APPENDIX A

GAS-PHASE ATMOSPHERIC CHEMISTRY OF ORGANIC COMPOUNDS

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ABSTRACT

The current knowledge of the gas-phase reactions occurring in the troposphere for organic chemicals is reviewed and evaluated, and areas of uncertainty are discussed.

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INTRODUCTION

Large quantities of chemical compounds are emitted into the atmosphere as a result of anthropogenic, biogenic and geogenic processes. These emissions lead to a complex array of chemical and physical transformations resulting in such apparently diverse effects as photochemical air pollution, acid deposition, long-range transport of chemicals, changes in the stratospheric ozone layer and global weather modification. Over the past approximately 15-20 years a vast amount of experimental work, involving laboratory, environmental chamber and ambient atmospheric studies, has been carried out concerning the chemical and physical processes occurring in the atmosphere. Because of the complexity of these processes, the use of computer models is necessary to elucidate and predict the effects of anthropogenic and biogenic emissions on the atmosphere. Such computer models have been used for several years to aid in the formulation of air pollution control strategies, and with the availability of ever more powerful computers, are being used to theoretically investigate the impacts of anthropogenic emissions of reactive organic gases, oxides of nitrogen and sulfur dioxide on the deposition of acidic species in North America and Europe.

Chemical mechanisms, with varying levels of detail, are integral components of these atmospheric computer modeling studies. For tropospheric chemistry applications, such as the modeling of local, urban and regional air pollution impacts and long range transport/acid deposition modeling studies, the detailed chemistry is exceedingly complex, and condensed chemical mechanisms must be utilized. While these detailed and condensed chemical mechanisms are tested against available environmental chamber data during their development, for several model applications (long range transport, acid deposition modeling and modeling of the clean troposphere) these chamber data are often of limited utility due to the differing organic and oxides of nitrogen concentration regimes and ratios in the environmental chamber experiments compared to those encountered in the modeling scenarios. Thus, the ultimate accuracy of the chemical mechanisms, whether of a detailed or condensed nature, are dependent on the accuracy of the input data, i.e., the rate constants and products of the many hundreds of elementary reactions which occur in the atmosphere.

It is evident that, in parallel with laboratory, ambient atmospheric, and chemical mechanism development and refinement studies, there must also be a continual program to critically evaluate and review the kinetics, mechanisms and reaction products of the chemical reactions relevant to the atmosphere, and to update these evaluations as new experimental and theoretical data become available. For the reactions of importance for chemical modeling of the stratosphere, the National Atmospheric and Space Administration (NASA) established a Panel for Data Evaluation in 1977. To date this panel has published eight, progressively updated and extended, compilations of kinetic and photochemical data for use by modelers in computer simulations of stratospheric chemistry, with the most recent such evaluation appearing in September 1987 (DeMore et al., 1987). In a parallel program, the CODATA Task Group on Chemical Kinetics has critically evaluated the kinetic and photochemical data relevant to middle atmospheric chemistry (10-55 km altitude). The first evaluation appeared in 1980 (Baulch et al., 1980), and two further supplements have been published (Baulch et al., 1982, 1984).

However, these comprehensive evaluations have been concerned primarily with stratospheric modeling (although, obviously, a majority of the reactions covered are also applicable to tropospheric modeling needs), and only organic compounds containing up to three carbon atoms are dealt with (Baulch et al., 1980, 1982, 1984; DeMore et al., 1987). The troposphere, and in particular, the polluted troposphere, contains hundreds of differing organic species of much greater complexity, and there is a need for critical evaluations of the chemical reactions occurring for these more complex organic compounds. Critical review and evaluations of the kinetics and mechanisms of the gas-phase reactions of the hydroxyl (OH) radical and of ozone (O_3) with organic compounds under atmospheric conditions have recently been published (Atkinson and Carter, 1984; Atkinson, 1986a). In addition, and highly relevant to the present evaluation and review, the tropospheric chemistry of eight hydrocarbons (n-butane, 2,3-dimethylbutane, ethene, propene, 1-butene, trans-2-butene, toluene and m-xylene) and their degradation products (Atkinson and Lloyd, 1984) and of the alkanes (Carter and Atkinson, 1985) has been reviewed and evaluated. Despite these extremely useful evaluations, it is evident that there is a need to evaluate the tropospheric chemistry of the various classes of organic compounds emitted into the troposphere from both anthropogenic and biogenic sources, in a manner analogous to the recent evaluation of the atmospheric chemistry of the alkanes of Carter and Atkinson (1985).

This has been carried out in this review, which deals with the chemistry of the major classes of organics of importance in the troposphere. The inorganic reactions which occur in the troposphere are not dealt with here, since these were reviewed and evaluated by Atkinson and Lloyd (1984) and are the focus of the comprehensive and ongoing NASA and CODATA (now IUPAC) evaluations (Baulch et al., 1980, 1982, 1984; Atkinson et al., 1988a; DeMore et al., 1985, 1987). In this review the previous evaluations noted above are extensively utilized. Thus the recommendations of Atkinson and Carter (1984) and Atkinson (1986a) [updated where necessary] are used for the O_3 and OH radical reactions, respectively, and the section dealing with the alkanes is based upon the review of Carter and Atkinson (1985). Since this review and evaluation is an update and extension of the review of Atkinson and Lloyd (1984), extensive use, again updated where necessary, is made of that article whenever possible.

The reactions of organic compounds under tropospheric conditions are dealt with in the following sections:

(1) reactions of alkyl, alkoxy and alkyl peroxy radicals which are intermediate radical species in the degradation reaction schemes of most organics.

(2) reactions of aldehydes and ketones, including α-dicarbonyls. These classes of organics are again common "first generation" products formed from the tropospheric degradation reactions of many classes of organics.

(3) reactions of alkanes.

(4) reactions of haloalkanes.

(5) reactions of monoalkenes and di- and trialkenes.

(6) reactions of haloalkenes.

(7) reactions of alkynes.

(8) reactions of alcohols, ethers, esters, unsaturated carbonyls, carboxylic acids and hydroperoxides.

(9) reactions of nitrogen-containing organic compounds.

(10) reactions of sulfur-containing organic compounds.

(11) reactions of aromatic hydrocarbons and substituted aromatics, including the polycyclic aromatic hydrocarbons expected to be present in the gas phase.

Only gas-phase processes are discussed; while highly important under many tropospheric conditions, reactions occurring in the particulate and/or aerosol phase (including fog, rain and cloud drops), on surfaces (heterogeneous reactions), and gas- to particle conversion processes are beyond the scope of this review. Clearly, this present review is only one step of a hopefully ongoing critical review process for the atmospheric reactions of organic compounds, and regular updating will be required.

I. REACTIONS OF ALKYL (R), ALKOXY (RO) AND ALKYL PEROXY (RO_2) RADICALS

These radicals are common intermediate species formed during the atmospheric degradation reactions of most organic compounds, and their reactions under atmospheric conditions can be treated by class.

Alkyl (R) radicals

Alkyl and substituted alkyl radicals are formed from the initial reactions of several classes of organic compounds with OH radicals, NO_3 radicals and O_3. For example, alkanes react with OH and NO_3 radicals via H atom abstraction

$$OH + RH \rightarrow H_2O + R$$

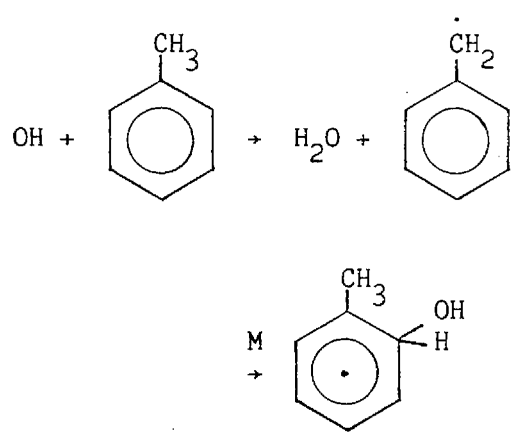
$$NO_3 + RH \rightarrow HNO_3 + R$$

and alkenes react with OH and NO_3 radicals by OH or NO_3 radical addition to the >C=C< double bond

$$OH + {>}C{=}C{<} \rightarrow {>}\dot{C}-C(OH){<}$$

$$NO_3 + {>}C{=}C{<} \rightarrow {>}\dot{C}-C(ONO_2){<}$$

to yield alkyl or β-substituted alkyl radicals. The haloalkanes and haloalkenes react via analogous pathways to form haloalkyl radicals. For the aromatic hydrocarbons, OH radical reaction leads to the initial formation of benzyl and hydroxycyclohexadienyl radicals (or alkyl-substituted homologues), for example, from toluene,



The available kinetic and mechanistic data show that most of these alkyl and substituted alkyl radicals react with O_2 to form an alkyl peroxy radical.

$$R + O_2 \rightarrow RO_2$$

The kinetic data presently available for the O_2 addition pathway are given in Table 1. In addition, Ruiz et al. (1981) and Morgan et al. (1982), have shown that the reaction of O_2 with allyl (CH_2=CH-CH_2) radicals proceeds via addition, with the rate constant being in the fall-off region at 413-427 K at total pressures of $\leq$50 torr of argon diluent (Morgan et al., 1982). At approximately 380 K and 50 torr total pressure of argon, the bimolecular rate constant for addition of O_2 to the alkyl radical is 4×10^{-13} cm^3 $molecule^{-1}$ s^{-1} (Morgan et al., 1982).

At elevated temperatures these reactions of alkyl radicals with O_2 have been assumed to also occur via the H atom abstraction pathway, for example

$$C_2H_5 + O_2 \rightarrow CH_2{=}CH_2 + HO_2$$

However, this is now recognized not to be a parallel reaction route, but to occur from the activated RO_2 adduct (Slagle et al., 1984a, 1985; McAdam and Walker, 1987)

$$R + O_2 \rightleftarrows [RO_2^*] \rightarrow HO_2 + \text{alkene}$$
$$[RO_2^*] \xrightarrow{M} RO_2$$

Hence at the high pressure limit at room temperature and below, peroxy radical formation is the sole reaction process. Klais et al. (1979) have also shown that the previously postulated reaction pathway for the reaction of CH_3 radicals with O_2

$$CH_3 + O_2 \rightarrow HCHO + OH$$

Table 1. Bimolecular Rate Constants at the High-Pressure Limit k for the Addition Reaction of Alkyl and Substituted-Alkyl Radicals with O_2 at Around Room Temperature

Alkyl radical	10^{12} x k (cm^3 molecule^{-1} s^{-1})	T (K)	Reference
Methyl	1.8 ± 0.2	298	DeMore et al. (1987)
	1.1[a]	298	
Ethyl	4.4 ± 0.5	295	Plumb and Ryan (1981)
	4.3[a]	295	
	5.3 ± 0.2	298	Munk et al. (1986a)
	5.0 ± 0.3	325	
	4.5 ± 0.2	346	
	4.2 ± 0.2	376	
	3.7 ± 0.2	400	
1-Propyl	5.5 ± 0.9	298 ± 3	Ruiz and Bayes (1984)
	5.7	297	Slagle et al. (1985)
2-Propyl	14.1 ± 2.4	298 ± 3	Ruiz and Bayes (1984)
	8.3 ± 0.4	Room temperature	Munk et al. (1986b)
1-Butyl	7.5 ± 1.4	300	Lenhardt et al. (1980)
2-Butyl	16.6 ± 2.2	300	Lenhardt et al. (1980)
2-Methyl-2-propyl	23.4 ± 3.9	300	Lenhardt et al. (1980)
2-Methyl-1-propyl	2.9 ± 0.7	298 ± 3	Wu and Bayes (1986)
2,2-Dimethyl-1-propyl	1.6 ± 0.3	298 ± 3	Wu and Bayes (1986)
Cyclopentyl	17 ± 3	293	Wu and Bayes (1986)
Cyclohexyl	14 ± 2	298 ± 3	Wu and Bayes (1986)
3-Hydroxy-2-butyl	28 ± 18	300	Lenhardt et al. (1980)
$CH_3\dot{C}O$	2.0 ± 0.4	Room temperature	McDade et al. (1982)

(continued)

Table 1 (continued) - 2

Alkyl radical	10^{12} x k (cm^3 molecule^{-1} s^{-1})	T (K)	Reference
$C_6H_5\dot{C}O$	5.7 ± 1.4	Room temperature	McDade et al. (1982)
CF_3	~8	295	Ryan and Plumb (1982)
	10.0 ± 0.3	300	Cooper et al. (1980)
	9 ± 2	233-373	Caralp et al. (1986)
CF_2Cl	6.0 ± 1.0 4.7[a]	298 298	Caralp and Lesclaux (1983)
CCl_3	5.1 ± 0.5	300	Cooper et al. (1980)
	~2.5	295	Ryan and Plumb (1984)
Benzyl	0.99 ± 0.77	Room temperature	Ebata et al. (1981)
	1.12 ± 0.11 0.997 ± 0.08 1.03 ± 0.04	295 350 372	Nelson and McDonald (1982)
2-Methylbenzyl	1.2 ± 0.07	Room temperature	Ebata et al. (1981)
4-Methylbenzyl	1.1 ± 0.10	Room temperature	Ebata et al. (1981)

[a]Value at 760 torr total pressure calculated from the fall-off expression.

is of totally negligible importance, having a rate constant of <3 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} at 368 K.

Hence for the alkyl, haloalkyl, hydroxy-substituted (other than α-hydroxy substituted) alkyl, benzyl and methyl-substituted benzyl and allyl radicals (of general formula $R_1R_2R_3C$ where R_1, R_2 and R_3 are alkyl, vinyl, halogen or aromatic groups), the reaction with O_2 proceeds via addition to form a peroxy radical, with a room temperature rate constant of ~10^{-12} cm^3 $molecule^{-1}$ s^{-1} at atmospheric pressure. For the smaller alkyl or haloalkyl radicals these reactions are in the fall-off regime between second- and third-order kinetics, but are reasonably close to the high-pressure rate constant at 760 torr of air. Thus, under atmospheric conditions these reactions with O_2 will be the sole loss process of these alkyl type radicals, and other reactions need not be considered.

It is clear that for only a small number of the alkyl-type radicals has the reaction with O_2 been studied, with most proceeding via O_2 addition to form the peroxy radical. However, α-hydroxy radicals, hydroxycyclohexadienyl radicals, and vinyl radicals react by other routes.

The simplest α-hydroxy radical, $\dot{C}H_2OH$, reacts rapidly with O_2 to form the HO_2 radical (Radford, 1980; Wang et al., 1984; Grotheer et al., 1985; Dóbé et al., 1985)

$$\dot{C}H_2OH + O_2 \rightarrow HCHO + HO_2$$

with a room temperature rate constant of (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) 2^{+2}_{-1} (Radford, 1980); 1.4 ± 0.4 (Wang et al., 1984), 9.5 ± 2.5 (Grotheer et al., 1985), 10.6 ± 2.5 (Dóbé et al., 1985). The most recent data are to be preferred (Demore et al., 1987), with a rate constant of

9.6×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K being recommended. With a rate constant of this magnitude, reaction with O_2 will be the sole loss process of CH_2OH radicals in the atmosphere. Product studies have shown that the higher (C_2-C_4) α-hydroxy radicals also react via H-atom abstraction to yield the corresponding carbonyls (Carter et al., 1979a; Ohta et al., 1982)

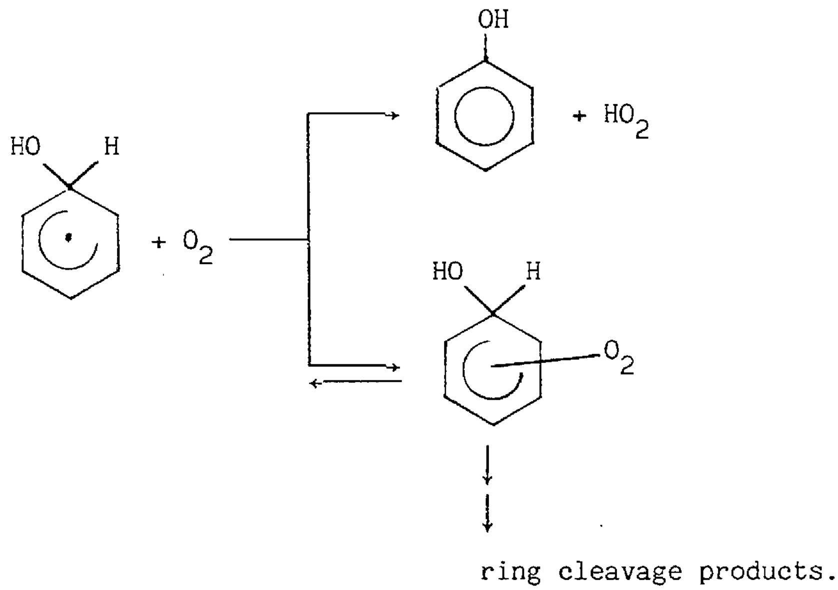
$$RR_1\dot{C}OH + O_2 \rightarrow RCOR_1 + HO_2$$

As discussed by Atkinson and Lloyd (1984) and Atkinson (1986a), the expected radical resulting from O_2 addition to $\dot{C}H_2OH$, $\dot{O}OCH_2OH$, is also presumably formed from the reaction of HO_2 radicals with HCHO

$$HO_2 + HCHO \rightleftarrows HOOCH_2\dot{O} \rightarrow \dot{O}OCH_2OH$$

This suggests that the exothermicity of the $O_2 + CH_2OH$ reaction leads to rapid decomposition of the energy-rich $OOCH_2OH$ radical (and other $RR_1C(OH)OO^{\cdot}$ radicals).

Hydroxycyclohexadienyl and methyl-substituted hydroxycyclohexadrenyl radicals are formed from OH radical addition to the aromatic hydrocarbons. As discussed in Section (XI) below, the subsequent reactions of these hydroxycyclohexadienyl radicals lead to formation of phenols and to aromatic ring cleavage. These observed products suggest that reaction with O_2 occurs (see, for example, Atkinson and Lloyd, 1984)



However, Zellner et al. (1985) have directly observed that while the hydroxycyclohexadienyl radical reacts rapidly with NO and NO_2 at 298 K,

$$C_6H_6OH + NO \rightarrow \text{products}$$
$$k = (1.0 \pm 0.5) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$C_6H_6OH + NO_2 \rightarrow \text{products}$$
$$k = (8.5 \pm 2.1) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$$

no observable reaction with O_2 was found (with a rate constant of $\lesssim 10^{-13}$ $cm^3\ molecule^{-1}\ s^{-1}$ being suggested by their data). However, this upper limit to the O_2 reaction rate constant does not preclude the O_2 reaction being dominant under atmospheric conditions. More recent evidence suggesting that these O_2 reactions are not important under atmospheric conditions arises from the hydroxyaromatic and nitroarene data of Atkinson et al. (1987a) for naphthalene and biphenyl (see Section XI).

Slagle et al. (1984b) have investigated the kinetics of the reaction of the vinyl radical with O_2, and observed that the rate constant is pressure independent, with

$$k = 6.6 \times 10^{-12} e^{126/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 297-602 K. The magnitude of this rate constant, and the almost zero temperature dependence, strongly suggest the initial formation of a $C_2H_3O_2$ adduct. However, the lack of a pressure dependence and the observation of HCHO and HCO radicals as products of this reaction show that the reaction proceeds via

$$^{\bullet}C_2H_3 + O_2 \rightarrow [H_2C{=}CHO\dot{O}] \rightarrow HCHO + HCO$$

Presumably the homologues of the vinyl radical react analogously.

<u>Alkyl peroxy (RO_2) radicals</u>

These radicals are formed from the addition of O_2 to the alkyl radicals, as discussed above:

$$R + O_2 \xrightarrow{M} RO_2$$

Under tropospheric conditions, RO_2 radicals react with NO, via two pathways,

$$RO_2 + NO \rightarrow RO + NO_2 \qquad \text{(a)}$$

$$RO_2 + NO \xrightarrow{M} RONO_2 \qquad \text{(b)}$$

with HO_2 radicals,

$$RO_2 + HO_2 \rightarrow ROOH + O_2$$

(and possibly other products)

and RO_2 radicals (either a self-reaction or a reaction with other alkyl peroxy radicals)

$$RO_2 + RO_2' \rightarrow \text{products.}$$

The reaction pathways which occur depend on the NO to HO_2 and/or RO_2 radical concentration ratios; and in the troposphere reaction with NO is expected to dominate for NO mixing ratios $\gtrsim$30 ppt (Logan et al., 1981; Logan, 1983). The reaction of RO_2 radicals with NO_2

$$RO_2 + NO_2 \xrightarrow{M} RO_2NO_2$$

are generally unimportant under tropospheric conditions due to the rapid thermal decomposition of the alkyl peroxynitrates back to reactants. These reactions are discussed in the following sections.

<u>Reaction with NO</u>

The kinetic data obtained using absolute measurement techniques are given in Table 2. The studies of Cox and Tyndall (1979, 1980), Sander and Watson (1980), Ravishankara et al. (1981), Simonaitis and Heicklen (1981) and Plumb et al. (1981) for the CH_3O_2 reaction appear to be free of possible experimental problems and are in good agreement. Based largely upon these studies NASA (DeMore et al., 1987) and CODATA (Baulch et al.,

Table 2. Absolute Rate Constant Data for the Reaction of RO_2 Radicals with NO

R	10^{12} x k (cm^3 molecule^{-1} s^{-1})	T (K)	Reference
CH_3O_2	>1	a	Anastasi et al. (1978)
	8.0 ± 2.0	295 ± 2	Plumb et al. (1979)
	2.92 ± 0.12	a	Adachi and Basco (1979a)
	6.5 ± 2.0	298	Cox and Tyndall (1979,1980)
	7.1 ± 1.4	298	Sander and Watson (1980)
	8.4 ± 1.5 8.6 ± 1.1 9.0 ± 1.1 7.8 ± 1.2 7.8 ± 1.4	240 250 270 298 339	Ravishankara et al. (1981)
	13.5 ± 1.4 17.0 ± 2.2 7.7 ± 0.9 6.3 ± 0.5	218 218 296 365	Simonaitis and Heicklen (1981)
	8.6 ± 2.0	295	Plumb et al. (1981)
	7 ± 2	298	Zellner et al. (1986)
$CH_3CH_2O_2$	2.66 ± 0.17	a	Adachi and Basco (1979b)
	8.9 ± 3.0	295	Plumb et al. (1982)
$(CH_3)_2CHO_2$	3.5 ± 0.3	a	Adachi and Basco (1982a)
$(CH_3)_3CO_2$	>1	a	Anastasi et al. (1978)
CF_3O_2	14.5 ± 2.0	298[b]	Dognon et al. (1985)
	17.8 ± 3.6	295	Plumb and Ryan (1982)
CF_2ClO_2	16 ± 3	298[b]	Dognon et al. (1985)
$CFCl_2O_2$	16 ± 2	a	Lesclaux and Caralp (1984)
	14.5 ± 2.0	298[b]	Dognon et al. (1985)

(continued)

Table 2 (continued) - 2

R	10^{12} x k (cm^3 molecule^{-1} s^{-1})	T (K)	Reference
CCl_3O_2	18.6 ± 2.8	295	Ryan and Plumb (1984)
	17.0 ± 2.0	298[b]	Dognon et al. (1985)

[a]Room temperature, not reported.
[b]Studied over the temperature range ~230-430 K, individual rate constants other than at 298 K not reported.

1984) recommended that for the reaction of CH_3O_2 radicals with NO

$$k(CH_3O_2 + NO) = 4.2 \times 10^{-12} e^{(180 \pm 180)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$= 7.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

This rate constant expression was also recommended by Atkinson and Lloyd (1984). The rate constant determined by Plumb et al. (1982) for $C_2H_5O_2$ is, within the cited experimental errors, identical to that for the CH_3O_2 radical.

Hence, consistent with the treatment of Atkinson and Lloyd (1984), the rate constant for the reaction of all alkyl peroxy (RO_2) and acyl peroxy (RCO_3) radicals with NO is recommended to be

$$k(RO_2 + NO) = k(RCO_3 + NO)$$

$$= 4.2 \times 10^{-12} e^{180/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$= 7.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

The reaction of CH_3O_2 with NO has been shown to proceed primarily via the reaction

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

(Pate et al., 1974; Ravishankara et al., 1981; DeMore et al., 1987; Zellner et al., 1986), and Plumb et al. (1982) have shown that the reaction of $C_2H_5O_2$ radicals with NO yields NO_2 with a yield of ≥ 0.80.

However, for the larger alkyl peroxy radicals, Darnall et al. (1976), Atkinson et al. (1982, 1983a, 1984a, 1987b) and Takagi et al. (1981) have shown that the reaction pathway

$$RO_2 + NO \rightarrow [ROONO] \rightarrow RONO_2$$

becomes important. The product data of Atkinson et al. (1982, 1983a, 1984a, 1987b) show that for the secondary alkyl peroxy radicals the rate constant ratio $k_a/(k_a + k_b)$, where k_a and k_b are the rate constants for the reaction pathways (a) and (b), respectively, at room temperature and atmospheric pressure

$$RO_2 + NO \xrightarrow{M} RONO_2 \qquad (a)$$

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (b)$$

increases monotonically with the carbon number of the RO_2 radical (Table 3). Furthermore, for a given alkyl peroxy radical the rate constant ratio $k_a/(k_a + k_b)$ is pressure- and temperature-dependent, increasing with increasing pressure and with decreasing temperature (Atkinson et al., 1983a, 1987b). The pressure and temperature-dependent rate constant ratios k_a/k_b for secondary alkyl peroxy radicals are fit by the fall-off expression (Carter and Atkinson, 1988) [note that earlier evaluations of Atkinson et al. (1983a), Carter and Atkinson (1985) and Atkinson (1986) utilized the ratio $k_a/(k_a + k_b)$ rather than k_a/k_b (see Carter and Atkinson, 1988)].

Table 3. Experimental Rate Constant Ratios $k_a/(k_a + k_b)$ for the Reaction of Secondary Alkyl Peroxy Radicals with NO at ~299 K and 740 Torr Total Pressure of Air

Carbon Number n	$k_a/(k_a + k_b)^a$	Peroxy Radical
3	0.042 ± 0.003	2-Propyl
4	0.090 ± 0.008	2-Butyl
5	0.129 ± 0.016, 0.134 ± 0.002	2-Pentyl
	0.131 ± 0.016, 0.146 ± 0.009	3-Pentyl
	0.141 ± 0.003, 0.150 ± 0.004	2-Methyl-3-butyl
6	0.209 ± 0.032	2-Hexyl
	0.230 ± 0.031	3-Hexyl
	0.160 ± 0.015	Cyclohexyl
	0.190 ± 0.018	2-Methyl-3-pentyl + 2-Methyl-4-pentyl
	0.162 ± 0.009, 0.178 ± 0.017	3-Methyl-2-pentyl
7	0.291 ± 0.022, 0.301 ± 0.049	2-Heptyl
	0.323 ± 0.048, 0.325 ± 0.014	3-Heptyl
	0.285 ± 0.015, 0.301 ± 0.045	4-Heptyl
8	0.323 ± 0.024	2-Octyl
	0.348 ± 0.032	3-Octyl
	0.329 ± 0.032	4-Octyl

[a]At 298-300 K and 735-740 torr total pressure (from Atkinson et al. 1982, 1983a, 1984a, 1987b). The indicated error limits are two least-squares standard deviations, but do not take into account errors due to GC-FID calibrations of the alkanes and alkyl nitrates, nor of the estimation procedure used to derive the rate constant ratios from the observed alkyl nitrate yields.

$$\frac{k_a}{k_b} = \left(\frac{Y_o^{300}[M](T/300)^{-m_o}}{1 + \frac{Y_o^{300}[M](T/300)^{-m_o}}{Y_\infty^{300}(T/300)^{-m_\infty}}} \right) F^z \qquad \text{(I)}$$

where

$$z = \left\{ 1 + \left[\log \left(\frac{Y_o^{300}[M](T/300)^{-m_o}}{Y_\infty^{300}(T/300)^{-m_\infty}} \right) \right]^2 \right\}^{-1}$$

and $Y_o^{300} = \alpha\ e^{\beta n}$, where n is the number of carbon atoms in the alkyl peroxy radical and α and β are constants. The most recent evaluation of the experimental data, (Carter and Atkinson, 1988) leads to

$Y_\infty^{300} = 0.826$

$\alpha = 1.94 \times 10^{-22}$ cm^3 molecule^{-1}

$\beta = 0.97$

$m_o = 0$

$m_\infty = 8.1$

and

$F = 0.411$

Although the rate constant ratios k_a/k_b at room temperature and atmospheric pressure for secondary RO_2 radicals depend primarily on the number of carbon atoms in the RO_2 molecule, the corresponding rate constant ratios for primary and tertiary RO_2 radicals are significantly lower, by a factor of ~2.5 for primary and a factor of ~3.3 tertiary alkyl peroxy radicals (Atkinson et al., 1987b; Carter and Atkinson, 1988). Accordingly,

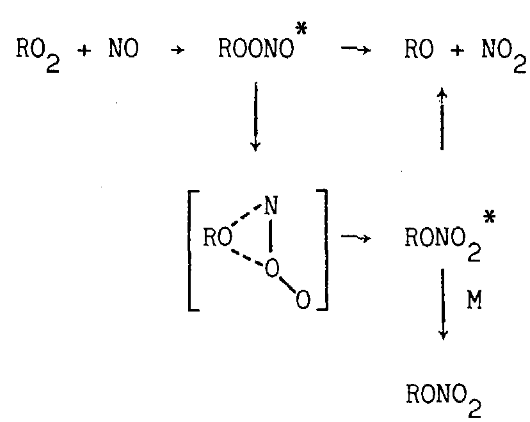
$$(k_a/k_b)_{\text{primary}} \simeq 0.40\ (k_a/k_b)_{\text{secondary}}$$

and

$$(k_a/k_b)_{\text{tertiary}} \simeq 0.3\ (k_a/k_b)_{\text{secondary}}$$

It should be noted that the use of the above equations to calculate rate constant ratios k_a/k_b is solely applicable to alkyl peroxy radicals. Thus, although no definitive data exist, computer modeling data suggest (Carter and Atkinson, 1985) that the rate constant ratios for δ-hydroxyalkyl peroxy radicals (for example $RCHOHCH_2CH_2CH(OO)R'$) are much lower than for the corresponding alkyl peroxy radicals.

