CHAPTER

6

Rates and Mechanisms of Gas-Phase Reactions in Irradiated Organic – NO_x – Air Mixtures

The myriad organics found in the troposphere, in combination with a variety of potential oxidizing species, can easily conjure up a nightmare in terms of the chemistry and kinetics needed to fully understand the gas-phase chemistry of organic–NO_x mixtures in the lower atmosphere. Fortunately, through studies over the past three decades, a great deal has been learned regarding which oxidants are important for each class of organics. One can use this information to examine the most important types of reactions, which once understood, can be readily extrapolated to other organic compounds.

Let us first review the oxidants that have been recognized for some time as important in the troposphere, as well as atomic chlorine, for which there is increasing evidence of a contribution in marine regions.

A. SOURCES OF OXIDANTS IN THE TROPOSPHERE: OH, O_3, NO_3, HO_2, AND Cl

The major recognized oxidants for organics in the troposphere are OH and O_3, with a contribution from NO_3 at night. The hydroperoxyl free radical, HO_2, as we shall see, also reacts readily with aldehydes but does not significantly impact tropospheric chemistry due to a rapid reverse reaction. It is, of course, responsible for converting NO to NO_2, ultimately leading to the production of O_3, as well as a whole host of compounds included under the umbrella of NO_y. The HO_2 + NO reaction also generates OH, so understanding the sources of HO_2 is important in understanding sources of OH. Because there is increasing evidence for the production of atomic chlorine in marine areas (although its source is unknown), we shall briefly discuss this as well.

1. OH

The major source of OH in remote areas is the photolysis of O_3 to electronically excited $O(^1D)$, followed by its reaction with water vapor:

$$O_3 + h\nu(\lambda \lesssim 336\ \text{nm}) \rightarrow O(^1D) + O_2, \quad (1)$$

$$O(^1D) + H_2O \rightarrow 2OH, \quad (2a)$$

$$O(^1D) \overset{M}{\rightarrow} O(^3P). \quad (2b)$$

It should be noted that only a portion of the $O(^1D)$ formed generates OH via reaction (2a); the remainder is deactivated to ground-state $O(^3P)$, reaction (2b), which then re-forms O_3. For example, at 50% RH and 300 K at the earth's surface, about 10% of the $O(^1D)$ formed generates OH. As a result, as discussed later in this chapter, the relative importance of (2a) decreases at higher altitudes due to the decrease in water vapor. This is also an important source in polluted areas, where, however, there are additional sources as well. These include the photolysis of gaseous nitrous acid (HONO) and hydrogen peroxide (H_2O_2):

$$HONO + h\nu(\lambda < 400\ \text{nm}) \rightarrow OH + NO, \quad (3)$$

$$H_2O_2 + h\nu(\lambda < 370\ \text{nm}) \rightarrow 2OH. \quad (4)$$

In addition, in the presence of NO concentrations larger than ~ 10 ppt, sources of HO_2 are, in effect, sources of OH:

$$HO_2 + NO \rightarrow OH + NO_2. \quad (5)$$

Because most of the OH sources are photolytic in nature (exceptions being production via the reactions of O_3 with alkenes, free radicals produced by the thermal decomposition of compounds such as PAN or peroxynitric acid, HO_2NO_2, or the nighttime reactions of NO_3), OH is a major oxidant primarily during daylight hours.

2. O_3

Tropospheric O_3 is known to be formed upon photolysis of NO_2 in air, first suggested by Blacet (1952):

$$NO_2 + h\nu(\lambda \lesssim 420\text{ nm}) \rightarrow NO + O(^3P), \quad (6)$$

$$O(^3P) + O_2 \overset{M}{\rightarrow} O_3. \quad (7)$$

While elevated NO_x levels are clearly associated with anthropogenic emissions (see Chapter 2), there are also small concentrations due to natural processes. Hence small concentrations of O_3 are also formed via the reactions of natural VOC and NO_x discussed later in this chapter. Finally, the periodic intrusion of stratospheric air with its relatively high concentrations of O_3 provides an additional source of tropospheric ozone.

Although the photolysis of NO_2 is the major source of O_3, ozone is sufficiently long-lived that it can be transported downwind and survive into the nighttime hours. Hence it is a player in tropospheric chemistry throughout the day and night.

3. NO_3

The nitrate radical is formed by the reaction of NO_2 with O_3:

$$NO_2 + O_3 \rightarrow NO_3 + O_2. \quad (8)$$

As discussed in Chapter 4, NO_3 only exists in sufficient concentrations to play a role in nighttime chemistry, due to its strong absorption of light in the visible and subsequent photodissociation.

4. HO_2

Any reactions that produce H or HCO in the troposphere act as HO_2 sources:

$$H + O_2 \overset{M}{\rightarrow} HO_2, \quad (9)$$

$$HCO + O_2 \rightarrow HO_2 + CO. \quad (10)$$

Thus, formaldehyde photolysis is a major source of HO_2 during the day:

$$HCHO + h\nu(\lambda \lesssim 370\text{ nm}) \rightarrow H + HCO. \quad (11)$$

The photolysis of higher aldehydes, RCHO, also forms HCO (see Chapter 4) and hence HO_2:

$$RCHO + h\nu \rightarrow R + HCO. \quad (12)$$

However, as discussed in Chapter 4, the absorption spectrum of higher aldehydes cuts off at shorter wavelengths than formaldehyde. This, combined with higher quantum yields for radical production in the 290- to 340-nm range and the fact that HCHO produces $2HO_2$ essentially immediately upon dissociation, makes the photolysis of aldehydes larger than formaldehyde less important at equal concentrations of the aldehydes.

The reactions of some alkoxy radicals generated in the VOC oxidation sequence, for example those of CH_3O and C_2H_5O radicals discussed in more detail later, with O_2 also generate HO_2:

$$RCH_2O + O_2 \rightarrow RCHO + HO_2. \quad (13)$$

The alkoxy radical originates in the oxidation of a VOC to an alkyl radical by any of the oxidants described here or, alternatively, in the thermal decomposition of species such as PAN which gives the CH_3 radical. In short, HO_2 is a natural consequence of the oxidation of organics.

Finally, the decomposition of peroxynitric acid, HO_2NO_2, which is strongly temperature dependent, generates HO_2 directly:

$$HO_2NO_2 \leftrightarrow HO_2 + NO_2. \quad (14, -14)$$

5. Cl

In marine areas, wave action generates airborne droplets of seawater from which the water can evaporate, leaving a suspended particle of the dissolved solids. Because this is mainly NaCl, the possibility exists for the generation of atomic chlorine via the reactions of NaCl with gaseous species such as N_2O_5 or $ClONO_2$ (see reviews by Finlayson-Pitts, 1993; Graedel and Keene, 1995; Andreae and Crutzen, 1997; Finlayson-Pitts and Pitts, 1997; De Haan *et al.*, 1999; and Hemminger, 1999), e.g.,

$$N_2O_{5(g)} + NaCl_{(s)} \rightarrow ClNO_{2(g)} + NaNO_{3(s)}, \quad (15)$$

$$ClONO_{2(g)} + NaCl_{(s)} \rightarrow Cl_{2(g)} + NaNO_{3(s)}. \quad (16)$$

(Chlorine nitrate is formed from the reaction of ClO with NO_2.) These reactions also occur when NaCl is in the aqueous phase, in competition with the hydrolysis of N_2O_5 and $ClONO_2$, i.e., above the deliquescence point of NaCl in sea salt (e.g., Behnke *et al.*, 1997). Photolysis then generates chlorine atoms, e.g.,

$$ClNO_2 + h\nu \rightarrow Cl + NO_2, \quad (17)$$

$$Cl_2 + h\nu \rightarrow 2Cl. \quad (18)$$

It is likely that there are as yet ill-defined aqueous-phase reactions in the airborne seawater droplets that release photochemically labile chlorine gases. For example, Oum *et al.* (1998a) have shown that Cl_2 is formed when sea salt aerosols above their deliquescence point are irradiated at 254 nm in the presence of O_3, generating OH which initiates Cl^- oxidation.

Such reactions may also be important in other situations in the troposphere. For example, Shaw (1991) has observed salt particles as far as 900 km inland in Alaska, and chloride salts are used on many roads in cold climates in the wintertime. In addition, in the plumes from oil well burning in Kuwait, salt particles were observed, due to the brine that was mixed with the oil in the wells (e.g., see Cahill *et al.*, 1992).

Direct evidence for the potential importance of Cl as an organic oxidant comes from recent measurements of inorganic chlorine-containing species other than HCl in the marine troposphere in midlatitudes (Keene *et al.*, 1993; Pszenny *et al.*, 1993). In particular, Cl_2 has been identified using atmospheric pressure ionization mass spectrometry (API-MS) in a coastal region (Spicer *et al.*, 1998). Interestingly, the concentrations, up to 150 ppt, are much higher than can be explained by any known chemistry, again highlighting the contribution of some as yet unidentified chemistry in the marine boundary layer. During the day, any Cl_2 formed will absorb strongly in the 300- to 400-nm region (Chapter 4), and dissociate, generating atomic chlorine.

Indirect evidence for the involvement of atomic chlorine in the chemistry of marine atmospheres comes from the measurement of simple organics, where their relative rates of decay frequently cannot be matched assuming attack only by OH (Wingenter *et al.*, 1996). Estimates of the peak concentrations of atomic chlorine range from $\sim 10^3$ to 10^6 radicals cm^{-3} in the marine boundary layer (e.g., Pszenny *et al.*, 1993; Singh *et al.*, 1996a). However, on a global scale, the concentrations are likely much smaller. For example, Rudolph *et al.* (1996) and Singh *et al.* (1996b) have examined the budget for tetrachloroethene (TCE), which reacts relatively rapidly with Cl compared to OH. The measured atmospheric concentrations of TCE are consistent with the known emissions and removal solely by reaction with OH, from which an upper limit for the *global annual average* Cl atom concentrations was estimated to be $\leq 10^3$ atoms cm^{-3}. However, most of it is in the marine boundary layer (MBL) so that these averaged values may not be inconsistent with peak MBL concentrations of 10^4–10^6 atoms cm^{-3}.

In short, while there is evidence that atomic chlorine is generated from sea salt reactions and contributes to organic oxidations in the marine boundary layer, the nature and strength of the sources remain to be elucidated.

B. LIFETIMES OF TYPICAL ORGANICS IN THE TROPOSPHERE

To pare the list of VOC oxidations down to the most important processes, we can calculate the effective lifetimes of organics with respect to reactions with each of the oxidants listed in the previous section. Since these natural lifetimes are defined as $\tau = 1/k_p[X]$, we also need to assume an average concentration for the oxidant, [X]. We can therefore take a typical organic from each of the major classes (alkane, alkene, aromatic, etc.) and compare the individual lifetimes for reaction with OH, O_3, NO_3, etc. Those reactions having very long lifetimes are insignificant with respect to their contribution to tropospheric chemistry and hence can be ignored for the purposes of this discussion.

Table 6.1 shows such a set of calculated lifetimes for the oxidants discussed in Section A. The most significant reactions are as follows:

Alkanes: OH, to a lesser extent NO_3, and in the marine boundary layer (MBL) Cl
Alkenes: OH, O_3, NO_3, and to a lesser extent Cl (MBL)
Alkynes: OH, Cl (MBL)
Aromatics: OH, Cl (MBL)
Aldehydes: OH, NO_3, (HO_2), Cl (MBL)

TABLE 6.1 Estimated Lifetimes of Representative Organics in the Troposphere[a]

Organic	OH (1×10^6 cm^{-3})	O_3 (100 ppb)	NO_3 (50 ppt)	HO_2 (2×10^8 cm^{-3}, 8 ppt)	Cl (1×10^4 cm^{-3})
n-Butane	5 days	≥ 1300 yr	205 days		5 days
trans-2-Butene	4.3 h	36 min	35 min		~4 days
Acetylene	14 days	≥ 400 days	≥ 188 days		~22 days[c]
Toluene	2 days	≥ 400 days	138 days[d]		20 days
HCHO	1.2 days	≥ 463 days	16 days	18/h[b]	16 days

[a] $\tau = 1/k_p$[oxidant] = time for the organic to fall to $1/e$ of its initial value; except as shown here, rate constants are found in text.

[b] Note: This is only for the forward reaction. Since the adduct decomposes back to reactants under most atmospheric conditions. The effective atmospheric lifetime is much longer.

[c] Based on k ($Cl + C_2H_2$) = 5.3×10^{-11} cm^3 $molecule^{-1}$ s^{-1} from $k_0 = 5.7 \times 10^{-30}$ cm^6 $molecule^{-2}$ s^{-1}, $k_\infty = 2.3 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and $F_c = 0.6$ (Atkinson *et al.*, 1997a).

[d] Using $k = 6.8 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1994).

The HO_2–aldehyde reaction is in parentheses because, as we shall see later, it is a reversible reaction that is sufficiently fast in the reverse direction under typical tropospheric conditions that no overall reaction, in effect, occurs.

Each of these reactions, both the kinetics and mechanisms, are discussed in the remainder of this chapter.

C. REACTIONS OF ALKANES

1. Hydroxyl Radical (OH)

The hydroxyl radical has a strong tendency to abstract a hydrogen atom whenever possible, forming the thermodynamically stable water molecule. In the case of alkanes, the reaction is therefore

$$OH + RH \rightarrow R + H_2O. \qquad (19)$$

Table 6.2 summarizes rate constants for some OH–alkane reactions; for recent recommendations for other alkanes, see Atkinson (1994, 1997a) and Atkinson *et al.* (1997a).

The temperature dependence is given in the form $k = BT^n e^{-C/T}$, where n is usually taken as 2, except for CH_4. This fit procedure provides curvature in the Arrhenius plot similar to that which is observed. Donahue *et al.* (1998a) propose an alternate form of the

TABLE 6.2 Rate Constants and Temperature Dependence[a,b] for Reaction of OH Radicals with Some Alkanes

Alkane	k (10^{-12} cm^3 molecule^{-1} s^{-1}) at 298 K	B (10^{-18} cm^3 molecule^{-1} s^{-1})	C (K)	n	D (10^{-9} K cm^3 s^{-1})	F (K)
Methane	0.00618	0.0965	1082	2.58		
Ethane	0.254	15.2	498	2	1.24	1042
Propane	1.12	15.5	61	2	1.32	616
n-Butane	2.44	16.9	−145	2	1.68	456
2-Methylpropane	2.19	11.6	−225	2	0.75	257
n-Pentane	4.0	24.4	−183	2	2.46	414
2-Methylbutane	3.7					
2,2-Dimethylpropane	0.85	18.0	189	2		
n-Hexane	5.45	15.3	−414	2	2.10	284
2-Methylpentane	5.3					
3-Methylpentane	5.4					
2,3-Dimethylbutane	5.8	12.4	−494	2		
n-Heptane	7.0	15.9	−478	2		
2,2-Dimethylpentane	3.4					
2,2,3-Trimethylbutane	4.2	8.5	−516	2		
n-Octane	8.7	27.6	−378	2		
2,2,4-Trimethylpentane	3.6	20.8	−196	2		
2,2,3,3-Tetramethylbutane	1.05	19.1	144	2		
n-Nonane	10.0	25.1	−447	2		
n-Decane	11.2	31.3	−416	2		
n-Undecane	12.9					
n-Dodecane	13.9					
n-Tridecane	16					
n-Tetradecane	18					
n-Pentadecane	21					
n-Hexadecane	23					
Cyclopropane	0.084					
Cyclobutane	1.5					
Cyclopentane	5.02 (4.8)[c]	25.7	−235	2	1.97	253
Cyclohexane	7.21 (7.2)[c]	28.8	−309	2	2.36	227
Cycloheptane	13				4.25	256
Methylcyclohexane	10 (9.4)[c]					

[a] The parameters B and C give the temperature dependence in the form $k = BT^n e^{-C/T}$, where $C = E_a/R$. From Atkinson (1997a).

[b] The parameters D and $F = E_a/R$ are for the temperature dependence in the form recommended by Donahue *et al.* (1998a): $k(T) = De^{-F/T}/[T(1 - e^{-1.44\upsilon_1/T})^2(1 - e^{-1.44\upsilon_2/T})]$, where two bends at $\upsilon_1 = 300$ cm^{-1} and one bend at $\upsilon_2 = 500$ cm^{-1} are treated explicitly.

[c] Kramp and Paulson (1998).

temperature dependence consistent with a simplified form of transition state theory:

$$k(T) = \frac{De^{-F/T}}{T(1 - e^{-1.44\nu_1/T})^2(1 - e^{-1.44\nu_2/T})},$$

where υ_1 is the degenerate C−H−O bend frequency (cm^{-1}) and υ_2 is the H−O−H bend frequency (cm^{-1}). Table 6.2 also shows the parameters D and $F = E_a/R$ for this form of the temperature dependence using $\upsilon_1 = 300\ cm^{-1}$ and $\upsilon_2 = 500\ cm^{-1}$.

The first thing that stands out in Table 6.2 is that the $OH-CH_4$ rate constant, 6.2×10^{-15} cm^3 $molecule^{-1}$ s^{-1}, is much smaller than those for the higher alkanes, a factor of 40 below that for ethane. This relatively slow reaction between OH and CH_4 is the reason that the focus is on "non-methane hydrocarbons" (NMHC) in terms of ozone control in urban areas. Thus, even at a typical peak OH concentration of 5×10^6 molecules cm^{-3}, the calculated lifetime of CH_4 at 298 K is 373 days, far too long to play a significant role on urban and even regional scales. Clearly, however, this reaction is important in the global troposphere (see Chapter 14.B.2b).

Second, the room temperature rate constants increase with increasing size and complexity of the alkane and are of the order of 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the largest alkanes. To put this in perspective, a diffusion-controlled reaction, i.e., one that occurs on every collision of the reactants, is of the order of $\sim(3-5) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Thus for the larger alkanes, reaction occurs in approximately one in 10 collisions, which is quite a fast process.

As discussed in Chapter 5, kinetic theories predict that the preexponential factor should have a temperature dependence that manifests itself in curved Arrhenius plots if the reactions are studied over a sufficiently broad temperature range. This is the case for OH−alkane reactions, where there has been great interest in the high-temperature kinetics for combustion systems. Table 6.2 also shows the temperature dependence for the OH reactions in the form $k = BT^n e^{-C/T}$, where $C = E_a/R$ and in the form recommended by Donahue *et al.* (1998a).

The C−H bond strength is largest for primary C−H bonds at $\sim$101 kcal mol^{-1}, decreasing to $\sim$98 kcal mol^{-1} for secondary and $\sim$96 kcal mol^{-1} for tertiary C−H bonds (Lide, 1998−1999). Hence one expects that, all else being equal, a tertiary C−H will react faster than a secondary C−H, which in turn will react faster than a primary C−H. Greiner (1970), whose measurements of the absolute rate constants for OH reactions in the mid-1960s provided the first clue of the potential importance of OH in the troposphere, suggested that the rate constant for the overall reaction, k^{tot}, could be treated as the sum of contributions from each type of abstractable hydrogen in the following manner:

$$k^{tot} = N_p k_p + N_s k_s + N_t k_t. \qquad (A)$$

k_p, k_s, and k_t represent rate constants for the abstraction of primary, secondary, and tertiary hydrogens, respectively, and N_p, N_s, and N_t are the corresponding numbers of each kind of hydrogen. If the rate constants (k^{tot}) for a number of simple alkanes are known, the experimental data can be fit to obtain best values for k_p, k_s, and k_t. These can then be used to predict the rate constant for the reaction of OH with an alkane where experimental measurements have not been made.

This type of structure−reactivity relationship (SRR) works reasonably well for the simple alkanes. However, clearly one would expect that the nature of adjacent groups would also have an effect on the rate constant, albeit a smaller one than the type of C−H bond. A variant of the approach in Eq. (A) is to use rate constants per primary, secondary, or tertiary *group* modified by factors reflecting the adjacent groups. In this case,

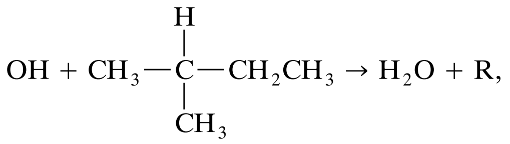
$$k'_p(CH_3X) = k^*_p F(X),$$

$$k'_s(CH_2XY) = k^*_s F(X)F(Y),$$

$$k'_t(CHXYZ) = k^*_t F(X)F(Y)F(Z),$$

where k^*_p, k^*_s, and k^*_t are the rate constants for the CH_3- *group*, the $-CH_2-$ *group*, and the $>CH-$ *group*, respectively, and the F factors reflect how the rate constants for the individual groups are modified by adjacent groups, X, Y, and Z. Recommended values (Kwok and Atkinson, 1995; Atkinson, 1997a) of these group rate constants are $k^*_p = 1.36 \times 10^{-13}$, $k^*_s = 9.34 \times 10^{-13}$, and $k^*_t = 1.94 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. The modifying F parameters at 298 K are taken as 1.00 for $X = CH_3$ and 1.23 for all of the other simple alkyl groups, $-CH_2-$, $>CH-$, and $>C<$. Other correction factors must be included for cyclic compounds (Atkinson, 1997a).

For example, the rate constant for the reaction of OH with 2-methylbutane,



$$OH + CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle H}{C}}-CH_2CH_3 \rightarrow H_2O + R,$$

can be estimated as follows:

$$k^{tot} = 2\left[k^*_p F(>CH-)\right] + k^*_t[F(CH_3-)F(CH_3-)F(-CH_2-)]$$

$$\begin{aligned}
&+ k_s^*[F(>\mathrm{CH}-)F(\mathrm{CH_3}-)] + k_p^*F(-\mathrm{CH_2}-)\\
&= 2(1.36\times10^{-13})[1.23]\\
&\quad +(1.94\times10^{-12})[1.0\times1.0\times1.23]\\
&\quad +(9.34\times10^{-13})[1.23\times1.00]\\
&\quad +(1.36\times10^{-13})(1.23)\\
&= (0.335+2.39+1.15+0.167)\times10^{-12}\\
&= 4.0\times10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}.
\end{aligned}$$

This is within 10% of the recommended value (Table 6.2) of 3.7×10^{-12} cm^3 molecule^{-1} s^{-1}.

A similar approach can be used for estimating rate constants with a variety of other organics such as alkenes, alcohols, and nitrates, although the agreement is not as good in many cases (Kwok and Atkinson, 1995).

In addition to this type of empirical approach, there are several other approaches that are related more directly to specific properties of the organic, such as the C–H bond dissociation enthalpies (Heicklen, 1981; Jolly *et al.*, 1985), ionization energy (Gaffney and Levine, 1979), or NMR shifts (Hodson, 1988). In addition, molecular orbital calculations (Klamt, 1993) and transition state theory (Cohen and Benson, 1987) have been applied.

2. Nitrate Radical (NO_3)

Like OH, the nitrate radical also abstracts a hydrogen atom, forming nitric acid and an alkyl radical:

$$NO_3 + RH \rightarrow HNO_3 + R. \tag{20}$$

The kinetics and mechanisms of nitrate radical reactions with alkanes and a variety of other organics relevant to the atmosphere are discussed in detail in two excellent reviews by Wayne *et al.* (1991) and Atkinson (1991). The kinetics of the NO_3–alkane reactions are summarized in Table 6.3, where it can be seen that, with the exception of methane, they are in the range 10^{-18}–10^{-16} cm^3 molecule^{-1} s^{-1}.

While these reactions are much slower than the corresponding OH reactions, the nighttime peak concentrations of NO_3 under some conditions are much larger than those of OH during the day, ~400 ppt vs 0.4 ppt. Even given the differences in concentration, however, as seen from the lifetimes in Table 6.1, the nitrate radical reaction is still relatively slow. While the removal of the alkanes by NO_3 is thus not expected to be very significant under most tropospheric conditions, reaction (20) can contribute to HNO_3 formation and the removal of NO_x from the atmosphere.

TABLE 6.3 Rate Constants at Room Temperature for Reaction of NO_3 Radicals with Alkanes[a]

Alkane	k (10^{-17} cm^3 molecule^{-1} s^{-1})
Methane	< 0.1
Ethane	0.14[b]
Propane	1.7[b]
n-Butane	4.59
2-Methylpropane	10.6
n-Pentane	8.7
2-Methylbutane	16
n-Hexane	11
2,3-Dimethylbutane	44
Cyclohexane	14
n-Heptane	15
n-Octane	19
n-Nonane	23

[a] From Atkinson (1997a).

[b] Estimated from group contributions as described in text.

The rate constants for the simple alkanes can be empirically fit by assigning rate constants to the primary and secondary C–H groups, along with substituent factors F used to modify these rate constants. The best fit to the data at 298 K are found for the following values (Atkinson, 1997a):

$$k_p^* = 7.0\times10^{-19}, \qquad F(\mathrm{CH_3}-) = 1.00,$$

$$k_s^* = 1.22\times10^{-17}, \qquad F(-\mathrm{CH_2}-) = 1.67.$$

However, this approach is not accurate for branched chain alkanes (Atkinson, 1997).

3. Chlorine Atoms (Cl)

Table 6.4 summarizes the rate constants for the reactions of chlorine atoms with alkanes. Structure–reactivity relationships have again been developed for

TABLE 6.4 Rate Constants for the Reactions of Cl Atoms with Alkanes[a]

Alkane	$k^{298\,\mathrm{K}}$ (10^{-11} cm^3 molecule^{-1} s^{-1})	A (10^{-12} cm^3 molecule^{-1} s^{-1})	E_a/R (K)
Methane	0.010	9.6	1350
Ethane	5.9	81	95
Propane	13.7	120	−40
n-Butane	21.8	218	0
Isobutane	14.3		
n-Pentane	28		
n-Hexane	34		
n-Heptane	39		
n-Octane	46		
n-Nonane	48		
n-Decane	55		

[a] From Atkinson (1997a); temperature dependence is in form $k = Ae^{-E_a/RT}$.

298 K (Atkinson, 1997a):

$$k_p^* = 3.5 \times 10^{-11}, \quad F(CH_3–) = 1.00,$$

$$k_s^* = 9.3 \times 10^{-11}, \; F(–CH_2–) = F(>CH–) = F(>C<) = 0.79,$$

$$k_t^* = 6.8 \times 10^{-11}.$$

The reaction involves abstraction of a hydrogen atom to form HCl:

$$Cl + RH \rightarrow HCl + R. \qquad (21)$$

D. REACTIONS OF ALKYL (R), ALKYLPEROXY (RO_2), AND ALKOXY (RO) RADICALS IN AIR

As already seen, the reactions of OH, NO_3, and Cl with alkanes generate alkyl radicals. We shall see in the subsequent sections of this chapter that the production of alkyl radicals of various types is a general characteristic of organic oxidations. Here we will trace the atmospheric fates of typical alkyl radicals formed in OH, NO_3, and Cl atom oxidations of alkanes. However, the principles are general and can be applied to those formed by the reactions of other organics such as alkenes as well.

1. Alkyl Radicals (R)

The only fate of alkyl radicals in air is reaction with O_2:

$$R + O_2 \overset{M}{\rightarrow} RO_2. \qquad (22)$$

For the case where R is a methyl group, the reaction is in the falloff region at 1 atm, and for C_2H_5, it is close to the high-pressure limit. For C_3H_7 and above, a value for the effective second-order rate constant, k_∞, of $\sim(0.8–2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} means that the lifetime of an alkyl radical at $\sim$1 atm in air is $\sim$10 ns.

A second possible channel, in which the alkene and HO_2 are formed from decomposition of the excited RO_2^* intermediate before it is stabilized, is very small; thus, this channel is $< 1\%$ for $C_2H_5 + O_2 \rightarrow (C_2H_5O_2)^* \rightarrow C_2H_4 + HO_2$ and $< 0.13\%$ for $C_3H_7 + O_2 \rightarrow (C_3H_7O_2)^* \rightarrow C_3H_6 + HO_2$ at 1 atm pressure and room temperature but becomes important at higher temperatures, e.g., in combustion systems (Kaiser, 1995; Benson, 1996; Kaiser and Wallington, 1996a).

2. Alkylperoxy Radicals (RO_2)

Alkylperoxy radicals (RO_2) in the atmosphere react primarily with NO, HO_2, and other RO_2. Reaction with the nitrate radical, NO_3, at night, has been recently recognized as being important as well. A less important reaction is that with NO_2. There are two excellent reviews of RO_2 chemistry by Lightfoot *et al.* (1992) and Wallington *et al.* (1992), including the thermochemistry, spectroscopy, kinetics, and mechanisms. The reader should consult these for references to the original work in this area.

a. Reactions with NO

The reactions of RO_2 with NO are quite fast and do not vary significantly with the nature of the alkyl group (Wallington *et al.*, 1992; Lightfoot *et al.*, 1992; Masaki *et al.*, 1994; Maricq and Szente, 1996; Eberhard and Howard, 1996, 1997). The recommended rate constants at 298 K are 7.5×10^{-12} cm^3 molecule^{-1} s^{-1} for $R = CH_3$ and $(8–9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for all other R groups (Atkinson, 1997a; Eberhard and Howard, 1997).

The major path produces alkoxy radicals (RO) and NO_2:

$$RO_2 + NO \rightarrow RO + NO_2. \qquad (23a)$$

There is a second path for the larger RO_2 radicals corresponding to addition of the NO and followed by isomerization to form an alkyl nitrate:

$$RO_2 + NO \rightarrow RONO_2. \qquad (23b)$$

The mechanism is postulated to be (Darnall *et al.*, 1976)

$$\begin{tikzcd} RO_2 + NO \arrow[r] & (ROONO)^* \arrow[r] \arrow[d] & RO + NO_2, \quad (23a) \\ & (RONO_2)^* \arrow[r, "M"] & RONO_2. \quad (23b) \end{tikzcd}$$

Hence one would expect the second channel to depend on the size of the radical and to show some pressure dependence as well as a negative temperature dependence, all of which are found to be the case.

Table 6.5 shows the fraction of the total reaction forming the stable alkyl nitrate, i.e., the branching ratio $k_{23b}/(k_{23a} + k_{23b})$ for some simple alkylperoxy radicals at 1 atm and room temperature. The ratio is smaller for primary and tertiary RO_2; in general, the ratio k_{23b}/k_{23a} for primary and tertiary alkylperoxy radicals is about 40 and 30%, respectively, of that for secondary RO_2 (Atkinson, 1997a).

It can be seen from the data in Table 6.5 that the fraction of the total RO_2 + NO reaction that forms the stable alkyl nitrate at 1 atm can be substantial, as much as 35% for the larger radicals. (However, more recent measurements by Aschmann *et al.* (1999) give lower nitrate yields for the hexyl, heptyl, and octyl alkylperoxy radicals, ranging from 15% for the sum of (2-hexyl + 3-hexyl) to 24% for the sum of (2-octyl + 3-octyl + 4-octyl RO_2.) It is thought that such reactions may be significant sources of such alkyl nitrates and perhaps form part of the "missing NO_y" (see Section E.3).

TABLE 6.5 Yields of $RONO_2$ in RO_2 + NO Reactions at Room Temperature and 1 atm[a]

R	Branching ratio = $k_{23b}/(k_{23a}+k_{23b})$
Ethane	
Ethyl	≤0.014
Propane	
1-Propyl	0.020
2-Propyl	0.05
n-Butane	
1-Butyl	≤0.04
2-Butyl	0.083
Isobutane	
2-Methyl-1-propyl	0.075
tert-Butyl	0.18
n-Pentane	
1-Pentyl	0.06
2-Pentyl	0.13
3-Pentyl	0.12
Isopentane	
2-Methyl-1-butyl	0.040
2-Methyl-2-butyl	0.044–0.056
2-Methyl-3-butyl	0.074–0.15
3-Methyl-1-butyl	0.043
n-Pentane	
n-Pentyl	0.51
n-Hexane	
1-Hexyl	0.12
2-Hexyl	0.22[b]
3-Hexyl	0.22[b]
2-Methylpentane	
2-Methyl-2-pentyl	0.035
3-Methylpentane	
3-Methyl-2-pentyl	0.14–0.16
n-Heptane	
1-Heptyl	0.20
2-Heptyl	0.32[b]
3-Heptyl	0.31[b]
4-Heptyl	0.29[b]
n-Octane	
1-Octyl	0.36
2-Octyl	0.35[b]
3-Octyl	0.34[b]
4-Octyl	0.32[b]

[a] Adapted from Lightfoot *et al.* (1992).

[b] Aschmann *et al.* (1999) have measured 0.15 for the sum of (2-hexyl + 3-hexyl), 0.19 for (2-heptyl + 3-heptyl + 4-heptyl), and 0.24 for (2-octyl + 3-octyl + 4-octyl).

There is evidence that in some cases, the alkoxy radical formed in the RO_2 + NO reaction contains sufficient excess energy that it can decompose under atmospheric conditions. This is the case, for example, for some of the alkoxy radicals formed in the oxidation of alternate CFCs (see Chapter 13.D.2a). It has also been postulated for the alkoxy radical formed from the NO reaction with $HOCH_2CH_2O_2$, formed in the OH + C_2H_4 reaction (Orlando *et al.*, 1998). In the latter case, about 25% of the excited $(HOCH_2CH_2O)^*$ decomposes to HCHO + CH_2OH, with the remainder being stabilized. The stabilized radicals then decompose to HCHO + CH_2OH or react with O_2.

b. Reactions with HO_2 and RO_2

Alternate fates of RO_2 are reactions with HO_2 or with other RO_2 radicals:

$$RO_2 + HO_2 \rightarrow ROOH + O_2, \tag{24a}$$

$$\rightarrow \text{Carbonyl compound} + H_2O + O_2, \tag{24b}$$

$$\rightarrow ROH + O_3, \tag{24c}$$

$$RO_2 + R'O_2 \rightarrow \text{Products}. \tag{25}$$

The reaction of simple alkylperoxy radicals with HO_2 is believed to occur primarily by path (24a) to form the hydroperoxide, although for more complex RO_2 radicals there is some evidence for some contribution of the other paths. The rate constant (k_{24}) at room temperature is 5.2×10^{-12} for R = CH_3, increasing to 7.7×10^{-12} for C_2H_5 and $\sim 1.5 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for the larger radicals (Lightfoot *et al.*, 1992; Fenter *et al.*, 1993; Atkinson, 1997a).

The self-reaction of RO_2 radicals, i.e., $RO_2 + RO_2$, or their reaction with alkylperoxy radicals of different structure, i.e., $RO_2 + R'O_2$ as shown in reaction (25), is complex. In principle, one expects an excited intermediate $(ROOOOR)^*$ to be formed, which could decompose by a number of different paths; i.e., the overall reaction could be one of the following paths:

$$RO_2 + RO_2 \rightarrow 2RO + O_2, \tag{25a}$$

$$\rightarrow ROH + RCHO + O_2, \tag{25b}$$

$$\rightarrow ROOR + O_2. \tag{25c}$$

The term "branching ratio" is used to describe the relative importance of each path. Thus the branching ratio for (25a) is the fraction of the total reaction proceeding by this path and is given by $k_{25a}/(k_{25a} + k_{25b} + k_{25c})$. Clearly, the sum of the branching ratios for a reaction must add up to 1.0.

Table 6.6 gives some of the values of the recommended rate constants for the self-reaction, k_{25}, and

TABLE 6.6 Recommended Rate Constants and Branching Ratios at Room Temperature for the Self-Reactions of Some RO_2 Radicals[a]

		Branching ratios		
RO_2	$k_{25}^{298\,\mathrm{K}}$ ($\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$)	(25a) ($2RO + O_2$)	(25b) ($ROH + RCHO + O_2$)	(25c) ($ROOR + O_2$)
CH_3O_2	3.7×10^{-13}	0.33 ± 0.05[b]	~ 0.67[f]	Minor
		0.30 ± 0.08[c]	~ 0.70[f]	
		0.41 ± 0.04[d]		< 0.006[d]
$HOCH_2CH_2O_2$	2.3×10^{-12}	0.50[e]	0.50	
$C_2H_5O_2$	6.4×10^{-14}	0.63 ± 0.06[b,c]	0.32[g]	0.05[c]
$n\text{-}C_3H_7O_2$	3×10^{-13}			
$i\text{-}C_3H_7O_2$	1×10^{-15}	0.56	0.44	0
$HOCH(CH_3)CH(CH_3)O_2$	6.7×10^{-13}[e]	~ 0.2[e]		
$t\text{-}C_4H_9O_2$	2×10^{-17}			
$HOC(CH_3)_2C(CH_3)_2O_2$	4×10^{-15}[e]	1.0[e]		

[a] Rate constants from IUPAC recommendations (Atkinson *et al.*, 1997a).

[b] Lightfoot *et al.* (1992).

[c] Wallington *et al.* (1992).

[d] Tyndall *et al.* (1998).

[e] Boyd and Lesclaux (1997).

[f] Calculated assuming path c is negligible.

[g] Calculated from the branching yields of the other two paths.

where there are available data, the branching ratios. For the simple alkylperoxy radicals, the contribution of path (c) to form a peroxide and O_2 is generally small, whereas both paths (a) and (b) contribute significantly at room temperature. The self-reaction of primary RO_2 occurs with the highest rate constant, $\sim 10^{-13}$, that of secondary RO_2 is slower at $\sim 10^{-15}$, and that of tertiary RO_2 is even slower at 10^{-17} $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. Kirchner and Stockwell (1996) have parameterized the rate constants for the self-reactions in the form

$$k\ (\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) = 2 \times 10^{-14} \exp\left[3.8A - 5\alpha + \frac{3N}{1 + 0.02N^2}\right],$$

where $A = 0$ for simple alkyl radicals and 1 if there are additional oxygen atoms in the alkyl group, α is the number of R or RO groups attached to the $-COO$ group, and N is the number of carbon atoms in the RO_2. This gives values within about a factor of three of measured rate constants and can be used for $N \leq 7$. For larger RO_2, the value calculated with $N = 7$ is recommended since the rate constants do not increase significantly beyond that. This formulation is not appropriate for use for peroxy radicals derived from the reactions of OH with terminal alkenes or for those with functional groups containing oxygen attached to the terminal carbon, e.g., $(HO)(R_1)(R_2)COO$ (Kirchner and Stockwell, 1996).

Atkinson (1997a) recommends values of 2.5×10^{-13}, 5×10^{-15}, and 2×10^{-17} $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ for the self-reaction of primary, secondary, and tertiary RO_2 radicals, respectively, with uncertainties of at least a factor of five. For the cross-reaction of two different radicals R_aO_2 and R_bO_2, the recommendation is $k \sim 2(k_a k_b)^{0.5}$, based on Madronich and Calvert (1990), where k_a and k_b are the self-reaction rate constants for each of the two radicals. This generally gives rate constants within a factor of two of the experimental value for the cases where such rate constants are available. However, in some cases when the RO_2 self-reaction is fast, e.g., for $CH_3C(O)O_2$, the cross combination reactions with CH_3O_2 or $C_2H_5O_2$ also tend to be fast (e.g., Villenave and Lesclaux, 1996).

c. Reactions with NO_3

Simple alkyl peroxy radicals have been shown to react with NO_3, e.g., for CH_3O_2:

$$CH_3O_2 + NO_3 \rightarrow CH_3O + NO_2 + O_2. \quad (26)$$

The rate constant is in the range of $(1-3) \times 10^{-12}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K (e.g., Biggs *et al.*, 1994a, 1994b; Kukui *et al.*, 1995; Daële *et al.*, 1995), similar to that for the $CH_3C(O)O_2$ reaction with NO_3 (4×10^{-12} $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$; Canosa-Mas *et al.*, 1996). Although there are few data on the range of possible NO_3^- peroxy radical reactions, as discussed in more detail later, it appears that such reactions may be very important at night (e.g., Platt *et al.*, 1990; Canosa-Mas *et al.*, 1996; Kirchner and Stockwell, 1996).

d. Reactions with NO_2

Alkylperoxy radicals can also react with NO_2 in a three-body reaction to form a peroxynitrate, RO_2NO_2:

$$RO_2 + NO_2 \overset{M}{\rightarrow} ROONO_2.$$

This reaction is in the falloff region at 1 atm for R = CH_3 and C_2H_5 but for larger radicals is effectively in the high-pressure limit with a rate constant $\sim 9 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. The reaction is reversible in that the peroxynitrates thermally decompose in the reverse of this reaction. As we shall see, this reaction of RO_2 with NO_2 is not significant compared to its reactions with NO, HO_2, or other RO_2 under most tropospheric conditions.

e. Fate of RO_2 under Typical Tropospheric Conditions

To compare the relative importance of these potential atmospheric fates of RO_2 under typical polluted conditions, and particularly the relative importance of the NO reaction, let us take the $C_2H_5O_2$ radical as an example. The lifetime of $C_2H_5O_2$ with respect to reaction with NO, HO_2, or $C_2H_5O_2$ at peak concentrations of 20 ppb, 40 ppt, and 40 ppt, respectively, can then be calculated from $\tau = 1/k[X]$ as 0.2, 1.3×10^2 s and 1.6×10^4 s, respectively. (Note that the NO and HO_2/RO_2 peaks will not occur simultaneously.) At night, with an NO_3 concentration of 100 ppt, the lifetime would be ~ 135 s, assuming a rate constant of 3×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. In short, in areas impacted by anthropogenic emissions, the reaction of RO_2 with NO will predominate.

One can then ask under what conditions the reaction of RO_2 with NO will be equivalent in rate to that with HO_2. To make this calculation, one can estimate the concentration of NO at which $k_{23}[NO] = k_{24}[HO_2]$. Since $k_{23} \sim k_{24} \sim 1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, this suggests that the removal of RO_2 by HO_2 will compete with that by NO when the concentrations of these two, HO_2 and NO, are equal. Typical peak HO_2 concentrations in polluted areas are believed to be of the order of 10^9 cm^{-3}, corresponding to ~ 40 ppt. "Average" HO_2 concentrations may more typically be $(1–2) \times 10^8$ cm^{-3}, corresponding to concentrations of 4–8 ppt. Such equivalent small concentrations of NO are found in the remote troposphere and, under such conditions, reactions of RO_2 with HO_2 or other RO_2 can become quite important (see Section J.2b).

