Air Pollution Science for the 21st Century
J. Austin, P. Brimblecombe and W. Sturges, editors

Chapter 11

Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer

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Abstract

The chemical processing of pollutants emitted into the atmosphere leads to a variety of oxidised products, which are commonly referred to as secondary pollutants. Such pollutants are often formed on local or regional scales in the planetary boundary layer, and may have direct health impacts and/or play wider roles in global atmospheric chemistry. In the present review, a comparatively detailed description of our current understanding of the chemical mechanisms leading to the generation of secondary pollutants in the troposphere is provided, with particular emphasis on chemical processes occurring in the planetary boundary layer. Much of the review is devoted to a discussion of the gas-phase photochemical transformations of nitrogen oxides (NO_x) and volatile organic compounds (VOCs), and their role in the formation of ozone (O_3). The chemistry producing a variety of other oxidants and secondary pollutants (e.g., organic oxygenates; oxidised organic and inorganic nitrogen compounds), which are often formed in conjunction with O_3, is also described. Some discussion of nighttime chemistry and the formation of secondary organic aerosols (SOA) in tropospheric chemistry is also given, since these are closely linked to the gas-phase photochemical processes. In many cases, the discussion of the relative importance of the various processes is illustrated by observational data, with emphasis generally placed on conditions appropriate to the UK and northwest continental Europe.

First published in Atmospheric Environment 34 (2000) 2499–2527

1. Introduction

The emission of a variety of pollutant gases (e.g., nitrogen oxides, NO_x, and volatile organic compounds, VOCs) into the troposphere may present a health risk either directly, or as a result of their oxidation. This can lead to a variety of secondary oxidised products, many of which are potentially more harmful than their precursors. Because much of the chemistry is driven by the presence of sunlight, the oxidised products are commonly referred to as *secondary photochemical pollutants*, and include photochemical oxidants such as ozone (O_3). The production of elevated levels of O_3 at ground level is of particular concern, since it is known to have adverse effects on human health, vegetation (e.g., crops) and materials (PORG, 1997). Established air quality standards for O_3 are frequently exceeded, and the formulation of control policies is therefore a major objective of environmental policy (UNECE, 1992,1993,1994). Nevertheless, other pollutants that are formed on local or regional scales in the planetary boundary layer may also have direct health impacts (e.g. peroxy acetyl nitrate, PAN), and/or play wider roles in global atmospheric chemistry.

Photochemical air pollution, first identified in Los Angeles in the 1940s, is now a widespread phenomenon in many of the world's population centres (e.g., see NRC, 1991; PORG, 1997). Consequently, considerable attention has been given to identifying and quantifying chemical processes leading to the generation of O_3 and other secondary photochemical pollutants in the planetary boundary layer. This has involved the laboratory study of many hundreds of chemical reactions, and a significant body of evaluated chemical kinetics and photochemical data has accumulated for elementary atmospheric reactions (e.g., Atkinson et al., 1997a,b; DeMore et al., 1997). Computer models have provided a useful means of assembling these data, and of describing the likely behaviour and interconversion of various atmospheric pollutants, and such models play a central role in policy development and implementation. This work has been driven, of course, by the need to interpret the results of field studies of atmospheric chemical processes. In recent years, an enormous variety of observational data has become available for molecular and free radical species involved in atmospheric chemical processes in both polluted and clean environments.

The aim of this review is to provide a comparatively detailed description of our current understanding of the chemical mechanisms leading to the generation of secondary photochemical pollutants in the troposphere, with particular emphasis on chemical processes occurring in the planetary boundary layer. Much of the review is devoted to a discussion of the gas-phase photochemical transformations of nitrogen oxides and volatile organic compounds, and their role in the formation of O_3. The chemistry producing a variety of

other oxidants and secondary pollutants, which are often formed in conjunction with O_3, is also described. Some discussion of nighttime chemistry and the formation and role of secondary organic aerosols (SOA) in tropospheric chemistry is also given, since these are closely linked to the gas-phase photochemical processes. Where possible, the relative importance of the various processes is discussed and illustrated by observational data, with emphasis generally placed on conditions appropriate to the UK and northwest continental Europe. Although some reference to heterogeneous reactions and aqueous uptake is made, multiphase chemical processes are not considered in detail, and the reader is referred to other texts (e.g., Jonson and Isaksen, 1993; Ravishankara, 1997) for further information on this important area of tropospheric chemistry.

