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Atmospheric chemistry of VOCs and NO_x

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Abstract

The present status of knowledge of the gas-phase reactions of inorganic O_x, HO_x and NO_x species and of selected classes of volatile organic compounds (VOCs) [alkanes, alkenes, aromatic hydrocarbons, oxygen-containing VOCs and nitrogen-containing VOCs] and their degradation products in the troposphere is discussed. There is now a good qualitative and, in a number of areas, quantitative understanding of the tropospheric chemistry of NO_x and VOCs involved in the photochemical formation of ozone. During the past five years much progress has been made in elucidating the reactions of alkoxy radicals, the mechanisms of the gas-phase reactions of O_3 with alkenes, and the mechanisms and products of the OH radical-initiated reactions of aromatic hydrocarbons, and further progress is expected. However, there are still areas of uncertainty which impact the ability to accurately model the formation of ozone in urban, rural and regional areas, and these include a need for: rate constants and mechanisms of the reactions of organic peroxy ($R\dot{O}_2$) radicals with NO, NO_3 radicals, HO_2 radicals and other $R\dot{O}_2$ radicals; organic nitrate yields from the reactions of $R\dot{O}_2$ radicals with NO, preferably as a function of temperature and pressure; the reaction rates of alkoxy radicals for decomposition, isomerization, and reaction with O_2, especially for alkoxy radicals other than those formed from alkanes and alkenes; the detailed mechanisms of the reactions of O_3 with alkenes and VOCs containing $>C{=}C<$ bonds; the mechanisms and products of the reactions of OH-aromatic adducts with O_2 and NO_2; the tropospheric chemistry of many oxygenated VOCs formed as first-generation products of VOC photooxidations; and a quantitative understanding of the reaction sequences leading to products which gas/particle partition and lead to secondary organic aerosol formation. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction and Overview

The troposphere is the region of the Earth's atmosphere in which we live and into which chemical compounds are generally emitted as a result of human activities (an exception being the exhaust from present and future supersonic transports). As described below, emissions of oxides of nitrogen ($NO_x = NO + NO_2$), volatile organic compounds (VOCs) and sulfur compounds (including SO_2 and reduced sulfur compounds) lead to a complex series of chemical and physical transformations which result in such effects as the formation of ozone in urban and regional areas (National Research Council, 1991) as well as in the global troposphere (Logan, 1985), acid deposition (Schwartz, 1989), and the formation of secondary particulate matter through gas/particle partitioning of both emitted chemical compounds and the atmospheric reaction products of VOCs, NO_x, SO_2 and organosulfur compounds (Pankow, 1987; Bidleman, 1988; Odum et al., 1996,1997).

This article deals with the gas-phase chemistry of VOCs and NO_x, including a brief discussion of the role

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of VOCs and NO_x in the formation of particulate matter. No discussion is given here of dry and wet deposition of gases and particles, nor of aqueous-phase chemistry occurring in aerosols and rain-, fog- and cloud-water [dry deposition is dealt with by Wesely and Hicks (2000), and aqueous-phase and heterogeneous reactions are dealt with by Jacob (2000)]. The tropospheric chemistry of hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and organosulfur compounds is also not dealt with here, and the chemistry of polycyclic aromatic hydrocarbons (PAH) is only touched on briefly in Section 6. The HCFCs and HFCs, potential replacements for the chlorofluorocarbons (CFCs), play a negligible role in the formation of ozone in urban and regional areas (Hayman and Derwent, 1997), and their chemistry is reviewed and evaluated on an ongoing basis by the National Aeronautics and Space Administration (NASA) Panel for Data Evaluation [the most recent being DeMore et al. (1997)] and the International Union of Pure and Applied Chemistry (IUPAC) Sub-Committee on Gas Kinetic Data Evaluation for Atmospheric Chemistry [the most recent covering HCFC and HFC chemistry being Atkinson et al. (1997a)]. The tropospheric chemistry of organosulfur compounds and of volatile PAH has been reviewed and evaluated elsewhere (Atkinson and Arey, 1994; DeMore et al., 1997; Atkinson et al., 1997a,b), and these references should be consulted for further details.

The troposphere extends from the Earth's surface to the tropopause at 10–18 km, with the height of the tropopause depending on latitude and season, being highest at the tropics and lowest at the polar regions during wintertime (McIlveen, 1992). The troposphere is characterized by generally decreasing temperature with increasing altitude, from an average of 289 K at ground level to 210–215 K at the tropopause. In the atmosphere, pressure decreases monotonically with increasing altitude, from an average of 1013 millibar (mb) at the Earth's surface to 140 mb at 14 km (the average altitude of the tropopause). The lowest kilometer or so of the troposphere contains the planetary boundary layer and inversion layers, with vertical mixing between the boundary and inversion layers and the free troposphere above them being hindered. The troposphere is well-mixed and its composition is 78% N_2, 21% O_2, 1% Ar, 0.036% CO_2, varying amounts of water vapor depending on altitude and temperature, and minute amounts of a number of trace gases.

Molecular oxygen, O_2, and ozone, O_3, in the stratosphere [the maximum concentration of O_3 in mid-latitudes occurs at an altitude of $\sim$ 20–25 km (World Meteorological Organization, 1995)] absorb ultraviolet radiation below $\lesssim 290$ nm, and hence only solar radiation of wavelength $\gtrsim 290$ nm is transmitted through the stratospheric ozone layer into the troposphere, and impacts the Earth's surface (Seckmeyer and McKenzie, 1992). Any depletion of stratospheric ozone allows shorter wavelength radiation to be transmitted through the stratosphere into the troposphere (Kerr and McElroy, 1993; Madronich et al., 1995; Kirchhoff et al., 1997), leading to increased photodissociation rates in the troposphere and not yet fully understood effects on tropospheric chemistry (Tang and Madronich, 1995).

Because of the presence of high mixing ratios of O_3 in the stratospheric ozone layer, with a peak mixing ratio of $\sim 10 \times 10^{-6}$ (World Meteorological Organization, 1995), there is net transport of O_3 by eddy diffusion from the stratosphere into the troposphere (Logan, 1985; Roelofs et al., 1997). In addition to this net downward transport of O_3 from the stratosphere, O_3 is formed photochemically in the troposphere from the interactions of VOCs and NO_x in the presence of sunlight (Logan, 1985; Roelofs et al., 1997). These sources of tropospheric O_3 are balanced by in situ photochemical destruction and by dry deposition at the Earth's surface (Logan, 1985; Ayers et al., 1992,1996; Roelofs et al., 1997). The chemical processes involved in the photochemical formation and destruction of tropospheric O_3 are briefly discussed below, after discussion of emissions and sources of VOCs and NO_x in the troposphere.

The result of downward transport of stratospheric ozone, in situ formation and destruction, and dry deposition at the Earth's surface is the presence of ozone in the "clean" natural troposphere (Logan, 1985). Ozone mixing ratios at "clean" remote sites at ground level are in the range $(10\text{–}40) \times 10^{-9}$ (Logan, 1985; Oltmans and Levy, 1994) and tend to increase with increasing altitude (Logan, 1994).

1.1. Organic compounds in urban and rural atmospheres

Large quantities of VOCs are emitted into the troposphere from anthropogenic and biogenic sources (World Meteorological Organization, 1995; Guenther et al., 1995,2000; Hein et al., 1997; Sawyer et al., 2000; Placet et al., 2000). Methane is emitted into the atmosphere from both biogenic (natural wetlands) and anthropogenic (domestic ruminants, rice paddies, landfills, biomass burning, and fossil-fuel related emissions) sources (World Meteorological Organization, 1995; Hein et al., 1997). The estimated world-wide emissions of methane are $\sim$ 155–240 million tonnes yr^{-1} from biogenic sources and $\sim$ 350–375 million tonnes yr^{-1} from anthropogenic sources (World Meteorological Organization, 1995; Intergovernmental Panel on Climate Change, 1996; Hein et al., 1997). Large quantities of non-methane organic compounds (NMOC), including isoprene (2-methyl-1,3-butadiene), a series of $C_{10}H_{16}$ monoterpenes, $C_{15}H_{24}$ sesquiterpenes, and oxygenated VOCs (including methanol, 2-methyl-3-buten-2-ol, 6-methyl-5-hepten-2-one, *cis*-3-hexen-1-ol, *cis*-3-hexenylacetate, and linalool) are emitted from vegetation (Arey et al., 1991;

Winer et al., 1992; Guenther et al., 1995,2000; König et al., 1995). NMOC are also emitted into the troposphere from a variety of anthropogenic sources, including combustion sources (vehicle and fossil-fueled power plant emissions), fuel storage and transport, solvent usage, emissions from industrial operations, landfills, and hazardous waste facilities (Sawyer et al., 2000; Placet et al., 2000). Literature estimates of the USA. and world-wide emissions of NMOC are ~ 20 million tons yr^{-1} and ~ 60–140 million tons yr^{-1}, respectively, from anthropogenic sources and ~ 29 million tonnes yr^{-1} and ~ 1150 million tonnes (of carbon) yr^{-1}, respectively, from biogenic sources (National Research Council, 1991; Lamb et al., 1993; World Meteorological Organization, 1995; Guenther et al., 1995).

Organic compounds present in the atmosphere are partitioned between the gas and particle phases (Pankow, 1987; Bidleman, 1988; Finizio et al., 1997), and the phase in which a chemical exists in the atmosphere can significantly influence its dominant tropospheric removal process(es) and lifetime (Bidleman, 1988). For partitioning proceeding by surface adsorption, gas/particle partitioning depends on the liquid-phase (or sub-cooled liquid-phase) vapor pressure, P_L, at the ambient atmospheric temperature, the surface area of the particles per unit volume of air, θ, and the nature of the particles and of the chemical being adsorbed. The fraction of the chemical present in the particle phase, ϕ, depends on these parameters through an equation of the form (Pankow, 1987; Bidleman, 1988),

$$\phi = c\theta/(c\theta + P_L) \tag{I}$$

where c is a parameter which depends on the chemical being adsorbed and on the nature of the particle. To a first approximation, chemical compounds with liquid-phase vapor pressures of $P_L < 10^{-6}$ Pa ($< 10^{-8}$ Torr) at the ambient atmospheric temperature are present in the particle phase, and those with values of $P_L > 1$ Pa ($> 10^{-2}$ Torr) at the ambient atmospheric temperature exist essentially totally in the gas-phase (Eisenreich et al., 1981; Bidleman, 1988). Chemicals with intermediate values of P_L are present in both the gas and particle phases and are often termed semi-volatile organic compounds (SOCs). Because of the variation of P_L with temperature, for a given particle surface area a decrease in ambient atmospheric temperature will increase the fraction of the SOC present in the particle phase [Eq. (I)].

For partitioning proceeding by absorption into particulate organic matter, it is assumed that the particulate organic matter behaves as octanol, with the partitioning between the particles and air depending on the octanol-air partition coefficient K_{OA} (Finizio et al., 1997). With the data-base presently existing, the two approaches appear complementary (Finizio et al., 1997).

1.2. Oxides of nitrogen

In addition to emissions of methane and NMOC into the troposphere, oxides of nitrogen are also emitted into, or produced in, the troposphere. NO is emitted from soils and natural fires and is formed in situ in the troposphere from lightning (National Research Council, 1991; World Meteorological Organization, 1995), and is emitted from combustion processes such as vehicle emissions and fossil-fueled power plants (National Research Council, 1991) [see also Guenther et al., 2000; Placet et al., 2000; Sawyer et al., 2000]. The estimated USA and world-wide emissions of NO_x (including formation from lightning) are ~ 1 million tons yr^{-1} and ~ 10 million tonnes yr^{-1} (as N), respectively, from biogenic or natural sources, and ~ 6 million tons yr^{-1} and ~ 40 million tons yr^{-1} (as N), respectively, from anthropogenic sources (National Research Council, 1991; World Meteorological Organization, 1995). In urban areas, NMOC and NO_x from anthropogenic sources dominate over NMOC and NO_x from biogenic sources, and the reverse is generally the case in rural and remote areas, with, for example, isoprene dominating over anthropogenic NMOC in the southeastern USA. (Geron et al., 1994,1995).

1.3. Formation of hydroxyl radicals in the "clean" troposphere

The presence of relatively low levels of O_3 in the troposphere is important, because photolysis of O_3 at wavelengths $\gtrsim 290$ nm occurs in the troposphere to form the excited oxygen, $O(^1D)$, atom (DeMore et al., 1997; Atkinson et al., 1997b). $O(^1D)$ atoms are either deactivated to ground-state oxygen, $O(^3P)$ atoms, or react with water vapor to generate OH radicals (DeMore et al., 1997; Atkinson et al., 1997b).

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \qquad (\lambda \leqslant 335\ \text{nm}) \tag{1}$$

$$O(^1D) + M \rightarrow O(^3P) + M \qquad (M = N_2, O_2) \tag{2}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (M = \text{air}) \tag{3}$$

$$O(^1D) + H_2O \rightarrow 2OH \tag{4}$$

At 298 K and atmospheric pressure with 50% relative humidity, ~ 0.2 OH radicals are produced per $O(^1D)$ atom formed. Photolysis of O_3 in the presence of water vapor is a major tropospheric source of OH radicals, especially in the lower troposphere where water vapor mixing ratios are high. As discussed below, other sources of OH radicals in the troposphere include the photolysis of nitrous acid (HONO), the photolysis of formaldehyde and other carbonyls in the presence of NO, and the dark reactions of O_3 with alkenes.

As shown later in this article, the hydroxyl (OH) radical is the key reactive species in the troposphere, reacting with all organic compounds apart from the chlorofluorocarbons (CFCs) and those Halons not containing H atoms (Atkinson, 1989,1994; DeMore et al., 1997; Atkinson et al., 1997a). Using direct spectroscopic techniques (see, for example, Brauers et al., 1996; Mount et al., 1997; Mather et al., 1997), peak daytime OH radical concentrations in the range $(2–10)\times10^6$ molecule cm^{-3} have been measured at close to ground level at two mid-latitude northern hemisphere sites during August/September time-periods. A diurnally and annually averaged global tropospheric OH radical concentration has also been estimated by comparing the emissions of methylchloroform (1,1,1-trichloroethane) with its atmospheric concentrations and taking into account the atmospheric loss processes for methyl chloroform (mainly gas-phase reaction with the OH radical), resulting in a diurnally, seasonally and annually averaged 24-h OH radical concentration of 1.0×10^6 molecule cm^{-3} (Prinn et al., 1995; Hein et al., 1997). Note that OH radicals are formed only during daylight hours from the photolysis of O_3 (and from the photolysis of HONO, HCHO and other carbonyls), and it has been suggested that OH radical formation from the reactions of O_3 with alkenes during both daytime and nighttime could be important (Paulson and Orlando, 1996).

1.4. *Formation of nitrate radicals in the troposphere*

The presence of NO in the troposphere from natural and anthropogenic sources is followed by the reactions,

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (5)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (6)$$

leading to the formation of the nitrate (NO_3) radical (DeMore et al., 1997; Atkinson et al., 1997b). Because the nitrate radical photolyzes rapidly,

$$NO_3 + h\nu \rightarrow NO + O_2 \qquad (\sim 10\%), \quad (7a)$$

$$NO_3 + h\nu \rightarrow NO_2 + O(^3P) \qquad (\sim 90\%) \quad (7b)$$

with a lifetime due to photolysis of ~ 5 s for overhead sun, and reacts rapidly with NO, NO_3 radical concentrations remain low during daylight hours but can increase to measurable levels during nighttime. Measurements made over the past 15 years show nighttime NO_3 concentrations at around ground level over continental areas ranging up to 1×10^{10} molecule cm^{-3} [a mixing ratios of 430×10^{-12}] (Atkinson et al., 1986; Mihelcic et al., 1993; Platt and Heintz, 1994).

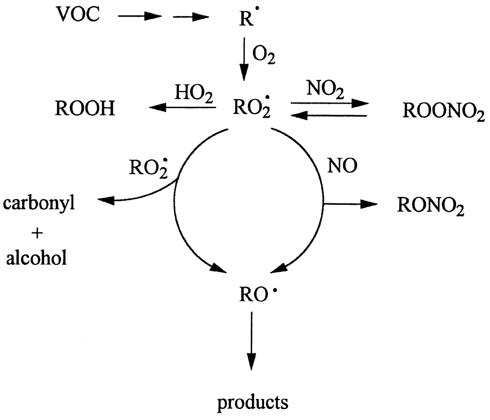
1.5. *Overview of VOC–NO_x–O_x–HO_x chemistry in the troposphere*

In the troposphere, VOCs are removed by the physical processes of wet and dry deposition (which are not discussed here), and are transformed by the chemical processes of photolysis, reaction with hydroxyl (OH) radicals, reaction with nitrate (NO_3) radicals and reaction with O_3 (National Research Council, 1991; Atkinson, 1994,1995).

In addition to tropospheric chemistry involving O_x, NO_x and VOCs, the involvement of Cl and Br atoms in VOC and O_3 chemistry has been observed in the lower Arctic troposphere during springtime (see, for example, Le Bras and Platt, 1995; Barrie and Platt, 1997). Observations made in the Arctic during springtime provide evidence for the occurrence of reactions of alkanes, alkyl nitrates, ethene and acetylene with Cl atoms (Bottenheim et al., 1990; Kieser et al., 1993; Jobson et al., 1994; Muthuramu et al., 1994; Ramacher et al., 1997) and for the depletion of O_3 by BrO_x chemistry and the reactions of ethene and acetylene with Br atoms (Bottenheim et al., 1990; Kieser et al., 1993; Jobson et al., 1994; Hausmann and Platt, 1994; Ramacher et al., 1997; Tuckermann et al., 1997). The sources of active chlorine and bromine are postulated to be through heterogeneous reactions involving chloride and bromide salt particles (including sea-salt aerosols) as discussed in, for example, McConnell et al. (1992) and Oum et al. (1998).

While to date this halogen atom-initiated destruction of tropospheric O_3 has been observed only in Arctic regions, it is possible that similar occurrences occur in other localities (Kreher et al., 1997). It should be recognized that while Cl and Br atom-initiated chemistry can be important in certain situations, with reaction with the Cl atom then potentially being a major removal process for alkanes (and possibly other VOCs), assessments of the impact of Cl atom-initiated removal of VOCs in the global troposphere (Singh et al., 1996; Rudolph et al., 1996) and in the global marine boundary layer (Rudolph et al., 1997) indicate that Cl atom chemistry plays, at most, a minor role with average Cl atom concentrations of $\lesssim 10^3$ molecule cm^{-3} in the global troposphere and $\lesssim 10^4$ molecule cm^{-3} in the global marine boundary layer (Singh et al., 1996; Rudolph et al., 1996,1997). No discussion of tropospheric ClO_x and BrO_x chemistry or of the reactions of Cl and Br atoms with VOCs is given here, and the NASA and IUPAC evaluations (DeMore et al., 1997; Atkinson et al., 1997a,1999) and Atkinson (1997a) should be consulted for details.

The atmospheric chemistry of the various classes of VOCs were discussed by the National Research Council (1991) and recent reviews and evaluations of various aspects of VOC tropospheric chemistry have been published within the past few years (Atkinson, 1994,1997a; DeMore et al., 1997; Atkinson et al., 1997a,1999). Details of this chemistry are discussed in Sections 3–8 below. In general, the degradation/transformation reactions of VOCs which occur in the troposphere can be represented by Scheme 1, with the important intermediate radicals being alkyl or substituted alkyl radicals ($\dot{R}$), alkyl peroxy



Scheme 1.

or substituted alkyl peroxy radicals ($R\dot{O}_2$), and alkoxy or substituted alkoxy radicals ($R\dot{O}$).

There are, however, certain reactions which lead to product species whose subsequent reactions are unique and differ from those of $\dot{R}$, $R\dot{O}_2$ and $R\dot{O}$ radicals formed from alkanes, alkenes and other VOCs. As discussed in Sections 5 and 6, these include the formation of biradicals from the O_3 reactions with alkenes and the formation of hydroxycyclohexadienyl radicals from the OH radical reactions with aromatic hydrocarbons.