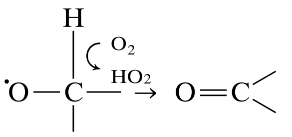
In addition, the reaction of RO_2 with NO_3 at night can become significant. For example, at HO_2 of 4 ppt and NO_3 of 10 ppt, which have been reported in a relatively clean marine region (Carslaw *et al.*, 1997), the lifetimes of RO_2 relative to reaction with these species are comparable at $\sim 10^3$ s. Kirchner and Stockwell (1996) predict that in more polluted areas, the RO_2 + NO_3 reactions may be important. For example, under conditions chosen to be representative of aged polluted air masses mixing with rural air masses, they calculate that 77% of the total RO_2 at night reacts with NO_3; overall (both day and night), however, only 0.66% is removed by reaction with NO_3.

The relative magnitude of the RO_2 + NO reaction compared to the RO_2 + HO_2 or RO_2 reactions is a critical factor in ozone formation in the troposphere. As discussed in more detail in Section J, if RO_2 + NO predominates, NO_2 is formed and through its photolysis to $O(^3P)$, O_3 is ultimately generated. On the other hand, the RO_2 + HO_2/RO_2 reactions can lead to the formation of stable products such as ROOH, without conversion of an NO to NO_2. In this case, no O_3 is formed and indeed, through its photolysis to form OH radicals and subsequent reactions with HO_2 and OH, destruction of O_3 occurs.

3. Alkoxy Radicals (RO)

The reactions of RO_2 with NO and with RO_2 generate alkoxy radicals (RO). Alkoxy radicals have several possible atmospheric fates, depending on their particular structure. These include reaction with O_2, decomposition, and isomerization; as we shall see, reactions with NO and NO_2 are unlikely to be important under most tropospheric conditions. Atkinson *et al.* (1995b) and Atkinson (1997b) have reviewed reactions of alkoxy radicals and β-hydroxyalkyl radicals:

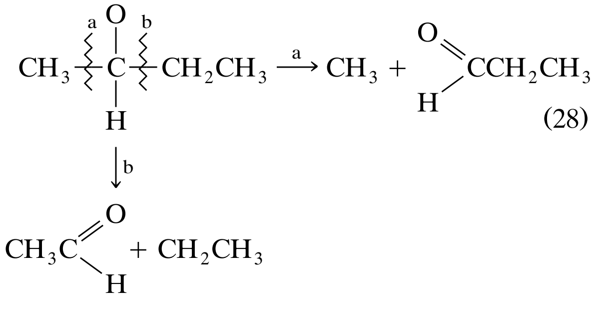
- Reaction with O_2: If the carbon to which the alkoxy oxygen is attached also has a hydrogen, this H can be abstracted to give HO_2 and a carbonyl compound:



(27)

This reaction may proceed via the initial addition of O_2 to give a trioxy intermediate (–C–OOO•) followed by rearrangement and elimination of HO_2 (e.g., Jungkamp *et al.*, 1997). Atkinson (1997a, 1997b) recommends rate constants of 9.5×10^{-15} and 8×10^{-15} cm^3 $molecule^{-1}$ s^{-1} at 298 K for primary RCH_2O and secondary R_1R_2CHO radicals, respectively.

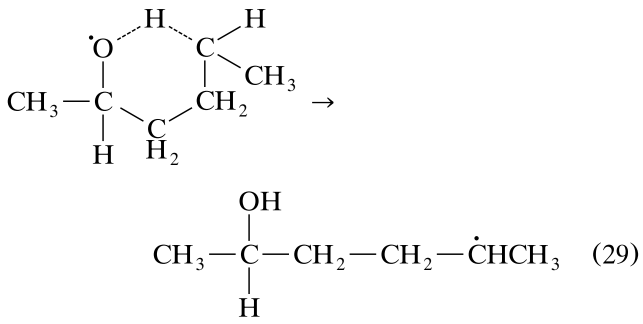
- Scission of a C–C bond:



(28)

Scission to produce the larger alkyl radical dominates. For example, in the case of the 2-butoxy radical in Eq. (28), path (b) dominates over path (a) by more than two orders of magnitude (see Atkinson, 1997b, and references therein).

- If the alkoxy radical has four or more carbon atoms and can form a 6-membered transition state via the alkoxy oxygen abstracting H from a C–H bond, an intramolecular isomerization may occur:



$$CH_3-\underset{H}{\overset{OH}{C}}-CH_2-CH_2-\dot{C}HCH_3 \quad (29)$$

Structure–reactivity relationships have also been developed for these isomerizations. For H abstraction from a CH_3–X, CH_2–XY, or CH–XYZ, respectively, through a 6-membered transition state, rate constants of 1.6×10^5, 1.6×10^6, and 4×10^6 s^{-1}, respectively, are recommended (Atkinson, 1997a, 1997b). These are corrected for neighboring group effects using $F(-CH_3) = 1.0$, $F(-CH_2-) = F(>CH-) = F(>C<) = 1.27$, and $F(-OH) = 4.3$.

- Reaction with NO or NO_2:

$$RO + NO \overset{M}{\rightarrow} RONO, \quad (30)$$

$$RO + NO_2 \overset{M}{\rightarrow} RONO_2. \quad (31)$$

The latter reactions with NO and NO_2 are less likely than the first three possibilities. With $k_{30} \sim k_{31} \sim 3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K and 1 atm pressure, the pseudo-first-order rate of reaction, k_{30}[NO] or k_{31}[NO_2], is ~75 s^{-1} at 100 ppb of NO or NO_2. For a species such as $(CH_3)_3CO^{\bullet}$ that can only decompose (and then only relatively slowly), these reactions could be responsible for ~10% of the alkoxy radical reaction at the relatively high NO and NO_2 concentrations of 100 ppb.

Table 6.7 compares the estimated rates of reaction with O_2, decomposition, and isomerization for some alkoxy radicals with different structures. It is important to recognize that there is a great deal of uncertainty in many of these estimates, and this is an area that clearly requires more research. However, given these caveats, it is clear that where isomerization is possible, it usually predominates at room temperature. (Note, however, that this will be slower at the lower temperatures found at higher altitudes.) When isomerization is not feasible, e.g., for the smaller alkoxy radicals or for branched species, reaction with O_2 is always significant and usually predominates.

As the size of the alkane increases, so does the relative importance of isomerization. For example, consider the competition between isomerization and reaction with O_2 for the *n*-pentoxy radical:

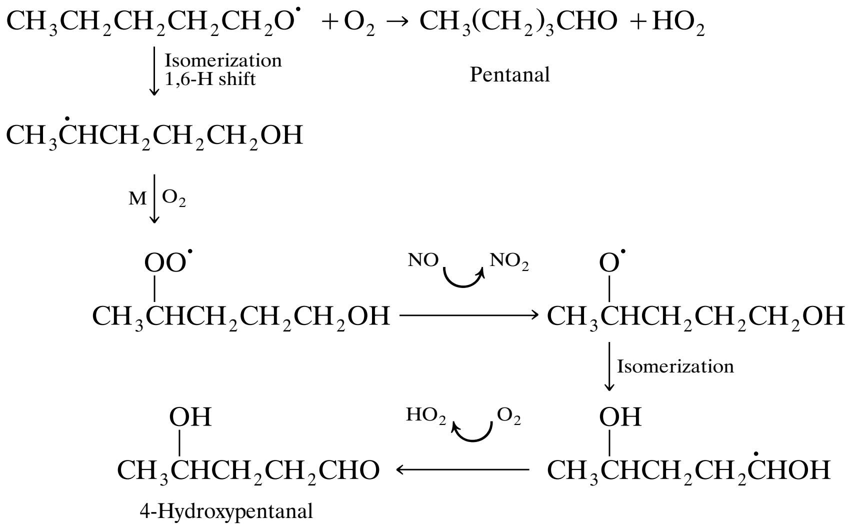
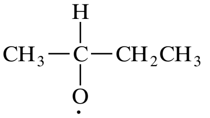
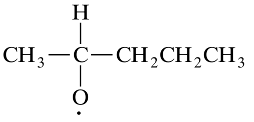
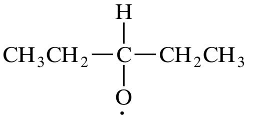
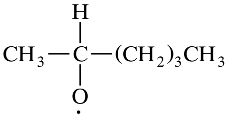
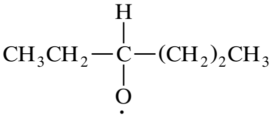
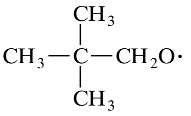


TABLE 6.7 Rates (s^{-1}) of Alkoxy Radical Reactions at 298 K and 1 atm Air[a]

RO	Decomposition	Reaction with O_2[b]	Isomerization
$CH_3O\cdot$	5.3×10^{-2}	1×10^4	
$C_2H_5O\cdot$	0.3	5×10^4	
$n\text{-}C_4H_9O\cdot$	5.8×10^2	5×10^4	2.0×10^5
 $CH_3-\underset{\underset{\cdot}{O}}{\overset{H}{C}}-CH_2CH_3$	2.3×10^4	4×10^4	
$(CH_3)_3CO\cdot$	1×10^3		
 $CH_3-\underset{\underset{\cdot}{O}}{\overset{H}{C}}-CH_2CH_2CH_3$	1.7×10^4	4×10^4	2×10^5
 $CH_3CH_2-\underset{\underset{\cdot}{O}}{\overset{H}{C}}-CH_2CH_3$	1.6×10^4	4×10^4	
 $CH_3-\underset{\underset{\cdot}{O}}{\overset{H}{C}}-(CH_2)_3CH_3$	2.8×10^4	4×10^4	2×10^6
 $CH_3CH_2-\underset{\underset{\cdot}{O}}{\overset{H}{C}}-(CH_2)_2CH_3$	3.4×10^4	4×10^4	2×10^5
$(CH_3)_3COCH_2O\cdot$	1.1×10^{-3}	3.8×10^6	2.0×10^5
 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2O\cdot$	9.8×10^3	2.4×10^4	$\geq 7 \times 10^4$

[a] Adapted from Atkinson (1994, 1997a, 1997b) and Atkinson *et al.* (1995b).

[b] Shown as $k[O_2]$ (s^{-1}), based on recommended rate constants for RO + O_2 (Atkinson, 1997a).

The last step, forming 4-hydroxypentanal, which overall is net hydrogen abstraction from an α-hydroxy radical to form a carbonyl compound and HO_2, is characteristic of this type of radical; it is discussed later in more detail with respect to the reaction of the smallest α-hydroxy radical, CH_2OH, with O_2 to form HCHO + HO_2.

The relative importance of the two pathways is reflected in the ratio of the yields of the hydroxycarbonyls compared to the carbonyl products with the same number of carbons as the parent compound as well as in the absolute yields of the latter products. Thus the carbonyl product yields decrease from 70% for the *n*-butane reaction to 0.7% for the *n*-octane reaction; at the same time, the ratio of hydroxycarbonyl products to carbonyls increases from 0.14 to 50 (Kwok *et al.*, 1996a). In short, isomerization becomes increasingly more important for the larger alkoxy radicals.

A study by Eberhard *et al.* (1995) illustrates the differences in the importance of the various paths that are associated with what may appear at first glance to be small changes in structure. They assessed the relative importance of the various reaction paths for the 2-hexoxy and 3-hexoxy radicals expected from the abstraction of a hydrogen in either the 2- or 3-position, respectively (e.g., by OH or NO_3), followed by addition of O_2 and reaction with NO. Based on the final product yields, they estimated the branching ratios for each possible reaction path. Figure 6.1 shows the possible reactions of each of these alkoxy radicals and the branching ratios they calculate, which are in reasonable agreement with the estimates shown in Table 6.7.

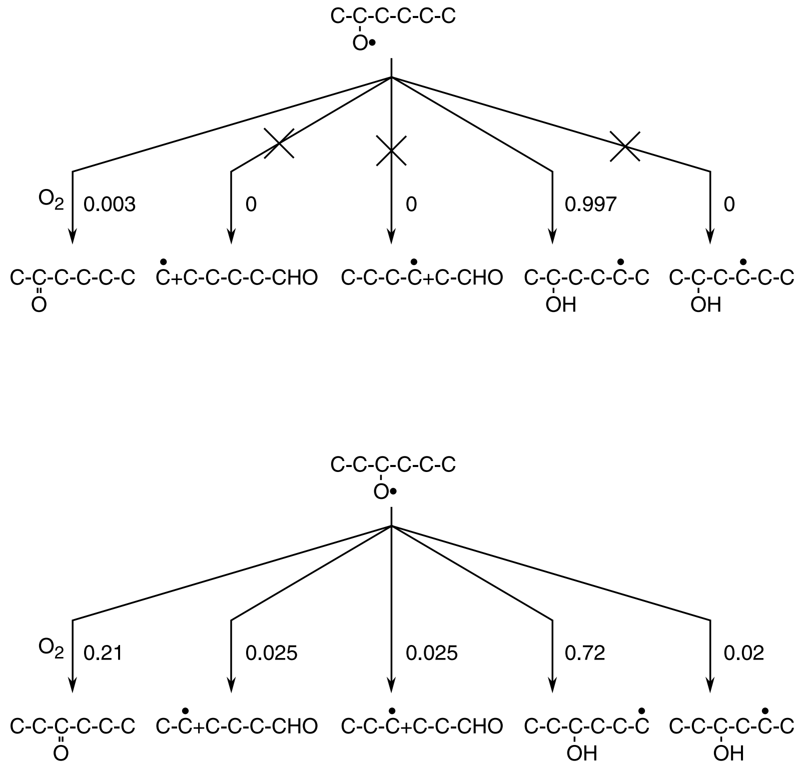


FIGURE 6.1 Possible fates of the 2-hexoxy and 3-hexoxy free radicals (adapted from Eberhard *et al*., 1995).

It should be noted that some alkoxy radicals derived from oxygenated compounds may have some unique chemistry in addition to these reactions. For example, Tuazon *et al*. (1998b) have shown that alkoxy radicals derived from OH + acetate reactions, i.e., $R_1C(O)OCH(O^{\bullet})R_2$, rearrange and decompose to $R\dot{C}O$ and the acid RC(O)OH.

4. Summary of R, RO_2, and RO Radical Reactions in the Troposphere

In summary, alkyl radicals, R, are all converted to alkylperoxy radicals, RO_2, in the troposphere. RO_2 reacts with NO, except in very remote regions where the concentration of NO is of the order of ~40 ppt or less. The reaction converts NO to NO_2 and hence acts as a source of O_3 via the NO_2 photolysis. For the larger alkylperoxy radicals, a substantial portion of the RO_2 + NO reaction also gives the stable alkyl nitrate, $RONO_2$.

As discussed in more detail in Section J.2.b, in remote regions where the NO concentrations are very low, reactions of RO_2 with other peroxy radicals such as HO_2 and RO_2 occur. Finally, under very high concentrations of NO_2, RO_2 may react with NO_2.

The alkoxy radical, RO, generated by RO_2 reactions can react with O_2, decompose, or undergo an isomerization, depending on the structure of the radical. At very high NO_x concentrations for a few alkoxy radicals, reactions with NO and NO_2 may also occur to a small extent. Figure 6.2 summarizes these possibilities.

E. REACTIONS OF ALKENES (INCLUDING BIOGENICS)

1. Hydroxyl Radical (OH)

As for other organics in the atmosphere, the OH radical is a major oxidant for alkenes. Table 6.8 gives the rate constants for some OH–alkene reactions as well as their temperature dependence in Arrhenius form. Several points are noteworthy: (1) the reactions are very fast, approaching 10^{-10} cm^3 $molecule^{-1}$ s^{-1} for the larger alkenes; (2) the rate constants have a pressure dependence; (3) the apparent Arrhenius activation energies are "negative."

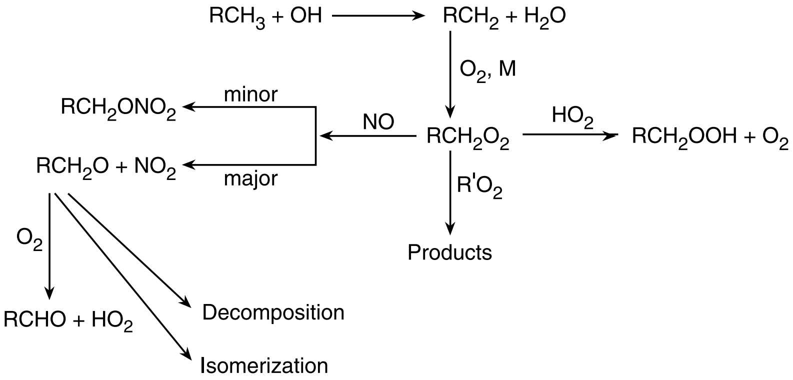


FIGURE 6.2 Summary of alkane oxidation by OH in air.

TABLE 6.8 Rate Constants and Temperature Dependence[a] for the Reactions of OH Radicals with Alkenes[e] at 1 atm Total Pressure of Air[b]

Alkene	k^c (10^{-12} cm^3 molecule^{-1} s^{-1})	A (10^{-12} cm^3 molecule^{-1} s^{-1})	E_a/R (K)
Ethene	8.52	1.96	−438
Propene	26.3	4.85	−504
1-Butene	31.4	6.55	−467
cis-2-Butene	56.4	11.0	−487
trans-2-Butene	64.0	10.1	−550
2-Methylpropene	51.4	9.47	−504
1-Pentene	31.4		
cis-2-Pentene	65		
trans-2-Pentene	67		
Cyclopentene	67		
3-Methyl-1-butene	31.8	5.32	−533
2-Methyl-1-butene	61		
2-Methyl-2-butene	86.9	19.2	−450
1-Hexene	37		
Cyclohexene	67.7		
1-Heptene	40		
trans-2-Heptene	68		
Cycloheptene	74		
1,3-Butadiene	66.6	14.8	−448
2-Methyl-1,3-butadiene (isoprene)	101	25.4	−410
Camphene	53		
2-Carene	80		
Limonene	171		
α-Phellandrene	313		
β-Phellandrene	168		
α-Pinene	53.7	12.1	−444
β-Pinene	78.9	23.8	−357
α-Terpinene	363		
γ-Terpinene	177		
Terpinolene	225		
Methyl vinyl ketone	18.8[d]		
Methacrolein	33.5[d]		

[a] $k = Ae^{-E_a/RT}$; valid only for the 250–425 K range.

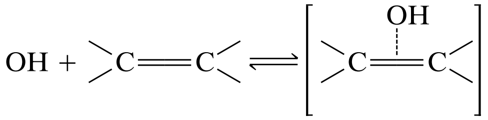
[b] From Atkinson (1997a).

[c] High-pressure limiting rate constants (k_∞) except for C_2H_4 and C_3H_6.

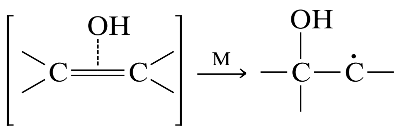
[d] From Atkinson (1994).

[e] See Fig. 6.22 for structures of biogenics.

These observations are consistent with the primary reaction path being addition of OH to the double bond to form an adduct or intermediate that can decompose back to the reactants, or be stabilized:



(32, −32)



(33)

This mechanism has been confirmed by the mass spectrometric observation of the OH–alkene adducts themselves (e.g., Morris *et al.*, 1971; Hoyermann and Sievert, 1983). Only at low pressures for the smaller alkenes is decomposition back to reactants significant.

However, this does illustrate the importance of understanding the fundamental mechanisms in order to extrapolate to atmospheric conditions reliably. A number of experimental techniques used for studying gas-phase kinetics and mechanisms require low pressures and, under these conditions, decomposition of the OH–alkene adduct can predominate. As long as the fundamental mechanisms are understood and the kinetics determined as a function of pressure, extrapolation to atmospheric conditions is possible. Clearly, confirmation using studies at atmospheric pressure is also important.

Hydrogen atom abstraction can occur to a small extent, particularly with larger and more highly branched compounds. However, the contribution of this path is, overall, relatively small. For example, for the reaction with 3-methyl-1-butene, where there is a weaker allylic C–H bond, ~5–10% of the reaction proceeds by abstraction at 1 atm in air (Atkinson *et al.*, 1998).

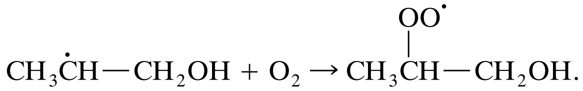
For all but the two smallest alkenes, ethene and propene, the rate constants are at their high-pressure limits at 1 atm, and even for these two compounds, the effective rate constant is within ~10% of k_∞.

In the case of unsymmetrical alkenes, the OH radical can add to either end of the double bond. There is evidence that, as expected, it preferentially adds to form the secondary radical. For example, for the propene reaction (Cvetanovic, 1976), ~65% of the adducts formed correspond to (34a) and 35% to (34b):

$$OH + CH_3CH{=}CH_2 \rightarrow CH_3\dot{C}H{-}CH_2OH, \quad (34a)$$

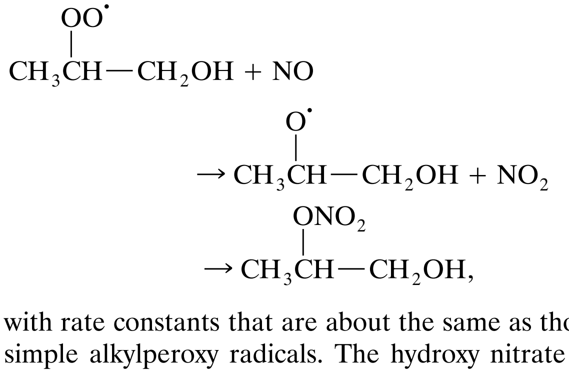
$$\rightarrow CH_3CH(OH){-}\dot{C}H_2. \quad (34b)$$

Because the β-hydroxyalkyl radicals formed are substituted alkyl radicals, they react with O_2 to form alkylperoxy radicals, e.g.,



$$CH_3\dot{C}H{-}CH_2OH + O_2 \rightarrow CH_3\overset{\overset{\displaystyle OO^{\bullet}}{|}}{C}H{-}CH_2OH. \quad (35)$$

These β-hydroxyalkyperoxy radicals undergo the same reaction discussed earlier for RO_2 radicals, i.e., reaction primarily with NO,



$$CH_3\overset{\overset{\displaystyle OO^{\bullet}}{|}}{C}H{-}CH_2OH + NO$$

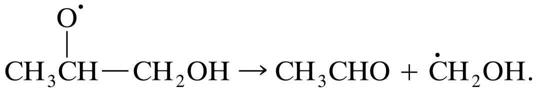
$$\rightarrow CH_3\overset{\overset{\displaystyle O^{\bullet}}{|}}{C}H{-}CH_2OH + NO_2 \quad (36a)$$

$$\rightarrow CH_3\overset{\overset{\displaystyle ONO_2}{|}}{C}H{-}CH_2OH, \quad (36b)$$

with rate constants that are about the same as those for simple alkylperoxy radicals. The hydroxy nitrate yields for some simple C_4–C_6 alkenes are ~2–6%, about half those for simple alkyl radicals (Table 6.5) (e.g., O'Brien *et al.*, 1998; Chen *et al.*, 1998). At low concentrations of NO, these RO_2 radicals also react with HO_2 and other RO_2 radicals (e.g., see Hatakeyama *et al.*, 1995; and Tuazon *et al.*, 1998a).

There is increasing evidence that for some reactions, the RO_2 + NO reaction produces a fraction of the alkoxy radicals with sufficient energy that they decompose immediately. For example, Orlando *et al.* (1998) observed that in the reaction of OH with C_2H_4, approximately 25% of the $HOCH_2CH_2O$ radicals generated in the reaction of $HOCH_2CH_2OO$ with NO decomposed before they could be collisionally stabilized. Similar observations have been made for RO_2 from the reactions of alternate CFCs (see Chapter 13).

The β-hydroxyalkoxy radicals such as that formed in (36a) can, in principle, react as discussed earlier, i.e., with O_2, decompose, or, for the larger radicals, undergo intramolecular isomerization. For the small alkenes ($\leq C_4$), decomposition appears to be the most important process (e.g., Tuazon *et al.*, 1998a). For example, for the β-hydroxyalkoxy radical formed in (36a), the primary fate is



$$CH_3\overset{\overset{\displaystyle O^{\bullet}}{|}}{C}H{-}CH_2OH \rightarrow CH_3CHO + \dot{C}H_2OH. \quad (37)$$

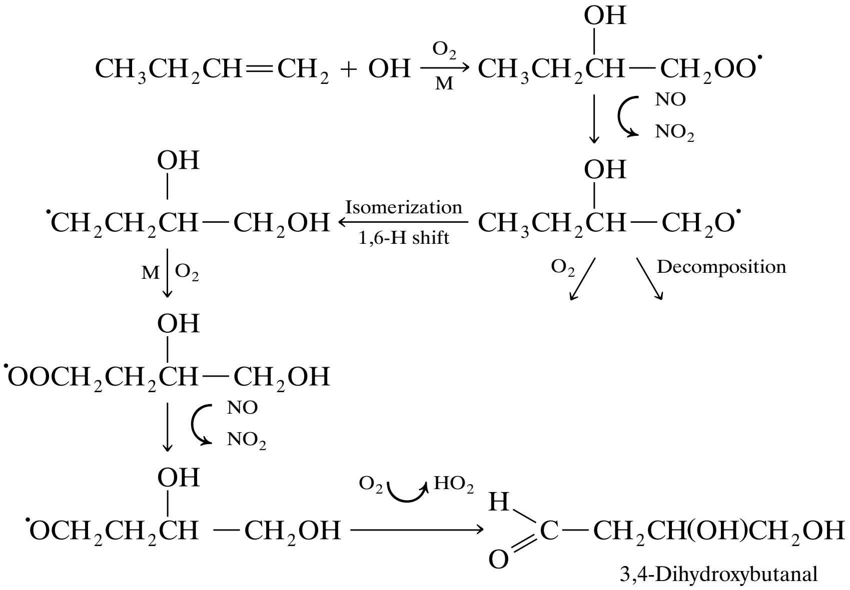
In the case of the stabilized alkoxy radical formed in the ethene reaction, decomposition and reaction with

O_2 are both important at 1 atm in air (Niki *et al.*, 1981; Orlando *et al.*, 1998):

$$CH_2(OH)CH_2\dot{O} + O_2 \rightarrow CH_2(OH)CHO + HO_2, \qquad (38)$$

$$CH_2(OH)CH_2\dot{O} \rightarrow HCHO + \dot{C}H_2OH. \qquad (39)$$

For the β-hydroxyalkoxy radicals formed from alkenes C_5 and larger, there is experimental evidence that isomerization starts to dominate (e.g., see Atkinson *et al.*, 1995d; Kwok *et al.*, 1996b). Thus, isomerization followed by reaction with O_2, NO, etc., ultimately leads to the formation of dihydroxycarbonyl compounds. For the reaction of OH with 1-butene, for example, isomerization of one of the alkoxy radicals ultimately leads to 3,4-dihydroxybutanal in competition with its decomposition and reaction with O_2:



3,4-Dihydroxybutanal

The yields of such dihydroxycarbonyl products have been measured to increase continuously from 0.04 for 1-butene to 0.6 for the 1-octene reaction (Kwok *et al.*, 1996b). The low yield for 1-butene reflects the fact that only one of the two possible alkoxy radicals formed can undergo isomerization via a 6-membered transition state.

The carbon-centered hydroxy-containing radical $\dot{C}H_2OH$ formed in reactions (37) and (39) is encountered frequently as an intermediate in tropospheric organic oxidations. It is commonly referred to as an α-hydroxy radical. These types of radicals react in a characteristic manner with O_2:

$$\cdot CH_2OH + O_2 \rightarrow HCHO + HO_2,$$
$$k = 9.4 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$
$$\text{(Atkinson } et\ al.\text{, 1997a).} \qquad (40)$$

The larger α-hydroxy radicals react in a similar manner:

$$\dot{C}R_1R_2OH + O_2 \rightarrow R_1R_2C{=}O + HO_2. \qquad (41)$$

Interestingly, the mechanism appears to involve the initial addition of O_2 to the carbon radical, followed by isomerization and decomposition:

$$\cdot CH_2OH + O_2 \rightarrow \cdot OOCH_2OH$$
$$\leftrightarrow HOOCH_2O \rightarrow HO_2 + HCHO. \qquad (40)$$

For example, no deuterium isotope effect is observed on the rate constant when CH_2OD is substituted for CH_2OH (Grotheer *et al.*, 1988; Pagsberg *et al.*, 1989), as would be expected if a direct hydrogen abstraction were occurring.

Similar principles apply to more complex alkenes. One such case is that of isoprene, an important biogenically produced hydrocarbon:

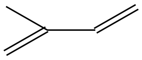

Isoprene

Figure 6.3 shows some of the major pathways in the

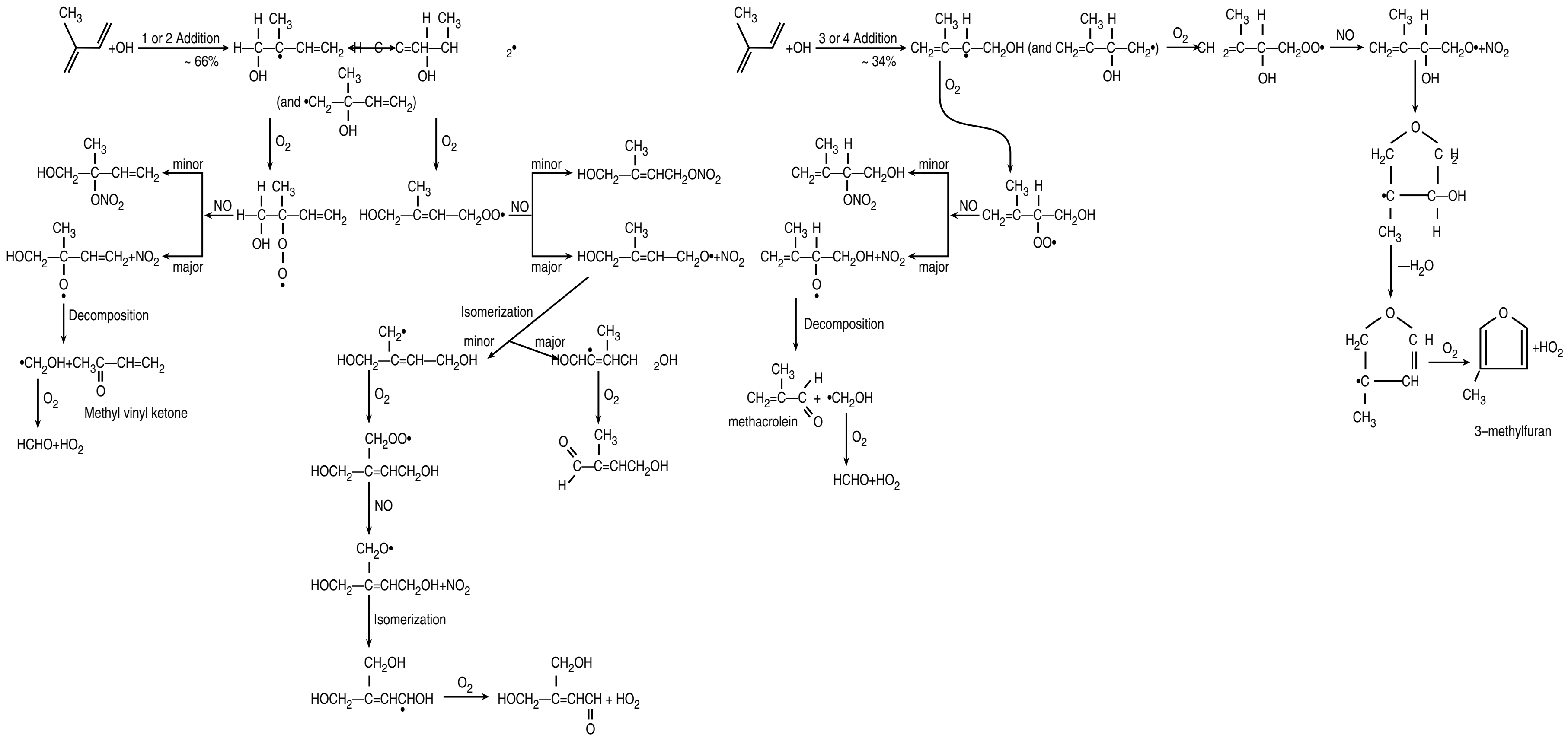


FIGURE 6.3 Some major pathways in the reaction of OH with isoprene (adapted from Carter and Atkinson, 1996).

OH–isoprene reaction. Detailed mechanisms have been developed by several groups (e.g., Paulson and Seinfeld, 1992b; Carter and Atkinson, 1996; Zimmermann and Poppe, 1996). Addition to the 1- (or 2-) position gives methyl vinyl ketone, whereas OH addition to the 3- (or 4-) position yields methacrolein. (Note that the O_3 reaction also generates these products, e.g., Aschmann and Atkinson, 1994.) Small yields of 3-methylfuran have also been reported (e.g., Atkinson *et al.*, 1989; Tuazon and Atkinson, 1990; Paulson *et al.*, 1992a). However, together these account for only about 60% of the total reaction (Tuazon and Atkinson, 1990; Paulson *et al.*, 1992a; Carter and Atkinson, 1996). There is experimental evidence for another path in which isomerization of the double bond to the 2,3-position occurs after the initial addition of the OH; subsequent addition of O_2 and the usual reactions of RO_2 and RO give the hydroxycarbonyls $CHOC(CH_3)=CHCH_2OH$ and $HOCH_2C(CH_3)=CHCHO$ (Kwok *et al.*, 1995).

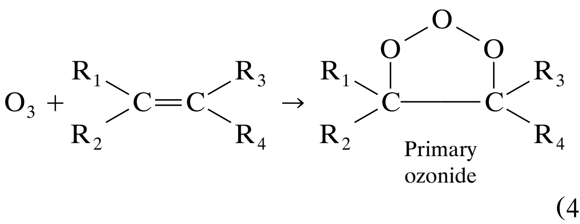
As shown in Fig. 6.3 and as expected by analogy to the chemistry of simple alkenes, organic nitrates are formed in small yields from the reaction of the peroxy radicals with NO_2. For example, Chen *et al.* (1998) report the formation of seven different organic nitrates in this system, with a total yield of 4.4%. This formation of organic nitrates may be important as a minor NO_x sink in forested regions, however. For example, Starn *et al.* (1998a,b) estimated that the isoprene nitrates comprise 0.5–2% of the NO_y during the day but up to 9% at night in a rural area in the state of Tennessee.

2. Ozone (O_3)

The room temperature rate constants for the reactions of O_3 with some alkenes are given in Table 6.9. While the values are many orders of magnitude smaller than those for the corresponding OH reactions, the fact that tropospheric ozone concentrations are so much larger makes these reactions a significant removal process for the alkenes.

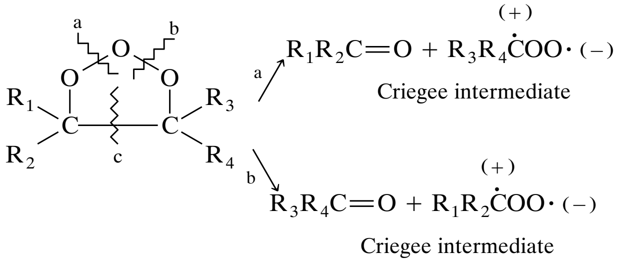
Despite many decades of research, the mechanisms of ozone–alkene reactions in the gas phase are still not well understood, certainly not as well understood as the corresponding reactions in the condensed phases. Figure 6.4 compares the overall characteristics of these reactions in the gas and condensed phases.

It is well known that the initial step in the reaction is the addition of O_3 across the double bond to form what is known as a primary ozonide, or molozonide:



(42)

This primary ozonide is not stable. One of the two peroxy O–O bonds (marked *a* or *b* in Eq. 43) and the C–C bond (marked *c*) cleave simultaneously to give an aldehyde or ketone and an intermediate called the Criegee intermediate, named after the German chemist who originally proposed this mechanism (e.g., see Criegee, 1975):



(43)

TABLE 6.9 Rate Constants and Temperature Dependence[a] for the Gas-Phase Reactions of O_3 with Some Alkenes[b]

Alkene	k (10^{-18} cm^3 molecule^{-1} s^{-1})	A (10^{-15} cm^3 molecule^{-1} s^{-1})	E_a/R (K)
Ethene	1.6	9.14	2580
Propene	10.1	5.51	1878
1-Butene	9.64	3.36	1744
2-Methylpropene	11.3	2.70	1632
cis-2-Butene	125	3.22	968
trans-2-Butene	190	6.64	1059
1-Pentene	10.0		
Cyclopentene	570	1.8	350
2-Methyl-2-butene	403	6.51	829
1-Hexene	11.0		
Cyclohexene	81.4	2.88	1063
cis-3-Methyl-2-pentene	450		
trans-3-Methyl-2-pentene	560		
2,3-Dimethyl-2-butene	1130	3.03	294
1,3-Butadiene	6.3	13.4	2283
2-Methyl-1,3-butadiene	12.8	7.86	1913
Myrcene	470		
2-Carene	230		
3-Carene	37		
Limonene	200		
α-Phellandrene	2980		
β-Phellandrene	47		
α-Pinene	86.6	1.01	732
β-Pinene	15		
α-Terpinene	2.1×10^4		
γ-Terpinene	140		
Terpinolene	1880		
Methyl vinyl ketone	5.6[c]		
Methacrolein	1.2[c]		

[a] $k = Ae^{-E_a/RT}$.

[b] From Atkinson (1997a) and Atkinson *et al.* (1997a); for structures of biogenics, see Fig. 6.22.

[c] Average of Grosjean and Grosjean (1998a) and Neeb *et al.* (1998b).

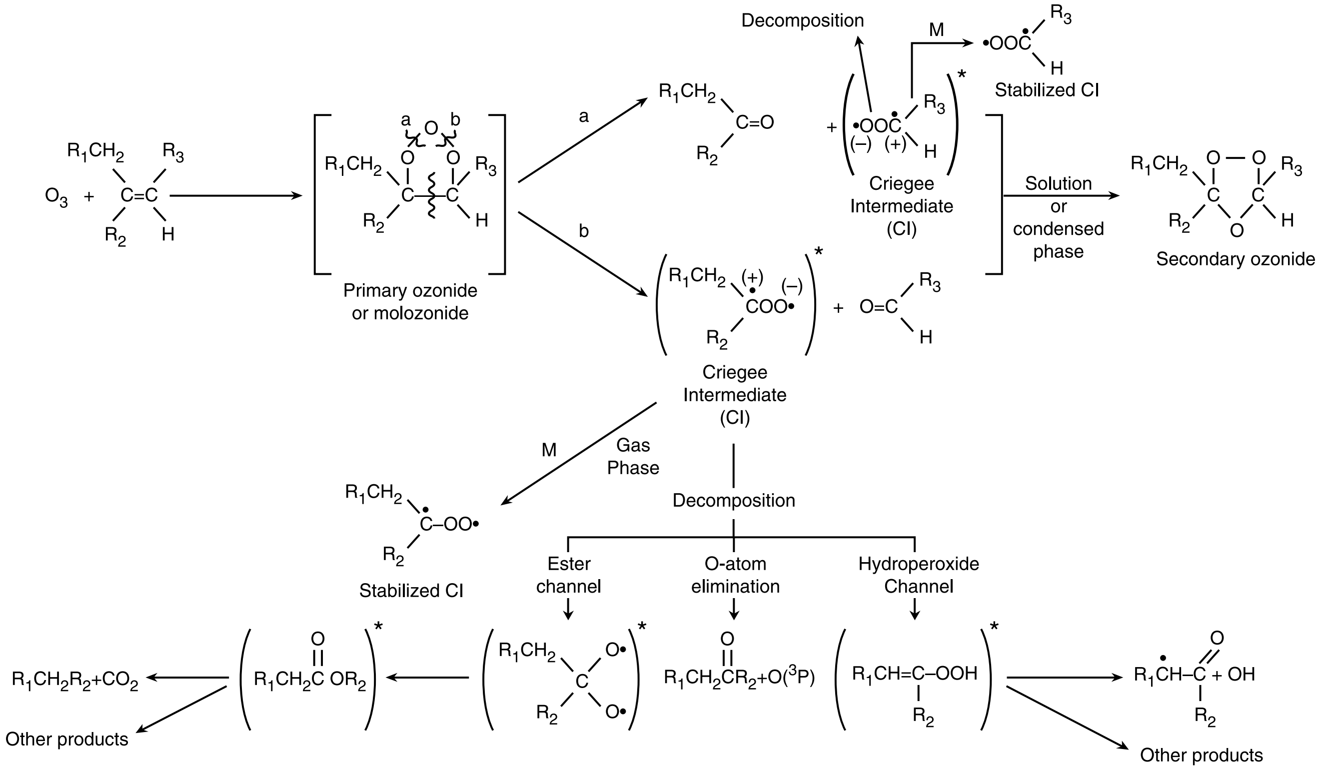
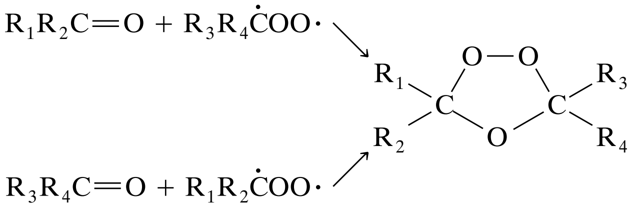


FIGURE 6.4 Overall mechanisms of O_3–alkene reactions in the gas and condensed phase, respectively.