These alkyl nitrate forming reactions are postulated to occur via the mechanism (Atkinson et al., 1983a)



For the haloalkyl peroxy radicals CX_3O_2, where X = F or Cl, the room temperature reaction rate constants are all ~(1.5-1.9) x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Table 2), a factor of ~2 higher than those for the alkyl peroxy radicals. Dognon et al. (1985) have determined rate constants for the reactions of CF_3O_2, CF_2ClO_2, $CFCl_2O_2$ and CCl_3O_2 with NO over the temperature range ~230-430 K. Negative temperature dependences were observed, with the values of n in the expression $k = k_{298} (T/298)^{-n}$ being 1.2 ± 0.2, 1.5 ± 0.4, 1.3 ± 0.2 and 1.0 ± 0.2 for CF_3O_2, CF_2ClO_2, $CFCl_2O_2$ and CCl_3O_2, respectively. These negative temperature dependences are equivalent, over this temperature range, to an Arrhenius activation energy of -720 cal $mole^{-1}$. Use of this Arrhenius activation energy leads to

$$k(CX_3O_2 + NO; X = F, Cl) = 5.0 \times 10^{-12} e^{360/T} cm^3 molecule^{-1} s^{-1}$$

$$= 1.67 \times 10^{-11} cm^3 molecule^{-1} s^{-1} \text{ at } 298 K$$

which is recommended in the absence of further data. The available data (Lesclaux and Caralp, 1984; Dognon et al., 1985) suggest that these reactions of the haloalkylperoxy radicals with NO proceed via

$$CX_3O_2 + NO \rightarrow CX_3O + NO_2$$

Reaction with NO_2

The kinetic data obtained using absolute experimental methods are given in Table 4. The most recent studies of Sander and Watson (1980) and Ravishankara et al. (1980) for CH_3O_2 show that this reaction is in the fall-off regime between second- and third-order kinetics below atmospheric

Table 4. Absolute Room Temperature Rate Constants for the Gas Phase Reactions of RO_2 and RCO_3 Radicals with NO_2 at the High-Pressure Limit

RO_2	10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})	Reference
CH_3O_2	1.6 ± 0.3[a] (540 torr N_2)	Cox and Tyndall (1979, 1980)
	1.53 ± 0.07 (53-580 torr O_2 + Ar)	Adachi and Basco (1980)
	8.0 ± 1.0	Sander and Watson (1980)
	7	Ravishankara et al. (1980)
$C_2H_5O_2$	1.25 ± 0.07	Adachi and Basco (1979c)
$(CH_3)_2CHO_2$	5.65 ± 0.17	Adachi and Basco (1982a)
$(CH_3)_3CO_2$	≳0.5	Anastasi et al. (1978)
$CFCl_2O_2$	6.0 ± 1.0	Lesclaux and Caralp (1984)
$CH_3C(O)O_2$	6.0 ± 2.0 (714 torr O_2)	Addison et al. (1980)
	6.1	Basco and Parmar (1987)

[a]At 275 K.

pressure at room temperature, and this is in agreement with the CH_3OONO_2 thermal decomposition data of Reimer and Zabel (1986). The data of Adachi and Basco (1980) appear to have been in error due to interferences by the $CH_3O_2NO_2$ product with the spectroscopic technique used, and this was probably also the case for their studies of the $C_2H_5O_2$ and $(CH_3)_2CHO_2$ radical reactions.

For CH_3O_2, Ravishankara et al. (1980) fit the data for $M=N_2$ from their study and that of Sander and Watson (1980), which are in excellent agreement, to the fall-off expression

$$k = \left(\frac{k_o(T)[M]}{1 + \frac{k_o(T)[M]}{k_\infty(T)}} \right) F^{\left\{1 + [\log (k_o(T)[M]/k_\infty(T)]^2\right\}^{-1}} \qquad (I)$$

with

$$F = 0.4$$

$$k_o(T) = 2.2 \times 10^{-30} (T/298)^{-2.5} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

and

$$k_\infty(T) = 7 \times 10^{-12} (T/298)^{-3.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Hence $k = 3.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 760 torr total pressure.

This expression, which was recommended by Atkinson and Lloyd (1984), is slightly different to the NASA (DeMore et al., 1987) and CODATA (Baulch et al., 1982) evaluations, but gives a better fit to the experimental data. For the $\geq C_2$ alkyl peroxy radicals, apart from the lower limit to the rate constants for $(CH_3)_3CO_2$ derived by Anastasi et al. (1978), only the suspect data of Adachi and Basco (1979c, 1982a) are available. Atkinson and Lloyd (1984) recommended that the limiting high-pressure rate constants for the $\geq C_2$ alkyl peroxy radicals are identical to that for CH_3O_2,

$$k_{\infty}(RO_2 + NO_2) = 7 \times 10^{-12} (T/298)^{-3.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The pressures at which these reactions will exhibit kinetic fall-off behavior from the second- to third-order regime will decrease as the size of the RO_2 radical increases, and it is expected that at room temperature and 760 torr total pressure these $\geq C_2$ alkyl peroxy reactions will be close to the limiting high-pressure region.

For the acyl peroxy (RCO_3) radicals, rate constants are available only for the $CH_3C(O)OO$ radical (Addison et al., 1980; Basco and Parmar, 1987). Both studies, which are in good agreement, show that the rate constant is pressure dependent [in agreement with the data of Reimer and Zabel (1986) on the thermal decomposition of $CH_3C(O)OONO_2$]. Basco and Parmar (1987) have fitted their data (obtained at room temperature) to the Troe fall-off equation, and obtain:

$$F = 0.19$$

$$k_o = 5.07 \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

and

$$k_{\infty} = 6.09 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This high-pressure limit is similar to that for the $RO_2 + NO_2$ reactions, and it is recommended that for all RCO_3 and RO_2 radical reactions have the same limiting high pressure rate constant at 298 K of

$$k(RO_2 + NO_2;\ RCO_3 + NO_2) = 7 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$$

For $CFCl_2O_2$, Lesclaux and Caralp (1984) and Lesclaux et al. (1986) fit their room temperature data to equation (I) with

$$F = 0.6$$

$$k_o = (3.5 \pm 0.5) \times 10^{-29}\ cm^6\ molecule^{-2}\ s^{-1}$$

and

$$k_\infty = (6.0 \pm 1.0) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$$

This reaction is hence reasonably close to the high pressure limit at 298 K and 760 torr total pressure ($k = 5.4 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}). In a recent temperature dependence study, Lesclaux et al. (1986) fit their data for $CFCl_2O_2$ with $k_o = (3.5 \pm 0.5) \times 10^{-29}\ (T/298)^{-(4.1 \pm 0.3)}$ cm^6 $molecule^{-2}$ s^{-1} and $k_\infty = (5.9 \pm 1.0) \times 10^{-12}\ (T/298)^{-(3.6 \pm 0.5)}$ cm^3 $molecule^{-1}$ s^{-1}. In the absence of further experimental data this expression should be used for the other CX_3O_2 (X = F or Cl) radicals.

These absolute rate data are supported by the relative rate data of Simonaitis et al. (1979) and Simonaitis and Heicklen (1979) for $CFCl_2O_2$ and CCl_3O_2 radicals, for which the rate constant ratios $k(CX_3O_2 + NO_2)/k(CX_3O_2 + NO) = 0.58 \pm 0.10$ ($CFCl_2O_2$) and 0.68 (CCl_3O_2) were obtained at 1 atmosphere pressure of N_2, independent of temperature over the range 268-298 (CCl_3O_2) and 286-305 K ($CFCl_2O_2$). Thus the limiting high pressure rate constants for the reactions of CX_3O_2 radicals with NO_2 are similar to those for RO_2 and RCO_3 radicals.

These reactions of alkyl peroxy and haloalkyl peroxy radicals with NO_2 all proceed via combination to yield the corresponding peroxynitrates

$$RO_2 + NO_2 \xrightarrow{M} ROONO_2$$

(Niki et al., 1978a, 1980; Edney et al., 1979; Spence et al., 1978; Hendry and Kenley, 1979; Gay et al., 1976; Simonaitis and Heicklen, 1979; Simonaitis et al., 1979).

Reaction with HO_2 Radicals

Relatively few data exist for the reactions of HO_2 radicals with RO_2 radicals. Cox and Tyndall (1979, 1980) used molecular modulation spectroscopy to study the reaction of HO_2 radicals with CH_3O_2 over the temperature range 274-337 K. Assuming, in agreement with Sander and Watson (1981), that the CH_3O_2 radical absorption cross-section is independent of temperature, with $\sigma(CH_3O_2) = 3.9 \times 10^{-18}$ cm^2 at 250 nm, the rate constants given in Table 5 were obtained. A product was observed which adsorbed strongly in the wavelength region 210-280 nm, and attributed to CH_3OOH. At $\lesssim$250 nm the spectrum of this product was reasonably similar to that reported by Molina and Arguello (1979), supporting the conclusion that the reaction proceeds via

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$$

More recently, McAdam et al. (1987) and Kurylo et al. (1987) have determined the absorption cross-sections of CH_3O_2 (and HO_2) and also measured the rate constant for the reaction of CH_3O_2 with HO_2 at 298 K (Table 5).

Table 5. Absolute Rate Constant Data for the Gas-Phase Reactions of RO_2 Radicals with HO_2

RO_2	10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})	T (K)	Reference
CH_3O_2	8.5 ± 1.2	274	Cox and Tyndall (1980)
	6.5 ± 1.0	298	
	3.5 ± 0.5	338	
	6.4 ± 1.0	298	McAdam et al. (1987)
	2.9 ± 0.4	298	Kurylo et al. (1987)
$C_2H_5O_2$	6.3 ± 0.9	295	Cattrell et al. (1986)
	7.3 ± 1.0	248	Dagaut et al. (1988a)
	6.0 ± 0.5	273	
	5.3 ± 1.0	298	
	3.4 ± 1.0	340	
	3.1 ± 0.5	380	

For the reaction of $C_2H_5O_2$ with HO_2, kinetic data have recently been reported by Cantrell et al. (1986) and Dagaut et al. (1988a). The rate constants derived in these studies depend on the absorption cross-sections measured or assumed for the HO_2 and RO_2 radicals. Furthermore, the ultraviolet absorption bands of these species overlap, resulting in the potential for significant overall uncertainties to be associated with the reported measurements of these radical-radical reaction rate constants.

The data given in Table 5 show that while the reported 298 K rate constants for the reaction of HO_2 radicals with CH_3O_2 radicals vary by a factor of 2, those for the reaction of HO_2 radicals with $C_2H_5O_2$ radicals are in good agreement. Rather than recommend a specific study, a rate constant at 298 K for the reactions of HO_2 radicals with RO_2 radicals of

$$k(HO_2 + RO_2) = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

is indicated, with a likely overall uncertainty of ± a factor of 2. The temperature dependent studies for both of the reactions studied to date yield negative temperature dependencies equivalent to E/R values of -1300 K (Cox and Tyndall, 1980) and -650 K (Dagaut et al., 1988a). A value of E/R = -1000 K is chosen to yield

$$k(HO_2 + RO_2) = 1.75 \times 10^{-13} e^{1000/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Reaction with RO_2 Radicals

Numerous studies of the self reactions of RO_2 radicals have been carried out, and the data obtained are listed in Table 6. These data are discussed below:

Table 6. Kinetic Data for the Gas-Phase Combination Reactions of RO_2 Radicals

RO_2	$10^{13} \times k_{obs}$ (cm^3 $molecule^{-1}$ s^{-1})	T (K)	Reference
CH_3O_2	4.0	298	DeMore et al. (1987)[a]
$C_2H_5O_2$	1.10 ± 0.09 1.0 ± 0.1[b]	Room temperature	Adachi et al. (1979)
	0.948 ± 0.130 1.10 ± 0.15 1.33 ± 0.19 1.51 ± 0.21 1.68 ± 0.23	303 333 373 423 457	Anastasi et al. (1983)
	0.52	298	Munk et al. (1986a)
	1.30 ± 0.16 (0.84[b])	268-347.5	Cattell et al. (1986)
	0.59[c]	298	Dagaut et al. (1988a)
$CH_3CH_2CH_2O_2$	3.84 ± 0.33	Room temperature	Adachi and Basco (1982b)
$(CH_3)_2CHO_2$	0.0135 ± 0.0008 0.0181 ± 0.0020 0.0269 ± 0.0020 0.0418 ± 0.0050 0.0591 ± 0.0033	300 313 333 353 373	Kirsch et al. (1978)
	0.0203 ± 0.0058	Room temperature	Adachi and Basco (1982b)
	0.53 ± 0.05	Room temperature	Munk et al. (1986b)
$(CH_3)_3CO_2$	0.000256 0.00088	298 325	Anastasi et al. (1978)
	0.000256	Room temperature	Parkes (1975)
	0.000188[c]	298	Kirsch et al. (1978)
$CH_3C(O)O_2$	25 ± 10	302 ± 1	Addison et al. (1980)
	80 ± 15	Room temperature	Basco and Parmar (1985)

[a]Evaluation.
[b]Estimated rate constant for the elementary reaction (see text).
[c]Calculated from cited Arrhenius expression.

$\underline{CH_3O_2 + CH_3O_2 \rightarrow \text{products}}$

The majority of kinetic and product studies concerning the self-reactions of RO_2 radicals have concerned this reaction. However, since the rate constants have been derived from measurements of k/σ and σ, where σ is the absorption cross section, and most studies were carried out at different wavelengths, comparison of the reported data is somewhat difficult. Absorption spectra and cross-sections have been reported from several studies. The most recent NASA evaluation (DeMore et al., 1987) used the absorption cross-sections determined by Hochanadel et al. (1977) to reevaluate the room temperature literature rate constants, yielding

$$k_{obs}(CH_3O_2 + CH_3O_2) = 4.0 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty of ± a factor of 1.5, where k_{obs} is the experimentally measured rate constant which may include contributions from secondary reactions. Combined with the temperature dependence of Sander and Watson (1981), this leads to (DeMore et al., 1987)

$$k_{obs}(CH_3O_2 + CH_3O_2) = 1.9 \times 10^{-13}\ e^{220/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

Kan and Calvert (1979) and Kurylo et al. (1987) have shown that, in contrast to the combination reaction of HO_2 radicals, H_2O vapor has no effect on the measured rate constant for combination of CH_3O_2 radicals at room temperature.

However, secondary reactions of the products of this reaction will result in these measured values being upper limits to the true elementary rate constant. The reaction proceeds via the pathways:

$$CH_3O_2 + CH_3O_2 \rightarrow 2\ CH_3O + O_2 \quad (a)$$

$$\rightarrow HCHO + CH_3OH + O_2 \quad (b)$$

$$\rightarrow CH_3O_2CH_3 + O_2 \quad (c)$$

Quantitative data for these reaction pathways have been obtained by Parkes (1975), using molecular modulation spectroscopy, and more recently by Kan et al. (1980) and Niki et al. (1981a) using FT-IR absorption spectroscopy. These data are in good agreement and Atkinson and Lloyd (1984) recommend

$$k_a/k_{overall} = 0.35$$

$$k_b/k_{overall} = 0.57$$

and

$$k_c/k_{overall} = 0.08$$

with the ratios $k_a/k_{overall}$ and $k_c/k_{overall}$ being uncertain by ±30%. Hence, secondary reactions of CH_3O radicals, for example

$$CH_3O + CH_3O_2 \rightarrow CH_3OOH + HCHO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$CH_3O_2 + HO_2 \rightarrow products$$

lead to the observed rate constant being an upper limit to the "true" rate constant. Kan et al. (1980) have assessed the influence of secondary reactions in this system and estimate that the value of $k_{overall}$ is some 12% lower than the observed rate constant. Thus, it is recommended that

$$k(CH_3O_2 + CH_3O_2) = 3.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, and

$$k(CH_3O_2 + CH_3O_2) = 1.7 \times 10^{-13} e^{220/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

<u>$C_2H_5O_2 + C_2H_5O_2 \rightarrow$ Products</u>

Room temperature rate constants have been determined for this reaction by Adachi et al. (1979), Anastasi et al. (1983), Munk et al. (1986a), Cattell et al. (1986) and Dagaut et al. (1988a) and, as seen from Table 6, the measured rate constants range over a factor of ~2. The reported temperature dependencies are zero (Cattell et al., 1986) or slightly positive (Anastasi et al., 1983; Dagaut et al., 1988a). This reaction can proceed via the channels

$$C_2H_5O_2 + C_2H_5O_2 \rightarrow 2\ C_2H_5O + O_2 \quad \text{(a)}$$

$$\rightarrow C_2H_5OH + CH_3CHO + O_2 \quad \text{(b)}$$

$$\rightarrow C_2H_5OOC_2H_5 + O_2 \quad \text{(c)}$$

Niki et al. (1982a) obtained the rate constant ratios $k_a/k_b = 1.3 \pm 0.16$ and $k_c/k_b \leq 0.22$, which leads to $k_a/k_{overall} = 0.52$ to 0.56, $k_b/k_{overall} = 0.40$ to 0.44, and $k_c/k_{overall} \leq 0.09$. Anastasi et al. (1983) determined that $k_a/k_b = 1.75 \pm 0.05$ at 302 K, 2.12 ± 0.10 at 333 K, and 2.45 ± 0.15 at 373 K, with channel (c) contributing $\lesssim$5% of the overall reaction.

Using the recent kinetic data of Cattell et al. (1986) with $k_a/k_b = 1.5$ and $k_c/k_a \sim 0$ yields the elementary rate constants, corrected for secondary reactions, of

$$k_a = 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k_b = 3.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

both independent of temperature over the small range of ~270-350 K.

$\underline{CH_3CH_2CH_2O_2 + CH_3CH_2CH_2O_2 \rightarrow \text{Products}}$

The sole reported data concerning this reaction are those of Adachi and Basco (1982b), who obtained a value of

$$k_{obs} = (3.8 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at room temperature. No determination of the products formed were made, and this rate constant is an upper limit to the "true" rate constant for this reaction.

$(CH_3)_2CHO_2\cdot + (CH_3)_2CHO_2\cdot \rightarrow$ Products

This reaction has been investigated by Kirsch et al. (1978, 1979), Cowley et al. (1982), Adachi and Basco (1982b), and Munk et al. (1986b), with the only temperature dependence study being that of Kirsch et al. (1978) over the range 300-373 K using molecular modulation spectroscopy. The rate constant reported by Munk et al. (1986b) is over an order of magnitude higher than the other data given in Table 6. One wonders if it is possible that they were not studying only the reactions of the isopropylperoxy radical.

These observed rate constants are again upper limits to the "true" rate constant because of the influence of secondary reactions of the isopropoxy radicals formed in reaction (b)

$$2(CH_3)_2CHO_2 \rightarrow (CH_3)_2CHOH + (CH_3)_2CO + O_2 \qquad (a)$$

$$\rightarrow 2(CH_3)_2CHO + O_2 \qquad (b)$$

and Kirsch et al. (1979) and Cowley et al. (1982) obtained, from a product analysis study, the rate constant ratios

$$k_b/k_a = 1.39 \pm 0.04 \text{ at } 302 \text{ K}$$

$$= 1.84 \pm 0.04 \text{ t } 333 \text{ K}$$

$$= 2.80 \pm 0.08 \text{ at } 373 \text{ K}$$

From these data and the observed rate constants of Kirsch et al. (1978), the Arrhenius expressions for reaction pathways (a) and (b) were derived (Cowley et al., 1982)

$$k_a = 4.1 \times 10^{-14}\ e^{-1440/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$= 3.3 \times 10^{-16}\ cm^3\ molecule^{-1}\ s^{-1}$$

at 298 K, with an estimated uncertainty of ±25% at 298 K;

$$k_b = 2.3 \times 10^{-12}\ e^{-2560/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$= 4.3 \times 10^{-16}\ cm^3\ molecule^{-1}\ s^{-1}$$

at 298 K with an estimated uncertainty of ±30% at 298 K. These expressions of Cowley et al. (1982) are recommended, with large uncertainties.

$\underline{(CH_3)_3CO_2\cdot + (CH_3)_3\dot{C}O_2 \rightarrow \text{Products}}$

Rate constants for the combination of t-butylperoxy radicals have been obtained by Parkes (1975) and Anastasi et al. (1978) using molecular modulation and flash photolysis techniques, respectively.

These data are in excellent agreement and, using an absorption cross-section for the t-butylperoxy radical of 4.0×10^{-18} cm^2 at 240 nm (Anastasi et al., 1978), yield an observed rate constant at 298 K of

$$k_{obs} = (2.6 \pm 0.8) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

with an activation energy of ~8.8 kcal mol^{-1} (Anastasi et al. 1978) over the narrow temperature range of 298-325 K. This temperature dependence is consistent with the Arrhenius expression obtained by Kirsch et al. (1978) of

$$k_{obs} = 1.7 \times 10^{-10} e^{-4775/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Kirsch and Parkes (1981) have shown that the initial reaction leads predominantly to t-butoxy radicals, pathway (a), with pathway (b) being ~14% of the overall reaction at 298 K, decreasing rapidly with temperature.

$$(CH_3)_3CO_2\cdot + (CH_3)_3CO_2\cdot \rightarrow 2(CH_3)_3CO^\cdot + O_2 \quad \text{(a)}$$

$$\rightarrow (CH_3)_3COO(CH_3)_3 + O_2 \quad \text{(b)}$$

$$\rightarrow \text{other products} \quad \text{(c)}$$

$\underline{CH_3CO_3 + CH_3CO_3 \rightarrow \text{Products}}$

This combination reaction has recently been studied by Addison et al. (1980) using molecular modulation absorption spectroscopy, and Basco and Parmar (1985) using a flash photolysis technique. The room temperature rate constants obtained disagree by a factor of ~3. While no recommendation can be made, it appears that this combination reaction is rapid.

In addition to these RO_2 self-combination reaction studies, rate constants for the reactions of CH_3O_2 with $(CH_3)_3CO_2$ and with $CH_3C(O)O_2$ have been deduced (Parkes, 1975; Addison et al., 1980), with values at room temperature of

$$k[CH_3O_2 + (CH_3)_3CO_2] \sim 1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k[CH_3O_2 + CH_3C(O)O_2] = 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Because of the inherent complexities of these experimental systems, no recommendations can be made.

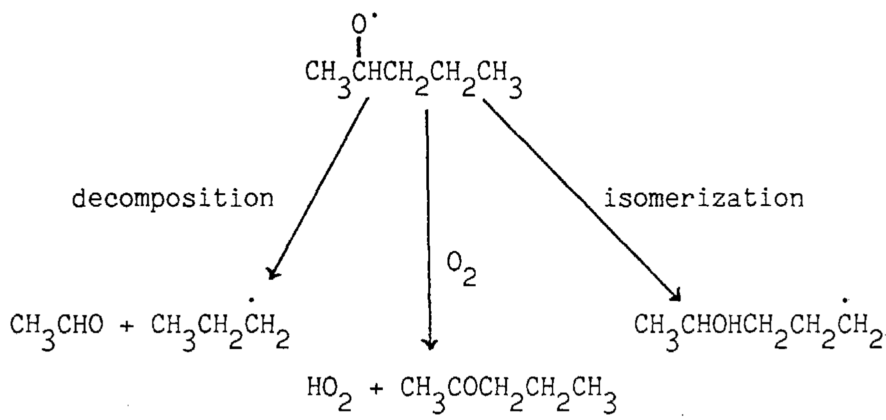
In the absence of more experimental data, the rate constants and product ratios obtained for the $C_2H_5O_2$, $(CH_3)_2CHO_2$ and $(CH_3)_3CO_2$ radicals are recommended as being reasonably representative of other primary, secondary and tertiary alkylperoxyradicals, and similarly with CH_3CO_3 radicals. Furthermore, the use of a rate constant at 298 K of

$$5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

is recommended for the reaction of HO_2 radicals with all peroxy radicals (this being the major cross-combination reaction occurring).

<u>Alkoxy Radical Reactions</u>

It is now recognized that under atmospheric conditions the major alkoxy radical removal processes involve reaction with O_2, unimolecular decomposition and unimolecular isomerization (see, for example, Atkinson and Lloyd, 1984; Carter and Atkinson, 1985). These reactions are shown for the case of the 2-pentoxy radical:



In addition, reactions with NO and NO_2, though minor under most conditions, must be considered.

<u>Reaction with O_2</u>

Absolute rate constants for the reactions of alkoxy radicals with O_2 have been determined for CH_3O (Sanders et al., 1980; Gutman et al., 1982; Lorenz et al., 1985; Wantuck et al., 1987), C_2H_5O (Gutman et al., 1982), and $(CH_3)_2CHO$ (Balla et al., 1985) radicals. The rate constants obtained are given in Table 7.

For the reaction of CH_3O radicals with O_2, the rate constants of Gutman et al. (1982), Lorenz et al. (1985) and Wantuck et al. (1987) are in good agreement. These data are well fitted (Wantuck et al., 1987) by the double Arrhenius expression

$$k(CH_3O + O_2) = 1.5 \times 10^{-10}\ e^{-6028/T} + 3.6 \times 10^{-14} e^{-880/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

For the temperature range applicable to the troposphere, $T \approx 200\text{-}300$ K, this expression reduces to

Table 7. Absolute Rate Constants for the Reactions of O_2 with Alkoxy Radicals

Radical	10^{15} x k (cm^3 $molecule^{-1}$ s^{-1})	T (K)	Reference
CH_3O	<2	295	Sanders et al. (1980)
	4.7	413	Gutman et al. (1982)
	6.0	475	
	10.7	563	
	12.7	608	
	1.9[a]	298	Lorenz et al. (1985)
	2.3 ± 0.2	298	Wantuck et al. (1987)
	1.9 ± 0.2	298	
	4.0 ± 0.2	348	
	4.7 ± 0.3	423	
	4.4 ± 0.1	423	
	4.6 ± 0.2	423	
	7.2 ± 0.6	498	
	14 ± 1	573	
	12 ± 3	573	
	14 ± 1	573	
	30 ± 1	673	
	67 ± 4	773	
	140 ± 10	873	
	360 ± 110	973	
C_2H_5O	8.0	296	Gutman et al. (1982)
	9.8	353	
$(CH_3)_2CHO$	7.55 ± 0.30	294	Balla et al. (1985)
	7.06 ± 0.56	295	
	6.90 ± 0.37	296	
	8.22 ± 0.28	296	
	8.65 ± 0.26	314	
	7.48 ± 0.55	330	
	8.60 ± 0.36	346	
	9.16 ± 0.92	367	
	8.27 ± 0.80	384	

[a]Calculated from cited Arrhenius expression.

$$k(CH_3O + O_2) = 3.6 \times 10^{-14} e^{-880/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

which is similar to that of Lorenz et al. (1985) [obtained over the temperature range 298-450 K] of

$$k(CH_3O + O_2) = 5.5 \times 10^{-14} e^{-1000/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This Arrhenius expression of Lorenz and Zellner (1985) is recommended [at 200 K, a 15% difference occurs between the rate constants calculated from the expressions of Lorenz et al. (1985) and Wantuck et al. (1987)].

For the ethoxy radical Gutman et al. (1982) obtained rate constants at 296 and 353 K. Combining these data of Gutman et al. (1982) with an estimated Arrhenius preexponential factor of 3.7×10^{-14} cm^3 molecule^{-1} s^{-1} (from the preexponential factor for $CH_3O + O_2$, which yields 1.85×10^{-14} cm^3 molecule^{-1} s^{-1} per abstractable H atom) leads to the expression for the ethoxy radical, and for primary alkoxy radicals in general, of

$$k(\text{prim-alkoxy} + O_2) = 3.7 \times 10^{-14} e^{-460/T} \text{ cm}^33 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$= 7.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

Balla et al. (1985) determined absolute rate constants for the reaction of O_2 with the $(CH_3)_2CHO$ radical over the temperature range 294-384 K, and obtained the Arrhenius expression

$$k((CH_3)_2CHO + O_2) = 1.51 \times 10^{-14} e^{-(196 \pm 141)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Combining these rate constants of Balla et al. (1985) for the reaction of the isopropoxy radical with O_2, and the estimated preexponential factor of 1.8×10^{-14} cm^3 $molecule^{-1}$ s^{-1}, the following Arrhenius expression for secondary alkoxy radicals of

$$k(\text{sec-alkoxy} + O_2) = 1.8 \times 10^{-14} e^{-260/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$= 7.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

is derived. These rate constant recommendations for primary and secondary alkoxy radicals are slightly different than those recommended by Carter and Atkinson (1985). These rate constants are expected to be applicable to substituted alkoxy radicals formed from, for example, the alkenes after initial OH radical reaction (for example, $HOCH_2CH_2O$).

Alkoxy Radical Decompositions

There have been a number of studies of these reactions in the gas phase. For the non-substituted alkoxy radicals; i.e., those formed from alkanes, the most useful of these experimental studies are those of Batt and co-workers (Batt, 1979a and references therein; Batt and Robinson, 1982) who determined the decomposition rates for a series of alkoxy radicals relative to their reaction rates with NO at ~400-470 K. Because of uncertainties concerning the absolute rates of the reference reactions and the relatively limited temperature range employed, the Arrhenius parameters, and thus the room temperature rate constants, for these reactions are subject to significant uncertainties.

As discussed by Carter and Atkinson (1985), while there have been several attempts to develop systematic schemes for estimating the

Arrhenius parameters for these reactions (Baldwin et al., 1977; Batt, 1979a; Choo and Benson, 1981), discrepancies have arisen primarily due to the differing thermochemical estimates used in the analyses of the experimental data. Batt and co-workers (Batt, 1979a) used the competition between the reactions

$$RO \rightarrow \text{decomposition}$$

$$RO + NO \rightarrow RONO$$

The rate constant for the RO + NO combination is derived for the decomposition rate constant data of RONO and an assumed zero temperature dependence for the RO + NO combination reaction. Carter and Atkinson (1985) used the alkoxy radical decomposition rates given by Batt (1979a) and Batt and Robinson (1982) since these data appeared to yield a reasonably self-consistent data set concerning the reactions of alkoxy radicals with O_2, NO and NO_2. Batt (1979a) derived a value of ~4 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the reaction of RO radicals with NO, while Choo and Benson (1981) recommended a value of ~1 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, both being independent of temperature. The recent study of Balla et al. (1985) on the kinetics of the reaction of $(CH_3)_2CHO$ radicals with NO yields a rate constant at ~400 K of ~(2.5-3.0) x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, a factor of ~1.5 lower than estimated by Batt and co-workers (Batt, 1979a). Furthermore, a negative temperature dependence equivalent to an Arrhenius activation energy of -0.62 kcal $mole^{-1}$ was determined by Balla et al. (1985). This leads to the preexponential factor for the RO + NO combination reaction being lowered by a factor of 3 over that used by Batt

(1979a), with a negative temperature dependence of ~-0.6 kcal $mole^{-1}$. Thus,

$$k(RO + NO) = 1.3 \times 10^{-11} e^{300/T} cm^3 molecule^{-1} s^{-1}$$

This expression is consistent with the rate constant of (2.08 ± 0.12) x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} determined by Sanders et al. (1980) in the presence of 15 ± 5 torr of SF_6 diluent (this reaction would still be in the fall-off regime under these conditions). Hence the Carter and Atkinson (1985) estimated preexponential factors for alkoxy radical decompositions will be lowered by a factor of 4, and the Arrhenius activation energies decreased by 0.6 kcal $mole^{-1}$.

The technique discussed by Carter and Atkinson (1985) involves the estimation of the Arrhenius preexponential factor, A, for the decompositions, and derivation of the Arrhenius activation energies, E_{decomp}, by correlation with the heats of reaction (ΔH_{decomp}). The A factors for decomposition to an alkyl radical and the corresponding carbonyl are now given by

$$A = n \times 2.7 \times 10^{14} s^{-1}$$

where n is the reaction path degeneracy. In agreement with the earlier work of Baldwin et al. (1977) and Batt (1979a), an Evans-Polanyi plot of the Arrhenius activation energies, E_{decomp} (decreased by 0.6 kcal $mole^{-1}$ as discussed above), against the calculated heats of reaction, ΔH_{decomp}, yields a good straight line with no obvious effect of the leaving alkyl group, with

$$E_{decomp} = 11.4 + 0.70\ \Delta H_{decomp}$$

where E_{decomp} and ΔH_{decomp} are both in kcal mole^{-1}.

Table 8 summarizes the estimated heats of reaction and the calculated Arrhenius parameters and rate constants at 298 K for the classes of alkoxy radical decomposition which may be important in alkane photooxidations. The heats of reaction were estimated using the group additivity method of Benson (1976).

Dobé et al. (1986) have used a technique similar to that of Batt and co-workers to study the decomposition of the 2-pentoxy radical. Using the rate constant for the combination reaction of RO with NO given above, the data of Dobé et al. (1986) lead to a rate constant for 2-pentoxy decomposition to CH_3CHO and $CH_3CH_2CH_2$ of

$$k(\text{decomposition}) = 4.9 \times 10^{13}\ e^{-6700/T}\ s^{-1}$$

$$= 8.4 \times 10^{3}\ s^{-1} \text{ at } 298 \text{ K}$$

This is a factor of 1.9 higher than predicted from Table 8; considering the relatively long extrapolation from 363-418 K to 298 K this is reasonably good agreement.