The simplest VOC degradation scheme is that for methane (DeMore et al., 1997; Atkinson et al., 1999), and the tropospheric degradation of methane in the presence of NO leading to first-generation products is

$$OH + CH_4 \rightarrow H_2O + \dot{C}H_3 \quad (8)$$

$$\dot{C}H_3 + O_2 \xrightarrow{M} CH_3\dot{O}_2 \quad (9)$$

$$CH_3\dot{O}_2 + NO \rightarrow CH_3\dot{O} + NO_2 \quad (10)$$

$$CH_3\dot{O} + O_2 \rightarrow HCHO + HO_2 \quad (11)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (12)$$

$$\textit{NET}: OH + CH_4 + 2NO + 2O_2 \rightarrow OH + HCHO + H_2O + 2NO_2$$

The tropospheric reactions of methane and of its degradation products HCHO and CO are dealt with in the NASA and IUPAC evaluations (DeMore et al., 1997; Atkinson et al., 1999), and these articles should be consulted for further details. Reactions with methane and CO are the dominant loss process for the OH radical concentration in the "clean" troposphere, and calculations indicate that increases in tropospheric methane concentrations will reduce the OH radical concentration (Intergovernmental Panel on Climate Change, 1996), thus further increasing methane concentrations in a feedback loop.

O_3 is formed photochemically from the photolysis of NO_2,

$$NO_2 + h\nu \rightarrow NO + O(^3P) \quad (13)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (M = \text{air}) \quad (3)$$

and because O_3 reacts rapidly with NO

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (5)$$

reactions (13), (3) and (5) result in a photoequilibrium between NO, NO_2 and O_3 with no net formation or loss of O_3, as shown in Fig. 1A.

However, in the presence of VOCs (including methane and NMOCs of biogenic origin in the "clean" troposphere and anthropogenic plus biogenic VOCs in urban and rural areas), the degradation reactions of VOCs lead to the formation of intermediate $R\dot{O}_2$ and HO_2 radicals. These HO_2 and $R\dot{O}_2$ radicals react with NO, converting NO to NO_2,

$$HO_2 + NO \rightarrow OH + NO_2 \quad (12)$$

$$R\dot{O}_2 + NO \rightarrow R\dot{O} + NO_2 \quad (14)$$

which then photolyzes to form O_3 (Fig. 1B). As evident from Fig. 1B, this process results in net formation of O_3.

Note that the photolysis of O_3 to form $O(^1D)$ atoms with subsequent reaction of $O(^1D)$ atoms with water vapor to form OH radicals [reaction (1) followed by reaction (4)] is a net loss of tropospheric O_3 [in contrast, reaction (1) followed by reactions (2) and (3) leads to no net loss (or formation) of O_3]. In the absence of NO or at

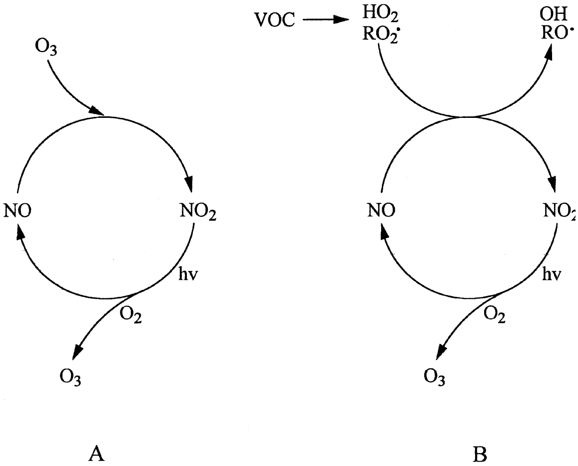


Fig. 1. Schematics of the reactions involved in NO-to-NO_2 conversion and O_3 formation in (A) NO–NO_2–O_3 systems in the absence of VOCs, and (b) NO–NO_2–O_3 systems in the presence of VOCs.

sufficiently low NO concentrations (which are defined below), reactions of O_3 with OH and HO_2 radicals

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (15)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad (16)$$

are additional loss processes for tropospheric ozone.

Net photochemical formation of O_3 vs. net photochemical loss of O_3 in the troposphere therefore depends on the NO concentration, and is determined by the rate of the reaction of the HO_2 radical with NO

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (12)$$

versus those for the reactions

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (17)$$

and

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad (16)$$

and also by the rates of the reactions of $R\dot{O}_2$ radicals with NO

$$R\dot{O}_2 + NO \rightarrow R\dot{O} + NO_2 \qquad (14)$$

compared to those for reactions of $R\dot{O}_2$ radicals with the HO_2 radical.

$$R\dot{O}_2 + HO_2 \rightarrow ROOH + O_2 \qquad (18)$$

Based on the rate constants for these reactions of HO_2 and $R\dot{O}_2$ radicals and the tropospheric concentrations of HO_2 radicals and NO, net photochemical O_3 formation occurs for NO mixing ratios $\gtrsim(10\text{–}30) \times 10^{-12}$ while net photochemical O_3 destruction occurs for NO mixing ratios $\lesssim(10\text{–}30) \times 10^{-12}$ (Logan, 1985).

As an example of net formation of O_3 from the tropospheric degradation of VOCs in the presence of NO, combining the net overall reaction for methane oxidation given above

$$OH + CH_4 + 2NO + 2O_2 \rightarrow OH + HCHO + H_2O + 2NO_2$$

with the photolysis of NO_2 in air to form NO plus O_3 [reaction (13) followed by reaction (3)], leads to the overall process

$$OH + CH_4(+h\nu) \rightarrow OH + HCHO + H_2O + 2O_3$$

forming O_3 and regenerating the OH radical.

Any factors which affect OH radical concentrations and the number of molecules of NO converted to NO_2 therefore affect the rate of O_3 formation and the amount of O_3 formed; such factors include radical sources and sinks, NO_x sinks, and reaction pathways with differing numbers of NO molecules converted to NO_2 in a VOC's degradation mechanism. Uncertainties in these aspects of a VOC's degradation mechanism translate into corresponding uncertainties in the ozone forming potential of that VOC.

In addition to the reactions of NO and NO_2 with O_3,

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (5)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (6)$$

NO_2 reacts with NO_3 to form dinitrogen pentoxide (N_2O_5, the anhydride of nitric acid) in a reversible process.

$$NO_3 + NO_2 \overset{M}{\rightleftarrows} N_2O_5 \qquad (19)$$

Although no homogeneous gas-phase reaction of N_2O_5 with water vapor to form nitric acid has been observed (Mentel et al., 1996; Atkinson et al., 1997b), wet and dry deposition of N_2O_5 and uptake of N_2O_5 by aerosols can be important nighttime loss processes for NO_x (see Jacob, 2000; Wesely and Hicks, 2000).

Additional gas-phase reactions involved in NO_x tropospheric chemistry include the reactions of OH radicals with NO and NO_2.

$$OH + NO \overset{M}{\rightarrow} HONO \qquad (20)$$

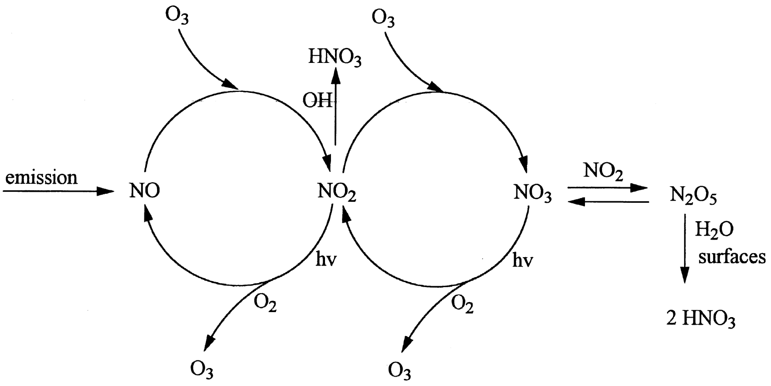
$$OH + NO_2 \overset{M}{\rightarrow} HNO_3 \qquad (21)$$

The OH radical reaction with NO_2 is a major loss process for NO_x during daytime and is an important loss process for OH radicals in urban airsheds with elevated NO_2 concentrations (Ehhalt et al., 1991). Important tropospheric NO_x reactions for "clean" tropospheric conditions are shown in Scheme 2 (omitting the minor photolysis pathway of the NO_3 radical to form $NO + O_2$).

The OH radical reaction with NO to form nitrous acid (HONO) is in photoequilibrium with the photolysis of HONO

$$HONO + h\nu \rightarrow OH + NO \qquad (22)$$

Formation of HONO during nighttime has been observed in urban areas (as well as in the dark in environmental chambers) and is attributed to the heterogeneous hydrolysis of NO_2 on aerosol and particulate matter surfaces (Lammel and Cape, 1996) (see also Jacob, 2000). The rapid photolysis of this nighttime-generated HONO after sunrise leads to an early morning pulse of OH radicals and hence acts as an initiator to urban photochemistry (Harris et al., 1982).



Scheme 2.

As noted above, the reaction of HO_2 radicals with NO [reaction (12)] converts HO_2 radicals to the more reactive OH radicals. While HO_2 radicals also react with NO_2

$$HO_2 + NO_2 \overset{M}{\rightleftarrows} HO_2NO_2 \tag{23}$$

the rapid thermal decomposition of HO_2NO_2 (DeMore et al., 1997; Atkinson et al., 1997b) renders this reaction unimportant in the lower troposphere.

2. Inorganic reactions

The kinetics, mechanisms and products of the gas-phase reactions of inorganic species in the troposphere are now generally well understood and the salient points of the O_x–HO_x–NO_x interactions have been presented and briefly discussed above. The reactions of O_x species [$O(^3P)$ and $O(^1D)$ atoms and O_3], HO_x species [H atoms, OH and HO_2 radicals, H_2O and H_2O_2], NO_x species, and SO_2 and H_2S and their reaction products are reviewed and evaluated on an on-going basis by the NASA and IUPAC data evaluation panels, with the most recent of these evaluations being NASA Evaluation No. 12 (DeMore et al., 1997) and IUPAC Supplement VI (Atkinson et al., 1997b). The few major changes in rate constants or mechanisms of inorganic reaction in either the NASA or IUPAC evaluations over the past several years is indicative of the generally good understanding of the majority of inorganic reactions important in the troposphere.

However, there are certain specific reactions or areas of uncertainty that impact the ability to quantitatively understand the formation, cycling and losses of O_3 and NO_x in the troposphere (in some cases specifically in the boundary layer), and these are noted below.

2.1. *O_3 photodissociation quantum yields for $O(^1D)$ atom formation*

Recent studies [see DeMore et al. (1997) and Atkinson et al. (1997b) and references therein] have shown that $O(^1D)$ atom formation from O_3 occurs at wavelengths > 320 nm, and therefore that the OH radical formation rate in the troposphere is higher than calculated using the recommendations of the earlier NASA and IUPAC evaluations. There are still uncertainties in the quantum yields for O_3 photodissociation to yield $O(^1D)$ atoms at wavelengths $\geqslant 320$ nm; for example, NASA (DeMore et al., 1997) recommends a quantum yield of zero for $\lambda > 325$ nm while IUPAC (Atkinson et al., 1997b) recommends a non-zero quantum yield out to 335 nm.

2.2. *Rate constant for the reaction of the OH radical with NO_2*

As noted above, the combination reaction of the OH radical with NO_2 to form nitric acid is the major daytime loss process for NO_x in the troposphere, and is a significant loss process for OH radicals in polluted urban atmospheres with elevated NO_x levels (Ehhalt et al., 1991) and in "smog" chamber experiments. Despite the importance of this reaction, there are significant discrepancies in the published room temperature rate constants at around atmospheric pressure (see Forster et al., 1995; Donahue et al., 1997 and references therein). Indicative of these discrepancies, the NASA (DeMore et al., 1997) and IUPAC (Atkinson et al., 1997b) recommended rate constants at 298 K and 760 Torr total pressure of air differ considerably, with second-order rate constants of 8.7×10^{-12} and 1.42×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively. The studies of Anastasi and Smith (1976), Wine et al. (1979) and Robertshaw and Smith (1982) carried out at $\geqslant 490$ Torr total pressure of N_2, Ar, CF_4

or SF_6 diluents suggest a rate constant of $\sim 1.1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K and 760 Torr of N_2, in the middle of the NASA and IUPAC recommendations, while the most recent study of Donahue et al. (1997) recommends a second-order rate constant of 9.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K and 760 Torr of N_2. It therefore appears that a second-order rate constant of $\sim 1.0 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} should be appropriate for 760 Torr of air at 298 K, and that the IUPAC recommended rate constant (Atkinson et al., 1997b) is too high.

2.3. N_2O_5 loss processes

As discussed above, N_5O_5 is formed from the reaction of NO_2 with the NO_3 radical [reaction (19)] and may be present during nighttime hours. The recent study of Mentel et al. (1996) shows that the homogeneous gas-phase reaction of N_2O_5 with water vapor

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{24}$$

is very slow, with a measured rate constant at 293 K of $(2.6 \times 10^{-22} + 1.9 \times 10^{-39}[H_2O])$ cm^3 $molecule^{-1}$ s^{-1}. While this measured rate constant may be due, at least in part, to reactions of N_2O_5 at the reaction chamber walls, the effective rate constant at 293 K and all relative humidities is significantly lower (by up to an order of magnitude) than earlier direct measurements used in the most recent NASA (DeMore et al., 1997) and IUPAC (Atkinson et al., 1997b) recommendations. It is possible that no homogeneous gas-phase reaction of N_2O_5 with water vapor occurs, with the loss of N_2O_5 (and hence of NO_x) from the tropospheric boundary layer during nighttime being by dry deposition to surfaces (Wesely and Hicks, 2000) and efficient uptake to aerosols with hydrolysis to nitric acid (Jacob, 2000).

2.4. Heterogeneous formation of HONO

Nitrous acid is observed at mixing ratios $\gtrsim 10^{-9}$ during nighttime in polluted atmospheres (see, for example, Perner and Platt, 1979; Harris et al., 1982) and its rapid photolysis after sunrise then leads to an early morning “pulse” of OH radicals.

$$HONO + h\nu \rightarrow OH + NO \tag{22}$$

The analogous formation of HONO in “smog” chambers has been observed and extensively studied (see, for example, Sakamaki et al., 1983; Pitts et al., 1984; Akimoto et al., 1987), and attributed to the heterogeneous hydrolysis of NO_2,

$$2NO_2 + H_2O(+\text{wall}) \rightarrow HONO + HNO_3 \tag{25}$$

with the nitric acid remaining on the surface and the formation rate of HONO being first order in the NO_2 concentration. As discussed in the review article of Lammel and Cape (1996), despite claims to the contrary a totally analogous heterogeneous hydrolysis of NO_2 on airborne particle and aerosol surfaces appears to be responsible for ambient atmospheric formation of HONO (see also Jacob, 2000). However, quantification (or accurate parameterization) of the formation of HONO during both nighttime and daytime is needed to allow reliable calculation of the OH radical formation rate from HONO photolysis during daytime to be used in urban and regional airshed model applications.

2.5. Products of the tropospheric degradation of NH_3

In the absence of gaseous nitric acid, ammonia is chemically fairly long-lived in the troposphere and reacts relatively slowly with the OH radical to form the NH_2 radical. NH_2 radicals then react in the troposphere with O_3, NO and NO_2 (DeMore et al., 1997; Atkinson et al., 1997b). The kinetics of these reactions are known reasonably well (although cited uncertainties of up to a factor of 3 still exist in the NASA and IUPAC recommended rate constants for the O_3 and NO_2 reactions), and all three reactions need to be considered as a tropospheric loss process for NH_2 radicals. However, the products of the reactions of the NH_2 radical with O_3 and NO_2 are either not known (O_3 reaction) or the reaction channels are not quantitatively understood (the NO_2 reaction), and these uncertainties translate into uncertainties concerning the fate of the nitrogen originally contained in NH_3 (to NO_x, N_2 or N_2O). The important reaction of NH_3 with gaseous nitric acid to form ammonium nitrate particulate is discussed by Jacob (2000).

3. Organic reactions

While detailed discussions of the tropospheric chemistry of the various classes of VOCs are given in the sections below, the tropospheric reactions of VOCs share many reaction sequences in common, and certain areas of uncertainty which affect tropospheric ozone formation and NO_x cycling and removal are also common to almost all VOCs. Photolysis and the initial reactions of many VOCs with OH radicals and NO_3 radicals lead to the formation of alkyl or substituted alkyl ($\dot{R}$) radicals, and the reactions of O_3 with alkenes and other VOCs containing $>C{=}C<$ bonds lead to the formation of organic peroxy ($R\dot{O}_2$) radicals. A generalized tropospheric degradation scheme which is applicable for most VOCs is given in Scheme 1, showing that the intermediate organic radicals include alkyl (or substituted alkyl) radicals ($\dot{R}$), organic peroxy radicals ($R\dot{O}_2$) and alkoxy (or substituted alkoxy) radicals ($R\dot{O}$). There are areas of uncertainty common to all VOC degradation reaction schemes, two of which involve organic peroxy radicals.

3.1. Reactions of organic peroxy radicals

As shown in Scheme 1, organic peroxy radicals react with NO, NO_2, HO_2 radicals and organic peroxy radicals.

$$R\dot{O}_2 + NO \overset{M}{\rightarrow} RONO_2 \tag{14a}$$

$$R\dot{O}_2 + NO \rightarrow R\dot{O} + NO_2 \tag{14b}$$

$$R\dot{O}_2 + NO_2 \overset{M}{\rightleftarrows} ROONO_2 \tag{26}$$

$$R\dot{O}_2 + HO_2 \rightarrow ROOH + O_2 \tag{18}$$

$$RCH(O\dot{O})R' + RCH(O\dot{O})R' \rightarrow RCH(\dot{O})R' + RCH(\dot{O})R' + O_2 \tag{27a}$$

$$RCH(O\dot{O})R' + RCH(O\dot{O})R' \rightarrow RCH(OH)R' + RC(O)R' + O_2 \tag{27b}$$

Alkyl peroxynitrates thermally decompose rapidly back to reactants at around room temperature (Zabel, 1995; Atkinson et al., 1997a,1999), and hence the $R\dot{O}_2 + NO_2$ reaction is unimportant in the lower troposphere for R = alkyl or substituted alkyl (but not for R = acyl). In the troposphere, important reactions of $R\dot{O}_2$ radicals are with NO and HO_2 radicals, and the competition between these reactions determines whether net O_3 formation or net O_3 destruction occurs. To date, kinetic and product data for $R\dot{O}_2$ radical reactions with NO and with the HO_2 radical are available mainly for alkyl peroxy radicals formed from alkanes (Carter and Atkinson, 1989a; Atkinson, 1997a), and there is a definite need for kinetic and product data for the reactions of a wide variety of organic peroxy radicals with NO and HO_2 radicals.