2. Photochemical transformations of oxidised nitrogen species

2.1. Daytime interconversion of NO and NO_2

Nitrogen oxides are released into the troposphere from a variety of biogenic and anthropogenic sources (Logan, 1983; IPCC, 1995; Lee et al., 1997). Approximately 40% of the global emissions, and the largest single source, results from the combustion of fossil fuels, which almost exclusively leads to emission directly into the planetary boundary layer, mainly in the form of NO. A small fraction (generally $\leqslant 10\%$) may be released as NO_2 (PORG, 1997), or is produced close to the point of emission from the termolecular reaction of NO with O_2:

$$2NO + O_2 \rightarrow 2NO_2. \tag{1}$$

The rate of this reaction is strongly dependent on the NO concentration. Thus, at high levels typical of those close to points of emission, the rate of conversion of NO to NO_2 is rapid (e.g. ca. $0.5\%\,s^{-1}$ at 1000 ppmv NO), but the significance of reaction (1) decreases dramatically as NO is diluted, with a fractional conversion rate of only $5\times10^{-6}\,s^{-1}$ at 1 ppmv NO. Under most tropospheric conditions, reaction (1) is insignificant, and the dominant pathway by which NO is converted to NO_2 is via the reaction with O_3 (see Fig. 1):

$$NO + O_3 \rightarrow NO_2 + O_2. \tag{2}$$

At a typical boundary layer concentration of 30 ppbv O_3, this reaction occurs on a timescale of ca. 1 min. During daylight hours, however, NO_2 is converted back to NO as a result of photolysis, which also leads to the regeneration of

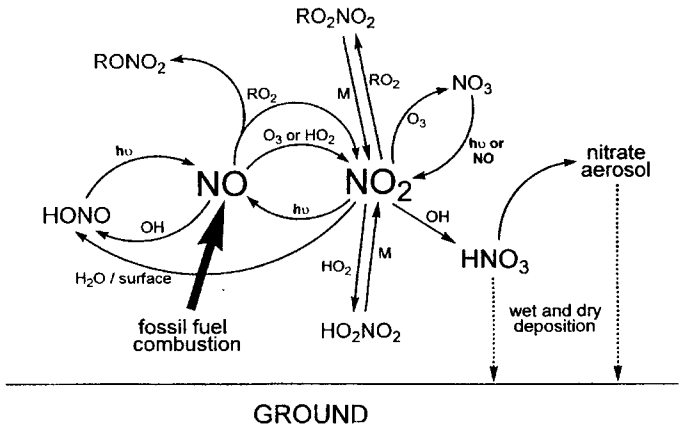

Figure 1. Daytime interconversions of oxidised nitrogen compounds in the troposphere.

O_3 as follows,

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

$$O(^3P) + O_2(+M) \rightarrow O_3(+M) \tag{4}$$

where M is a third body, most commonly N_2. Thus, reactions (2)–(4) constitute a cycle with no net chemistry. In the absence of competing interconversion reactions, this cycle leads to a photostationary state in which the concentrations of NO and NO_2 are related to the O_3 concentration by the following expression (Leighton, 1961):

$$[O_3] = (J_3[NO_2]/k_2[NO]) \tag{i}$$

where J_3 is the rate of NO_2 photolysis, and k_2 is the rate coefficient for the reaction of NO with O_3. As a result of this rapid interconversion, the behaviour of NO and NO_2 is highly coupled, and they are usually collectively referred to as NO_x. The lifetime of NO_2 with respect to photolysis in the boundary layer depends on latitude, season and time of day. Reported midsummer measurements of J_3 indicate that the minimum lifetime of NO_2 under conditions typical of the UK is of the order of 1.5 min, with a mean daylight lifetime of ca. 3 min (e.g., Carpenter et al., 1998). In the wintertime, this is typically a factor of two or three longer.