In the liquid phase, the Criegee intermediates have been assumed to be zwitterions and hence the term "Criegee zwitterion" is commonly used. In the gas phase, the structure is usually written as a biradical (although it may really be more zwitterionic in character; e.g., see Cremer *et al.*, 1993). Hence "Criegee biradical" is frequently used for this gaseous intermediate. Sander (1990), Bunnelle (1991), and Cremer *et al.* (1993) give a more detailed discussion of the structure and properties of the Criegee intermediate.

In any event, in the solvent cage in which they are formed in the liquid phase, or for higher molecular weight alkenes condensed on surfaces, the two fragments formed by decomposition of the primary ozonide are held in close proximity and recombine to form a secondary ozonide:



(44)

In addition to the effects of close proximity, the condensed phases act to remove excess energy in the fragments.

In the gas phase, however, two effects come into play. First, the two fragments formed on decomposition of the primary ozonide fly apart rapidly. As a result, the formation of secondary ozonides by recombination, reaction (44), does not occur to a significant extent in the gas phase [unless the mixture is doped with large quantities of an aldehyde or ketone to trap the Criegee intermediate (e.g., Neeb *et al.*, 1998a) or very high concentrations are used (e.g., Fajgar *et al.* (1996); Griesbaum *et al.* (1998)]. Second, there is no efficient mechanism for removal of excess energy from the carbonyl compound and the Criegee intermediate. The Criegee intermediate contains excess energy and either can be stabilized or decompose in a variety of ways. For example, for the two possible Criegee intermediates produced in the O_3–propene reaction, the following paths are possible (where the branching ratios are the IUPAC evaluation recommendations (Atkinson *et al.*, 1997a):

$$
\begin{aligned}
(\mathrm{H\dot{C}HOO}\cdot)^* + \mathrm{M} &\xrightarrow{0.37} \mathrm{H\dot{C}HOO}\cdot + \mathrm{M}, && (45a)\\
&\xrightarrow{0.12} \mathrm{HCO + OH}, && (45b)\\
&\xrightarrow{0.38} \mathrm{CO + H_2O}, && (45c)\\
&\xrightarrow{0.13} \mathrm{CO_2 + H_2}, && (45d)\\
&\xrightarrow{0} \mathrm{CO_2 + 2H}, && (45e)\\
&\xrightarrow{0} \mathrm{HCOOH}. && (45f)
\end{aligned}
$$

Neeb *et al.* (1998a) report branching ratios for (45a) of 0.50, (45b) + (45c) of 0.23, (45d) + (45e) of 0.23, and (45f) of 0.04.

$$
\begin{aligned}
\left(CH_3\dot{C}HOO\cdot\right)^* + M &\xrightarrow{0.15} CH_3\dot{C}HOO\cdot\,, && (46a)\\
&\xrightarrow{0.54} CH_3 + CO + OH, && (46b)\\
&\longrightarrow CH_3 + CO_2 + H, && (46c)\\
&\xrightarrow{(0.17 = c + d)} HCO + CH_3O, && (46d)\\
&\xrightarrow{0.14} CH_4 + CO_2, && (46e)\\
&\xrightarrow{0} CH_3OH + CO. && (46f)
\end{aligned}
$$

Table 6.10 gives the ranges of observed yields of the stabilized Criegee intermediates at 1 atm pressure in air and at room temperature. Clearly, significant decomposition of the intermediates occurs under typical tropospheric conditions.

The fraction of the primary ozonide decomposition that goes by path a in reaction (43) vs path b for unsymmetrical alkenes has been determined from the product yields in a number of studies (e.g., see series of papers by Grosjean and co-workers and Atkinson and co-workers). One might expect, based on thermochemical arguments, that the decomposition giving the more stable, i.e., more highly substituted, biradical would be preferred, and this is indeed what has been observed (e.g., see Horie and Moortgat, 1991; Grosjean *et al.*, 1994c; Atkinson *et al.*, 1995c; and Grosjean and Grosjean, 1997, 1998a). Atkinson (1997a) recommends, based on the literature, the following branching ratios:

$$
\begin{aligned}
O_3 + R_1CH{=}CH_2 &\xrightarrow{0.5} (R_1\dot{C}HOO\cdot)^* + HCHO,\\
&\xrightarrow{0.5} R_1CHO + (H\dot{C}HOO\cdot)^*,
\end{aligned}
$$

$$
\begin{aligned}
O_3 + R_1R_2C{=}CH_2 &\xrightarrow{0.65} (R_1R_2\dot{C}OO\cdot)^* + HCHO,\\
&\xrightarrow{0.35} R_1C(O)R_2\\
&\qquad + (H\dot{C}HOO\cdot)^*,\\
O_3 + R_1R_2C{=}CHR_3 &\xrightarrow{0.65} (R_1R_2\dot{C}OO\cdot)^* + R_3CHO,\\
&\xrightarrow{0.35} R_1C(O)R_2\\
&\qquad + (R_3\dot{C}HOO\cdot)^*.
\end{aligned}
$$

TABLE 6.10 Yields of Stabilized Criegee Intermediates at Room Temperature and 1 atm Air[a]

Alkene	Yield
Ethene	0.35–0.47
Propene	0.25–0.44
2-Methylpropene	0.17
cis-2-Butene	0.18
trans-2-Butene	0.19–0.42
2,3-Dimethyl-2-butene	0.30
1-Octene	0.22
Cyclopentene	0.05
Cyclohexene	0.03
Cycloheptene	0.03
1-Methylcyclohexene	0.10
Methylenecyclohexane	0.22
α-Pinene	0.13
β-Pinene	0.25

[a] From Hatakeyama and Akimoto (1994) and Atkinson (1994, 1997a); see these for original references.

While free radicals were reported in ozone–alkene reactions as long ago as 1958 by Saltzman, the importance and magnitude of these processes have only relatively recently been appreciated by the atmospheric chemistry community. Of greatest significance is the production of OH in these reactions, which was first observed in these systems in a vibrationally excited state, $OH^{\neq}$, probably from the initial production of H atoms, followed by the well-known reaction $H + O_3 \rightarrow OH^{\neq} + O_2$ (Finlayson *et al.*, 1972). Rapid secondary reactions of OH with the parent alkene complicates interpretation of the original O_3–alkene mechanism and products. In addition, in kinetic studies where the loss of the alkene is followed, the derived rate constants may be too large unless the contribution of OH secondary reactions is taken into account or it is scavenged from the system. However, more important than the implications for laboratory studies are those for the role of ozone–alkene reactions in tropospheric chemistry. Thus, in addition to producing carbonyl compounds that can photolyze to generate free radicals, ozone–alkene reactions contribute directly to the generation of free radicals via reactions such as (45) and (46). This will be especially important at night when there are no photolytic sources of OH.

Table 6.11 gives some measured yields of OH in some ozone–alkene reactions. These have been determined by trapping the OH, e.g., using a large excess of cyclohexane (e.g., Grosjean *et al.*, 1994c; Grosjean and Grosjean, 1997) or 2-butanol (e.g., Chew and Atkinson, 1996), and measuring the major "OH-trap" products such as cyclohexanone and cyclohexanol (Atkinson *et al.*, 1992; Aschmann *et al.*, 1997a) and butanone, respectively (e.g., Chew and Atkinson, 1996), under conditions where the formation of OH via the $HO_2 + O_3$ reaction is minimized. Other approaches include trapping by CO to form CO_2 (e.g., Gutbrod *et al.*, 1997b) or following the loss of pairs of tracer organics that react with OH (e.g., Schäfer *et al.*, 1997; Paulson *et al.*, 1997; Marston *et al.*, 1998). In addition to the indirect measurements of OH, a direct measurement of its production using laser-induced fluorescence has been carried out for the reactions of O_3 with ethene, *trans*-2-butene, 2,3-dimethyl-2-butene, and isoprene at 4- to 6-Torr pressures in N_2. Yields of OH from 0.4 to 0.8 were observed by Donahue *et al.* (1998b).

In short, O_3–alkene reactions generate OH, with yields approaching unity in the case of highly branched alkenes.

The mechanism of decomposition of the Criegee intermediates is believed to occur via several reaction channels shown for the $[(R_1CH_2)(R_2)\dot{C}HO\dot{O}]^*$ Criegee intermediate in Fig. 6.4. The oxygen-atom elimination channel for simple alkenes is not believed to be important. However, the ester and hydroperoxide channels are important and explain the production of free radicals such as OH. Theoretical calculations have shed some light on this (e.g., Gutbrod *et al.*, 1996, 1997a; Anglada *et al.*, 1996). Figure 6.5, for example, shows the calculations of Gutbrod *et al.* (1996) for the reaction of the Criegee intermediate $\dot{C}(CH_3)_2O\dot{O}$, formed in the reaction of O_3 with 2,3-dimethyl-2-butene. The path that forms the dioxinane intermediate has a higher activation barrier than that forming the unsaturated hydroperoxide, and the latter channel that leads to OH formation is predicted to predominate. The key to OH production is predicted to be an alkyl group in a *syn* position so that it can interact with the terminal oxygen (Gutbrod *et al.*, 1996, 1997a):

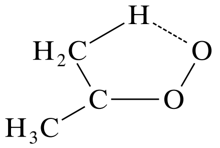


TABLE 6.11 Yields of OH from Gas-Phase O_3 – Alkene Reactions at 1 atm Pressure[a]

Alkene	OH yield
Ethene	0.12,[b] 0.08[h]
Propene	0.33,[a] 0.18[h]
1-Butene	0.41[a]
1-Pentene	0.37[f]
1-Hexene	0.32[f]
1-Heptene	0.27[f]
1-Octene	0.18[f]–0.45[c]
cis-2-Butene	0.41,[a] 0.17[h]
trans-2-Butene	0.64,[a] 0.24[h]
Cyclopentene	0.61[f]
Cyclohexene	0.68[a]
1-Methylcyclohexene	0.90[f]
2-Methylpropene	0.84[a]
2-Methyl-1-butene	0.83[a]
2-Methyl-2-butene	0.89[a]
2,3-dimethyl-2-butene	0.5[h]–1.0[a,d]
Limonene	0.86[b]
Myrcene	1.15[b]
α-Pinene	0.70–0.85[b,g,i]
β-Pinene	0.35[b]
Terpinolene	1.03[b]
Camphene	≤0.18[b]
1,3-Butadiene	0.08[a]
Isoprene	0.19–0.27[b,g,e,h]

[a] From Atkinson and Aschmann (1993) and Atkinson (1997a); Donahue *et al.* (1998) have reported OH yields of 0.4–0.8 at low pressures (4–6 Torr) in N_2 from the ethene, *trans*-2-butene, 2,3-dimethyl-2-butene, and isoprene reactions; see Fig. 6.22 for biogenics structures.

[b] From Atkinson *et al.* (1992).

[c] From Paulson and Seinfeld (1992a).

[d] From Niki *et al.* (1987).

[e] From Paulson *et al.* (1992b).

[f] From Atkinson *et al.* (1995a).

[g] Paulson *et al.* (1998); OH yield of 0.25 from O_3 + isoprene supersedes Paulson *et al.* (1992b) yield of 0.68.

[h] From Gutbrod *et al.* (1997b); the OH yields reported using this CO trapping method tend to be lower than those measured using other techniques.

[i] Chew and Atkinson (1996).

Grosjean *et al.* (1994c) propose that the hydroperoxide channel may also be responsible for the formation of hydroxycarbonyl and/or dicarbonyl products:

$$\begin{aligned} CH_3\dot{C}HOO\cdot &\rightarrow CH_2{=}CHOOH\\ &\rightarrow [CH(O)CH_2OH]^*\\ &\overset{M}{\rightarrow} CH(O)CH_2OH,\\ &\rightarrow H_2 + (CHO)_2. \end{aligned} \tag{47}$$

The generation of OH in O_3–alkene reactions has important implications for tropospheric chemistry. Thus the O_3–alkene reactions could be important free radical sources at dusk and during the night when photolytic sources of OH are minimal (e.g., Paulson and Orlando, 1996; Bey *et al.*, 1997; Paulson *et al.*, 1998). For example, Paulson and Orlando (1996) predicted that ~10–15% of the total radical production may be from O_3–alkene reactions in a typical rural area in the southeastern United States. As seen in Fig. 6.6, this reaction is expected to be most important at night.

There are a number of potential atmospheric fates of the stabilized Criegee intermediate. These include reactions with water vapor, SO_2, NO, NO_2, CO, and aldehydes and ketones. In the latter cases, the secondary ozonides are formed as discussed earlier. Neeb *et al.* (1998a) propose that the secondary ozonides are formed with sufficient excess energy that they may partly decompose rather than being stabilized; for the $CH_3CHO + \dot{C}H_2O\dot{O}$ reaction, for example, formation of both the stabilized secondary ozonide and HCHO and CO_2 was observed by Neeb *et al.* (1998a). Similarly, the reaction of the ethene Criegee intermediate, $\dot{C}H_2O\dot{O}$, with HCHO, observed to generate HCHO, HCOOH, and CO, was proposed to occur via an excited secondary ozonide that completely decomposes to

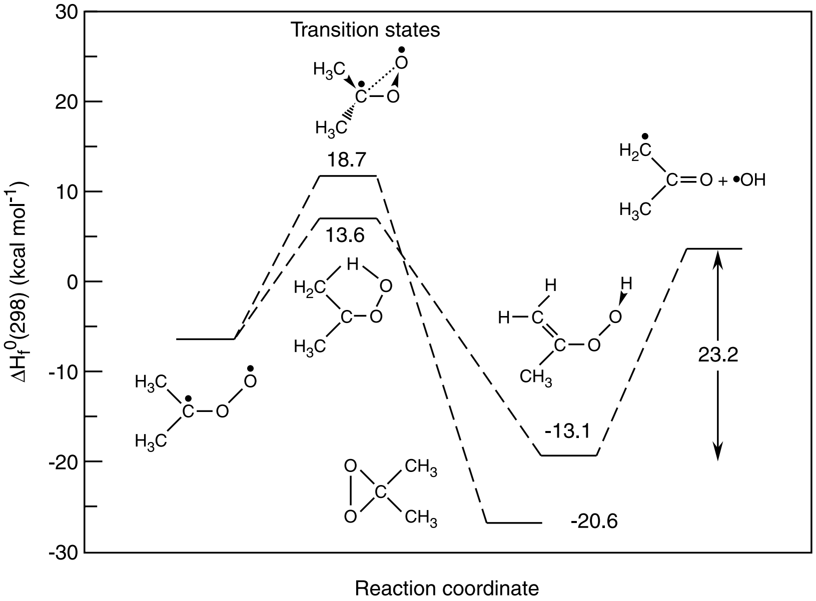
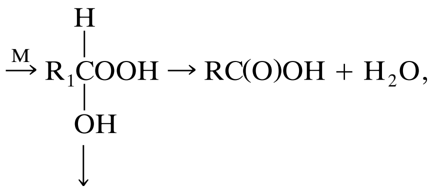


FIGURE 6.5 Calculated energetics of two possible reaction pathways for the Criegee intermediate $(CH_3)_2\dot{C}OO\cdot$ (adapted from Gutbrod *et al.*, 1996).

(HCHO + HCOOH), (HCHO + CO + H_2O), or (HCHO + HCO + OH).

The reaction with water vapor has a number of potential paths:

$$R_1H\dot{C}OO\cdot + H_2O \rightarrow R_1C(O)OH + H_2O, \quad (48a)$$



$$\xrightarrow{M} R_1\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}OOH \rightarrow RC(O)OH + H_2O, \quad (48b)$$

$$\downarrow$$

$$R_1CHO + H_2O_2. \quad (48c)$$

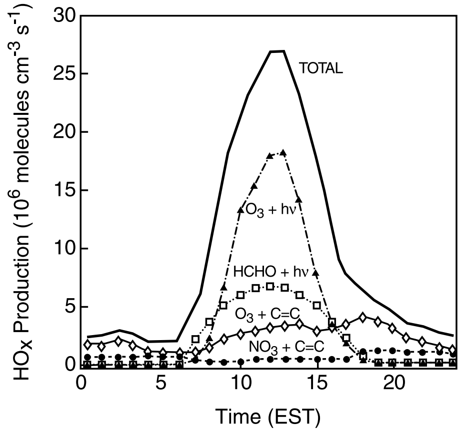


FIGURE 6.6 Calculated rates of HO_x radical generation from various sources for a rural forested site in the southeastern United States (adapted from Paulson and Orlando, 1996).

The formation of carboxylic acids in these reactions may be a significant source of organic acids in air. Reaction (48a) appears to occur by at least two mechanisms. Thus, the addition of isotopically labeled $H_2{}^{18}O$ leads to the formation of carboxylic acid, some of which contains the ^{18}O label and some of which does not (Hatakeyama *et al.*, 1981), suggesting mechanisms such as the following:

$$\begin{aligned} &R_1\dot{C}HOO\cdot + H_2{}^{18}O \\ &\rightarrow \left[R_1\dot{C}HOO \cdot H_2{}^{18}O\right]^* \\ &\rightarrow R_1CO^{18}OH, R_1C^{18}OOH + H_2O \\ &\rightarrow R_1COOH + H_2{}^{18}O. \end{aligned}$$

Analogous trapping reactions for the Criegee intermediate using such reactants as H_2O_2, CH_3OH, C_2H_5OH, and HCOOH have been observed for $\dot{C}H_2O\dot{O}$ from the ethene–O_3 reaction (e.g., Neeb *et al.*, 1996; Wolff *et al.*, 1997).

While it is often assumed that only the stabilized form of the Criegee intermediate undergoes such reactions, Moortgat and co-workers (Horie *et al.*, 1994) have suggested that in the ethene reaction, it is the excited form that reacts with water vapor to form the acid, while the reaction of the stabilized Criegee intermediate leads to a hydroxyhydroperoxide, corresponding to reaction (48b).

The formation of hydroxyhydroperoxides has only relatively recently been recognized, probably due to the difficulty in analyzing for these reactive species. An additional complication is that these hydroxyhydroperoxides are known to decompose in solution to H_2O_2 and the carbonyl compounds. This decomposition, reaction (48c), which can occur during analysis in solution or on the walls of the reaction chamber, may be responsible for the highly varying yields of H_2O_2 and hydroxyhydroperoxides reported in various studies (e.g., see Gäb *et al*., 1985, 1995; Hatakeyama and Akimoto, 1994; Horie *et al*., 1994; Hatakeyama *et al*., 1993; Hewitt and Kok, 1991; Simonaitis *et al*., 1991; Wolff *et al*., 1997; Neeb *et al*., 1997; and Sauer *et al*., 1999). At any rate, their formation is now accepted, although the yields as a function of water vapor concentration under typical atmospheric conditions are not well established for a variety of alkenes.

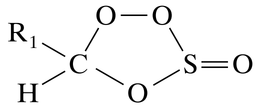
For example, in the isoprene reaction with O_3, H_2O_2 has been observed as a product, with its yield increasing as the relative humidity increased from 1 to 9% (Sauer *et al*., 1999). The yields of methacrolein and methyl vinyl ketone also increased simultaneously, as expected if they were also formed in part from the decomposition of an intermediate hydroxyhydroperoxide.

The reaction with SO_2 has been thought in the past to proceed via the direct formation of SO_3:

$$R_1\dot{C}HOO\cdot + SO_2 \rightarrow R_1CHO + SO_3. \quad (49)$$

However, as discussed in detail by Hatakeyama and Akimoto (1994), there is increasing evidence for the formation of an addition complex such as that proposed by Martinez and Herron (1981) and observed earlier by mass spectrometry by Schulten and Schurath (1975):

$R_1\dot{C}HOO\cdot + SO_2 \rightarrow$



(50)

In the presence of water vapor, the adduct then reacts with H_2O to generate sulfuric acid.

Other reactions proposed for the Criegee intermediate include

$$R_1\dot{C}HOO\cdot + NO \rightarrow R_1CHO + NO_2, \quad (51)$$

$$R_1\dot{C}HOO\cdot + NO_2 \rightarrow R_1CHO + NO_3, \quad (52)$$

$$R_1\dot{C}HOO\cdot + CO \rightarrow R_1CHO + CO_2. \quad (53)$$

TABLE 6.12 Range of Reported Rate Constants for the Reactions of the Criegee Intermediate with Some Gases[a] and Associated Lifetimes of the Criegee Intermediate under Polluted Tropospheric Conditions

Reactant	k (cm^3 molecule^{-1} s^{-1})	τ_{CI}[b] (s)
H_2O	1×10^{-15}–2×10^{-19}	0.003–400
CO	1×10^{-14}	8
HCHO	2×10^{-12}–2×10^{-16}	20–(2×10^5)
NO	7×10^{-12}	0.1
NO_2	7×10^{-13}–1×10^{-17}	1–10^5
SO_2	1.7×10^{-11}–3×10^{-15}	0.05–270

[a] Adapted from Hatakeyama and Akimoto (1994).

[b] Lifetime of Criegee intermediate assuming the following concentrations: H_2O, 4×10^{17} molecules cm^{-3}, corresponding to a relative humidity of ~50% at 298 K; CO, 0.5 ppm; HCHO, 1 ppb; NO, NO_2, SO_2, 50 ppb.

However, the relative importance of these reactions is highly uncertain. Table 6.12 gives one estimate of the range of possible rate constants for these reactions of the Criegee intermediate and the calculated lifetimes of the intermediate under some typical atmospheric conditions. Reaction with water vapor is expected to be the major fate of the Criegee intermediate, with perhaps some contribution by reaction with NO and/or SO_2 in more polluted atmospheres.

It should be noted that while the mechanism outlined in this section describes the overall features of O_3–alkene chemistry, there are also other minor paths as well. For example, small yields of epoxides that appear to be formed in the primary reaction have been observed as products of the reactions of some dienes and cycloalkenes (e.g., see Paulson *et al*., 1992b; and Atkinson *et al*., 1994a, 1994b). The reader should consult the rather extensive ozone literature for further details on both the condensed- and gas-phase reactions.

As discussed in Chapter 9, there are a variety of low-volatility organics, some of which are unsaturated, which are found in or on particles in the atmosphere, and these would be expected to undergo heterogeneous reactions with O_3. Consistent with this, de Gouw and Lovejoy (1998) report reaction probabilities of $\sim 10^{-2}$–10^{-3} for O_3 on organic liquids containing unsaturated sites.

3. Nitrate Radical (NO_3)

Table 6.13 gives the rate constants and temperature dependence for the reactions of the nitrate radical, NO_3, with some alkenes. The room temperature rate constants span about six orders of magnitude, approaching diffusion controlled for some of the biogenics. Those activation energies that have been measured are relatively small (or negative by a small amount), and the rate constants increase with increasing alkyl substitution at the double bond. This, plus the much larger values compared to the rate constants for reactions with alkanes where H-abstraction occurs, suggests

TABLE 6.13 Room Temperature Rate Constants and Temperature Dependence[a] for the Gas-Phase Reactions of the NO_3 Radical with Some Alkenes[b]

Alkene	k (cm^3 molecule^{-1} s^{-1}) at 298 K	A (cm^3 molecule^{-1} s^{-1})	E_a/R (K)
Ethene	2.1×10^{-16}	*c*	*c*
Propene	9.5×10^{-15}	4.6×10^{-13}	1156
1-Butene	1.4×10^{-14}	3.14×10^{-13}	938
2-Methylpropene	3.3×10^{-13}		
cis-2-Butene	3.5×10^{-13}		
trans-2-Butene	3.9×10^{-13}	*d*	*d*
2-Methyl-2-butene	9.4×10^{-12}		
2,3-Dimethyl-2-butene	5.7×10^{-11}		
1,3-Butadiene	1.0×10^{-13}		
2-Methyl-1,3-butadiene (isoprene)	6.8×10^{-13}	3.03×10^{-12}	446
Cyclopentene	5.3×10^{-13}		
Cyclohexene	5.9×10^{-13}	1.05×10^{-12}	174
Cycloheptene	4.8×10^{-13}		
Camphene	6.2×10^{-13}[f]	3.1×10^{-12}	481
2-Carene	1.9×10^{-11}		
3-Carene	9.1×10^{-12}		
Limonene	1.2×10^{-11}		
α-Pinene	5.9×10^{-12}[f]	3.5×10^{-13}	−841
β-Pinene	2.1×10^{-12}[f]	1.6×10^{-10}	1248
α-Phellandrene	7.3×10^{-11}		
β-Phellandrene	8.0×10^{-12}		
α-Terpinene	1.4×10^{-10}		
γ-Terpinene	2.9×10^{-11}		
Terpinolene	9.7×10^{-11}		
Methyl vinyl ketone	$< 6 \times 10^{-16}$[d]		
Methacrolein	3.3×10^{-15}[e]		

[a] $k = Ae^{-E_a/RT}$.

[b] From Atkinson (1994) and Atkinson *et al.* (1997a).

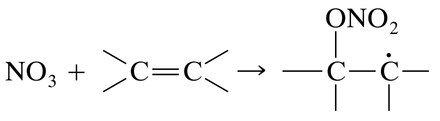
[c] Recommended temperature dependence is $k = 4.88 \times 10^{-18} T^2 e^{-2282/T}$ cm^3 molecule^{-1} s^{-1} from 290 to 523 K.

[d] Dlugokencky and Howard (1989) report a curved Arrhenius plot that can be matched from 204 to 378 K by $k = (1.78 \pm 0.36) \times 10^{-12} \exp[(-530 \pm 100)/T] + (1.28 \pm 0.26) \times 10^{-14} \exp[(570 \pm 110)/T]$; Atkinson (1997a) recommends $k = 1.22 \times 10^{-18} e^{382/T}$ cm^3 molecule^{-1} s^{-1} from 204 to 378 K.

[e] From Chew *et al.* (1998).

[f] From Martinez *et al.* (1998).

that NO_3 undergoes electrophilic addition to the double bond in much the same fashion as OH:



$$NO_3 + \;\rangle C{=}C\langle \;\rightarrow\; -\underset{|}{\overset{\overset{\displaystyle ONO_2}{|}}{C}}-\underset{|}{\overset{\bullet}{C}}- \qquad (54)$$

However, there is no pressure dependence of the rate constants over the range from about 1 Torr up to 1 atm, suggesting that the adduct does not decompose significantly back to reactants under atmospheric conditions.

This mechanism is consistent with the observation of significant yields of epoxide products and NO_2 for some alkenes (Olzmann *et al.*, 1994). For example, Fig. 6.7 shows the infrared spectrum of the minor products from the reaction of NO_3 with 2,3-dimethyl-2-butene at 740 Torr in air, after the spectra of the reactants and the major product, acetone, as well as of NO_2 and HNO_3 have been subtracted out. Bands due to the epoxide (in ~17% yield) are clearly seen, as well as bands due to 2,3-dinitroxy-2,3-dimethyl-2-butane. Together with acetone, these compounds account for 75% of the reacted alkene (Skov *et al.*, 1994).

Figure 6.8 summarizes the mechanism of the reaction of NO_3 with 2,3-dimethyl-2-butene (Skov *et al.*, 1994; Olzmann *et al.*, 1994). The addition of the NO_3 to a double bond is about 20 kcal mol^{-1} exothermic, so that the initially formed adduct is excited and either can be stabilized or decompose by breaking the weaker $CO{-}NO_2$ bond to form the epoxide and NO_2. The stabilized adduct can also decompose in a similar manner, in competition with its reaction with O_2. Under

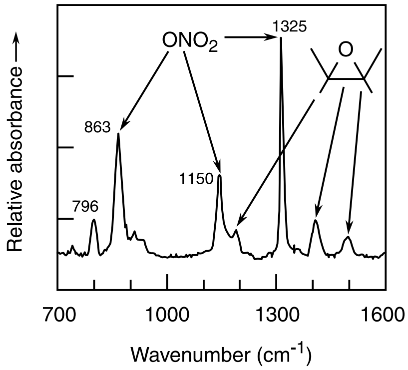


FIGURE 6.7 Infrared spectrum of products of the reaction of 2,3-dimethyl-2-butene with NO_3 (spectra of acetone, NO_2, and HNO_3 have been subtracted out) (adapted from Skov *et al.*, 1994).

surface-level tropospheric conditions, 1 atm total pressure in air, the epoxide yields are small but not insignificant. For example, epoxide yields of 7, 12, 18, and 28% from the reactions of isobutene, *trans*-2-butene, 1-butene, and propene, respectively, have been reported (Berndt and Böge, 1995).

The lifetime of the excited NO_3–alkene adducts is sufficiently long that rotation about the C–C bond leads to the same yields of *trans*- and *cis*-epoxides regardless of the configuration of the reactant alkene; for example, the reactions of both *cis*- and *trans*-2-butene give about 80% of the *trans* form of the product epoxide and 20% of the *cis* form (Benter *et al.*, 1994).

The peroxy radical formed in Fig. 6.8 is expected to react in air as discussed earlier, i.e., with NO, HO_2, RO_2, or NO_2. Since NO_3 itself reacts rapidly with NO, large concentrations of NO will not be present at the same time as NO_3. However, there may still be sufficient amounts for this to be a significant fate of the peroxy radical. Figure 6.9 traces the expected fates of this radical through to stable organic products. The dinitroxybutane is formed from the alkoxy radical–NO_2 reaction and acetone from the alkoxy radical decomposition. The observation of smaller amounts of other aldehydes and formaldehyde also suggests a small contribution from a 1,4-H shift and subsequent reactions of the alkyl radical thus formed (Hjorth *et al.*, 1990).

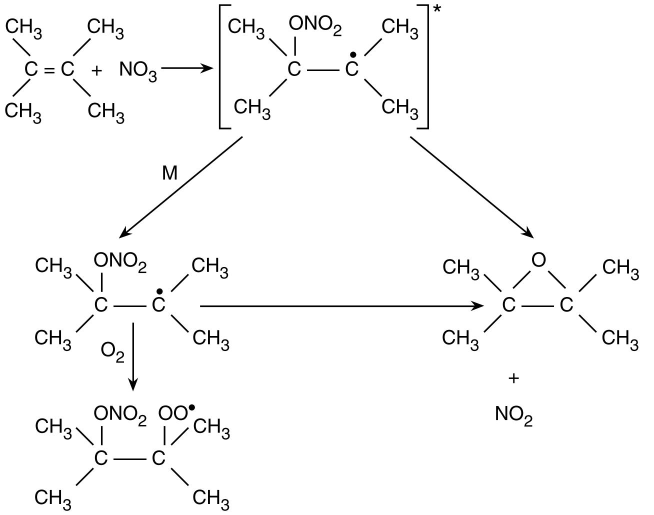


FIGURE 6.8 Mechanism of the NO_3 reaction with 2,3-dimethyl-2-butene (adapted from Skov *et al.*, 1994).

The results of laboratory studies of the mechanism of NO_3 radical reactions with alkenes tend to be slanted toward observing polyfunctional organics containing more than one nitro group. The reason for this is that the thermal decomposition of N_2O_5,

$$N_2O_5 \leftrightarrow NO_3 + NO_2, \qquad (55, -55)$$

is often used as the source of NO_3. As a result, relatively high concentrations of NO_2 may also be present, and depending on the concentration regimes employed, these can trap the alkylperoxy and alkoxy radicals more efficiently than would normally be the case in the atmosphere. On the other hand, sources such as the reaction of fluorine atoms with HNO_3,

$$F + HNO_3 \rightarrow HF + NO_3, \qquad (56)$$

are normally used at low pressures (~Torr) and in the absence of air because such conditions are needed to generate the halogen atoms. Under these conditions, the products may be quite different from those at 1 atm in air. For example, the yields of epoxides are much greater, typically approaching 100%, under these low-pressure, low -O_2 conditions (Skov *et al.*, 1994; Berndt and Böge, 1995).

However, it is interesting that vicinal dinitrates have been measured in air with higher concentrations at night, as would be expected if nitrate radical reactions were the source. For example, Schneider *et al.* (1998) measured the diurnal variation of a series of alkyl nitrates in rural air in Germany and found higher nighttime levels of vicinal dinitrates. They attributed these to the addition of NO_3 to double bonds, formation of the alkylperoxy radical, and then reaction with NO, with the minor channel in the RO_2 + NO reaction leading to a second nitrate group on the adjacent carbon.

As seen from the rate constants in Table 6.13, the reactions of biogenic hydrocarbons with NO_3 are quite fast, so this reaction is expected to be a major fate of these biogenics at night and to also contribute to the removal of NO_x. The lifetime of isoprene with respect to reaction with NO_3 at 50 ppt, for example, is only about 20 min.. Addition of NO_3 occurs primarily at the 1-position and leads in the absence of NO to the

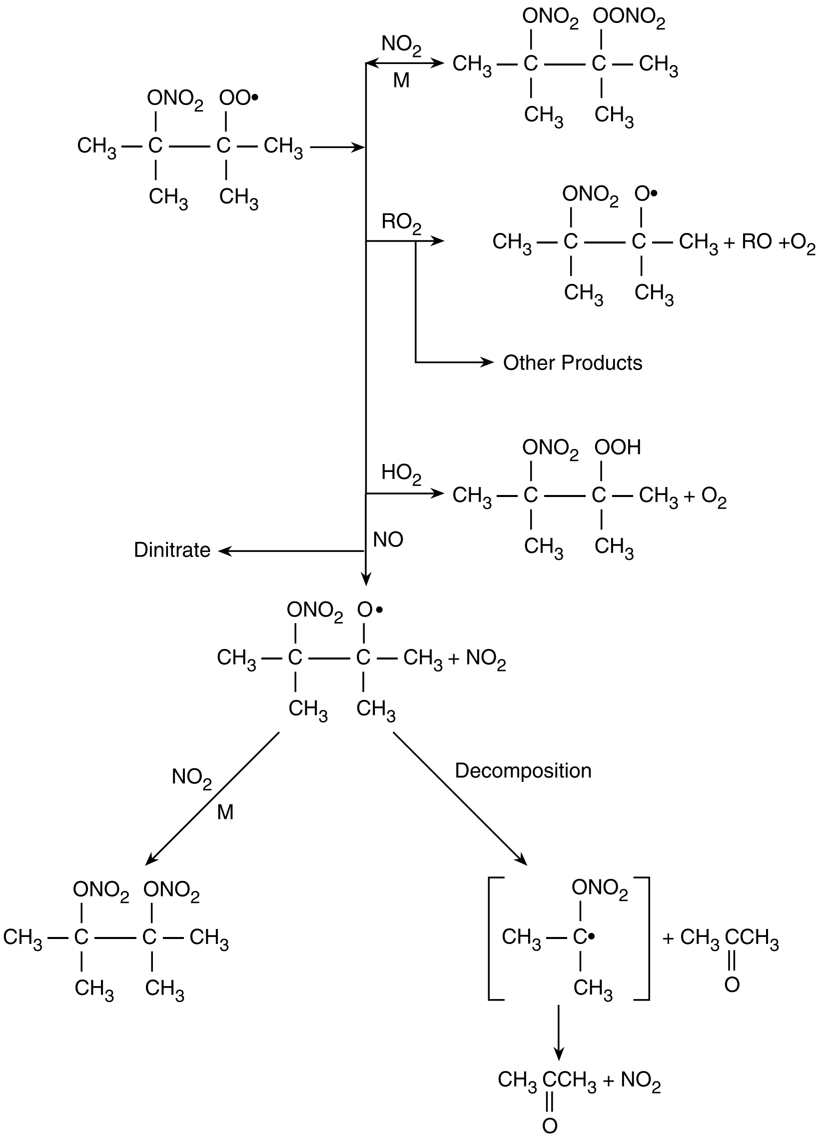
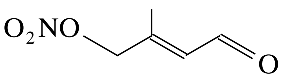


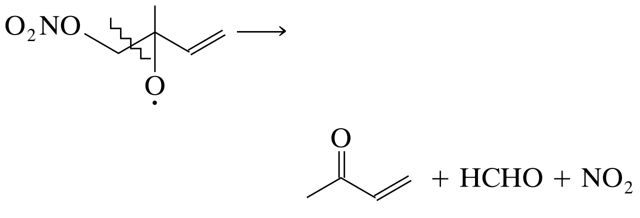
FIGURE 6.9 Expected atmospheric fates of peroxy radical formed in NO_3 addition to 2,3-dimethyl-2-butene.

formation of 4-nitroxy-3-methyl-2-butenal as a major product (e.g., Jay and Stieglitz, 1989; Barnes *et al.*, 1990; Skov *et al.*, 1992; Kwok *et al.*, 1996c; Berndt and Böge, 1997):



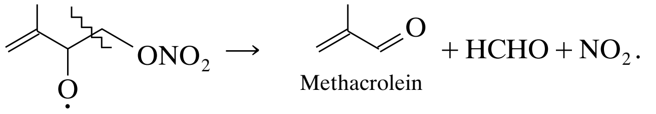
4-Nitroxy-3-methyl-2-butenal

Also formed are a variety of hydroxynitrates, nitrooxyhydroperoxides, and hydroxycarbonyls anticipated from the reactions of alkylperoxy and alkoxy radicals formed after the initial addition of NO_3 to the double bond (e.g., Kwok *et al.*, 1996c). The yield of 4-nitroxy-3-methyl-2-butenal decreases with increasing NO concentrations, while the yields of methyl vinyl ketone and methacrolein increase (Berndt and Böge, 1997). This has been attributed to the decomposition of the alkoxy radicals formed after 1,2-addition, e.g.,



Methyl vinyl ketone

and after 3,4-addition, respectively:



In addition, in the nighttime atmosphere, reaction of the RO_2 radicals with NO_3 may occur as discussed earlier. As a result, the products of the isoprene–NO_3 reaction in the atmosphere will depend on the concentrations of NO, NO_3, HO_2, and RO_2.

Field studies suggest that the nitrate radical reaction can also be a major contributor to isoprene decay at night, as well as contributing to the formation of organic nitrates in air. For example, Starn *et al.* (1998b) found that when the product of NO_2 and O_3 (which form NO_3) was high in a forested region in the southeastern United States, isoprene often decayed rapidly at dusk. This reaction of NO_3 with isoprene was estimated to be the major sink for NO_3 under some conditions in this area.

The reader is referred to two excellent reviews of NO_3 chemistry by Wayne *et al.* (1991) and Atkinson (1991) for further details.

The plethora of multifunctional products anticipated from nitrate radical reactions with alkenes (Fig. 6.8) may well be in part responsible for what is commonly referred to as "missing NO_y." In brief, one can measure total NO_y using techniques such as the "master blaster" described in Chapter 11, in which one converts all oxygenated nitrogen-containing species into NO using a Au/CO converter and then measures the total NO. At the same time, one can measure various individual components of NO_y (NO, NO_2, HNO_3, PAN, etc.) separately and determine whether their sum accounts for the observed NO_y. As discussed in detail in Chapter 11.A.4a, the sum of the individual compounds is often less than the measured NO_y, and this difference, which is not accounted for, is termed "missing NO_y." Given the mixture of potential nitrogen-containing organics formed in the NO_3 radical reactions (e.g., Figs. 6.8 and 6.9), as well as in NO_2 reactions with organic free radicals (see earlier), it is perhaps not surprising that in many air masses species other than NO_x, HNO_3, PAN, and particulate nitrate are present at significant concentrations. It remains a challenge to identify and measure such species in a specific and sensitive manner.

4. Chlorine Atoms (Cl)

Table 6.14 gives the rate constants for the reactions of chlorine atoms with some simple alkenes and some biogenic hydrocarbons. As expected, the reactions are all very fast, approaching the collision-controlled regime.

TABLE 6.14 Some Reported Values of the Rate Constants for the Reactions of Chlorine Atoms with Some Alkenes at 1 atm Total Pressure and 298 K

Alkene	k (10^{-10} cm^3 molecule^{-1} s^{-1})
Ethene	0.99[a] 1.2[b] 1.2[c]
Propene	2.3[a] 2.7[b] 2.5[d]
1-Butene	2.2[a]
1,3-Butadiene	4.2[a] 5.6[e]
Isoprene	4.6[h] 5.5[e] 2.8[f]
(1*R*)-(+)-α-Pinene	4.8[g]
(1*S*)-(−)-α-Pinene	4.6[g]
3-Carene	5.6[g]
Myrcene	6.6[g]
p-Cymene	2.1[g]
Methyl vinyl ketone	2.0[g]

[a] Stutz *et al.* (1998).

[b] Atkinson and Aschmann (1985), corrected to k(Cl + n-butane) = 2.18×10^{-10} cm^3 molecule^{-1} s^{-1}.

[c] Kaiser and Wallington (1998), based on reported values of k_0 and k_∞.

[d] Kaiser and Wallington (1996).

[e] Bierbach *et al.* (1996).

[f] Bedjanian *et al.* (1998); this is the value of k_∞.

[g] Finlayson-Pitts *et al.* (1999).

[h] Ragains and Finlayson-Pitts (1997).

The reaction proceeds primarily by addition to a double bond to form a chlorine-containing alkyl radical, which then adds O_2 to ultimately generate characteristic chlorine-containing oxygenated products. For example, 1-chloro-3-methyl-3-buten-2-one is formed in the absence of NO from the addition of chlorine atoms to the 4-position of isoprene, followed by secondary reactions of the alkyl radical with O_2 etc. This product might therefore be expected to be a reaction product in the low-NO_x environment of the marine boundary layer (Nordmeyer *et al.*, 1997).

A small portion of the reaction proceeds by what appears to be abstraction of the allylic hydrogen atom from the weaker C–H bond (e.g., Lee and Rowland, 1977). In the case of the isoprene reaction, for example, about 15% of the overall reaction at 1 atm pressure and room temperature proceeds by abstraction (Ragains and Finlayson-Pitts, 1997). It should be noted, however, that this net hydrogen abstraction may not be a simple abstraction per se but rather proceed via an addition–elimination reaction (e.g., Kaiser and Wallington, 1996b; Ragains and Finlayson-Pitts, 1997).