Organic peroxy radicals also react with NO_3 radicals (Ray et al., 1996; Canosa-Mas et al., 1996; Helleis et al., 1996; Atkinson et al., 1999), and this reaction pathway can be important during nighttime (Mihelcic et al., 1993).

$$R\dot{O}_2 + NO_3 \rightarrow R\dot{O} + NO_2 + O_2 \tag{28}$$

3.2. Organic nitrate formation

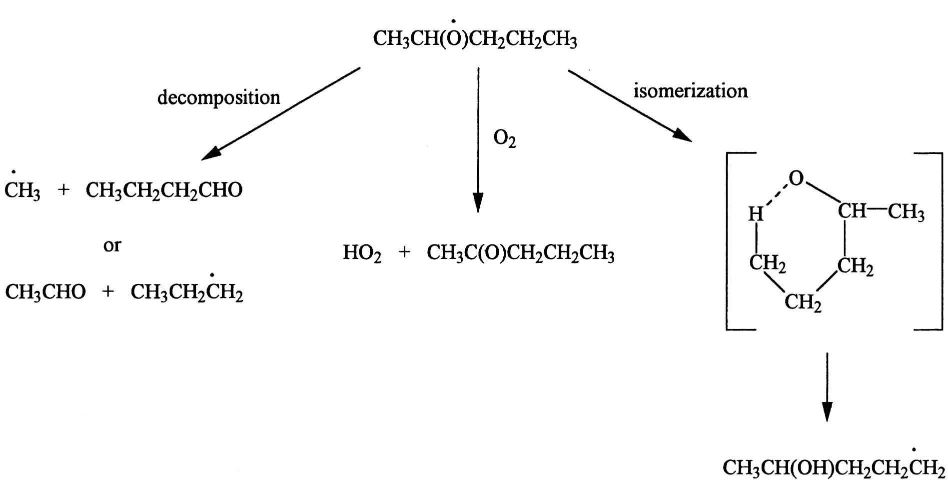
Organic nitrates ($RONO_2$) are formed in one channel [reaction (14a)] of the reaction of organic peroxy radicals with NO, and organic nitrate formation is a sink for both radicals and NO_x. Thus, a less than unit conversion of NO to NO_2 and of $R\dot{O}_2$ to $R\dot{O}$ in this reaction (and of NO to NO_2 in subsequent reactions in the degradation scheme leading to first-generation products) results in a lowered formation of O_3 and of HO_2 radicals. Accurate knowledge of the formation yields of organic nitrates from the $R\dot{O}_2 + NO$ reactions is crucial to accurate predictions of ozone formation in "smog" chambers as well as in the ambient atmosphere. Because the formation yields of organic nitrates are significantly temperature and pressure dependent, decreasing with increasing temperature and with decreasing pressure (Carter and Atkinson, 1989a; Atkinson, 1994,1997a), it is necessary to have pressure and temperature dependent organic nitrate yield data and/or methods available for accurate calculation of organic nitrate yields (or of the rate constant ratios k_{14a}/k_{14b}). To date, experimentally measured organic nitrate formation yield data are available only for 18 secondary alkyl peroxy radicals formed from the NO_x-air photooxidations of C_2–C_8 *n*-alkanes and for four other alkyl and β-hydroxyalkyl peroxy radicals formed from alkanes and alkenes (Carter and Atkinson, 1989a; Atkinson, 1994,1997a). Additional yield data are needed for organic nitrates formed from the wide variety of VOCs observed in ambient air.

3.3. Reactions of alkoxy radicals

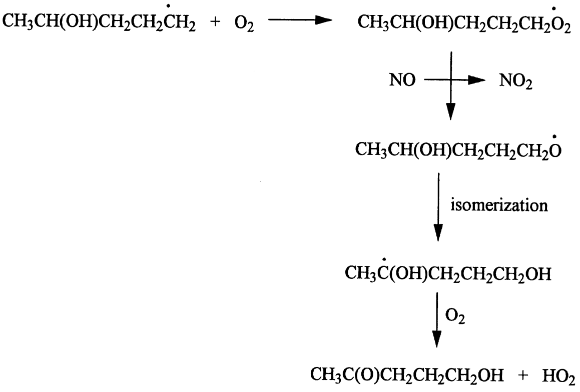
As shown in Scheme 1, alkoxy radicals are formed as intermediate radicals during the tropospheric degradations of VOCs. The subsequent reactions of alkoxy radicals determine the products formed and the amount of NO converted to NO_2 by $R\dot{O}_2$ and HO_2 radicals, and hence the amounts of O_3 formed. In the troposphere, alkoxy radicals can react with O_2, unimolecularly decompose, or isomerize by a 1,5-H shift through a 6-membered transition state (Atkinson, 1997a,b). Taking the 2-pentoxy radical formed from the OH radical reaction with *n*-pentane in the presence of NO as an example, these reactions are shown in Scheme 3.

The alkyl and δ-hydroxyalkyl radicals formed from the decomposition and isomerization pathways, respectively, react further by reaction schemes analogous to those shown in Scheme 1. For example, the subsequent reactions of the $CH_3CH(OH)CH_2CH_2\dot{C}H_2$ radical formed by isomerization of the 2-pentoxy radical (see Scheme 3) in the presence of NO lead to formation of the δ-hydroxycarbonyl 5-hydroxy-2-pentanone (Scheme 4). Reactions of α-hydroxyalkyl radicals such as $CH_3\dot{C}(OH)CH_2CH_2CH_2OH$ with O_2 are discussed in Section 5.

The products formed and the number of NO-to-NO_2 conversions involved therefore depend on the alkoxy radical reaction pathway. For example, reaction of a C_n-alkoxy radical with O_2 leads to a C_n-carbonyl and 1 NO-to-NO_2 conversion in addition to that to form the C_n-alkoxy radical. Decomposition of a C_n-alkoxy radical leads to two or more carbonyl or carbonyl/hydroxycarbonyl products each containing less carbon atoms than the original C_n-alkoxy radical and $\geqslant 2$ NO-to-NO_2 conversions in addition to that to form the C_n-alkoxy



Scheme 3.



Scheme 4.

radical (the precise number of NO-to-NO_2 conversions depends on the fate of the second-generation alkoxy radical formed from the alkyl radical produced in the C_n-alkoxy radical decomposition). Isomerization of a C_n-alkoxy radicals generally leads to a C_n-hydroxycarbonyl and 2 NO-to-NO_2 conversions in addition to that to form the original C_n-alkoxy radical.

There now appears to be a semi-quantitative understanding of the tropospheric reactions of alkoxy radicals formed from alkanes and of β-hydroxyalkoxy radicals formed from the OH radical-initiated reactions of alkenes (Atkinson, 1997a,b), and this understanding appears to hold for substituted alkoxy radicals formed from certain other classes of VOCs (see, for example, Shu et al., 1997; Aschmann et al., 1997a). However, we do not have such an understanding of the reactions of alkoxy radicals of structure $>\mathrm{C}(\dot{\mathrm{O}})\mathrm{OR}$ (R = alkyl) formed from ethers and glycol ethers, nor for alkoxy radicals of structure $-\mathrm{C(O)OCH}(\dot{\mathrm{O}})\mathrm{R}$ (R = alkyl) formed from esters, and this may also be the case for alkoxy radicals containing other structural features.

3.4. *Wet and dry deposition of VOCs and of their reaction products*

Dry deposition is dealt with by Wesely and Hicks (2000) and wet deposition has been previously discussed by Bidleman (1988), and these processes are not discussed here. Wet and dry deposition of VOCs and, more likely, of VOC reaction products (and especially multifunctional products of low vapor pressure and/or high aqueous solubility) is important in terms of ozone formation. These physical processes remove VOCs and/or their reaction products from the troposphere and these species are hence no longer involved in the radical-chain processes which convert NO to NO_2 and result in O_3 formation.

4. Tropospheric chemistry of alkanes and haloalkanes

4.1. *Alkanes*

The tropospheric chemistry of alkanes leading to first-generation products has been recently reviewed and evaluated (Atkinson, 1997a), and the discussion below is based on that review which should be consulted for further details. Alkanes do not photolyze in the troposphere, nor react at measurable rates with O_3. Alkanes react with OH radicals, NO_3 radicals, and Cl atoms and, as shown in Table 1, the OH radical reaction is calculated to generally dominate as the tropospheric loss process (National Research Council, 1991; Atkinson, 1995). As for other saturated organic compounds, these atom and

Table 1
Calculated lifetimes for selected volatile organic compounds with respect to photolysis, reaction with the OH radical, reaction with the NO_3 radical, and reaction with O_3

	Lifetime due to			
Organic	OH[b]	NO_3[c]	O_3[d]	Photolysis[e]
Propane	10 day	$\sim$ 7 yr	$>$ 4500 yr	
n-Butane	4.7 day	2.8 yr	$>$ 4500 yr	
n-Octane	1.3 day	240 day		
2,2,4-Trimethylpentane	3.2 day	1.4 yr		
Ethene	1.4 day	225 day	10 day	
Propene	5.3 h	4.9 day	1.6 day	
trans-2-Butene	2.2 h	1.4 h	2.1 h	
Isoprene	1.4 h	50 min	1.3 day	
α-Pinene	2.6 h	5 min	4.6 h	
Limonene	50 min	3 min	2.0 h	
Benzene	9.4 day	$>$ 4 yr	$>$ 4.5 yr	
Toluene	1.9 day	1.9 yr	$>$ 4.5 yr	
m-Xylene	5.9 h	200 day	$>$ 4.5 yr	
1,2,4-Trimethylbenzene	4.3 h	26 day	$>$ 4.5 yr	
Styrene	2.4 h	3.7 h	1.0 day	
Phenol	5.3 h	9 min		
o-Cresol	3.3 h	2 min	65 day	
Formaldehyde	1.2 day	80 day	$>$ 4.5 yr	4 h
Acetaldehyde	8.8 h	17 day	$>$ 4.5 yr	6 day
Butanal	5.9 h			
Benzaldehyde	11 h	18 day		
Acetone	53 day	$>$ 11 yr		$\sim$ 60 day
2-Butanone	10 day			$\sim$ 4 day
2-Pentanone	2.4 day			
Glyoxal	1.1 day			5 h
Methylglyoxal	9.3 h		$>$ 4.5 yr	2 h
2,3-Butanedione	49 day			1 h
cis-Butanedial	2.6 h			$\sim$ 10 min
cis-3-Hexene-2,5-dione	2.1 h	1.5 day		$\sim$ 30 min
cis, *trans*-2,4-Hexadiendial	1.3 h	8.8 day		1.9 h
Pinonaldehyde	2.9 h	2.3 day	$>$ 2.2 yr	
Methanol[f]	12 day	1 yr		
Ethanol	3.5 day	26 day		
2-Butanol	1.3 day	17 day		
Dimethyl ether	4.1 day	180 day		
Diethyl ether	11 h	17 day		
Methyl *tert*-butyl ether	3.9 day	72 day		
Ethyl *tert*-butyl ether	1.3 day	4.2 day		
tert-Butyl formate	16 day			
Methacrolein	4.1 h	11 day	15 day	$\sim$ 1 day
Methyl vinyl ketone	6.8 h	$>$ 385 day	3.6 day	$\sim$ 2 day
Ethyl acetate	6.9 day	10 yr		
tert-Butyl acetate	21 day			
Linalool	50 min	3 min	55 min	
6-Methyl-5-hepten-2-one	50 min	4 min	1.0 h	
3-Methyl-2-buten-3-ol	2.1 h	3.8 day	1.7 day	
Methyl hydroperoxide[f]	2.1 day			$\sim$ 5 day
Ethyl nitrate	66 day			$\sim$ 7 day
2-Butyl nitrate	13 day			15–30 day

[a] Rate constants at $\sim$ 298 K are taken from Alvarado et al. (1998), Atkinson (1989,1991,1994,1997a), Atkinson et al. (1995b,1997a,1999), Bierbach et al. (1994b), Clemitshaw et al. (1997), El Boudali et al. (1996), Grosjean and Grosjean (1994), Klotz et al. (1995), Langer and Ljundström (1994a,b,1995), Le Calvé et al. (1997a,b), Plum et al. (1983), Raber and Moortgat (1996), Rudich et al. (1995,1996), Smith et al. (1996), Talukdar et al. (1993,1997a,b) and Tuazon et al. (1985). Where no lifetime is given, this is because of a lack of kinetic data; however, none of the loss processes for which data are not available are expected to be significant.

[b] For a 12-h daytime average OH radical concentration of 2.0×10^6 molecule cm^{-3} (see text).

[c] For a 12-h nighttime average NO_3 radical concentration of 5×10^8 molecule cm^{-3} (see text).

[d] For a 24-h average O_3 concentration of 7×10^{11} molecule cm^{-3} (see text).

[e] For overhead sun.

[f] Wet and dry deposition also expected to be important.

radical reactions proceed by H-atom abstraction from the C–H bonds:

$$\left.\begin{array}{l}\mathrm{OH}\\ \mathrm{NO_3}\\ \mathrm{Cl}\end{array}\right\} + \mathrm{RH} \rightarrow \dot{\mathrm{R}} + \left\{\begin{array}{l}\mathrm{H_2O},\\ \mathrm{HNO_3},\\ \mathrm{HCl}\end{array}\right. \tag{29}$$

Under all tropospheric conditions, alkyl radicals react rapidly, and solely, with O_2 to form an alkyl peroxy ($R\dot{O}_2$) radical, with rate constants at 298 K and atmospheric pressure of $\gtrsim 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1997a).

$$\dot{\mathrm{R}} + \mathrm{O_2} \overset{\mathrm{M}}{\rightarrow} \mathrm{R\dot{O}_2} \tag{30}$$

As shown in Scheme 1 and discussed in Section 3, alkyl peroxy radicals can react with NO, NO_2, HO_2 radicals, $R\dot{O}_2$ radicals and NO_3 radicals in the troposphere, with the dominant reaction(s) depending on the relative concentrations of NO, NO_2, HO_2 radicals, $R\dot{O}_2$ radicals and NO_3 radicals. While the self-reactions of alkyl peroxy radicals and their reactions with other $R\dot{O}_2$ radicals are often important in laboratory studies, the reactions of $R\dot{O}_2$ radicals with NO, NO_2, and HO_2 radicals are expected to dominate in the troposphere, with reaction with the NO_3 radical potentially being important during nighttime.

The reactions of $R\dot{O}_2$ radicals with NO_2 form alkyl peroxynitrates.

$$\mathrm{R\dot{O}_2} + \mathrm{NO_2} \overset{\mathrm{M}}{\rightarrow} \mathrm{ROONO_2} \tag{26}$$

However, because the alkyl peroxynitrates rapidly thermally decompose back to reactants, with thermal decomposition lifetimes of ~ 0.1–1 s at 298 K and atmospheric pressure (Zabel, 1995; Atkinson et al., 1997a,1999), these $R\dot{O}_2 + NO_2$ reactions can be neglected in the lower troposphere.

Reaction with NO leads to the formation of an alkoxy ($R\dot{O}$) radical plus NO_2 and, for $R\dot{O}_2$ radicals with $\geqslant 3$ carbon atoms, an alkyl nitrate ($RONO_2$).

$$\mathrm{R\dot{O}_2} + \mathrm{NO} \overset{\mathrm{M}}{\rightarrow} \mathrm{RONO_2} \tag{14a}$$

$$\mathrm{R\dot{O}_2} + \mathrm{NO} \rightarrow \mathrm{R\dot{O}} + \mathrm{NO_2} \tag{14b}$$

The formation yields of alkyl nitrates from reaction (14) increases with increasing pressure and decreasing temperature, and for secondary $R\dot{O}_2$ radicals the alkyl nitrate yields also increase with increasing carbon number in the $R\dot{O}_2$ radical. Carter and Atkinson (1989a) used the experimental data then available to propose a relationship between the rate constant ratio k_{14a}/k_{14b} and temperature, pressure, and number of carbon atoms in the secondary alkyl peroxy radical, with

$$\frac{k_{14_a}}{k_{14_b}} = \left(\frac{Y_0\,[M]\,(T/300)^{-m_0}}{1 + \dfrac{Y_0\,[M]\,(T/300)^{-m_0}}{Y_\infty\,(T/300)^{-m_\infty}}}\right) F^z, \tag{II}$$

where

$$z = \left\{1 + \left[\log_{10}\left(\frac{Y_0\,[M]\,(T/300)^{-m_0}}{Y_\infty\,(T/300)^{-m_\infty}}\right)\right]^2\right\}^{-1} \tag{III}$$

and $Y_0 = ae^{bn}$, n is the number of carbon atoms in the $R\dot{O}_2$ radical, and a and b are constants. The k_{14a}/k_{14b} ratios for primary and tertiary $R\dot{O}_2$ radicals were scaled by factors of ~ 0.40 and ~ 0.3, respectively (Carter and Atkinson, 1989a). However, as noted in Section 3, the data-base is restricted to a relatively few (18) secondary $R\dot{O}_2$ radicals and even fewer primary (2) and tertiary (2) $R\dot{O}_2$ radicals, and further experimental studies of the alkyl nitrate yields from alkyl peroxy radicals and hydroxyalkyl peroxy radicals (and especially for δ-hydroxyalkyl peroxy radicals formed after alkoxy radical isomerizations) are urgently needed as a function of temperature and pressure.

Based on the kinetic data available for a number of alkyl peroxy radicals with NO, the overall reaction rate constant appears to be independent of the alkyl group and of pressure, with rate constants of

$$k(\mathrm{CH_3\dot{O}_2} + \mathrm{NO}) = 2.9 \times 10^{-12} e^{285/T}\ \mathrm{cm^3\ molecule^{-1} s^{-1}}$$

and

$$k(\mathrm{R\dot{O}_2} + \mathrm{NO}) = 2.7 \times 10^{-12} e^{360/T}\ \mathrm{cm^3\ molecule^{-1} s^{-1}}$$

being recommended by Atkinson (1997a) for $CH_3\dot{O}_2$ and $\geqslant C_2$ $R\dot{O}_2$ radicals, respectively.

The reactions of $R\dot{O}_2$ radicals with the HO_2 radical form hydroperoxides (Atkinson, 1997a; Atkinson et al., 1997a,1999),

$$\mathrm{R\dot{O}_2} + \mathrm{HO_2} \rightarrow \mathrm{ROOH} + \mathrm{O_2} \tag{18}$$

with the hydroperoxides undergoing wet and dry deposition, photolysis, and reaction with the OH radical (Atkinson et al., 1997a,1999; Wesely and Hicks, 2000). While product studies at room temperature have reported the formation of hydroperoxides in unit yield within the experimental uncertainties, there is still a possibility that a second minor reaction pathway leading to carbonyl formation exists (Jenkin et al., 1988), as observed for the reaction of the $CH_3OCH_2\dot{O}_2$ radical with HO_2 (Wallington et al., 1993).

$$\mathrm{CH_3OCH_2\dot{O}_2} + \mathrm{HO_2} \rightarrow \mathrm{CH_3OCHO} + \mathrm{H_2O} + \mathrm{O_2} \tag{31}$$

Based on the literature rate constants for the reactions of five alkyl peroxy radicals with the HO_2 radical, Atkinson (1997a) recommended that for the $\geqslant C_3$ alkyl peroxy radicals,

$$k(R\dot{O}_2 + HO_2) = 1.9 \times 10^{-13}\, e^{1300/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

with an uncertainty at 298 K of a factor of 2 [individual recommendations were made for the rate constants of the corresponding reactions of the $CH_3\dot{O}_2$ and $C_2H_5\dot{O}_2$ radicals (Atkinson, 1997a; Atkinson et al., 1999)].

The combination reactions of $R\dot{O}_2$ radicals proceed by two pathways, one forming the corresponding alkoxy radical(s) and the other forming an alcohol plus a carbonyl. For example, for the self-reaction of the 2-propyl peroxy radical.

$$2(CH_3)_2CHO\dot{O} \rightarrow 2(CH_3)_2CH\dot{O} + O_2 \qquad (27a)$$

$$2(CH_3)_2CHO\dot{O} \rightarrow CH_3C(O)CH_3 + CH_3CH(OH)CH_3 + O_2 \qquad (27b)$$

The reactions of $CH_3\dot{O}_2$ and $C_2H_5\dot{O}_2$ radicals with the NO_3 radical have been studied (Helleis et al., 1996; Ray et al., 1996; Atkinson et al., 1999 and references therein), with the reactions proceeding by

$$R\dot{O}_2 + NO_3 \rightarrow R\dot{O} + NO_2 + O_2 \qquad (28)$$

Rate constants at 298 K for the reactions of the $CH_3\dot{O}_2$ and $C_2H_5\dot{O}_2$ radicals with the NO_3 radical are in the range $(1\text{–}3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Helleis et al., 1996; Ray et al., 1996; Atkinson et al., 1999).

The dominant tropospheric reactions of alkyl peroxy radicals are with NO, NO_2 (to form thermally unstable alkyl peroxynitrates), and HO_2 radicals, with reaction with the NO_3 radical potentially being important during nighttime. Alkoxy radicals are therefore formed directly from the reactions of $R\dot{O}_2$ radicals with NO and the NO_3 radical and indirectly (and with generally significantly less than unit yield) through hydroperoxide formation via the HO_2 radical reaction. [Photolysis of hydroperoxides, ROOH, is expected to produce the $R\dot{O}$ radical plus the OH radical, as occurs for CH_3OOH.]