Other daytime chemical processes interconverting the NO_x species generally involve free radicals. Of particular importance are the hydroperoxy radical (HO_2) and organic peroxy radicals (RO_2), which are mainly produced in the troposphere as intermediates in the photochemical oxidation of carbon monoxide (CO) and volatile organic compounds, as described in Section 3. Both HO_2

and RO_2 provide additional NO to NO_2 conversion routes to supplement reaction (2):

$$HO_2 + NO \rightarrow OH + NO_2, \tag{5}$$

$$RO_2 + NO \rightarrow RO + NO_2. \tag{6a}$$

However, since conversion of NO to NO_2 as a result of these reactions does not consume O_3, the subsequent photolysis of NO_2 (reaction (3)), followed by reaction (4), represents a net source of O_3. These reactions form the core of photochemical O_3 production in the troposphere for which NO_x, organic compounds and sunlight are essential ingredients, as discussed further in Section 3. The net production rate of O_3 resulting from this *fast photochemistry* is given by the expression:

$$d[O_3]/dt = (k_5[HO_2] + \Sigma k_{6a}[RO_2])[NO]. \tag{ii}$$

The production rate is very variable, because the peroxy radical concentration is a strong function of factors such as location, season, time of day and cloud cover. However, for an ambient NO concentration of 1–2 ppbv (typical of a UK rural site) and a total peroxy radical concentration of ca. 10 pptv, which has been observed in the UK under summertime conditions (Clemitshaw et al., 1997a), O_3 production rates of the order of 5–10 ppbv h^{-1} may be calculated.

Reactions (5) and (6a) also perturb the photostationary state, and observed deviations from equation (i) are therefore often interpreted in terms of the presence of significant concentrations of the peroxy radicals (Ridley et al., 1992; Cantrell et al., 1993a,1997a; Kleinman et al., 1995; Hauglustaine et al., 1996; Carpenter et al., 1998). A modified equation allowing for deviations can be defined as follows:

$$[O_3] + \Psi_{ox} = (J_3[NO_2]/k_2[NO]) \tag{iii}$$

where "Ψ_{ox}" represents the observed deviation, which is usually termed the *missing oxidant* (Cantrell et al., 1993b) and is effectively the ambient level of oxidising free radicals expressed as an O_3-*equivalent concentration*. If the observed deviation is a consequence of reactions (5) and (6a), then

$$\Psi_{ox} = \{(k_5[HO_2]/k_2) + (\Sigma k_{6a}[RO_2]/k_2)\} \tag{iv}$$

and the net O_3 production rate is $k_2[NO]\cdot\Psi_{ox}$. When significant deviations from the photostationary state are observed, Ψ_{ox} tends to show a diurnal variation consistent with that expected for photochemically derived free radicals (e.g., Cantrell et al., 1993c; Cape et al., 1994), and their capacity for oxidising

NO to NO_2 can readily be compared with that due to O_3. Where simultaneous measurements are available, Ψ_{ox} usually shows a positive correlation with the total ambient concentration of peroxy radicals, $[HO_2] + \Sigma[RO_2]$, measured using the chemical amplification technique (e.g., Cantrell et al., 1993b). However, the precise calculation of the total peroxy radical concentration from measurements of Ψ_{ox} using equation (iv) is often not possible, since the value of k_{6a} depends on the structure of the RO_2 radical, with currently measured values for a variety of radicals covering a range of more than a factor of three (e.g., Atkinson et al., 1997a). It is also possible that deviations from Eq. (i) result from reactions other than (5) and (6a) (e.g., see Calvert and Stockwell, 1983), and peroxy radical concentrations calculated by this method are typically higher than measured values by as much as factors of 2 to 4 (Cantrell et al., 1992,1993a,1996a,b,1997a; Hauglustaine et al., 1996; Volz-Thomas et al., 1998). These large discrepancies either imply significant errors in the measured data for NO_x, O_3, J_3 and peroxy radicals, or infer the presence of unidentified species which oxidise NO to NO_2, or both (Ridley et al., 1992; Cantrell et al., 1996a,1997a).