Clearly, in view of the above discussion, these estimated alkoxy radical decomposition rate constants are subject to significant uncertainties, and direct determinations of these rate constants, obviating the need for reference reactions, are needed. It should also be noted that these decomposition reactions may be in the fall-off region between first-order and second-order kinetics at room temperature and

Table 8. Estimated Arrhenius Parameters and Room Temperature Rate Constants for Decompositions of Alkoxy Radicals

Reaction[a]	R·	ΔH_d[b] (kcal $mole^{-1}$)	E_d (kcal $mole^{-1}$)	k(298 K)[c] (s^{-1})
	$CH_3\cdot$	13.4	20.8	1.5×10^{-1}
	$-CH_2\cdot$	9.1	17.8	2.4×10^{1}
$RCH_2O\cdot \rightarrow R\cdot + HCHO$	>CH·	8.6	17.4	4.7×10^{1}
	⋟C·	6.9	16.2	3.5×10^{2}
	$CH_3\cdot$	9.0	17.7	2.8×10^{1}
	$-CH_2\cdot$	4.7	14.7	4.5×10^{3}
$RCH(O\cdot)-R' \rightarrow R\cdot + R'CHO$	>CH·	4.2	14.3	8.8×10^{3}
	⋟C·	2.5	13.2	5.6×10^{4}
	$CH_3\cdot$	6.6	16.0	5.0×10^{2}
	$-CH_2\cdot$	2.3	13.0	7.9×10^{4}
$R-C(O\cdot)(R'')-R' \rightarrow R\cdot + R'C(=O)R''$	>CH·	1.8	12.7	1.3×10^{5}
	⋟C·	0.1	11.5	1.0×10^{6}

[a] Thermochemical estimates based on R'-, R"- = $-CH_3$. Arrhenius parameters for R'-, R"- = CH_3-, >CH-, and ⋟C- are assumed to be identical.
[b] Estimated using group additivity and bond dissociation energies tabulated by Benson (1976).
[c] Calculated using $A = 2.7 \times 10^{14}\ s^{-1}$, and thus applicable only for a reaction path degeneracy of 1.

atmospheric pressure (Batt, 1979a; Batt and Robinson, 1982; Al Akeel and Waddington, 1984). For the two alkoxy radicals for which pressure dependent decomposition rate constants have been observed [2-propoxy and 2-methyl-2-propoxy (t-butoxy)] the rate constants at room temperature and atmospheric pressure are apparently reasonably close to the limiting high pressure values (Batt and Robinson, 1982; Al Akeel and Waddington, 1984) [see also Table II in Baldwin et al. (1977), which predicts that for C_3 and higher alkoxy radicals, the corrections for fall-off behavior are small, being less than a factor of 2 at room temperature and atmospheric pressure]. Since the estimation procedure given above yields the limiting high pressure rate constants, the possibility that the reaction may not be at its high pressure and thus the true rate constants under atmospheric conditions may be lower should be recognized.

The above discussion has dealt with the reactions of alkoxy radicals formed from the alkanes, and the decompositions of other alkoxy radicals such as $HOCH_2CH_2\dot{O}$ formed from ethene and $CH_3COCH(\dot{O})CH_3$ formed from 2-butanone need to be considered.

For radicals of the structure RCOCH(O)R′, the use of the above methods and equations used to estimate alkoxy radical deposition rates yields decomposition rates at the high pressure limit of:

for

$$CH_3COCH_2O \rightarrow CH_3CO + HCHO$$

$$k_{298} \simeq 1.0 \times 10^4\ s^{-1}$$

for

$$\underset{\displaystyle CH_3COCHCH_3}{\overset{O^{\cdot}}{|}} \rightarrow CH_3CO + CH_3CHO$$

$$k_{298} = 6.5 \times 10^5 \ s^{-1}$$

[these are somewhat uncertain due to uncertainties in the values of ΔH_f calculated for the alkoxy radicals (Benson, 1976)]. The reactions of these radicals with O_2 at 760 torr total pressure and 298 K are estimated to have rates of $4.1 \times 10^4 \ s^{-1}$ and $3.9 \times 10^4 \ s^{-1}$, respectively. It is hence predicted for the $CH_3COCH(O)CH_3$ radical that decomposition will dominate over reaction with O_2 by ~170:1. This prediction is in good agreement with experimental data (Batt, 1979b), and the estimation method outlined above appears to be applicable to these $RCOCH(\dot{O})R'$ radicals.

These estimates of the rate constants for the reaction of alkoxy radicals with O_2 and for decomposition predict that for the reactions

$$CH_3CH(O^{\cdot})C_2H_5 + O_2 \rightarrow CH_3C(=O)C_2H_5 + HO_2 \qquad (a)$$

$$CH_3CH(O^{\cdot})C_2H_5 \rightarrow CH_3CH(=O) + \dot{C}_2H_5 \qquad (b)$$

$k_b/k_a = 6.0 \times 10^{17}$ cm^3 $molecule^{-1}$ at 298 K. This rate constant ratio is a factor of approximately 4-5 lower than the direct measurements of k_b/k_a of Carter et al. (1979b) and Cox et al. (1981) of 3.1×10^{18} molecule cm^{-3} at 303 K and 2.6×10^{18} molecule cm^{-3} at 296 K, respectively. In view of the fact that thermochemical estimates of heats of reaction, and hence of the estimated Arrhenius activation energies, are uncertain to at least ~1 kcal

$mole^{-1}$, the minimum expected uncertainties in such rate constant ratio estimates are a factor of ~5 at 298 K.

Similarly, for radicals such as CH_3OCH_2O formed in the atmospheric degradation of dimethyl ether, the above estimation method predicts a decomposition rate at 298 K of 0.3 s^{-1}, in contrast to a rate of 4×10^4 s^{-1} for reaction with O_2. Hence reaction with O_2 to yield CH_3OCHO should dominate, and this is experimentally observed (Tuazon, unpublished data).

For the alkoxy radicals $RR_1COHC(O)R_2R_3$ formed from the alkenes, however, estimations and experimental data are in serious disagreement (Baldwin et al., 1977; Batt, 1979a,c; Golden, 1979; Niki et al., 1978b). Thus, based upon the thermochemistries of the reactions

$$RR_1COH\overset{O^{\cdot}}{\overset{|}{C}}R_2R_3 \rightarrow RR_1\dot{C}OH + R_2COR_3$$

and the estimation methods given above, the decompositions

$$HOCH_2CH_2O^{\cdot} \rightarrow \dot{C}H_2OH + HCHO$$

and

$$CH_3CHOH\overset{O}{\overset{|}{C}}HCH_3 \rightarrow CH_3CHO + CH_3\dot{C}HOH$$

have calculated rate constants at 298 K of ~10 s^{-1} and 4.5×10^3 s^{-1}, respectively, compared to estimated rates for reaction with O_2 (at 760 torr total pressure of air) of ~4×10^4 s^{-1} for both radicals. Hence, it is predicted (as discussed previously by Baldwin et al., 1977; Golden, 1979; Batt, 1979a,c) that reaction with O_2 will totally dominate for the ethene system and dominate for the 2-butenes.

However, experimentally, the $RR_1COHC(\dot{O})R_2R_3$ radicals decompose, with, at room temperature and 1 atmosphere or air, decomposition dominating for the $\geq C_3$ radicals, and with decomposition and reaction with O_2 being competitive for the $HOCH_2CH_2O^{\cdot}$ radical (Niki et al., 1978b, 1981b; Atkinson and Lloyd, 1984). Thus, for the $HOCH_2CH_2O$ radical the rate constant ratio k_b/k_a for the reactions

$$HOCH_2CH_2\dot{O} \rightarrow \dot{C}H_2OH + HCHO \qquad (a)$$

$$HOCH_2CH_2\dot{O} + O_2 \rightarrow HOCH_2CHO + HO_2 \qquad (b)$$

is $(5.4 \pm 1.0) \times 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1} at room temperature (~298 K) (Niki et al., 1981b). Using $k_b \sim 8 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} (see above), this yields

$$k_a \sim 1.5 \times 10^5 \ s^{-1}$$

at ~298 K and 700 torr total pressure. For the higher ($\geq C_3$) homologues of these radicals, the decomposition rates are expected to increase, as observed experimentally (Niki et al., 1978b; Atkinson et al., 1985). Thus, for these $\geq C_3$ homologues decomposition rates of $\gtrsim 4 \times 10^5$ s^{-1} are estimated.

Alkoxy Radical Isomerizations. No direct experimental data are available, but isomerization rate constants have been estimated initially by Carter (unpublished data, 1976) and subsequently, and in more detail, by Baldwin et al. (1977). The major relevant available experimental data concern measurements of the rate constant ratio for the reactions

$$\overset{O^{\cdot}}{\overset{|}{C}}H_2CH_2CH_2CH_3 \rightarrow \overset{OH}{\overset{|}{C}}H_2CH_2CH_2CH_2^{\cdot} \qquad (a)$$

$$\overset{O^{\cdot}}{\overset{|}{C}}H_2CH_2CH_2CH_3 + O_2 \rightarrow H\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 + HO_2 \qquad (b)$$

from product yields determined in n-butane-NO_x-air (Carter et al., 1979b), HONO-n-butane-air (Cox et al., 1981) and n-butyl nitrite-air photolyses (Niki et al., 1981c). Rate constant ratios of k_a/k_b of 1.65 $\times 10^{19}$ molecule cm^{-3} at 303 K (Carter et al., 1979b), 1.9 x 10^{19} molecule cm^{-3} at 298 ± 2 K (Niki et al., 1981c) and 1.5 x 10^{19} molecule cm^{-3} at 296 K (Cox et al., 1981) were derived from these studies. These rate constant ratios are in good agreement, with an average value of k_a/k_b = 1.7 x 10^{19} molecule cm^{-3} at ~299 K. Using the rate constant estimated as described above for k_b, this leads to a rate constant of k_a = 1.3 x 10^5 s^{-1} at 299 K, a factor of ~4 lower than the estimate of Baldwin et al. (1977). Considering the large uncertainties in the estimation technique, this estimate is actually in fairly good agreement with the experimental data.

However, the data of Dóbé et al. (1986) for the isomerization of the 2-pentoxy radical lead to an isomerization rate of ~4 x 10^3 s^{-1} at 298 K, significantly lower than the thermochemical estimates. The reasons for this discrepancy are not presently known, but may be due to the difficulties in quantitatively monitoring the end-products of this isomerization reaction (Dóbé et al., 1986).

As carried out by Carter and Atkinson (1985), the estimated Arrhenius parameters of Baldwin et al. (1977) have been modified to yield values of k_a which are a factor of 4 lower at 298 K, and the resulting Arrhenius parameters are given in Table 9 for 1,4-H shift and 1,5-H shift

Table 9. Estimated Arrhenius Parameters and Room Temperature Rate Constants for 1,4- and 1,5-H Shift Isomerizations of Alkoxy Radicals

Type of H-Shift	Ring Strain[a] (kcal $mole^{-1}$)	Type of H Abstracted	E(Abstraction)[b] (kcal $mole^{-1}$)	E_a(Isom)[c] (kcal $mole^{-1}$)	A[d] (s^{-1})	k(298 K) (s^{-1})
		$-CH_3$	7.7	13.6	2.5×10^{11}	2.6×10^{1}
		$-CH_2-$	4.6	10.5	1.7×10^{11}	3.4×10^{3}
1,4	5.9	>CH-	4.6	10.5	8.3×10^{10}	1.7×10^{3}
		$-CH_2OH$	6.5	12.4	1.7×10^{11}	1.4×10^{2}
		-CH(OH)-	3.4[e]	9.3	8.3×10^{10}	1.3×10^{4}
		$-CH_3$	7.7	8.2	1.3×10^{11}	1.3×10^{5}
1,5	0.5	$-CH_2-$	4.6	5.1	8.4×10^{10}	1.5×10^{7}
		>CH-	4.6	5.1	4.2×10^{10}	7.6×10^{6}
		$-CH_2OH$	6.5	7.0	8.4×10^{10}	6.2×10^{5}
		-CH(OH)-	3.4[e]	3.9	4.2×10^{10}	5.8×10^{7}

[a]As estimated by Baldwin et al. (1977).
[b]E(abstraction) = activation energy for abstraction by RO in bimolecular systems (i.e., no ring strain). Estimates of Baldwin et al. (1977), increased by 0.5 kcal $mole^{-1}$, used.
[c]E_a(Isom) = E(abstraction) + ring strain.
[d]Estimates of Baldwin et al. (1977), decreased by a factor of 1.9 (see text), used.
[e]Baldwin et al. (1977) did not give an estimate for this abstraction. It is assumed that replacing -H with -OH decreases E(abstraction) by 1.2 kcal $mole^{-1}$, based on their estimates for abstraction from $-CH_3$ and $-CH_2$-groups.

isomerizations of alkoxy radicals [the A factors of Baldwin et al. (1977) have been reduced by a factor of 1.9, and their estimated abstraction activation energies have been increased by 0.5 kcal $mole^{-1}$]. These estimates, however, must still be considered to be highly uncertain, and clearly further studies of these isomerization rate constants are needed.

While 1,2-, 1,3-, and 1,$\geq$6-H shifts, via 3, 4 and $\geq$7 member ring transition states, are also possible, the strain energies for the 3, 4 and 7-10 member rings are all higher than that estimated for the 1,4-H shift. Thus other H-atom shifts are expected to be much slower than 1,4-H shifts, which are themselves of marginal importance (Baldwin et al., 1977).

<u>Reactions of RO Radicals with NO and NO_2</u>. Alkoxy radicals can also react with NO and NO_2 under atmospheric conditions

$$RO + NO \rightarrow RONO$$
$$\rightarrow HONO + R'O$$

and

$$RO + NO_2 \rightarrow RONO_2$$
$$\rightarrow HNO_3 + R'O$$

Absolute rate constants have been measured for the reactions of CH_3O and $(CH_3)_2CHO$ radicals with NO and NO_2, and the data are given in Table 10. The rate constants for the reactions of CH_3O with NO and NO_2 measured by Sanders et al. (1980) and Lorenz et al. (1984) and by McCaulley et al. (1985), respectively, are in the fall-off region between second and third order kinetics (Gutman et al., 1982). The data of Lorenz et al. (1984) show that at 298 K the high pressure second order rate constant for the

Table 10. Absolute Rate Constants for Reaction of RO Radicals with NO and NO_2

Radical	Reactant	T (K)	P (torr)	10^{11} x k (cm^3 molecule^{-1} s^{-1})	Reference
CH_3O	NO	293	15 ± 5 (SF_6)	2.08 ± 0.12	Sanders et al. (1980)
			9.8 (He)	1.1 ± 0.2	
		298	190 (He)	2.5 ± 0.5	Lorenz et al. (1984)
	NO_2	250	4 (He)	0.531 ± 0.093	McCaulley et al. (1985)
		298	4 (He)	0.318 ± 0.049	
		390	4 (He)	0.120 ± 0.033	
		473	4 (He)	0.109 ± 0.027	
$(CH_3)_2CHO$	NO	295	1	4.01 ± 0.21	Balla et al. (1985)
		296	50	3.31 ± 0.12	
		296	10	3.28 ± 0.07	
		297	10	3.54 ± 0.09	
		319	10	3.44 ± 0.07	
		341	10	3.10 ± 0.11	
		359	10	2.89 ± 0.10	
		378	10	2.68 ± 0.07	
	NO_2	295	1-10	3.68 ± 0.16	Balla et al. (1985)
		340	10	2.59 ± 0.25	
		384	10	3.03 ± 0.15	

reaction of CH_3O with NO is $\gtrsim 2.5 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, with a low pressure bimolecular rate constant of ~4×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K, the latter corresponding to the H-atom abstraction route. Similar data arise from the study of McCaulley et al. (1985) for the corresponding NO_2 reaction, from which the abstraction channel was concluded to have a rate constant of

$$k\ (CH_3O + NO_2) = 9.6 \times 10^{-12}\ e^{-1150/T}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$= 1.2 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1} \text{ at } 298\ K.$$

For both addition reactions, negative temperature dependencies were observed (though these were in, or may have been in, the fall-off regions).

The kinetic data obtained by Balla et al. (1985) for the reactions of the $(CH_3)_2CHO$ radical with NO and NO_2 are at the high pressure limit, and show that these reactions have rate constants at room temperature of (3-4) x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, with, for the NO reaction, a slight negative temperature dependence.

A large amount of relative rate data have been obtained, and these are discussed in detail by Atkinson and Lloyd (1984). These relative rate data show that for the reaction of RO radicals with NO, the addition rate constants at ~400 K are ~3×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, with an uncertainty of ± a factor of 3. For the CH_3O radical, this reaction has not reached the limiting high-pressure second-order limit at 700 torr total pressure of N_2, being ~20% below the high pressure limit at this pressure. For the RO + NO reactions, the H-atom abstraction process appears to be insignificant for R=CH_3, with k $\lesssim 1.5 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at

383-423 K (Batt and Rattray, 1979). Higher H-atom abstraction rate constants have been reported for the higher alkoxy radicals (see Atkinson and Lloyd, 1984; Morabito and Heicklen, 1985), with values of (3-6) x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at ~400 K being typical.

For the RO reactions with NO_2, the relative rate data suggest that

$$k(RO + NO)/k(RO + NO_2) \sim 2 \pm 1$$

at ~400 K, and that the H-atom abstraction channel is negligible [with the most recent relative rate data yielding H-atom abstraction rate constants of ~1.5 x 10^{-13} cm^3 $molecule^{-1}$ s^{-1} for CH_3O and $(CH_3)_2CHO$ radicals (Batt and Rattray, 1979; Batt, 1979b)].

The relative rate data are reasonably consistent with the few absolute rate constants available, and allow the following general recommendations for all RO radicals to be made:

$$k_{\infty}(RO + NO) = 1.3 \times 10^{-11}\ e^{300/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$= 3.6 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1} \text{ at } 298\ K,$$

with the H-atom abstraction rate constants being of minor importance at temperatures below 298 K.

$$k_{\infty}(RO + NO_2) \simeq 1.3 \times 10^{-11}\ e^{300/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$\simeq 3.6 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1} \text{ at } 298\ K,$$

with the H-atom abstraction process being of negligible importance at $\leq$298 K.

II. REACTIONS OF ALDEHYDES, KETONES AND α-DICARBONYLS

The aliphatic aldehydes and ketones are formed as intermediate "stable" chemical products during the atmospheric degradation reactions of a wide variety of organic compounds. These carbonyls arise from the reactions of the alkyl peroxy and alkoxy radicals discussed in Section I above. In addition, a number of α-dicarbonyls (for example, glyoxal, methylglyoxal and biacetyl) are formed as intermediate reactive products from the aromatic hydrocarbons (Darnall et al., 1979; Takagi et al., 1980; Atkinson et al., 1983b; Bandow and Washida, 1985a,b; Bandow et al., 1985; Tuazon et al., 1984a, 1986; Shepson et al., 1984; Dumdei and O'Brien, 1984; Gery et al., 1985). In the atmosphere, these carbonyls can photolyze and react with OH, NO_3 and HO_2 radicals, and these atmospheric reaction pathways are reviewed in this section. The corresponding atmospheric reactions of other classes of carbonyls such as the 1,4-unsaturated dicarbonyls are dealt with in Section XI.

Photolysis

In order to evaluate or calculate the photolysis rates of carbonyls under atmospheric and environmental chamber conditions, the radiation flux J, the carbonyl absorption cross-section, σ, and the photolytic quantum yield, ϕ, all as a function of wavelength, need to be known. Thus

$$k_{photolysis} = \int_{\sim 290\ nm}^{\sim 800\ nm} J_\lambda \sigma_\lambda \phi_\lambda d_\lambda$$

The radiation flux, J, is either experimentally measured or calculated for clear sky conditions and is not dealt with further here. The absorption cross-sections and quantum yields are obtained from experimental studies, and the available data are discussed below.

Formaldehyde. The absorption cross-sections and quantum yields have been most recently evaluated by NASA (DeMore et al., 1987) and IUPAC (Atkinson et al., 1988a). The most recent IUPAC recommendation (Atkinson et al., 1988a) accepts the absorption cross-section data of Moortgat et al. (1983). At longer wavelengths these absorption cross-sections are higher than those measured by Bass et al. (1980), but are confirmed by recent unpublished data of Biermann (University of California, Riverside). The recommended absorption cross-sections and quantum yields for the processes

$$HCHO + h\nu \rightarrow H + HCHO \qquad (a)$$

$$HCHO + h\nu \rightarrow H_2 + CO \qquad (b)$$

as recommended by the IUPAC panel (Atkinson et al., 1988a) are given in Table 11, although the higher wavelength resolution data of Moortgat et al. (1983 and references therein) should be used for modeling purposes (see Atkinson et al., 1988a).

Acetaldehyde. The quantum yields for the photolysis of acetaldehyde have been reviewed and evaluated by Atkinson and Lloyd (1984) and Baulch et al. (1984), based on the experimental studies of Horowitz and Calvert (1982), Horowitz et al. (1982) and Meyrahn et al. (1982). The recommended values as a function of wavelength are similar to within approximately 10%. The absorption cross-sections have also been reviewed by Baulch et

Table 11. Absorption Cross Sections, σ, and Quantum Yields, ϕ, for the Photolysis of HCHO (from Atkinson et al., 1988a)

λ (nm)	10^{20} σ(cm^2)[a] 298 K	ϕ_a	ϕ_b
270	0.95	0.38	0.43
280	1.80	0.57	0.32
290	2.93	0.73	0.24
300	4.06	0.78	0.21
310	4.60	0.78	0.22
320	4.15	0.62	0.38
330	3.21	0.27	0.66
340	2.22	0	0.56[b]
350	1.25	0	0.21[b]
360	0.18	0	0.03[b]

[a]The values are averaged for 10 nm intervals centered on the indicated wavelength.
[b]760 torr total pressure of air.

al. (1982, 1984), and their recommendation is in good agreement with the recent values of Horowitz and Calvert (1982). The absorption cross-sections and quantum yields for the processes,

$$CH_3CHO + h\nu \rightarrow CH_4 + CO \quad \text{(a)}$$

$$CH_3CHO + h\nu \rightarrow CH_3 + CHO \quad \text{(b)}$$

$$CH_3CHO + h\nu \rightarrow CH_3CO + H \quad \text{(c)}$$

as evaluated by Baulch et al. (1984), are given in Table 12. The pathway to form ketene plus H_2 is negligible (Horowitz and Calvert, 1982; Horowitz et al., 1982).

<u>Propanal</u>. The sole data available for the photodissociation quantum yields for propanal arise from the studies of Shepson and Heicklen (1982a,b) and Heicklen et al. (1986). The more recent study of Heicklen et al. (1986) supercedes the previous work from the same laboratory. For the photodissociation

$$CH_3CH_2CHO + h\nu \rightarrow C_2H_5 + CHO \quad \text{(a)}$$

data were obtained at 294, 302, 313, 325 and 334 nm, with the quantum yields in air at 760 torr total pressure and 298 K being 0.89, 0.85, 0.50, 0.26 and 0.15 at these wavelengths, respectively. The quantum yield for the non-radical forming process

$$CH_3CH_2CHO + h\nu \rightarrow C_2H_6 + CO \quad \text{(b)}$$

Table 12. Absorption Cross Sections, σ, and Quantum Yields ϕ_a and ϕ_b for CH_3CHO photolysis (at 1 atm air) [from Baulch et al., 1984]

Wavelength	10^{20} σ/cm^2	ϕ_a	ϕ_b
260	2.0	0.46	0.31
270	3.4	0.31	0.39
280	4.5	0.05	0.58
290	4.9	0.01	0.53
295	4.5	0.0	0.48
300	4.3		0.43
305	3.4		0.37
315	2.1		0.17
320	1.8		0.10
325	1.1		0.04
330	0.69		0.0
335	0.38		
340	0.15		
345	0.08		

was observed to be essentially zero at wavelengths >313 nm. Absorption cross-sections have been presented by Calvert and Pitts (1966).

Butanal. The absorption cross-sections are as given by Calvert and Pitts (1966), and the gas-phase photolysis has been studied by Forgeteg et al. (1978, 1979) at 313 nm. At high pressure of added C_4F_8, the quantum yields of the processes

$$C_3H_7CHO + h\nu \rightarrow C_3H_7 + CHO \quad (a)$$

$$C_3H_7CHO + h\nu \rightarrow C_2H_4 + CH_3CHO \quad (b)$$

were reported to be $\phi_b = 0.18$, and $\phi_a \sim 0.3$. Other photolysis pathways account for <5% of the overall quantum yield at 313 nm.

Higher Aldehydes. Absorption cross-section data are given by Calvert and Pitts (1966) for iso-butyraldehyde, and quantum yield data have been measured by Desai et al. (1986). At one atmosphere of air and room temperature the quantum yields for $(CH_3)_2CH + HCO$ production were measured to be at the wavelengths: 253.7 nm, 0.20; 280.3 nm, 0.45; 302.2 nm, 0.55; 312.8 nm, 0.88; 326.1 nm, 0.88; and 334.1 nm, 0.69. For the higher aldehydes no quantum yield data are available, and further work is clearly needed concerning the photolysis of aldehydes (and ketones) under atmospheric conditions.

Acetone. The photodissociation of acetone has recently been studied under simulated atmospheric conditions by Gardner et al. (1984) and Meyrahn et al. (1986). Unfortunately, there are significant discrepancies between the results obtained from the studies of Gardner et al. (1984) and Meyrahn et al. (1986), with respect to both the quantum yields for radical production and the effects of pressure on the quantum yields. At total pressures >350 torr of air, the quantum yield of the process

$$CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3$$

was found to be 0.077 ± 0.0022 in the study of Gardner et al. (1984), independent of wavelength over the range 279-313 nm, and independent of temperature over the range 272-300 K.

Meyrahn et al. (1986) could not avoid the effects of secondary reactions, and added NO_2 to scavenge CH_3CO radicals to yield PAN ($CH_3C(O)OONO_2$). At 750 torr total pressure of air the quantum yields for CH_3CO formation were determined to be 0.55 at 280 nm, 0.30 at 290 nm, 0.15 at 300 nm, 0.05 at 310 nm, 0.028 at 320 nm, and ~0.033 at 330 nm. The absorption cross-section was also measured by Meyrahn et al. (1986). In addition, Cox et al. (1980) have reported an average photodissociation quantum yield of 0.33 ± 0.06 for the wavelength region 280-330 nm, which is not consistent with the data of Gardner et al. (1984). The data of Meyrahn et al. (1986) are hence recommended, being more consistent with the variation of photodissociation quantum yields with wavelength observed for other ketones and with the data of Cox et al. (1980).

2-Butanone. Absorption cross-section data are given by Calvert and Pitts (1966). No definitive quantum yield data are available. By analogy with the quantum yields for the carbonyls discussed above, the photodissociation quantum yield is expected to be significantly less than unity. In fact, Carter et al. (1986) used a quantum yield for radical production of approximately 0.1 to fit environmental chamber irradiations of NO_x-2-butanone-air mixtures.

Higher Ketones. No data are available concerning the photodissociation quantum yields for the higher ketones. As for acetone, these quantum yields are likely to be low. However, since these compounds also react with the OH radical, it is expected that the OH radical reactions will be the dominant atmospheric loss process.

α-Dicarbonyls. The α-dicarbonyls for which experimental data are available are glyoxal, methylglyoxal and biacetyl. The absorption cross-sections have been measured and reported by Plum et al. (1983) over the wavelength regions 240-470 nm. In this wavelength region, two distinct absorption bands are observed, one from approximately 340-470 nm and a second from approximately 230-340 nm. Plum et al. (1983) studied the photolysis of these α-dicarbonyls in the longer wavelength band, although no wavelength resolution was carried out and only average photodissociation quantum yields could be derived. The α-dicarbonyl photolysis rates were determined relative to the measured photodissociation rate of NO_2 in the environmental chamber employed. The data obtained showed that photodissociation did occur in the longer wavelength band, and effective quantum yields (assuming a constant photodissociation quantum yield for wavelengths >325 nm) of 0.029 ± 0.018, 0.107 ± 0.030 and 0.158 ± 0.024 for glyoxal, methylglyoxal and biacetyl were derived.

For glyoxal, formaldehyde was observed as a product, showing that the process

$$(CHO)_2 + h\nu \rightarrow HCHO + CO$$

must occur, with the HCHO yield corresponding to 13% of the glyoxal photolyzed (Plum et al., 1983). Other photodissociation pathways obviously occur. In the shorter wavelength band, Langford and Moore (1984) observed the formation of HCO radicals from the photolysis of glyoxal at 308 nm, with an estimated quantum yield of 0.4 ± 0.2. Clearly, further work is necessary, but the available data suggest photodissociation into two HCO radicals with an appreciable quantum yield in the 230-340 nm absorption band, with photolysis to predominantly non-radical products [HCHO + CO and H_2 + 2 CO (Osamura et al. (1981)] occurring with low quantum yield in the first long wavelength band.

For methylglyoxal and biacetyl the photodissociation pathways are less well understood. However, the formation of PAN as a product of irradiated NO_x-methylglyoxal or biacetyl-air mixtures and the observation of the $CH_3C(O)OO$ radical from the photolysis of biacetyl-O_2 mixtures (Cox et al., 1980) shows that the photolysis paths

$$CH_3COCHO + h\nu \rightarrow CH_3CO + CO$$

$$CH_3COCOCH_3 + h\nu \rightarrow 2\ CH_3CO$$

must occur. Indeed, Cox et al. (1980) have reported an average photodissociation quantum yield of 0.98 ± 0.15 for biacetyl for the 280-330 nm wavelength region.

<u>Hydroxyl Radical Reactions</u>. The kinetics and mechanisms of the OH radical reactions with carbonyl compounds have been reviewed and evaluated by Atkinson (1986a), and updated evaluations for HCHO and CH_3CHO have been carried out for the IUPAC evaluation (Atkinson et al., 1988a). The

kinetic data for the simpler aldehydes and ketones, either as the recommended values or those measured but not recommended for lack of sufficient studies, are given in Table 13. All of these reactions proceed via overall H-atom abstraction, although it should be noted that for the aldehydes the initial reaction possibly involves OH radical addition to the >C=O bond system. Thus:

$$OH + HCHO \rightarrow H_2O + HCO$$

$$OH + RCHO \rightarrow H_2O + RCO$$

As noted in Section I, the HCO radical reacts rapidly with O_2

$$HCO + O_2 \rightarrow HO_2 + CO$$

while the RCO radicals rapidly add O_2 to form the corresponding acyl peroxy radicals (RC(O)OO).

For glyoxal, Niki et al. (1985) have shown that the resulting HCOCȮ radical can either decompose or react with O_2

$$HCOCO \rightarrow HCO + CO \qquad (a)$$

$$HCOCO + O_2 \rightarrow HCOC(O)OO \qquad (b)$$

$$\rightarrow 2\ CO + HO_2 \qquad (c)$$

Table 13. Room Temperature Rate Constants k and Arrhenius Parameters, $k = Ae^{-E/RT}$, for the Reaction of OH Radicals with Carbonyl Compounds. Except as Indicated, Taken from Atkinson (1986)

Carbonyl	10^{12} k (298 K) cm^3 $molecule^{-1}$ s^{-1}	10^{12} x A cm^3 $molecule^{-1}$ s^{-1}	E/R (K)
HCHO[a]	11	16	110
CH_3CHO[a]	16	5.6	-310
CH_3CH_2CHO	20		
$CH_3CH_2CH_2CHO$	23		
$(CH_3)_2CHCHO$	27		
$CH_3(CH_2)_3CHO$	27		
$(CH_3)_2CHCH_2CHO$	28		
$(CH_3)_3CCHO$	27		
$HOCH_2CHO$[b]	10		
CH_3COCH_3[a]	0.23	1.7	600
$CH_3COCH_2CH_3$[c]	1.1	2.3	170
$CH_3COCH_2CH_2CH_3$	4.6		
$CH_3CH_2COCH_2CH_3$	1.8		
$CH_3COCH_2CH_2CH_2CH_3$	9.0		
$CH_3CH_2COCH_2CH_2CH_3$	6.8		
$(CHO)_2$	11		
CH_3COCHO	17		
$CH_3COCOCH_3$[d]	2.3	1.1	450

[a]From Atkinson et al. (1988a).
[b]From Niki et al. (1987a).
[c]From Wallington and Kurylo (1987a).
[d]From Dagaut et al. (1988b).

with $k_b \sim k_c$ and $k_a/k_b = 3.5 \times 10^{18}$ molecule cm^{-3}. Thus, at 298 K and 760 torr total pressure of air, addition of O_2 occurs 40% of the time, while formation of CO and HO_2 occurs the remaining 60% of the time. For methylglyoxal, the corresponding CH_3COCO radical is expected to decompose more rapidly, and hence O_2 addition to yield $CH_3COC(O)OO$ should be less important.