The tropospheric reactions of alkoxy radicals (reaction with O_2, unimolecular decomposition and isomerization by a 1,5-H shift through a 6-membered transition state) have been discussed in Section 3 above and by Atkinson (1997a,b). Absolute rate constants are available for the reactions of the methoxy, ethoxy and 1- and 2-propoxy radicals with O_2 (Atkinson, 1997a,b; Mund et al., 1998; Atkinson et al., 1999). Based on the measured rate constants for the reactions of O_2 with methoxy, ethoxy and 2-propoxy radicals, Atkinson (1997a,b) suggested that the rate constants for the reaction of alkoxy radicals with O_2, k_{O_2}, at 298 K are given by

$$k_{O_2} = 4.0 \times 10^{-19}\, n\, e^{-(0.28\Delta H_{O_2})}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}},$$

where n is the number of abstractable H atoms and ΔH_{O_2} is the enthalpy of the alkoxy radical reaction with O_2 (in kcal mol^{-1}). This suggested dependence of k_{O_2} on ΔH_{O_2} needs to be confirmed. For the alkoxy radicals formed from alkanes, the values of ΔH_{O_2} for $RCH_2\dot{O}$ radicals are generally similar to that for the ethoxy radical and the values of ΔH_{O_2} for $R\acute{R}CH\dot{O}$ radicals are generally similar to that for the 2-propoxy radical, and the rate constants k_{O_2} are then calculated to be in the range $(8\text{–}10) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 1997a,b) [and similar to those measured for the ethoxy and 1- and 2-propoxy radical reactions].

For the decomposition reactions of alkoxy radicals, Atkinson (1997b) reviewed the literature data and used the approach of Choo and Benson (1981) to derive a method to calculate the decomposition rate constants. Specifically, using the Arrhenius expression $k_d = A_d e^{-E_d/RT}$, where E_d is the Arrhenius activation energy for the decomposition in kcal mol^{-1}, Atkinson (1997a,b) proposed that

$$A_d = 2 \times 10^{14}\, d\ \mathrm{s^{-1}}$$

where d is the reaction path degeneracy, and

$$E_d = a + b\Delta H_d$$

with $b = 0.36$ and $a = \{2.4(\mathrm{IP}) - 8.1\}$, where IP is the ionization potential (in eV) of the leaving radical and ΔH_d is the enthalpy of the decomposition reaction in kcal mol^{-1}. Values of a for common leaving radicals (in kcal mol^{-1}) are then (Atkinson, 1997a,b): $\dot{C}H_3$, 15.5; $R\dot{C}H_2$, 11.1 (including ethyl, 11.4, and 1-propyl, 11.3); $R\acute{R}\dot{C}H$, 9.3 (including 2-propyl, 9.6); $R\acute{R}R\dot{C}$, 7.9 (including *tert*-butyl, 8.0); and $RCH = \dot{C}H$, 11.7 (including $CH_2{=}\dot{C}H$, 11.7). This empirical approach fits the decomposition rate constant data for the alkoxy radicals formed from alkane photooxidations (see Atkinson (1997b) for a detailed discussion).

For the case of alkoxy radical isomerizations, to date there is no evidence for isomerization via a 5-membered transition state (Eberhard et al., 1995), and hence only isomerization reactions involving a 6-membered transition state are considered. Direct evidence for the occurrence of alkoxy radical isomerization arises from the study of Eberhard et al. (1995), involving the identification and quantification of the 2,4-dinitrophenylhydrazine derivatives of 2-hydroxy-5-hexanone and 1-hydroxy-4-hexanone formed after isomerization of the 2- and 3-hexoxy radicals, respectively, and from the in situ atmospheric pressure ionization mass spectrometry (API-MS) studies of the OH radical-initiated reactions of *n*-butane through *n*-octane and *n*-pentane-d_{12} through *n*-octane-d_{18} of Atkinson et al. (1995a) and Kwok et al. (1996a). Estimates of the rate constant ratios $(k_{\mathrm{isom}} + k_{\mathrm{decomp}})/k_{O_2}$ are available at room temperature for the 1- and 2-butoxy, 2- and 3-pentoxy, and 2- and 3-hexoxy radicals (Atkinson et al., 1995a; Atkinson, 1997b), showing that this rate constant ratio is an order of magnitude or more higher for the 1-butoxy, 2-pentoxy, and 2- and 3-hexoxy radicals than for the 2-butoxy and 3-pentoxy radicals. This observation is consistent with the dominance of isomerization over decomposition for the 1-butoxy, 2-pentoxy, and 2- and 3-hexoxy radicals at 298 K and atmospheric pressure.

The rate constant ratios for the 1-butoxy, 2-pentoxy, and 2- and 3-hexoxy radicals [with $(k_{\text{isom}} + k_{\text{decomp}})/k_{O_2} \sim k_{\text{isom}}/k_{O_2}$], together with values of $k_{\text{isom}}/k_{\text{decomp}}$ obtained by Atkinson and Aschmann (1995) for the $RCH_2C(CH_3)(OH)CH_2C(\dot{O})(CH_3)_2$ radicals (R = H and CH_3), allow rate constants at 298 K for the isomerization of alkoxy radicals proceeding by H-atom abstraction from $-CH_3$ and $-CH_2-$ groups of $2 \times 10^5\ s^{-1}$ and $2 \times 10^6\ s^{-1}$ to be derived (Atkinson, 1997b). Atkinson (1997a,b) has used these rate constants to propose a method of estimating rate constants for alkoxy radical isomerization as a function of temperature. This estimation method then allows rate constants for the isomerization of the δ-hydroxyalkoxy radicals, $RCH(OH)–C–C–C(\dot{O})\acute{R}$, encountered in alkane photooxidations (see Scheme 4) to be calculated, and these second isomerizations (Schemes 3 and 4), if feasible, are calculated to be faster than the first isomerization shown in Scheme 3 and to dominate over reaction with O_2 (and also generally over decomposition).

The estimation methods proposed by Atkinson (1997a,b) allow the rates of the decomposition, isomerization and reaction with O_2 of alkoxy radicals involved in alkane photooxidations to be estimated (including at temperatures other than 298 K). However, there are no experimental absolute or relative rate data available for most alkoxy radicals, and especially for hydroxyalkoxy radicals of structure $RCH(OH)–C–C–C(\dot{O})\acute{R}$. Absolute rate constants for all three reactions of alkoxy and hydroxyalkoxy radicals are required to revise or confirm the present semi-quantitative knowledge of these reactions.

4.2. Aerosol formation from alkanes

The amounts of aerosol formed in the photooxidations of methylcyclohexane and *n*-octane were studied by Wang et al. (1992), and the average aerosol yields by mass were 9% for methylcyclohexane and < 0.001% for *n*-octane. The greater propensity for cycloalkanes to produce secondary organic aerosol than straight chain alkanes may well be linked to their formation of multifunctional products such as hydroxydicarbonyls, as observed by Aschmann et al. (1997b) from the OH radical-initiated reaction of cyclohexane in the presence of NO.

4.3. Haloalkanes

Apart from the HCFCs and HFCs, potential replacements for the CFCs and whose chemistry is reviewed and evaluated by the NASA (DeMore et al., 1997) and IUPAC (Atkinson et al., 1997a) panels, haloalkanes such as bromopropanes and analogous halogenated compounds are being considered for use as solvents. The dominant tropospheric reactions of these haloalkanes are with the OH radical, and the subsequent reactions are analogous to those discussed above for the alkanes and shown schematically in Scheme 1, except that the alkoxy radicals formed contain a halogen atom(s). In addition to reaction with O_2, decomposition by C–C bond scission and isomerization through a six-membered transition state, these halogenated alkoxy radicals can also decompose by elimination of a Cl or Br atom (World Meteorological Organization, 1995); for example for the $CH_3CH_2CH(\dot{O})Br$ radical formed after H-atom abstraction from the 1-position of 1-bromopropane.

$$CH_3CH_2CH(\dot{O})Br \rightarrow CH_3CH_2CHO + Br \tag{32}$$

$$CH_3CH_2CH(\dot{O})Br + O_2 \rightarrow CH_3CH_2C(O)Br + HO_2 \tag{33}$$

Clearly, product studies need to be carried out for these haloalkanes to determine the product distribution formed and the detailed reaction mechanisms.

5. Tropospheric chemistry of alkenes and haloalkenes

5.1. Alkenes

As noted in Section 1, alkenes are emitted into the troposphere from anthropogenic sources (mainly combustion sources such as vehicle exhaust), and isoprene (2-methyl-1,3-butadiene), $C_{10}H_{16}$ monoterpenes, and $C_{15}H_{24}$ sesquiterpenes are emitted from vegetation. In the troposphere, alkenes react with OH radicals, NO_3 radicals, and O_3, and all three of these reactions must be considered in assessing the transformation processes of a specific alkene (National Research Council, 1991; Atkinson, 1995), as evident from Table 1. These reactions proceed wholly (NO_3 radical and O_3 reactions) or mainly (OH radical reaction) by initial addition to the >C=C< bond(s) (Atkinson, 1989,1994,1997a). The recent review and evaluation of Atkinson (1997a) should be consulted for additional details, and the following discussion is taken largely from that article.

5.2. Reaction with the OH radical

The major initial reaction pathway involves OH radical addition to either carbon atom of the >C=C< bond to form β-hydroxyalkyl radicals, as shown, for example, for 1-butene.

$$OH + CH_3CH_2CH{=}CH_2 \xrightarrow{M} CH_3CH_2\dot{C}HCH_2OH \text{ or } CH_3CH_2CH(OH)\dot{C}H_2 \tag{34}$$

In addition to the major OH radical addition pathway, H-atom abstraction from the C–H bonds of the alkyl substituent groups around the $>C{=}C<$ bond(s) also occurs as a minor process (Atkinson, 1989,1994,1997a). As for the alkyl radicals discussed above in Section 4, in the troposphere the β-hydroxyalkyl radicals react rapidly and solely with O_2 to form β-hydroxyalkyl peroxy radicals.

$$CH_3CH_2CH(OH)\dot{C}H_2 + O_2 \overset{M}{\rightarrow} CH_3CH_2CH(OH)CH_2O\dot{O} \qquad (35)$$

For conjugated dienes [for example, 1,3-butadiene and 2-methyl-1,3-butadiene (isoprene)], the β-hydroxyalkyl radical formed after OH radical addition at the 1- or 4-positions of the C=C–C=C unit can isomerize to an allylic δ-hydroxyalkyl radical.

$$HOCH_2\dot{C}(CH_3)CH{=}CH_2 \leftrightarrow HOCH_2C(CH_3){=}CH\dot{C}H_2 \qquad (36)$$

Totally analogous to the reactions of alkyl peroxy radicals (see Sections 3 and 4 and Scheme 1), β- and δ-hydroxyalkyl peroxy radicals react with NO, NO_2 (to form thermally labile hydroxyalkyl peroxynitrates), HO_2 radicals and organic peroxy radicals (and presumably also with the NO_3 radical). The reaction with NO forms either the hydroxyalkoxy radical plus NO_2 or the hydroxyalkyl nitrate,

$$CH_3CH_2CH(OH)CH_2O\dot{O} + NO \overset{M}{\rightarrow} CH_3CH_2CH(OH)CH_2ONO_2 \qquad (14a)$$

$$CH_3CH_2CH(OH)CH_2O\dot{O} + NO \rightarrow CH_3CH_2CH(OH)CH_2\dot{O} + NO_2 \qquad (14b)$$

with measured β-hydroxyalkyl nitrate yields at room temperature and atmospheric pressure of air of ~ 1.5–1.7% for the $CH_3CH(O\dot{O})CH_2OH$ and $CH_3CH(OH)CH_2O\dot{O}$ radicals formed from propene (Shepson et al., 1985) and $3.7 \pm 0.9\%$ for the $CH_3CH(OH)CH(O\dot{O})CH_3$ radical formed from *cis*-2-butene (Muthuramu et al., 1993). The measured rate constants for the reactions of the hydroxyalkyl peroxy radicals $HOCH_2CH_2\dot{O}_2$ and $(CH_3)_2C(OH)CH_2\dot{O}_2$ with NO (see Atkinson, 1997a) are within a factor of 2 of the recommendation for the corresponding alkyl peroxy radical reactions (Atkinson, 1997a) and suggest that the same recommended rate constant applies for all hydroxyalkyl peroxy radicals.

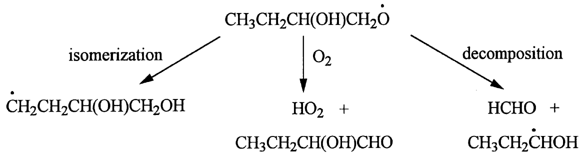
The HO_2 radical reactions with β-hydroxyalkoxy radicals appear to form hydroxyalkyl hydroperoxides, as shown for the $HOCH_2CH_2\dot{O}_2$ radical (Barnes et al., 1993; Hatakeyama et al., 1995),

$$HOCH_2CH_2O\dot{O} + HO_2 \rightarrow HOCH_2CH_2OOH + O_2 \qquad (37)$$

and API-MS analyses provide evidence for the analogous reactions of the β-hydroxyalkyl peroxy radicals formed after OH radical addition to a series of methyl-substituted ethenes in the absence of NO (Tuazon et al., 1998a). Rate constants have been measured for the reactions of four β-hydroxyalkyl peroxy radicals with the HO_2 radical (Atkinson, 1997a), and these rate constants are similar to the recommended rate constant for the corresponding $\geqslant C_3$ alkyl peroxy radical reactions (Atkinson, 1997a; see Section 4 above).

Analogous to the alkoxy radicals formed from the alkanes, the β-hydroxyalkoxy radicals react with O_2, unimolecularly decompose, or isomerise via a 1,5-H shift through a six-member transition state (Atkinson, 1997a,b). Scheme 5 shows the possible reactions of the $CH_3CH_2CH(OH)CH_2\dot{O}$ radical formed after OH radical addition to the internal carbon atom of the $>C{=}C<$ bond in 1-butene.

At room temperature and atmospheric pressure of air, the $HOCH_2CH_2\dot{O}$ radical formed after OH radical addition to ethene reacts with O_2 and thermally decomposes (Niki et al., 1981; Barnes et al., 1993; Orlando et al., 1998), while the β-hydroxyalkoxy radicals formed after OH radical addition to propene, 1-butene, 2-methylpropene, *cis*- and *trans*-2-butene, 2-methyl-2-butene and 2,3-dimethyl-2-butene primarily decompose (Niki et al., 1978,1987; Atkinson et al., 1985; Tuazon et al., 1998a). However, API-MS analyses have shown that the β-hydroxyalkoxy radicals formed after OH radical addition to 1-pentene, 1-hexene, 1-heptene and 1-octene also isomerize in competition with decomposition (Kwok et al., 1996b), and isomerization of the β-hydroxyalkoxy radicals formed after OH radical addition to several of the monoterpenes also occurs (Aschmann et al., 1998). The empirical estimation method proposed by Atkinson (1997a,b) to calculate the rates of decomposition, isomerization and reaction with O_2 of alkoxy radicals is also applicable to the β-hydroxyalkoxy radicals formed after OH radical addition to alkenes (Atkinson, 1997a,b) and there is semi-quantitative agreement between the literature data concerning the dominant reaction pathways



Scheme 5.

and the estimation method predictions (Atkinson, 1997a,b).

α-Hydroxyalkyl radicals such as $\dot{C}H_2OH$ and $CH_3\dot{C}HOH$ react rapidly with O_2 to form the corresponding carbonyl plus the HO_2 radical (Atkinson, 1997a), as shown, for example, for the $CH_3CH_2\dot{C}HOH$ radical formed in the decomposition pathway in Scheme 5.

$$CH_3CH_2\dot{C}HOH + O_2 \rightarrow CH_3CH_2CHO + HO_2. \quad (38)$$

The β-hydroxyalkoxy radicals formed after OH radical addition to isoprene are $HOCH_2C(CH_3)(\dot{O})CH{=}CH_2$, $\dot{O}CH_2C(CH_3)(OH)CH{=}CH_2$, $CH_2{=}C(CH_3)CH(\dot{O})CH_2OH$ and $CH_2{=}C(CH_3)CH(OH)CH_2\dot{O}$, and the dominant reaction of these hydroxyalkoxy radicals at room temperature and atmospheric pressure of air is decomposition to form HCHO plus methyl vinyl ketone $[CH_3C(O)CH{=}CH_2]$ or HCHO plus methacrolein $[CH_2{=}C(CH_3)CHO]$, depending on which $>C{=}C<$ bond the OH radical adds to (Atkinson, 1997a).

$$\begin{array}{l} HOCH_2C(CH_3)(\dot{O})CH{=}CH_2 \\ \quad \rightarrow \dot{C}H_2OH + CH_3C(O)CH{=}CH_2 \\ \qquad \downarrow O_2 \\ \quad HCHO + HO_2 \end{array} \quad (39)$$

The two other hydroxyalkoxy radicals formed after OH radical addition to isoprene are the $HOCH_2C(CH_3){=}CHCH_2\dot{O}$ and $\dot{O}CH_2C(CH_3){=}CHCH_2OH$ radicals, which are predicted to isomerize at room temperature and atmospheric pressure of air (Atkinson, 1997a).

$$\begin{array}{l} HOCH_2C(CH_3){=}CHCH_2\dot{O} \\ \quad \rightarrow HO\dot{C}HC(CH_3){=}CHCH_2OH \\ \qquad\qquad \downarrow O_2 \\ \quad HC(O)C(CH_3){=}CHCH_2OH + HO_2 \end{array} \quad (40)$$

It may be noted that, although the reaction of these δ-hydroxyalkoxy radicals with O_2 is not expected to compete with isomerization (Atkinson, 1997a), the O_2 reactions of the two radicals $HOCH_2C(CH_3){=}CHCH_2\dot{O}$ and $\dot{O}CH_2C(CH_3){=}CHCH_2OH$ lead to the same products as formed from their isomerizations. For example, for the $\dot{O}CH_2C(CH_3){=}CHCH_2OH$ radical,

$$\begin{array}{l} \dot{O}CH_2C(CH_3){=}CHCH_2OH + O_2 \\ \quad \rightarrow HC(O)C(CH_3){=}CHCH_2OH + HO_2 \end{array} \quad (41)$$

which is the same product as formed from isomerization of the $HOCH_2C(CH_3){=}CHCH_2\dot{O}$ radical [reaction (40)].