5. Nitrogen Dioxide (NO_2)

NO_2 can add to the double bond of conjugated dienes, but the reaction is generally slow, ranging from 1×10^{-20} cm^3 $molecule^{-1}$ s^{-1} for 2,3-dimethyl-2-butene to 1.3×10^{-17} cm^3 $molecule^{-1}$ s^{-1} for α-phellandrene (see Atkinson, 1997a, for a review). Addition of NO_2 to one of the double bonds generates an alkyl radical that reacts as expected, i.e., adds O_2 to form RO_2 etc. This reaction is not likely to be significant under most atmospheric conditions; for example, at 0.1 ppm NO_2, the lifetime of α-phellandrene is about 9 h, much longer than its lifetimes with respect to reaction with OH and O_3 (see Problem 9). However, it may be important in some laboratory systems where high NO_x concentrations are used. For example, it may be responsible for the observed generation of OH in the dark reaction of isoprene and other conjugated dienes (e.g., Atkinson *et al.*, 1984) with NO_2 in the presence of NO in the dark (Tuazon and Atkinson, 1990) (see Problem 10). Harrison *et al.* (1998) have also proposed that it could be responsible for some of the observed NO to NO_2 conversion during some air pollution episodes at night in London.

F. REACTIONS OF ALKYNES

1. Hydroxyl Radical (OH)

The only significant loss of alkynes is reaction with OH, for which a pressure dependence is observed. Table 6.15 gives the high-pressure limiting rate constants for the OH reactions with acetylene, propyne, 1-butyne, and 2-butyne. The reaction of acetylene approaches the high-pressure limit at several thousand Torr (see Problem 5). However, for the larger alkynes, the reactions are essentially at the high-pressure limit at 1 atm (and room temperature).

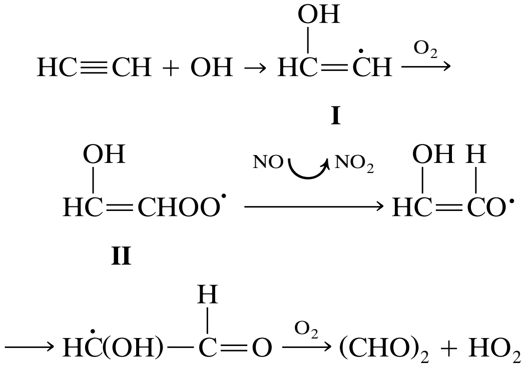
TABLE 6.15 High-Pressure Limiting Rate Constants (k_∞) for the Reaction of OH Radicals with Alkynes at 298 K[a]

Alkyne	**k_∞(OH) (10^{-12} cm^3 $molecule^{-1}$ s^{-1})**
Acetylene	0.90
Propyne	5.9
1-Butyne	8.0
2-Butyne	27.4

[a] From Atkinson (1994) and Atkinson *et al.* (1997a).

The magnitude of the rate constants, their observed pressure dependence, and the products of the reactions are consistent with the mechanism involving the initial addition of OH to the triple bond. For example, the OH–1-butyne reaction at 298 K is about a factor of three faster than the reaction with n-butane (see Table 6.2), despite the fact that it has fewer abstractable hydrogens and the $\equiv$C–H bond is much stronger than a primary –C–H bond (~125 vs ~100 kcal mol^{-1}). In addition, a pressure dependence is not consistent with a simple hydrogen atom abstraction (see Chapter 5.A.2).

The reactions give as major products the corresponding dicarbonyls; i.e., acetylene gives glyoxal [$(CHO)_2$], propyne gives methylglyoxal [CH_3COCHO], and 2-butyne gives biacetyl [$(CH_3CO)_2$] (Schmidt *et al.*, 1985; Hatakeyama *et al.*, 1986). This is consistent with the following reaction sequence:



$$HC{\equiv}CH + OH \rightarrow \underset{\textbf{I}}{H\overset{\overset{OH}{|}}{C}{=}\dot{C}H} \xrightarrow{O_2}$$

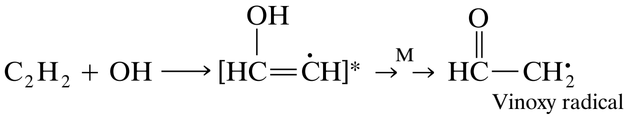
$$\underset{\textbf{II}}{H\overset{\overset{OH}{|}}{C}{=}CHOO^{\bullet}} \xrightarrow{NO \curvearrowright NO_2} H\overset{\overset{OH}{|}}{C}{=}\overset{\overset{H}{|}}{C}O^{\bullet}$$

$$\longrightarrow H\dot{C}(OH)-\overset{\overset{H}{|}}{C}{=}O \xrightarrow{O_2} (CHO)_2 + HO_2 \quad (57)$$

Formic acid is another product, possibly from the rearrangement and decomposition of the intermediate **II** (Hatakeyama *et al.*, 1986).

Siese and Zetzsch (1995) and Bohn and Zetzsch (1998) have studied the OH–C_2H_2 reaction using FP-RF (see Chapter 5.B.3) and observed biexponential decays of OH. They propose that the adduct **I** has two channels in its reaction with O_2, rather than one as shown above, and that one of the two generates OH and glyoxal, a small portion of which is excited and decomposes to HCO.

The vinoxy radical has also been observed as an intermediate (Schmidt *et al.*, 1985), suggesting that a portion of the initial adduct isomerizes:



$$C_2H_2 + OH \longrightarrow [H\overset{\overset{OH}{|}}{C}{=}\dot{C}H]^* \xrightarrow{M} \underset{\text{Vinoxy radical}}{H\overset{\overset{O}{\|}}{C}-CH_2^{\bullet}} \quad (58)$$

The vinoxy radical reacts rapidly with O_2 with a high-pressure limiting rate constant $k_\infty = (1.9 \pm 0.2) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at $P \geq 400$ Torr (Zhu and Johnston, 1995). While the reaction leads to glyoxal formation, the production of glyoxal is delayed compared to the disappearance of the vinoxy radical, suggesting that a long-lived adduct with O_2 is first formed and then subsequently decomposes, in part to glyoxal,

$$\mathrm{CH(O)\dot{C}H_2 + O_2 \rightarrow \left[CH(O)CH_2O\dot{O}\right] \rightarrow \rightarrow (CHO)_2 + OH,} \quad (59)$$

perhaps along with the regeneration of OH, which Schmidt *et al.* (1985) also observed in the presence of O_2. However, Zhu and Johnston (1995) observed the yield of glyoxal from reaction (59) to be only 15%, whereas Hatakeyama *et al.* (1986) measured glyoxal yields in the OH–C_2H_2 reaction of ~70%. Thus reaction (59) cannot be the major path for glyoxal formation in the OH + C_2H_2 reaction. Another reaction proposed for the vinoxy radical (Gutman and Nelson, 1983) is reaction (60):

$$\mathrm{CH(O)CH_2\cdot + O_2 \rightarrow OH + HCHO + CO.} \quad (60)$$

In short, while the overall features of OH–alkyne reactions are understood, more research needs to be done, especially on the alkynes larger than acetylene.

G. REACTIONS OF SIMPLE AROMATIC HYDROCARBONS

1. Hydroxyl Radical (OH)

The reactions of simple aromatic hydrocarbons with OH provide a classic example of how kinetics can be used to elucidate reaction mechanisms. Figure 6.10 shows a semilogarithmic plot of the decay of OH in the presence of a great excess of toluene from 298 to 424 K at ~100 Torr total pressure in argon. While one would expect such plots to be linear (Chapter 5.B.1), this is only observed to be the case at temperatures below 325 K and above about 380 K; at the intermediate temperatures, the plots are clearly curved.

Even more unusual behavior is observed for the temperature dependence of the rate constant. Figure 6.11 shows these data in Arrhenius form for the reactions of toluene and 1,2,3-trimethylbenzene. At the higher temperatures, the Arrhenius plot is linear with a normal activation energy (i.e., the rate constant increases with increasing temperature). However, as the temperature is lowered, there is a sharp discontinuity in the plot and at lower temperatures the temperature dependence is reversed; i.e., the rate constants decrease with increasing temperature.

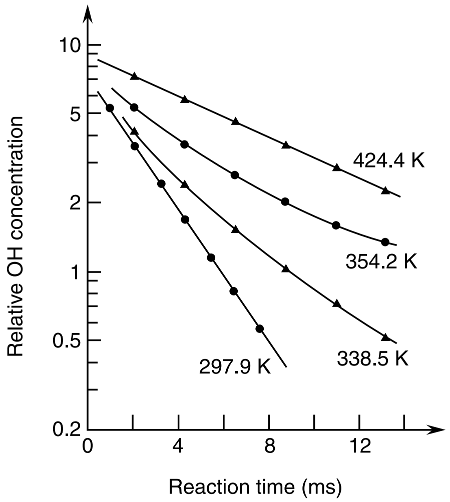
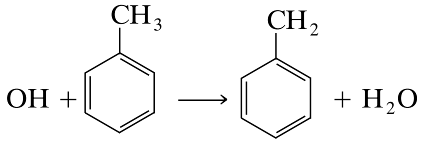


FIGURE 6.10 Semilogarithmic plots of OH decays as a function of reaction time in the presence of a great excess of toluene (~5 × 10^{13} cm^{-1}) at temperatures from 297.9 to 424.4 K and in ~100 Torr argon (adapted from Perry *et al.*, 1977).

These results are now known to reflect the occurrence of two, quite different mechanisms over this temperature range. At the higher temperatures, abstraction of a hydrogen atom occurs, in the case of the substituted benzenes from the alkyl side chains, where the C–H bonds are weaker (~85 kcal mol^{-1} vs ~110 kcal mol^{-1} for C–H bonds in benzene):



(61)

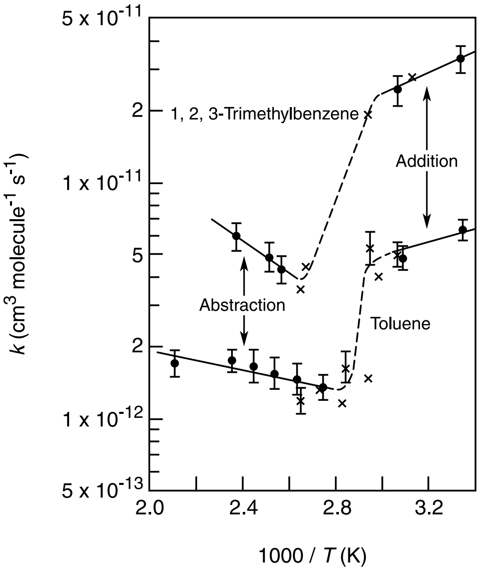
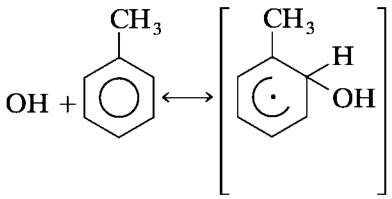


FIGURE 6.11 Arrhenius plots of log *k* vs 1000/T for the reaction of OH with toluene and 1,2,3-trimethylbenzene: (●) exponential OH decays observed; (×) nonexponential OH decays observed (adapted from Perry *et al.*, 1977).

The temperature dependence is that expected for a hydrogen abstraction; i.e., the rate constant increases with temperature (left side of Fig. 6.11).

As the temperature is lowered, the abstraction slows down but another reaction, addition of OH to the aromatic ring, takes place:



(62, −62)

Theoretical calculations support the expectation that the preferred site of initial OH attack is *ortho* to the methyl group (Andino *et al.*, 1996), but addition to the other positions also occurs. If the OH–aromatic adduct, which contains ~18 kcal mol^{-1} excess energy, is not stabilized, it decomposes back to reactants, reaction (−62). The existence of the adduct in the case of the OH–benzene reaction has been observed spectroscopically (Fritz *et al.*, 1985; Knispel *et al.*, 1990; Markert and Pagsberg, 1993; Bjergbakke *et al.*, 1996). As expected for such a mechanism, the rate constants at temperatures below ~300 K exhibit a pressure dependence at lower pressures. At higher temperatures, the rate of decomposition of the excited adduct back to reactants is higher, so the net contribution of adduct formation to the overall reaction is small compared to H-abstraction.

Conversely, at the lower temperatures, the rate constant for H-abstraction is small while, at the same time, the rate of adduct decomposition is lowered. As a result, at the lower temperatures (right side of Fig. 6.11), adduct formation predominates and a "negative" temperature dependence, as well as a dependence on pressure is observed for the overall rate constant. In the intermediate region, both addition and abstraction are occurring at significant rates, leading to the curved OH decay plots in Fig. 6.10 and the discontinuities in the Arrhenius plots of Fig. 6.11.

Table 6.16 shows the room temperature rate constants for the reactions of OH with some simple aromatics as well as the branching ratio for abstraction, i.e., the ratio $k_{61}/(k_{61} + k_{62})$. Abstraction accounts for less than about 10% of the reaction at room temperature for those alkylbenzenes studied to date. It is noteworthy that the reactions are all quite fast, even that for benzene being within approximately two orders of magnitude of diffusion controlled.

The products of the abstraction path are easily predictable, based on our understanding of the fates of alkyl radicals produced in alkane reactions (see Sections C and D). For example, in the case of toluene, the alkyl radical formed in reaction (61) adds O_2 and ultimately forms benzaldehyde and smaller amounts of benzyl nitrate, as shown in Fig. 6.12.

TABLE 6.16 Rate Constants at Room Temperature for OH – Aromatic Hydrocarbon Reactions and Branching Ratios for the Abstraction Reaction[a]

Aromatic	k (10^{-12} cm^3 $molecule^{-1}$ s^{-1})	Branching ratio for abstraction
Benzene	1.2	0.05
Toluene	6.0 (5.5)[b]	0.07–0.12
Ethylbenzene	7.1	
o-Xylene	13.7	0.05–0.10
m-Xylene	23.6 (22.0)[b]	0.04
p-Xylene	14.3	0.08
n-Propylbenzene	6.0	
Isopropylbenzene	6.5	
o-Ethyltoluene	12.3	
m-Ethyltoluene	19.2	
p-Ethyltoluene	12.1	
1,2,3-Trimethylbenzene	32.7	0.06
1,3,5-Trimethylbenzene	57.5 (57.3)[b]	0.03
tert-Butylbenzene	4.6	

[a] From Atkinson (1994).

[b] Numbers in parentheses from Kramp and Paulson (1998).

The greatest uncertainty in the mechanism is the fate of the stabilized OH–aromatic adduct. It had been assumed that it would react with O_2 and ultimately lead to the formation of oxygenated compounds. However, there is also some evidence that the kinetics of the reaction of the adduct with O_2 may be sufficiently slow at room temperature that the reaction with NO_2 may be competitive at the relatively high concentrations of NO_2 used in laboratory studies of these reactions. The rate constants at room temperature for the reactions with O_2 and NO_2 have been reported to be $\sim 5 \times 10^{-16}$ and $\sim 3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, respectively (Knispel *et al.*, 1990; Goumri *et al.*, 1991), in which case the removal of the adduct by these two pathways at 1 atm in air would be equal only at the very high NO_2 concentration of ~3.5 ppm. While these kinetic data suggest that the adduct will react with O_2 under atmospheric conditions, in many labora-

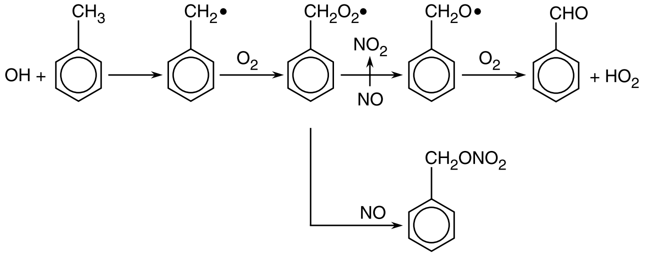
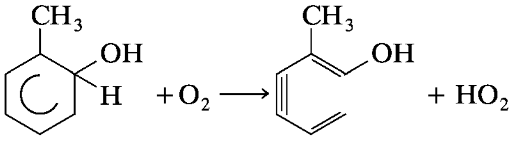


FIGURE 6.12 Mechanism of formation of benzyl nitrate and benzaldehyde from reaction from the methyl side group of toluene.

tory studies where higher NO_x levels are used, a significant portion of the OH–aromatic adducts may be trapped by NO_2, rather than reacting with O_2. As a result, the products from some laboratory studies may not be directly applicable to ambient air.

More recent measurements (Bjergbakke *et al.*, 1996) report the observation of the $HO\text{-}C_6H_6O_2$ peroxy radical by UV absorption (which has been controversial; see Koch, 1997, and Pagsberg, 1997). This study reports rate constants for the $OH\text{-}C_6H_6$ adduct of $\sim 5 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} with O_2 and 1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} with NO_2, in which case reaction of the adduct with NO_2 is not expected to be important. This is clearly an area that warrants further study in order to be able to extrapolate reliably the results of laboratory studies to atmospheric conditions.

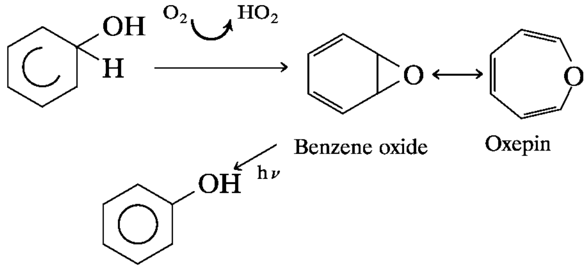
Species such as cresol are known to be products of the toluene oxidation and have commonly been assumed to be formed via reactions such as (63)



(63)

The actual mechanism may not be as simple as implied by this equation, however. For example, Narita and Tezuka (1982) have shown that, in the solution phase oxidation at least, some of the cresol product contains an oxygen atom from the O_2. In addition, in the case of reaction of benzene, phenol may be formed by direct displacement of a hydrogen atom by OH (Bjergbakke *et al.*, 1996; Koch, 1997; Pagsberg, 1997).

There are also data suggesting that O_2 reacts with the OH–aromatic adduct by abstraction of the hydroxyl hydrogen to give an epoxide that photolyzes to the alcohol. Such epoxides are known to be in equilibrium with the isomeric oxepins. For the benzene reaction, for example, the formation of phenol may occur via the following mechanism:



For example, Klotz *et al.* (1997, 1998) have shown that benzene oxide/oxepin photolyzes in sunlight to give phenol with a yield of 43.2 ± 4.5%. This reaction mechanism is therefore feasible for the formation of phenol in the benzene–OH reaction. However, photolysis of toluene 1,2-oxide/2-methyloxepin gave *o*-cresol only in small yields, 2.7 ± 2.2% (Klotz *et al.*, 1998); this suggests that cresols formed in the OH–toluene reaction come primarily from the direct reaction (63) of the OH adduct with O_2, in contrast to the conclusions of Moschonas *et al.* (1999).

A variety of smaller multifunctional oxygenated compounds are also found as products of the gas-phase OH–aromatic reactions. Table 6.17 shows the yields of the smallest dicarbonyl compounds from these reactions, which, while small, are not insignificant. In addition to these products, a variety of other multifunctional compounds are typically found, the numbers, types, and concentrations of these products depending on the analytical methodologies used, the reaction conditions, and the skill and imagination of the experimentalist! Table 6.18, for example, shows some products observed in the photooxidation of toluene in air where the loss is due to attack by OH (Dumdei *et al.*, 1988). In this particular study, ~44% of the reacted toluene could be accounted for by the products shown in Table 6.18.

Similarly, Yu *et al.* (1997) and Yu and Jeffries (1997) report a total of 50 products from the oxidation of

TABLE 6.17 Fractional Yields of Dicarbonyl Compounds from the OH Reaction with Some Aromatic Hydrocarbons at 1 atm Total Pressure and 298 K[a]

Aromatic	Glyoxal $(CHO)_2$	Methylglyoxal CH_3COCHO	Biacetyl $(CH_3CO)_2$
Benzene	0.21		
Toluene	0.08–0.15	0.08–0.15	
o-Xylene	0.03–0.09	0.12–0.25	0.09–0.26
m-Xylene	0.09–0.13	0.27–0.42	
p-Xylene	0.12–0.24	0.11	
1,2,3-Trimethylbenzene	0.06–0.07	0.15–0.18	0.32–0.45
1,2,4-Trimethylbenzene	0.05–0.08	0.36	0.05–0.11
1,3,5-Trimethylbenzene		0.60–0.64	

[a] From Atkinson (1994).

TABLE 6.18 Some Products Observed in the Photooxidation of Toluene[a]

Species	Percentage yield
$CH_3C(O)CHO$	7.7
$(CHO)_2$	5.8
Methylbutenedial	5.8
C_6H_5CHO	5.0
(Hydroxymethyl)butenedial	3.4
Peroxyacetyl nitrate	3.3
Oxoheptadienal	2.7
CH_3COOH	1.8
HCHO	1.0
Hexadienal	1.0
Hydroxyoxoheptadienal	1.0
Hydroxydioxohexenal	0.8
Dioxohexenal	0.7
Hydroxyoxohexenal	0.6
Hydroxyhexadienal	0.6
Methyl vinyl ketone	0.5
Methylfuran	0.5
Hydroxyoxobutanal	0.5
Hexadienedial	0.3
Hydroxymethyl vinyl ketone	0.3
Butenedial	0.3
Hydroxybutenedial	0.2
CH_3CHO	0.2
Pentadienal	0.1
Acrolein	0.06
Pyruvic acid	0.06
Total	44.2

[a] From Dumdei *et al.* (1988); see also Yu *et al.* (1997).

toluene in air in the presence of NO_x. These include additional compounds from those in Table 6.18, such as benzoquinones and epoxides, the latter hypothesized to be formed from an epoxide type of structure predicted theoretically for the OH–aromatic–O_2 adduct in one study (Bartolotti and Edney, 1995). Kwok *et al.* (1997) have studied the reactions of OH with *o*-, *m*-, and *p*-xylene and identified a variety of open-chain multifunctional products, including

$$HC(O)CH{=}CHCHO\,,$$

$$CH_3C(O)CH{=}CHCHO\,,$$

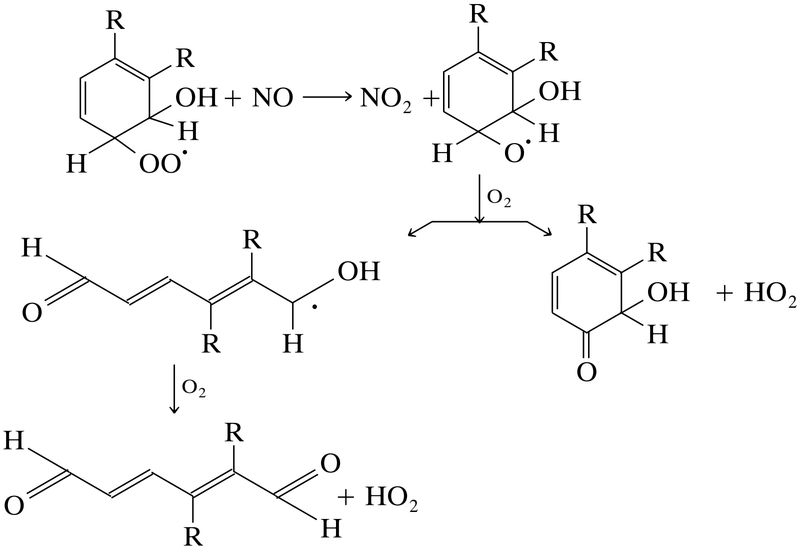
$$CH_3C(O)CH{=}CHC(O)CH_3\,,$$

$$CH_3C(O)C(CH_3){=}CHCH{=}CHCHO\,,$$

and their isomers. It is typical of such aromatic oxidations that only ~40–70% of the reacted parent organic can be accounted for in measured products.

Figure 6.13 shows one postulated reaction sequence taking the adduct to methylglyoxal and butenedial. This represents just one of many possible reaction paths. OH can also add to the ring at the *meta* or *para* positions, in addition to the *ortho* position shown in Eq. (62). The addition of O_2, shown in Fig. 6.13 to occur at the 1-position relative to the OH group, could also occur at the 3- or 5-positions. Ring-cleavage products are also observed in the absence of NO_x (Atkinson and Aschmann, 1994; Seuwen and Warneck, 1996). Subsequent cyclization of the peroxy radical to form allylically stabilized five-membered bicyclic radicals is expected to be the most energetically favored, with the formation of nonallylically stabilized biradicals being endothermic (Andino *et al.*, 1996).

Theoretical studies also suggest that some of the peroxy radicals formed by addition of O_2 to the OH–aromatic adducts may react with NO in competition with cyclization (Andino *et al.*, 1996), generating NO_2 and an aromatic peroxy radical that may subsequently form phenolic and unsaturated derivatives through reactions with O_2:



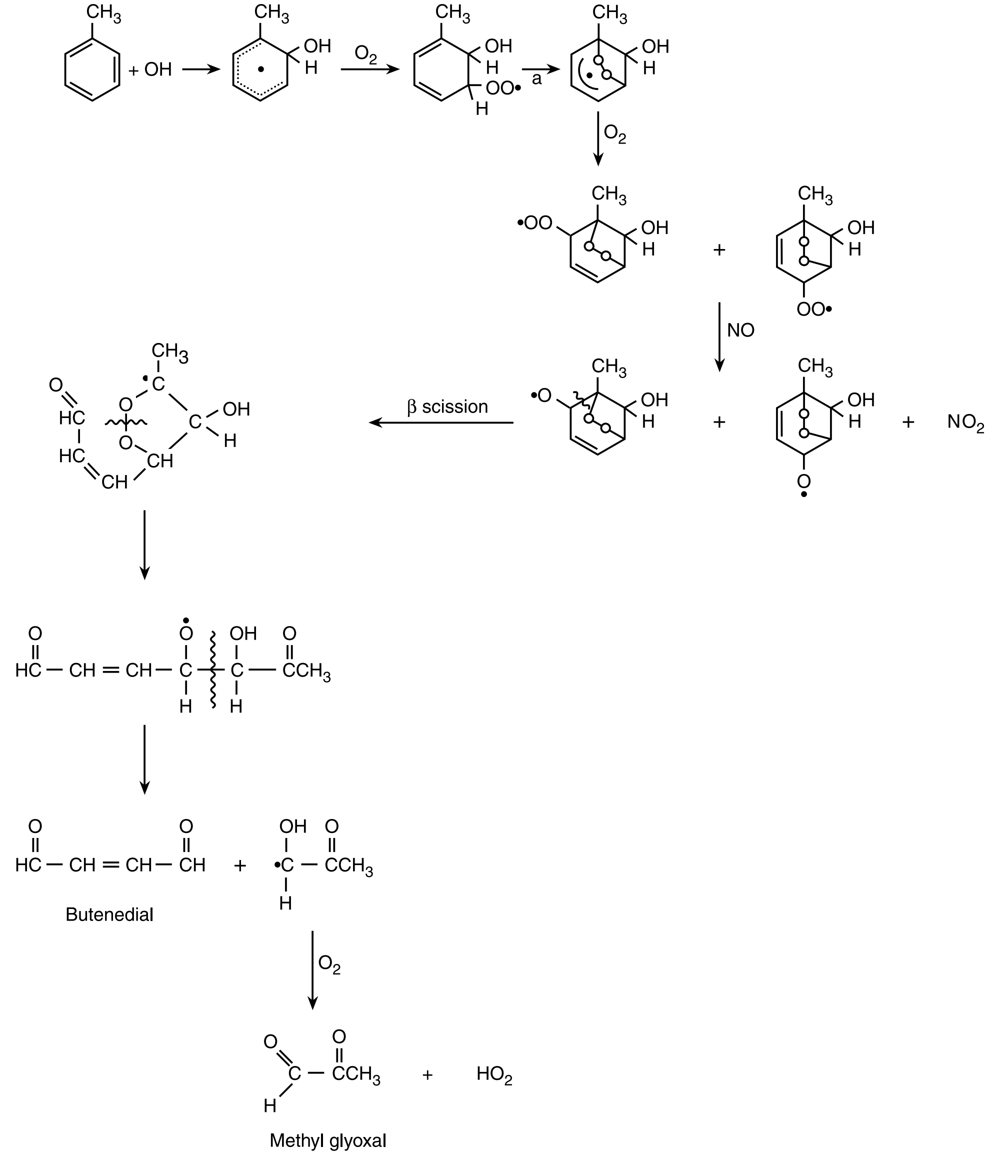


FIGURE 6.13 One postulated fate of the OH–toluene adduct in air.

The simplest phenoxy radical, C_6H_5O, does not react with O_2 ($k < 5 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}) but does react with NO ($k = 1.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) and with NO_2 ($k = 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}), suggesting that reactions with NO_x will be its primary fate in the troposphere (Platz *et al.*, 1998b). However, this may not be the case for the larger, hydroxylated phenoxy radicals from the OH–aromatic–O_2–NO reaction sequence.

In short, there are a multitude of potential reaction pathways that must be considered in OH–aromatic reactions, and the details of the mechanism remain to be elucidated.

The formation of multifunctional, highly reactive "products" such as butenedial may be responsible for much of the missing carbon in these reactions. Such products will also react rapidly with OH, with O_3, and, when present, with NO_3, as well as photolyze. For example, Fig. 6.14 shows the infrared spectrum obtained after a mixture of the *cis* and *trans* forms of butenedial were photolyzed using fluorescent lamps with wavelengths $320 \leq \lambda \leq 480$ nm and the absorptions due to the products CO, CO_2, HCHO, and HCOOH were subtracted out (Bierbach *et al.*, 1994). Most of the remaining bands are due to the product 3*H*-furan-2-one formed from an intramolecular rearrangement of butenedial.

Reaction of butenedial with OH was also shown to give maleic anhydride as a major product (along with glyoxal). Figure 6.15 shows possible mechanisms for

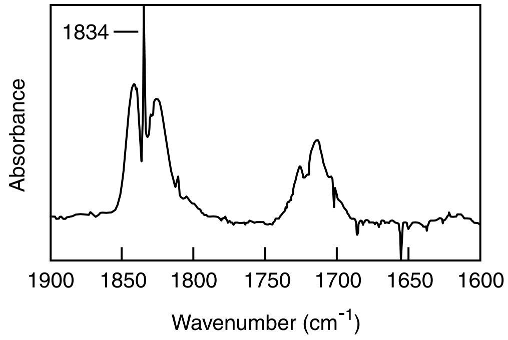
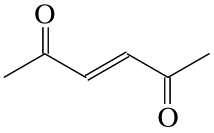


FIGURE 6.14 Infrared spectrum due primarily to 3-H-furan-2-one formed in the photolysis of butenedial after subtraction of bands due to CO, CO_2, HCHO, and HCOOH (adapted from Bierbach *et al.*, 1994).

formation of maleic anhydride from butenedial, which is itself formed in the toluene–OH oxidation.

Further complicating mechanistic understanding is the possibility of different isomers of some of the multifunctional products. For example, one of the products of the *p*-xylene–OH reaction is 3-hexene-2,5-dione:



As shown in Fig. 6.16, it is expected to react with OH to form 4-hydroxyhexane-2,3,5-trione, which, as Wiesen *et al.* (1995) have shown, exists in equilibrium with the enediol form. Further reaction of the enediol with OH forms the trione shown in Fig. 6.16. Wiesen *et al.* (1995) suggest that such polyketones could account for 25–30% of the carbon, which would improve the carbon balance in OH–aromatic reactions considerably.

In short, the mechanism of OH–aromatic reactions remains today one of the least understood areas in tropospheric chemistry.

2. Nitrate Radical (NO_3)

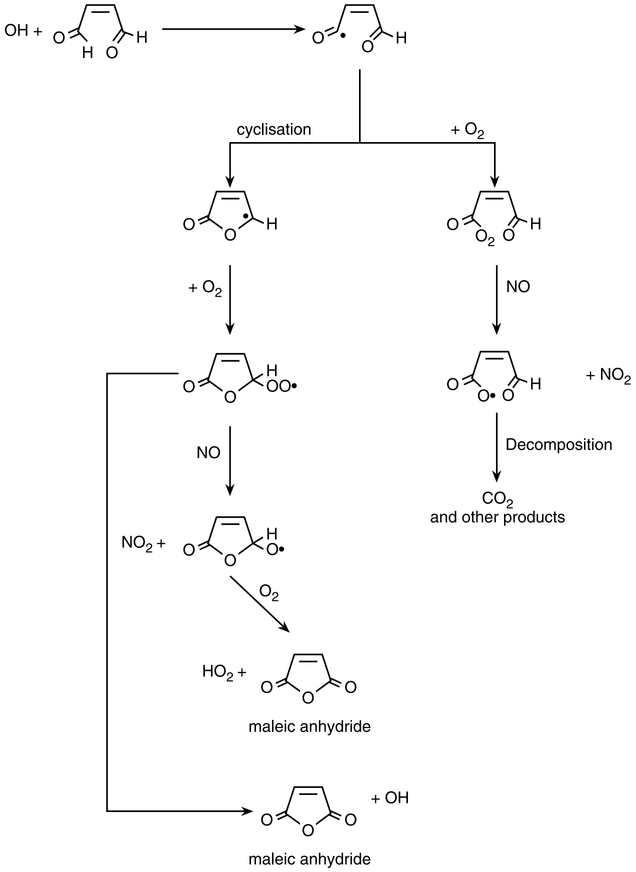
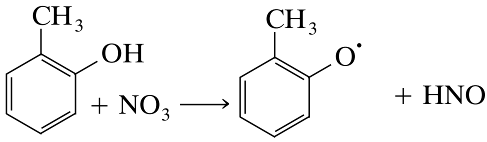


FIGURE 6.15 Postulated reaction scheme from the reaction of *cis*-butenedial with OH (adapted from Bierbach *et al.*, 1994).

As seen in Table 6.1, the reactions of the nitrate radical with the simple aromatic hydrocarbons are generally too slow to be important in the tropospheric decay of the organic. However, one of the products of the aromatic reactions, the cresols, reacts quite rapidly with NO_3. *o*-Cresol, for example, reacts with NO_3 with a room temperature rate constant of 1.4×10^{-11} cm^3 molecule^{-1} s^{-1}, giving a lifetime for the cresol of only ~1 min at 50 ppt NO_3. This rapid reaction is effectively an overall hydrogen abstraction from the phenolic OH (although the mechanism is likely not a direct abstraction process; e.g., Atkinson, 1994):



(64)

3. Chlorine Atoms (Cl)

Chlorine atoms react with aromatic hydrocarbons, but only at a significant rate with those having saturated side chains from which the chlorine atom can abstract a hydrogen or unsaturated side chains to which it can add. For example, the rate constant for the Cl atom reaction with benzene is 1.3×10^{-15} cm^3 molecule^{-1} s^{-1} (Shi and Bernhard, 1997). On the other hand, the rate constants for the reactions with toluene and *p*-xylene are 0.59×10^{-10} and 1.5×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively (Shi and Bernhard, 1997), and that for reaction with *p*-cymene is 2.1×10^{-10} cm^3 molecule^{-1} s^{-1} (Finlayson-Pitts *et al.*, 1999). Hence

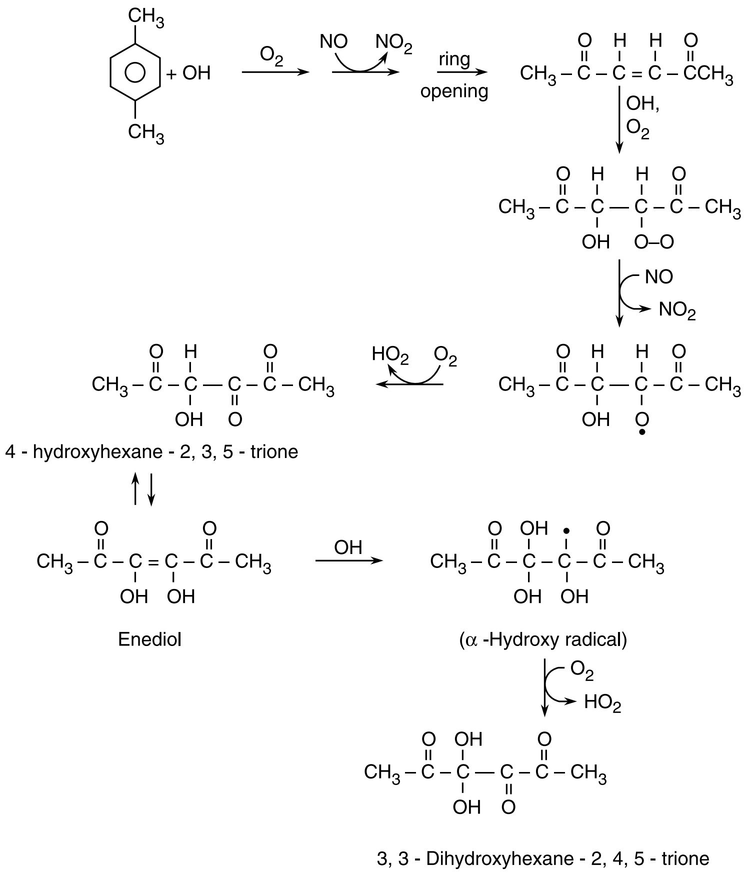


FIGURE 6.16 Formation of polyketones in the OH reaction with *p*-xylene (adapted from Wiesen *et al.*, 1995).

reactions of aromatic hydrocarbons with chlorine atoms will be significant primarily for those species having reactive groups attached to the ring.

H. REACTIONS OF OXYGEN-CONTAINING ORGANICS

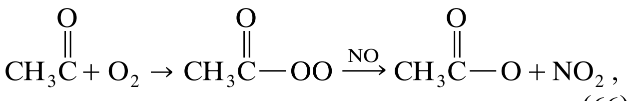
1. Reactions of OH, NO_3, and Cl

Table 6.19 gives the room temperature rate constants for the reactions of some oxygen-containing organics with OH as well as with NO_3 and with chlorine atoms. As expected, the OH reactions are reasonably fast, ranging from $\sim 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} with acetone to more than 10^{-11} cm^3 $molecule^{-1}$ s^{-1} with the aldehydes, furan, and, in general, compounds having an alkyl group larger than $-CH_3$. Chlorine atoms also react very quickly. The NO_3 reactions in most cases are sufficiently slow that OH is the only significant tropospheric oxidant on a global basis for these oxygenated compounds. However, NO_3 can play a role in aldehyde oxidations, especially at night when OH levels are very low.