For the aldehydes and ketones, the positions of OH radical H-atom abstraction and the partial OH radical reaction rate constant at that position can be calculated using the estimation technique of Atkinson (1986b; 1987). As an example, the OH radical reaction with 2-butanone is calculated to proceed via the pathways

$$OH + CH_3CH_2COCH_3 \rightarrow H_2O + CH_2CH_2COCH_3 \qquad (46\%)$$

$$\rightarrow H_2O + CH_3CHCOCH_3 \qquad (46\%)$$

$$\rightarrow H_2O + CH_3CH_2COCH_2 \qquad (8\%)$$

The subsequent reactions involve O_2 addition to these radicals followed by the various reactions discussed above in Section I.

Ozone Reactions. For the carbonyls dealt with in this section which do not contain >C=C< bonds the reactions with O_3 are of negligible atmospheric importance, and indeed only upper limits to the rate constants of $<10^{-20}$ cm^3 $molecule^{-1}$ s^{-1} have been obtained for HCHO, CH_3CHO, $(CHO)_2$ and CH_3COCHO (Atkinson and Carter, 1984).

Nitrate Radical Reactions. For the carbonyl compounds dealt with in this section, rate constant data are available only for HCHO and CH_3CHO

(Atkinson et al., 1988a and references therein). Most of these studies are relative to the equilibrium constant for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$, and unfortunately, there are significant uncertainties in the value of this equilibrium constant (DeMore et al., 1987). For the reactions of the NO_3 radical with HCHO and CH_3CHO, the most recent NASA (DeMore et al., 1987) and IUPAC (Atkinson et al., 1988a) recommendations are in good agreement, with (DeMore et al., 1987; Atkinson et al., 1988a)

$$k(NO_3 + HCHO) = 6.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

and (Atkinson et al., 1988a)

$$k(NO_3 + CH_3CHO) = 1.4 \times 10^{-12} e^{-1860/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 264-374 K

$$= 2.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

With rate constants of this magnitude, these reactions with the NO_3 radical are of minimal atmospheric importance as an aldehyde loss process, and the NO_3 radical reaction rate constants for the ketones are expected to be lower, in the range of 10^{-17} to 10^{-16} cm^3 molecule^{-1} s^{-1} at room temperature. However, these NO_3 radical reactions with the aldehydes during nighttime hours can be important with respect to the products formed (Stockwell and Calvert, 1983; Cantrell et al., 1985, 1986). Thus, as with the corresponding OH radical reactions, these NO_3 radical reactions proceed via H-atom abstraction

$$NO_3 + RCHO \rightarrow HNO_3 + RCO \quad (R = H, \text{alkyl})$$

and the production of HO_2 and RC(O)OO radicals during nighttime hours can be significant.

<u>HO_2 Radical Reactions</u>. While the HO_2 radical has been shown to react with HCHO (Su et al., 1979a,b; Niki et al., 1980; Veyret et al., 1982; Barnes et al., 1985), data are not available for other aldehydes. The room temperature rate constants obtained cover a range of a factor of 10, from 1 x 10^{-14} cm^3 $molecule^{-1}$ s^{-1} (Su et al., 1979a,b) to 1.1 x 10^{-13} cm^3 $molecule^{-1}$ s^{-1} (at 273 K) [Barnes et al., 1985]. The initial reaction involves addition of HO_2,

$$HO_2 + HCHO \rightarrow HOOCH_2O$$

followed by rapid isomerization of this intermediate species via a six-membered transition state

$$HOO\dot{C}H_2O \rightarrow OOCH_2OH$$

Su et al. (1979a,b) and Barnes et al. (1985) have proposed that the $OOCH_2OH$ species can back-decompose to the HO_2 + HCHO reactants (presumably via the intermediacy of $HOOCH_2O$). That the $OOCH_2OH$ species is formed in this HO_2 radical reaction is shown by the formation, in the presence of NO_2, of the peroxy nitrate $HOCH_2OONO_2$ (Niki et al., 1980). While further work is clearly necessary on this, and other analogous reaction(s), the data of Barnes et al. (1985) are recommended, i.e.,

$k(HO_2 + HCHO \rightarrow HOCH_2OO) = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 273 K

and

$k(HOCH_2OO \rightarrow HO_2 + HCHO) = 20$ s^{-1} at 273 K.

With this rapid back-decomposition rate of the $HOCH_2OO$ radical, the reaction of HO_2 radicals with HCHO is expected to be of minor importance.

III. ALKANES

The atmospheric chemistry of the alkanes has been reviewed and discussed in detail by Carter and Atkinson (1985), and the kinetics and mechanisms of the reactions with OH radicals and with O_3 have recently been reviewed and evaluated (Atkinson and Carter, 1984; Atkinson, 1986a). The gas-phase reaction of the alkanes with O_3 are of negligible importance as an atmospheric loss process, since the available data show that the rate constants for these reactions at room temperature are $<10^{-23}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Carter, 1984). Under atmospheric conditions, the potential loss processes for the alkanes involve gas-phase reactions with OH and NO_3 radicals.

OH Radical Reactions

The kinetics and mechanisms of the reactions of the OH radical with alkanes have been critically reviewed and evaluated by Atkinson (1986a). Rate constants have been determined over significant temperature ranges for a number of alkanes, and it is evident, as expected from theoretical considerations, that the Arrhenius plots are curved. Accordingly, the three-parameter expression

$$k = C\, T^2\, e^{-D/T}$$

has been used. The recommended 298 K rate constants and the parameters C and D given by Atkinson (1986a) are shown in Table 14 for alkanes of relevance to tropospheric chemistry. Room temperature rate constants for other alkanes for which recommendations were not given (generally due to only single studies being carried out) are also given in Table 14.

These OH radical reactions proceed via H-atom abstraction from the C-H bonds and, as discussed by Atkinson (1986a,b), the rate constants for these OH radical reactions with alkanes can be fit to within a factor of 2 over the temperature range 250-1000 K by consideration of the CH_3-, $-CH_2$- and >CH- groups in the alkane and the substituent groups around these CH_3-, $-CH_2$- and >CH- groups. Thus

$$k(CH_3\text{-}X) = k^{o}_{prim}\, F(X)$$

$$k(X\text{-}CH_2\text{-}Y) = k^{o}_{sec}\, F(X)\, F(Y)$$

and

$$k\left(X\text{-}CH\begin{smallmatrix} Y \\ Z \end{smallmatrix}\right) = k^{o}_{tert}\, F(X)\, F(Y)\, F(Z)$$

where k^{o}_{prim}, k^{o}_{sec} and k^{o}_{tert} are the OH radical rate constants per $-CH_3$, $-CH_2$- and >CH-group, respectively, and F(X), F(Y) and F(Z) are the substituent factors for X, Y and Z substituent groups. As derived by Atkinson (1986b, 1987)

Table 14. Rate Constants at 298 K and Parameters C and D in $k=CT^2e^{-D/T}$ for the Reaction of OH Radicals with Alkanes (from Atkinson, 1986a)

Alkane	10^{12} x k (298 K) cm^3 $molecule^{-1}$ s^{-1}	10^{18} x C cm^3 $molecule^{-1}$ s^{-1}	D (K)
Methane	0.00841	6.95	1280
Ethane	0.274	13.7	444
Propane	1.18	12.7	-14
n-Butane	2.53	a	a
2-Methylpropane	2.37	9.58	-305
n-Pentane	4.04		
2-Methylbutane	3.9		
2,2-Dimethylpropane	0.852	17.5	-179
n-Hexane	5.58		
2-Methylpentane	5.5		
3-Methylpentane	5.6		
2,2-Dimethylbutane	2.6		
2,3-Dimethylbutane	6.2	b	b
n-Heptane	7.2		
2,4-Dimethylpentane	5.1		
2,2,3-Trimethylbutane	4.1		
n-Octane	8.72	c	c
2,2,4-Trimethylbutane	3.66	d	d
2,2,3,3-Tetramethylbutane	1.06	18.7	-133
n-Nonane	10.0		
n-Decane	11.2		
n-Undecane	13.3		

Table 14 (continued) - 2

Alkane	10^{12} x k (298 K) cm^3 $molecule^{-1}$ s^{-1}	10^{18} x C cm^3 $molecule^{-1}$ s^{-1}	D (K)
n-Dodecane	13.9		
n-Tridecane	15.5		
Cyclopropane	0.07		
Cyclobutane	1.2		
Cyclopentane	5.2		
Cyclohexane	7.38	e	e
Cycloheptane	13.1		
Methylcyclohexane	10.3		

[a]Arrhenius expression of $k = 1.55 \times 10^{-11} e^{-540/T}$ cm^3 $molecule^{-1}$ s^{-1} recommended (300-500 K).
[b]Independent of temperature over the range ~300-500 K.
[c]Arrhenius expression of $k = 3.12 \times 10^{-11} e^{-380/T}$ cm^3 $molecule^{-1}$ s^{-1} recommended (300-500 K).
[d]Arrhenius expression of $k = 1.62 \times 10^{-11} e^{-443}$ cm^3 $molecule^{-1}$ s^{-1} recommended (300-500 K).
[e]Arrhenius expression of $k = 2.73 \times 10^{-11} e^{-390/T}$ cm^3 $molecule^{-1}$ s^{-1} recommended (300-500 K).

$$k^{o}_{prim} = 4.47 \times 10^{-18}\ T^{2}\ e^{-303/T}\ \mathrm{cm^{3}\ molecule^{-1}\ s^{-1}},$$

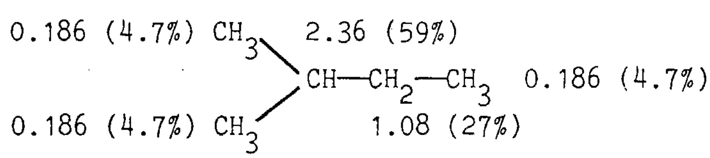
$$k^{o}_{sec} = 4.32 \times 10^{-18}\ T^{2}\ e^{233/T}\ \mathrm{cm^{3}\ molecule^{-1}\ s^{-1}},$$

$$k^{o}_{tert} = 1.89 \times 10^{-18}\ T^{2}\ e^{711/T}\ \mathrm{cm^{3}\ molecule^{-1}\ s^{-1}},$$

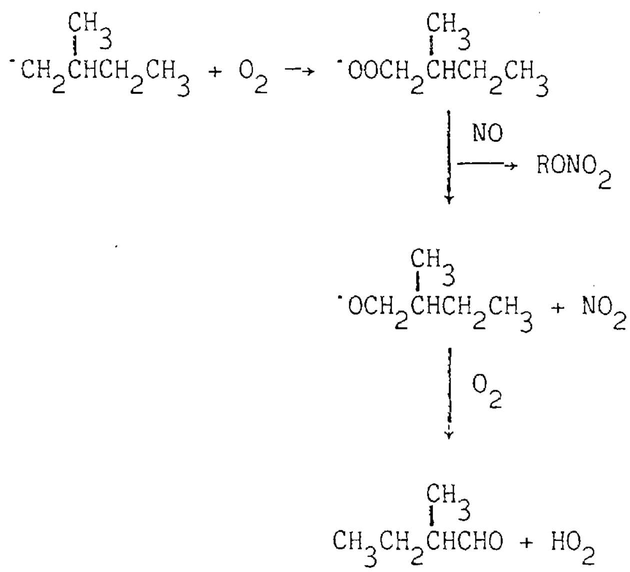
$$F(-CH_3) = 1.00$$

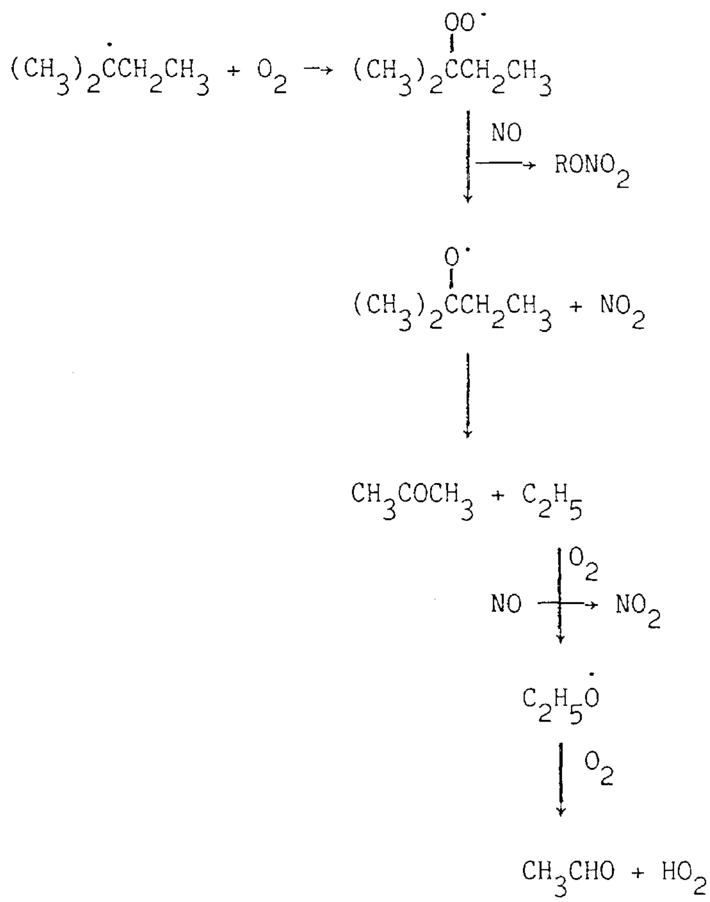
$$F(-CH_2-) = F(>CH-) = F(>C<) = e^{76/T} = 1.29 \text{ at } 298\ K.$$

This estimation technique not only allows the calculation of OH radical reaction rate constants for alkanes for which experimental data do not exist, but also allows the isomeric alkyl radical distribution to be calculated for a given alkane. Thus, for example, for 2-methylbutane the calculated OH radical reaction rate constants at 298 K at the various carbon atoms are (in units of 10^{-12} $\mathrm{cm^{3}\ molecule^{-1}\ s^{-1}}$)



The percentages of OH radical reaction calculated to occur at each of the carbons are also given. These alkyl radicals then react as discussed above in Sections I and II, and the expected subsequent reaction sequences in the presence of NO are as follows (where $RONO_2$ is the corresponding alkyl nitrate formed from the alkyl peroxy radicals).





$$(CH_3)_2CH\dot{C}HCH_3 + O_2 \rightarrow (CH_3)_2CHCH(OO^{\cdot})CH_3$$

$$\downarrow NO \quad (\rightarrow RONO_2)$$

$$(CH_3)_2CHCH(O^{\cdot})CH_3 + NO_2$$

$$\downarrow$$

$$(CH_3)_2\dot{C}H + CH_3CHO$$

$$\downarrow O_2,\ NO \quad (\rightarrow RONO_2)$$

$$(CH_3)_2CH\dot{O} + NO_2$$

$$\downarrow O_2$$

$$CH_3COCH_3 + HO_2$$

$$(CH_3)_2CHCH_2\dot{C}H_2 + O_2 \rightarrow (CH_3)_2CHCH_2CH_2O\dot{O}$$

$$\downarrow NO \quad (\rightarrow RONO_2)$$

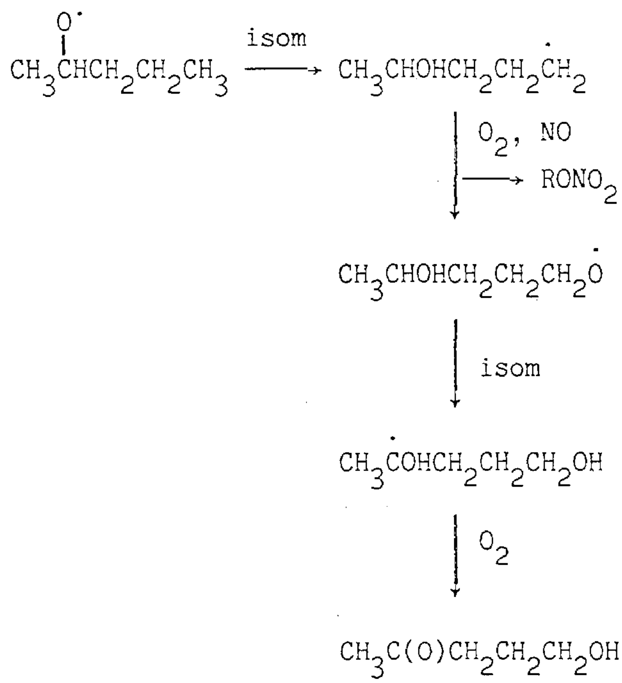
$$(CH_3)_2CHCH_2CH_2O^{\cdot} + NO_2$$

$$\downarrow O_2$$

$$(CH_3)_2CHCH_2CHO + HO_2$$

In the absence of NO, the alkyl peroxy radicals will react with HO_2 and RO_2 radicals.

For the longer chain ($>C_3$) alkanes, alkoxy radical isomerization can also occur in addition to decomposition and reaction with O_2 (Section I and Carter and Atkinson, 1985). For example, for the 2-pentoxy radical



It should be noted, however, that this reaction sequence has not been experimentally confirmed, and the fraction of the reaction of the δ-hydroxyalkyl peroxy radical reacting with NO to yield the corresponding δ-hydroxyalkyl nitrate has not been experimentally determined. The limited data available concerning alkyl nitrate formation from these hydroxy-substituted alkyl peroxy radicals (from computer model fits to environmental chamber data) suggest that this alkyl nitrate formation is minimal, and Carter and Atkinson (1985) recommend that this fractional alkyl nitrate formation from the reaction

$$RCHOHCH_2CH_2CH(OO^{\cdot})R' + NO \rightarrow RCHOHCH_2CH_2CH(ONO_2)R'$$

is essentially zero.

NO_3 Radical Reactions

It has been shown that the NO_3 radical reacts with the alkanes, with room temperature rate constants being in the 10^{-17} to 10^{-16} cm^3 $molecule^{-1}$ s^{-1} range (Atkinson et al., 1988b). These kinetic data were obtained using a relative rate technique. Using rate constants for the reactions of NO_3 radicals with n-heptane and 2,3-dimethylbutane of 1.36×10^{-16} and 4.06×10^{-16} cm^3 $molecule^{-1}$ s^{-1} at 296 K, respectively (Atkinson et al., 1988b), the rate constants given in Table 15 are derived. Under atmospheric conditions, the nighttime reactions of the alkanes with the NO_3 radical can be calculated to be typically a factor of 100 less important as an atmospheric loss process compared to the daytime OH radical reaction.

These NO_3 radical reactions, similar to the OH radical reactions, proceed via H-atom abstraction from the C-H bonds

$$NO_3 + RH \rightarrow HNO_3 + R$$

followed by the alkyl radical reactions. The distribution of alkyl radical isomers formed from the more complex alkanes are not known, but the reactivities of primary, secondary and tertiary C-H bonds are anticipated to be tertiary >> secondary >> primary.

Table 15. Rate Constants for the Reaction of NO_3 Radicals with Alkanes at 296 ± 2 K (Taken from Atkinson et al., 1988b)

Alkane	10^{16} x k (cm^3 $molecule^{-1}$ s^{-1})[a]
n-Butane	0.6
n-Pentane	0.8
n-Hexane	1.1
n-Heptane	1.4
n-Octane	1.8
n-Nonane	2.4
2-Methylpropane	1.0
2,3-Dimethylbutane	4.1
Cyclohexane	1.3

[a]Uncertainty limits are of the order of ±15-35%.

IV. HALOALKANES

The kinetics and mechanisms of the OH radical and O_3 reactions with the haloalkanes have recently been reviewed and evaluated by Atkinson (1986a) and Atkinson and Carter (1984), respectively. The gas-phase reactions of the haloalkanes with O_3 are of negligible importance as an atmospheric loss process, since the available data show that the rate constants for these reactions are $<10^{-20}$ cm^3 $molecule^{-1}$ s^{-1} at room temperature (Atkinson and Carter, 1984). The potential tropospheric loss processes for the haloalkanes then involve reaction with OH and NO_3 radicals and photolysis. To date, no data exist for the NO_3 radical reactions, but by analogy with the alkanes it is expected that these NO_3 radical reactions will be slow (with rate constants $< 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} at room temperature for the C_1 and C_2 haloalkanes at room temperature).

OH Radical Reactions

The kinetics and mechanisms of the reactions of the OH radical with the haloalkanes have been critically reviewed and evaluated by Atkinson (1986a). Rate constants have been determined over significant temperature ranges for a number of haloalkanes, and the Arrhenius plots are curved, as expected from theoretical considerations. Atkinson (1986a) accordingly evaluated the data in terms of the modified expression

$$k = C\ T^2\ e^{-D/T}$$

The recommended 298 K rate constants and the parameters C and D given by Atkinson (1986a) are given in Table 16 for haloalkanes of tropospheric interest, together with the room temperature rate constants for other haloalkanes for which recommendations were not made.

For the haloalkanes containing F, Cl and Br substituents, these OH radical reactions proceed by H atom abstraction, and in the absence of experimental data the estimation technique of Atkinson (1986a,b, 1987) can be used to calculate the distribution of haloalkyl radicals formed. Garraway and Donovan (1979) have reported that CF_3I and other non-hydrogen-containing iodine containing haloalkanes such as C_2F_5I and C_3F_7I react with OH radicals, presumably by I atom abstraction to form HOI and the corresponding haloalkyl radical. The atmospheric reactions of the haloalkyl radicals have been dealt with in Section I above.

Photolysis

Photolysis is a potentially important tropospheric loss process for the haloalkanes, especially for those containing multiple Cl and/or Br atoms and no H atoms (thus precluding OH radical reaction). Absorption cross-sections for CCl_4, $CFCl_3$, CF_2Cl_2, CHF_2Cl, CH_3Cl and CH_3CCl_3 are tabulated in the NASA evaluation (DeMore et al., 1985, 1987). Absorption cross-sections for other haloalkanes have been measured by Chou et al (1978), Robbins (1977), Hubrich and Stuhl (1980), Hubrich et al. (1977), Vanlaethem-Meuree et al. (1978), Green and Wayne (1976/77) and Molina et al. (1982). The absorption spectra are unstructured and continuous, and the photodissociation quantum yields are expected, consistent with experimental observations for CCl_4, $CFCl_3$ and CF_2Cl_2 (Baulch et al.,

Table 16. Room Temperature Rate Constants and Temperature Dependencies ($k = CT^2e^{-D/T}$) for the Gas-Phase Reactions of the OH Radical with Haloalkanes (from Atkinson, 1986a)

Haloalkane	10^{14} x k(298 K) cm^3 $molecule^{-1}$ s^{-1}	10^{18} x C cm^3 $molecule^{-1}$ s^{-1}	D (K)
CH_3Cl	4.4	3.5	585
CH_3Br	3.9	1.2	296
CH_2FCl	4.4	3.8	604
CH_2Cl_2	14	8.5	500
CHF_2Cl	0.47	1.5	1000
$CHFCl_2$	3.0	1.7	479
$CHCl_3$	10	6.3	504
CF_3Br	<0.1		
CF_2Cl_2	<0.04		
CF_2ClBr	<0.1		
$CFCl_3$	<0.05		
CCl_4	<0.4		
CH_3CH_2Cl	40		
CH_3CHF_2	3.4		
CH_2ClCH_2Cl	22		
CH_2BrCH_2Br	25		
CH_3CF_2Cl	0.36	2.1	1171
CH_3CCl_3	1.2	5.9	1129
CH_2FCF_3	0.85	1.3	769
CH_2ClCF_2Cl	~1.5		
$CHFClCF_3$	1.0	0.91	624
$CHCl_2CF_3$	3.4	a	a

[a] $k = 1.2 \times 10^{-12} e^{-1056/T}$ cm^3 $molecule^{-1}$ s^{-1} over the range 245-375 K.

1982), to be unity, and at shorter wavelengths (<230 nm) two halogen atoms can be simultaneously in the primary process. The halogen atom produced is a Br atom for bromine-containing haloalkanes and a Cl atom for haloalkanes containing Cl atoms but no Br atoms.

$$CF_2ClBr + h\nu \rightarrow CF_2Cl + Br$$

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$$

The subsequent reactions of the haloalkyl radicals formed have been discussed in Section I above.

In general, photolysis of the fluorochloroalkanes is insignificant in the troposphere. Indeed, photolysis of CF_3Br is extremely slow in the troposphere, with a calculated lifetime of >1000 yr (Molina et al., 1982). Only for haloalkanes containing one Br and one Cl atom (for example, CF_2ClBr) or two Br atoms (such as CF_2Br_2) or more does photolysis in the troposphere become important (Molina et al., 1982).

V. ALKENES

As discussed by Atkinson and Lloyd (1984), Atkinson and Carter (1984) and Atkinson (1986a), the atmospheric loss processes of the alkenes are by reaction with OH and NO_3 radicals and O_3. The conjugated dialkenes also react with NO_2, and this reaction could be of some importance in environmental chamber experiments carried out at NO_2 concentrations higher than ambient.

OH Radical Reactions

The kinetics and mechanisms of the reactions of the OH radical with the alkenes, cycloalkenes and dialkenes have been reviewed and evaluated by Atkinson (1986a). For ethene and the methyl-substituted ethenes the OH radical reaction proceeds essentially totally by OH radical addition to the carbon-carbon double bond, with H atom abstraction from the side chains accounting for <5% of the total reaction for propene and 2-methylpropene (Hoyermann and Sievert, 1979, 1983) at room temperature and <10% for cis- and trans-2-butene (Hoyermann and Sievert, 1983). For 1-butene, the recent data of Hoyermann and Sievert (1983) and Atkinson et al. (1985) show that H atom abstraction accounts for <10% of the overall reaction at room temperature. To date, only for 1,3- and 1,4-cyclohexadiene has H atom abstraction been shown to occur to any significance (Ohta, 1984), with this process accounting for 8.9% and 15.3% of the overall OH radical reactions with 1,3- and 1,4-cyclohexadiene, respectively, at room temperature. However, for the alkenes with side chains, a small amount of H atom abstraction must occur, with this process contributing only a small fraction of the overall reaction. Assuming that H atom abstraction from substituent alkyl groups occurs at the same rate as in the alkanes (Atkinson, 1987), then this H atom abstraction pathway is generally insignificant. For an extreme case, H atom abstraction in 1-heptene is then calculated to account for 10-15% of the overall OH radical reaction.

The rate constants for these OH radical reactions with the alkenes are at, or are very close to, the high pressure second-order kinetic limit at atmospheric pressure. For ethene, this high pressure limit appears to be attained at approximately 760 torr of air diluent gas. Thus, the high pressure second order rate constants will be reasonably applicable throughout the troposphere. The room temperature rate constants and temperature dependent parameters for the reactions of the OH radical with a series of atmospherically important alkenes, cycloalkenes and dialkenes are given in Table 17.

As discussed above, except for 1,3- and 1,4-cyclohexadiene (and presumably also the corresponding cycloheptadienes), OH radical addition to the >C=C< bond is the dominant reaction pathway. The OH radical can add to either carbon atom of the double bond(s), and Cvetanovic (1976) has reported that for propene addition to the terminal carbon occurs 65% of the time

$$OH + CH_3CH{=}CH_2 \rightarrow \underset{(\sim 35\%)}{CH_3\overset{OH}{\overset{|}{C}}H\dot{C}H_2} \text{ and } \underset{(\sim 65\%)}{CH_3\dot{C}HCH_2OH}$$

The β-hydroxyalkyl radicals then rapidly add O_2 under atmospheric conditions, as discussed in Section I above. In the presence of NO, these β-hydroxyalkyl peroxy radicals form NO_2 plus the corresponding β-hydroxyalkoxy radical, with a small amount of β-hydroxyalkyl nitrate also being formed (Shepson et al., 1985)

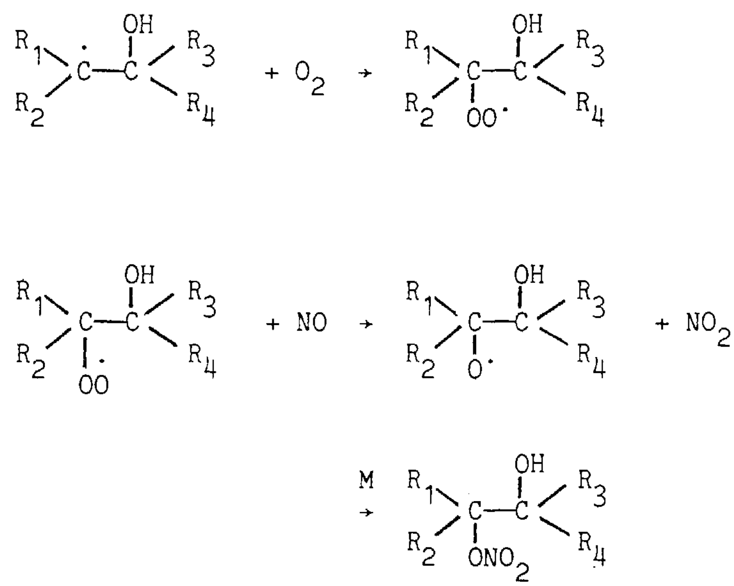
Table 17. Rate Constants k at 298 K and Arrhenius Parameters ($k = Ae^{-E/RT}$) for the Reaction of OH Radicals with Alkanes at the High Pressure Limit (from Atkinson, 1986a)

Alkene	10^{12} x k(298 K) (cm^3 $molecule^{-1}$ s^{-1})	10^{12} x A (cm^3 $molecule^{-1}$ s^{-1})	E/R(K)
Ethene	8.54	2.15	-411
Propene	26.3	4.85	-504
1-Butene	31.4	6.53	-468
1-Pentene	31.4		
3-Methyl-1-butene	31.8	5.32	-533
1-Hexene	37		
3,3-Dimethyl-1-butene	28.4		
1-Heptene	40		
2-Methylpropene	51.4	9.51	-503
2-Methyl-1-butene	60.7		
cis-2-Butene	56.1	10.9	-488
cis-2-Pentene	65.1		
trans-2-Butene	63.7	10.1	-549
trans-2-Pentene	67		
2-Methyl-2-butene	86.9	19.2	-450
2,3-Dimethyl-2-butene	110		
Cyclopentene	67.0		
Cyclohexene	67.4		
Cycloheptene	74.1		
1-Methylcyclohexene	95		

(continued)

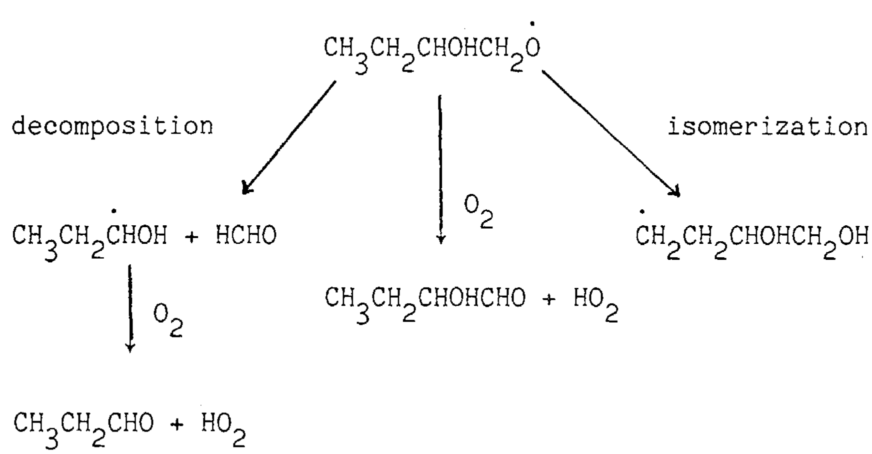
Table 17 (continued) - 2

Alkene	$10^{12} \times k(298\ K)$ ($cm^3\ molecule^{-1}\ s^{-1}$)	$10^{12} \times A$ ($cm^3\ molecule^{-1}\ s^{-1}$)	E/R(K)
α-Pinene	53.2	12.0	-444
β-Pinene	78.2	23.6	-357
Δ^3-Carene	87.0		
d-Limonene	169		
1,3-Butadiene	66.8	13.9	-468
2-Methyl-1,3-butadiene	101	25.5	-409



At atmospheric pressure and room temperature, Shepson et al. (1985) determined yields of $CH_3CHOHCH_2ONO_2$ and $CH_3CH(ONO_2)CH_2OH$ of approximately 0.016 for each nitrate.

