all organic nitrates are assumed to photolyze using the absorption cross sections recommended by IUPAC (Atkinson et al, 1997a, 1999) for isopropyl nitrate. As discussed there, the quantum yield for NO₂ formation is assumed to be unity. In view of this, all organic nitrate photolysis reactions are represented by the general mechanism



The subsequent reactions of the alkoxy radicals are then derived using the general methods discussed in Section II.C.10.

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