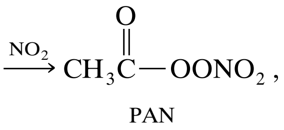
Aldehydes. Reactions with aldehydes occur by abstraction of the relatively weak ($\sim$87 kcal mol^{-1}) aldehydic hydrogen:

$$\mathrm{OH(NO_3, Cl) + RCHO} \rightarrow \mathrm{RCO + H_2O\ (HNO_3, HCl).} \qquad (65)$$

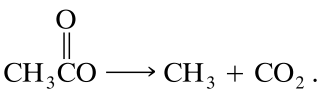
The RCO radical produced then adds O_2 as expected. For example, for acetaldehyde, reaction (65) is followed by



$$\mathrm{CH_3\overset{\overset{\displaystyle O}{\|}}{C} + O_2 \rightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}OO \xrightarrow{NO} CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}O + NO_2}, \qquad (66)$$

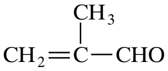
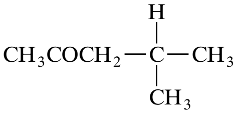
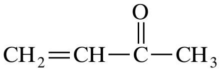
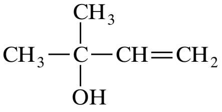
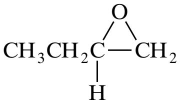


$$\xrightarrow{NO_2} \underset{\text{PAN}}{\mathrm{CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}OONO_2}}, \qquad (67)$$



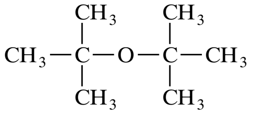
$$\mathrm{CH_3\overset{\overset{\displaystyle O}{\|}}{C}O \longrightarrow CH_3 + CO_2}. \qquad (68)$$

TABLE 6.19 Room Temperature Rate Constants (cm^3 $molecule^{-1}$ s^{-1}) for the Reactions of Some Oxygen-Containing Organics[a]

Organic	OH	NO_3	Cl
Aldehydes			
HCHO	9.2×10^{-12}	5.8×10^{-16}	7.3×10^{-11}[w]
CH_3CHO	1.6×10^{-11}	2.7×10^{-15}	7.2×10^{-11}
CH_3CH_2CHO	2.0×10^{-11}		1.2×10^{-10}
$(CHO)_2$	1.1×10^{-11}		
 $CH_2{=}C(CH_3){-}CHO$ Methacrolein	3.4×10^{-11}	$<8 \times 10^{-15}$[e]	
Ketones			
CH_3COCH_3	2.2×10^{-13}	$<3 \times 10^{-17}$	3.5×10^{-12}
 $CH_3COCH_2{-}CH(CH_3){-}CH_3$	1.4×10^{-11}		
 $CH_2{=}CH{-}C({=}O){-}CH_3$ Methyl vinyl ketone	1.9×10^{-11}	$<1.2 \times 10^{-16}$[e]	2.0×10^{-10}[x]
Alcohols			
CH_3OH	9.3×10^{-13}	2.4×10^{-16}	5.5×10^{-11}[c]
C_2H_5OH	3.2×10^{-12}	$<2 \times 10^{-15}$	9.4×10^{-11}
$n\text{-}C_3H_7OH$	5.5×10^{-12}		1.5×10^{-10}
$(CH_2OH)_2$	1.5×10^{-11}[k]		
$CH_3CH(OH)CH_2OH$	2.2×10^{-11}[k]		
 $CH_3{-}C(CH_3)(OH){-}CH{=}CH_2$ 2-Methyl-3-buten-2-ol	6.4×10^{-11}[f]	1.2×10^{-14}[e]	
Acids			
HCOOH	4.5×10^{-13}		2.0×10^{-13}
CH_3COOH	8×10^{-13}		2.8×10^{-14}
CH_3CH_2COOH	1.2×10^{-12}		
Epoxides			
	1.9×10^{-12}[b]		
Furans			
Furan	4.2×10^{-11}[c]	1.0×10^{-12}[t]	
2-Methylfuran	6.2×10^{-11}[c]	2.6×10^{-11}[t]	
3-Methylfuran	9.3×10^{-11}	$(1.3\text{–}2.9) \times 10^{-11}$[u,t]	
2-Ethylfuran	1.1×10^{-10}[c]		
2,5-Dimethylfuran	1.3×10^{-10}[c]	5.8×10^{-11}[t]	
Ethers			
CH_3OCH_3	3.0×10^{-12}		
$C_2H_5OC_2H_5$	1.3×10^{-11}		
$(CH_3CH_2CH_2CH_2)_2O$	2.9×10^{-11}[j]		
$CH_3OC(CH_3)_3$ (MTBE)	3.1×10^{-12}[g]		
$CH_3CH(OH)CH_2OCH_3$	2.1×10^{-11}[k]		
1,3,5-Trioxane ($C_3H_6O_3$)	6.0×10^{-12}[l]		1.0×10^{-10}[l]
$CH_3OCH_2OCH_3$	4.8×10^{-12}[m]		
$CH_3OCH_2CH_2OCH_3$	$(2.7\text{–}4.1) \times 10^{-11}$[n]		
$CH_3CH_2OC(CH_3)_3$ (ETBE)	8.8×10^{-12}[g]	8.71×10^{-15}[d]	

(*continues*)

TABLE 6.19 (*Continued*)

Organic	**OH**	**NO_3**	**Cl**
Ethers (*Continued*)			
 $CH_3{-}C(CH_3)_2{-}O{-}C(CH_3)_2{-}CH_3$ Di-*tert* butyl ether	$3.7 \times 10^{-12\,h}$	$2.8 \times 10^{-16\,h}$	$1.4 \times 10^{-10\,h}$
Formates, acetates, and other esters			
$HC(O)OCH_3$	$1.7 \times 10^{-13\,n}$		
$HC(O)OC_2H_5$	$8.5 \times 10^{-13\,n}$		
$HC(O)OC_4H_9$	$3.5 \times 10^{-12\,n}$		
$HC(O)C(CH_3)_3$	$7.5 \times 10^{-13\,n}$		
$CH_3C(O)OCH_3$	$3.2 \times 10^{-13\,o}$		
$C_2H_5C(O)OCH_3$	$8.3 \times 10^{-13\,s}$		
n-$C_4H_9C(O)OCH_3$	$4.8 \times 10^{-12\,s}$		
$CH_3C(O)OC_2H_5$	$1.7 \times 10^{-12\,o,v}$		
$CH_3C(O)OC_4H_9$	$5.5 \times 10^{-12\,o,v}$		
$CH_3C(O)OCH(CH_3)_2$	$3.8 \times 10^{-12\,p,v}$		
$CH_3C(O)OC(CH_3)_3$	$5.6 \times 10^{-13\,p,v}$		
$C_2H_5OCH_2CH_2C(O)OC_2H_5$	$2.3 \times 10^{-11\,q}$		
$CH_3OC(O)(CH_2)_xC(O)OCH_3$			
$x = 2$	$1.4 \times 10^{-12\,r}$		
$x = 3$	$3.3 \times 10^{-12\,r}$		
$x = 4$	$8.4 \times 10^{-12\,r}$		
Glycol ethers ($ROCH_2CH_2OH$)			
$R = CH_3$	$(1.1\text{–}1.4) \times 10^{-11\,i,m}$		
$R = C_2H_5$	$(1.5\text{–}1.9) \times 10^{-11\,i,m}$		
$R = C_3H_7$	$1.6 \times 10^{-11\,i}$		
$R = C_4H_9$	$1.9 \times 10^{-11\,i}$		

[a] Unless otherwise stated, from Atkinson *et al.* (1997a) or Atkinson (1994). The additional references cited are not intended to be comprehensive, but merely illustrative of studies of these reactions. [b] From Wallington *et al.* (1988). [c] From Bierbach *et al.* (1992). [d] From Langer and Ljungström (1994). [e] From Rudich *et al.* (1996). [f] From Rudich *et al.* (1995). [g] From Teton *et al.* (1996). [h] From Langer *et al.* (1996). [i] From Stemmler *et al.* (1996). [j] From Kramp and Paulson (1998). [k] From Aschmann and Atkinson (1998a). [l] From Platz *et al.* (1998a). [m] From Porter *et al.* (1997). [n] From Le Calvé *et al.* (1997a). [o] From El Boudali *et al.* (1996). [p] From Le Calvé *et al.* (1997b). [q] From Baxley *et al.* (1997). [r] From Aschmann and Atkinson (1998b). [s] From Le Calvé *et al.* (1997c). [t] From Kind *et al.* (1996). [u] From Alvarado *et al.* (1996). [v] From Picquet *et al.* (1998). [w] From DeMore *et al.* (1997) [x] From Finlayson-Pitts *et al.* (1999).

Ketones. Reactions of ketones are similar to those of alkanes, with abstraction by OH, NO_3, and Cl occurring from the alkyl chains. In the case of acetone, for example, these reactions generate the radical $CH_3COCH_2O_2$ in air. As for typical RO_2, this reacts rapidly with NO ($k^{298} = 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) and with NO_2 ($k^{298} = 6.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) (Sehested *et al.*, 1998b), giving calculated lifetimes with respect to reaction with 100 ppt each of NO and NO_2 of about 1 min. In remote areas where the NO_x concentrations can be much smaller (see later and Chapter 11), reactions of $CH_3COCH_2O_2$ with HO_2 and other RO_2 may also become important.

Photolysis of acetone also contributes significantly to its loss and is the dominant loss process in the upper troposphere (Gierczak *et al.*, 1998; see Section J.3).

The peroxynitrate $CH_3COCH_2OONO_2$ formed from the NO_2 reaction thermally decomposes, with a rate constant of ~3 s^{-1} at 700 Torr and 295 K. Sehested *et al.* (1998b) suggest that its lifetime with respect to thermal decomposition is sufficiently small even at the lower temperatures of the upper troposphere that this species cannot participate in long-range transport of NO_x, as is the case for PAN, and that in the upper troposphere, reaction of $CH_3COCH_2OONO_2$ with OH and photolysis will be major fates.

Alcohols. Reactions of the simple alcohols in air are of particular interest because of their use as alternate fuels, including as blends with gasoline (see Chapter 16.D). There are two possible abstraction sites for the reaction with methanol, the alcohol O–H or the alkyl

C–H. Since the alcohol O–H bond is stronger (~104 kcal mol^{-1}) than the alkyl C–H bond (~96 kcal mol^{-1}) (Lide, 1998–1999), one would expect that abstraction from the alkyl group would predominate, e.g., reaction (69a) would be faster than reaction (69b):

$$CH_3OH + OH \rightarrow CH_2OH + H_2O, \quad (69a)$$

$$\rightarrow CH_3O + H_2O. \quad (69b)$$

In agreement with these expectations, reaction (69a) does indeed appear to account for ~85% of the overall reaction (McCaulley *et al.*, 1989).

In the case of ethanol, three different hydrogen abstractions are possible:

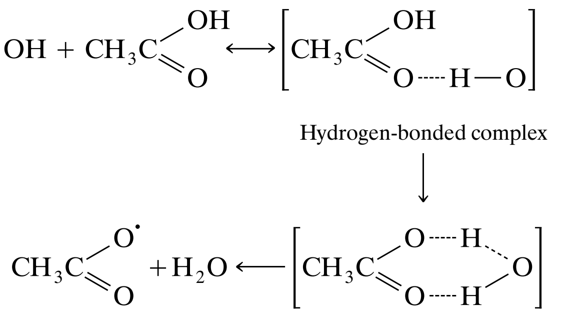
$$CH_3CH_2OH + OH \rightarrow CH_3\dot{C}HOH + H_2O, \quad (70a)$$

$$\rightarrow \cdot CH_2CH_2OH + H_2O, \quad (70b)$$

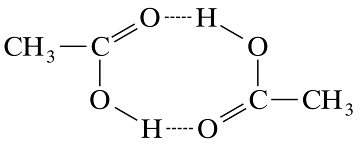
$$\rightarrow CH_3CH_2O\cdot + H_2O. \quad (70c)$$

Abstraction of the secondary hydrogen, reaction (70a), accounts for about 90% of the overall reaction, with the remainder split about equally between (70b) and (70c) (Atkinson *et al.*, 1997a). Similarly, the reaction of OH with 2-butanol and 2-pentanol proceeds predominantly by abstraction of the alkyl hydrogen of the –CH(OH) group (Chew and Atkinson, 1996; Baxley and Wells, 1998).

Carboxylic acids. The mechanism of the OH reaction with carboxylic acids is interesting in that it appears to undergo both addition to form a hydrogen-bonded complex, and abstraction. For the reactions with formic and acetic acids, for example, Singleton, Paraskevopoulos, and co-workers (Jolly *et al.*, 1986; Singleton *et al.*, 1988, 1989) proposed the following mechanism for the formation and reaction of the hydrogen-bonded complex:



Thus, it is the carboxylic hydrogen that is ultimately abstracted by this channel. This is consistent with the decrease in the room temperature rate constant upon deuterium substitution from 5.2×10^{-11} to 4.9×10^{-11} to 1.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for OH + CH_3COOH vs OH + CD_3COOH vs OH + CD_3COOD. Similarly, the rate constants for OH + HCOOH and DCOOH are identical (Wine *et al.*, 1985). That is, only deuteration of the acidic hydrogen has a large effect on the rate constant. The acid dimer also reacts about two orders of magnitude slower than the monomer, because the carboxylic hydrogen is tied up in hydrogen bonding in the dimers:



In competition with the formation and subsequent reaction of the OH–acid complex, there is also a direct hydrogen abstraction channel:

$$OH + CH_3COOH \rightarrow H_2O + \dot{C}H_2COOH.$$

In the case of acetic acid, this channel is small at room temperature. The relative rates of the two channels for formic, acetic, and propionic acids are discussed in detail by Singleton *et al.* (1989).

Overall, given the slowness of the reactions (lifetime ~26 days for HCOOH at [OH] = 1×10^6 radicals cm^{-3}) and the high solubilities and "stickiness" of these acids, they are likely removed primarily by wet and dry deposition rather than by reaction with OH.

OH radical reactions with other oxygen-containing organics such as ethers and glycol ethers, which are used as gasoline additives, solvents, and intermediates in chemical manufacturing, occur by hydrogen abstraction, as expected (e.g., see Wells *et al.* (1996) for the reaction of 2-ethoxy acetate, Stemmler *et al.* (1997) for the reaction of 2-butoxyethanol, and Tuazon *et al.* (1998b) for reactions of acetates). For example, Kerr and co-workers (Eberhard *et al.*, 1993) report that the OH-radical reaction with diethyl ether gives ethyl formate as the major product, with smaller amounts of ethyl acetate and acetaldehyde, as well as some other products that can be rationalized by the mechanisms discussed earlier (see Problem 6). The mechanism of the NO_3 radical reactions with furan and tetramethylfuran is treated by Berndt *et al.* (1997).

2. Hydroperoxyl Radical (HO_2)

Interestingly, while HO_2 is fairly unreactive toward most organics, it does react quite readily with HCHO and certain other aldehydes such as CH_3CHO, CH_3COCHO, and $(CHO)_2$:

$$HO_2 + H_2C{=}O \leftrightarrow OOCH_2OH \quad (71, -71)$$

followed by

$$\mathrm{OOCH_2OH \leftrightarrow HOOCH_2O \rightarrow HCHO + HO_2}.$$

Theoretical studies suggest reaction (71) occurs by a concerted process in which the H from HO_2 is transferred simultaneously to the oxygen of C=O, while the terminal oxygen of HO_2 adds to the carbon (Evleth *et al.*, 1993). The forward rate constant, k_{71}, is 7.9×10^{-14} cm^3 molecule^{-1} s^{-1}, leading to a lifetime of HCHO with respect to HO_2 of only 7 h at $[HO_2] = 5 \times 10^8$ radicals cm^{-3}. However, the reverse decomposition is also fast, $k_{-71} = 150$ s^{-1} at 298 K. If the rate constant for the reaction of the peroxy radical formed in (71) with NO is $\sim 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1},

$$\mathrm{OOCH_2OH + NO \rightarrow OCH_2OH + NO_2}, \quad (72)$$

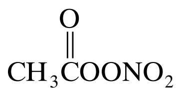
then even at 100 ppb NO, found only in highly polluted areas, the removal of $OOCH_2OH$ in reaction (72) would only be 13% of that via its decomposition, reaction (−71).

In short, while the addition of HO_2 to aldehydes is fast, the decomposition of the adduct back to reactants is sufficiently fast compared to alternate reactions that little net loss of the aldehyde occurs under most conditions.

I. REACTIONS OF NITROGENOUS ORGANICS

1. Peroxyacetyl Nitrate and Its Homologs

Shortly after the discovery of photochemical air pollution, Stephens and his co-workers (Stephens *et al.*, 1956; Stephens, 1987) applied long-path infrared spectroscopy to identifying and measuring products in the photooxidation of organic–NO_x mixtures. In the photooxidations of 3-methylheptane and, to a larger extent, 2,3-butanedione, a set of infrared bands that could not be assigned to known products was observed. These were assigned to a previously unobserved species, which was initially called "compound X." It was ultimately shown to be peroxyacetyl nitrate (PAN):



$$\mathrm{CH_3\overset{\overset{\displaystyle O}{\|}}{C}OONO_2}$$

PAN

For a detailed discussion of the discovery of PAN in the context of early studies of photochemical air pollution, the reader is referred to an article by Stephens (1987).

PAN is the simplest member of a series of compounds known as peroxyacyl nitrates, having the structure

$$\mathrm{R\overset{\overset{\displaystyle O}{\|}}{C}OONO_2}$$

The nomenclature for this homologous series is somewhat confused. The term "PANs" has been used historically to denote peroxyacyl nitrates, and this terminology continues to be used extensively in the literature, despite the lack of adherence to traditional IUPAC rules of nomenclature. Because the PANs can be considered to be mixed anhydrides of carboxylic acids and nitric acid, another suggestion (Roberts, 1990) has been "peroxyacetic nitric anhydride" for $CH_3C(O)OONO_2$ and "peroxy carboxylic nitric anhydrides" for the whole class of compounds. Although it does not follow the IUPAC rules, it would be consistent with the widespread use of the name "PAN" but also reflect the structure more accurately. Table 6.20 shows the structures and commonly used names of some PANs that have been observed in the atmosphere and/or in laboratory studies.

PAN is known to play an important role in tropospheric chemistry. As discussed in this section, its thermal decomposition releases both NO_2 and an organic free radical, so that it can act as an NO_x reservoir and ultimately as a source of OH in the dark. In addition, PAN is a strong lachrymator (eye irritant), is mutagenic in certain bacterial assays, and is phytotoxic to plants. Because of these broad effects on a variety of systems, its formation and reactions have been studied in some detail.

As seen earlier in this chapter, the oxidation of organics produces a variety of free radicals, some of which can form peroxyacyl nitrates. For example, acetaldehyde is a classic precursor to the PAN through the following reaction sequence:

$$\mathrm{CH_3CHO + OH \rightarrow CH_3CO + H_2O}, \quad (73)$$

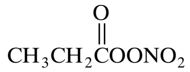
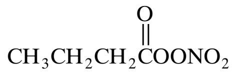
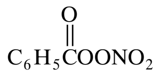
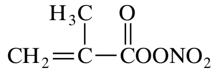
$$\mathrm{CH_3CO + O_2 + M \rightarrow CH_3C(O)OO + M}, \quad (74)$$

$$\mathrm{CH_3C(O)OO + NO_2 + M \leftrightarrow CH_3C(O)OONO_2 + M}. \quad (75, -75)$$

As expected for a termolecular reaction, reaction (74) proceeds through the formation of an excited intermediate that can decompose back to reactants at lower pressures. At 298 K and 1 atm pressure, $k_{74} = 3.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (e.g., Tyndall *et al.*, 1997), about half that for other alkyl radical reactions with O_2 discussed earlier.

A key feature of reaction (75) is that it is reversible; i.e., PAN thermally decomposes back to peroxyacetyl

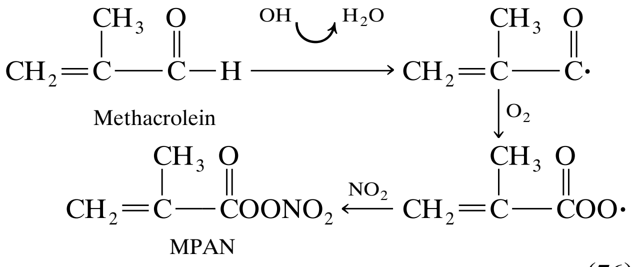
TABLE 6.20 Structures and Commonly Used Names for Some Peroxyacyl Nitrates Found in the Atmosphere and/or in Laboratory Studies

Name	Acronym	Structure
Peroxyacetyl nitrate (peroxyacetic nitric anhydride)	PAN	 $CH_3\overset{\overset{O}{\|}}{C}OONO_2$
Peroxypropionyl nitrate	PPN	 $CH_3CH_2\overset{\overset{O}{\|}}{C}OONO_2$
Peroxy-*n*-butyryl nitrate	PnBN	 $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}OONO_2$
Peroxybenzoyl nitrate	PBzN	 $C_6H_5\overset{\overset{O}{\|}}{C}OONO_2$
Peroxymethacryloyl nitrate	MPAN	 $CH_2{=}\overset{\overset{H_3C}{|}}{C}{-}\overset{\overset{O}{\|}}{C}OONO_2$

radicals and NO_2. Indeed, it is this thermal decomposition that accounts for most of the loss of PAN under typical conditions in the troposphere.

The simplest compound in the series, PAN, is also the one found in the highest concentrations in the atmosphere. While PAN, PPN, PnBN, PBzN, and MPAN have all been identified in ambient air, PAN predominates by a large margin, and it is only for PAN and, to a lesser extent, PPN that a large number of measurements have been reported (e.g., see Gaffney *et al.*, 1989; Roberts, 1990; Altshuller, 1993; Williams *et al.*, 1993; Grosjean *et al.*, 1993a, 1993b; Kleindienst, 1994; and Chapter 11.A.4g). Measurements in a number of locations around the world typically show PPN/PAN ratios of ~0.1–0.3. In highly polluted air, PAN has been observed to reach concentrations as high as 70 ppb.

The oxidation of isoprene, one of the most common biogenic hydrocarbons, is expected to lead to the formation of some MPAN. Thus, as treated earlier, one of the major products of isoprene oxidation is methacrolein. Its subsequent oxidation by OH is expected to form MPAN:



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}H \xrightarrow{OH\ \ H_2O} CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\overset{\overset{O}{\|}}{C}\cdot \xrightarrow{O_2} CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\overset{\overset{O}{\|}}{C}OO\cdot \xrightarrow{NO_2} CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\overset{\overset{O}{\|}}{C}OONO_2 \tag{76}$$

Like the other higher PANs, MPAN is expected to be formed in relatively small yields and indeed, this compound has been identified and measured in rural areas where isoprene is present (e.g., see Bertman and Roberts, 1991; Williams *et al.*, 1997; Nouaime *et al.*, 1998; and Roberts *et al.*, 1998). In one study in the rural southeastern United States, the MPAN concentration was found to track that of methacrolein but with a delay of several hours (Fig. 6.17); Nouaime *et al.* (1998) attributed this positive correlation to a more rapid formation of methacrolein compared to its rate of reaction to form MPAN.

Of all the possible fates for PANs in the atmosphere, thermal decomposition is usually the most important; e.g., for PAN

$$CH_3C(O)OONO_2 \overset{\Delta}{\rightarrow} CH_3C(O)OO + NO_2. \tag{77}$$

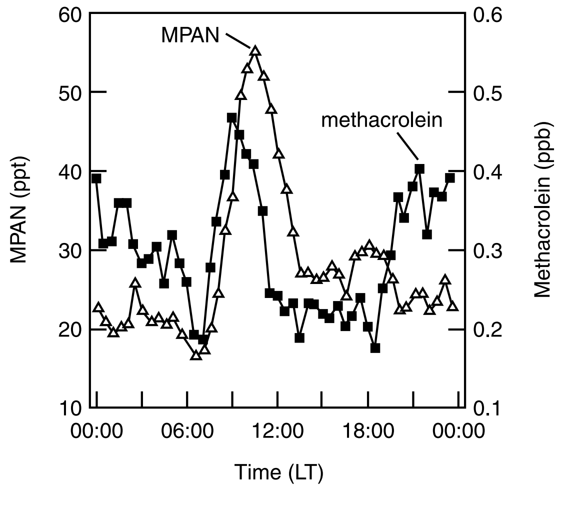


FIGURE 6.17 Diurnal variation of mean mixing ratios of MPAN and its precursor methacrolein measured near Nashville, Tennessee (adapted from Nouaime *et al.*, 1998).

Table 6.21 gives the Arrhenius parameters for the decomposition of various PANs and the rate constants and corresponding lifetimes for PAN. The decomposition is strongly temperature dependent, with long lifetimes, of the order of a year or more at low temperatures of ~215 K, and very short lifetimes, < 1 h, at the higher temperatures around 298 K.

The effective rate of decomposition depends on the ratio of NO to NO_2. Thus the acetylperoxy radical formed in the decomposition must be removed by further reaction, e.g., with NO,

$$CH_3C(O)OO + NO \rightarrow CH_3C(O)O + NO_2, \quad (78)$$

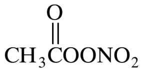
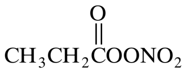
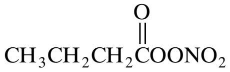
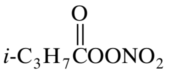
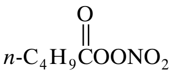
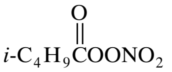
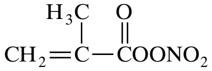
before it reacts back with NO_2 to regenerate PAN, reaction (75), in which case there has been no net reaction (see Problem 8). As a result, the ratio of rate constants k_{75}/k_{78} as well as the ratio of NO_2 to NO concentrations is important. This rate constant ratio has been measured to be $k_{75}/k_{78} \sim 0.4$ for both PAN and peroxypropionyl nitrate (e.g., see Seefeld *et al.*, 1997; Seefeld and Kerr, 1997; and Sehested *et al.*, 1998b). The $CH_3C(O)O$ radical rapidly decomposes to $CH_3 + CO_2$. In regions where NO levels are low, $CH_3C(O)OO$ can also be removed by reactions with other RC(O)OO, RO_2, HO_2, and NO_3, which then become important in determining the lifetime of PAN (Madronich and Calvert, 1990; Stockwell *et al.*, 1995).

This strong temperature dependence has important implications for the role of PAN, and its higher homologs, in the troposphere. Thus, when it is formed at lower temperatures or is transported into colder regions, it is stabilized and acts as an NO_x reservoir. When an air mass containing PAN is transported into warmer regions, however, the PAN decomposes, releasing both the NO_2 and the acetylperoxy free radical. If sufficient NO is present, the organic free radical reacts in the following manner:

$$CH_3C(O)OO + NO \rightarrow CH_3C(O)O + NO_2, \quad (78)$$

$$CH_3C(O)O \rightarrow CH_3 + CO_2, \quad (79)$$

TABLE 6.21 Rate Constants and Temperature Dependence[a] for the Thermal Decomposition of Some PANs

Compound	Temperature dependence	$k^{298\ K}$ (10^{-4} s^{-1})	τ^b (min)
 $CH_3C(=O)OONO_2$ PAN	$k_0 = 4.9 \times 10^{-3} \exp(-12{,}100/T)[N_2]$ $k_\infty = 5.4 \times 10^{16} \exp(-13{,}830/T)$ $F_c = 0.3$	3.3	50
 $CH_3CH_2C(=O)OONO_2$ PPN	$2 \times 10^{15} \exp(-12{,}800/T)$	4.4	38
 $CH_3CH_2CH_2C(=O)OONO_2$ PnBN	$3.2 \times 10^{18} \exp(-15{,}150/T)$	2.7	62
 $i\text{-}C_3H_7C(=O)OONO_2$ PiBN	$1.6 \times 10^{18} \exp(-15{,}000/T)$	2.2	76
 $n\text{-}C_4H_9C(=O)OONO_2$	$1.3 \times 10^{12} \exp(-10{,}870/T)$	1.8	93
 $i\text{-}C_4H_9C(=O)OONO_2$	$2.5 \times 10^{9} \exp(-15{,}800/T)$	2.4	69
 $CH_2{=}C(CH_3){-}C(=O)OONO_2$ MPAN	$1.6 \times 10^{16} \exp(-13{,}488/T)$	3.5	48

[a] For PAN and PPN, from Atkinson *et al.* (1997a); for MPAN, from Roberts and Bertman (1992); for PnBN, PiBN, and *n*- and *i*-$C_4H_9C(O)OONO_2$, from Grosjean *et al.* (1994a, 1994b) over a limited temperature range (291–299 K). Note that PAN is not in the high-pressure limit at 298 K and 1 atm, whereas the higher homologs are.

[b] Assuming no back reaction with NO_2 (see text).

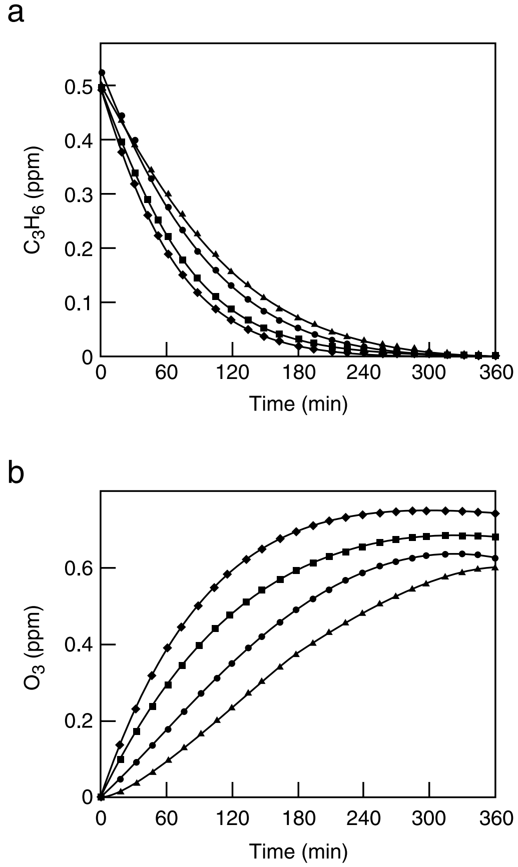


FIGURE 6.18 Concentration–time profiles in an environmental chamber for (a) propene and (b) O_3 as a function of increasing initial concentrations of PAN. Temperature ~30°C, relative humidity ~60%, [NO] = [NO_2] = 0.26 ppm, [C_3H_6] = 0.5 ppm. (▲) No added PAN; (●) 0.06 ppm PAN added; (■) 0.13 ppm PAN added; (◆) 0.26 ppm added PAN (adapted from Carter *et al.*, 1981a).

followed by the reaction of CH_3 with O_2, etc., to form HCHO and HO_2, or HCHO, CH_3OH, and CH_3OOH under low-NO$_x$ conditions. As a result of this chemistry, it was suggested by Hendry and Kenley (1979) that PAN should act as an accelerator for photochemical smog formation, and indeed this is the case. Figure 6.18, for example, shows that in smog chamber studies, the loss of propene and the formation of O_3 are accelerated by the addition of PAN (Carter *et al.*, 1981a).

At lower temperatures such as those found in the Arctic, the majority of NO$_y$ is often present in the form of PAN because of its thermal stability. For example, 50–90% of NO$_y$ may exist in the form of PAN in the Arctic spring (Bottenheim *et al.*, 1986; Barrie and Bottenheim, 1991; Jaffe, 1993). It is also interesting that, in relatively "clean," low-NO$_x$ regions at higher temperatures, PANs may also tie up significant amounts of NO$_x$ (Singh *et al.*, 1985; Madronich and Calvert, 1990).

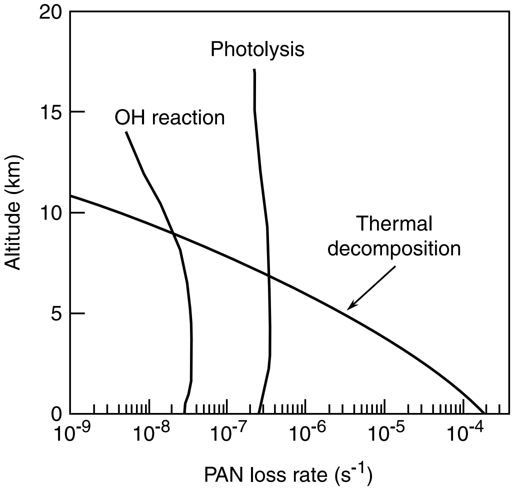


FIGURE 6.19 Calculated first-order loss rates of PAN due to thermal decomposition, OH reaction, and photolysis as a function of altitude (assuming diurnally averaged actinic fluxes for 30°N, July 4) (adapted from Talukdar *et al.*, 1995).

The reaction of OH with PAN and its homologs appears to be sufficiently slow, $k < 3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (Talukdar *et al.*, 1995), that it cannot compete with thermal decomposition. For example, Figure 6.19 shows the calculated loss rates for PAN in the atmosphere as a function of altitude (Talukdar *et al.*, 1995). Photolysis (see Chapter 4.J) only becomes important above 5 km, and the reaction with OH does not compete at any altitude.

For a detailed treatment of peroxyacyl nitrates, see the recent reviews by Gaffney *et al.*, 1989; Roberts, 1990; Altshuller, 1993; and Kleindienst, 1994.

2. Alkyl Nitrates and Nitrites

a. Alkyl Nitrates

As discussed earlier in this chapter, alkyl nitrates ($RONO_2$) are expected to be formed as minor products of the RO_2 + NO reaction, especially in the case of larger alkylperoxy radicals where as much as ~30–35% of the reaction may give stabilized alkyl nitrates rather than RO + NO_2. It is noteworthy that while NO$_x$ levels tend to be low in "clean" areas, modeling studies by Madronich and Calvert (1990) suggest that a significant fraction (~30–70%) of NO$_y$ may be tied up as various alkyl nitrates (including multifunctional nitrates) in these regions.

The absorption cross sections and photochemistry of alkyl nitrates are discussed in Chapter 4.J, where the

TABLE 6.22 Room Temperature Rate Constants for the Reactions of OH with Some Simple Alkyl Nitrates at 298 K[a]

Alkyl nitrate	$k^{298\text{K}}$ (10^{-13} cm^3 molecule^{-1} s^{-1})
CH_3ONO_2	0.35, 0.30,[b] 0.24[c]
$C_2H_5ONO_2$	4.9, 2.0,[b], 1.8[c]
n-$C_3H_7ONO_2$	7.3
i-$C_3H_7ONO_2$	4.9, 2.9[c]
$CH_3CH(ONO_2)CH_2CH_3$	9.2
$CH_3CH(ONO_2)CH_2CH_2CH_3$	18.5
$CH_3CH_2CH(ONO_2)CH_2CH_3$	11.2
$CH_3CH_2CH(ONO_2)(CH_2)_4CH_3$	38.8

[a] From Atkinson *et al.* (1997a) and Atkinson (1994).

[b] Kakesu *et al.* (1997), from 304 to 310 K for CH_3ONO_2 and from 298 to 310 K for $C_2H_5ONO_2$.

[c] Talukdar *et al.* (1997).

photolysis appears to occur via breaking the O–NO_2 bond. However, the absorption cross sections are not large, and hence the lifetimes with respect to photolysis are quite long, of the order of a week or more at the earth's surface and several days at higher altitudes where the solar flux is larger (e.g., see Clemitshaw *et al.*, 1997).

Reaction with OH is, however, reasonably rapid as might be expected and is of the same order of magnitude as the OH–alkane reactions. Table 6.22, for example, shows the room temperature rate constants for the reactions of OH at 298 K with some alkyl nitrates. With 2-butyl nitrate as an example, the lifetime with respect to the OH reaction with OH at 1×10^6 radicals cm^{-3} is about 13 days, comparable to the photolysis rate. As with the alkanes, abstraction of a hydrogen atom occurs to form an alkyl radical, whose fate is the same as discussed in Section 6.D earlier.

b. Alkyl Nitrites

Alkyl nitrites (RONO) absorb light strongly in the actinic region, dissociating to form RO + NO. Because of this rapid photolysis, other reactions such as that with OH cannot compete, and alkyl nitrites have not been generally observed in the troposphere at significant concentrations.

3. Amines, Nitrosamines, and Hydrazines

a. Amines

Aliphatic amines are emitted from a variety of sources, including feedlots, sewage treatment, waste incineration, and industrial activities (e.g., Schade and Crutzen, 1995). They have also been measured in nonurban areas (e.g., see Van Neste *et al.*, 1987; Gorzelska and Galloway, 1990; and Eisele and Tanner, 1990). Because they do not absorb light in the actinic region (Calvert and Pitts, 1966), they are not removed by photolysis. Hence reactions with atmospheric oxidants such as OH and O_3 are the major removal processes for these organic nitrogen compounds. Reaction with HNO_3 may also occur in polluted urban areas.

Table 6.23 gives the rate constants for the reactions of OH and O_3 with some simple alkyl amines at room

TABLE 6.23 Room Temperature Rate Constants and Estimated Atmospheric Lifetimes for the Gas-Phase Reactions of Some Alkyl Amines and Amides with OH[a] and O_3[b]

	OH		O_3	
Amine or amide	k (10^{-11} cm^3 molecule^{-1} s^{-1})	τ^c (h)	k (10^{-18} cm^3 molecule^{-1} s^{-1})	τ^d
CH_3NH_2	2.2,[a] 1.7[e]	13	0.0074	~2 yr
$C_2H_5NH_2$	2.8, 2.4[e]	10		
$(CH_3)_2NH$	6.5[a,e]	4	1.67	67 h
$(CH_3)_3N$	6.1,[a] 3.6[e]	5	7.84	14 h
$(CH_3)_3CNH_2$	1.2[f]	23		
$CH_3NHC(O)CH_3$	0.52[g]	53		
$CH_3NHC(O)C_2H_5$	0.76[g]	37		
$(CH_3)_2NC(O)CH_3$	1.4[g]	20		

[a] From Atkinson (1989).

[b] From Tuazon *et al.* (1994).

[c] Assuming [OH] = 1×10^6 radicals cm^{-3}.

[d] Assuming [O_3] = 100 ppb = 2.5×10^{12} molecules cm^{-3}.

[e] Carl and Crowley (1998).

[f] Koch *et al.* (1996).

[g] Koch *et al.* (1997).

temperatures and the associated atmospheric lifetimes under typical, moderately polluted tropospheric conditions. As might be expected, OH reacts quite rapidly with the simple amines. Perhaps somewhat surprising, however, are the relatively rapid reactions of di- and trimethylamine with O_3.

The N–H bond strength in CH_3NH_2 is ~100 kcal mol^{-1}, stronger than the C–H bond at 93 kcal mol^{-1}. Similarly, in $(CH_3)_2NH$, the N–H bond strength is ~92 kcal mol^{-1}, compared to 87 kcal mol^{-1} for the C–H bond. One might expect abstraction of a C–H hydrogen to predominate in these reactions, and this appears to be the case. For example, for $(CH_3)_2NH$, Lindley *et al.* (1979) report that 63% of the reaction occurs by (80a),

$$OH + (CH_3)_2NH \rightarrow H_2O + CH_2NHCH_3, \quad (80a)$$

and the remainder by (80b):

$$OH + (CH_3)_2NH \rightarrow H_2O + (CH_3)_2N \quad (80b)$$

The subsequent reactions of the alkyl radical formed in reaction (80a) and the dimethylamino radical in (80b) are expected to be as follows:

$$(CH_3)_2N + O_2 \rightarrow \text{Products}$$

$$[\text{e.g., } CH_2 = NCH_3 + HO_2 \text{ or } (CH_3)_2NOO?], \quad (81)$$

$$(CH_3)_2N + NO \overset{M}{\rightarrow} (CH_3)_2NNO, \quad (82)$$

$$(CH_3)_2N + NO_2 \rightarrow (CH_3)_2NNO_2, \quad (83a)$$

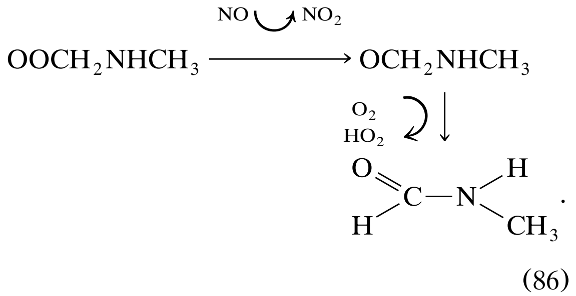
$$\rightarrow HONO + CH_2 = NCH_3, \quad (83b)$$

$$(CH_3)_2N + (CH_3)_2NNO_2 \rightarrow$$

$$(CH_3)_2NN(CH_3)_2 + NO_2, \quad (84)$$

$$2(CH_3)_2N \rightarrow (CH_3)_2NN(CH_3)_2, \quad (85)$$

$$CH_2NHCH_3 + O_2 \longrightarrow$$



$$OOCH_2NHCH_3 \xrightarrow{NO \curvearrowright NO_2} OCH_2NHCH_3 \xrightarrow{O_2 \curvearrowright HO_2} HC(O)NHCH_3.$$

(86)

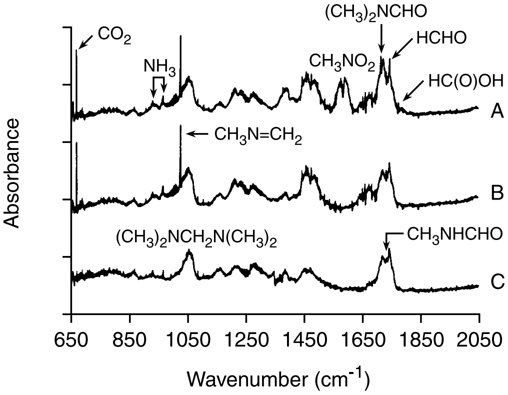
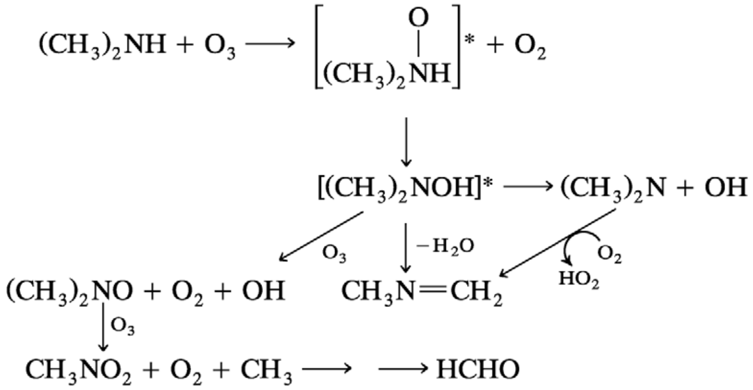


FIGURE 6.20 Infrared spectrum of the products of reaction of 19 ppm $(CH_3)_2NH$ with 5.5 ppm O_3 at room temperature and in 740 Torr air: (A) product spectrum; (B) after subtraction of $(CH_3)_2NCHO$, CH_3NO_2, HCHO, and HCOOH absorptions; (C) after subtraction of $(CH_3)N{=}CH_2$ and CO_2 absorptions (adapted from Tuazon *et al.*, 1994).

Most of the products predicted by this reaction scheme have been observed in laboratory studies, including dimethylnitramine [$(CH_3)_2NNO_2$], HONO, tetramethylhydrazine [$(CH_3)_2NN(CH_3)_2$], and small amounts of methylformamide as products of the photooxidation of dimethylamine (e.g., see Pitts *et al.*, 1978; and Tuazon *et al.*, 1978). In addition, HCHO, CO, and small amounts of dimethylformamide were identified in these studies.

It is noteworthy that the dimethylamino radical reaction with O_2 is about a factor of ~10^6–10^7 slower than its reactions with NO and NO_2. For example, Lindley *et al.* (1979) measured the ratio of rate constants $k_{81}/k_{82} = 1.5 \times 10^{-6}$ and $k_{81}/k_{83a} = 3.9 \times 10^{-7}$. Thus, at ~10 ppb NO_x, reactions of the nitrogen-centered radical with NO and NO_2, in addition to O_2, become important. This is perhaps not surprising, given that NH_2 radicals also react extremely slowly with O_2, with an upper limit of 6×10^{-21} cm^3 $molecule^{-1}$ s^{-1} (Tyndall *et al.*, 1991).

There are few kinetic or product studies of the reactions of O_3 with simple amines. Figure 6.20 shows the infrared spectrum of the products of the reaction of dimethylamine with O_3 (Tuazon *et al.*, 1994). The major products observed are $CH_3N{=}CH_2$, CH_3NO_2, HCHO, CH_3NHCHO, $(CH_3)_2NCHO$, $(CH_3)_2NCH_2N(CH_3)_2$, HCOOH, and CO_2. The major nitrogen-containing products were explained by Tuazon and co-workers by the following mechanism:The



(87)

CH_3NHCHO arises from the reaction of the OH generated in the system with the parent amine to form the CH_2NHCH_3 alkyl radical, followed by reaction (86). *N,N,N′,N′*-Tetramethyldiaminomethane, $(CH_3)_2NCH_2N(CH_3)_2$, seen in Fig. 6.20C, was shown to be formed in the reaction of dimethylamine with the product HCHO:

$$2(CH_3)_2NH + HCHO \rightarrow (CH_3)_2NCH_2N(CH_3)_2 + H_2O. \quad (88)$$

Further reaction of this product with O_3 was shown to give $(CH_3)_2NCHO$, observed as a product in Fig. 6.20A.