The β-hydroxyalkoxy radicals can then decompose, react with O_2 or isomerize, as discussed in Section I above. Thus, for the alkoxy radical formed after internal addition of the OH radical to 1-butene:



The experimental data for the simpler alkenes show that, at room temperature, under atmospheric conditions decomposition dominates over reaction with O_2. Indeed, for the $\geq C_3$ alkanes the reaction with O_2 is negligible and only the products arising from decomposition are observed at room temperature and atmospheric pressure. For ethene, Niki et al. (1981b) have shown that both reaction with O_2 and decomposition of the $HOCH_2CH_2\dot{O}$ radical occurs

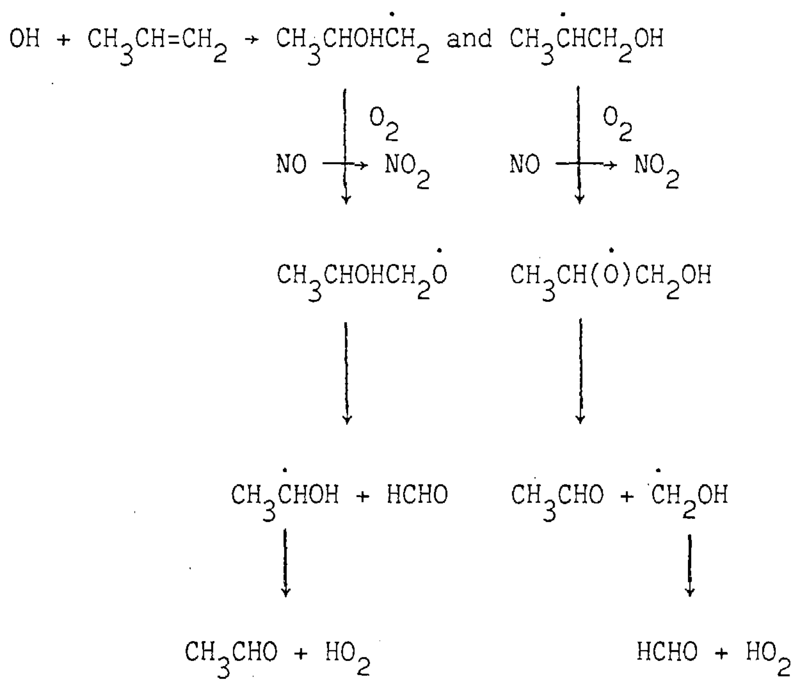
$$HOCH_2CH_2\dot{O} \rightarrow \dot{C}H_2OH + HCHO \qquad (a)$$

$$HOCH_2CH_2\dot{O} + O_2 \rightarrow HOCH_2CHO + HO_2 \qquad (b)$$

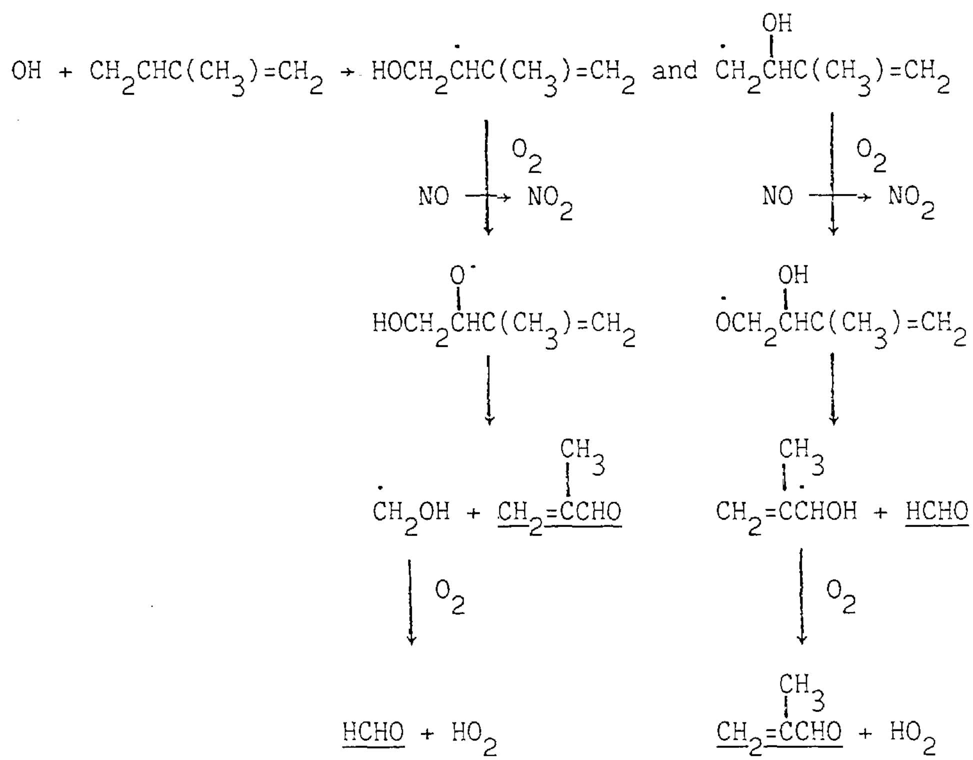
with $k_b/k_a = (5.4 \pm 1.0) \times 10^{-20}$ at 298 K.

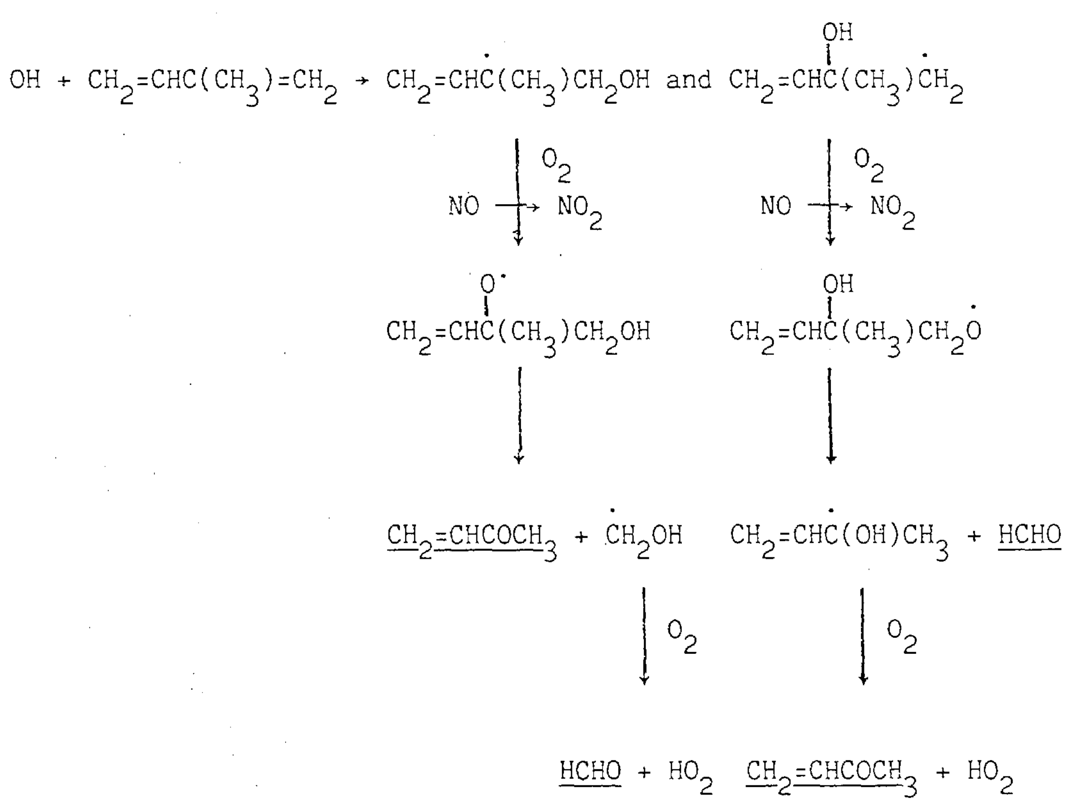
For the $CH_3CH_2CHOHCH_2\dot{O}$ radical formed from 1-butene, the experimental data of Atkinson et al. (1985) show that isomerization is not important. This observation is in accord with the estimates of Atkinson and Lloyd (1984).

Hence, apart from ethene, for which reaction of the $HOCH_2CH_2\dot{O}$ radical with O_2 and decomposition are competitive at 298 K and atmospheric pressure, the β-hydroxyalkoxy radicals formed subsequent to OH radical reactions with the simpler alkenes decompose. For propene the reaction scheme in the presence of NO is then



Similar reaction schemes have been expected to apply to the conjugated dialkenes. For example, for isoprene (2-methyl-1,3-butadiene) the reaction sequence is expected to be (Lloyd et al., 1983) [with the reactions at the two double bonds being dealt with separately, and neglecting nitrate formation (initial stable products are underlined)]:


OH + CH2CHC(CH3)=CH2 → HOCH2CHC(CH3)=CH2 and CH2CHC(CH3)=CH2
OH
O2
NO → NO2
O2
NO → NO2
O
HOCH2CHC(CH3)=CH2
OH
OCH2CHC(CH3)=CH2
CH3
CH2OH + CH2=CCHO
CH3
CH2=CCHOH + HCHO
O2
O2
HCHO + HO2
CH3
CH2=CCHO + HO2


OH + CH2=CHC(CH3)=CH2 → CH2=CHC(CH3)CH2OH and CH2=CHC(CH3)CH2
OH
O2
NO → NO2
O2
NO → NO2
O
CH2=CHC(CH3)CH2OH
OH
CH2=CHC(CH3)CH2O
CH2=CHCOCH3 + CH2OH
CH2=CHC(OH)CH3 + HCHO
O2
O2
HCHO + HO2
CH2=CHCOCH3 + HO2

The products formed depend on which double bond OH radical addition occurs at, but not at which carbon atom of the particular double bond. For conjugated dialkenes, the estimation technique of Ohta (1983) allows the fraction of the overall OH radical addition reaction proceeding at each >C=C< double bond to be calculated [note that this information cannot be obtained from the estimation technique of Atkinson (1986a)]. Thus, for isoprene, OH radical addition to the CH_2=CH- and CH_2=C< bonds

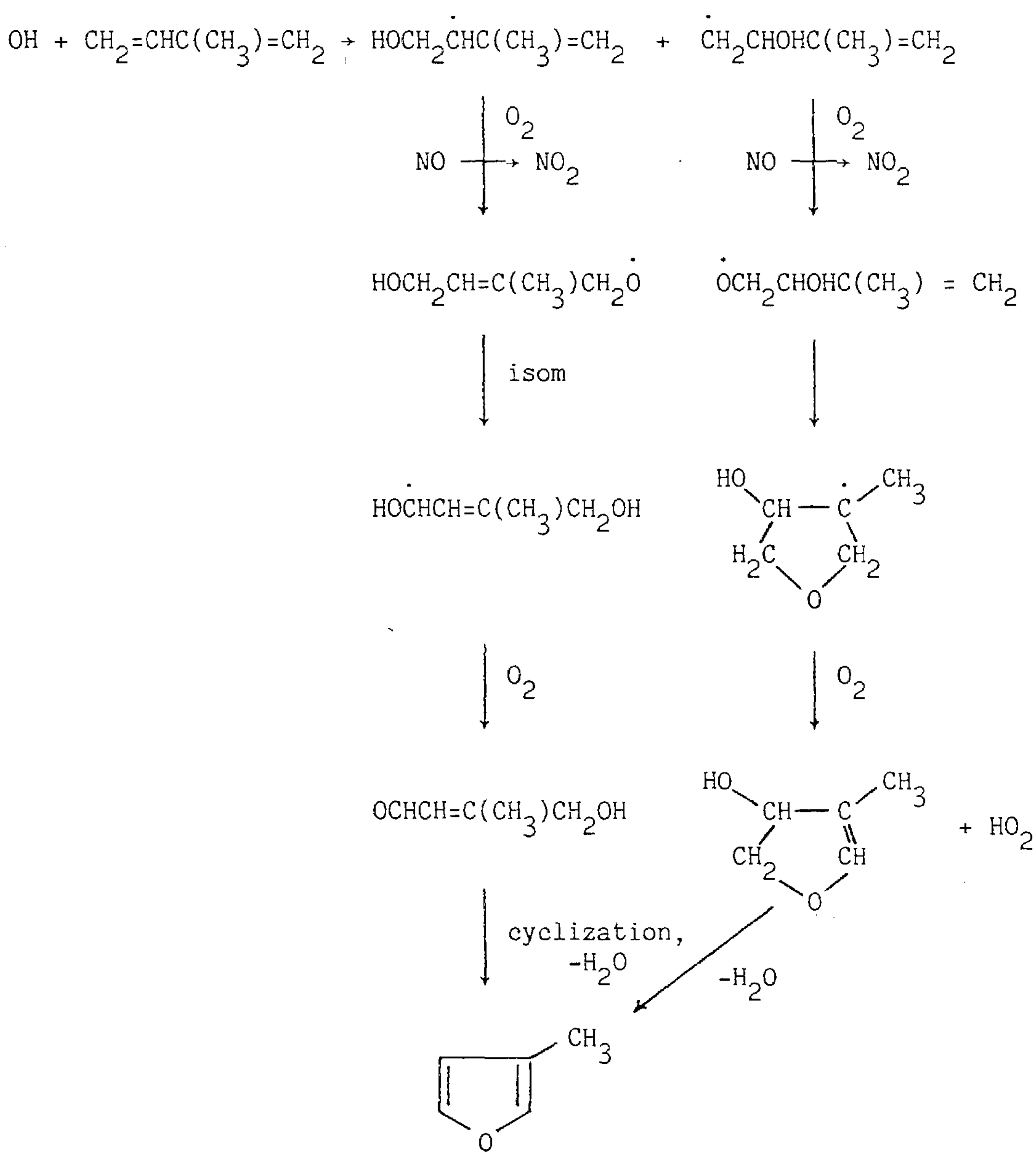
$$OH + CH_2{=}CHC(CH_3){=}CH_2 \rightarrow HOCH_2\text{-}\dot{C}HC(CH_3){=}CH_2 \text{ and } \dot{C}H_2CH(OH)C(CH_3){=}CH_2 \quad (a)$$

$$\rightarrow CH_2{=}CHC(OH)(CH_3)\dot{C}H_2 \text{ and } CH_2{=}CH\dot{C}(CH_3)CH_2OH \quad (b)$$

is calculated to be in the ratio k_a/k_b = 34/66. The reactions of the products have been dealt with in Section II above (carbonyls) or in Section VIII below (α,β-unsaturated carbonyls).

However, two recent studies of the products formed from the gas-phase reaction of the OH radical with isoprene show that methyl vinyl ketone and methacrolein (together with their co-product HCHO) do not account for the entire reaction pathway. Thus, Gu et al. (1985) observed that at room temperature and atmospheric pressure of air or O_2 the major products were methyl vinyl ketone, methacrolein and 3-methylfuran in approximate respective yields of 16%, 23% and 5%. More recently, Tuazon et al. (unpublished data, 1988) have observed methyl vinyl ketone, methacrolein and HCHO as products, with yields of ~30%; ~20% and ~60%, respectively, with the HCHO yield being in reasonable agreement with the sum of the methyl vinyl ketone and methacrolein yields. Additionally, 3-methylfuran is a product of this reaction (with a yield of 4.4%). These data of Tuazon et al. show that ~40% of the overall reaction pathways are not presently accounted for by the reaction scheme presented by Lloyd et al. (1983) [see above], and IR absorption bands due to other products were indeed observed.

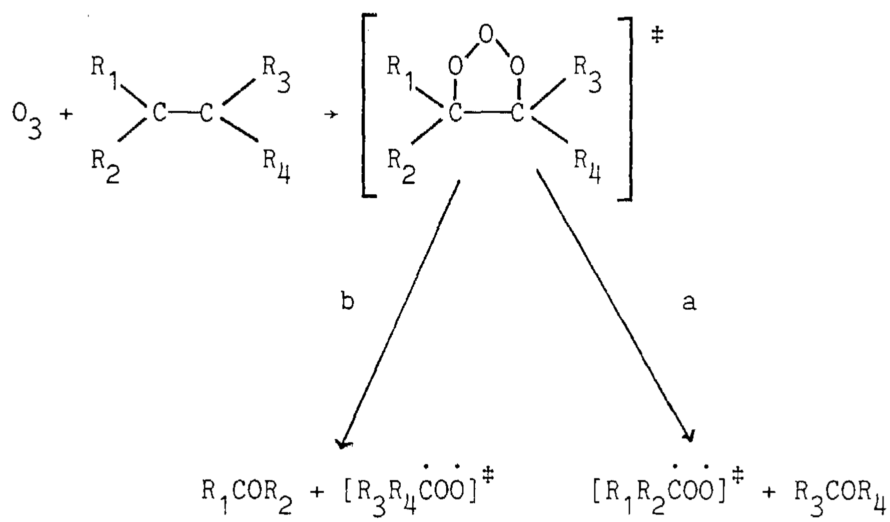
The production of 3-methylfuran presumably occurs by one of two routes



and initial OH radical addition at the other >C=C< bond will also yield 3-methylfuran by these schemes.

O_3 Reaction

The kinetics and mechanisms of the gas-phase reactions of O_3 with the alkanes, cycloalkenes and dialkenes have been reviewed and evaluated by Atkinson and Carter (1984). The kinetic data for alkenes of atmospheric importance [updated to take into account the more recent studies of Bahta et al. (1984) and Bennett et al. (1987)] are given in Table 18. These reactions proceed by initial O_3 addition to the >C=C< bond to yield an energy-rich ozonide which rapidly decomposes to a carbonyl and an initially energy-rich biradical.



where [ ]‡ denotes an energy-rich species. Based upon the data of Herron and Huie (1978), it is assumed that $k_a \sim k_b$ for the alkene systems. The energy-rich biradicals can then be collisionally stabilized or unimolecularly decompose.

$$[R_1R_2\dot{C}O\dot{O}]^{\ddagger} + M \rightarrow R_1R_2\dot{C}O\dot{O} + M$$

$$[R_1R_2\dot{C}O\dot{O}]^{\ddagger} \rightarrow \text{products.}$$

Table 18. Rate Constants k at 298 K and Arrhenius Parameters ($k = Ae^{-E/RT}$) for the Gas-Phase Reactions of O_3 with Alkenes, Cycloalkenes and Dialkenes (from Atkinson and Carter, 1984, except as indicated)

Alkene	10^{18} x k(298 K) (cm^3 $molecule^{-1}$ s^{-1})	10^{15} x A (cm^3 $molecule^{-1}$ s^{-1})	E/R (K)
Ethene[a]	1.7	12	2630
Propene	11.3	13.2	2105
1-Butene	11.0	3.46	1713
1-Pentene	10.7		
1-Hexene	11.7		
1-Heptene	17.3		
2-Methyl-2-propene	12.1	3.55	1693
cis-2-Butene	130	3.52	983
cis-2-Pentene	209		
trans-2-Butene	200	9.08	1136
trans-2-Pentene	315		
2-Methyl-2-butene	423	6.17	798
2,3-Dimethyl-2-butene	1160	3.71	347
Cyclopentene[b]	275-813		
Cyclohexene[b]	104-160		
Cycloheptene	319		
α-Pinene	84	0.96	731
β-Pinene	21		
Δ^3-Carene	120		
d-Limonene	640		
1,3-Butadiene[c]	7.5	26	2430
2-Methyl-1,3-butadiene	14.3	12.3	2013

[a]From Atkinson et al. (1988a).
[b]Includes the data of Bennett et al. (1987).
[c]Includes the data of Bahta et al. (1984).

The fraction of the initially formed biradical which is collisionally stabilized is thus expected to be pressure dependent, and this has been confirmed by the study of Hatakeyama et al. (1984), in which the stabilized biradicals formed from a variety of alkenes were "trapped" by reaction with SO_2 to form sulfate. For the trans-2-butene system, the fraction of the biradical stabilized was a function of the total pressure of air, increasing from essentially zero at zero total pressure to a high-pressure limit of 0.185 attained at ~600 torr total pressure of air. At one atmosphere total pressure, the fractional amount of stabilized biradicals formed from ethene, propene, trans-2-butene and 2-methyl-2-propene were 0.390, 0.254, 0.185 and 0.174, respectively (Hatakeyama et al., 1984). This yield of stabilized biradicals from ethene is in excellent agreement with previous values of 0.38 (Su et al., 1980), 0.37 (Kan et al., 1981) and 0.35 (Niki et al., 1981d), and that for trans-2-butene agrees well with the stabilized biradical yield of 0.18 obtained by Niki et al. (1977) from cis-2-butene.

Thus, at ~760 torr total pressure of air and ~298 K the fractions of $[\dot{C}H_2O\dot{O}]^{\ddagger}$ and $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ stabilized from the ethene and 2-butene systems are 0.37 and 0.18, respectively. Assuming that $k_a = k_b$ for the decomposition routes of the initially formed ozonide and that the $[\dot{C}H_2O\dot{O}]^{\ddagger}$ and $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ biradicals formed from propene react identically to those formed from ethene and the 2-butenes, these stabilization yields predict a total stabilized biradical yield from propene ($\dot{C}H_2O\dot{O}$ plus $CH_3\dot{C}HO\dot{O}$) of 0.275, in good agreement with the observed yield of 0.254 ± 0.023 (Hatakeyama et al., 1984).

However, the data of Hatakeyama et al. (1984) for the stabilized biradical yield from 2-methyl-2-propene (0.174) are not consistent with the above data for the stabilization yield of $[\dot{C}H_2O\dot{O}]^{\ddagger}$ (0.37) and the stabilization yield of ~0.30 for the $[(CH_3)_2\dot{C}O\dot{O}]^{\ddagger}$ biradical in the 2,3-dimethyl-2-butene system (Niki et al., 1987b). This suggests that the stabilization yields of these biradical species, as may be expected, are dependent on the reaction system in which they are formed.

Data concerning the decomposition pathways of the energy-rich biradicals are available mainly for $[\dot{C}H_2O\dot{O}]^{\ddagger}$, $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ and $[(CH_3)_2\dot{C}O\dot{O}]^{\ddagger}$ (Atkinson and Lloyd, 1984; Atkinson and Carter, 1984; Niki et al., 1987b). For the $[\dot{C}H_2O\dot{O}]^{\ddagger}$ biradical, formed from the reaction of O_3 with ethene, the recommendation of Atkinson and Lloyd (1984) yields (at ~760 torr total pressure of air and 298 K):

$$[\dot{C}H_2O\dot{O}]^{\ddagger} \xrightarrow{M} \dot{C}H_2O\dot{O} \qquad 37\%$$

$$\longrightarrow CO_2 + H_2 \qquad \sim 13\%$$

$$\longrightarrow CO + H_2O \qquad \sim 44\%$$

$$\longrightarrow H + HCO_2 \qquad \sim 6\%$$

$$HCO_2 \longrightarrow H + CO_2$$

Thus, for the reaction of O_3 with ethene at 760 torr total pressure of air and room temperature, the overall reaction stoichiometry is

$$O_3 + CH_2{=}CH_2 \rightarrow HCHO + 0.37\ \dot{C}H_2O\dot{O} + 0.12\ HO_2 + 0.13\ H_2 + 0.19\ CO_2 + 0.44\ CO + 0.44\ H_2O$$

For the $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ biradical, a fraction of 0.18 is stabilized at 298 K and atmospheric pressure. Based upon the recommendations of Atkinson and Lloyd (1984) for the decomposition routes, the reactions of this biradical under atmospheric conditions is given by

$$[CH_3\dot{C}HO\dot{O}]^{\ddagger} \xrightarrow{M} CH_3\dot{C}HO\dot{O} \qquad (18\%)$$

$$\rightarrow CH_3 + CO + OH \qquad (\sim 30\%)$$

$$\rightarrow CH_3 + CO_2 + H \qquad (\sim 32\%)$$

$$\rightarrow HCO + CH_3O \qquad (\sim 6\%)$$

$$\rightarrow CH_4 + CO_2 \qquad (14\%)$$

Thus, when combined with reactions of the $[\dot{C}H_2O\dot{O}]^{\ddagger}$ biradical, the overall stoichiometry of the reaction of O_3 with propene at ~760 torr total pressure and 298 K is then expected to be

$$O_3 + CH_3CH{=}CH_2 \rightarrow 0.50\ HCHO + 0.50\ CH_3CHO + 0.185\ \dot{C}H_2O\dot{O}$$

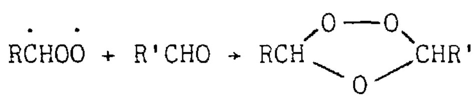
$$+ 0.09\ CH_3\dot{C}HO\dot{O} + 0.25\ HO_2 + 0.15\ OH$$

$$+ 0.03\ CH_3O + 0.31\ CH_3O_2 + 0.07\ CH_4$$

$$+ 0.065\ H_2 + 0.325\ CO_2 + 0.40\ CO + 0.22\ H_2O$$

However, Carter et al. (1986) observed from computer model simulations of propene-NO_x-air irradiations that the radical formation from this scheme is too high. Clearly further study of the products arising from the reaction of O_3 with propene under atmospheric pressure are needed.

The stabilized biradicals are known to react with aldehydes, SO_2, CO, H_2O, and NO_2, and it is expected that they will also react with NO.



$$R\dot{C}HO\dot{O} + SO_2 \xrightarrow{H_2O} RCHO + H_2SO_4$$

$$R\dot{C}HO\dot{O} + CO \rightarrow \text{products}$$

$$R\dot{C}HO\dot{O} + H_2O \rightarrow RCOOH + H_2O$$

$$R\dot{C}HO\dot{O} + NO_2 \rightarrow RCHO + NO_3$$

$$R\dot{C}HO\dot{O} + NO \rightarrow RCHO + NO_2$$

Based upon the available data for the reactions of $\dot{C}H_2O\dot{O}$ radicals with these reactants [with rate constants relative to the reaction of $\dot{C}H_2O\dot{O}$ with SO_2 of: HCHO, ~0.25 (Su et al., 1980); CO, 0.0175 (Su et al., 1980); H_2O, $(2.3 \pm 1) \times 10^{-4}$ (Suto et al., 1985) and NO_2, 0.014 (Manzanares et al., 1985)], it appears that the reaction of stabilized biradicals with water vapor will be their dominant loss process, leading to the formation of carboxylic acids.

Recently Niki et al. (1987b) have studied the products and mechanism of the reaction of O_3 with 2,3-dimethyl-2-butene under atmospheric conditions. A fraction of 0.25-0.30 of the initially energy-rich biradical $[(CH_3)_2\dot{C}O\dot{O}]^{\ddagger}$ was observed to be stabilized at atmospheric pressure, with the major decomposition route of this biradical involving the isomerization

$$[(CH_3)_2\dot{C}O\dot{O}]^{\ddagger} \rightarrow [CH_3C(OOH){=}CH_2]$$

followed by dissociation of this unsaturated hydroperoxide intermediate

$$[CH_3C(OOH){=}CH_2] \rightarrow CH_3COCH_2 + OH$$

The above discussion shows that only for the reaction of O_3 with ethene (and maybe 2,3-dimethyl-2-butene) are the products reasonably well known. Even for propene there are significant uncertainties in the radicals formed and their yields under atmospheric conditions.

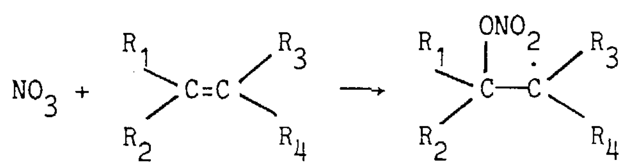
NO_3 Radical Reaction

The rate constants for the gas-phase reactions of the NO_3 radical with a large number of alkenes, cycloalkenes and dialkenes have been determined using absolute and relative rate methods. A reliable absolute rate constant at room temperature is available for trans-2-butene (Ravishankara and Mauldin, 1985; Dlugokencky and Howard, 1988), and this enables the recent relative rate constant data of Atkinson et al. (1988b) to be placed on an absolute basis. The room temperature rate constants for a series of atmospherically important alkenes are given in Table 19.

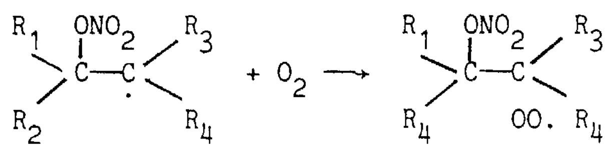
Table 19. Room Temperature Rate Constants k for the Reaction of NO_3 Radicals with a Series of Alkenes (from Atkinson et al., 1988b)

Alkene	k (cm^3 $molecule^{-1}$ s^{-1})
Ethene	2.1×10^{-16}
Propene	9.4×10^{-15}
1-Butene	1.2×10^{-14}
2-Methylpropene	3.1×10^{-13}
cis-2-Butene	3.5×10^{-13}
trans-2-Butene	3.9×10^{-13}
2-Methyl-2-butene	9.3×10^{-12}
2,3-Dimethyl-2-butene	5.7×10^{-11}
Cyclopentene	4.6×10^{-13}
Cyclohexene	5.3×10^{-13}
Cycloheptene	4.8×10^{-13}
α-Pinene	5.8×10^{-12}
β-Pinene	2.4×10^{-12}
Δ^3-Carene	1.0×10^{-11}
d-Limonene	1.3×10^{-11}
1,3-Butadiene	9.8×10^{-14}
2-Methyl-1,3-Butadiene	5.9×10^{-13}

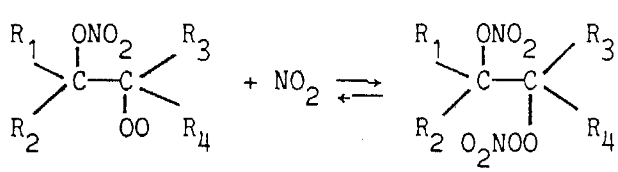
These reactions proceed by NO_3 radical addition to the >C=C< bond, with H atom abstraction being totally insignificant,



followed by rapid addition of O_2

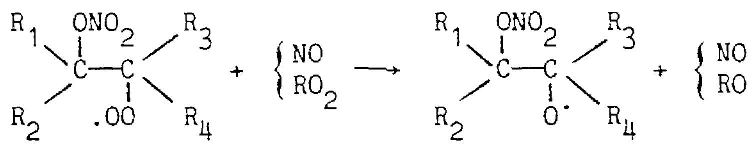


When NO_3 radicals are present, NO concentrations are extremely low, and these β-nitratoalkyl peroxy radicals will then either react with HO_2 and other RO_2 radicals, or reversibly add NO_2 to yield the thermally unstable nitrato peroxynitrates



Because of the expected rapid thermal decomposition of the peroxy nitrates, these species act as a temporary reservoir of the β-nitratoalkyl peroxy radicals. Of course, if NO is present at sufficiently high concentrations to react with the peroxy radicals, then the corresponding alkoxy radical will be formed (this radical can also be formed from the

RO_2 + RO_2 radical reactions)



These alkoxy radicals can then react with O_2, decompose or isomerize, as discussed in Section I above. For the major β-nitratoalkoxy radical formed from the reaction of NO_3 radicals with propene (by NO_3 radical addition at the terminal carbon atom), Shepson et al. (1985) showed that decomposition and reaction with O_2 both occur

$$CH_3CH(O)CH_2ONO_2 \rightarrow CH_3CHO + HCHO + NO_2$$

$$CH_3CH(O)CH_2ONO_2 + O_2 \rightarrow CH_3COCH_2ONO_2 + HO_2$$

NO_2 Reactions

NO_2 has been shown to react with conjugated dialkenes with rate constants at room temperature of $>10^{-20}$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 1984b; Ohta et al., 1986). These reactions are of negligible importance as an atmospheric loss process of the alkenes and dialkenes, but may be marginally important in environmental chamber experiments carried out at high NO_2 concentrations. The articles of Atkinson et al. (1984), Niki et al. (1986) and Ohta et al. (1986) should be consulted for further details of the kinetics and mechanisms of these reactions.