5.3. Reaction with the NO_3 radical

The reactions of the NO_3 radical with alkenes proceed essentially entirely by initial addition of the NO_3 radical to form a β-nitrooxyalkyl radical (Atkinson, 1991,1994,1997a).

$$\begin{array}{l} NO_3 + CH_3CH{=}CH_2 \overset{M}{\rightarrow} CH_3\dot{C}HCH_2ONO_2 \\ \qquad \text{or } CH_3CH(ONO_2)\dot{C}H_2 \end{array} \quad (42)$$

The subsequent reactions of the nitrooxyalkyl radicals are analogous to those of the hydroxyalkyl radicals formed from the corresponding OH radical reactions (Atkinson, 1991,1994,1997a). Analogous to the OH radical reactions, conjugated dienes such as 1,3-butadiene and isoprene will also lead to δ-nitrooxyalkyl radicals. If NO_3 radicals are present in the troposphere, then NO will be at low concentrations due to the rapid reaction of NO with the NO_3 radical (and of NO with O_3). Nitrooxyalkyl peroxy radicals are therefore expected to react primarily with NO_2, to form thermally unstable peroxy nitrates such as $CH_3CH(OONO_2)CH_2ONO_2$, NO_3 radicals, HO_2 radicals and organic peroxy radicals, with self-reactions of nitrooxyalkyl peroxy radicals or combination reactions with other peroxy radicals being important in laboratory studies. Taking isoprene as an example and based on the in situ FT–IR spectroscopy study of Skov et al. (1992) and the gas chromatography and in situ API–MS study of Kwok et al. (1996c), the dominant nitrooxyalkyl peroxy radical formed is the $O_2NOCH_2C(CH_3){=}CHCH_2\dot{O}_2$ radical (Skov et al., 1992) and its reactions appear to be,

$$\begin{array}{l} O_2NOCH_2C(CH_3){=}CHCH_2\dot{O}_2 + NO_2 \\ \quad \rightleftarrows O_2NOCH_2C(CH_3){=}CHCH_2OONO_2 \end{array} \quad (43)$$

$$\begin{array}{l} O_2NOCH_2C(CH_3){=}CHCH_2\dot{O}_2 + HO_2 \\ \quad \rightarrow O_2NOCH_2C(CH_3){=}CHCH_2OOH + O_2 \end{array} \quad (44)$$

$$\begin{array}{l} O_2NOCH_2C(CH_3){=}CHCH_2\dot{O}_2 + R\dot{O}_2 \\ \quad \rightarrow \alpha O_2NOCH_2C(CH_3){=}CHCH_2OH \\ \qquad + (1-\alpha)O_2NOCH_2C(CH_3){=}CHCHO \\ \qquad + R\dot{O}_2 \text{ products} + O_2 \end{array} \quad (45)$$

$$\begin{array}{l} O_2NOCH_2C(CH_3){=}CHCH_2\dot{O}_2 + R\dot{O}_2 \\ \quad \rightarrow O_2NOCH_2C(CH_3){=}CHCH_2\dot{O} \\ \qquad + R\dot{O} + O_2 \end{array} \quad (46)$$

followed by reactions of the nitrooxyalkoxy radical $O_2NOCH_2C(CH_3){=}CHCH_2\dot{O}$, presumably by reaction with O_2 and/or isomerization.

$$O_2NOCH_2C(CH_3){=}CHCH_2\dot{O} + O_2 \rightarrow O_2NOCH_2C(CH_3){=}CHCHO + HO_2 \quad (47)$$

$$O_2NOCH_2C(CH_3){=}CHCH_2\dot{O} \rightarrow O_2NO\dot{C}HC(CH_3){=}CHCH_2OH \downarrow HC(O)C(CH_3){=}CHCH_2OH + NO_2 \quad (48)$$

However, to date there are no a priori methods available to quantitatively predict the relative or absolute importance of the various reaction channels and products formed in these reactions, and the empirical estimation method of Atkinson (1997b) for alkoxy radical reactions has not been applied to nitrooxyalkoxy radicals.

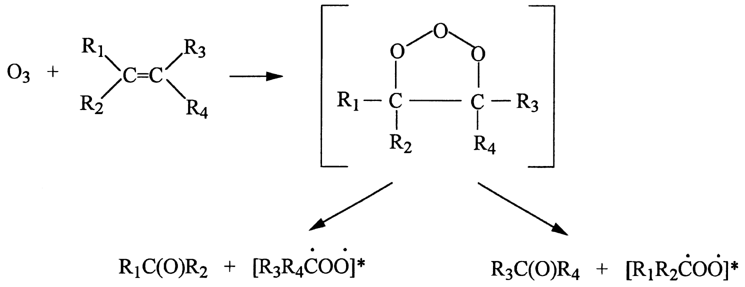
5.4. Reaction with O_3

O_3 initially adds to the $>C{=}C<$ bond to form an energy-rich primary ozonide, which rapidly decomposes, as shown in Scheme 6, to form two sets of carbonyl plus biradical, where $[\,]^{\ddagger}$ denotes an energy-rich species (Atkinson, 1997a).

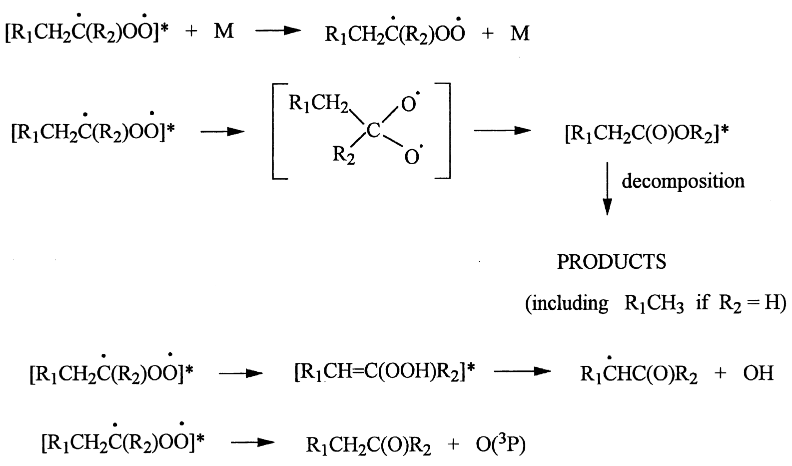
Recent studies have shown that the relative importance of the two decomposition pathways of the primary ozone to form the two sets of carbonyl plus biradical products depends on the structure of the alkene and hence on the structures of the carbonyl and, especially, the biradical(s) formed (Atkinson, 1997a). It appears that the two decomposition pathways of the primary ozonide are of approximately equal importance for alkenes of structure $RCH{=}CH_2$, $R_1CH{=}CHR_2$, and $R_1R_2C{=}CR_3R_4$, but that for alkenes of structure $R_1R_2C{=}CH_2$ and $R_1R_2C{=}CHR_3$ the primary ozonide decomposes preferentially to form the dialkyl-substituted biradical $[R_1R_2\dot{C}O\dot{O}]^{\ddagger}$ plus HCHO or R_3CHO.

The fate of the initially energy-rich biradicals is presently not well understood. The biradicals can be collisionally stabilized or decompose by a number of pathways, as shown in Scheme 7.

For the *trans*-2-butene reaction the stabilization pathway is pressure dependent, with a stabilization yield extrapolated to zero pressure of zero (Hatakeyama et al., 1984). However, for the reaction of O_3 with ethene, both



Scheme 6.



Scheme 7.

Niki et al. (1983) and Hatakeyama et al. (1986) observed that a significant fraction of the $[\dot{C}H_2O\dot{O}]^*$ biradicals was thermalized even at low pressure [0.235 at 10 Torr (Hatakeyama et al., 1986)].

The isomerization/decomposition reactions of the "energy-rich" biradicals include the reaction channels postulated by Martinez et al. (1981) and Niki et al. (1987), involving "O-atom elimination", the "ester channel" and the "hydroperoxide" channel, as shown in Scheme 7. $O(^3P)$ atom elimination has not been observed for alkenes at room temperature and atmospheric pressure of air (Atkinson, 1997a,and references therein) and the evidence for the occurrence of the "ester" channel involves the elimination of CO_2 and the formation of an RH product from biradicals of the structure $[R\dot{C}HO\dot{O}]^*$, including the formation of methane from the reaction of O_3 with *cis*- and *trans*-2-butene through the intermediary of the $[CH_3\dot{C}HO\dot{O}]^*$ biradical

$$[CH_3\dot{C}HO\dot{O}]^* \rightarrow CH_4 + CO_2 \tag{49}$$

and the formation of butanal from the reaction of O_3 with cyclopentene through the intermediary of the $[HC(O)CH_2CH_2CH_2\dot{C}HO\dot{O}]^*$ biradical (Atkinson, 1997a and references therein).

$$[HC(O)CH_2CH_2CH_2\dot{C}HO\dot{O}]^* \rightarrow CH_3CH_2CH_2CHO + CO_2 \tag{50}$$

However, OH radicals are formed from the reactions of O_3 with alkenes (Paulson et al., 1997; Donahue et al., 1998), often in unit or close to unit yield (Atkinson, 1997a). For acyclic alkenes and cycloalkenes not containing terminal $=CH_2$ groups, OH radical formation generally increases with the number of alkyl substituent groups or, equivalently, with the number of alkyl substituents on the biradicals. This formation of OH radicals from the reactions of O_3 with alkenes leads to secondary reactions of the OH radical with the alkene and, unless the OH radicals are scavenged, the nominal "O_3 reaction" involves OH radical reactions and hence the products observed and their yields may not be those for the O_3 reactions (see, for example, Hakola et al., 1994). The formation of OH radicals is postulated to occur via the "hydroperoxide" channel; for example, for the $[(CH_3)_2\dot{C}O\dot{O}]^*$ biradical formed from the reaction of O_3 with 2,3-dimethyl-2-butene (Niki et al., 1987; Gutbrod et al., 1996).

$$[(CH_3)_2\dot{C}O\dot{O}]^* \rightarrow [CH_3C(OOH){=}CH_2]^* \rightarrow OH + CH_3C(O)\dot{C}H_2 \tag{51}$$

For the $[\dot{C}H_2O\dot{O}]^*$ biradical, the OH radical is calculated to arise from decomposition of the biradical (Donahue et al., 1998)

$$[\dot{C}H_2O\dot{O}]^* \rightarrow OH + H\dot{C}O \tag{52}$$

While it has been assumed for several years that the radicals formed and measured from the O_3 reactions with alkenes (and other VOCs containing $>C{=}C<$ bonds) are indeed OH radicals (Niki et al., 1987; Paulson et al., 1992; Atkinson et al., 1992), only recently has direct evidence been reported from the laser-induced fluorescence observation of OH radicals in reacting O_3–alkene–N_2 mixtures (Donahue et al., 1998) [although at low total pressures]. The direct spectroscopic observation of OH radicals by Donahue et al. (1998) and the relative rate kinetic studies of Paulson et al. (1997) and Marston et al. (1998) indicate that the conclusion of Schäfer et al. (1997), that the radicals formed are not OH radicals (or not solely OH radicals), is incorrect.

Assuming that the OH radicals formed in these reactions arise via the hydroperoxide channel, then the organic co-product radicals [for example, the $CH_3C(O)\dot{C}H_2$ radical formed together with the OH radical from the $[(CH_3)_2\dot{C}O\dot{O}]^*$ biradical in reaction (51)] will react as described in Section 3 and Scheme 1, leading to a variety of carbonyl, hydroxycarbonyl and hydroperoxycarbonyl products (Niki et al., 1987; Atkinson, 1997a). To date, these reactions have not been quantitatively elucidated for any biradical.

Other biradical decomposition channels occur, including the formation of ketene $[CH_2CO]$ from biradicals of the structure $[CH_3\dot{C}HO\dot{O}]^*$ (Tuazon et al., 1997).

$$[CH_3\dot{C}HO\dot{O}]^* \rightarrow CH_2CO + H_2O \tag{53}$$

While there have been significant (and largely qualitative or semi-quantitative) advances in our knowledge of the isomerization/decomposition reactions of the energy-rich biradicals over the past few years (in fact, since 1992), there is still a need to quantitatively elucidate these reactions.

The other important aspect of O_3-alkene reactions concerns the subsequent reactions of the thermalized biradicals in the troposphere (as well as under conditions relevant to "smog" chamber experiments). The thermalized biradicals are known to react with aldehydes, SO_2, CO, H_2O and NO_2 (see, for example, Atkinson, 1997a; Atkinson et al., 1997a,1999), and it is expected that they will also react with NO. Based upon the available data for the reactions of the $\dot{C}H_2O\dot{O}$ biradical with these reactants, with rate constants relative to the reaction of the $\dot{C}H_2O\dot{O}$ biradical with SO_2 of: HCHO, ~ 0.25 (Su et al., 1980); CO, 0.0175 (Su et al., 1980); H_2O, $(2.3 \pm 1) \times 10^{-4}$ (Suto et al., 1985) and $(8.3 \pm 3.6) \times 10^{-4}$ (Becker et al., 1993); and NO_2, 0.014 (Manzanares et al., 1985), it appears that the reaction of the thermalized $\dot{C}H_2O\dot{O}$ biradical with water vapor will be its dominant loss process under tropospheric conditions. The rate constant ratio for the reactions of the $(CH_3)_2\dot{C}O\dot{O}$ biradical with water vapor and SO_2 of $(4.1 \pm 2.2) \times 10^{-4}$ measured by Becker et al. (1993) is similar to the values for the

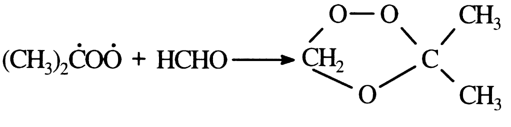
$\dot{C}H_2O\dot{O}$ biradical (Suto et al., 1985; Becker et al., 1993), suggesting that the various biradicals react similarly.

The reaction of the $\dot{C}H_2O\dot{O}$ biradical with water vapor proceeds by initial formation of hydroxymethyl hydroperoxide [$HOCH_2OOH$], which can decompose (probably heterogeneously) to either $HC(O)OH + H_2O$ or, less likely, to $HCHO + H_2O_2$ (Neeb et al., 1997).

$$\begin{tikzcd} \dot{C}H_2O\dot{O} + H_2O \arrow[r] & HOCH_2OOH \arrow[r] \arrow[d] & HC(O)OH + H_2O \\ & HCHO + H_2O_2 & \end{tikzcd} \qquad (54)$$

The reactions of biradicals of structure $R\dot{C}HO\dot{O}$ and $R\acute{R}\dot{C}O\dot{O}$ with water vapor have not been directly studied to date; such studies are clearly needed to identify and quantify the products of these biradical reactions with water vapor. Gäb et al. (1985), Becker et al. (1990,1993), Simonaitis et al. (1991), Hewitt and Kok (1991), Hatakeyama et al. (1993) and Horie et al. (1994) have reported the formation of H_2O_2 and organic hydroperoxides from the reactions of O_3 with alkenes, and the formation of H_2O_2 has been attributed to the reactions of biradicals with water vapor. There are significant quantitative discrepancies between these studies, and these may be related to the analytical methods used (Atkinson, 1997a). The IR spectroscopic data of Becker et al. (1990,1993) and Horie et al. (1994) show that for the alkenes studied the molar formation yields of H_2O_2 in the presence of $(3\text{–}5) \times 10^{17}$ molecule cm^{-3} of water vapor are in the range 0.001–0.018.

In laboratory systems, other reaction pathways of the thermalized biradicals can be important and may need to be considered in certain "smog" chamber experiments (especially any carried out at low water vapor concentrations and/or at high reactant concentrations). The reaction of the $\dot{C}H_2O\dot{O}$ biradical with acetaldehyde and the reactions of the more complex biradicals such as $CH_3\dot{C}HO\dot{O}$ and $(CH_3)_2\dot{C}O\dot{O}$ with formaldehyde and other aldehydes lead to the formation of secondary ozonides (Niki et al., 1977,1987; Neeb et al., 1996a; Horie et al., 1997).



(55)

However, the formation of ethene ozonide is not observed during the reaction of O_3 with ethene. Neeb et al. (1995) have shown that earlier proposals that the reaction of the $\dot{C}H_2O\dot{O}$ biradical with HCHO forms $HOCH_2OCHO$ were incorrect. Neeb et al. (1995) postulated that the $\dot{C}H_2O\dot{O}$ biradical reacts with formic acid, HC(O)OH, to form hydroperoxymethyl formate,

$$\dot{C}H_2O\dot{O} + HC(O)OH \rightarrow HOOCH_2OCHO \qquad (56)$$

which decomposes to formic acid anhydride, HC(O)OCHO, plus H_2O, and that $HOOCH_2OCHO$ was previously incorrectly identified as $HOCH_2OCHO$. The formation of hydroperoxymethyl formate from the reaction of the $\dot{C}H_2O\dot{O}$ biradical with HC(O)OH has been confirmed by Thamm et al. (1996). Neeb et al. (1996b) have shown that the $\dot{C}H_2O\dot{O}$ biradical also reacts with acetic acid and methanol (ROH, with $R{=}CH_3CO$ and CH_3, respectively) to form $ROCH_2OOH$,

$$\dot{C}H_2O\dot{O} + ROH \rightarrow ROCH_2OOH \qquad (57)$$

analogous to reaction (56) with HC(O)OH (for which R=HCO). The reaction of the $\dot{C}H_2O\dot{O}$ biradical with SO_2 has been discussed by Hatakeyama and Akimoto (1992,1994) [see also Atkinson, 1997a], and under tropospheric conditions the reaction leads to the formation of sulfuric acid and HCHO (Hatakeyama and Akimoto, 1994).

5.5. *Aerosol formation from alkenes*

A number of studies have been carried out to investigate the amount of aerosol formed in the photooxidations of alkenes and to identify and quantify the compounds responsible for this aerosol formation (Pandis et al., 1991; Palen et al., 1992,1993; Wang et al., 1992; Zhang et al., 1992; Odum et al., 1996; Hoffmann et al., 1997; Forstner et al., 1997a). These studies have involved the photooxidations (and in some cases reaction with O_3) of the anthropogenic alkenes 1-octene (Wang et al., 1992; Palen et al., 1993; Forstner et al., 1997a), 1-decene (Forstner et al., 1997a) and the biogenic alkenes isoprene, α- and β-pinene, 3-carene, limonene, ocimene and *trans*-caryophyllene (Pandis et al., 1991; Palen et al., 1992; Zhang et al., 1992; Odum et al., 1996; Hoffmann et al., 1997). While the aerosol yield [defined as (mass of aerosol formed/amount of alkene reacted)] depends on the organic aerosol mass (or surface area) present, consistent with Eq. (I) based on gas/particle partitioning, these studies allow the alkenes to be approximately ranked according to their ability to generate secondary organic aerosol. The aerosol yields measured in these studies ranged from negligible for isoprene (Pandis et al., 1991), a few percent for 1-octene, 1-decene, ocimene and α-pinene, to $\sim$ 30–40% for β-pinene and limonene, up to $\sim$ 100% for *trans*-caryophyllene (realizing that the yields depend on the initial conditions, the major reactive species (OH radicals, NO_3 radicals or O_3) and the aerosol mass or surface area in the chamber). Hoffmann et al. (1997) observed that for the biogenic monoterpenes and sesquiterpenes studied, the O_3 reactions were responsible for much of the aerosol formation.

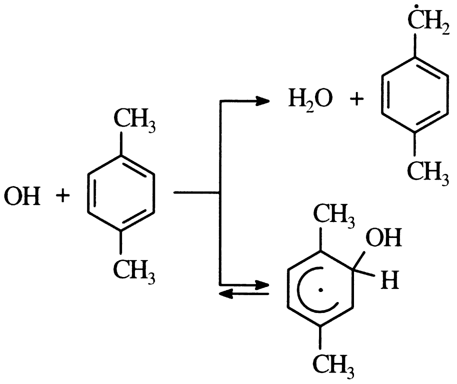
5.6. Haloalkenes

A number of haloalkenes are emitted into the atmosphere, including trichloroethene and tetrachloroethene. The major tropospheric loss process for the haloalkenes is by reaction with the OH radical [halogenation generally decreases the reactivity towards O_3 and the NO_3 radical compared to the reactivities of the alkene with the same degree and position of substituents around the $>C{=}C<$ bond (Atkinson and Carter, 1984; Atkinson, 1991,1994)]. The OH radical reactions proceed mainly by addition, analogous to the alkene reactions. The reaction mechanisms are expected to be analogous to those for the OH radical-initiated reactions of the alkenes, except that the intermediate halogenated hydroxyalkoxy radicals can decompose by Cl or Br atom elimination in addition to decomposition by C–C bond scission, reaction with O_2, and isomerization.

6. Tropospheric chemistry of aromatic compounds

6.1. Aromatic hydrocarbons

Benzene and the alkyl-substituted benzenes such as toluene, ethylbenzene, the xylenes, and the trimethylbenzenes react with OH radicals and NO_3 radicals (Atkinson, 1989,1991,1994,1995), with the OH radical reactions dominating as the tropospheric removal process (Atkinson, 1995) (Table 1). The OH radical reactions proceed by H-atom abstraction from the C–H bonds of the alkyl substituent groups (or from the C–H bonds of the aromatic ring in the case of benzene), and by OH radical addition to the aromatic ring to form a hydroxycyclohexadienyl or alkyl-substituted hydroxycyclohexadienyl radical (hereafter termed an OH-aromatic adduct) (Atkinson, 1989,1994). For example, for *p*-xylene:



(58a)

(58b)

The OH radical addition pathway is reversible at elevated temperatures due to thermal decomposition of the OH-aromatic adduct (Atkinson, 1989,1994), and the lifetimes of the OH-benzene and OH-toluene adducts due to thermal decomposition are each ~ 0.2–0.3 s at 298 K and ~ 0.025 s at 325 K (Knispel et al., 1990; Atkinson, 1989,1994).