It should be noted, however, that in studies of amine photooxidations, it is generally true that a significant fraction of the reacted parent amine remains unaccounted for in the identified products. Clearly, the mechanisms and products are complex and warrant further investigation.

b. Nitrosamines

One difficulty in studying the photooxidation of amines is the rapid reaction in the dark with nitrous acid to form nitrosamines (Hanst *et al.*, 1977; Pitts *et al.*, 1978):

$$R_2NH + HONO \leftrightarrow R_2NNO + H_2O. \quad (89)$$

As discussed in Chapter 7.B.3, NO_2 undergoes a surface reaction with water, which is perhaps enhanced at the air–water interface, forming HONO:

$$2NO_2 + H_2O \xleftrightarrow{\text{surface}} HONO + HNO_3. \quad (90)$$

Thus, in the course of preparing reactant mixtures for photooxidation studies under typical atmospheric conditions where both NO_2 and water vapor are present, it is essentially impossible to avoid the production of some HONO, and in the case of studies of amine reactions, some nitrosamines. However, this too is quite relevant, since nitrosamines are carcinogenic in experimental animals. In addition, there are a number of sources that emit nitrosamines directly into the air, including leather tanneries, rocket fuels, tire and amine factories, and tobacco smoke (e.g., see Fine, 1980).

The major atmospheric fate of the *N*-nitrosamines such as *N*-nitrosodimethylamine is photolysis (Tuazon *et al.*, 1984):

$$(CH_3)_2NNO + h\nu \rightarrow (CH_3)_2N + NO. \quad (91)$$

The dimethylamino radical then reacts as described earlier.

c. Hydrazines

Hydrazines see widespread use as fuels, for example, in the space shuttle and as a source of emergency power in the F-16 fighter plane. As a result of the industrial and fuel uses of hydrazines, with their accompanying transport and storage, some emissions to the atmosphere occur and hence there is interest in their atmospheric reactions.

Hydrazines do not photolyze in the actinic UV, but reactions with OH and O_3 must be considered. The rate constants for reaction of OH with N_2H_4 and CH_3NHNH_2 are $(6.1 \pm 1.0) \times 10^{-11}$ and $(6.5 \pm 1.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively, essentially independent of temperature over the range 298–424 K (Harris *et al.*, 1979). At an OH concentration of 1×10^6 cm^{-3}, the lifetimes of both N_2H_4 and CH_3NHNH_2 will be $\sim$4–5 h. Harris and co-workers (1979) estimate that the rate constant for the reaction of OH with 1,1-dimethylhydrazine is $\sim(5 \pm 2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, so that its lifetime with respect to OH will be similar, $\sim$6 h.

Reaction with O_3 is also relatively fast. Tuazon *et al.* (1981) estimate that the rate constant for the N_2H_4–O_3 reaction at 294–297 K is $\sim 1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}. This corresponds to a lifetime of about 1 h at an O_3 concentration of 0.1 ppm. The rate constants for the O_3–CH_3NHNH_2 and O_3–$(CH_3)_2NNH_2$ reactions were too fast to measure under their experimental conditions; the reactions of $\sim$1–3 ppm O_3 with 0.4–4 ppm CH_3NHNH_2 and $\sim$2 ppm O_3 with $\sim$0.2–2 ppm $(CH_3)_2NNH_2$ were complete in less than 2–3 min.

From these data, the rate constants must be $>10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}, and the lifetimes of these two hydrazines must be less than 7 min at 0.1 ppm O_3.

The mechanism of the reaction of hydrazines with O_3 has been investigated using FTIR (Tuazon *et al.*, 1981; Carter *et al.*, 1981b). In the case of N_2H_4, the major product was H_2O_2, and N_2O appeared as a minor product; these are consistent with the following mechanism:

Initiation

$$H_2NNH_2 + O_3 \rightarrow H_2N\text{—}\dot{N}H + OH + O_2 \quad (92)$$

Propagation

$$H_2N\text{—}\dot{N}H + O_2 \rightarrow HN\text{=}NH + HO_2 \quad (93)$$

$$HN\text{=}NH + O_3 \rightarrow HN\text{=}\dot{N} + OH + O_2 \quad (94)$$

$$H_2NNH_2 + OH \rightarrow H_2N\text{—}\dot{N}H + H_2O \quad (95)$$

Product Formation

$$HN\text{=}\dot{N} \rightarrow H + N_2 \quad (96)$$

$$H + O_2 \xrightarrow{M} HO_2 \quad (97)$$

$$HO_2 + HO_2 \xrightarrow{M, H_2O} H_2O_2 + O_2 \quad (98)$$

According to this mechanism, most of the nitrogen in the hydrazine would form N_2, which would not have been detected in this system. The diazene HN=NH would be expected to react with OH radicals:

$$HN\text{=}NH + OH \rightarrow HN\text{=}\dot{N} + H_2O, \quad (99)$$

and ultimately form N_2 and H_2O_2 via reactions (96)–(98).

Interestingly, this reaction has been used as a nonphotolytic OH source for kinetic studies because of the production of OH in the initial reaction (92) between O_3 and N_2H_4 (Tuazon *et al.*, 1983a).

Figure 6.21 shows an FTIR spectrum taken during the studies by Tuazon *et al.* (1981) of the reaction of CH_3NHNH_2 with O_3 (the absorption bands from NH_3 which form from the slow decay of the hydrazine in the dark have been subtracted from the spectra). After initial injection of O_3, with the hydrazine present in excess, the observed products were methyl hydroperoxide (CH_3OOH), diazomethane (CH_2N_2), H_2O_2, methyldiazene ($CH_3N\text{=}NH$), HCHO, CH_3OH, and traces of CH_3ONO_2. After a second injection of O_3 into the system so that O_3 was in excess, $CH_3N\text{=}NH$ and CH_2N_2 disappear, and higher yields of CH_3OOH, CH_3OH, and HCHO result. Ninety-two percent of the initial carbon atoms could be accounted for in the observed products, but at least 95% of the initial nitrogen in CH_3NHNH_2 could not be found, indicating it likely formed N_2.

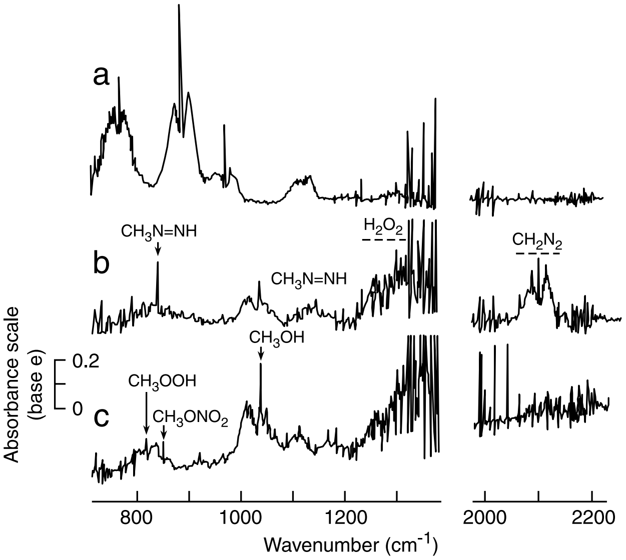


FIGURE 6.21 FTIR spectra taken during reaction of CH_3NHNH_2 with O_3: (a) 3.68 ppm CH_3NHNH_2 before reaction; (b) 2 min after injection of 2.8 ppm O_3; (c) 2.8 ppm O_3 injected 38 min after first injection (spectrum taken 2 min after second injection). NH_3 absorptions have been subtracted from (a) and (b), and both NH_3 and O_3 absorptions from (c) (adapted from Tuazon *et al.*, 1981).

The reaction mechanism proposed by Tuazon *et al.* (1981, 1982) to explain these results is analogous to that for N_2H_4. In this case, the intermediate $CH_3N\text{=}NH$ formed in the reaction analogous to (93) was identified by FTIR. Reactions (100a) and (100b) explain the formation of CH_2N_2:

$$CH_3N\text{=}NH + O_3 \xrightarrow{O_2} CH_2N_2 + OH + O_2 + HO_2, \quad (100a)$$

$$CH_3N\text{=}NH + O_3 \rightarrow CH_2N_2 + H_2O + O_2. \quad (100b)$$

In excess O_3, CH_2N_2 can react via (100c):

$$CH_2N_2 + O_3 \rightarrow HCHO + O_2 + N_2. \quad (100c)$$

The formation of CH_3OOH, HCHO, CH_3OH, and CH_3ONO_2 is expected from secondary reactions of the methyl radical as discussed earlier in this chapter.

The reaction of 1,1-dimethylhydrazine with O_3 gave the carcinogen *N*,*N*-dimethylnitrosamine as the major product in ~60% yields within 2- to 3-min reaction time (Tuazon *et al.*, 1981). Minor products were HCHO, H_2O_2, HONO, and perhaps NO_x. For a discussion of the complex mechanisms, the reader should consult the original reference.

NO_2 has also been shown to react with 1,1-dimethylhydrazine in air, forming HONO and tetramethyltetrazine-2, $(CH_3)_2NN{=}NN(CH_3)_2$ (Tuazon *et al.*, 1983b). The reaction is also proposed to involve abstraction of a hydrogen from the weak N–H bond by NO_2, forming HONO. The tetramethyltetrazine-2 is hypothesized to be formed by the addition of NO_2 to the $(CH_3)_2NNH$ radical, followed by decomposition to $(CH_3)_2N_2$ + HONO and the self-recombination of the $(CH_3)_2N_2$ radicals (Tuazon *et al.*, 1982). The apparent overall rate constant for the reaction was 2.3×10^{-17} cm^3 molecule^{-1} s^{-1} so that the lifetime of 1,1-dimethylhydrazine at an NO_2 concentration of 0.1 ppm would be ~5 h. Since the lifetimes with respect to 0.1 ppm O_3 or 1×10^6 OH radicals cm^{-3} are ~7 min and 6 h, respectively, the reaction of NO_2 can contribute to the atmospheric reactions of the hydrazine only at low O_3 levels.

Hydrazine, monomethylhydrazine, and asymmetrical dimethylhydrazine have also been shown to react rapidly ($k > 10^{-15}$ cm^3 molecule^{-1} s^{-1}) with HNO_3 in the gas phase to form the corresponding hydrazinium nitrate aerosols (Tuazon *et al.*, 1982).

J. CHEMISTRY OF REMOTE REGIONS

Gas-phase chemistry in remote areas is, in most cases, analogous to that in more polluted regions. The major difference is in lower NO_x emissions and hence concentrations. In addition, in continental regions, there are substantial emissions of biogenic organics, many of which are highly reactive toward OH, O_3, NO_3, and Cl atoms and in oceanic regions, dimethyl sulfide (DMS), which reacts with OH, NO_3, and Cl atoms.

As discussed briefly in Chapter 1 and in more detail in Chapter 14, it is unlikely that there are any regions at the earth's surface that have not been significantly impacted by anthropogenic emissions. Even over the central Atlantic and Pacific Oceans, for example, significant contributions to the chemistry from anthropogenic emissions are often observed (e.g., Parrish *et al.*, 1993b; Dickerson *et al.*, 1995). One means of testing for anthropogenic emissions is the use of a correlation between CO and O_3. CO is generated primarily from combustion processes in vehicles and industrial processes (e.g., Fig. 2.7 and Table 2.1), and its chemistry is the relatively slow reaction with OH (lifetime of ~90 days at an OH concentration of 5×10^5 cm^{-3}). As a result, as an air mass containing VOC and NO_x ages and undergoes the photochemical reactions discussed earlier, O_3 is formed. Such air masses therefore often have both increased O_3 and CO, with $\Delta[O_3]/\Delta[CO] \sim 0.3$–$0.4$ being typical (e.g., Dickerson *et al.*, 1989; Chin *et al.*, 1994; Wang *et al.*, 1996; Harris *et al.*, 1998; Parrish *et al.*, 1993b, 1998; Kajii *et al.*, 1998). This relationship is impacted, of course, by other factors as well such as the production of CO in the oxidation of VOC and by the deposition of O_3 during transport, for which corrections can be estimated (e.g., Chin *et al.*, 1994).

In this section, we discuss briefly the distinguishing chemistry associated with remote regions of the troposphere, including continental and marine areas, focusing primarily on regions of minimal anthropogenic influence. There is increasing evidence of interesting chemistry in the upper troposphere, which is also discussed. Finally, we briefly treat some unusual chemistry occurring in the Arctic, which is characterized by long periods of darkness and low temperatures during winter followed by long periods of sunlight.

1. Emissions of Biogenic Organics

As discussed briefly in Chapter 2, there are substantial biogenic emissions of VOC. (We exclude a discussion of methane, since it is of low reactivity and its chemistry is quite straightforward; see Chapter 14 for a discussion of its implications for global climate change.) On a global basis, the total may exceed anthropogenic emissions by as much as an order of magnitude (see Tables 2.1 and 2.2 and the volume edited by Hewitt, 1999). In urban areas, of course, their contributions are relatively less important. For example, Benjamin *et al.* (1997) report that biogenic hydrocarbons in the South Coast Air Basin of southern California are ~10% of the total VOC emission inventory on a typical summer day. The contribution of biogenic organics to urban O_3 formation is of course variable, depending on the particular locations (e.g., Chameides *et al.*, 1988; Roselle *et al.*, 1991; Pierce *et al.*, 1998; see also Chapter 16).

Several thousand different biogenic VOCs have been identified (e.g., Isidorov *et al.*, 1985; Graedel *et al.*, 1986; Puxbaum, 1997; Helas *et al.*, 1997; Fall, 1999). The most well known are ethene, isoprene, and the monoterpenes emitted by terrestrial plants. As discussed in this section, it has been increasingly recognized that there are biogenic emissions of oxygen-containing organics, from small alcohols such as methanol to larger aldehydes, ketones, and alcohols such as 2-methyl-3-buten-2-ol. Figures 6.22 and 6.23 summarize some of the VOC that have been observed and possible mechanisms of production (Fall, 1999). Different compounds are produced in different parts of the plant and by different physiological processes; the

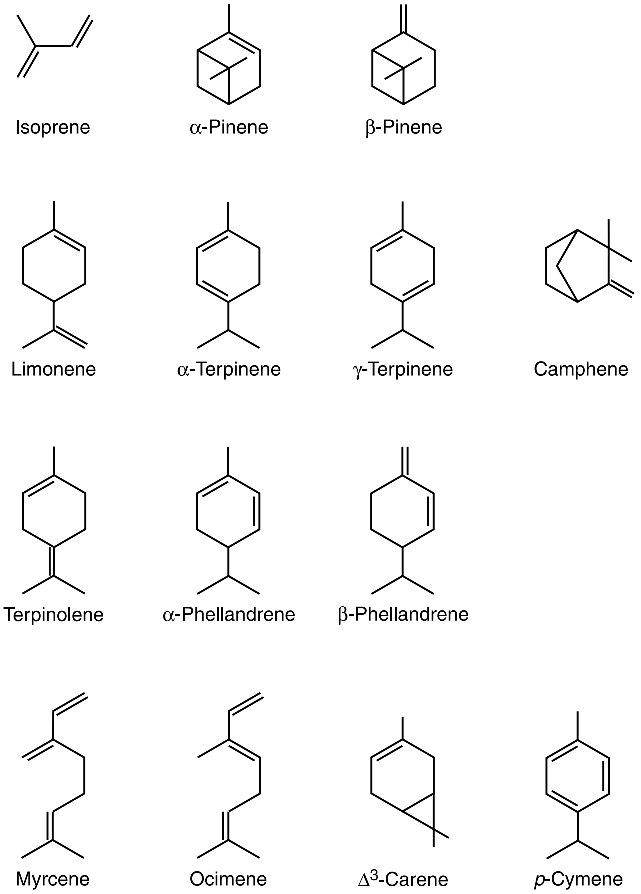
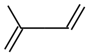


FIGURE 6.22 Chemical structures of some biogenically emitted hydrocarbons.

present understanding of these processes is reviewed by Fall (1999).

Ethene is a plant hormone emitted at a rate of several teragrams per year from plants; smaller amounts are emitted by soils and oceans (Rudolph, 1997). Interestingly, the emissions of ethene as well as some other VOCs (see later) increase significantly (by as much as factors of one to two orders of magnitude) when the plant is stressed, for example by mechanical means, high temperatures, or lack of water.

Isoprene is the major single, non-methane VOC emitted by plants:



Isoprene

Significant amounts of larger hydrocarbons are also generated by plants and emitted to the atmosphere. The larger hydrocarbon compounds generally fall under the classification of isoprenoids, or terpenoids, consisting of groups of 5-carbon isoprene type units (although they are not formed from isoprene). The monoterpenes are the C_{10} compounds, sesquiterpenes the C_{15} compounds, diterpenes the C_{20} compounds, triterpenes the C_{30} compounds, and tetraterpenes the C_{40} compounds.

Table 6.24, for example, shows one estimate of the annual global emissions of isoprene, other monoterpenes, and VOCs as well as methane (Guenther, 1999). Emissions of isoprene are believed to be about four times those of the other monoterpenes and about equal to all other VOCs.

Hardwood species such as oaks, poplars, aspen, and ironwood are generally isoprene emitters. However, even within plant families, not all species are isoprene emitters. For example, while North American oaks emit isoprene, many European oak species do not. For example, Steinbrecher *et al.* (1997) measured the emissions of isoprene and monoterpenes from five species of Mediterranean oak; two of them were strong isoprene emitters, whereas the other three did not emit significant amounts. Similarly, Kesselmeier *et al.* (1998) measured emissions of isoprene and monoterpenes from a Holm oak and a white oak growing side by side; the white oak was a strong isoprene emitter, whereas the Holm oak was a strong monoterpene emitter.

In addition to deciduous trees such as some oaks, isoprene is also emitted from other plants, including shrubs, gorse, vines, ferns, and plants characteristic of tropical savannas and peatlands characteristic of boreal regions (e.g., Guenther *et al.*, 1996a,b; Cao *et al.*, 1997; Owen *et al.*, 1998; Janson and De Serves, 1998; Guenther, 1999; Fall, 1999). Isoprene emissions have been reported to be correlated with successional patterns; for example, Klinger *et al.* (1998) report higher isoprene emissions in the early to mid-successional savanna ecosystems, compared to the later, rainforest development. Other sources (all believed to be relatively small) include marine phytoplankton (e.g., Bonsang *et al.*, 1992; Moore *et al.*, 1994; Milne *et al.*, 1995; Broadgate *et al.*, 1997), bacteria and fungi (e.g., Kuzma *et al.*, 1995), the breath of humans and other mammals (e.g., Gelmont *et al.*, 1981; Mendis *et al.*, 1994; Phillips *et al.*, 1994; Jones *et al.*, 1995; Foster *et al.*, 1996; Sharkey, 1996; Fenske and Paulson, 1999), and some industrial processes (e.g., Guenther, 1999).

Isoprene production by plants is very sensitive to light as well as temperature (e.g., Sanadze and Kalandadze, 1966; Tingey *et al.*, 1979). Figure 6.24a shows the production of isoprene from an aspen leaf when light in the photosynthetically active range is turned on and off (Monson *et al.*, 1991; Fall, 1999). When the light is switched on, isoprene emissions rise and when it is turned off, fall even more rapidly. Figure 6.24b shows

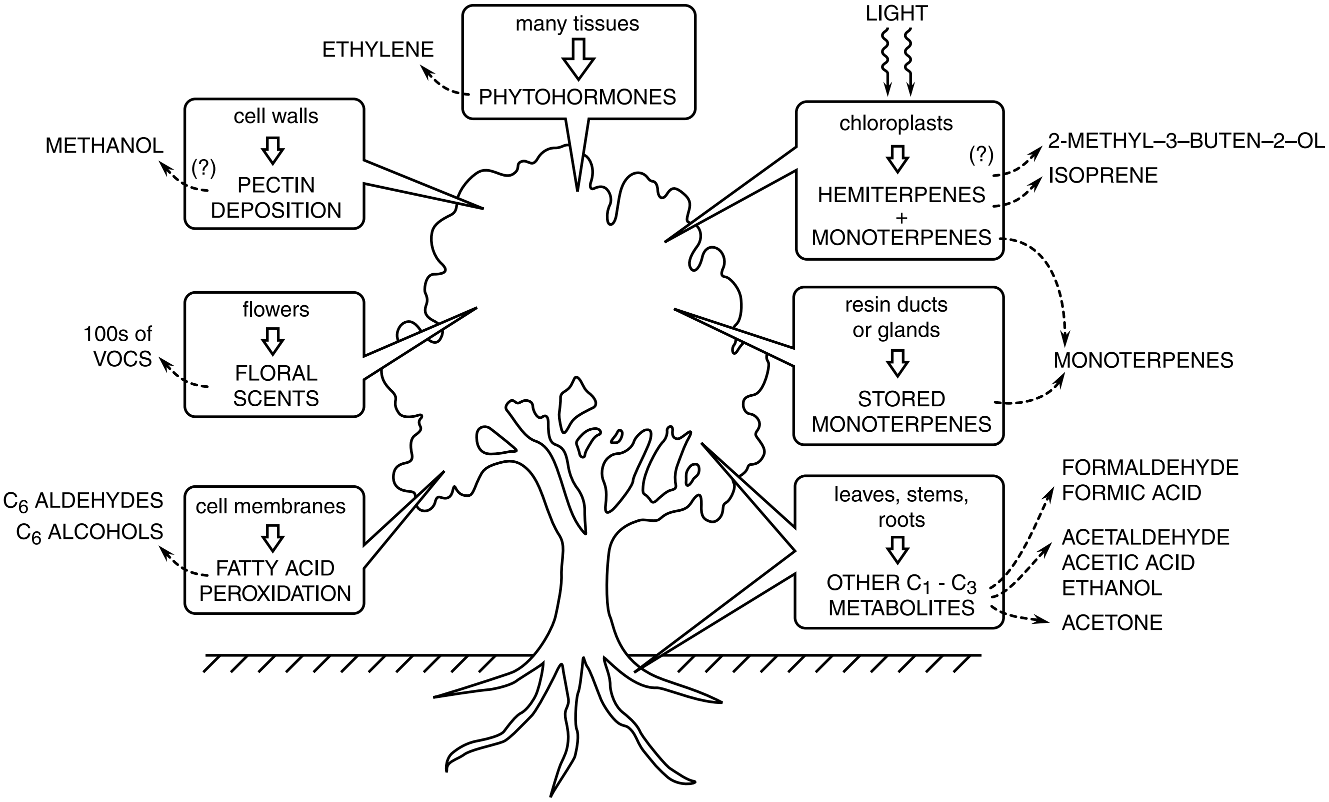


FIGURE 6.23 Schematic diagram of mechanisms of production of some biogenically emitted VOCs (adapted with permission from Fall, 1999).

the emissions as a function of this light intensity; the emissions rise rapidly and approach (but do not reach) a plateau (Monson *et al.*, 1992; Fall, 1999). Finally, Fig. 6.25 shows the effect of temperature on the isoprene emission rate; emissions rise to a temperature of ~40–45 °C and then rapidly fall (e.g., Monson *et al.*, 1992; Sharkey and Singsaas, 1995; Fall and Wildermuth, 1998; Fall, 1999). These influences of light and temperature are believed to be major factors in the variable emissions of isoprene measured in field studies (e.g., Lamb *et al.*, 1996; Guenther *et al.*, 1996b; Geron *et al.*, 1997; Owen *et al.*, 1997; Guenther and Hills, 1998; Drewitt *et al.*, 1998).

This dependence on light levels and temperature is believed to be due to the mechanism of production of isoprene in the plant, which involves the enzyme isoprene synthetase and dimethylallyl diphosphate (DMAPP) as a precursor to isoprene (e.g., see Silver and Fall, 1995; and Monson *et al.*, 1995). Either the enzyme, the formation of DMAPP, or both may be light sensitive (Wildermuth and Fall, 1996). The temperature effect has been attributed to effects on the enzyme, increasing its activity initially and then leading to irreversible denaturation (and/or possibly membrane damage) (Fall and Wildermuth, 1998).

Conifers tend to be sources of a variety of larger terpenoids, a major component of which are the C_{10} monoterpenes (Table 6.24). The structures of some of these are shown in Fig. 6.22. The mechanisms of the formation of these hydrocarbons in plants are closely linked, so that emissions of more than one monoterpene often occur together. For example, geranyl

TABLE 6.24 Estimated Global Annual Biogenic VOC Emissions (Tg yr^{-1})[a]

Source	Isoprene	Monoterpenes	Other VOCs[b]
Canopy foliage	460	115	500
Terrestrial ground cover and soils	40	13	50
Flowers	0	2	2
Ocean and freshwater	1	<0.001	10
Animals, humans, and insects	0.003	<0.001	0.003
Anthropogenic (including biomass burning)	0.01	1	93
Total	~500	~130	~650

[a] From Guenther (1999) and references therein.

[b] Other VOCs include all volatile organic compounds other than methane, isoprene, and monoterpenes.

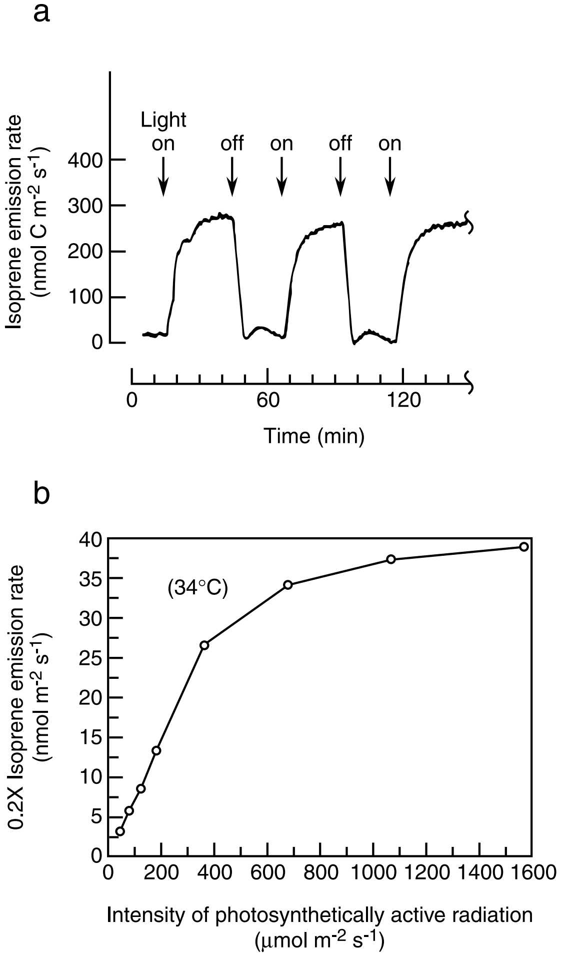


FIGURE 6.24 Effect of light on isoprene emission rate from (a) aspen leaf and (b) velvet bean leaf (adapted from Monson *et al.*, 1991, 1992; and Fall, 1999).

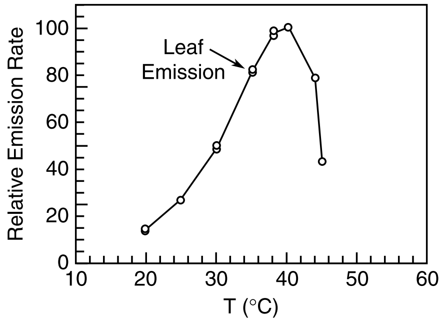


FIGURE 6.25 Effect of willow leaf temperature on isoprene emission rate (adapted from Fall and Wildermuth, 1998; and Fall, 1999).

diphosphate is a precursor for α- and β-pinene, limonene, and myrcene, whose generation involves the enzyme limonene synthase (e.g., see Fall, 1999). In contrast to isoprene, which does not have a reservoir in leaves in many cases, monoterpenes are generated and stored in the plant prior to emission so that in general, their emission to the atmosphere is not as closely tied to short-term controls over their biosynthesis (e.g., Monson *et al.*, 1995; Fall, 1999).

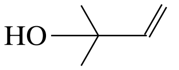
Emissions of monoterpenes have been observed from a variety of plants, including pines (e.g., Juuti *et al.*, 1990; Guenther *et al.*, 1994; Street *et al.*, 1997; Staudt *et al.*, 1997), resin in pine forests (e.g., Pio and Valente, 1998), spruce (Street *et al.*, 1996), some deciduous trees such as oaks (e.g., Benjamin *et al.*, 1996; Street *et al.*, 1997; Kesselmeier *et al.*, 1998), and gorse (e.g., Cao *et al.*, 1997). Interestingly, as for ethene, increased emissions have been observed when plants are stressed (Fall, 1999). For example, Juuti *et al.* (1990) report that the monoterpene emission rates from a Monterey pine increased by factors of 10–50 during rough handling.

As for isoprene, emission rates of the monoterpenes increase with temperature, although different plant species exhibit different temperature sensitivities and different compounds can also show different dependencies on temperature (e.g., Tingey *et al.*, 1980; Loreto *et al.*, 1996; Owen *et al.*, 1997; Schween *et al.*, 1997; Drewitt *et al.*, 1998). The temperature dependence of monoterpene emissions is often taken into account by multiplying the base emission rate at a reference temperature T_s by the factor $e^{[\beta(T-T_s)]}$, where T is the leaf temperature and β is a coefficient that reflects the temperature sensitivity of emissions (e.g., Guenther *et al.*, 1993). Light also affects monoterpene emissions but does not appear to be as significant as for isoprene (e.g., Tingey *et al.*, 1980; Loreto *et al.*, 1996; Guenther *et al.*, 1996b).

Larger hydrocarbons such as the C_{15} sesquiterpenes also have biogenic sources such as sage (Arey *et al.*, 1995).

As shown in Table 6.24, oceans and freshwater are not believed to be major sources of VOC to the atmosphere. As indicated earlier, isoprene is thought to be generated in small amounts in the oceans by marine phytoplankton. In addition, a variety of small hydrocarbons have been identified both in seawater and in the air above it, including alkanes (ethane, propane, *n*-butane, isobutane, *n*-pentane, isopentane, and *n*-hexane), alkenes (ethene, propene, 1- and 2-butene, isobutene, 1-pentene, and 1-hexene), and acetylene (e.g., Arlander *et al.*, 1990; Rudolph and Johnen, 1990; Bonsang *et al.*, 1991; Plass-Dülmer *et al.*, 1993). While some of these may be due to long-range transport from the continents (Rudolph and Johnen, 1990), it appears that the ocean is indeed a source of most, if not all, of these light hydrocarbons. A major organic found in ocean areas is dimethyl sulfide (DMS), whose oxidation products are believed to play a significant role in particle formation and hence radiative properties in the marine boundary layer (see Chapters 8.E.1 and 14.C). DMS also plays a major role in determining the lifetime and fate of NO_3 (Carslaw *et al.*, 1997).

In addition to hydrocarbons, biogenic processes also produce a number of oxygen-containing organics. One of the most important appears to be 2-methyl-3-buten-2-ol (MBO), first identified in a forested area by Goldan *et al.* (1993):



2-Methyl-3-buten-2-ol

Direct emissions of this compound from loblolly pine as well as from lodgepole and ponderosa pines were subsequently demonstrated (Guenther *et al.*, 1996b; Harley *et al.*, 1998). The concentrations of MBO measured by Goldan *et al.* (1993) were factors of 4–7 times those of isoprene, indicating the potential importance of this compound in the chemistry of remote regions. Its emissions appear to be regulated by temperature and light, similar to that of isoprene. This may be due to formation from a common precursor such as DMAPP (Fall, 1999).

Figure 6.26 shows the structures of some oxygen-containing compounds for which there is evidence of direct biogenic emissions. (3*Z*)-Hexenol and (3*Z*)-

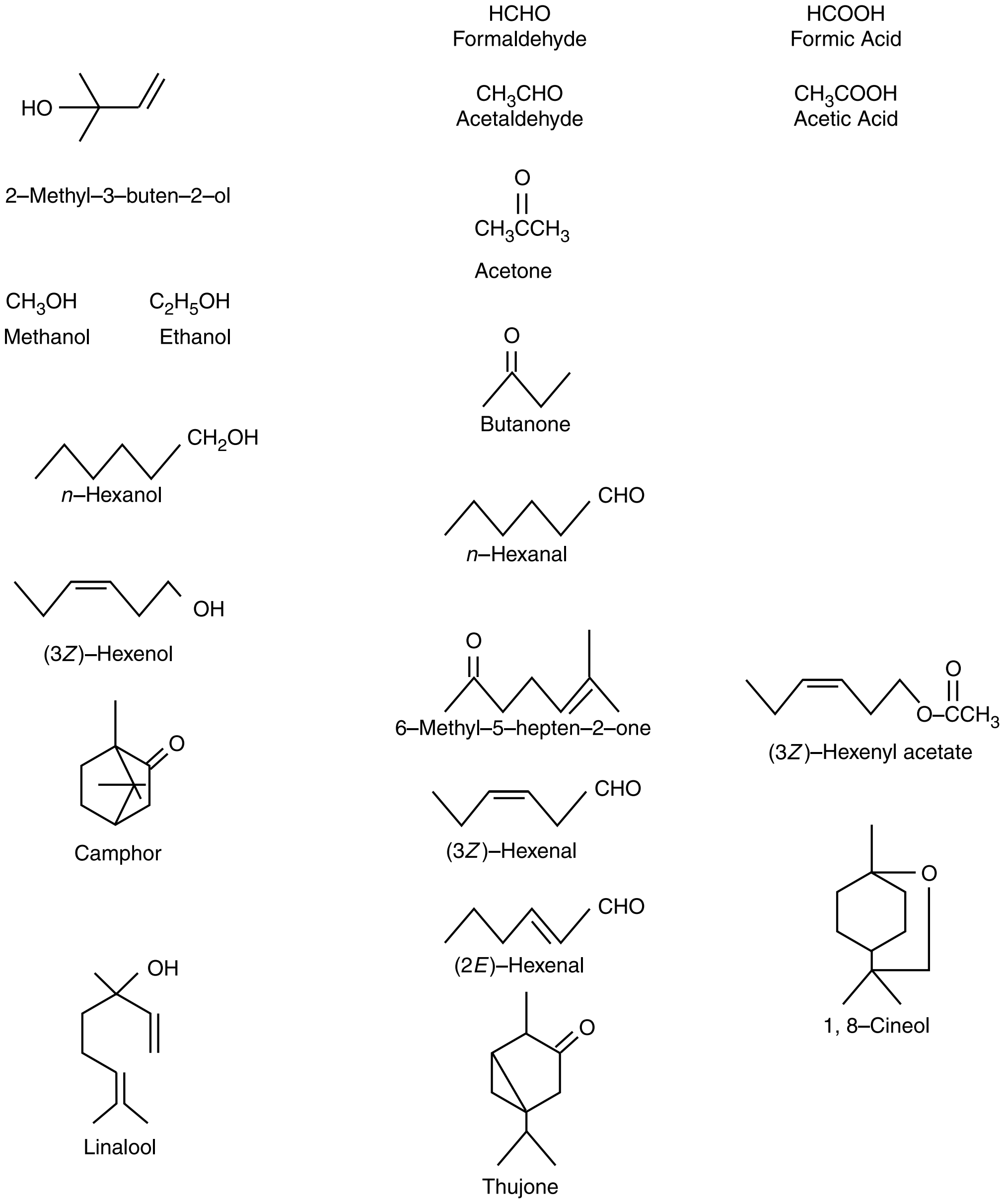


FIGURE 6.26 Structures of some oxygen-containing organics with biogenic emission sources.

hexenyl acetate, for example, are emitted by a number of plant species. For example, Arey *et al.* (1991a) identified emissions of these compounds from more than a dozen different agricultural plants in California as well as from Valley Oak and Whitethorn, and Kirstine *et al.* (1998) reported emissions from grass and clover. Such emissions are enhanced by mechanical damage. For example, Kirstine *et al.* (1998) reported that the emissions of (3*Z*)-hexenol and (3*Z*)-hexenyl acetate increased by three orders of magnitude when the grass and clover were mowed! A second, even larger, emission of these and other organics during the subsequent drying of the plants has been observed (de Gouw *et al.*, 1999).These compounds as well as other volatile C_6 aldehydes and alcohols are generated by the biochemical degradation of α-linolenic acid in the plants (Fall, 1999). Similarly, the breakdown of linoleic acid gives *n*-hexanal and *n*-hexanol.

Other examples of emissions of larger oxygen-containing organics include camphor, cineole, and thujone which are emitted by California sagebrush (Arey *et al.*, 1995), cineole from pines and eucalyptus (Staudt *et al.*, 1997), the unsaturated alcohol linalool from the blossoms of Valencia orange trees (Arey *et al.*, 1991b) and from certain pines (Kesselmeier *et al.*, 1997; Staudt *et al.*, 1997), and eucalyptol from grass and clover (e.g., Kirstine *et al.*, 1998). Ciccioli *et al.* (1997) measured emissions in a Mediterranean region known as the Mediterranean Pseudosteppe and found that not only isoprene but also a range of C_6–C_{10} aldehydes, linalool, and acetic acid were emitted by the vegetation.

In addition to these larger VOCs, there are biogenic sources of a wide variety of small alcohols, aldehydes, ketones, and acids. For example, emissions of methanol and acetone have been reported from plant leaves, grass, and clover (e.g., MacDonald and Fall, 1993; Nemecek-Marshall *et al.*, 1995; Fall and Benson, 1996; Kirstine *et al.*, 1998). Table 6.25 shows some of the compounds measured in grass and clover emissions (Kirstine *et al.*, 1998). Clearly, a wide variety of oxygen-containing species are emitted from this one source alone. Direct emissions of formaldehyde, acetaldehye, and formic and acetic acids have been observed from oaks and pines (Kesselmeier *et al.*, 1997).

TABLE 6.25 Some Oxygen-Containing Organics Observed in Emissions from Grass and Clover[a]

	Percentage of total carbon	
Compound	**Grass**	**Clover**
Methanol	11–15	15.1
Ethanol	16–21	0.4
Acetaldehyde	13–16	0.3
Acetone	11–16	22.9
Propanol	2	< 0.1
2-Methyl-2-propenal	1	< 0.1
2,3-Butanedione	1	< 0.1
Butanone	0.4–2	50.0
3-Methylbutanal	1	< 0.1
Pentanal	1	< 0.1
2-Pentanone	0.2–0.8	< 0.1
Hexanal	4	< 0.1
4-Methyl-2-pentanone	0.5–1.1	< 0.1
Benzaldehyde	0.9–1.9	< 0.1
Nonanal	0.3–1.1	< 0.1
Eucalyptol	1	0.1

[a] Adapted from Kirstine *et al.* (1998).

Consistent with the direct observation of the emissions are field measurements in remote areas. For example, Fehsenfeld *et al.* (1992) measured the composition of VOC at two rural locations in the United States, summarized in Fig. 6.27. Alcohols and carbonyl compounds comprise 40–70% of the total. Of these, a significant portion appear to be direct emissions, with methanol being a major contributor to the oxygen-containing portion. Similarly, Singh *et al.* (1995) reported relatively high concentrations of methanol and acetone in the free troposphere, at least a portion of which may be due to biogenic emissions. For example, based on a comparison of measurements and model predictions, Wang *et al.* (1998) propose that biogenic emissions account for about 40% of the acetone on a global basis.

As is expected, there are also a variety of oxygen-containing organics found in rural and remote areas, which are oxidation products of the directly emitted biogenics. For example, in areas with significant isoprene emissions, the oxidation products methyl vinyl ketone (MVK), methacrolein (MACR), and 3-methylfuran are also typically present (e.g., Yokouchi *et al.*, 1993; Montzka *et al.*, 1993, 1995; Biesenthal *et al.*, 1998; Helmig *et al.*, 1998b). Biesenthal and Shepson (1997) suggest that MVK and MACR may also be generated by automobile exhaust, based on the correlation of these compounds with CO in an urban area.