VI. HALOALKENES

The kinetics and mechanisms of the gas-phase reactions of the haloalkenes with O_3 and OH radicals have been reviewed and evaluated by Atkinson and Carter (1984) and Atkinson (1986a), respectively. The loss processes which are potentially important in the troposphere involve reaction with OH and NO_3 radicals and with O_3.

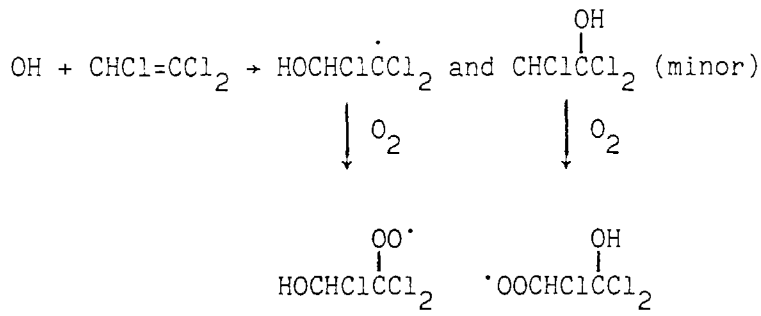
OH Radical Reactions

The kinetics and mechanisms of the gas-phase reactions of the haloalkanes with the OH radical have been reviewed by Atkinson (1986a). More recent kinetic and product data have been reported by Edney et al. (1986a,b), Tuazon et al. (1988) and Winer et al. (1987). Room temperature rate constants and temperature dependent parameters for the atmospherically important haloalkenes are given in Table 20. These reactions proceed entirely, or essentially entirely, by OH radical addition to the $>C=C<$ bond, and are at the second-order high pressure limit at atmospheric pressure. Indeed, since the limiting high-pressure rate constant for $CH_2=CHCl$ is attained at a total pressure of argon of <50 torr, these reactions will be at the high pressure second-order limit throughout the troposphere. The OH radical adds preferentially to the least halogen substituted carbon atom of the $>C=C<$ bond, and the resulting substituted alkyl radical will rapidly add O_2 under atmospheric conditions:

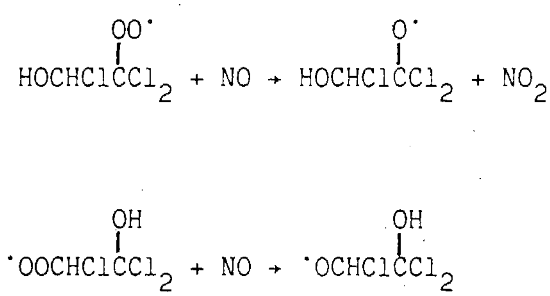
Table 20. Rate Constants k at Room Temperature and Arrhenius Parameters ($k = Ae^{-E/RT}$) for the Reaction of OH Radicals with Haloalkenes

Haloalkene	10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})	10^{12} x A (cm^3 $molecule^{-1}$ s^{-1})	E/R(K)
CH_2=CHCl[a]	6.60	1.48	-390
CH_2=CCl_2[b]	8.11		
cis-CHCl-CHCl[b]	2.38	0.563	-427
trans-CHCl=CHCl[b]	1.80		
CHCl=CCl_2[a]	2.36		
CCl_2=CCl_2[a]	0.167	9.64	1209
CH_2=$CHCH_2Cl$[c]	17		
cis-CH_2ClCH=CHCl[b]	8.45		
trans-CH_2ClCH=CHCl[b]	14.4		

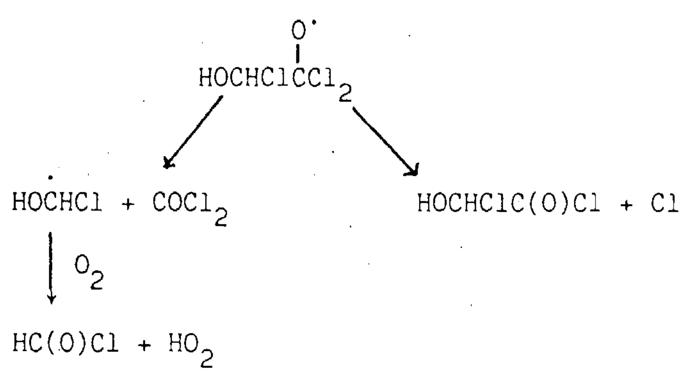
[a]From Atkinson (1986a).
[b]From Tuazon et al. (1988).
[c]From Edney et al. (1986a) and Winer et al. (1987).

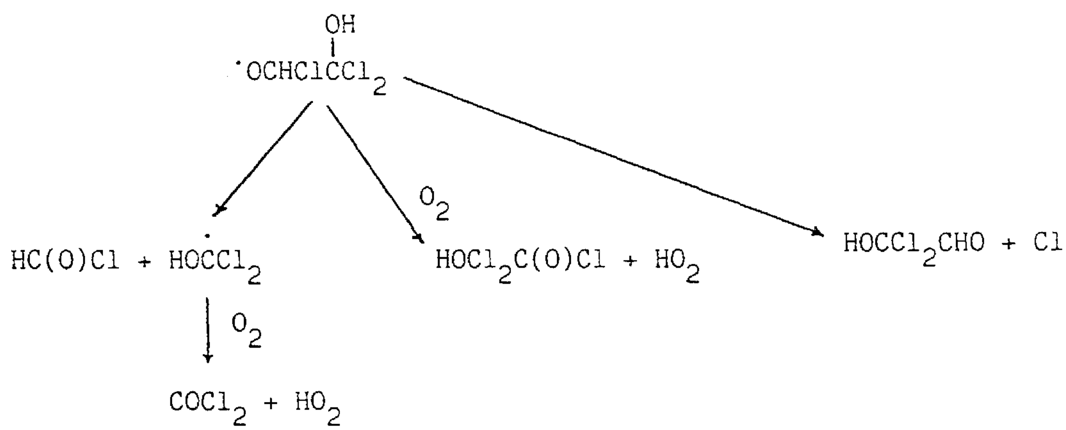


In the absence of sufficient NO, these peroxy radicals will react with HO_2 and other RO_2 radicals. In the presence of sufficiently high concentrations of NO, reaction with NO will occur to yield NO_2 and the corresponding alkoxy radical.



The subsequent reactions of these hydroxy-haloalkoxy radicals are not totally understood (Tuazon et al., 1988); reaction with O_2, decomposition or Cl atom elimination are possible:





The available data (Edney et al., 1986a,b; Tuazon et al., 1988) show that Cl atom elimination occurs during the OH radical reactions with all of the chloroethenes except for CH_2=CHCl, and this process competes with other decomposition processes of the alkoxy radical. For vinyl chloride, a unit yield of HCHO and HC(O)Cl are observed (Tuazon et al., 1988). For the remaining chloroethenes, the fraction of the overall alkoxy radical proceeding by C-C bond decomposition is approximately as follows: cis-1,2-dichloroethene, ~0.3; trans-1,2-dichloroethene, ~0.35; 1,1-dichloroethene, ~0.7-0.75; trichloroethene, ~0.4; and tetrachloroethene, ~0.25, with the remainder of the overall reactions occurring by O_2 reaction with and/or Cl atom elimination from the alkoxy radicals.

For allyl chloride, the observed products are CH_2ClCHO and HCHO in similar yield (~25%), together with smaller, and similar, amounts of $HOCH_2CHO$ and HC(O)Cl (Winer et al. 1987). Edney et al. (1986a) observed a further variety of products, including $CH_2ClCOCH_2Cl$ which shows that Cl atoms were involved in secondary reactions in their system. Addition of OH radicals to the >C=C< bond is expected to be the major (~98%) initial reaction pathway, leading (in the presence of NO) to the alkoxy radicals $\dot{O}CH_2CHOHCH_2Cl$ and $HO\dot{C}H_2CH(\dot{O})CH_2Cl$. Decomposition of these lead to the products observed by Winer et al. (1987)

$$\dot{O}CH_2\underset{}{\overset{OH}{C}}HCH_2Cl \rightarrow HCHO + CH_2Cl\dot{C}HOH$$

$$CH_2Cl\dot{C}HOH \xrightarrow{O_2} CH_2ClCHO + HO_2$$

and

$$HOCH_2\overset{O^{\cdot}}{C}HCH_2Cl \rightarrow CH_2ClCHO + \dot{C}H_2OH$$

$$\dot{C}H_2OH \xrightarrow{O_2} HCHO + HO_2$$

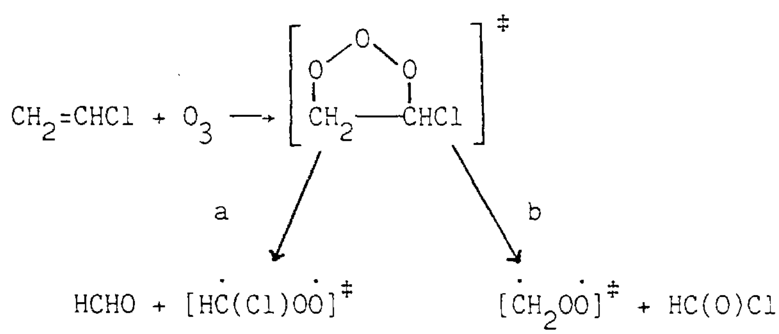
$$\rightarrow HOCH_2CHO + \dot{C}H_2Cl$$

$$\dot{C}H_2Cl \xrightarrow{O_2} HC(O)Cl + HO_2$$

Reaction of the $^{\cdot}OCH_2CHOHCH_2Cl$ radical with O_2 to yield $CH_2ClCHOHCHO$ may occur, accounting, at least in part, for the other product(s) not observed by Winer et al. (1987). Photolysis of HC(O)Cl in the irradiated NO_x-air system employed by Edney et al. (1986a) to produce Cl atoms with subsequent chain reactions involving Cl atoms may explain many of the other products observed by Edney et al. (1986a). The products of the reaction of OH radicals with <u>cis</u>- and <u>trans</u>-1,3-dichloropropenes in the presence of NO were HC(O)Cl and CH_2ClCHO in essentially unit yield, irrespective of the 1,3-dichloropropene isomer. This observation shows that the alkoxy radicals $CH_2ClCHOHCHCl\dot{O}$ and $CH_2ClCH(\dot{O})CHClOH$ must both decompose with essentially unit efficiency, similar to the $\geq C_3$ alkenes.

O_3 Reaction

The kinetics and mechanisms of the gas-phase reactions of O_3 with the haloalkenes have been reviewed and evaluated by Atkinson and Carter (1984), and data have since been reported for allyl chloride [CH_2=$CHCH_2Cl$] (Edney et al., 1986a; Winer et al., 1987). The measured rate constants at room temperature for the reaction of O_3 with atmospherically important haloalkenes are given in Table 21. No temperature dependencies have been measured to date. The reactivities of the haloalkenes with respect to reaction with O_3 are much lower than the analogous alkenes, and these O_3 reactions are of minor or negligible importance as a haloalkenes loss process in the troposphere. As for the alkenes, these reactions proceed by O_3 addition to the >C=C< bond, followed by rapid decomposition of this energy-rich ozonide:



In contrast to the alkene reactions, for which it is generally assumed that $k_a \sim k_b$, Zhang et al. (1983) have determined that $k_a/k_b \sim 3.2$ for the decomposition of the ozonide formed from this reaction of O_3 with vinyl chloride, and that the fraction of the initially energy rich $[\dot{C}H_2O\dot{O}]^{\ddagger}$ biradical which is stabilized at atmospheric pressure is 0.25. This lower fraction of stabilization of the $[\dot{C}H_2O\dot{O}]^{\ddagger}$ biradical formed from vinyl

Table 21. Room Temperature Rate Constants k for the Reactions of O_3 with a Series of Haloalkenes (from Atkinson and Carter, 1984, except as indicated)

Haloalkene	k (cm^3 $molecule^{-1}$ s^{-1})
CH_2=CHCl	2.4×10^{-19}
CH_2=CCl_2	3.7×10^{-21}
cis-CHCl=CHCl	$<5 \times 10^{-21}$
trans-CHCl=CHCl	1.2×10^{-19}
CHCl=CCl_2	$<3 \times 10^{-20}$
CCl_2=CCl_2	$<2 \times 10^{-23}$
CH_2=$CHCH_2Cl$[a]	1.6×10^{-18}
cis-CHCl=$CHCH_2Cl$	1.5×10^{-19}
trans-CHCl=$CHCH_2Cl$	6.7×10^{-19}

[a]From Edney et al. (1986a) and Winer et al. (1987).

chloride than from ethene was rationalized by the fact that $[\dot{C}H_2O\dot{O}]^{\ddagger}$ formed from vinyl chloride is ~10 kcal mol^{-1} more energized than $[\dot{C}H_2O\dot{O}]^{\ddagger}$ formed from ethene.

From a study of the reaction of O_3 with trans-1,2-dichloroethene, Niki et al. (1983a, 1984) have shown that the $[H\dot{C}(Cl)O\dot{O}]^{\ddagger}$ biradical reacts via

$$[H\dot{C}(Cl)O\dot{O}]^{\ddagger} \xrightarrow{M} H\dot{C}(Cl)O\dot{O} \quad (\sim 23\%)$$

$$\rightarrow HC(O)Cl + O(^3P) \quad (\sim 20\%)$$

$$\left.\begin{array}{l}\rightarrow Cl + H + CO_2 \\ \rightarrow Cl + OH + CO \\ \rightarrow \text{other products}\end{array}\right\} \quad (\sim 57\%)$$

Furthermore, it was proposed that the stabilized $H\dot{C}(Cl)O\dot{O}$ radical reacts with water (homogeneously or heterogeneously) to yield peroxyformic acid

$$H\dot{C}(Cl)O\dot{O} + H_2O \rightarrow HC(O)OOH + HCl$$

Peroxyformic acid yields of 0.04, 0.09, 0.23 and 0.10 were observed from the reactions of O_3 with CH_2=CHCl, cis-CHCl=CHCl, trans-CHCl=CHCl and CH_2=CCl_2, respectively (Niki et al., 1982b).

The major products from the reactions of O_3 with cis- and trans-1,3-dichloropropene were determined to be HC(O)Cl (initial yield ~0.7), CH_2ClCHO (yield ~0.4) and CH_2ClCOOH (Tuazon et al., 1984b). These products can be formed by the general schemes shown above for the alkenes and the haloalkenes.

NO_3 Radical Reaction

Rate constants have been determined at room temperature for the reaction of NO_3 radicals with the chloroethenes and allyl chloride (Table 22). These kinetic data indicate that these NO_3 radical reactions will be a minor loss process for the haloalkenes under tropospheric conditions. These reactions are expected to proceed by NO_3 radical addition to the >C=C< bond, totally analogous to the NO_3 radical reactions with the alkenes. Although no product or mechanistic data are available, the subsequent reactions are expected to be analogous to those for the alkenes, with the added complication that Cl atom elimination may occur.

Table 22. Room Temperature Rate Constants k for the Reactions of NO_3 Radicals with Haloalkenes (from Atkinson et al., 1988b)

Haloalkene	10^{16} x k (cm^3 $molecule^{-1}$ s^{-1})
CH_2=CHCl	4.5
CH_2=CCl_2	13
cis-CHCl=CHCl	1.5
trans-CHCl=CHCl	1.1
CHCl=CCl_2	2.9
CCl_2=CCl_2	<0.62
CH_2=$CHCH_2$Cl	5.6

VII. ALKYNES

The potentially important reactions of the alkynes are with OH and NO_3 radicals and O_3. At the present time, for the simpler alkynes kinetic and product data are available for acetylene, propyne, 1-butyne, and 2-butyne.

OH Radical Reaction

The limiting high-pressure second-order rate constants at room temperature are given in Table 23. For acetylene, the rate constant is in the fall-off region between second- and third-order kinetics below ~1000 torr (Schmidt et al., 1985; Wahner and Zetzsch, 1985). At 298 K and 760 torr total pressure of air, Atkinson (1986a) recommended that k(acetylene) = 7.8×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, with an Arrhenius activation energy of 0.46 kcal mol^{-1}. At 298 K, the rate constant for acetylene is given by

$$k = \left(\frac{k_o[M]}{1 + \frac{k_o[M]}{k_\infty}} \right) 0.6^{\left\{1 + [\log_{10} k_o[M]/k_\infty]^2 \right\}^{-1}}$$

with

$$k_o = 4 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

and

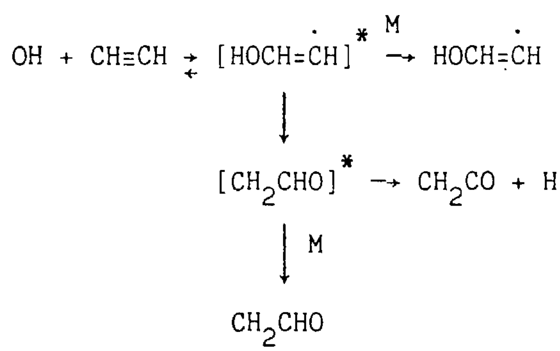
$$k_\infty = 8.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

For the other alkynes studied to date, the rate constants determined at 760 torr total pressure of air are probably the high pressure limiting values.

Table 23. Room Temperature Rate Constants k for the Reaction of OH Radicals with Alkynes at the High-Pressure Limit (from Atkinson, 1986a)

Alkyne	10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})
Acetylene	0.87
Propyne	5.8
1-Butyne	8.0
2-Butyne	29

These reactions proceed by initial OH radical addition to the -C≡C- bond. The OH-acetylene adduct can isomerize to the vinoxy (CH_2CHO) radical with subsequent decomposition or reaction. At low pressures, the formation of ketene has been observed, and this process may explain the observation of a bimolecular reaction with room temperature rate constant of ~$(5 \pm 3) \times 10^{-14}$ cm^3 $molecule^{-1}$ (Schmidt et al., 1985). Thus, the reaction probably proceeds via



For atmospheric purposes any "direct" formation of ketene is of negligible importance [with $\leq$0.5% of ketene being observed from acetylene (Hatakeyama et al., 1986)], with the majority of the reaction proceeding through the formation of a stabilized OH-acetylene adduct. Schmidt et al. (1985) observed the intermediate formation of the vinoxy radical, with glyoxal being a major product. In the presence of O_2, OH radicals were efficiently regenerated (Schmidt et al., 1985),

$$CH_2CHO + O_2 \rightarrow (CHO)_2 + OH$$

Hatakeyama et al. (1986) investigated the products of the reactions of OH and OD radicals with acetylene, propyne and 2-butyne. Glyoxal, methylglyoxal and biacetyl, respectively, were observed products from these reactions in both the absence and presence of NO_x. For acetylene, formic acid was also observed in appreciable (40 ± 10%) yield. The reaction of OH radicals with acetylene thus appears to proceed via (at the high pressure limit),

$$OH + CH{\equiv}CH \rightleftarrows [HOCH{=}\dot{C}H]$$

$$[HOCH{=}\dot{C}H] + M \rightarrow HOCH{=}\dot{C}H + M$$

$$HOCH{=}CH \rightarrow CH_2CHO \xrightarrow{O_2} (CHO)_2 + OH$$

$$HOCH{=}\dot{C}H + O_2 \rightarrow HOCH{=}CHO\dot{O}$$

$$HOCH{=}CHO\dot{O} \rightarrow HCO + HCOOH$$

$$HOCH{=}CHO\dot{O} + NO \rightarrow HO\dot{C}HCHO + NO_2$$

$$\downarrow O_2$$

$$(CHO)_2 + HO_2$$

The amount of reaction leading directly to OH formation, without conversion of NO to NO_2, is uncertain at the present time. The product yields obtained by Hatakeyama et al. (1986) were as follows: from acetylene, HCOOH, 0.4 ± 0.1; (CHO_2), 0.7 ± 0.3; from propyne, HCOOH, 0.12 ± 0.02; CH_3COCHO, 0.53 ± 0.03; and from 2-butyne, CH_3COOH, 0.12 ± 0.01 and $CH_3COCOCH_3$, 0.87 ± 0.07. Other products must thus be formed from propyne.

O_3 Reactions

Kinetic data have been determined for the reactions of O_3 with acetylene, propyne, 1-butyne, 2-butyne and butadiyne (Atkinson and Carter, 1984). There are significant discrepancies between the various studies, and no recommendations were made by Atkinson and Carter (1984). The most recent data of Atkinson and Aschmann (1984) give rate constants at 294 ± 2 K of (in cm^3 $molecule^{-1}$ s^{-1} units): acetylene, 7.8 x 10^{-21}; propyne, 1.4 x 10^{-20}, and 1-butyne, 2.0 x 10^{-20}. These rate constants are sufficiently low that the O_3 reactions are of negligible importance as an alkyne loss process. No definitive product data are available, although α-dicarbonyls have been observed from the reaction of O_3 with acetylene, propyne, 1-butyne and 2-butyne (DeMore, 1971).

NO_3 Radical Reactions

Rate constants, or upper limits to the rate constants, have been determined at room temperature for the reaction of NO_3 radicals with acetylene and propyne (Atkinson et al., 1988b). Based upon a rate constant for the reaction of NO_3 radicals with ethene of 2.14 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 1988b), rate constants (in cm^3 $molecule^{-1}$ s^{-1} units) of $\leq$3.5 x 10^{-17} and 1.8 x 10^{-16} are obtained for acetylene and propyne, respectively, at 296 ± 2 K. These relative rate data are in reasonable agreement with the absolute rate constants at 295 ± 2 K of (5.1 ± 3.5) x 10^{-17} cm^3 $molecule^{-1}$ s^{-1} and (2.66 ± 0.32) x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} for acetylene and propyne, respectively, reported by Canosa-Mas et al. (1986). These reactions are sufficiently slow that they can be neglected for atmospheric purposes.

VIII. OXYGEN-CONTAINING ORGANIC COMPOUNDS

In this section, the atmospheric chemistry of those oxygen-containing organic compounds which are either emitted into the troposphere directly or are formed in the atmosphere as degradation products of other organics is dealt with. The atmospheric chemistry of the simple aliphatic aldehydes, ketones and α-dicarbonyls has been discussed above in Section II.

A. Alcohols

The alcohols of interest in urban atmospheres are primarily methanol, ethanol and, to a lesser extent, the C_3 and C_4 species. The gas-phase reactions with the NO_3 radical are slow (Wallington et al., 1987a), with upper limits to the room temperature rate constants of $<6 \times 10^{-16}$, $<9 \times 10^{-16}$ and $<2.3 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} for methanol, ethanol and 2-propanol, respectively. While no kinetic data are available for the gas-phase reactions of O_3 with the alcohols (Atkinson and Carter, 1984), the reactions are expected to be of negligible importance as an atmospheric loss process. Thus the only loss process which requires consideration is that by reaction with the OH radical. The room temperature rate constants and temperature dependencies for the OH radical reactions with the alcohols are given in Table 24.

These OH radical reactions proceed by H-atom abstraction from both the C-H and O-H bonds. For methanol, the rate constant ratio $k_a/(k_a + k_b)$, where k_a and k_b are the rate constants for the reactions,

Table 24. Room Temperature Rate Constants k and Arrhenius Parameters ($k = Ae^{-E/RT}$) for the Gas-Phase Reactions of the OH Radical with a Series of Alcohols, Ethers, Carboxylic Acids, Esters, Epoxides, Hydroperoxides, α,β-Unsaturated Carbonyls and 1,4-Unsaturated Dicarbonyls

Organic	10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})	10^{12} x A (cm^3 $molecule^{-1}$ s^{-1})	E/R(K)
Methanol[a]	0.90	9.1	690
Ethanol[a]	3.4	9.3	300
1-Propanol[a]	5.3		
2-Propanol[a]	5.6	5.6	0
1-Butanol[b]	8.3		
Dimethyl ether[c]	3.0	10.4	372
Diethyl ether[c]	13		
Methyl t-butyl ether[d]	3.1	5.1	155
Formic acid[a]	0.48	0.48	0
Acetic acid[a]	0.74	1.3	170
Methyl formate[e]	0.23		
Methyl acetate[e]	0.34	0.83	260
Ethyl acetate[e]	1.5	2.3	131
n-Propyl acetate[e]	3.5		
Ethene oxide[c]	0.081	11	1460
Propene oxide[c]	0.52		
Methyl hydroperoxide[c]	11		
t-Butyl hydroperoxide[c]	3.0		

(continued)

Table 24 (continued) - 2

Organic	10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})	10^{12} x A (cm^3 $molecule^{-1}$ s^{-1})	E/R(K)
Acrolein[c]	20		
Methacrolein[c]	31	20	-134
Crotonaldehyde[c]	36		
Methyl vinyl ketone[c]	19	3.3	-514
<u>cis</u>-3-Hexene-2,5-dione	63		
<u>trans</u>-3-Hexene-2,5-dione	53		

[a]Atkinson et al. (1988a).
[b]Wallington and Kurylo (1987b).
[c]Atkinson (1986a).
[d]Wallington et al. (1988a).
[e]Wallington et al. (1988b).

$$OH + CH_3OH \rightarrow H_2O + CH_3O \quad (a)$$

$$OH + CH_3OH \rightarrow H_2O + CH_2OH \quad (b)$$

have been determined to be 0.10-0.15 at 298 K (Atkinson, 1986a and references therein). For ethanol, Meier et al. (1985) have shown that the initial OH radical reaction forms CH_3CHOH 75 ± 15% of the overall reaction pathway at room temperature. The estimation technique of Atkinson (1986a,b) allows the distribution of initially formed radicals to be approximately determined for the higher alcohols, and the subsequent reactions of these radicals are then as discussed in Section I above.

B. Ethers

The ethers of main interest are dimethyl ether, diethyl ether, and methyl *tert*-butyl ether. The reactions of the aliphatic saturated ethers with O_3 and NO_3 radicals are expected to be of negligible importance as atmospheric loss processes [with an upper limit to the rate constant for the reaction of NO_3 radicals with CH_3OCH_3 of $<3 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K being the only available data (Wallington et al., 1986a)]. Hence the major, if not sole, atmospheric loss process will be by reaction with the OH radical. The available kinetic data for these reactions are given in Table 24. The expected reaction schemes (based upon the calculated values of ΔH_{decomp} and the discussion of Section I) for dimethyl ether and methyl *tert*-butyl ether in the presence of NO are as follows (neglecting the possibility of small amounts of nitrate formation from methyl *tert*-butyl ether):

Dimethyl ether:

$$OH + CH_3OCH_3 \rightarrow H_2O + CH_3O\dot{C}H_2$$

$$\downarrow O_2$$

$$CH_3OCH_2O\dot{O}$$

$$\downarrow NO \rightarrow NO_2$$

$$CH_3OCH_2\dot{O}$$

$$\downarrow O_2$$

$$CH_3OCHO + HO_2$$

Methyl t-butyl ether

$$OH + CH_3OC(CH_3)_3 \rightarrow H_2O + \dot{C}H_2OC(CH_3)_3$$

$$\rightarrow H_2O + CH_3OC(CH_3)_2\dot{C}H_2$$

followed by:

$$(CH_3)_3CO\dot{C}H_2 \xrightarrow[NO_2]{O_2,\ NO} (CH_3)_3COCH_2\dot{O}$$

$$\downarrow O_2$$

$$(CH_3)_3COCHO + HO_2$$

$$CH_3OC(CH_3)_2\dot{C}H_2 \xrightarrow[\downarrow NO_2]{O_2,\ NO} CH_3OC(CH_3)_2CH_2\dot{O}$$

$$CH_3OC(CH_3)_2CH_2\dot{O} \xrightarrow{O_2} CH_3OC(CH_3)_2CHO + HO_2$$

C. Carboxylic Acids

The carboxylic acids of interest in polluted urban atmospheres are formic and acetic acid. Again, although no data have been reported for the NO_3 radical or O_3 reactions, the only important gas-phase atmospheric removal process is expected to be by OH radical reaction. The OH radical rate constants are given in Table 24. For HCOOH, the OH radical reaction proceeds to form mainly CO_2 and an H-atom, although the reaction dynamics are not yet known. No product data are available for the OH radical reaction with CH_3COOH. Since these OH radical reactions are slow, with calculated atmospheric lifetimes due to OH radical reaction of approximately 50 days, the major process removing these compounds from the gas phase will be by wet or dry deposition, with incorporation into raindrops or cloud and fog water being of importance from the viewpoint of acid deposition.

D. Esters

Analogous to the alcohols, ethers and carboxylic acids, the only important gas-phase atmospheric loss process for the simple esters is expected to be by OH radical reaction, and rate constants are given in Table 24 for the esters for which data are available. These data show that the reaction proceeds by H atom abstraction from the -OR group, for example

$$OH + CH_3C(O)OCH_3 \rightarrow H_2O + CH_3C(O)OCH_2$$

No product data for this class of organic compounds are available, but the subsequent reactions of the initially formed radicals are expected to be as discussed in Section II. For example, for the radical formed from methyl acetate, in the presence of NO:

$$CH_3C(O)O\dot{C}H_2 + O_2 \rightarrow CH_3C(O)OCH_2OO\cdot$$

$$\downarrow NO \rightarrow NO_2$$

$$CH_3C(O)OCH_2\dot{O} \xrightarrow{O_2} CH_3C(O)OCHO + HO_2$$

$$\downarrow$$

$$HCHO + CH_3CO_2$$

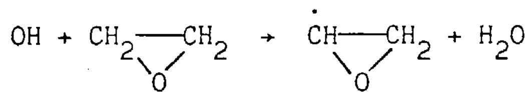
$$\downarrow$$

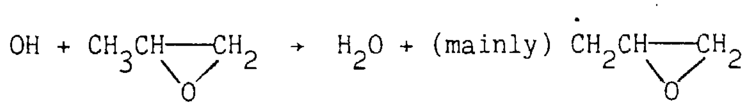
$$CH_3 + CO_2$$

with the relative importance of O_2 reaction versus decomposition of the alkoxy radical being uncertain at the present time.