The H-atom abstraction pathway accounts for $\leqslant 10\%$ of the overall OH radical reactions with benzene and the methyl-substituted benzenes at room temperature and atmospheric pressure (Atkinson, 1994). The tropospheric reactions of the benzyl and alkyl-substituted benzyl radicals formed from the pathway involving H-atom abstraction from the alkyl-substituent groups are analogous to those for alkyl radicals discussed in Sections 3 and 4 above [and can be considered phenyl-substituted alkyl radicals] (Atkinson, 1994). For example, the reactions for the benzyl radical, $C_6H_5\dot{C}H_2$, in the presence of NO are:

$$C_6H_5\dot{C}H_2 + O_2 \xrightarrow{M} C_6H_5CH_2O\dot{O} \tag{59}$$

$$C_6H_5CH_2O\dot{O} + NO \xrightarrow{M} C_6H_5CH_2ONO_2 \tag{60a}$$

(benzyl nitrate),

$$C_6H_5CH_2O\dot{O} + NO \rightarrow C_6H_5CH_2\dot{O} + NO_2 \tag{60b}$$

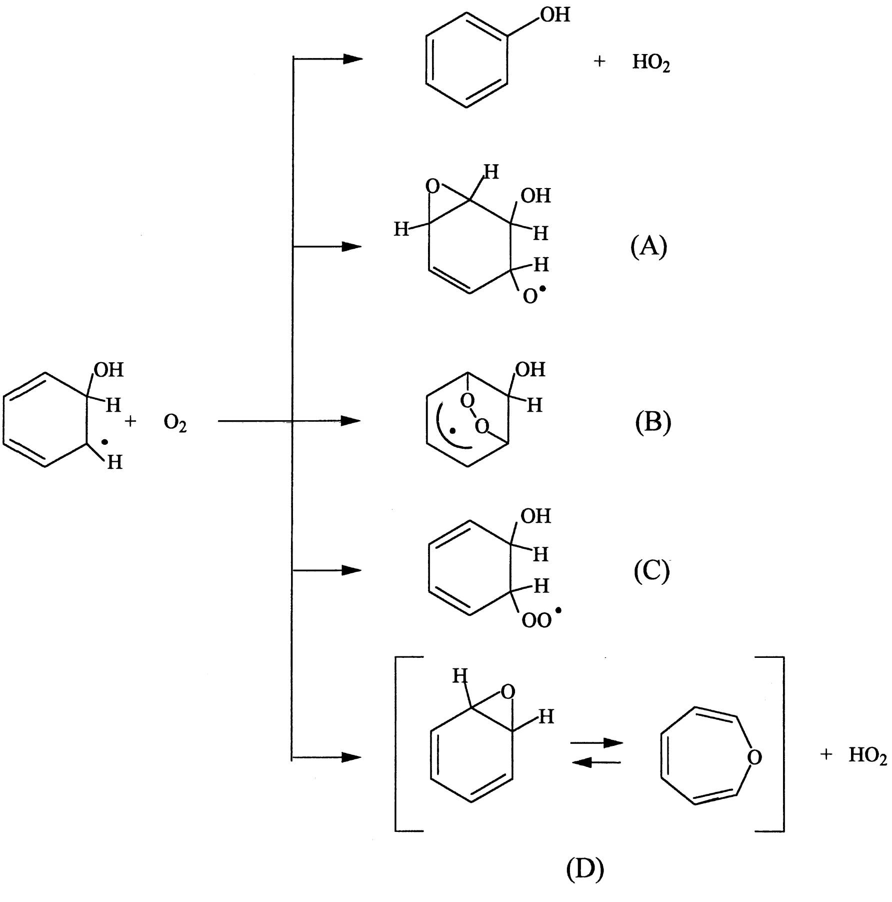
$$C_6H_5CH_2\dot{O} + O_2 \rightarrow C_6H_5CHO + HO_2 \tag{61}$$

The benzyl nitrate yield from the reaction of NO with the benzyl peroxy radical is ~ 10–12% at room temperature and atmospheric pressure (Atkinson, 1994).

Clearly, the major reaction pathway involves the formation of the OH-aromatic adduct(s). The ultraviolet absorption spectra of the OH-benzene (Fritz et al., 1985; Zellner et al., 1985; Knispel et al., 1990; Bjergbakke et al., 1996) and OH-toluene (Markert and Pagsberg, 1993) adducts have been observed, and the reactions of the OH-benzene, OH-toluene and OH-xylene adducts with NO, NO_2, and O_2 have been studied by several groups (Atkinson, 1994, and references therein; Zetzsch and Koch, 1994; Koch et al., 1994; Atkinson and Aschmann, 1994; Bjergbakke et al., 1996) using both direct and indirect methods. No reactions with NO have been observed (Knispel et al., 1990; Koch et al., 1994). However, reactions of the OH-benzene, OH-toluene and OH-xylene adducts with O_2 and NO_2 are observed, with room temperature rate constants of $(1.8\text{–}20) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} and $(2.5\text{–}3.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively (Knispel et al., 1990; Zetzsch and Koch, 1994; Koch et al., 1994). These kinetic data show that in the lower troposphere, including in polluted urban airmasses, the dominant reaction of the OH-alkylbenzene adducts is with O_2 [the O_2 and NO_2 reactions are of equal importance for NO_2 mixing ratios of $\sim (1\text{–}15) \times 10^{-6}$].

The uncertainty in the tropospheric degradation mechanism of aromatic hydrocarbons concerns the mechanisms and products of the reactions of the OH-aromatic adducts with NO_2 and, especially, O_2. While the reaction with NO_2 is expected to be generally of minor importance in the troposphere, it can be important or even dominant in laboratory product studies carried out at elevated NO_x concentrations or in exhaust plumes from combustion sources containing elevated levels of NO_2. Scheme 8 shows postulated reactions of the OH-benzene adduct with O_2, leading to phenol, an epoxide-alkoxy radical (A) (Bartolotti and Edney, 1995), a bicycloalkyl radical (B) (Bartolotti and Edney, 1995; Andino et al., 1996), a peroxy radical (C) (Bartolotti and Edney, 1995; Andino et al., 1996), and benzene oxide/oxepin (D) (Klotz et al., 1997). The epoxide-alkoxy radical (A), bicycloalkyl radical (B) and the peroxy radical (C) are the lowest-energy isomers derived from quantum mechanical calculations (Bartolotti and Edney, 1995; Andino et al. 1996).

Schemes 9–12 show possible subsequent reactions of the species (A) through (D) (Bartolotti and Edney, 1995; Andino et al., 1996; Klotz et al., 1997), leading to the formation of ring-opened unsaturated carbonyls, dicarbonyls and epoxy-carbonyls. Product studies carried out to date under simulated atmospheric conditions for benzene, toluene, and the xylenes generally account for only ~ 30–50% of the reaction products (Atkinson, 1994), which include phenolic compounds and ring-opened dicarbonyls (Atkinson, 1994; Bierbach et al., 1994a). On a molar basis the reported yields of the α-dicarbonyls glyoxal, methylglyoxal and 2,3-butanedione account for ~ 20–50% of the overall OH radical reaction pathways (Atkinson, 1994), and for *o*-xylene the 2,3-butanedione yield decreases with increasing participation of the NO_2 reaction (Atkinson and Aschmann, 1994). 3-Hexene-2,5-dione, the expected co-product to the α-dicarbonyl glyoxal, has been reported as a product of the OH radical-initiated reactions of *p*-xylene (Becker and Klein, 1987; Becker et al., 1992; Bierbach et al., 1994a; Kwok et al., 1997) and 1,2,4-trimethylbenzene (Tagaki et al., 1982). The formation of other ring-opened unsaturated carbonyls have been reported (Atkinson, 1994 and references therein; Becker

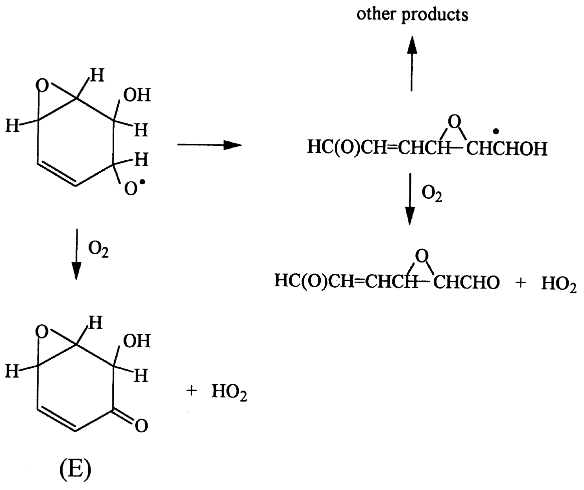


Scheme 8.

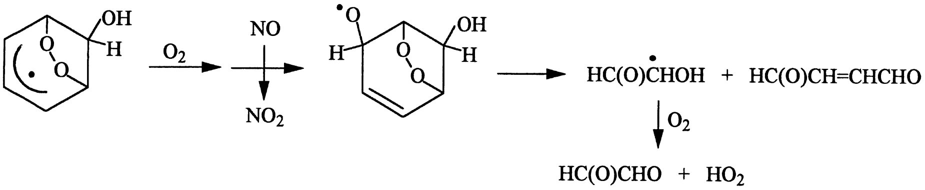
et al., 1992; Bierbach et al., 1994a; Kwok et al., 1997; Yu et al., 1997; Yu and Jeffries, 1997), although no quantitative yield data have been published to date.

The API-MS data of Kwok et al. (1997) concerning the products of the OH radical-initiated reactions of *o*-, *m*- and *p*-xylene (including partially and fully deuterated xylenes) in the presence and absence of NO_x and the O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine derivatization data of Yu et al. (1997) and Yu and Jeffries (1997) are not inconsistent with the OH-xylene adduct reactions with O_2 proceeding by all five pathways shown in Scheme 8. Kwok et al. (1997) did not observe the formation of dimethyl-2-hydroxycyclo-3,5-hexadien-1-ones [(F) in Scheme 11], consistent with the expectation that decomposition of the intermediate alkoxy radical dominates over reaction with O_2 (Atkinson, 1997b). Taking the xylenes as an example, the qualitative studies of Kwok et al. (1997), Yu et al. (1997) and Yu and Jeffries (1997) indicate the formation of C_4-C_6 unsaturated dicarbonyls such as HC(O)CH=CHCHO (from *o*-xylene only), $CH_3C(O)CH=CHCHO$ and $CH_3C(O)CH=CHC(O)CH_3$, and their isomers, C_8 di-unsaturated dicarbonyls such as $CH_3C(O)CH=CHCH=CHC(O)CH_3$ (and its isomers), C_8 unsaturated epoxy-carbonyls, and C_8 epoxycyclohexenones. The C_4–C_6 unsaturated dicarbonyls are the expected co-products to the α-dicarbonyls glyoxal, methylglyoxal and 2,3-butanedione.

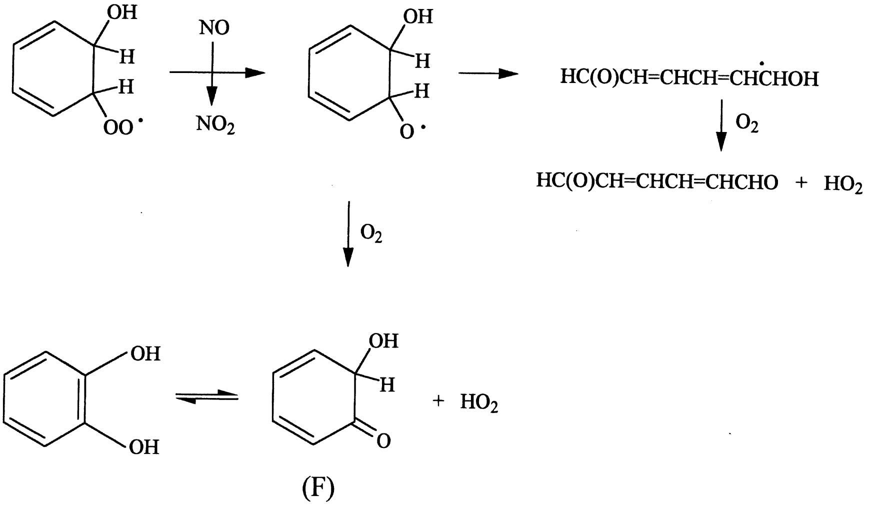
The unsaturated 1,4-dicarbonyls and di-unsaturated 1,6-dicarbonyls formed in Schemes 10–12 are highly reactive (Tuazon et al., 1985; Becker et al., 1992; Bierbach



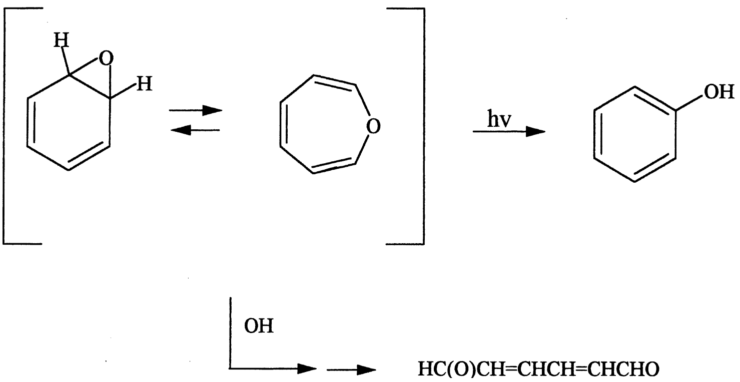
Scheme 9.



Scheme 10.



Scheme 11.



Scheme 12.

et al., 1994a,b; Klotz et al., 1995) and react (at least in part) to form α-dicarbonyls (Bierbach et al., 1994b; Klotz et al., 1995). However, the prompt formation of α-dicarbonyls and unsaturated 1,4-dicarbonyls observed by Darnall et al. (1979) and Kwok et al. (1997) suggests the involvement of the bicycloalkyl radicals (B). Additionally, if the ion peaks observed by Kwok et al. (1997) in their API-MS analyses at 155, 161, and 164 and 165 from the xylene-h_{10}, xylene-dimethyl-d_6 and xylene-d_{10} reactions, respectively, and the products observed by Yu and Jeffries (1997) were due to ring-opened unsaturated epoxy-dicarbonyls and epoxycyclohexenones (E) (Scheme 9), then it appears that the epoxide-alkoxy radical (A) predicted by Bartolotti and Edney (1995) is formed from reaction of the OH-aromatic adducts with O_2.

Klotz et al. (1997) have reported a rate constant for the reaction of benzene oxide/oxepin with the OH radical of $(1.00 \pm 0.04) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K, a factor of ~ 80 more reactive than benzene, and the dimethyl homologs are expected to be more reactive yet. Thus, for the benzene reaction the formation of benzene oxide/oxepin will be difficult to detect because its steady-state concentration will be a factor of ~ 80 lower than the benzene concentration and the benzene oxide/oxepin reaction products will look very much like "first-generation" products. Whether or not methyl-substituted benzene oxides/oxepins are formed may be able to be answered through studies of the OH radical-initiated reactions of the more reactive xylenes and trimethylbenzenes, for which the rate constant ratio k(OH + methyl-substituted benzene oxide/oxepin)/k(OH + aromatic) is expected to be $\leqslant 10$ [the room temperature rate constants for the reaction of the OH radical with methyl-substituted benzene oxide/oxepins are presumably $\leqslant (3\text{–}4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (see Atkinson (1989,1994,1997a) for kinetics of OH radical reactions with VOCs)].

Clearly, the detailed reaction mechanisms of the OH-aromatic adducts under tropospheric conditions are not presently understood, and approximately 50% of the products have not been quantified. Mechanistic and product data (and especially quantitative data for the formation yields of the various potential unsaturated dicarbonyls and unsaturated epoxycarbonyls) are needed to elucidate the reactions of the OH-aromatic adducts with O_2 and NO_2, and to determine the first-generation products whose tropospheric chemistry then need to be studied.

The situation is somewhat similar for the gas-phase reactions of the OH radial with polycyclic aromatic hydrocarbons (PAH) such as naphthalene, 1- and 2-methylnaphthalene and biphenyl. The rate constants for the initial reactions are known (Atkinson and Arey, 1994), as are the initial reaction pathways (at least qualitatively) which involve initial addition to the aromatic rings and H-atom abstraction from the alkyl substituent groups or, for acenaphthylene, OH radical addition to the $>C{=}C<$ bond in the cyclopenta-fused ring (Atkinson and Arey, 1994). The relative importance of the reactions of the OH-PAH adducts with O_2 and NO_2 are not known, but must differ from the OH-monocyclic aromatic adducts because the nitro-PAH formed after the NO_2 reaction with the OH-aromatic adducts are observed in ambient air at concentrations reasonably consistent with laboratory product studies carried out at elevated NO_2 concentrations (Arey et al., 1990; Atkinson and Arey, 1994). In fact, it may well be the case that the OH-PAH adducts react dominantly with NO_2 under conditions representative of urban air masses (see also the discussion concerning the NO_3 radical-initiated reactions below).

Analogous to the reactions of the OH radical with the aromatic hydrocarbons, the NO_3 radical reactions with monocyclic aromatic hydrocarbons and PAH proceed by H-atom abstraction from the C-H bonds of the alkyl substituent groups and by reversible addition to the aromatic rings to form an NO_3-aromatic adduct

(Atkinson, 1991,1994; Atkinson and Arey, 1994; Atkinson et al., 1994). Because of the rapid thermal decomposition of the NO_3-monocyclic aromatic adducts, with an estimated lifetime at 298 K due to thermal decomposition of $\sim 10^{-8}$ s (Atkinson, 1991), addition of the NO_3 radical to the aromatic ring is of no importance in the troposphere for monocyclic aromatic hydrocarbons. The observed slow reactions of the alkyl-substituted benzenes therefore proceed by H-atom abstraction from the C–H bonds of the alkyl groups, and this is confirmed by the observation of a significant deuterium isotope effect for toluene, *o*- and *p*-xylene (Atkinson, 1991; Rindone et al., 1991; Chiodini et al., 1993) and of no observable reaction in the case of benzene (Atkinson, 1991).

For the PAH, although it appears that thermal decomposition of the NO_3-PAH adduct back to reactants is still rapid, reactions with NO_2 and O_2 (and possibly decomposition to products other than the reactants) are competitive with the thermal decomposition pathway (Atkinson, 1991; Atkinson et al., 1994). For the NO_3-naphthalene adduct, Atkinson et al. (1994) obtained an upper limit for the rate constant ratio $k(O_2 + NO_3\text{-naphthalene adduct})/k(NO_2 + NO_3\text{-naphthalene adduct})$ of $< 4 \times 10^{-7}$ at 298 ± 2 K and atmospheric pressure, showing that at a mixing ratio of NO_2 of 80×10^{-9} the NO_3-naphthalene adduct reacts $\geqslant 50\%$ of the time with NO_2, and this may well be the situation at lower NO_2 mixing ratios. Again, ambient atmospheric measurements provide strong evidence for the reaction of the NO_3-naphthalene and NO_3-methylnaphthalene adducts with NO_2 (to form, in part, nitro-PAH) at NO_2 concentrations encountered in urban areas (Gupta et al., 1996). Further work to define the relative importance of the OH-PAH adducts and NO_3-PAH adducts with O_2 and NO_2 are needed for a more quantitative understanding of the atmospheric chemistry of volatile PAH and their role in the in situ tropospheric formation of nitro-PAH.

6.2. Styrenes

Styrene [$C_6H_5CH{=}CH_2$] and its methyl-substituted homologs react with OH radicals, NO_3 radicals, and O_3 (Atkinson, 1994) (see Table 1). The magnitude of the rate constants and the products formed from these reactions (Atkinson, 1994) show that they proceed by initial addition at the $>C{=}C<$ bond in the substituent group, and styrene behaves as a phenyl-substituted ethene. Accordingly, the reaction mechanisms and the products formed are analogous to those for the corresponding reactions of alkenes.