Indeed, separating out direct emissions and the formation by oxidation in air of other biogenics is not straightforward. For example, 6-methyl-5-hepten-2-one (Fig. 6.26) has been reported in air in different locations by a number of groups (e.g., Ciccioli *et al.*, 1993a, 1993b; König *et al.*, 1995; Helmig *et al.*, 1996). However, the reaction of O_3 with organics containing the structural group $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}C–$ also gives this compound (e.g., Fruekilde *et al.*, 1998), as expected from the earlier discussion of mechanisms of ozonolysis and studies of struc-

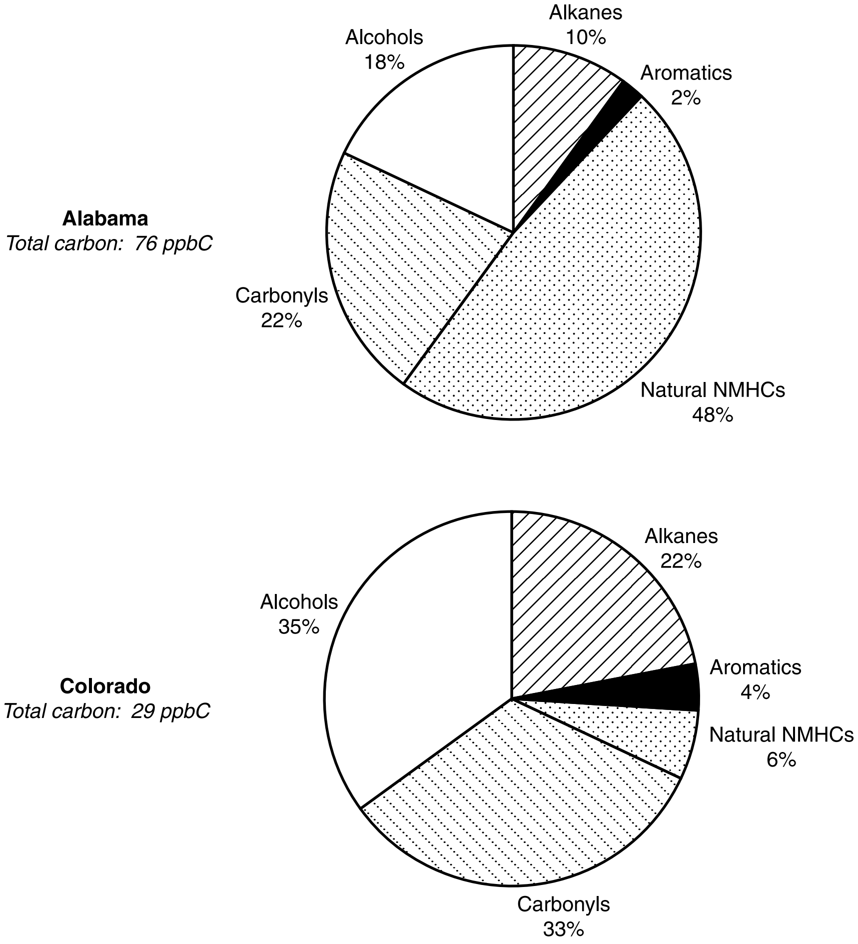


FIGURE 6.27 Distribution of organics observed in rural areas in Alabama and Colorado, respectively (adapted from Fehsenfeld *et al*., 1992).

turally similar compounds such as linalool, $(CH_3)_2C{=}CHCH_2CH_2C(CH_3)(OH)CH{=}CH_2$ (e.g., Shu *et al*., 1997). For example, ozonolysis of squalene (Fig. 6.28) was demonstrated to form gaseous 6-methyl-5-hepten-2-one, acetone, and geranyl acetone, respectively. 4-Oxopentanal was also formed from the further oxidation of 6-methyl-5-hepten-2-one (Grosjean *et al*., 1996; Smith *et al*., 1996; Fruekilde *et al*., 1998). These compounds were also observed when leaves of common vegetation found in the Mediterranean were exposed to O_3. Furthermore, these products could be formed from the reaction of glass wool that had been in contact with human skin, which also contains squalene as a lipid; such observations suggest the importance of avoiding contamination of samples during measurements of biogenic organics.

In short, while a variety of oxygen-containing biogenic organics have been observed to be generated from plants and most are likely direct emissions, care must be taken to distinguish such direct emissions from possible formation from oxidation of larger biogenic hydrocarbons and/or, in some cases, contamination during sample handling.

2. Chemistry

a. Biogenic Hydrocarbons

Although some of the biogenic VOCs are relatively simple compounds such as ethene, most are quite complex in structure (e.g., Figs. 6.22 and 6.26). Furthermore, they tend to be unsaturated, often with multiple double bonds. As a result, they are very reactive (see Chapter 16.B) with OH, O_3, NO_3, and Cl atoms (e.g., Atkinson *et al*., 1995a). In addition, because they are quite large and of relatively low volatility, their polar oxidation products are even less volatile. This makes elucidating reaction mechanisms and quantifying product yields quite difficult. For a review of this area, see Atkinson and Arey (1998).

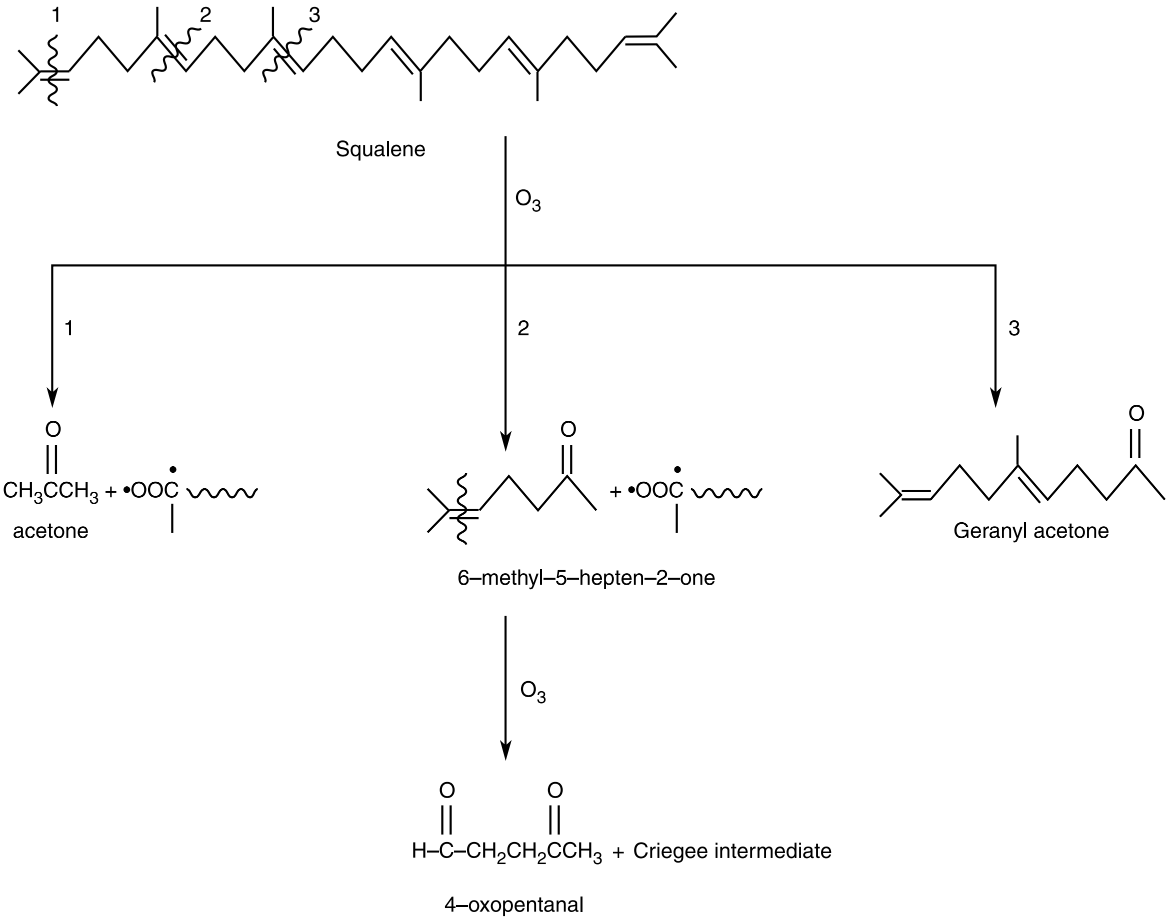
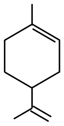
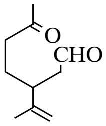
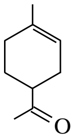
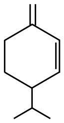
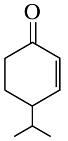
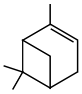
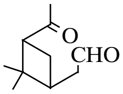
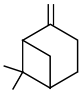
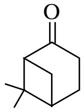
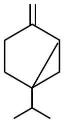
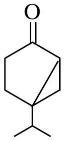
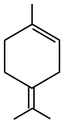
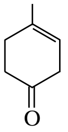
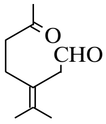


FIGURE 6.28 Oxidation of squalene to 6-methyl-5-hepten-2-one, acetone, geranyl acetone, and 4-oxopentanal (adapted from Fruekilde *et al*., 1998).

Some of the reactions, e.g., that of isoprene with OH and NO_3, were discussed earlier in this chapter. Table 6.26 summarizes some of the major products observed in the gas-phase reactions of several other biogenic hydrocarbons with OH and O_3 (Atkinson, 1997a). These products are anticipated, based on the mechanisms described earlier in this chapter. As also expected, the yields of these major products generally do not account for 100% of the reactant lost, and there are a number of other products, including multifunctional species, that are also formed. As an example, the formation of more than 30 individual products has been observed from the reaction of α-pinene with O_3 in air, some of which are unidentified, and the same is true for the Δ^3-carene reaction (Yu *et al*., 1998). Products included hydroxy oxoacids, hydroxy dicarbonyls, and dicarbonyls. The formation of low-volatility products that form particles (e.g., Hoffmann *et al*., 1998; Jang and Kamens, 1999) is likely responsible for a significant fraction of the products missing from the gas phase. For example, Jang and Kamens (1999) have identified a variety of multifunctional oygenated products in aerosol particles from the α-pinene reaction with O_3, including diacids such as 2,2-dimethylcyclobutane-1,3-dicarboxylic acid and pinic acid. These diacids have sufficiently low vapor pressures that they are believed to contribute significantly to the formation of particles in this system.

This is supported by studies of the aerosol composition in forested areas. For example, Kavouras *et al*. (1998) identified *cis*- and *trans*-pinonic acids as well as pinonaldehyde and nopinone in particles in a forest in Portugal. The diurnal variations of the pinonic acids and formic acid were similar, peaking in the afternoon as expected if they were formed by the reaction of O_3 with α-pinene. On the other hand, the concentrations of pinonaldehyde, expected from the oxidation of α-pinene by OH, O_3, and NO_3, and nopinone, from the oxidation of β-pinene, were the smallest in the after-

TABLE 6.26 Some Products and Their Yields Observed in the Gas-Phase Reactions of Some Biogenic Hydrocarbons with OH and O_3[a]

Biogenic	**Structure**	**Product**	**OH reaction yield**	**O_3 reaction yield**
Limonene			0.29 ± 0.06[b]	
			0.20 ± 0.03[b]	≤ 0.04[b]
		HCHO		0.10[e]
β-Phellandrene			0.29 ± 0.07[c]	0.29 ± 0.06[c]
α-Pinene			0.28 ± 0.05[b] 0.56 ± 0.04[d]	0.143 ± 0.024[g]
		CH_3COCH_3	0.11 ± 0.03[f]	
β-Pinene			0.27 ± 0.04[b] 0.79 ± 0.08[d]	0.23 ± 0.05[b] 0.22[e]
		HCHO	0.54 ± 0.05[d]	0.42[e]
		CH_3COCH_3	0.085 ± 0.018[f]	
Sabinene			0.17 ± 0.03[b]	0.50 ± 0.09[b]
Terpinolene			0.26 ± 0.06[b]	0.40 ± 0.06[b]
			0.08 ± 0.02[b]	

[a] Adapted from Atkinson (1997a).

[b] Hakola *et al*. (1994).

[c] Hakola *et al*. (1993).

[d] Hatakeyama *et al*. (1991); yields may be too high due to contribution from other products to IR absorption.

[e] Grosjean *et al*. (1993a).

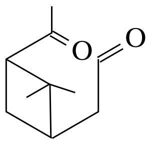
[f] Aschmann *et al*. (1998).

[g] Alvarado *et al*. (1998b).

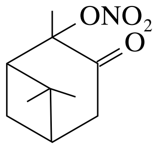
noon, likely reflecting their simultaneous removal by reaction with OH and/or photolysis.

The atmospheric oxidation of biogenic hydrocarbons appears to be a significant source of CO on a global level, accounting for ~10–20% of the total (e.g., Hatakeyama *et al.*, 1991; Miyoshi *et al.*, 1994; Röckmann *et al.*, 1998).

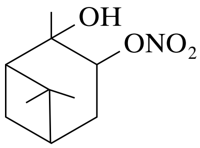
Nighttime reactions of biogenics with NO_3 are also important. As seen in Table 6.13, many of these reactions are very fast, leading to relatively short lifetimes of the biogenics at night. For α-pinene, for example, the lifetime with respect to reaction with 50 ppt NO_3 is only ~2 min. Again the reactions produce a number of multifunctional products, in this case many of them containing the nitrate group. For example, Wängberg *et al.* (1997) found total organic nitrate yields of about 14% in the NO_3–α-pinene reaction, which included 3-oxopinane 2-nitrate (3% yield) and 2-hydroxypinane 3-nitrate (5% yield), as well as the major product pinonaldehyde (62% yield):



Pinonaldehyde



3-Oxopinane 2-nitrate



2-Hydroxypinane 3-nitrate

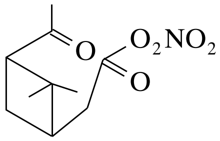
It is interesting that the reactions of α-terpinene and α-phellandrene with NO_3 also gave the corresponding aromatic, *p*-cymene, in significant yields (6 and 22%, respectively), suggesting an additional path producing $NO_2 + H_2O$ + aromatic (Berndt *et al.*, 1996).

Since 2-methyl-3-buten-2-ol is now recognized as being emitted in significant quantities, its kinetics and mechanisms of oxidation are also of interest. Reaction with OH is fast, with the rate constant reported to be in the range of $(4–7) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (Rudich *et al.*, 1995; Fantechi *et al.*, 1998a; Ferranto *et al.*, 1998). As expected, the reaction proceeds primarily by addition to the double bond. The major products of the reaction in air are $CHOCH_2OH$ (glycoaldehyde), acetone, and HCHO (Grosjean and Grosjean, 1995; Fantechi *et al.*, 1998b; Ferranto *et al.*, 1998) (see Problem 12).

2-Methyl-3-buten-2-ol also reacts with O_3 and NO_3, with the rate constants for these reactions being 1×10^{-17} and $\sim(1–2) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, respectively (Grosjean and Grosjean, 1994; Rudich *et al.*, 1996; Hallquist *et al.*, 1996; Fantechi *et al.*, 1998a). Major products of the O_3 reaction have been reported to be acetone, HCHO, HCOOH, and possibly 2-hydroxy-2-methylpropanal. Major products of the NO_3 reaction are acetone and organic nitrates, peroxy nitrates, and carbonyl nitrates (e.g., Fantechi *et al.*, 1998b). These are consistent with the mechanisms of reaction of O_3 and NO_3 discussed earlier in this chapter.

As anticipated from their structures, the products formed from the initial reactions of the biogenics (Table 6.26) are also highly reactive with OH, O_3, and NO_3. For example, the rate constants (Alvarado *et al.*, 1998a) for the reaction of pinonaldehyde with OH, O_3, and NO_3 are 4.8×10^{-11}, $< 2 \times 10^{-20}$, and 2×10^{-14} cm^3 $molecule^{-1}$ s^{-1}, respectively (see also Glasius *et al.*, 1997; and Hallquist *et al.*, 1997), leading to a lifetime of ~6 h with respect to the OH reaction (at an [OH] of 1×10^6 radicals cm^{-3}) and ~11 h with respect to the reaction with 50 ppt NO_3. Photolysis is also important, with a photolysis lifetime of ~3 h for 50°N on July 1, assuming a quantum yield of one (Hallquist *et al.*, 1997).

Again, the reaction products are complex. For example, the NO_3 reaction has been reported to give 3-acetyl-2,2-dimethylcyclobutane acetylperoxynitrate (Wängberg *et al.*, 1997; Nozière and Barnes, 1998):



3-Acetyl-2,2-dimethylcyclobutane acetylperoxynitrate

A review of the gas-phase oxidation products is given by Calogirou *et al.* (1999).

The chemistry of dimethyl sulfide, a major biogenic in marine areas, is discussed in Chapter 8.E.1.

b. General Remote Boundary Layer Chemistry

The most universal characteristic of remote regions compared to those clearly subject to anthropogenic influences is the low NO_x (see Crutzen, 1995, for a review). Under these conditions, OH is generated by the photolysis of O_3 to $O(^1D)$, followed by its reaction with water vapor, which occurs in competition with deactivation to $O(^3P)$:

$$O_3 + h\nu \rightarrow O(^1D) + O_2, \tag{101}$$

$$O(^1D) + H_2O \rightarrow 2OH, \tag{102a}$$

$$+ M \rightarrow O(^3P) + M. \tag{102b}$$

In remote marine regions where there are not significant sources of large, biogenic VOCs, OH is removed by reaction with CO and CH_4:

$$OH + CO \xrightarrow{O_2} HO_2 + CO_2, \qquad (103)$$

$$OH + CH_4 \xrightarrow{O_2} CH_3O_2 + H_2O. \qquad (104)$$

Both HO_2 and OH can react with O_3:

$$HO_2 + O_3 \rightarrow OH + 2O_2, \qquad (105)$$

$$OH + O_3 \rightarrow HO_2 + O_2. \qquad (106)$$

In the absence of NO, radical–radical reactions of HO_2 and of RO_2 occur. The self-reaction of HO_2 is both pressure and water concentration dependent:

$$HO_2 + HO_2 \xrightarrow{M, H_2O} H_2O_2 + O_2. \qquad (107)$$

As indicated by the involvement of water vapor and an inert third body, this reaction has several channels (see DeMore *et al.*, 1997, for a review). There is both a bimolecular channel, which is pressure independent, and a termolecular channel, which is pressure dependent. In addition, the rate constant increases in the presence of gaseous water, suggesting that the reaction proceeds through a mechanism such as

$$HO_2 + H_2O \leftrightarrow (HO_2 \cdot H_2O),$$

$$HO_2 + (HO_2 \cdot H_2O) \rightarrow \rightarrow H_2O_2 + O_2 + H_2O,$$

$$2(HO_2 \cdot H_2O) \rightarrow H_2O_2 + O_2 + 2H_2O.$$

The binding energy of the $HO_2 \cdot H_2O$ complex has been calculated to be 6.9 kcal mol^{-1} (Aloisio and Francisco, 1998). The recommended overall rate constant (in units of cm^3 $molecule^{-1}$ s^{-1}) for reaction (107) is given by (DeMore *et al.*, 1997)

$$k_{107} = [2.3 \times 10^{-13} e^{600/T} + 1.7 \times 10^{-33}[M] e^{1000/T}] \times \{1 + 1.4 \times 10^{-21}[H_2O] e^{2200/T}\}.$$

At 1 atm pressure, 298 K, and 50% relative humidity, $k_{107} = 5.5 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (see Problem 13). The pressure and water vapor dependences are quite significant. For example, Stockwell (1995) points out that the relative error can be as much as 75% near the earth's surface and 30% at 10 km, leading to underestimates of the rate of formation of H_2O_2 and overestimates of the rates of formation of organic peroxides (formed from $HO_2 + RO_2$; see the following) and of O_3.

In addition to the HO_2 self-reaction, there are also HO_2–RO_2 and RO_2–RO_2 reactions:

$$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2, \qquad (108)$$

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2, \qquad (109a)$$

$$\rightarrow 2CH_3O + O_2. \qquad (109b)$$

Although reaction (108) is generally accepted to represent the major, if not sole, reaction path, it has been suggested by Ayers *et al.* (1997), based on measurements of HCHO in clean marine air, that a portion may proceed by an alternate path to produce HCHO + H_2O + O_2. As discussed earlier, path (109a) is the major path in the CH_3O_2 self-reaction at room temperature, with a branching ratio of ~0.7 and the remainder occurring via (109b); however, k_{109a}/k_{109b} is temperature dependent, with the relative importance of reaction (109b) decreasing at lower temperatures. For example, the recommended temperature dependence for these channels gives a branching ratio for (109b) of ~0.13 at 245 K compared to 0.3 at 298 K (Atkinson *et al.*, 1997a).

The result of this chemistry is the photochemical destruction of O_3 and the formation of peroxides.

On the other hand, when sufficient concentrations of NO are present, HO_2 and RO_2 both react with NO:

$$HO_2 + NO \rightarrow OH + NO_2, \qquad (110)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2, \qquad (111)$$

As discussed earlier, the NO_2 then photolyzes to $O(^3P)$, which adds to O_2 to form O_3. Under these conditions, O_3 will be formed. The concentration of NO at which this crossover from ozone destruction to ozone formation occurs is central to the chemistry of both remote and polluted regions.

At night, there can be significant concentrations of NO_3 radicals present, along with HO_2 and RO_2. HO_2 reacts with NO_3,

$$HO_2 + NO_3 \rightarrow OH + NO_2 + O_2, \qquad (112)$$

with a recommended rate constant of 3.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K (DeMore *et al.*, 1997). Given that this rate constant is similar to that for the HO_2 self-reaction under typical tropospheric conditions near the surface, this reaction can be a significant contributor to the removal of HO_2 at night. It accomplishes the same thing as NO, i.e., converts HO_2 to OH and generates NO_2.

In addition to gas-phase chemistry, aqueous-phase chemistry discussed in Chapter 8.C.3 taking place in clouds can also be important in remote regions. For example, modeling studies by Lelieveld and Crutzen (1990) suggest that clouds may decrease the net production of O_3 by uptake of HO_2, dissociation to $H^+ +$ O_2^-, and reaction of O_3 with O_2^- in cloud droplets.

A test of our understanding of the chemistry of remote regions thus requires measurements of not only

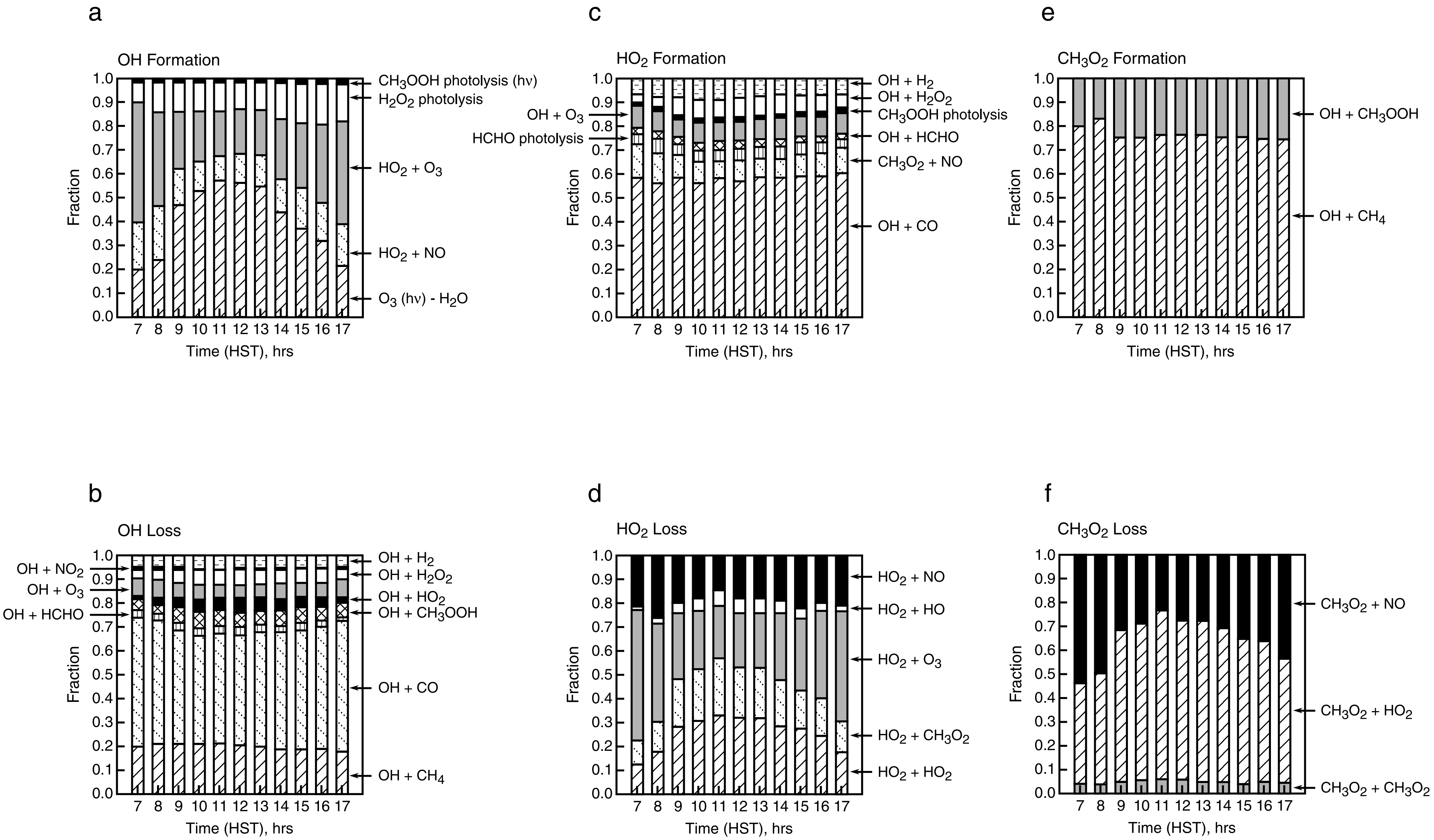


FIGURE 6.29 Estimated rates of formation and loss of OH, HO_2, and CH_3O_2 in what is primarily free tropospheric air (adapted from Cantrell *et al.*, 1996).

stable species such as O_3, CO, CH_4, and NO but also free radicals such as HO_2, RO_2, and OH. Such studies have been carried out in a number of locations (see Chapter 11.A.4), including remote regions. For example, Cantrell *et al.* (1996) measured total peroxy radical concentrations ($HO_2 + RO_2$) at the Mauna Loa Observatory and compared them to model calculations. On one day in which mostly free tropospheric air reached the sampling site, the measurements and model calculations were in relatively good agreement. However, on other days, the measured values were significantly smaller than predicted. This was hypothesized as being due to the possible loss of peroxy radicals on aerosol particles and/or reaction of OH with unidentified organics.

Figure 6.29 shows the estimated rates of removal and formation of OH, HO_2, and CH_3O_2 for the day having primarily free tropospheric air at the sampling site. The photolysis of O_3 to $O(^1D)$ is estimated to be a major source of OH, but not the only source, with its contribution varying from ~ 20 to 55% of the total rate of OH production. The major source of HO_2 is the reaction of OH with CO, which is also the major sink for OH. Interestingly, the production of CH_3O_2 is predicted to occur to a small, but significant, extent from the reaction of OH with CH_3OOH formed in the $HO_2 + CH_3O_2$ reaction.

Figure 6.30 shows the predicted rates of O_3 formation and loss for the day corresponding to Fig. 6.29. The net is a loss of O_3; i.e., the air mass is in the low-NO_x regime.

Penkett, Ayers, Galbally, and co-workers have measured $[HO_2 + RO_2]$ radicals using the radical amplifier technique described in Chapter 11.A.4, peroxides, O_3, and the photolysis rate of O_3, $J(O^1D)$, in remote marine air. Assuming that reaction (109) is sufficiently slow compared to reaction (108) that it can be ignored, steady-state analysis can be applied to OH, HO_2, and RO_2 to give the following expressions (Penkett *et al.*, 1997):

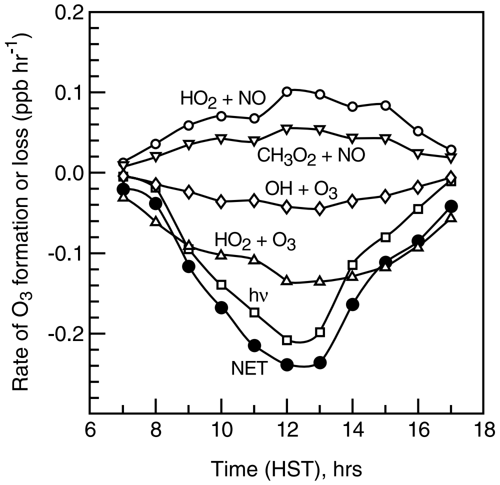


FIGURE 6.30 Calculated rates of processes leading to the formation and loss of O_3 for conditions of primarily free tropospheric air (see also Fig. 6.29) (adapted from Cantrell *et al.*, 1996).

$$d[OH]/dt = (2f)J(O^1D)[O_3] + k_{105}[HO_2][O_3] - k_{103}[OH][CO] - k_{104}[OH][CH_4] \approx 0. \quad (B)$$

In Eq. (B), f is the fraction of $O(^1D)$ that reacts with water vapor to form OH,

$$f = k_{102b}[H_2O]/\{k_{102a}[H_2O] + k_{102b}[M]\},$$

and is typically about 0.1.

$$d[HO_2]/dt = k_{103}[CO][OH] - k_{105}[HO_2][O_3] - 2k_{107}[HO_2]^2 - k_{108}[HO_2][CH_3O_2] \approx 0, \quad (C)$$

$$d[CH_3O_2]/dt = k_{104}[OH][CH_4] - k_{108}[CH_3O_2][HO_2] \approx 0. \quad (D)$$

The net change in the free radical concentration (i.e., $OH + HO_2 + CH_3O_2$) is given by the sum of Eqs. (B)–(D):

$$d[OH + HO_2 + CH_3O_2]/dt = (2f)J(O^1D)[O_3] - 2k_{107}[HO_2]^2 - 2k_{108}[HO_2][CH_3O_2]. \quad (E)$$

Under steady-state conditions, the net change is 0.

If the $[HO_2]/\{[HO_2] + [RO_2]\}$ ratio is a constant, α, then a rate constant representing both the $HO_2 + HO_2$ and $HO_2 + CH_3O_2$ reactions, k_{sum}, can be formulated:

$$k_{sum} = \alpha^2 k_{107} + \alpha(1-\alpha)k_{108}. \quad (F)$$

Setting the right-hand side of Eq. (E) to 0 and using the composite rate constant defined by Eq. (F), one can show (see Problem 11) that

$$\{[HO_2] + [RO_2]\} = \left\{fJ(O^1D)[O_3]/k_{sum}\right\}^{0.5}. \quad (G)$$

That is, the peroxy radical concentrations in the absence of NO should vary with the square root of $J(O^1D)$ under conditions of relatively constant O_3 concentrations.

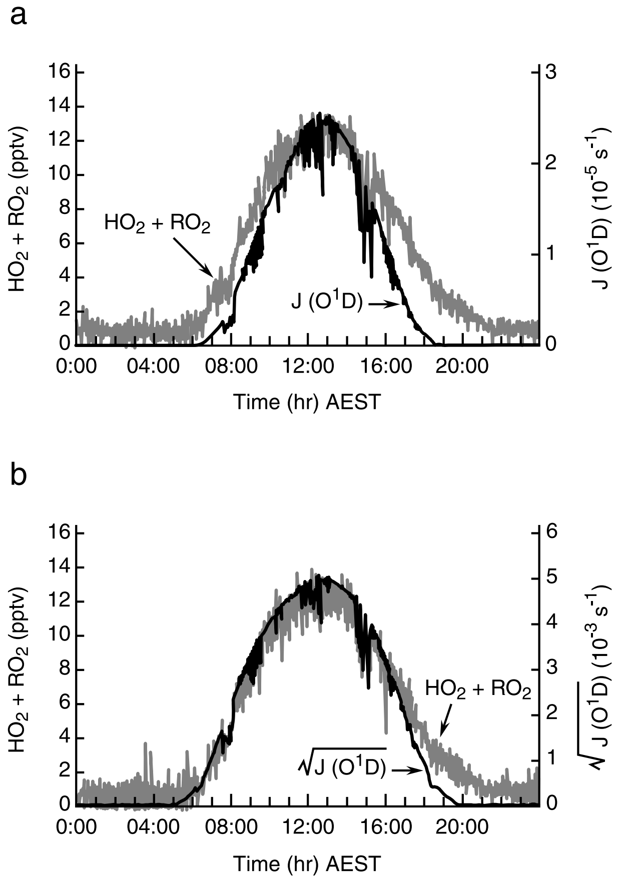


FIGURE 6.31 Measured peroxy radical concentrations ($[HO_2]$ + $[RO_2]$) and ozone photolysis rate $J(O^1D)$ (a) or $\{J(O^1D)\}^{0.5}$ (b) in clean marine air at Cape Grim, Tasmania (adapted from Penkett *et al.*, 1997).

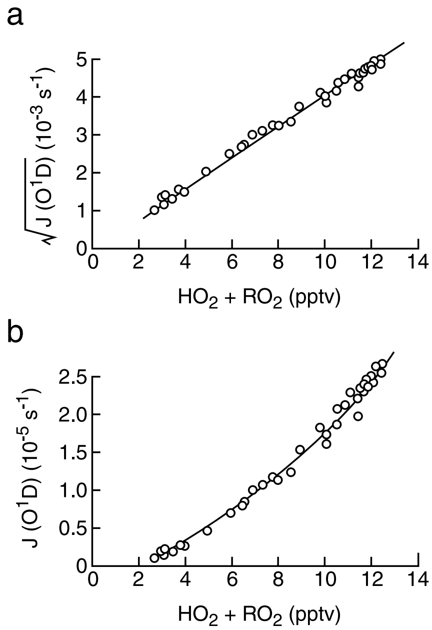


FIGURE 6.32 Measured concentrations of $HO_2 + RO_2$ as a function of (a) square root of ozone photolysis rate $\{J(O^1D)\}^{0.5}$ and (b) $J(O^1D)$ for a clean marine air mass at Cape Grim, Tasmania. Lines are guides for the eye only (adapted from Penkett *et al.*, 1997).

Figure 6.31 shows plots of measured peroxy radical concentrations for low-NO_x conditions at Cape Grim, Tasmania (Penkett *et al.*, 1997). Overlaid are plots of $J(O^1D)$ and $\{J(O^1D)\}^{0.5}$. The plot of $\{J(O^1D)\}^{0.5}$ provides a better match. The slower decay in the peroxy radical concentration at dusk is due to the slow decay due to self-reactions, with some contribution from the $CH_3O_2 + O_3$ reaction ($k \sim 1 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}; Tyndall *et al.*, 1998) and perhaps a small contribution from deposition (Monks *et al.*, 1996).

The relationship between $\{J(O^1D)\}^{0.5}$ and $\{[HO_2] + [RO_2]\}$ is better illustrated in Fig. 6.32, which shows plots of both the square root and first power of $J(O^1D)$ against the measured peroxy radical concentrations; the square root plot is linear, while the first-order plot curves significantly.

This chemistry suggests that under low-NO_x conditions, there should be net photochemical destruction of O_3 accompanied by the formation of peroxides. That is, there should be a negative correlation between O_3 and peroxides, which has indeed been observed to be the case in remote regions (e.g., see Penkett *et al.*, 1995).

The relationship between the peroxy radical concentration and the ozone photolysis rate constant for these higher NO conditions can be again approximated using steady-state analysis (Penkett *et al.*, 1997; Carpenter *et al.*, 1997). While OH is recycled in its reactions with CO and CH_4 via HO_2, it is permanently removed at higher NO_x concentrations by the reaction of OH with NO_2, forming nitric acid:

$$OH + NO_2 \xrightarrow{M} HONO_2. \tag{113}$$

Thus the steady-state concentration of OH is given by

$$[OH] = \frac{(2f)J(O^1D)[O_3]}{k_{113}[NO_2]}, \tag{H}$$

where k_{113} is the effective second-order rate constant. However, the OH concentration is also determined by its interconversion with HO_2 and CH_3O_2. Treating the OH + CO and HO_2 + NO as one cycle and OH + CH_4 and CH_3O_2 + NO as another,

$$k_{103}[OH][CO] = k_{110}[HO_2][NO], \tag{I}$$

$$\begin{aligned} k_{104}[OH][CH_4] &= k_{111}[CH_3O_2][NO] \\ &\cong k_{110}[CH_3O_2][NO], \end{aligned} \tag{J}$$

since the rate constants for reactions (111) and (110) are similar. Adding (I) and (J), one obtains

$$\{[HO_2] + [CH_3O_2]\} = \frac{[OH]}{k_{110}[NO]}\{k_{103}[CO] + k_{104}[CH_4]\}, \quad (K)$$

and using Eq. (H) for [OH], this becomes:

$$\{[HO_2] + [CH_3O_2]\} = \frac{(2f)J(O^1D)[O_3]}{k_{113}[NO_2]}\left\{\frac{k_{103}[CO] + k_{104}[CH_4]}{k_{110}[NO]}\right\}. \quad (L)$$

That is, in the presence of sufficient quantities of NO that HO_2 and CH_3O_2 react primarily with NO rather than with each other, the total concentration of peroxy radicals should vary directly with the photolysis rate constant for O_3 rather than with its square root as was the case at low NO.

Figure 6.33 shows a plot of the total peroxy radical concentrations measured at Mace Head, Ireland, as a function of either the square root or the first power of $J(O^1D)$ (Carpenter *et al.*, 1997). Consistent with Eq. (L), the concentrations vary with the first power under these conditions.

From such studies, Carpenter *et al.* (1997) conclude that the crossover point between O_3 destruction and formation occurs at NO concentrations of ~55 ± 30 ppt at Mace Head, Ireland, in the late spring and 23 ± 20 ppt at Cape Grim, Tasmania, during the summer.

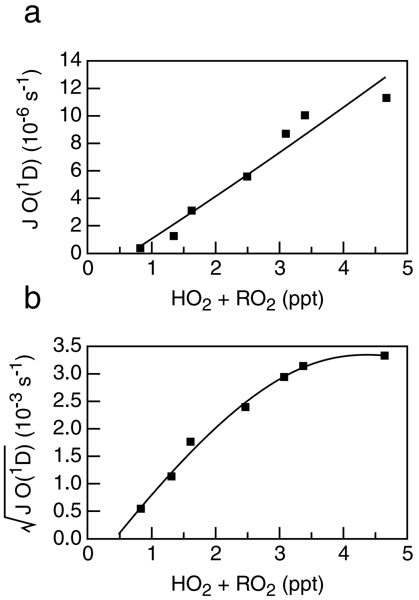


FIGURE 6.33 Measured concentrations of $HO_2 + RO_2$ as a function of (a) ozone photolysis rate, $J(O^1D)$, or (b) $\{J(O^1D)\}^{0.5}$ under polluted conditions at Mace Head, Ireland. Lines are guides for the eye (adapted from Carpenter *et al.*, 1997).

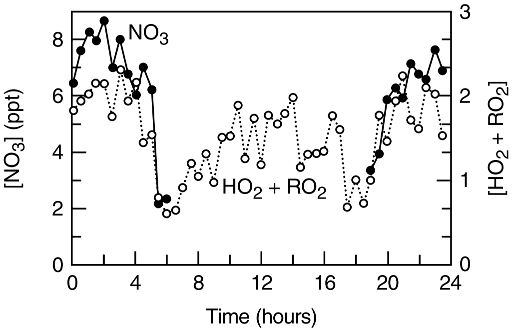


FIGURE 6.34 Measured diurnal variation of NO_3 and HO_2 + RO_2, respectively, at Weybourne, U.K. (adapted from Carslaw *et al.*, 1997).

As discussed earlier in this chapter, NO_3 drives nighttime chemistry. Through its reactions with organics, it would be expected to generate HO_2 and RO_2 at night and hence NO_3 and peroxy radical concentrations should be related. Figure 6.34 shows one set of measurements of these species in a coastal marine boundary layer at Weybourne, U.K. (Carslaw *et al.*, 1997). The temporal profile of peroxy radicals at night follows that of NO_3; during the day, there are additional sources, of course, through OH and O_3 reactions. Carslaw *et al.* (1997) suggest that the reactions of HO_2, and perhaps $CH_3SCH_2O_2$ (from DMS oxidation), with NO_3 at night may also be important.

3. Upper Troposphere

While a great deal is known about the chemistry of the lower troposphere, particularly the boundary layer, as well as the stratosphere (see Chapters 12 and 13), much less is known about the upper troposphere, the region between the two. This region has attracted increasing attention for a number of reasons, including the potential impact of commercial aircraft. Of particular concern is understanding the formation and fate of O_3, whose concentration in this region is important for its role as a greenhouse gas (see Chapter 14.B), in addition to its role in the photochemical reactions.

Measurements made in this region have raised questions regarding our understanding of the chemistry involved, as well as the transport processes that can affect ozone in this region (e.g., Suhre *et al.*, 1997). Figure 6.35, for example, shows one set of measurements of OH as a function of solar zenith angle at an altitude of 11.8 km near Hawaii (Wennberg *et al.*, 1998). Also shown are model predictions based on the

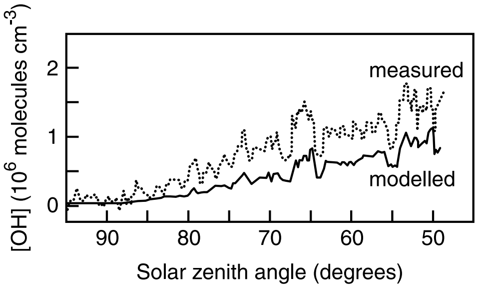


FIGURE 6.35 Measured OH concentrations at an altitude of 11.8 km near Hawaii and concentrations predicted using simple chemistry (adapted from Wennberg *et al.*, 1998).

simple O_3–H_2O–OH–CO–CH_4 chemistry outlined earlier. The measured concentrations of OH are significantly larger than predicted by the model, indicating that there are additional sources of OH and other free radicals.

In general, for a compound to reach the upper troposphere in sufficient concentrations to impact the chemistry, it must not react rapidly in the lower troposphere. However, more reactive compounds can be rapidly transported (on the time scale of a few minutes) from the surface to the upper troposphere through convective events (e.g., thunderstorms) (e.g., Gidel, 1983; Chatfield and Crutzen, 1984; Chatfield and Alkezweeny, 1990; Pickering *et al.*, 1992; Wang *et al.*, 1995; Kley *et al.*, 1996; Mahlman, 1997; Kley, 1997; Jaeglé *et al.*, 1998a; Talbot *et al.*, 1998). As a result, some compounds with relatively short tropospheric lifetimes can be carried into the upper troposphere and act as free radical sources.

The additional source of HO_x free radicals has been proposed to be the photolysis of compounds such as CH_3COCH_3, HCHO, CH_3OOH, and H_2O_2 carried into the upper troposphere by such convective transport (e.g., Chatfield and Crutzen, 1984; Singh *et al.*, 1995; Arnold *et al.*, 1997a, 1997b; McKeen *et al.*, 1997; Prather and Jacob, 1997; Jaeglé *et al.*, 1997, 1998a; Folkins *et al.*, 1998; Lee *et al.*, 1998). Thus, inclusion of acetone photolysis improves the agreement between the measured and modeled values of OH. Figure 6.36, for example, shows the measured and calculated values of OH with and without acetone photolysis in the model as well as calculated rates of production of HO_x from the photolysis of O_3 and acetone, respectively (Wennberg *et al.*, 1998). At higher altitudes where acetone photolysis predominates, the agreement between the measurements and model is good. At lower altitudes, however, measured OH is still larger than the predicted values even with acetone photolysis, indicating a significant contribution of other species, perhaps compounds such as CH_3OOH, as well.