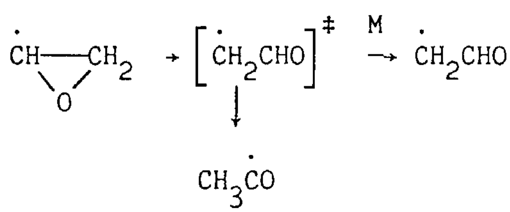
E. <u>Epoxides</u>

The major epoxides of interest are ethene oxide and propene oxide. Again, OH radical reaction is expected to be the dominant atmospheric removal process, and the rate constants for these reactions are given in Table 24 for those epoxides for which data are available. This OH radical reaction will proceed by initial H atom abstraction





Only for ethene oxide has a product study been carried out. For the higher epoxides, the distribution of initially formed radicals can be estimated using the technique of Atkinson (1986b) with, as shown, propene oxide being calculated to yield mainly the $\dot{C}H_2\overset{O}{C}HCH_2$ radical. Presumably due to the large amount of ring strain, the initially formed radical (if the radical center is a part of the 3-membered ring system) may rapidly undergo ring cleavage, for example:



Lorenz and Zellner (1984) have observed the vinoxy (CH_2CHO) radical in appreciable (0.23 at 298 K and 60 torr total pressure of helium) yield from the OH radical reaction with ethene oxide. No product data are available for the higher epoxides.

F. Hydroperoxides

To date, data concerning the atmospheric chemistry of the hydroperoxides are only available for methyl hydroperoxide (CH_3OOH) and *tert*-butyl hydroperoxide [$(CH_3)_3OOH$]. The expected gas-phase atmospheric loss processes for this class of organic compounds are by photolysis and OH radical reaction. The absorption cross section of CH_3OOH has been evaluated by NASA (DeMore et al., 1987), and the quantum yield is expected to be unity.

$$CH_3OOH + h\nu \rightarrow CH_3O + OH$$

The available room temperature rate constants for the OH radical reactions of CH_3OOH and $(CH_3)_3COOH$ are given in Table 24. For CH_3OOH, the study of Niki et al. (1983b) shows that the OH radical reaction proceeds by two pathways

$$OH + CH_3OOH \rightarrow H_2O + CH_2OOH \qquad (a)$$

$$OH + CH_3OOH \rightarrow H_2O + CH_3OO \qquad (b)$$

with $k_a/(k_a + k_b) = 0.4$ at 298 K. The CH_2OOH radical is expected to rapidly decompose

$$CH_2OOH \rightarrow HCHO + OH$$

to regenerate the OH radical directly.

G. α,β-Unsaturated Carbonyls

The α,β-Unsaturated carbonyls of major interest are acrolein, methacrolein and methyl vinyl ketone, these being formed from the atmospheric degradation reactions of 1,3-butadiene (acrolein) and 2-methyl-1,3-butadiene [isoprene] (methacrolein and methyl vinyl ketone). The major atmospheric removal processes for this class of organic compounds are expected to be reaction with O_3 and with OH and NO_3 radicals. As shown by the recent data for acrolein (Gardner et al., 1987), photolysis appears to be of minor importance as a loss process [with a lifetime of acrolein of ~10 days at 40° zenith angle (Gardner et al., 1987)].

The kinetics of the gas-phase reactions of the NO_3 radical with acrolein and crotonaldehyde have been determined (Atkinson et al., 1988b), and the rate constants at 296 ± 2 K are 1.2×10^{-15} and 5.1×10^{-15} cm^3 $molecule^{-1}$ s^{-1}, respectively. These reactions are expected to be analogous to the OH radical reactions (see below) in that the NO_3 radical reaction with acrolein is expected to proceed mainly by H-atom abstraction from the -CHO group:

$$NO_3 + CH_2{=}CHCHO \rightarrow HNO_3 + CH_2{=}CH\dot{C}O$$

while the reaction with crotonaldehyde will proceed by H-atom abstraction from the -CHO group and NO_3 radical addition to the >C=C< bond

$$NO_3 + CH_3CH{=}CHCHO \rightarrow HNO_3 + CH_3CH{=}CH\dot{C}O$$

$$\rightarrow CH_3CH(ONO_2)\dot{C}HCHO \text{ and }$$

$$CH_3\dot{C}HCH(ONO_2)CHO$$

These NO_3 radical reactions will be of generally minor significance as atmospheric loss processes of the α,β-unsaturated carbonyls. The room temperature rate constants for the gas-phase reactions of O_3 with acrolein, methacrolein, crotonaldehyde and methyl vinyl ketone have been measured (Atkinson and Carter, 1984) with rate constants of (in units of 10^{-18} cm^3 $molecule^{-1}$ s^{-1}) 0.28, 1.1, 0.9 and 4.8, respectively. As for the alkenes and haloalkenes, these O_3 reactions proceed by initial addition to the >C=C< bonds. Again, these O_3 reactions are of minor importance as atmospheric loss processes.

The major atmospheric loss process of the α,β-unsaturated carbonyls is with the OH radical, and the room temperature rate constants and Arrhenius parameters for this reaction for acrolein, methacrolein, crotonaldehyde and methyl vinyl ketone are given in Table 24. For the aldehydes, these OH radical reactions occur by H-atom abstraction from the -CHO group and OH radical addition to the >C=C< bond:

$$OH + CH_2{=}CHCHO \rightarrow H_2O + CH_2{=}CH\dot{C}O \quad (a)$$

$$\rightarrow HOCH_2\dot{C}HCHO \text{ and } \dot{C}H_2CHOHCHO \quad (b)$$

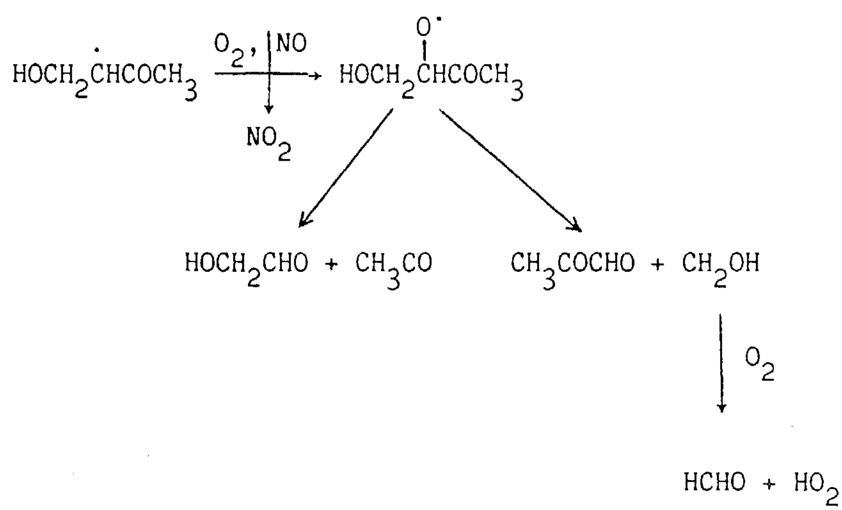
For acrolein the major reaction pathway appears to be H-atom abstraction from the -CHO group, while for crotonaldehyde and methacrolein both reaction pathways occur (Atkinson, 1986a). The subsequent reactions of the initially formed radicals will be as discussed in Section I.

For the α,β-unsaturated ketones such as methyl vinyl ketone the only reaction pathway (since H-atom abstraction from the substituent alkyl groups will be slow) involves OH radical addition to the >C=C< bond:

$$OH + CH_2{=}CHCOCH_3 \rightarrow HOCH_2\dot{C}HCOCH_3$$

$$\rightarrow \dot{C}H_2CHOHCOCH_3$$

The subsequent reactions of these radicals are as dealt with in Section I; i.e., in the presence of NO



Formation of $HOCH_2CHO + CH_3CO$ is calculated (Benson, 1976) to be ~10 kcal mol^{-1} more exothermic than the formation of $CH_3COCHO + CH_2OH$, and this is in accord with the product data of Tuazon et al. (unpublished data, 1988).

H. 1,4-Unsaturated Carbonyls

The 1,4-unsaturated carbonyl compounds have been postulated to be formed in the atmospheric degradation of the aromatic hydrocarbons (see, for example, Atkinson and Lloyd, 1984), and 3-hexene-2,5-dione ($CH_3COCH=CHCOCH_3$) has been observed in small yield from the photooxidation of 1,2,4-trimethylbenzene (Takagi et al., 1982) and, in larger yield, from p-xylene (Becker and Klein, 1987). Experimental data are only available for the atmospherically important reactions of cis- and trans-3-hexene-2,5-dione (Tuazon et al., 1985; Becker and Klein, 1987). These isomers were observed to react with O_3, with rate constants at 298 ± 2 K of 1.8 x 10^{-18} and 8.3 x 10^{-18} cm^3 $molecule^{-1}$ s^{-1} for cis- and trans-3-hexene-2,5-dione, respectively (Tuazon et al., 1985). The measured OH radical reaction rate constants are given in Table 24. Photolysis of both isomers was also observed, with the major pathway in the spectral region employed (>320 nm) being photoisomerization to the other isomer (Tuazon et al., 1985; Becker and Klein, 1987). Based upon these data, it appears that photolysis (other than photoisomerization) and reaction with the OH radical will be the dominant atmospheric removal processes.

Unfortunately, no definitive product data have been obtained for the OH radical reactions with these 1,4-unsaturated carbonyls, although a speculative discussion of the likely reactions of this class of organic compounds and their rates and mechanisms has been given by Atkinson and Lloyd (1984). However, until it can be determined whether or not these compounds are indeed formed to any significant extent from the degradation of aromatic hydrocarbons or other organic emissions, speculation about the atmospheric reactions of these chemicals is not warranted.

IX. SULFUR-CONTAINING ORGANIC COMPOUNDS

The organosulfur compounds which need to be considered are methyl mercaptan (CH_3SH), dimethyl sulfide (CH_3SCH_3) and dimethyl disulfide (CH_3SSCH_3). The atmospherically important reactions of these organosulfur species have been evaluated by the IUPAC data panel (Atkinson et al., 1988a), and the recommendations of that evaluation are used here. The potentially significant atmospheric loss processes for these chemicals are by reaction with OH and NO_3 radicals and with O_3. Photolysis (Calvert and Pitts, 1966) is expected to be of negligible importance due to the high reactivity of these compounds toward the OH radical. Only for dimethyl sulfide has the kinetics of the O_3 reaction been studied, with an upper limit for this reaction of 8.3×10^{-19} cm^3 $molecule^{-1}$ s^{-1} at room temperature (Atkinson and Carter, 1984). Atkinson and Carter (1984) recommend that the gas-phase reactions of O_3 with these organosulfur compounds be considered to be unimportant as an atmospheric loss process, and thus only the OH and NO_3 radical reactions need to be dealt with.

OH Radical Reactions

The room temperature rate constants and Arrhenius parameters for the OH radical reactions with CH_3SH, CH_3SCH_3 and CH_3SSCH_3 are given in Table 25. For CH_3SH (and CD_3SH), no effect of either total pressure or of the presence of O_2 on the rate constant has been observed (Hynes and Wine, 1987), and a simple Arrhenius expression is sufficient. The lack of a kinetic isotope effect (Atkinson, 1986a; Hynes and Wine, 1987) and the product data of Hatakeyama and Akimoto (1983) show that this OH radical reaction with CH_3SH proceeds by initial addition of the OH radical to the S atom, followed by reactions to yield SO_2, CH_3SO_3H (methanesulfonic acid)

Table 25. Room Temperature Rate Constants k and Arrhenius Parameters ($k = Ae^{-E/RT}$) for the Gas-Phase Reactions of the OH Radical with Selected Organosulfur Compounds (from Atkinson et al., 1988a, except as indicated)

Organic	$10^{12} \times k$ (cm^3 $molecule^{-1}$ s^{-1})	$10^{12} \times A$ (cm^3 $molecule^{-1}$ s^{-1})	E/R(K)
CH_3SH	33	9.9	-356
CH_3SCH_3	$4.4 + \frac{(4.1 \times 10^{-17}[O_2])}{(1 + 4.1 \times 10^{-20}[O_2]}$	a	a
CH_3SSCH_3[b]	205	51	-414

[a]See text.
[b]From Atkinson (1986a).

and HCHO. Hatakeyama and Akimoto (1983) suggested that the initial adduct decomposes to CH_3S and H_2O, followed by reactions of CH_3S radicals.

$$OH + CH_3SH \rightarrow CH_3\dot{S}(OH)H \rightarrow CH_3S + H_2O$$

In the presence of alkyl nitrites (used to generate OH radicals in the experimental system used), Hatakeyama and Akimoto (1983) observed the formation of CH_3SNO, with the N atom coming from the alkyl nitrite (and not from NO), with subsequent photolysis of CH_3SNO giving rise to CH_3S radicals and hence to the observed products. The formation of CH_3SNO was attributed to the reaction of the $CH_3S(OH)H$ adduct with the alkyl nitrite

$$CH_3S(OH)H + RONO \rightarrow CH_3SNO + RCH_2OH + OH$$

For CH_3SSCH_3, the OH radical reaction also appears to proceed by OH radical addition (Hatakeyama and Akimoto, 1983; Atkinson, 1986a), leading to the production of CH_3S and CH_3SOH radicals, the subsequent reactions of which lead to the SO_2, HCHO and CH_3SO_3H products.

$$OH + CH_3SSCH_3 \rightarrow [CH_3SS(OH)CH_3] \rightarrow CH_3S + CH_3SOH$$

In contrast, for CH_3SCH_3 the OH radical reaction proceeds by two pathways; H atom abstraction from the C-H bonds and OH radical addition to the S atom

$$OH + CH_3SCH_3 \rightarrow H_2O + CH_3S\dot{C}H_2 \qquad (a)$$

$$\rightarrow CH_3S(OH)CH_3 \qquad (b)$$

The recent kinetic data of Hynes et al. (1986) [which were, in a preliminary form, incorporated and discussed in the review of Atkinson (1986a)] show that in the absence of O_2 the OH-CH_3SCH_3 adduct rapidly back-decomposes to the reactants. Thus, in the absence of O_2 the only reaction pathway observed is the H atom abstraction route, with a rate constant of (Atkinson et al., 1988a)

$$k_a = 9.6 \times 10^{-12} e^{-234/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$= 4.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}.$$

In the presence of O_2, the OH-CH_3SCH_3 adduct reacts

$$CH_3S(OH)CH_3 + O_2 \rightarrow \text{products}$$

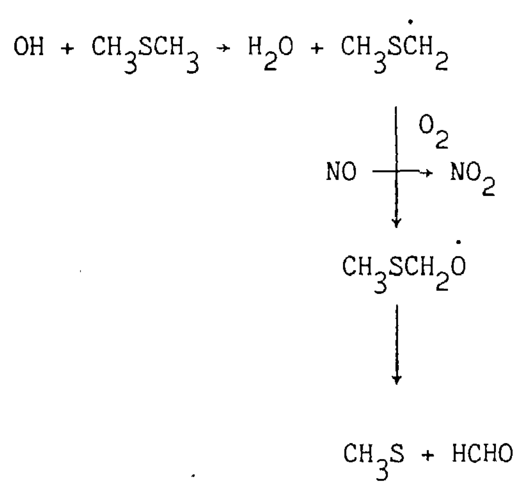
Thus, the observed rate constant for the OH radical addition pathway is dependent on the O_2 concentration, and based upon the kinetic data of Hynes et al. (1986), Atkinson et al. (1988a) recommend that

$$k_b = \frac{1.7 \times 10^{-42}\ e^{7810/T}\ [O_2]}{(1 + 5.5 \times 10^{-31}\ e^{7460/T}\ [O_2])}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range ~260-360 K. Hence, at 298 K and atmospheric pressure (760 torr) of air,

$$k(OH + CH_3SCH_3) = k_a + k_b = 6.2 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

The H-atom abstraction pathway is expected to proceed by the reactions



followed by reactions of the CH_3S radical (discussed below). However, the reactions subsequent to the formation of the $CH_3S(OH)CH_3$ radical, in the presence of O_2, are not known at present. Furthermore, the complexities of the experimental systems used to investigate the products of the OH-CH_3SCH_3 reaction under simulated atmospheric conditions [involving secondary reactions leading to enhanced loss processes of CH_3SCH_3 not involving OH radicals (Atkinson, 1986a; Wallington et al., 1986b)] do not allow the products of the OH radical reactions to be quantitatively determined.

NO_3 Radical Reactions

The kinetics of the gas-phase reactions of the NO_3 radical with several organosulfur species have recently been measured, and the rate constants recommended by Atkinson et al. (1988a) are given in Table 26 for CH_3SH, CH_3SCH_3 and CH_3SSCH_3. No definitive product or mechanistic data are available, but is appears that these reactions proceed by initial NO_3 radical addition, probably followed by rapid decomposition to, among other products, CH_3S radicals (Mac Leod et al., 1986). Speculative, and incomplete, reaction sequences have been presented by Mac Leod et al. (1986), and that reference should be consulted (although it must be recognized that much more work is necessary before any realistic reaction schemes can be proposed for use in urban airshed chemical mechanisms).

Reactions of the CH_3S Radical

The CH_3S radical is becoming recognized as a key intermediate in the atmospheric degradation reactions of organosulfur compounds, leading to the formation of SO_2, CH_3SO_3H and HCHO, and the atmospheric reactions of CH_3S thus need to be understood. To date, rate constants for the reactions of the CH_3S radical with NO, NO_2, O_2 and O_3 have been reported (Balla et al., 1986; Black and Jusinski, 1986). The reaction with NO is an addition reaction

$$CH_3S + NO \rightarrow CH_3SNO$$

and the rate constant is in the fall-off regime between second- and third-order kinetics below atmospheric pressure for $M = N_2$ (Balla et al.,

Table 26. Room Temperature Rate Constants k and Arrhenius Parameters ($k = Ae^{-E/RT}$) for the Gas-Phase Reactions of the NO_3 Radical with Selected Organosulfur Compounds (from Atkinson et al., 1988a)

Organic	10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})	10^{12} x A (cm^3 $molecule^{-1}$ s^{-1})	E/R(K)
CH_3SH	1.0	1.0	0
CH_3SCH_3	1.0	0.19	-500
CH_3SSCH_3	0.7	0.7	0

1986). At 295 K, Balla et al. (1986) fit their data for $M = N_2$ to the Troe expression

$$k = \left(\frac{k_o[M]}{1 + \frac{k_o[M]}{k_\infty}} \right) F^{\left\{1 + [\log (k_o[M]/k_\infty)]^2 \right\}^{-1}}$$

with

$k_o = 3.3 \times 10^{-29}$ cm^6 molecule^{-2} s^{-1},

$k_\infty = 3.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}

and

$F = 0.60.$

At the high pressure limit (determined using SF_6 as the diluent gas),

$$k(CH_3S + NO) = 1.81 \times 10^{-12} e^{906/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The reaction of CH_3S radicals with NO_2 exhibits bimolecular kinetics with no marked pressure dependence, and the rate constant determined by Balla et al. (1986) is

$$k(CH_3S + NO_2) = 8.3 \times 10^{-11} e^{81/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$= 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

It is possible that this reaction forms $CH_3SO + NO$. The reaction of CH_3S radicals with O_2 is slow, with an upper limit to the rate constant of <2 x 10^{-17} cm^3 molecule^{-1} s^{-1} at room temperature (Balla et al., 1986). Black and Jusinski (1986) have reported, using a somewhat complex chemical system, an upper limit to the reaction of CH_3S radicals with O_3 of <8 x 10^{-14} cm^3 $molecule^{-1}$ s^{-1} at room temperature.

Although further kinetic and product data are clearly required for these reactions of the CH_3S radical, it appears that the major reaction in the polluted atmosphere will be with NO_2 [since the CH_3SNO formed from the NO reaction will rapidly photodissociate back to CH_3S + NO (Niki et al., 1983c) during daylight]. The situation is less clear for the "clean" troposphere until further, more definitive, rate data become available for the reaction of CH_3S radicals with O_2.

X. NITROGEN-CONTAINING ORGANIC COMPOUNDS

The nitrogen-containing organic compounds considered in this section are the simple aliphatic amines (and related alcohol amines), the alkyl nitrates expected to be formed in the atmosphere from the alkanes (see Section III), and peroxyacyl and peroxyalkyl nitrates. These are dealt with below.

Aliphatic Amines

The expected atmospheric loss processes for these compounds are by gas-phase reaction with nitric acid (HNO_3), OH and NO_3 radicals and O_3. The amines will react with gaseous HNO_3, in a manner similar to NH_3, to form their nitrate salts

$$RNH_2 + HNO_3 \rightarrow RNH_3^+ NO_3^-$$

although no rate data are currently available. Similarly, although it is expected that NO_3 radicals may react rapidly with the amines, no experimental data are available due to difficulties in studying these reactions in the absence of HNO_3.

The gas-phase reactions of the simple aliphatic amines with O_3 have been studied (Atkinson and Carter, 1984), and the measured room temperature rate constants range from 2×10^{-20} cm^3 $molecule^{-1}$ s^{-1} for methylamine to 1.0×10^{-17} cm^3 $molecule^{-1}$ s^{-1} for trimethylamine (although these rate constants must be viewed as upper limits because of the possibility if secondary reactions consuming the reactants). Due to the high rate constants for the OH radical reactions (see below), these O_3 reactions are calculated to be of minor significance under atmospheric conditions.

The rate constants for the OH radical reactions with the amines and alcohol amines are given in Table 27. While the reaction products are those corresponding to H atom abstraction, these reactions with the amines probably occur by initial OH radical addition to the N atom, followed by rapid decomposition of this adduct to products. For the reaction of OH radicals with $(CH_3)_2NH$, Lindley et al. (1979) determined the rate constant ratio $k_a/(k_a + k_b) = 0.37 \pm 0.05$ at room temperature, where k_a and k_b are the rate constants for the reaction pathways (a) and (b), respectively.

$$OH + (CH_3)_2NH \rightarrow H_2O + (CH_3)_2\dot{N} \qquad (a)$$

$$OH + (CH_3)_2NH \rightarrow H_2O + CH_3NH\dot{C}H_2 \qquad (b)$$

From these data and the kinetics of these reactions, it appears that for methylamine and ethylamine the OH radical reactions proceed by H atom abstraction from the N-H bonds, for dimethylamine H atom abstraction

Table 27. Room Temperature Rate Constants k and Arrhenius Parameters ($k = Ae^{-E/RT}$) for the Gas-Phase Reactions of the OH Radical with Selected Nitrogen-Containing Compounds [from Atkinson (1986a) except as indicated]

Organic	$10^{12} \times k$ (cm^3 $molecule^{-1}$ s^{-1})	$10^{12} \times A$ (cm^3 $molecule^{-1}$ s^{-1})	E/R(K)
Methylamine	22	10	-229
Ethylamine	28	15	-189
Dimethylamine	65	29	-247
Triethylamine	61	26	-252
2-Dimethylaminoethanol	80	80	0
2-Amino-2-methyl-1-propanol	28		
N-Nitrosodimethylamine	2.5		
Dimethylnitramine	3.8		
Methyl nitrate[a]	0.034		
Ethyl nitrate[b]	0.49		
1-Propyl nitrate[b]	0.49		
2-Propyl nitrate	0.18		
1-Butyl nitrate	1.4		
2-Butyl nitrate	0.67		
2-Pentyl nitrate	1.8		
3-Pentyl nitrate	1.1		
2-Methyl-3-butyl nitrate	1.7		
2,2-Dimethyl-1-propyl nitrate	0.85		
2-Hexyl nitrate	3.1		

(continued)

Table 27 (continued) - 2

Organic	10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})	10^{12} x A (cm^3 $molecule^{-1}$ s^{-1})	E/R(K)
3-Hexyl nitrate	2.7		
Cyclohexyl nitrate	3.3		
2-Methyl-2-pentyl nitrate	1.7		
3-Methyl-2-pentyl nitrate	3.0		
3-Heptyl nitrate	3.6		
3-Octyl nitrate	3.8		
Peroxyacetyl nitrate	0.14	1.2	650

[a]Gaffney et al. (1986).
[b]Kerr and Stocker (1986).

occurs from both the N-H and C-H bonds, and for trimethylamine the reaction proceeds by H atom abstraction from the C-H bonds. Atkinson (1986b) has formulated an estimation technique for the calculation of OH radical reaction rate constants (and the positions at which reaction occurs) for these related compounds.

The subsequent reactions are not totally understood at present, but Lindley et al. (1979) showed that for the reactions of the dimethylamino radical with O_2, NO and NO_2,

$$\left.\begin{aligned}(CH_3)_2N + O_2 &\xrightarrow{M} (CH_3)_2NOO \\ &\rightarrow CH_3N{=}CH_2 + HO_2\end{aligned}\right\} \quad \text{(a)}$$

$$(CH_3)_2N + NO \xrightarrow{M} (CH_3)_2NNO \quad \text{(b)}$$

(N-nitrosodimethylamine)

$$(CH_3)_2N + NO_2 \xrightarrow{M} (CH_3)_2NNO_2 \quad \text{(c)}$$

(dimethylnitramine)

$$\rightarrow CH_3N{=}CH_2 + HONO \quad \text{(d)}$$

$k_d/k_c = 0.22$, $k_a/k_c = 3.9 \times 10^{-7}$ and $k_a/k_b = 1.5 \times 10^{-7}$ at room temperature.

Thus, under polluted urban atmospheric conditions the major reaction of the dimethylamino radical will be with NO and/or NO_2. For the $CH_3NH\dot{C}H_2$ radical also formed from dimethylamine, Lindley et al. (1979) showed that reaction with O_2 occurs via

$$CH_3NHCH_2 + O_2 \rightarrow HO_2 + CH_3N{=}CH_2$$

The atmospheric reactions of N-nitrosodimethylamine and dimethylnitramine have been studied by Tuazon et al. (1983). The reactions of O_3 with these compounds are slow, with measured upper limits of $<1 \times 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1} for N-nitrosodimethylamine and $<3 \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1} for dimethylnitramine at 296 K. The room temperature rate constants for the OH radical reactions are given in Table 27, with the reactions being expected to proceed by H atom abstraction from the C-H bonds. For N-nitrosodimethylamine photolysis also occurs

$$(CH_3)_2NNO + h\nu \rightarrow (CH_3)_2N + NO$$

with a lifetime of approximately 5 min at 0^o zenith angle (Tuazon et al., 1983). Thus, the major atmospheric loss process for dimethylnitramine will be by OH radical reaction, while that for N-nitrosodimethylamine will be photolysis back to its precursors.

Alkyl Nitrates

Based upon laboratory studies concerning the formation of alkyl nitrates from the NO_x-air photooxidations of the alkanes, the major alkyl nitrates expected to be formed in the atmosphere are 2-propyl nitrate, 2-butyl nitrate, 2- and 3-pentyl nitrate, and 2- and 3-hexyl nitrate. Although no experimental data are available concerning the kinetics of the NO_3 radical or O_3 reactions, these are expected to be of no significance as atmospheric loss processes. The major loss processes are then reaction with the OH radical and photolysis. The room temperature OH radical reaction rate constants are given in Table 27 (no temperature dependent data are available). These reactions proceed by H atom abstraction from the C-H bonds, and in the absence of product data the estimation technique of Atkinson (1987) can be used to calculate the distribution of the nitratoalkyl radicals formed in these reactions. For example

$$OH + CH_3CH_2CH_2CH(ONO_2)CH_3 \rightarrow H_2O + \dot{C}H_2CH_2CH_2CH(ONO_2)CH_3 \qquad (11\%)$$

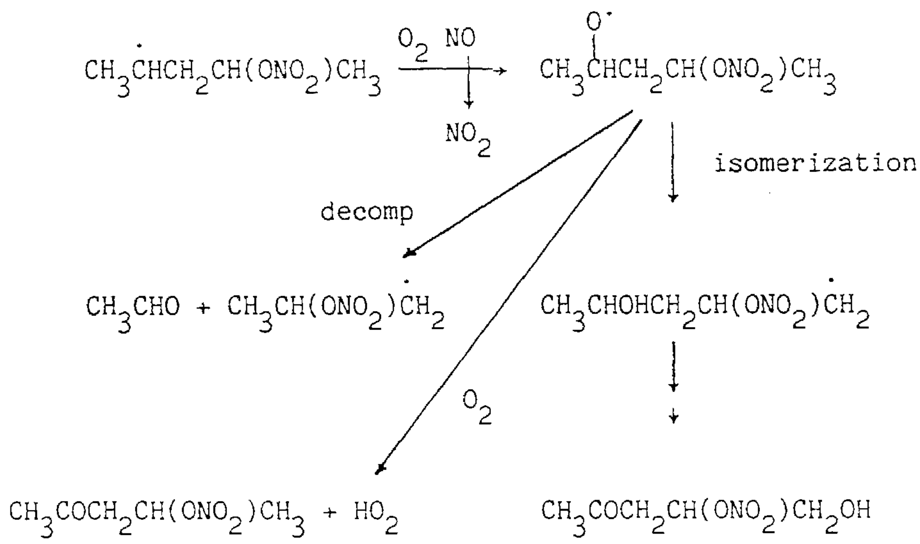
$$\rightarrow H_2O + CH_3\dot{C}HCH_2CH(ONO_2)CH_3 \qquad (61\%)$$

$$\rightarrow H_2O + CH_3CH_2\dot{C}HCH(ONO_2)CH_3 \qquad (13\%)$$

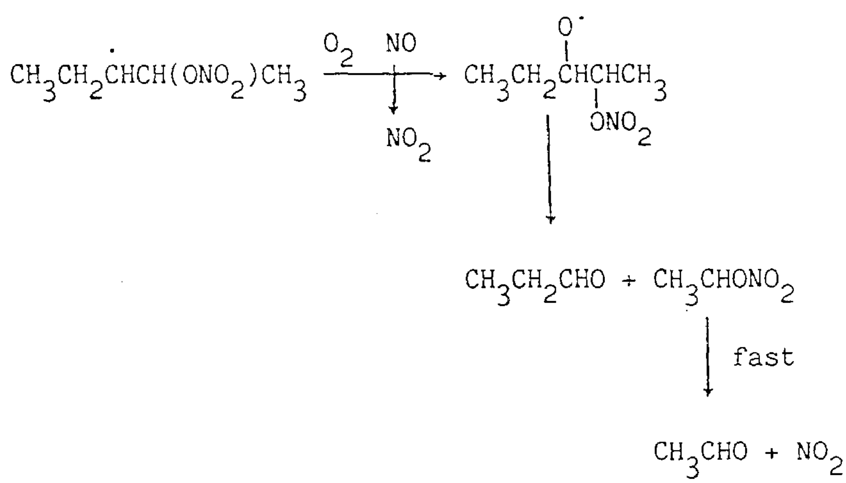
$$\rightarrow H_2O + CH_3CH_2CH_2\dot{C}(ONO)_2CH_3 \qquad (13\%)$$

$$\rightarrow H_2O + CH_3CH_2CH_2CH(ONO_2)\dot{C}H_2 \qquad (2\%)$$

The expected subsequent reactions of these radicals are, in the presence of NO_x, for example



with isomerization being expected to dominate (Section I)



The absorption cross sections of methyl nitrate have been measured by Taylor et al. (1980) and, assuming a quantum yield of unity (consistent with the broad featureless nature of the absorption band), an atmospheric lifetime of approximately 10 days due to photolysis is calculated. The absorption band positions and cross sections of the higher alkyl nitrates are probably similar (Calvert and Pitts, 1966), leading to similar photolysis lifetimes to that for methyl nitrate. Photolysis will lead to cleavage of the O-NO_2 bond

$$RONO_2 + h\nu \rightarrow RO + NO_2$$

followed by the reactions of the alkoxy radical (Section I).