6.3. Aromatic aldehydes

Kinetic data are available only for benzaldehyde and 2,4-, 2,5- and 3,4-dimethylbenzaldehyde (Atkinson, 1989 and references therein; Semadeni et al., 1995; Tse et al., 1997). Based on the rate constants for the reactions of benzaldehyde with OH radicals and NO_3 radicals (Atkinson, 1989,1991), benzaldehyde behaves similarly to an aliphatic aldehyde (Section 7), with reaction occurring almost exclusively at the –CHO group. However, the rate constants for the reactions of the OH radical with 2,4-, 2,5- and 3,4-dimethylbenzaldehyde are factors of ~ 3, ~ 3 and ~ 1.5 higher, respectively, than that for benzaldehyde, indicating that OH radical addition to the aromatic ring is important for these dimethylbenzaldehydes, and dominates for 2,4- and 2,5-dimethylbenzaldehyde.

6.4. Phenolic compounds

Phenol, the cresols, and the dimethylphenols have been reported as products of the OH radical-initiated reactions of benzene, toluene, and the xylenes, respectively (Atkinson, 1994, and references therein). Phenol, cresols, dimethylphenols and trimethylphenols react with OH radicals (Atkinson, 1994; Semadeni et al., 1995; Tse et al., 1997), NO_3 radicals (Atkinson, 1991,1994), and O_3 (Atkinson and Carter, 1984), with the reactions of the cresols with O_3 being slow. The major tropospheric transformation processes are therefore reaction with OH radicals and NO_3 radicals (Table 1). The OH radical reactions are analogous to the reactions of the OH radical with aromatic hydrocarbons in that the reactions proceed by H-atom abstraction from the C–H and O–H bonds of the substituent -OH and alkyl groups, and by OH radical addition to the aromatic ring (Atkinson, 1989). The H-atom abstraction pathway is of minor importance at room temperature, accounting for $\lesssim 10\%$ of the overall reaction for phenol and *o*-cresol (Atkinson, 1989). In the presence of NO_x, the phenoxy (or alkyl-substituted phenoxy) radical formed after H-atom abstraction from the -OH group appears to react with NO_2 to form 2-nitrophenol or alkyl-substituted 2-nitrophenols (Atkinson, 1991, 1994).

The dominant pathway for the OH radical reaction is via initial addition to the aromatic ring to form an OH-phenol adduct, which then reacts with O_2 or NO_2 (Knispel et al., 1990; Koch et al., 1994). The studies of Zetzsch and coworkers (Knispel et al., 1990; Koch et al., 1994) show that the OH-phenol and OH-*m*-cresol adducts do not react with NO, but react with NO_2 [with room temperature rate constants of $(3.6\text{–}4.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}] and O_2 [with room temperature rate constants of 3×10^{-14} cm^3 molecule^{-1} s^{-1} for the OH-phenol adduct(s) and 8×10^{-14} cm^3 molecule^{-1} s^{-1} for the OH-*m*-cresol adduct(s)]. Therefore, analogous to the situation for benzene, toluene and the xylenes, the OH-phenol and OH-cresol adducts will react only with O_2 in the troposphere. The products and mechanisms of the reactions of the OH-phenol and OH-cresol adducts with O_2 are not presently known.

The reactions of the NO_3 radical with phenolic compounds are rapid (Atkinson, 1991,1994), and lead to nitrophenol and alkyl-substituted nitrophenol formation in significant, but not unit, yields (Atkinson, 1994).

6.5. Aerosol formation from aromatics

A number of studies have been carried out to investigate the formation of aerosols from the photooxidations of aromatic hydrocarbons and to identify the chemical compounds present in the particulate phase (Wang et al., 1992; Odum et al., 1996,1997; Forstner et al., 1997b). Odum et al. (1997) conclude that aromatic hydrocarbons play a significant, and possibly dominant, role in the formation of secondary organic aerosol in urban areas. The product study of Forstner et al. (1997b) further suggests that it is the reactions of ring-opened first-generation (or second- and later generation) products which lead to aerosol formation, and this conclusion is consistent with FT-IR analyses of aerosol formed from the reaction of the OH radical with naphthalene in the presence of NO (Dekermenjian et al., 1999).

7. Tropospheric chemistry of oxygen-containing compounds

In this section, the tropospheric chemistry of the major oxygen-containing compounds emitted into the troposphere, or formed in situ in the troposphere as a result of atmospheric transformations, is discussed. The classes of oxygen-containing compounds considered are aliphatic aldehydes, ketones, α-dicarbonyls, unsaturated dicarbonyls, α,β-unsaturated carbonyls (many of which are formed in the troposphere), alcohols, ethers and glycol ethers, esters and hydroperoxides.

7.1. Aliphatic aldehydes, ketones, and α-dicarbonyls

The major tropospheric transformation processes for the aliphatic aldehydes (including benzaldehyde), ketones, and α-dicarbonyls are photolysis and reaction with the OH radical (Table 1). Reactions with O_3 have not been observed at room temperature, and the NO_3 radical and HO_2 radical reactions are of minor importance in the troposphere.

Absorption cross-sections are available for a number of aldehydes [formaldehyde, acetaldehyde, propanal, butanal, 2-methylpropanal, pinonaldehyde and caronaldehyde] (Martinez et al., 1992; Atkinson et al., 1999; Hallquist et al., 1997), ketones [acetone, 2-butanone and 2- and 3-pentanone] (Martinez et al., 1992; Hynes et al., 1992; Atkinson et al., 1999) and α-dicarbonyls [glyoxal, methylglyoxal and 2,3-butanedione] (Plum et al., 1983; Meller et al., 1991; Staffelbach et al., 1995; Zhu et al., 1996; Atkinson et al., 1999). For these carbonyls, the absorption cross-sections appear to be reliably known, apart from glyoxal for which the cross-sections of Plum et al. (1983) need to confirmed. Apparently reliable photodissociation quantum yields are available for formaldehyde, acetaldehyde and acetone (Atkinson et al., 1999), with some quantum yield data available for other C_3 and C_4 aldehydes and ketones (Raber and Moortgat, 1996; Atkinson et al., 1999). In some cases, the measured quantum yields are averages over large wavelength regions; for example, the 2-butanone data of Raber and Moortgat (1996) show an average photodissociation quantum yield of 0.34 ± 0.15 in one atmosphere of air for photolysis with sunlamps with a spectral distribution ranging from 275–380 nm with a broad maximum at 310 nm [the maximum absorption of 2-butanone is at 278 nm and extends out to ~ 345 nm (Martinez et al., 1992)]. The photodissociation quantum yield data for glyoxal and, especially, methylglyoxal have significant uncertainties (Plum et al., 1983; Staffelbach et al., 1995; Raber and Moortgat, 1996; Zhu et al., 1996) and data are needed as a function of wavelength at atmospheric pressure of air.

Rate constants are available for the reactions of the OH radical with $\leqslant C_5$ aliphatic aldehydes, a number of ketones, carbonyls formed from monoterpene photooxidations (including pinonaldehyde, nopinone, camphenilone, caronaldehyde and sabinaketone formed from α-pinene, β-pinene, camphene, 3-carene and sabinene, respectively), and for the α-dicarbonyls glyoxal, methylglyoxal and 2,3-butanedione (Atkinson, 1989,1994; Glasius et al., 1997; Hallquist et al., 1997; Atkinson et al., 1999; Alvarado et al., 1998). In the case of the NO_3 reactions, rate constants are available for the $\leqslant C_4$ aldehydes, certain C_5 and C_6 aldehydes, pinonaldehyde, caronaldehyde and sabinaketone, and an upper limit is available for acetone (Atkinson, 1991,1994; Atkinson et al., 1999; Glasius et al., 1997; Hallquist et al., 1997; D'Anna and Nielsen, 1997; Alvarado et al., 1998).

Photolysis is calculated to be the dominant tropospheric loss process for formaldehyde and the three α-dicarbonyls studied to date (glyoxal, methylglyoxal, and 2,3-butanedione) (Table 1). Photolysis is calculated to be competitive with the OH radical reaction as a tropospheric loss process for acetone (Table 1), while the OH radical reactions are expected to be the dominant loss process for the higher aldehydes and ketones (Atkinson, 1995; Table 1). The NO_3 radical reaction is of no importance in the troposphere for acetone and this is also likely to be the case for ketones in general. The NO_3 radical reactions are calculated to be a relatively minor nighttime loss process for aldehydes (Table 1). The long chemical lifetime of acetone (Table 1) is noteworthy, allowing acetone can be transported to remote regions of the troposphere.The reactions of the OH radical with aldehydes proceed mainly (or totally for HCHO) by H-atom abstraction from the -CHO group (Atkinson, 1989,1994).

$$OH + RCHO \rightarrow H_2O + R\dot{C}O \tag{62}$$

While the $H\dot{C}O$ radical reacts with O_2 by an abstraction pathway,

$$H\dot{C}O + O_2 \rightarrow HO_2 + CO \tag{63}$$

$R\dot{C}O$ (acyl) radicals with R = alkyl (or phenyl) react in the troposphere with O_2 by addition to form an acyl peroxy ($RC(O)O\dot{O}$) radical (Atkinson, 1994; Atkinson et al., 1999).

$$CH_3\dot{C}O + O_2 \overset{M}{\rightarrow} CH_3C(O)O\dot{O} \tag{64}$$

In the troposphere, acyl peroxy radicals react with NO, NO_2, HO_2 radicals and NO_3 radicals (Atkinson, 1994; Canosa-Mas et al., 1996; Atkinson et al., 1999), analogous to the corresponding reactions of the alkyl peroxy radicals dealt with in Section 4.

$$\begin{array}{l} CH_3C(O)O\dot{O} + NO \rightarrow CH_3C(O)\dot{O} + NO_2 \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad \dot{C}H_3 + CO_2 \end{array} \tag{65}$$

$$\begin{array}{l} CH_3C(O)O\dot{O} + NO_2 \overset{M}{\rightarrow} CH_3C(O)OONO_2 \\ \qquad\qquad \text{(peroxyacetyl nitrate; PAN),} \end{array} \tag{66}$$

$$CH_3C(O)O\dot{O} + HO_2 \rightarrow CH_3C(O)OH + O_3 \tag{67a}$$

$$CH_3C(O)O\dot{O} + HO_2 \rightarrow CH_3C(O)OOH + O_2 \tag{67b}$$

$$\begin{array}{l} CH_3C(O)O\dot{O} + NO_3 \rightarrow CH_3C(O)\dot{O} + NO_2 + O_2 \\ \qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad \dot{C}H_3 + CO_2 \end{array} \tag{68}$$

The reactions of PAN are dealt with in Section 8 below. In the presence of NO, the OH radical-initiated reaction of acetaldehyde therefore leads to the formation of HCHO, and the aldehyde degradation reactions "cascade" through the lower aldehydes to ultimately form HCHO.

The reactions of the OH radical with ketones proceed by H-atom abstraction from the various C–H bonds (Kwok and Atkinson, 1995), and the subsequent reactions of the substituted alkyl radicals produced in the initial reaction are analogous to those for the alkyl radicals discussed in Sections 3 and 4 above.

7.2. Alcohols

The dominant chemical loss process for aliphatic alcohols in the troposphere is by reaction with the OH radical (Atkinson, 1994; Atkinson et al., 1999) (Table 1). The OH radical reactions proceed by H-atom abstraction from the various C–H bonds and the O–H bond. For example, for ethanol,

$$OH + CH_3CH_2OH \rightarrow H_2O + CH_3CH_2\dot{O} \tag{69a}$$

$$OH + CH_3CH_2OH \rightarrow H_2O + CH_3\dot{C}HOH \tag{69b}$$

$$OH + CH_3CH_2OH \rightarrow H_2O + \dot{C}H_2CH_2OH \tag{69c}$$

with the reaction pathways (69a), (69b) and (69c) accounting for ~ 5%, ~ 90% and ~ 5%, respectively, of the overall reaction at 298 K (Atkinson, 1994; Atkinson et al., 1997a,1999). The radicals formed in reactions (69a), (69b), and (69c) react as discussed in Sections 4 and 5 to form acetaldehyde, acetaldehyde, and formaldehyde or glycolaldehyde ($HOCH_2CHO$), respectively (Atkinson, 1994; Atkinson et al., 1999). [Note that the $\dot{C}H_2CH_2OH$ radical formed in reaction (69c) is identical to that formed by OH radical addition to ethene]. The NO_3 radical reactions with secondary alcohols (for example, 2-propanol, 2-butanol and 4-heptanol) proceed mainly, if not exclusively, by H-atom abstraction from the C–H bond of the –CH(OH)– group, with the resulting α-hydroxyalkyl radical reacting with O_2 to form the corresponding carbonyl (Chew et al., 1998). For example, for 2-propanol:

$$\begin{array}{l} NO_3 + CH_3CH(OH)CH_3 \rightarrow HNO_3 \\ \qquad + CH_3\dot{C}(OH)CH_3 \\ \qquad\qquad \downarrow O_2 \\ \qquad CH_3C(O)CH_3 + HO_2. \end{array} \tag{70}$$

7.3. Ethers, glycol ethers and acetals

The aliphatic and cyclic ethers, glycol ethers and acetals [an example of an acetal being dimethoxymethane; $CH_3OCH_2OCH_3$] react with OH and NO_3 radicals, with the OH radical reaction dominating as a tropospheric loss process (Table 1). However, the NO_3 radical reactions are sufficiently important for certain ethers (for example, ethyl *tert*-butyl ether; Table 1) that they cannot be ignored. The OH radical reactions proceed by H-atom abstraction, mainly from the C–H bonds on the carbon atoms adjacent to the ether –O– atom (Atkinson, 1994; Kwok and Atkinson, 1995), with secondary C–H bonds being more reactive than primary C–H bonds (and a similar situation is expected for the NO_3 radical reactions).

$$\begin{array}{l} OH + CH_3OCH_2CH_2CH_2CH_3 \rightarrow H_2O \\ \qquad\qquad + CH_3O\dot{C}HCH_2CH_2CH_3. \end{array} \tag{71}$$

The alkoxy radicals formed after addition of O_2 and reaction with NO react as discussed in Sections 3 and 4.

For example:

$$CH_3CH_2CH_2CH(\dot{O})OCH_3 + O_2 \rightarrow CH_3CH_2CH_2C(O)OCH_3 + HO_2, \quad (72)$$

$$CH_3CH_2CH_2CH(\dot{O})OCH_3 \rightarrow CH_3CH_2CH_2CHO + CH_3\dot{O}, \quad (73a)$$

$$CH_3CH_2CH_2CH(\dot{O})OCH_3 \rightarrow CH_3CH_2\dot{C}H_2 + CH_3OCHO, \quad (73b)$$

$$CH_3CH_2CH_2CH(\dot{O})OCH_3 \rightarrow \dot{C}H_2CH_2CH_2CH(OH)OCH_3 \quad (74)$$

While rate constants are not yet available for the various reactions of the alkoxy radicals of structure $>C(\dot{O})OR$ (R = alkyl) formed from ethers and glycol ethers, it appears that the decomposition pathway typified by reaction (73b) is significantly more rapid than calculated using the estimation method proposed by Atkinson (1997a,b) for the alkoxy radicals formed from alkanes. Indeed, the decomposition pathway typified by reaction (73b) dominates in many cases (Atkinson, 1994), leading to the formation of esters which, especially for the formate esters, often have sufficiently low reactivity towards the OH radical (Atkinson, 1989,1994; Smith et al., 1995; Le Calvé et al., 1997a,b; Stemmler et al., 1997) that transport to remote regions is expected to occur. A better knowledge of the relative (and hopefully, absolute) rates of reaction of the various reaction pathways of alkoxy radicals of structure $>C(\dot{O})OR$ (R = alkyl) is needed before a priori predictions of the reaction mechanisms can be made. To date, the tropospheric degradation mechanisms of dimethyl ether, diethyl ether, methyl *tert*-butyl ether, ethyl *tert*-butyl ether and di-isopropyl ether appear to be well understood (Atkinson, 1994, and references therein), and data are available for a number of other ethers (Smith et al., 1995; Langer et al., 1996; Stemmler et al., 1997; Platz et al., 1997) and for certain glycol ethers (Stemmler et al., 1996; Tuazon et al., 1998b) and acetals (Wallington et al., 1997).

7.4. α,β-Unsaturated carbonyl compounds

This class of oxygen-containing compounds includes methacrolein [$CH_2{=}C(CH_3)CHO$] and methyl vinyl ketone [$CH_3C(O)CH{=}CH_2$], the tropospheric first-generation reaction products of isoprene. The dominant tropospheric reaction of the α,β-unsaturated carbonyls is with the OH radical, with the O_3 and NO_3 radical reactions being of relatively minor or negligible importance (Table 1), and with photolysis appearing to be of sufficient importance (Raber and Moortgat, 1996) that it cannot be neglected.

For the α,β-unsaturated aldehydes such as acrolein [$CH_2{=}CHCHO$], 2-butenal [$CH_3CH{=}CHCHO$], and methacrolein, the OH radical and NO_3 radical reactions proceed by H-atom abstraction from the C–H bond of the –CHO group and OH or NO_3 radical addition to the $>C{=}C<$ bond (Atkinson, 1989,1991,1994). For example, the reaction of the OH radical with methacrolein proceeds by:

$$OH + CH_2{=}C(CH_3)CHO \rightarrow H_2O + CH_2{=}C(CH_3)\dot{C}O \quad (\sim 50\%), \quad (75a)$$

$$OH + CH_2{=}C(CH_3)CHO \rightarrow HOCH_2\dot{C}(CH_3)CHO \text{ or } \dot{C}H_2C(OH)(CH_3)CHO \quad (\sim 50\%) \quad (75b)$$

The subsequent reactions of the acyl radical $CH_2{=}C(CH_3)\dot{C}O$ and of the β-hydroxyalkyl radicals $HOCH_2\dot{C}(CH_3)CHO$ and $\dot{C}H_2C(OH)(CH_3)CHO$ are analogous to those of the acyl ($R\dot{C}O$) and β-hydroxyalkyl radicals discussed above and in Section 5. However, for the β-hydroxyalkoxy radicals formed subsequent to OH radical addition to the $>C{=}C<$ bond of α,β-unsaturated carbonyls, the "first-generation" products depend on which carbon atom the OH radical addition occurs (Atkinson, 1994).

The reactions of the OH radical with α,β-unsaturated ketones proceed mainly by initial addition of the OH radical to the $>C{=}C<$ bond (Kwok and Atkinson, 1995), analogous to the corresponding pathway in the α,β-unsaturated aldehydes. The subsequent reactions of the resulting β-hydroxyalkyl radicals are analogous to those discussed in Section 5. The reactions of the β-hydroxyalkoxy radical reactions (Atkinson, 1994) are also analogous to those discussed in Section 5.

7.5. Unsaturated dicarbonyls

As discussed in Section 6 above, a number of unsaturated dicarbonyls (for example, $HC(O)CH{=}CHCHO$), di-unsaturated dicarbonyls (for example, $HC(O)CH{=}CHCH{=}CHCHO$) and unsaturated epoxy-dicarbonyls (for example,

$$HC(O)\overset{O}{CH{-}CH}CH{=}CHCHO)$$

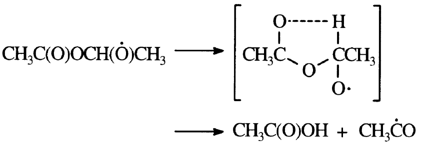
have been identified as products from the OH radical-initiated reactions of aromatic hydrocarbons. Because of the difficulties in preparing and handling these compounds, few data are available concerning their tropospheric chemistry. For the unsaturated dicarbonyls, room temperature rate constants have been measured for the gas-phase reactions of OH radicals with *cis*-butenedial [$HC(O)CH{=}CHCHO$] (Bierbach et al., 1994b), 4-oxo-2-pentenal [$CH_3C(O)CH{=}CHCHO$] (Bierbach et al., 1994b), and *cis*- and *trans*-3-hexene-2,5-dione [$CH_3C(O)CH{=}CHC(O)CH_3$] (Tuazon et al., 1985; Bierbach et al., 1994b), and for the O_3 reactions with *cis*- and *trans*-3-hexene-2,5-dione (Tuazon et al., 1985). Photolysis and products of the OH radical-initiated reactions have also been investigated (Tuazon et al., 1985; Becker and Klein, 1987; Bierbach et al., 1994b). These studies suggest that photolysis and reaction with the OH radical will be the important tropospheric loss processes (see also Table 1), except for the 3-hexene-2,5-diones for which photolysis, although rapid, leads primarily to *cis/trans* isomerization (Tuazon et al., 1985; Becker and Klein, 1987; Bierbach et al., 1994b).