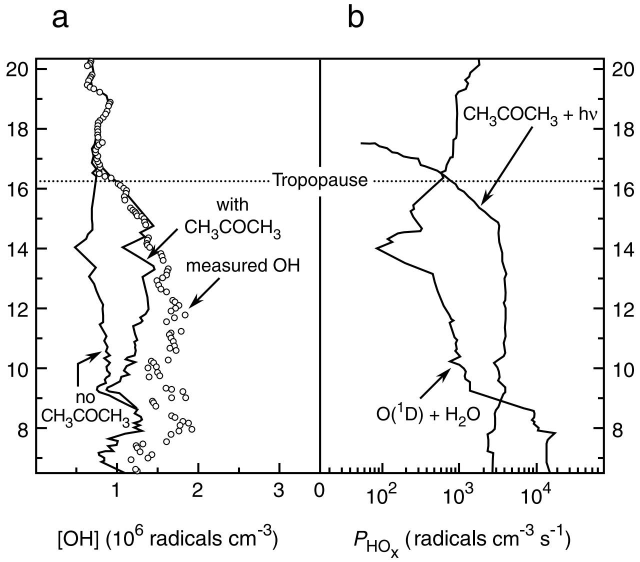


FIGURE 6.36 (a) Measured OH concentrations as a function of altitude and model-predicted concentrations without acetone photolysis and with acetone photolysis, respectively. (b) Calculated rates of HO_x production from O_3 and acetone photolysis, respectively, as a function of altitude. (Adapted from Wennberg *et al.*, 1998.)

Based on this chemistry, the production rate of O_3 is expected to be very sensitive to the NO concentration, increasing with NO (see also Chapter 16 for a discussion of the dependence of O_3 generation on NO_x). In this context, Folkins *et al.* (1998) suggest that acetone is likely the major contributor to enhanced ozone production in the upper troposphere, since increased CH_3OOH and H_2O_2 concentrations at 9- to 12-km altitude were observed only at very small NO concentrations, indicative of clean marine boundary layer air; under such low NO_x conditions, destruction rather than production of O_3 is expected.

Another significant uncertainty in our understanding of the chemistry of the upper troposphere involves oxides of nitrogen. The measured NO_x/NO_y ratios have been observed to be higher than expected based on model predictions (e.g., Jaeglé *et al.*, 1998b). The HNO_3/NO_x ratio in the free troposphere also appears to be smaller than expected (e.g., Liu *et al.*, 1992; Chatfield, 1994). One possible explanation is that there is some unrecognized chemistry reconverting NO_y back to NO_x (e.g., Chatfield, 1994) that would bring the measurements and model predictions into better agreement (e.g., Hauglustaine *et al.*, 1996). However, it has also been suggested that these observations may reflect additional injection of NO_x by convective transport, by lightning (e.g., McKeen *et al.*, 1997; Prather and Jacob, 1997; Jaeglé *et al.*, 1998b; Brunner *et al.*, 1998; Dias-Lalcaca *et al.*, 1998), or by uptake of HNO_3 in clouds. Another possibility is errors in the kinetics for NO_x and NO_y reactions in the models. For example, those for the OH + NO_2 and OH + HNO_3 reactions have been recently revised and bring the models and measurements into better agreement (see Chapters 7.B.1 and 7.E.2 and Problem 7.9).

Injection of air from the stratosphere into the upper troposphere is also very important under some conditions for determining the concentrations of various species in this region. For example, Suhre *et al.* (1997) measured high O_3 concentrations in the upper equatorial troposphere due to input from the stratosphere. Similarly, Dias-Lalcaca *et al.* (1998) carried out measurements of NO, NO_2, and O_3 in the tropopause region on flights of commercial passenger aircraft. Regions of very high ozone, up to 450 ppb, were encounted simultaneously with higher NO_x concentrations. These were attributed to air of stratospheric origin.

There has been a great deal of research activity on the effects of subsonic aircraft in the upper troposphere, with respect to impacts both on the chemistry and on the radiation balance through effects on clouds and O_3 (e.g., see April 15, May 1, and May 15, 1998, issues of *Geophysical Research Letters* and the July 27, 1998, issue of *Atmospheric Environment*). Aircraft emit a variety of pollutants, including NO_x, SO_2, and particles whose concentrations have provided "exhaust signatures" in some studies (e.g., Schlager *et al.*, 1997; Hofmann *et al.*, 1998).

Of particular concern is the impact of oxides of nitrogen emissions on O_3 (e.g., see Ehhalt *et al.*, 1992; and Ehhalt and Rohrer, 1995). As is typical of combustion systems, NO_x emissions are primarily in the form of NO (e.g., Schulte *et al.*, 1997). As discussed earlier in this chapter and elsewhere in this book (e.g., see Chapter 16), the impact of added NO_x on the generation of O_3 depends on existing levels. At low NO levels, added NO leads to increased O_3 formation. However, at sufficiently high NO_x, OH reacts with NO_2 to form HNO_3, effectively removing NO_x from the system and terminating ozone production. The level at which this occurs in the upper troposphere is ≈ 300 ppt NO (e.g., see Wennberg *et al.*, 1998; and Grooß *et al.*, 1998).

There is evidence from laboratory studies that heterogeneous reactions on sulfate particles may be important in the upper troposphere as well. For example, HCHO uptake into sulfuric acid solutions or ternary mixtures of sulfuric and nitric acids and water has been observed in laboratory studies (e.g., Tolbert *et al.*, 1993; Jayne *et al.*, 1996; Iraci and Tolbert, 1997). In sulfuric acid, the effective Henry's law constant at the low temperatures found in the upper troposphere and lower stratosphere is large, $\sim 10^6$–10^7 M atm^{-1}, and polymerization of the HCHO occurs as its concentration increases (Iraci and Tolbert, 1997). When HNO_3 is present, a reaction occurs that generates HONO and HCOOH:

$$HCHO + HNO_3 \rightarrow HONO + HCOOH. \quad (114)$$

NO_2 is also formed, perhaps by the subsequent reaction of HONO with HNO_3 (which is the reverse of the surface hydrolysis of NO_2 discussed in Chapter 7.B.3 thought to be a significant source of HONO in the troposphere):

$$HONO + HNO_3 \rightarrow 2NO_2 + H_2O. \quad (115)$$

These products were observed at room temperature, although their formation at the lower temperatures found in the upper troposphere could not be confirmed (Iraci and Tolbert, 1997). Such reactions may contribute to a conversion of HNO_3 to NO_x proposed by Chatfield (1994).

Similarly, the uptake of acetone into sulfuric acid–water solutions has been reported (Duncan *et al.*, 1998), with the formation of 4-methyl-3-penten-2-one and trimethylbenzene at temperatures above 200 K and 75 wt% H_2SO_4.

In short, although relatively little is known about the possibility of heterogeneous chemistry of organics in the upper troposphere, the results of initial laboratory studies suggest that this may be important.

4. Arctic

Atmospheric chemistry in the Arctic has been the subject of studies for many years, in part because of the observation of "Arctic haze" decades ago. This haze is composed of particles with significant amounts of sulfate, about half of which is due to long-range transport from other regions, particularly Eurasia during the winter (e.g., Barrie and Bottenheim, 1991; Polissar *et al.*, 1998a, 1998b).

As might be expected, levels of most pollutants are quite low in the Arctic when air is not being transported from populated regions. For example, during the spring in Alaska during periods of southerly wind flow, surface-level concentrations of small (C_2–C_5) hydrocarbons are 8 ppb C, O_3 is ~ 20–40 ppb, NO is < 10 ppt, NO_x is ~ 30 ppt, and NO_y is ~ 400 ppt (e.g., Doskey and Gaffney, 1992; Honrath and Jaffe, 1992; Sandholm *et al.*, 1992; Beine *et al.*, 1996). PAN tends to be a larger portion of NO_y than normally expected for "clean" regions, often in the range of 50–90% (e.g., Bottenheim *et al.*, 1986; Barrie and Bottenheim, 1991; Jaffe, 1993; Jaffe *et al.*, 1997). It forms an increasingly larger fraction of NO_y at higher altitudes due to stabilization with respect to thermal decomposition at lower temperatures (see Chapter 5.A.3c). For example, PAN was reported to be about 10% of NO_y near the surface, increasing to 45% at altitudes of 4.5–6.1 km over the Arctic (Sandholm *et al.*, 1992; Singh *et al.*, 1992).

An unusual phenomenon was reported in the Arctic in the mid-1980s. Ozone measured at ground level was observed to decrease rapidly to small concentrations, at times near zero (Bottenheim *et al.*, 1986; Oltmans and Komhyr, 1986). As seen in Fig. 6.37, an increase in bromide ion collected on filters (f-Br) was inversely correlated with the O_3 decrease (Barrie *et al.*, 1988; Oltmans *et al.*, 1989; Sturges *et al.*, 1993; Lehrer *et al.*, 1997); this could reflect either particle bromide or a "sticky" gas such as HBr that could be collected on the filter simultaneously. This correlation suggested that the loss of ozone was due to gas-phase chain reactions involving bromine such as

$$Br + O_3 \rightarrow BrO + O_2, \qquad (116)$$

$$BrO + BrO \rightarrow 2Br + O_2, \qquad (117a)$$

$$\rightarrow Br_2 + O_2, \qquad (117b)$$

$$Br_2 + h\nu \rightarrow 2Br, \qquad (118)$$

$$BrO + h\nu \rightarrow Br + O. \qquad (119)$$

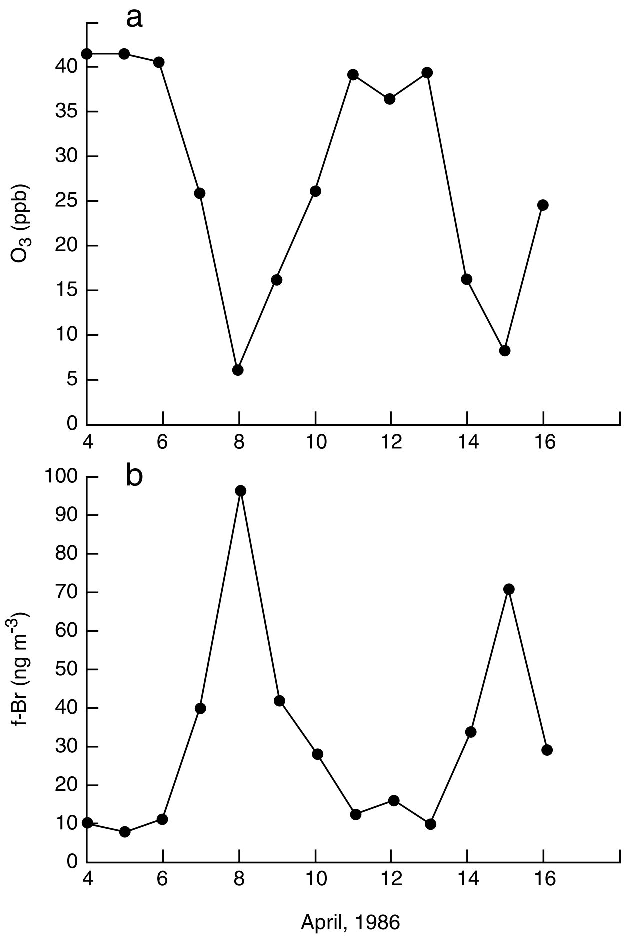


FIGURE 6.37 (a) Surface-level O_3 at Alert, Canada, and (b) filter-collected bromide (f-Br) during an ozone depletion episode (adapted from Barrie *et al.*, 1988).

Subsequently, additional reactions for the chain destruction of ozone were suggested, including one involving ClO (Le Bras and Platt, 1995):

$$ClO + BrO \rightarrow Br + Cl + O_2, \qquad (120a)$$

$$\rightarrow BrCl + O_2, \qquad (120b)$$

$$\rightarrow OClO + Br, \qquad (120c)$$

$$BrCl + h\nu \rightarrow Br + Cl, \qquad (121)$$

$$OClO + h\nu \rightarrow O + ClO. \qquad (122)$$

Such chain reactions imply low NO_x concentrations, which would otherwise terminate the chains by reacting with BrO and ClO to form $BrONO_2$ and $ClONO_2$, respectively. Unless the nitrates could be recycled rapidly back to active forms of the halogens, they would terminate the chain. NO_x concentrations do indeed appear to be small during O_3 depletion episodes. Beine *et al.* (1997), for example, measured $NO_x < 4.5$ ppt during O_3 depletion episodes in Norway.

In addition, mechanisms for regeneration of photochemically active bromine that involve aerosol particles or reactions on the snowpack have been proposed. For example, McConnell *et al.* (1992) and Tang and McConnell (1996) proposed that HBr and organobromine compounds could be converted to Br_2 through adsorption and reaction on ice and aerosol particles. Fan and Jacob (1992) suggested that HOBr, formed by the reaction of BrO with HO_2,

$$BrO + HO_2 \rightarrow HOBr + O_2, \qquad (123)$$

or by hydrolysis of bromine nitrate,

$$BrONO_2 + H_2O \rightarrow HOBr + HNO_3, \qquad (124)$$

would form Br_2 by reaction with Br^- in aerosol particles:

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O. \qquad (125)$$

Aranda *et al.* (1997) have shown in laboratory studies that CH_3O_2 also reacts with BrO in a manner analogous to the HO_2 reaction (123), with a rate constant at 298 K of 5.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. About 80% of the reaction generates HOBr + CH_2O_2, with the remainder forming Br + CH_3O + O_2. In either case, photochemically active bromine species are regenerated.

Crutzen and co-workers (Sander and Crutzen, 1996; Vogt *et al*., 1996) have developed a model for chemistry in the marine boundary layer at midlatitudes, in which autocatalytic cycles involving sea salt particles generate photochemically active gases such as BrCl, Br_2, and Cl_2. It is likely that such chemistry also occurs in the Arctic as well. In these cycles, reactions (125) and (126) in the condensed phase,

$$HOBr + Cl^- + H^+ \rightarrow BrCl + H_2O, \qquad (126)$$

followed by reactions such as (127)–(131), also occurring in the condensed phase,

$$BrCl + Br^- \leftrightarrow Br_2Cl^-, \qquad (127)$$

$$Br_2Cl^- \leftrightarrow Br_2 + Cl^-, \qquad (128)$$

$$BrCl + H_2O \leftrightarrow HOBr + Cl^- + H^+, \qquad (129)$$

$$BrCl + Cl^- \rightarrow BrCl_2^-, \qquad (130)$$

$$BrCl_2^- + H_2O \rightarrow HOBr + H^+ + 2Cl^-, \qquad (131)$$

lead to the generation of photochemically active halogens in the gas phase.

Much of this chemistry has been confirmed experimentally. For example, Kirchner *et al.* (1997) showed that HOBr reacts at 240 K with the surface of ice that has been doped with sea salt, generating gaseous BrCl and Br_2. The chemistry is similar to that at midlatitudes, only in this case occurs in a quasi-liquid layer on the ice surface. Figure 6.38 is a schematic diagram of this chemistry, for which many of the reaction kinetics in aqueous solution have been reported (e.g., Wang *et al*., 1994). Similar chemistry occurs in the interactions of HOBr with HCl on ice (Abbatt, 1994) and with aqueous aerosols of NaCl (Abbatt and Waschewsky, 1998) as well as in the reaction of O_3 with frozen seawater ice in the dark (Oum *et al*., 1998b); in the latter case, O_3 oxidizes Br^- to BrO^-/HOBr and the chemistry then leads to the generation of gaseous Br_2 through the chemistry in Fig. 6.38.

The central point is that photochemically active bromine, and perhaps chlorine (see following), compounds are generated that lead to the chain destruction of gaseous O_3 at ground level at polar sunrise.

However, what remains unknown is the source of the original bromine that initiates the chemistry. There have been a number of hypotheses, including the photolysis of bromoform which is generated by biological processes in the ocean (Barrie *et al*., 1988) or reactions of sea salt, either suspended in the air or deposited on, or associated with, the snowpack. These include photolysis of $BrNO_2$ formed from the reaction of sea salt particles with N_2O_5 (Finlayson-Pitts *et al*., 1990), the formation of HOBr from the oxidation of bromide by HSO_5^- (Mozurkewich, 1995), or the reaction of O_3 with bromide in frozen seawater ice (Oum *et al*., 1998b; De Haan *et al*., 1999).

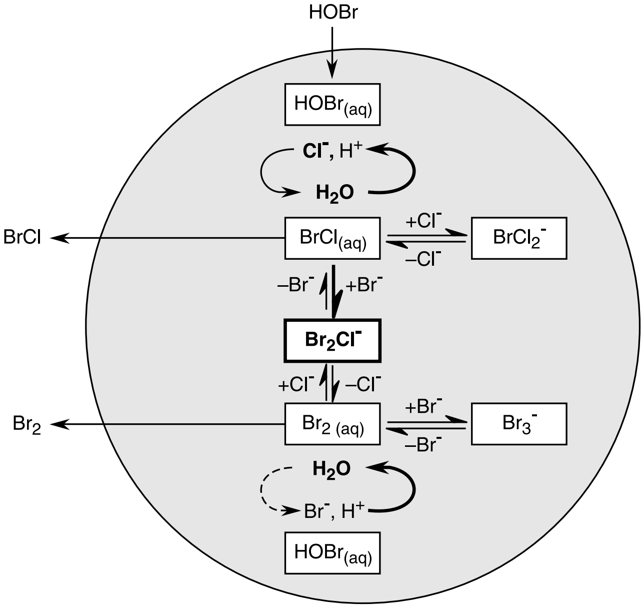


FIGURE 6.38 Schematic diagram of HOBr chemistry with sea salt particles/ice (graciously provided by T. Benter).

Supporting a seawater source for the halogens is the observation by Shepson and co-workers of significant amounts of as yet unidentified photolyzable chlorine as well as bromine compounds in the spring in the Arctic (Impey *et al*., 1997a, 1997b). In addition, Platt and co-workers have detected both BrO and ClO at the surface during ozone depletion events (Platt and Hausmann, 1994; Hausmann and Platt, 1994; Tuckermann *et al*., 1997).

It is also clear that during periods of low surface ozone, chlorine atoms are a major reactant for hydrocarbons (e.g., Jobson *et al*., 1994; Solberg *et al*., 1996; Ariya *et al*., 1998). Figure 6.39, for example, shows the measured ratios of isobutane, *n*-butane, and propane during an ozone depletion event (Jobson *et al*., 1994). These particular pairs of hydrocarbons were chosen to differentiate chlorine atom chemistry from OH reactions. Thus isobutane and propane have similar rate constants for reaction with Cl but different rate constants for reaction with OH. If chlorine atoms are responsible for the loss of these organics, their ratio should remain relatively constant in the air mass, as indicated by the line marked "Cl." Similarly, isobutane and *n*-butane have similar rate constants for removal by OH but different rate constants for reactions with

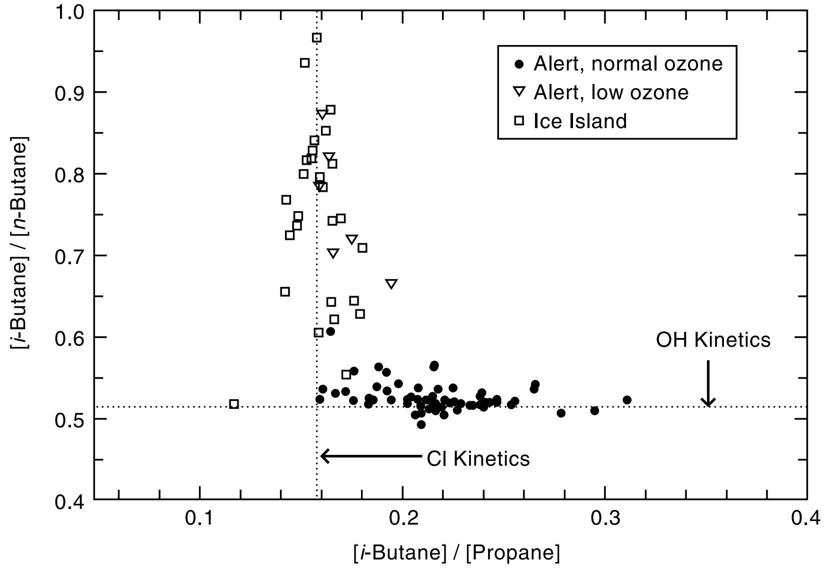


FIGURE 6.39 Decay of some simple alkanes during an episode of surface-level O_3 depletion at Alert, Canada, and at an ice island upwind. Also shown are the relative alkane concentrations for a "normal" time without O_3 depletion. The dotted lines show the ratios expected if the alkanes are being removed by Cl or OH, respectively (adapted from Jobson *et al.*, 1994).

chlorine atoms, and their ratio should remain constant if reaction with OH is the major removal process. As seen in Fig. 6.39, during ozone depletion events at Alert, Canada, and at an ice island upwind, the removal rates are consistent with chlorine atom reactions. On the other hand, in "normal ozone" conditions, the hydrocarbon loss is indicative of OH kinetics.

Aldehydes and ketones have also been measured during these ozone depletion events. Although these are expected to be generated from the oxidation of organics by chlorine atoms, the levels are not completely consistent with this as the only source. For example, Shepson *et al.* (1996) report that much higher concentrations of HCHO are observed than expected from such oxidation processes. High concentrations have been measured in the interstitial air in the snowpack in the presence of sunlight, suggesting that photochemical processes in the snowpack generate HCHO (Sumner and Shepson, 1999).

It is interesting that recent satellite observations (e.g., Richter *et al.*, 1998; Chance, 1998; Wagner and Platt, 1998; Hegels *et al.*, 1998) indicate that BrO is formed over large parts of the Arctic during spring, coincident with retreating sea ice and increasing radiation. Hopper *et al.* (1998) report that ozone depletion occurs in a layer above the sea ice, both observations again indicative of a seawater source for the bromine.

In short, a bromine-catalyzed destruction of surface-level ozone occurs over a wide area in the Arctic at polar sunrise. The mechanism likely involves regeneration of photochemically active bromine via heterogeneous reactions on aerosol particles, the snowpack, and/or frozen seawater. The source of the bromine is likely sea salt, but the nature of the reactions initiating this ozone loss remains to be identified. For a review, see the volume edited by Niki and Becker (1993) and an issue of *Tellus* (Barrie and Platt, 1997).

K. ATMOSPHERIC CHEMISTRY AND BIOMASS BURNING

Biomass burning is used for a variety of purposes, including clearing of forests for agricultural and grazing purposes, control of weeds and other unwanted plants, and removal of agricultural waste and stubble after harvest. Biomass fuels are also used for heating, cooking, and producing charcoal (Crutzen and Andreae, 1990; Levine *et al.*, 1995). While the burning of savannas has been the focus of many studies and is believed to contribute about 40% of the total carbon released by biomass burning each year, the other contributions, including burning of boreal forests, are also substantial during some time periods (Levine *et al.*, 1995). Indeed, there is evidence from changes in composition of the Greenland ice cores (see Chapter 14.E) for burning of boreal vegetation at high latitudes over the past approximately 800 years (e.g., Savarino and Legrand, 1998).

Emissions from biomass burning include a wide range of gases and particles, in quantities that in some cases can be significant not only locally and regionally but also on a global scale. Table 6.27, for example, shows one estimate of contributions of biomass burning to the global emissions of some of the emissions (Andreae, 1991). Clearly, biomass burning is important on a global scale, contributing to ozone formation over wide regions (see later) and through both ozone formation and particle emissions, impacting radiative properties regionally and hence potentially climate (e.g., Penner *et al.*, 1992; Kaufman and Fraser, 1997; Christopher *et al.*, 1996; Hobbs *et al.*, 1997; Portmann *et al.*, 1997).

The production of a wide range of compounds is associated with biomass burning. These include not only CO, CO_2, and NO_x but a variety of light hydrocarbons, CH_3Cl and CH_3Br, polycyclic aromatic hydrocarbons (see Chapter 10), HCHO, formic and acetic acids, CH_3OH, phenol, 2-hydroxyethanal, H_2O_2, methyl hydroperoxide, hydroxymethyl hydroperoxide, 1-hydroxyethyl hydroperoxide, NH_3, HCN, CH_3CN, HNO_3, PAN, H_2, some sulfur compounds such as SO_2 and COS, and particles (e.g., LeBel *et al.*, 1988; Hegg *et al.*, 1990; Cofer *et al.*, 1990; Levine, 1991; Rogers *et al.*, 1991; Andreae, 1991; Rudolph *et al.*, 1992; Laursen *et al.*, 1992; Reinhardt and Ward, 1995; Kuhlbusch and Crutzen, 1995; Yokelson *et al.*, 1996, 1997; Lee *et al.*, 1997, 1998; Nichol, 1998; Mauzerall *et al.*, 1998; Crutzen *et al.*, 1998).

Fires go through several different phases of burning, with emissions of different compounds tending to be associated with each phase. Most commonly, two phases, a flaming stage followed by a smoldering stage, have been considered. However, Yokelson *et al.* (1996) have suggested, based on their laboratory measurements of emissions from the burning of biomass materials, that a third pyrolysis stage, associated with unburned pyrolysis products from heating of the fuel, should also be considered.

The initial, hot, flaming stage of the fire is associated with emissions of CO_2, NO_x, N_2O, SO_2, and black/elemental carbon; during the second phase, CO, CH_4, NH_3, HCN, CH_3CN, and some light hydrocarbons such as ethane and acetylene are emitted (Fig. 6.40). Emissions of individual compounds are usually expressed as enhancement or emission factors relative to CO_2, defined as Δcompound/ΔCO_2, or relative to CO, Δcompound/ΔCO, where Δcompound is the difference between the concentration in the smoke plume and its background concentration outside the plume. (Corrections for the loss of CO by chemical reactions and for changes in the ratio due to dilution with air outside the plume, which contains different mixing ratios, must be taken into account; e.g., see Mauzerall *et al.*, 1998.)

TABLE 6.27 Estimated Emissions from Biomass Burning Compared to Global Emissions[a]

Species	Biomass burning (Tg of element / yr)	All sources (Tg of element / yr)	Biomass burning (%)
Carbon dioxide (gross from combustion)	3500	8700	40
Carbon dioxide (net from deforestation)	1800	7000	26
Carbon monoxide	350	1100	32
Methane	38	380	10
Nonmethane hydrocarbons[b]	24	100	24
Nitrous oxide	0.8	13	6
NO_x	8.5	40	21
Ammonia	5.3	44	12
Nitrous oxide	0.8	13	6
Sulfur gases	2.8	150	2
Carbonyl sulfide	0.09	1.4	6
Methyl chloride	0.51	2.3	22
Hydrogen	19	75	25
Tropospheric ozone[c]	420	1100	38
Total particulate matter	104	1530	7
Particulate organic carbon	69	180	39
Elemental carbon (black soot)	19	<22	>86

[a] From Andreae (1991); see for original references.
[b] Excluding isoprene and terpenes.
[c] Formed from reactions in air due to biomass burning.

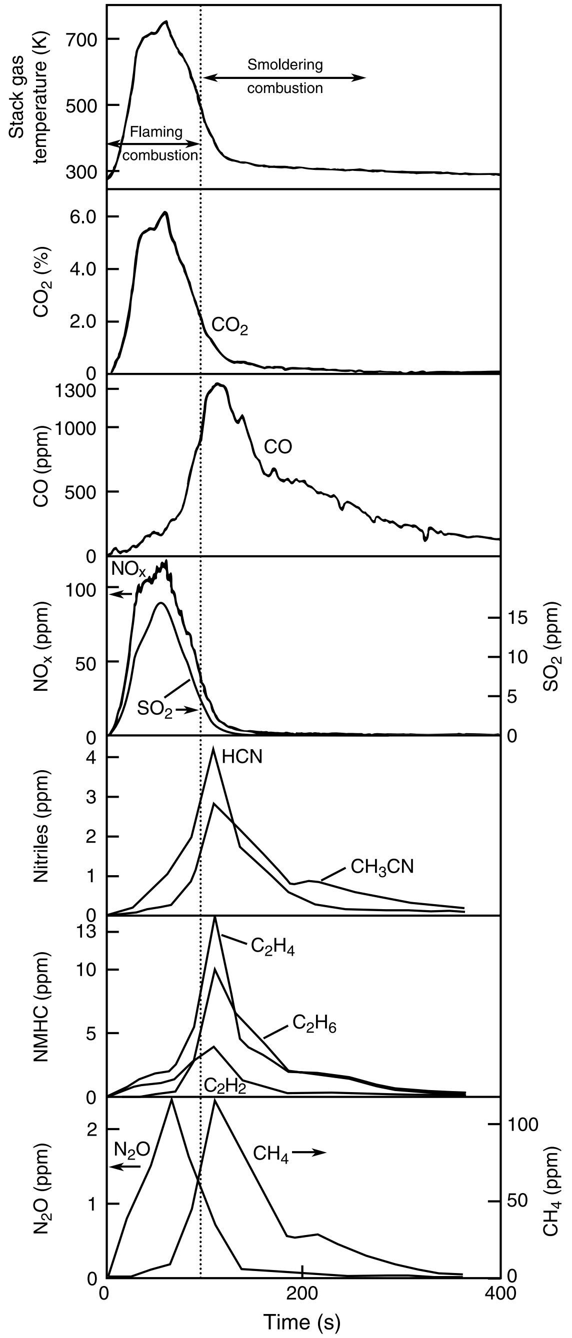


FIGURE 6.40 Stack gas temperature and emissions of various species from an experimental burning of grass in Venezuela (adapted from Crutzen and Andreae, 1990).

The use of *in situ* techniques such as FTIR in both laboratory and field studies has also permitted measurement of a variety of compounds associated with biomass burning that are difficult to analyze by traditional methods. For example, as seen in Fig. 6.41, Yokelson *et al.* (1996, 1997) have identified formic and acetic acids as well as methanol and 2-hydroxyethanal as products of burning during the smoldering phase in a laboratory study using FTIR. Remote infrared spectroscopy has also been used in field studies to detect such compounds as formic acid, methanol, ethene, and ammonia (Worden *et al.*, 1997), and remote sensing from satellites has been used to detect NO_2 and HCHO (Thomas *et al.*, 1998).

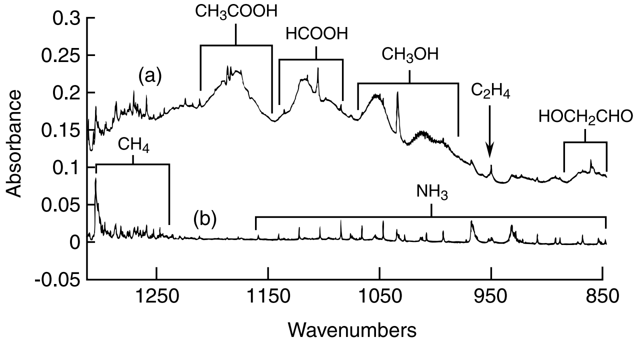


FIGURE 6.41 Infrared spectra of gases from burning a hardwood (a) when glowing combustion and white smoke are observed and (b) ~1 min later when there is no longer white smoke (adapted from Yokelson *et al.*, 1997).

In addition to the compounds that are directly emitted, there are a number of compounds formed in the plume from the VOC–NO$_x$ chemistry described earlier. In particular, the emissions from biomass burning have been observed to form elevated concentrations of O_3 over large regions (e.g., Fishman *et al.*, 1986, 1991; Logan and Kirchhoff, 1986; Cros *et al.*, 1992; Andreae *et al.*, 1994; Kim and Newchurch, 1996, 1998; Levy *et al.*, 1997; Mauzerall *et al.*, 1998; Jonquières *et al.*, 1998; Poppe *et al.*, 1998).

Mauzerall *et al.* (1998) measured a variety of species in plumes from biomass burning over the tropical South Atlantic Ocean as a function of the age of the plume and determined their enhancement ratios relative to both CO and CO_2. Species that are directly emitted by the biomass burning or formed rapidly are expected to be strongly correlated with CO at short times, but less so at longer times. CH_4, for example, was strongly correlated with CO, with a relatively constant enhancement ratio using CO_2 as the reference compound and a slight increase with age using CO, due to the small loss of CO. Similarly, HCHO and possibly H_2O_2 were correlated with CO in a manner suggesting direct emissions of these compounds, in agreement with measurements made by Lee *et al.* over the South Atlantic, Brazil, and southern Africa (1997, 1998).

On the other hand, species whose correlation with CO increases as the plume ages and with enhancement ratios that also increase with plume age are likely generated by chemical reactions in the plume. This was the case for O_3, as expected from known VOC–NO_x chemistry, with the enhancement ratio using CO as the reference increasing from 0.15 to 0.74 as the plume aged. Acetone also appeared to be formed as a secondary oxidation product, as did CH_3OOH.

Interconversion of various forms of oxides of nitrogen appeared to be occurring in the plume. Thus the enhancement ratio $\Delta NO_x/\Delta CO$ did not change substantially with the plume age, despite the fact that known chemistry of the primary emissions must be occurring. Mauzerall *et al.* (1998) postulate that continuing PAN decomposition to NO_2 helped to maintain this ratio at a relatively constant value. This was supported by measurements showing that in one fresh plume, PAN mixing ratios were larger than those of NO_x (by ~25%) and about a factor of 4 times that of HNO_3. However, after 5 days, PAN levels are about a third of those of HNO_3. It appears that PAN was the major form of NO_y initially but as the plume aged, it decomposed to NO_2, which was then ultimately oxidized to HNO_3.

Figure 6.42 shows the fraction of HO_x production due to O_3 photolysis as well as the contributions from photolysis of H_2O_2, CH_3OOH, HCHO, and acetone at different altitudes in a plume from biomass burning, based on measurements of these compounds (Lee *et al.*, 1998). O_3 photolysis becomes less important at higher altitudes due to lower water vapor concentrations which are needed to react with the $O(^1D)$ produced initially in order to generate OH. Formaldehyde becomes increasingly important at higher altitudes, with a significant contribution from H_2O_2 and in some cases, at high altitudes particularly, from CH_3OOH. Acetone is a minor contributor to the HO_x production.

Folkins *et al.* (1997) directly measured OH and HO_2 using an aircraft platform while descending through a plume from biomass burning. The measured concentrations of HO_x and the associated calculated rate of production of O_3 were much larger than expected based on the known chemistry. They suggested that, as for the clean upper troposphere, there must be an additional source of HO_x in biomass plumes.

In short, there is a rich and varied chemistry associated with the emissions from biomass burning, which have effects on local, regional, and global scales. A review of various aspects of biomass burning is found in the volume edited by Levine (1991).

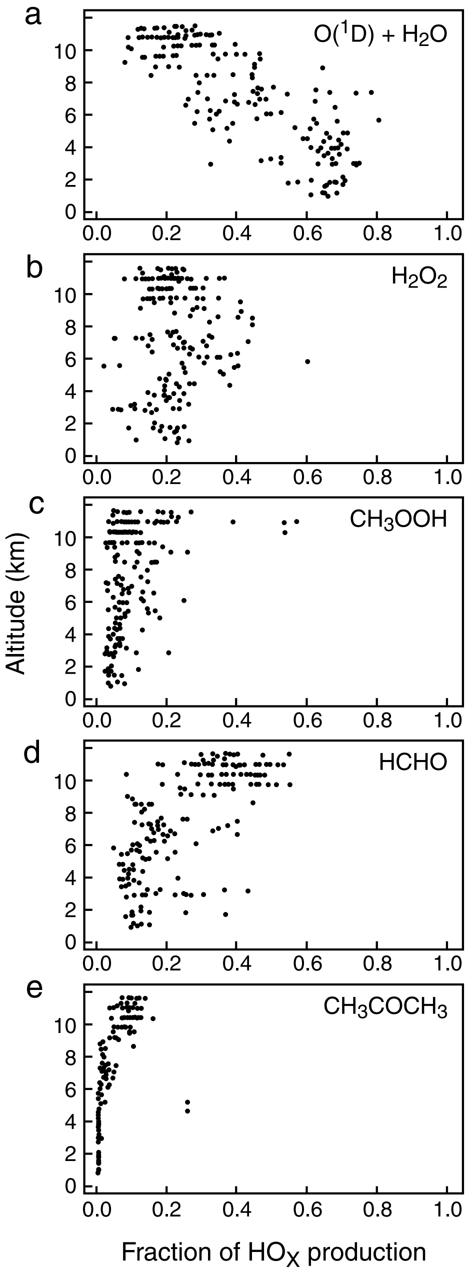


FIGURE 6.42 Fraction of HO_x from each radical source as a function of altitude over the tropical Atlantic Ocean (adapted from Lee *et al.*, 1998).

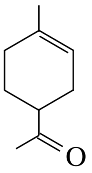
L. PROBLEMS

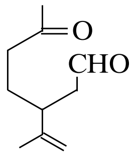
1. The individual lifetimes of *trans*-2-butene with respect to typical peak concentrations of OH, O_3, and NO_3 are given in Table 6.1. (a) Develop an expression for the overall "instantaneous" lifetime of an organic with respect to these three oxidants acting together at the same time. (b) Calculate the overall lifetime of this compound at concentrations of OH of 4×10^4 molecules cm^{-3}, of O_3 of 50 ppb, and of NO_3 of 100 ppt, which might be typical of a nighttime situation, using the rate constants given in this chapter.

2. Use the structure–reactivity relationship approach to calculate the rate constants for the reactions of OH with the following compounds and calculate the percentage difference from the recommended values in Table 6.2: (a) ethane, (b) *n*-butane, (c) 2-methylpentane, (d) 2,2-dimethylpentane, (e) 2,2,3-trimethylbutane, (f) *n*-nonane, (g) *n*-decane.

3. Use the structure-reactivity relationship approach to calculate the rate constants for the reactions of NO_3 with the following compounds and calculate the percentage difference from the recommended values in Table 6.3: (a) *n*-butane, (b) 2-methylbutane, (c) *n*-hexane, (d) 2,3-dimethylbutane, (e) *n*-octane, (f) *n*-nonane.

4. Two of the products of the OH reaction with limonene that have been observed are the following:





Show mechanisms that would form these products.

5. The OH–C_2H_2 reaction is not quite at the high-pressure limit at 1 atm. The OH–acetylene reaction occurs by addition of the OH to the triple bond. For the reaction at 300 K, $k_0 = 5.0 \times 10^{-30}$ cm^6 molecule^{-2} s^{-1}, $k_\infty = 9.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, and $F_C = 0.62$. (a) Calculate and plot the rate constant as a function of pressure up to 3000 Torr at 300 K. (b) What is the rate constant at 760 Torr and 300 K? How much different is this from the high-pressure limiting value?

6. Develop a mechanism for the photooxidation of diethyl ether in the presence of NO_x that explains why Eberhard *et al.* (1993) observed ethyl formate, ethyl acetate, and acetaldehyde as products.

7. Calculate the lifetimes of PPN with respect to thermal decomposition at temperatures of −30, 32, 70, and 120°F, respectively, assuming there is sufficient NO present to prevent the back reaction with NO_2 to regenerate PPN.

8. (a) It is pointed out in the text that the effective rate of decomposition of PAN depends on how much NO is present, relative to NO_2, to prevent the back reaction to regenerate PAN. Show that the lifetime of PAN with respect to its thermal decomposition as a function of the NO and NO_2 concentration and the rate constants k_{75}, k_{-75}, and k_{78} is given by $\tau = (1/k_{-75})(1 + k_{75}[NO_2]/k_{78}[NO])$. Assume that the acetylperoxy radical is in a steady state and that reactions 75, −75, and 78 represent the entire reaction system. (b) Calculate the lifetimes with respect to the thermal decomposition of PAN at 25°C at ratios of $[NO]/[NO_2]$ of 10, 1, and 0.1, respectively.

9. Use the rate constants provided in this chapter to show whether or not the reaction of NO_2 with α-phellandrene could compete with the OH, O_3, and NO_3 reactions for the removal of this compound from the atmosphere.

10. The OH radical has been observed to be formed in a dark reaction when isoprene, high concentrations of NO_2, and NO are present. Postulate a mechanism for this OH generation.

11. Show that Eq. (G), which indicates that the peroxy radical concentration should vary with the square root of the O_3 photolysis rate, can be derived from Eqs. (B)–(F).

12. Ferronato *et al.* (1998) have reported HCHO, $CHOCH_2OH$, and CH_3COCH_3 as major products of the reaction of the biogenically emitted 2-methyl-3-buten-2-ol with OH in air. Develop a likely mechanism for the formation of these products.

13. (a) Calculate and plot the rate constant for the HO_2 self-reaction as a function of relative humidity at 298 K in increments of 10% from 0 to 100% at 1 atm pressure. (b) By what factor will the rate constant for HO_2 self-reaction change from the surface at a pressure of 1 atm, temperature of 298 K, and 50% RH to the lower stratosphere, assuming a pressure of 100 Torr, a temperature of 220 K, and a water vapor mixing ratio of 5 ppm?

14. Assess the atmospheric fates of 1-pentene by answering the following questions:

(a) What are the potentially important tropospheric oxidants you have to consider, and what are typical concentrations of each oxidant under moderately polluted conditions?

(b) Calculate the lifetime of the organic with respect to each of the oxidants in (a). If the rate constant(s) you need are not available, estimate them based on those for analogous compounds.

(c) Show the mechanism of reaction of the organic with each of the important oxidants, following through to stable products in each case. Be sure to consider all possibilities. Be sure to consider all possible fates of reactive intermediates, and when some can be ruled out, state so explicitly.

(d) Suppose the oxidation occurs in a remote area where [NO] is close to 0. Trace the mechanism of the OH reaction through to one stable product under these conditions.

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