Peroxyacyl Nitrates and Peroxy Nitrates

Peroxyacetyl nitrate (PAN; $CH_3C(O)OONO_2$) and the higher members of this class of compounds are formed from the atmospheric degradation of many organics (see Section I). The reaction of OH radicals with PAN (the only peroxyacyl nitrate studied to date) is slow at tropospheric temperatures (Table 27) and this OH radical reaction is expected to be a significant atmospheric loss process for PAN only at the low temperatures encountered in the upper troposphere (Wallington et al., 1984). The major, and usually totally dominant, loss process for PAN in the atmosphere is by its thermal decomposition

$$CH_3C(O)OONO_2 \rightarrow CH_3C(O)OO + NO_2$$

Thus, PAN is in equilibrium with NO_2 and the $CH_3C(O)OO$ radical. In the presence of NO, the reaction

$$CH_3C(O)OO + NO \rightarrow CH_3C(O)O + NO_2$$

$$CH_3C(O)O \downarrow CH_3 + CO_2$$

leads to loss of PAN. The thermal decomposition rate constants for PAN are temperature and pressure dependent (Reimer and Zabel, 1986), being in the fall-off regime between first- and second-order kinetics below atmospheric pressure at room temperature. Using the Troe expression,

$$k = \left(\frac{k_o[M]}{1 + \frac{k_o[M]}{k_\infty}} \right) F^{\left\{ 1 + [N^{-1} \log k_o[M]/k_\infty]^2 \right\}^{-1}}$$

Reimer and Zabel (1986) derived (for $M=N_2$)

$$k_o = 6.3 \times 10^{-2}\ e^{-12783/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_\infty = 2.2 \times 10^{16}\ e^{-13437/T}\ s^{-1}$$

$$F = 0.27$$

and

$$N = 1.47,$$

with

$$k_o^{O_2}/k_o^{N_2} = 0.9 \pm 0.2$$

At 298 K and 760 torr total pressure of air,

$$k(PAN) = 4.2 \times 10^{-4}\ s^{-1}$$

in good agreement with the previous recommendation of Atkinson and Lloyd (1984) of 3.6×10^{-4} s^{-1} and with the atmospheric pressure data of

Schurath and Wipprecht (1980) [$k = 3.2 \times 10^{16}\ e^{-13592/T}\ s^{-1}$ at atmospheric pressure, $= 5.0 \times 10^{-4}\ s^{-1}$ at 298 K and atmospheric pressure]. The decomposition rates of the higher peroxyacyl nitrates are expected to be similar to that for PAN, although of course the decompositions will be closer to the high pressure limit at a given pressure than that for PAN, and at atmospheric pressure Schurath and Wipprecht (1980) determined that for peroxypropionyl nitrate (PPN; $C_2H_5C(O)OONO_2$),

$$k(PPN) = 1.6 \times 10^{17}\ e^{-14073/T}\ s^{-1}$$

$$= 5.0 \times 10^{-4}\ s^{-1} \text{ at 298 K and atmospheric pressure.}$$

For the peroxyalkyl nitrates, $ROONO_2$, the only significant atmospheric loss process is again thermal decomposition

$$ROONO_2 \rightarrow RO_2 + NO_2$$

with the thermal decomposition rate constant for CH_3OONO_2 being well into the fall-off regime at pressures of one atmosphere and below (Reimer and Zabel, 1986). Using the Troe fall-off expression

$$k = \left(\frac{k_o[M]}{1 + \frac{k_o[M]}{k_\infty}} \right) F^{\left\{ 1 + [N^{-1} \log k_o[M]/k_\infty]^2 \right\}^{-1}}$$

Reimer and Zabel (1986) derived for $M=N_2$

$$k_o = 8.5 \times 10^{-4}\ e^{-10317/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_\infty = 2.3 \times 10^{16}\ e^{-10770/T}\ s^{-1}$$

$$F = 0.47$$

and

$$N = 0.75 - 1.27 \log F = 1.17$$

with

$$k_o^{O_2}/k_o^{N_2} = 1.2 \pm 0.2$$

At 760 torr total pressure of air and 298 K,

$$k(CH_3OONO_2) = 2.2\ s^{-1}$$

The decomposition rates for the higher $ROONO_2$ species are expected to be similar to that for CH_3OONO_2, except that they will be closer to the high pressure first-order limit (which is 4.8 s^{-1} for CH_3OONO_2 at 298 K).

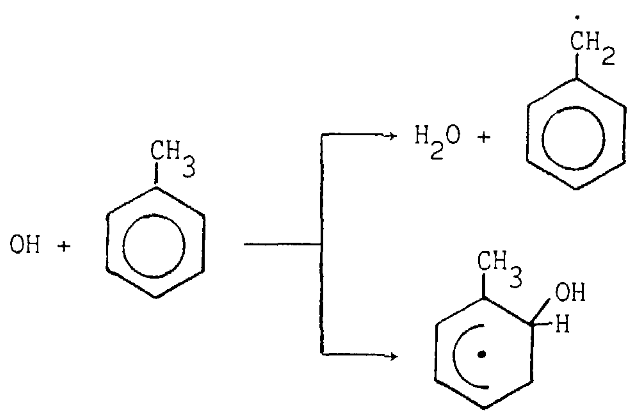
XI. AROMATIC COMPOUNDS

The aromatic compounds of concern in polluted urban atmospheres are the aromatic hydrocarbons and their aromatic ring-retaining products (aromatic aldehydes and phenolic compounds). In addition, there is recent concern over the atmospheric chemistry of the gas-phase polycyclic aromatic hydrocarbons. These are dealt with in this section.

Aromatic Hydrocarbons

The aromatic hydrocarbons react only very slowly with O_3 and with NO_3 radicals, with room temperature rate constants for the O_3 reactions of <1

x 10^{-20} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Carter, 1984) and for the NO_3 radical reactions of 10^{-17} to 10^{-16} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 1988b). Thus, atmospheric removal of the aromatic hydrocarbons by these reactions is of no importance. The only important atmospheric loss process is by reaction with the OH radical, and the room temperature rate constants for this reaction are given in Table 28. In general, the temperature dependencies of these rate constants are small below room temperature (Atkinson, 1986a). These OH radical reactions proceed by two routes; H atom abstraction from the C-H bonds of the alkyl substituent groups (or the ring C-H bonds for benzene) and OH radical addition to the aromatic ring



(a)

(b)

(plus other isomers)

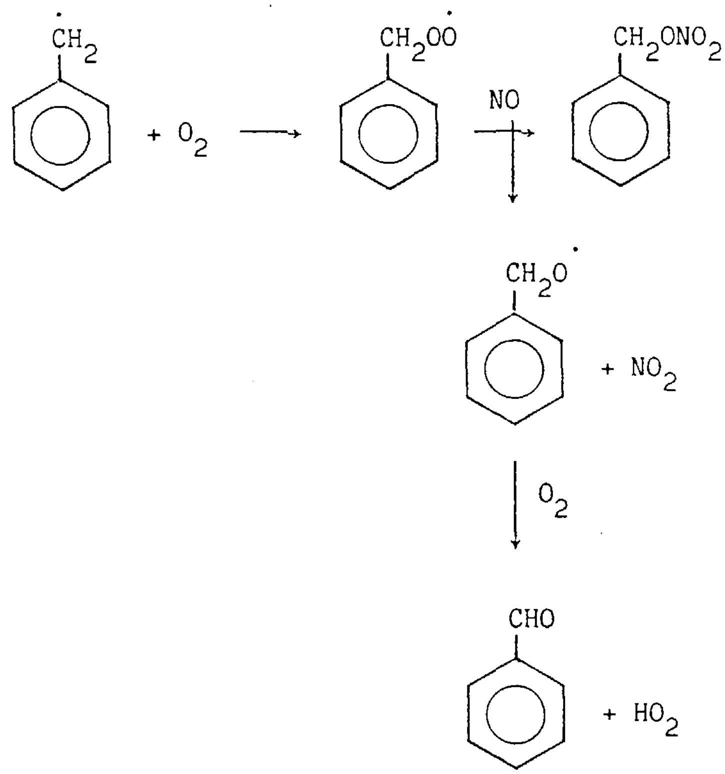
The H atom abstraction route is of minor importance, and the measured or estimated rate constant ratios $k_a/(k_a + k_b)$ at room temperature are also given in Table 28 (these are probably uncertain to a factor of approximately 2 for benzene, the xylenes and the trimethylbenzenes).

The reactions subsequent to the H atom abstraction route from the alkyl side chains are expected to be consistent with the data given in Section I, for example for the benzyl radical formed from toluene in the presence of NO

Table 28. Room Temperature Rate Constants for the Gas-Phase Reactions of the OH Radical with Aromatic Compounds and Rate Constant Ratios $k_a/(k_a + k_b)$

Aromatic	$10^{12} \times k$ (cm^3 $molecule^{-1}$ s^{-1})	$k_a/(k_a + k_b)$
Benzene	1.3[a]	0.07[a]
Toluene	6.0[a,d]	0.11[a], 0.08[b]
Ethylbenzene	7[a]	
n-Propylbenzene	7[a]	
Isopropylbenzene	7[a]	
t-Butylbenzene	5[a]	
o-Xylene	14[a,d]	0.09[a], 0.05[c]
m-Xylene	24[a,d]	0.04[a], 0.04[c]
p-Xylene	14[a,d]	0.09[a], 0.08[c]
o-Ethyltoluene	12[a]	
m-Ethyltoluene	20[a]	
p-Ethyltoluene	12[a]	
1,2,3-Trimethylbenzene	33[d]	0.05[a]
1,2,4-Trimethylbenzene	33[d]	0.04[a]
1,3,5-Trimethylbenzene	58[d]	0.03[a]
Benzaldehyde	13[a]	
Phenol	28[a]	
o-Cresol	40[a]	0.08[a]
m-Cresol	57[a]	
p-Cresol	44[a]	

[a]Atkinson (1986a); values of $k_a/(k_a + k_b)$ estimated from the reaction kinetics.
[b]Atkinson et al. (1983b).
[c]Bandow and Washida (1985a).
[d]Atkinson and Aschmann, unpublished data (1988).



The amount of nitrate formation (benzyl nitrate from the benzyl radical) is approximately 10% (Hoshino and Akimoto, 1978; Gery et al., 1985) at room temperature and atmospheric pressure. Similar reaction pathways account for the observation of the tolualdehydes from the xylene isomers (Bandow and Washida, 1985a).

The major pathway of the OH radical reaction is hence by OH radical addition to the aromatic ring to yield hydroxycyclohexadienyl or hydroxyalkylcyclohexadienyl radicals (reaction (b) above). The hydroxycyclohexadienyl radical (HCHD) has been observed by ultraviolet absorption spectroscopy for the OH radical reaction with benzene (Fritz et al., 1985; Zellner et al., 1985) and its reactions with O_2, NO and NO_2 studied (Zellner et al., 1985). At 298 K rate constants for the reactions of HCHD radicals with NO and NO_2 of

$$k(HCHD + NO) = (1.0 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(HCHD + NO_2) = (8.5 \pm 2.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

were determined (Zellner et al., 1985). No reaction of HCHD was observed with O_2 and, although no upper limit to the rate constant was given by Zellner et al. (1985), a value of

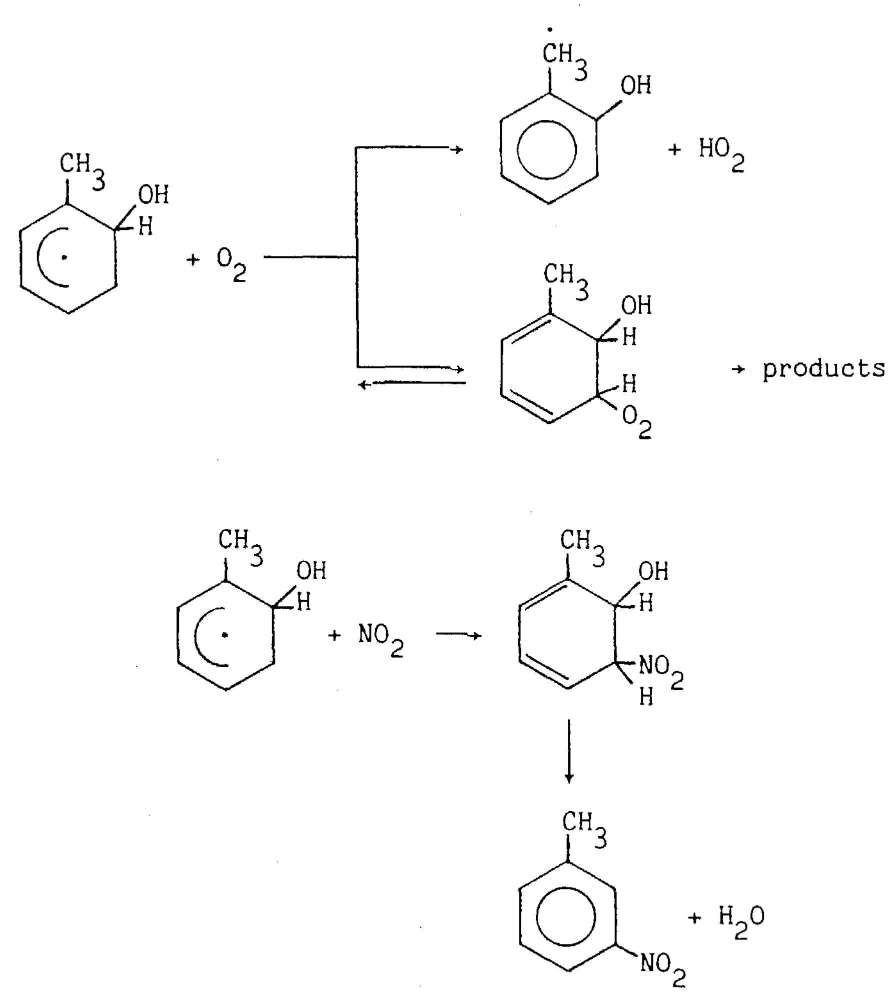
$$k(HCHD + O_2) < 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

can be estimated from their data. Since the O_2/NO_x concentration ratio is typically $\gtrsim 10^6$ under atmospheric conditions, these data do not allow an assessment of whether or not the O_2 reaction will be dominant in the atmosphere. It should be noted, however, that in a recent study Atkinson et al. (1987a) obtained data which suggest that at NO_x concentrations of approximately (1-4) x 10^{14} molecule cm^{-3}, the phenylhydroxycyclohexadienyl radical formed from biphenyl does not react with O_2.

Thus, at the present time the actual reactions removing the OH-aromatic adducts (i.e., hydroxycyclohexadienyl radicals) are not known, and it is distinctly possible that they do not react with O_2 under polluted urban atmospheric conditions. At present the only definitive data concerning the reactions subsequent to the addition reaction of OH radicals with the aromatic hydrocarbons are the products formed. For toluene, the most studied aromatic hydrocarbon, these include o-, m- and p-cresol, m-nitrotoluene, glyoxal, methylglyoxal, PAN (a secondary product which can be formed from the reactions of methylglyoxal), $CH_3COCOCH{=}CH_2$,

$CHOCOCH=CH_2$, $CH_3COCH=CH_2$, $CH_3CH=CHCH=CH_2$, $CHOC(OH)=CHCHO$, and $CH_3COCH=CHCH=CHCHO$.

The cresol yields from toluene have been determined in three recent studies, with reported yields of 0.13 ± 0.07 (Atkinson et al., 1983b), 0.13 (Leone et al., 1985) and 0.22 (Gery et al., 1985) for o-cresol, with the m- and p-cresol yields being much lower [with the o- : m- : p- yield ratio being approximately 80 : 5 : 15 (Hoshino et al., 1978; Gery et al., 1985)]. The reaction scheme postulated to account for the cresols and m-nitrotoluene has been (Atkinson et al., 1980; Killus and Whitten, 1982)



However, the recent study of 3-nitrobiphenyl formation from biphenyl throws doubt on this scheme since both the 3-nitrobiphenyl yield and the 3-nitrobiphenyl/2-hydroxybiphenyl yield ratio were observed to be independent, within the experimental errors, of the NO_2 concentration (Atkinson et al., 1987a).

The other products whose yields have been measured with some accuracy are the α-dicarbonyls for a series of aromatic hydrocarbons, and the data are given in Table 29. In addition, the expected co-products of the α-dicarbonyls have been observed (Takagi et al., 1982; Shepson et al., 1984; Becker and Klein, 1987), but generally only in small yields.

Thus, for toluene approximately 10% of the overall reaction occurs by H atom abstraction to form, in the presence of NO, benzaldehyde and benzyl nitrate. The cresols account for a further approximately 20% of the overall OH radical reaction, and glyoxal plus methylglyoxal (plus co-products) account for approximately 25% of the reaction, although the co-products are not known. The remaining reaction products, accounting for approximately 45% of the overall OH radical reaction, are not quantitatively known, although a variety of ring-cleavage products have been observed (Dumdei and O'Brien, 1984; Shepson et al., 1984).

Polycyclic Aromatic Hydrocarbons (PAH)

Kinetic data are available for several of the PAH, and these data are given in Table 30. Of particular interest is that the gas-phase PAH containing two or more six-membered fused ring react with N_2O_5 (Atkinson and Aschmann, 1987, 1988 and references therein). The OH radical (in the presence of NO_x) and N_2O_5 reactions lead to the formation of nitroarene products, and the yields of these products are given in Table 31.

Table 29. α-Dicarbonyl Yields from the OH Radical-Initiated Reactions of a Series of Aromatic Hydrocarbons

Aromatic	α-Dicarbonyl Yield[a] Glyoxal	Methyl-Glyoxal	Biacetyl	Reference
Benzene	0.207 ± 0.019			Tuazon et al. (1986)
Toluene	0.15 ± 0.04	0.14 ± 0.04		Bandow et al. (1985)
	0.105 ± 0.019	0.146 ± 0.006		Tuazon et al. (1986)
	0.098	0.106		Gery et al. (1985)
o-Xylene			0.18 ± 0.04	Darnall et al. (1979)
			0.260 ± 0.102	Takagi et al. (1980)
			0.137 ± 0.016	Atkinson et al. (1983b)
	0.08 ± 0.04	0.23 ± 0.03	0.10 ± 0.02	Bandow and Washida (1985a)
	0.087 ± 0.012	0.246 ± 0.020		Tuazon et al. (1986)
m-Xylene	0.13 ± 0.03	0.42 ± 0.05		Bandow and Washida (1985a)
	0.086 ± 0.011	0.319 ± 0.009		Tuazon et al. (1986)
p-Xylene	0.24 ± 0.02	0.12 ± 0.02		Bandow and Washida (1985a)
	0.225 ± 0.039	0.105 ± 0.034		Tuazon et al. (1986)
1,2,3-Trimethyl-	0.072 ± 0.001	0.18 ± 0.01	0.45 ± 0.02	Bandow and Washida (1985b)
benzene	0.058 ± 0.008	0.152 ± 0.025	0.316 ± 0.036	Tuazon et al. (1986)
1,2,4-Trimethyl-	0.078 ± 0.005	0.37 ± 0.01	0.11 ± 0.01	Bandow and Washida (1985b)
benzene	0.048 ± 0.005	0.357 ± 0.017	0.048 ± 0.009	Tuazon et al. (1986)
1,3,5-Trimethyl-		0.64 ± 0.03		Bandow and Washida (1985b)
benzene		0.602 ± 0.033		Tuazon et al. (1986)

[a]Indicated error limits are two standard deviations.

Table 30. Rate Constants for the Gas-Phase Reactions of PAH with OH and NO_3 Radicals, N_2O_5 and O_3 at Room Temperature

PAH	Rate Constant (cm^3 $molecule^{-1}$ s^{-1}) for Reaction with			
	OH	NO_3	N_2O_5	O_3
Naphthalene	2.2×10^{-11} [a]	b	1.4×10^{-17} [c]	$<2 \times 10^{-19}$ [d]
Biphenyl	7×10^{-12} [a]	b	$<2 \times 10^{-19}$ [c]	$<2 \times 10^{-19}$ [d]
1-Methylnaphthalene	5.3×10^{-11} [e]	b	3.3×10^{-17} [e]	$<1.3 \times 10^{-19}$ [e]
2-Methylnaphthalene	5.2×10^{-11} [f]	b	4.2×10^{-17} [e]	$<4 \times 10^{-19}$ [f]
2,3-Dimethylnaphthalene	7.7×10^{-11} [f]	b	5.7×10^{-17} [e]	$<4 \times 10^{-19}$ [f]
Acenaphthene	1.0×10^{-10} [g]	4.6×10^{-13} [g]	5.5×10^{-17} [g]	$<5 \times 10^{-19}$ [g]
Acenaphthylene	1.1×10^{-10} [g]	5.4×10^{-12} [g]	b	$\sim 5.5 \times 10^{-16}$ [g]
Phenanthrene	3.4×10^{-11} [h]			
Anthracene	1.3×10^{-10} [h]			

[a] Atkinson (1986a).
[b] No reaction observed.
[c] Atkinson et al. (1987a).
[d] Atkinson et al. (1984c).
[e] Atkinson and Aschmann (1987).
[f] Atkinson and Aschmann (1986).
[g] Atkinson and Aschmann (1988).
[h] Biermann et al. (1985).

Table 31. Nitroarene Products Formed from the Gas Phase Reactions of PAH Known to be Present in Ambient Air with OH Radicals (in the Presence of NO_x) and N_2O_5, Together with their Yields at Room Temperature and Atmospheric Pressure

PAH	Reaction with OH	Reaction with N_2O_5
Naphthalene	1-Nitronaphthalene (0.3%)[a]	1-Nitronaphthalene (17%)[a]
	2-Nitronaphthalene (0.3%)[a]	2-Nitronaphthalene (7%)[a]
Pyrene	2-Nitropyrene (~0.5%)[b]	4-Nitropyrene (~0.3%)[b]
	4-Nitropyrene (~0.05%)[b]	
Fluoranthene	2-Nitrofluoranthene (~5%)[b]	2-Nitrofluoranthene (~25-30%)[b]
	7-Nitrofluoranthene (~0.25%)[b]	
	8-Nitrofluoranthene (~0.25%)[b]	
Acephen-anthrylene	Two nitroarene isomers (~0.1%)[b,c]	None observed[c]
Biphenyl	3-Nitrobiphenyl (5%)[a]	No reaction observed[a]

[a]Atkinson et al. (1987a).
[b]Arey et al. (1988).
[c]Zielinska et al. (1988).

In addition (Atkinson et al., 1987a), 1- and 2-naphthol are formed from the OH radical reaction with naphthalene in approximately 5% yield each, and 2-hydroxybiphenyl is formed from biphenyl in approximately 20% yield (similar to that of o-cresol from toluene).

Aromatic Aldehydes

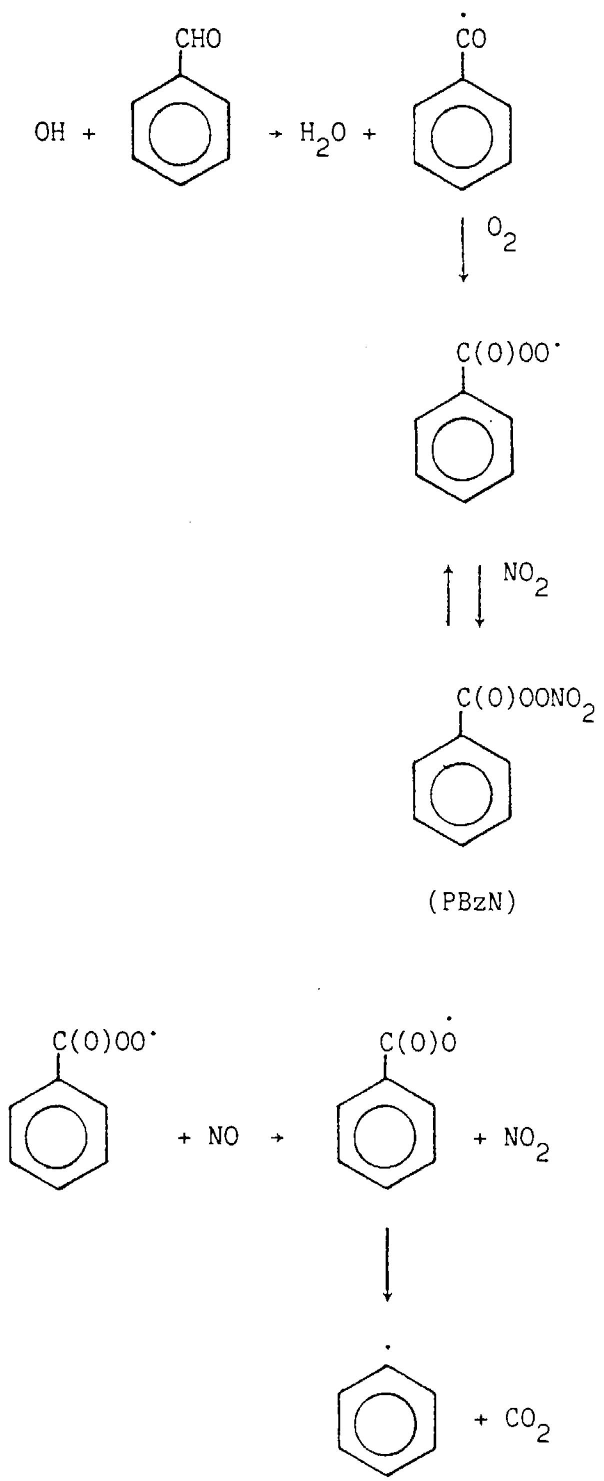
The only aromatic aldehyde which has been studied to any extent is benzaldehyde. The potential atmospheric reactions are photolysis and chemical reaction with OH and NO_3 radicals and O_3. No data are available concerning the O_3 reaction, but it is expected to be of no significance as an atmospheric loss process (Atkinson and Carter, 1984). The NO_3 radical reaction has a room temperature rate constant of 2.5×10^{-15} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 1988b), very similar to that for acetaldehyde. This NO_3 radical reaction is expected to proceed by H atom abstraction from the -CHO substituent group

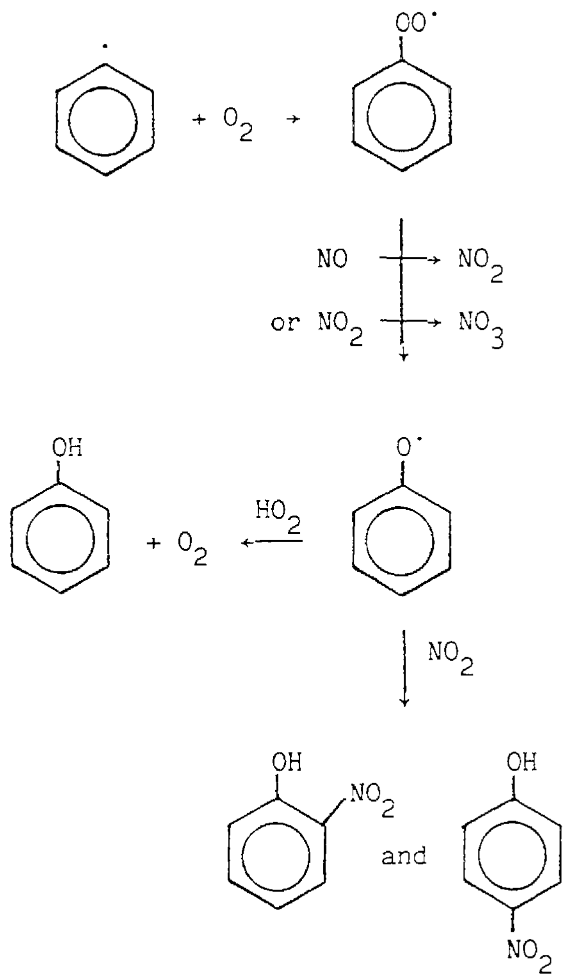
$$C_6H_5CHO + NO_3 \rightarrow HNO_3 + C_6H_5\dot{C}O$$

followed by reactions of the $C_6H_5\dot{C}O$ radical (see below).

The rate constant for the OH radical reaction at room temperature is given in Table 28. In terms of their importance as atmospheric loss processes, the OH radical reaction will dominate over the NO_3 radical reaction by approximately an order of magnitude. The OH radical reaction also proceeds by H atom abstraction from the -CHO group (OH radical addition to the aromatic ring is expected to be slower than the OH radical reaction with benzene since the -CHO group is electron withdrawing). Based upon the study of the Cl atom-initiated reaction of benzaldehyde of

Niki et al. (1979), the reactions after this H atom abstraction are expected to be:





This reaction sequence is also consistent with a recent study of Tuazon et al. (unpublished results, 1988) of the NO_3 radical reaction with phenol, which yields the phenoxy radical in the initial step.

Peroxybenzoyl nitrate (PBzN) is analogous to PAN in that it is in thermal equilibrium with NO_2 and the $C_6H_5C(O)OO$ radical. The thermal decomposition of PBzN has been studied by Ohta and Mizoguchi (1981) and Kenley and Hendry (1982), and rate constants of $8.5 \times 10^{14}\ e^{-12682/T}\ s^{-1}$ (Ohta and Mizoguchi, 1981) [$2.7 \times 10^{-4}\ s^{-1}$ at 298 K] and $1.6 \times 10^{15}\ e^{-13035/T}\ s^{-1}$ (Kenley and Hendry, 1982) [$1.6 \times 10^{-4}\ s^{-1}$ at 298 K] have been reported.

It is clear from experimental and computer modeling studies of the NO_x-air photooxidations of toluene that benzaldehyde photolyzes (Atkinson et al., 1980; Killus and Whitten, 1980; Gery et al., 1985; Leone et al., 1985). The absorption cross section has been given by Itoh (1987) and extends to 300 nm. The photodissociation quantum yields, the photodissociation products (in particular, whether the products are radical species or not) and their wavelength dependencies are, however, not presently known.

Phenolic Compounds

Phenol and the cresols are formed from the atmospheric degradation of benzene and toluene, respectively, and some data are available concerning the atmospheric reactions of these compounds. The potential atmospheric loss processes of phenolic compounds are reaction with NO_3 and OH radicals and with O_3, together with wet and/or dry deposition (these compounds are readily incorporated into rain and cloud water and fog). For the gas-phase reactions of O_3 with the cresol isomers, room temperature rate constants of (in units of 10^{-19} cm^3 $molecule^{-1}$ s^{-1}) 2.6, 1.9 and 4.7 for o-, m-, and p-cresol, respectively, have been measured (Atkinson and Carter, 1984). Reaction with O_3 will thus be a minor removal process for the phenolic compounds under atmospheric conditions.

The gas-phase reactions of the NO_3 radical with phenol and the cresols are rapid, with room temperature rate constants of: phenol, 3.6×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 1988b); o-cresol, 2.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 1984d, 1988b); m-cresol, 1.6×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 1984d, 1988b); and p-cresol, 2.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 1984d, 1988b). These reactions appear to proceed by H atom abstraction from the O-H bonds, leading to the formation of phenoxy and methylphenoxy radicals. The subsequent reactions of these radicals have been discussed above.

The room temperature rate constants for the gas-phase reactions of the OH radical with phenol and the cresols are given in Table 28. These reactions proceed mainly by OH radical addition to the aromatic ring (Atkinson, 1986a). No detailed knowledge of the products and mechanism of these OH radical reactions is known, although pyruvic acid ($CH_3COCOOH$) has been reported as a product (Grosjean, 1984).

Pyruvic acid photolyzes rapidly (Grosjean, 1983, 1985) with a photolysis rate, relative to that for photolysis of NO_2, of 0.033 under atmospheric conditions (Grosjean, 1985). The photolysis products of pyruvic acid are CO_2 and acetaldehyde (Yamamoto and Back, 1985)

$$CH_3COCOOH + h\nu \rightarrow CO_2 + CH_3CHO$$

Clearly, further work is needed concerning the atmospheric products and mechanisms of the reactions of phenolic compounds.

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