Klotz et al. (1995) have studied the kinetics and products of the gas-phase reactions of *trans,trans*- and *cis,trans*-2,4-hexadienedial [HC(O)CH=CHCH=CHCHO] and *trans,trans*-2-methyl-2,4-hexadienedial [$CH_3C(O)CH{=}CHCH{=}CHCHO$] with OH radicals, NO_3 radicals and O_3, and of their photolysis. These di-unsaturated dicarbonyls all react rapidly with the OH radical, with rate constants in the range $(0.9–1.2)\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 ± 2 K (Klotz et al., 1995), and the reaction products observed were *trans*-butenedial plus glyoxal from *trans,trans*- and *cis,trans*-2,4-hexadienedial and *trans*-butenedial plus methylglyoxal from *trans,trans*-2-methyl-2,4-hexadienedial. The products of the O_3 reactions (in the absence of an OH radical scavenger) are the same as those observed from the OH radical-initiated reactions in the presence of NO. The data reported (Klotz et al., 1995) indicate that in the troposphere the important loss processes of the di-unsaturated dicarbonyls are photolysis and reaction with the OH radical (Table 1).

To date, no studies have been reported concerning the tropospheric chemistry of the unsaturated epoxy-carbonyls.

7.6. Esters

The only important reactions of the aliphatic esters are with the OH radical (Table 1), and rate constants have been measured for a number of esters (Atkinson, 1989,1994; Smith et al., 1995; Veillerot et al., 1996; El Boudali et al., 1996; Le Calvé et al., 1997a,b; Stemmler et al., 1997). Tuazon et al. (1998c) have shown, from product studies of the OH radical-initiated reactions of ethyl acetate, isopropyl acetate and *tert*-butyl acetate, that intermediate alkoxy radicals of structure $RC(O)OCH(\dot{O})\dot{R}$ react via a novel rearrangement proceeding through a 5-membered transition state. For example, for the $CH_3C(O)OCH(\dot{O})CH_3$ alkoxy radical formed from ethyl acetate, this rearrangement leads to the formation of acetic acid plus an acetyl radical.



(76)

However, rate constants for this alkoxy radical rearrangement are not known.

7.7. Hydroperoxides

Hydroperoxides are formed in the gas phase from the reactions of organic peroxy radicals with the HO_2 radical (Atkinson, 1997a) and from the reactions of O_3 with alkenes through reactions of the biradicals with water vapor (see Section 5 above). The tropospheric chemistry of methyl hydroperoxide is dealt with in the IUPAC evaluations (Atkinson et al., 1999) and involves photolysis and reaction with the OH radical; wet and dry deposition may also be important tropospheric loss processes. For methyl hydroperoxide, photolysis and the OH radical reaction proceed by

$$CH_3OOH + h\nu \rightarrow CH_3\dot{O} + OH \tag{77}$$

$$OH + CH_3OOH \rightarrow H_2O + CH_3\dot{O}_2 \tag{78a}$$

$$\begin{array}{c} OH + CH_3OOH \rightarrow H_2O + \dot{C}H_2OOH \\ \downarrow \\ HCHO + OH \end{array} \tag{78b}$$

with $k_{78b}/(k_{78a}+k_{78b}) = 0.35$, independent of temperature over the range 220–430 K (Atkinson et al., 1999).

7.8. Other oxygenated compounds

There are other oxygenated compounds involved in the chemistry occurring in the troposphere, and these include the biogenic emissions and/or transformation products linalool [$(CH_3)_2C{=}CHCH_2CH_2C(CH_3)(OH)CH{=}CH_2$], 6-methyl-5-hepten-2-one [$(CH_3)_2C{=}CHCH_2CH_2C(O)CH_3$], *cis*-3-hexen-1-ol [$CH_3CH_2CH{=}CHCH_2CH_2OH$], *cis*-3-hexenyl acetate [$CH_3CH_2CH{=}CHCH_2CH_2OC(O)CH_3$] and 2-methyl-3-buten-2-ol [$(CH_3)_2C(OH)CH{=}CH_2$]. As expected, these compounds react with OH radicals, NO_3 radicals and O_3, mainly or totally by initial addition (Grosjean and Grosjean, 1994; Rudich et al., 1995,1996; Atkinson et al., 1995b; Calogirou et al., 1995; Grosjean et al., 1996; Smith et al., 1996; Shu et al., 1997; Aschmann et al., 1997a). The subsequent reaction mechanisms and products formed are consistent with the discussion in Section 5 for the corresponding reactions with alkenes, and the above articles should be consulted for details.

8. Tropospheric chemistry of nitrogen-containing compounds

The nitrogen-containing compounds of primary interest are the organic nitrates (including alkyl nitrates, hydroxynitrates and other organic nitrates) formed from the reactions of organic peroxy radicals with NO, and the peroxynitrates formed from the reactions of NO_2 with alkyl and acyl peroxy radicals. An important reaction of the peroxynitrates in the lower troposphere is thermal decomposition,

$$ROONO_2 \overset{M}{\rightarrow} R\dot{O}_2 + NO_2 \qquad (26)$$

$$RC(O)OONO_2 \overset{M}{\rightarrow} RC(O)O\dot{O} + NO_2 \qquad (79)$$

with thermal decomposition lifetimes at 298 K and atmospheric pressure of 0.1–1 s for the alkyl peroxynitrates $ROONO_2$ (Zabel, 1995; Atkinson et al., 1999), and ~ 30 min for the acyl peroxynitrates $RC(O)OONO_2$ (Zabel, 1995; Atkinson et al., 1999). Because the thermal decomposition rate constants decrease rapidly with decreasing temperature, the thermal decomposition lifetimes increase markedly with increasing altitude in the troposphere, and in the upper troposphere photolysis and reaction with the OH radical may be important for peroxynitrates.

Absorption cross-sections have been reported for methyl peroxynitrate [CH_3OONO_2] (Atkinson et al., 1999, and references therein) and peroxyacetyl nitrate [PAN; $CH_3C(O)OONO_2$] (Libuda and Zabel, 1995; Talukdar et al., 1995; Atkinson et al., 1999), and upper limits to the rate constant for the reaction of the OH radical with PAN over the temperature range 260–298 K have been obtained by Talukdar et al. (1995) [see Atkinson et al. (1999)]. For PAN, photolysis will dominate above ~ 7 km, with thermal decomposition dominating at lower altitudes (Talukdar et al., 1995).

The alkyl nitrates, $RONO_2$, undergo photolysis and reaction with the OH radical in the troposphere (Roberts, 1990; Atkinson, 1994; Atkinson et al., 1999). Absorption cross-sections have been measured for a series of alkyl nitrates by Zhu and Ding (1997), Talukdar et al. (1997a) and Clemitshaw et al. (1997), with generally good agreement between these studies (Atkinson et al., 1999). Photolysis involves cleavage of the $RO–NO_2$ bond,

$$RONO_2 + h\nu \rightarrow R\dot{O} + NO_2 \qquad (80)$$

and a photodissociation quantum yield for NO_2 formation of 1.0 ± 0.1 has been measured from the photolysis of ethyl nitrate at 308 nm (Zhu and Ding, 1997). The tropospheric lifetimes of the alkyl nitrates with respect to photolysis depend on season and altitude, and for a series of C_2–C_5 alkyl nitrates the photolysis lifetimes are calculated to be in the range 4–7 days at the equator, 5–8 days at 40° latitude during summer, and 20–36 days at 40° latitude during winter (Clemitshaw et al., 1997).

The reactions of the OH radical with the alkyl nitrates appear to involve H-atom abstraction from the C–H bonds, to form nitrooxyalkyl radicals (Talukdar et al., 1997b). It is expected that the subsequent reactions of these substituted alkyl radicals are similar to those for the alkyl radicals formed from the reactions of the OH radical with alkanes (Section 4). The OH radical reactions become important as tropospheric loss processes for the $\geqslant C_3$ alkyl nitrates (Table 1).

9. Reactivity with respect to ozone formation; incremental reactivity

As discussed in the sections above, VOCs are transformed in the troposphere by photolysis, reaction with the OH radical, reaction with the NO_3 radical (during nighttime), and reaction with O_3. In the presence of NO_x and sunlight, the degradation reactions of organic compounds lead to the conversion of NO to NO_2 and the formation of O_3 (Section 3). However, as evident from the range of tropospheric lifetimes for VOCs shown in Table 1, different VOCs react at differing rates in the troposphere. In large part because of these differing tropospheric lifetimes and rates of reaction, VOCs exhibit a range of reactivities with respect to the formation of ozone.

While there have been a number of methods of ranking VOC "reactivities", a reasonably fundamental understanding of reactivity has become popular since the late 1980's, with the concept of Incremental Reactivity (Carter and Atkinson, 1989b; Carter, 1994). Incremental Reactivity is defined as the amount of O_3 formed per unit amount of VOC added to, or subtracted from, an urban/rural VOC mixture in a given air mass.

$$\text{Incremental Reactivity} = \Delta[O_3]/\Delta[\text{VOC emitted}],$$

where $\Delta[O_3]$ is the change in the amount of ozone formed as a result of the change in the amount of VOC emitted, Δ[VOC]. This concept of incremental reactivity corresponds closely to control strategy conditions, in that the effects of reducing the emission of a VOC (or group of VOCs), or of replacing one VOC (or group of VOCs) by other VOC(s), on the ozone-forming potential of a complex mixture of VOC emissions are simulated. Indeed, this concept of incremental reactivity is used explicitly (and actually more accurately, as evident from the discussion below) in airshed computer model simulations of specific control strategies.

As shown in Table 1, reaction with the OH radical is the dominant tropospheric loss process for a majority of VOCs. For illustrative purposes, assuming that the VOC reacts with OH radicals to form an alkyl or substituted alkyl radical and that the intermediate alkoxy radical(s) react with O_2, a VOC degradation reaction scheme initiated by reaction with the OH radical in the presence of

NO can be written as

$$\mathrm{OH + RH \rightarrow \dot{R}} \tag{81}$$

$$\mathrm{\dot{R} + O_2 \rightarrow R\dot{O}_2} \tag{30}$$

$$\mathrm{R\dot{O}_2 + NO \rightarrow R\dot{O} + NO_2} \tag{14b}$$

$$\mathrm{R\dot{O} + O_2 \rightarrow carbonyl + HO_2} \tag{82}$$

$$\mathrm{HO_2 + NO \rightarrow OH + NO_2} \tag{12}$$

The net reaction is then,

$$\mathrm{OH + RH + 2NO \rightarrow carbonyl + 2NO_2 + OH}$$

and can be viewed as involving two separate reaction steps: (a) formation of organic peroxy ($\mathrm{R\dot{O}_2}$) radicals from reactions (81) and (30), and (b) conversion of NO to NO_2 and formation of radical and product species from these $\mathrm{R\dot{O}_2}$ radicals through reactions (14b), (82) and (12). This can be generalized further by considering all chemical loss processes of the VOC, and the net reaction

$$\mathrm{VOC(+OH, NO_3, O_3,} h\nu) \xrightarrow{O_2} \alpha \mathrm{R\dot{O}_2}$$

determines how fast $\mathrm{R\dot{O}_2}$ radicals are generated from the reactions of the VOC. The loss rate of the VOC is termed the "Kinetic Reactivity" and if the only reaction of the VOC is with the OH radical, then this is equivalent to the OH radical reaction rate constant. Note also that this definition of the Kinetic Reactivity is related to the lifetime of the VOC and hence to the fraction of the VOC reacted in the time-period being considered.

The second part of the reaction sequence,

$$\alpha \mathrm{R\dot{O}_2} + \beta \mathrm{NO(+NO_2)} \rightarrow \gamma \mathrm{NO_2} + \delta \mathrm{OH} + \varepsilon\mathrm{(products)}$$

leading to NO to NO_2 conversion, regeneration of OH radicals and formation of product species, is termed the "Mechanistic Reactivity". Incremental Reactivity is viewed as being comprised of these two terms:

$$\text{Incremental Reactivity} = (\text{Kinetic Reactivity}) \times (\text{Mechanistic reactivity}),$$

where the Kinetic Reactivity is the fraction of the VOC which reacts in a given time by whatever pathway (Carter, 1994). Thus, for a given Mechanistic Reactivity, the faster a VOC reacts in the atmosphere, the faster is the conversion of NO to NO_2 and the formation of O_3. The chemistry subsequent to the initial reaction(s) affects the ozone-forming potential of the VOC, through the Mechanistic Reactivity.

The following aspects of a chemical mechanism impact the formation of ozone: (a) the existence of NO_x sinks in the reaction mechanism ($\gamma < \beta$) leads to a lowering of the amount of ozone formed (examples are the formation of organic nitrates from the $\mathrm{R\dot{O}_2 + NO}$ reactions and of PAN from the $\mathrm{CH_3C(O)\dot{O}_2 + NO_2}$ reaction) [note that these reactions are also a sink for radicals], and (b) the generation or loss of radical species can lead to a net formation or loss of OH radicals ($\delta > 1$ or < 1, respectively), which in turn leads to an enhancement or suppression of OH radical concentrations in the entire airmass and hence to an enhancement or suppression of overall reactivity of all VOCs present through affecting the formation rate of $\mathrm{R\dot{O}_2}$ radicals. These effects vary in importance with the VOC/NO_x ratio (Carter and Atkinson, 1989b), with NO_x sinks being most important at high VOC/NO_x ratios (NO_x-limited conditions) and hence affecting the maximum ozone concentrations formed. The formation or loss of radicals is most important at low VOC/NO_x ratios, and this then affects the initial rate at which ozone is formed. Carter (1994) has proposed "reactivity scales" for VOCs, one of which is "Maximum Incremental Reactivity" (MIR), which is the incremental reactivity at a VOC/NO_x ratio which results in the highest incremental reactivity of the base-case VOC mixture used in the scenarios. Values of MIR for a large number of VOCs, relative to the MIR for the base-case VOC mix (the use of relative MIR values minimizes the effects of revisions/updates of the chemical mechanisms used), are tabulated by Carter (1994) and Carter (1997).

10. Conclusions and needed research

As should be evident from the discussion in the sections above, there is now a good qualitative and, in a number of areas, quantitative understanding of the tropospheric chemistry of NO_x and VOCs involved in the photochemical formation of ozone. Much progress has been made during the past two decades; during the past five years much progress has been made in elucidating the reactions of alkoxy radicals, the mechanisms of the gas-phase reactions of O_3 with alkenes, and the mechanisms and products of the OH radical-initiated reactions of aromatic hydrocarbons. This progress is expected to continue, in part through now-in-use advances in analytical methods for the identification and quantification of previously difficult, if not impossible, to detect product species such as hydroxycarbonyls, unsaturated-dicarbonyls, di-unsaturated-dicarbonyls, and unsaturated epoxycarbonyls.

As discussed in the sections above, there are still areas of uncertainty which impact the ability to accurately model the formation of ozone in urban, rural and regional areas, and these include:

- A need for quantitative knowledge of the rate constants and mechanism of the reactions of organic peroxy ($\mathrm{R\dot{O}_2}$) radicals with NO, HO_2 radicals, other $\mathrm{R\dot{O}_2}$ radicals and NO_3 radicals (the reactions with $\mathrm{R\dot{O}_2}$ radicals mainly to allow accurate modeling of environmental chamber NO_x–VOC–air irradiations).

- The need for additional data concerning the organic nitrates yields from the reactions of organic peroxy radicals with NO, preferably as a function of temperature and pressure.
- The reaction rates of alkoxy radicals for decomposition, isomerization and reaction with O_2, especially of alkoxy radicals other than those formed from alkanes and alkenes (for example, from hydroxy-compounds, ethers, glycol ethers and esters).
- The detailed mechanisms of the reactions of O_3 with alkenes and VOCs containing $>C{=}C<$ bonds. This involves understanding the reactions of the initially energy-rich biradicals and of the thermalized biradicals formed in these reactions.
- Studies of the thermal decompositions and other atmospherically-important reactions of the higher PANs, including, for example, of $CH_2{=}C(CH_3)C(O)OONO_2$ formed in the atmospheric photooxidation of isoprene.
- The products and mechanisms of the reactions of monoterpenes and oxygenated VOCs (including 2-methyl-3-buten-2-ol) emitted from vegetation with OH radicals, NO_3 radicals and O_3.
- The mechanisms and products of the reactions of OH-aromatic adducts with O_2 and NO_2.
- The tropospheric chemistry of many oxygenated VOCs formed as first-generation products of VOC photooxidations, including (but not limited to) carbonyls (including unsaturated dicarbonyls, di-unsaturated dicarbonyls, and unsaturated epoxy-carbonyls), hydroperoxides, and esters.
- A quantitative understanding of the reaction sequences leading to products which gas/particle partition and lead to secondary organic aerosol formation.

Advances in our knowledge of the kinetics, products and mechanisms of the tropospheric reactions of VOCs will result not only in more accurate chemical mechanisms for use in urban and regional airshed models, but also in more accurate estimates of VOC reactivities (see Section 9 above). In addition, though often not fully appreciated, detailed chemical mechanisms for the tropospheric photooxidations of VOCs can aid in the interpretation of ambient atmospheric measurements and in the evaluation of computer models of atmospheric chemistry against ambient data (see, for example, Montzka et al., 1995).

Additional Information

Since this article was completed, a number of publications have appeared which are relevant to the discussion and conclusions of this article. These include: $OH + NO_2$ kinetics: Brown et al., Chem. Phys. Lett., 299, 277–284 (1999) and Dransfield et al., Geophys. Res. Lett., 26, 687–690 (1999) which are in agreement with Donahue et al. (1997) with a rate constant at 298 K and 760 Torr of air of 9.0×10^{-12} cm^3 molecule^{-1} s^{-1}. $N_2O_5 + H_2O$: Wahner et al., Geophys. Res. Lett., 25, 2169–2172 (1998) conclude that a homogeneous gas-phase reaction does occur, with a rate constant of $k = \{2.5 \times 10^{-22}[H_2O] + 1.8 \times 10^{-39}[H_2O]^2\}$ cm^3 molecule^{-1} s^{-1} at 293 K. O'Brien et al., J. Phys. Chem. A, 102, 8903–8908 (1998) and Chen et al., J. Geophys. Res., 103, 25563–25568 (1998) have measured organic nitrate yields from the reactions of the intermediate β-hydroxyalkoxy radicals with NO for a series of alkenes (including isoprene). Pfeiffer et al., Chem. Phys. Lett., 298, 351–358 (1998) reported the in situ observation of OH radicals from the reactions of O_3 with alkenes under atmospheric conditions using laser induced fluorescence, and Sauer et al., Atmos. Environ., 33, 229–241 (1999) show that the biradicals formed from the reaction of O_3 with isoprene react with water vapor to form α-hydroxyhydroperoxides which decompose to form H_2O_2. Nozière et al., J. Geophys. Res., 104, 23645–23656 (1999) have additional product data of O_3 with α-pinene. Klotz et al., Chem. Phys. Lett., 231, 289–301 (1998); J. Phys. Chem. A, 102, 10289–10299 (1998) have investigated the photolysis of benzene oxide/oxepin and its methyl-homolog, and the products of the OH radical-initiated reaction of toluene, and conclude that the OH + toluene reaction does not proceed to any significant extent through formation of toluene oxide/methyloxepin.

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