Other chemical transformations of NO_x lead to the generation of a variety of inorganic and organic oxidised nitrogen compounds. Oxidised nitrogen species of atmospheric significance are usually collectively referred to as "NO_y", which is taken to consist of NO, NO_2, higher oxides (NO_3 and N_2O_5), oxyacids (HNO_3, HO_2NO_2 and HONO), organic peroxy nitrates (RO_2NO_2), organic nitrates ($RONO_2$) and aerosol nitrate. The component of NO_y excluding NO and NO_2 is sometimes defined as "NO_z" (Volz-Thomas et al., 1995; Colvile et al., 1996). The majority of these species are generated during daylight, and their formation and removal chemistry is described in the subsections which follow. The significance of the formation of the higher oxides (NO_3 and N_2O_5), is greatest for nighttime tropospheric chemistry, and is therefore discussed in Section 4.

2.2. The formation and removal of oxyacids of nitrogen

The addition reactions of the NO_x species with HO_x radicals (OH and HO_2) lead to the generation of the oxyacids, nitric acid (HNO_3), peroxynitric acid (HO_2NO_2) and nitrous acid (HONO). The reaction of OH with NO_2 to form HNO_3, is of particular importance, since it provides the predominant chemical removal route for NO_x during daylight, and therefore plays a major role in controlling its concentration:

$$OH + NO_2(+M) \rightarrow HNO_3(+M). \qquad (7)$$

The boundary layer lifetime of NO_2 with respect to this reaction is ca. 1 d for a typical background OH concentration of 0.04 pptv (10^6 molecule cm^{-3}), which decreases to ca. 2 h for an elevated OH concentration of 0.4 pptv (10^7 molecule cm^{-3}) consistent with a photochemical episode. HNO_3 is therefore usually a significant component of NO_z (e.g., Fahey et al., 1986; Nielsen et al., 1995; Singh et al., 1996; Aneja et al., 1996; Harrison et al., 1999). It is removed comparatively efficiently from the troposphere by both wet and dry deposition (Huebert and Robert, 1985; Hov et al., 1987; Derwent et al., 1988; Dentener, 1993), and also by adsorption on, or reaction with, the tropospheric aerosol (Cox, 1988; Fenter et al., 1995).

The addition reaction of HO_2 with NO_2 leads to the formation of HO_2NO_2:

$$HO_2 + NO_2(+M) \rightleftharpoons HO_2NO_2(+M). \tag{8}$$

The lifetime of NO_2 with respect to this reaction in the sunlit boundary layer is typically of the order of 2 h ([HO_2] = 10 pptv; 2.5×10^8 molecule cm^{-3}). However, HO_2NO_2 is thermally unstable and only has a lifetime of the order of 30 s with respect to decomposition by the reverse reaction at 288 K and atmospheric pressure. Consequently, NO_2 is readily regenerated and the contribution of HO_2NO_2 to NO_z is believed to be limited, although this has not been confirmed by direct observations.

The addition reaction of OH with NO leads to the production of HONO, with the boundary layer lifetime of NO with respect to this reaction being ca. 2 d for [OH] = 0.04 pptv (10^6 molecule cm^{-3}), and ca. 5 h for [OH] = 0.4 pptv (10^7 molecule cm^{-3}):

$$OH + NO(+M) \rightarrow HONO(+M). \tag{9}$$

Once again, HONO only acts as a temporary reservoir for NO_x, because it is readily photolysed by near ultraviolet radiation, such that its photolysis lifetime is typically less than 1 h (see Section 3):

$$HONO + h\nu \rightarrow OH + NO. \tag{10}$$

As a result, HONO is unable to accumulate significantly during daylight hours, and is often undetectable or close to detection limits of current HONO instrumentation (30–100 pptv). Where daytime measurements of HONO are possible, it provides a potential tracer for OH radicals, provided its photolysis rate (J_{10}) and the concentration of NO are also measured:

$$[OH] = J_{10}[HONO]/k_9[NO]. \tag{v}$$

This relation only holds, however, if reaction (9) is the sole (or dominant) daytime source of HONO.

Observational data are consistent with the existence of additional thermal sources of HONO, which may operate throughout the diurnal cycle, leading to an accumulation of HONO during the night, followed by photolysis at sunrise (e.g. Harris et al., 1982; Kessler and Platt, 1984; Harrison et al., 1996). The available information is consistent with HONO production from heterogeneous reactions involving the NO_x species and H_2O, for which the following have been postulated:

$$2NO_2(g) + H_2O(ads) \rightarrow HNO_3(ads) + HONO(g), \quad (11)$$

$$NO(g) + NO_2(g) + H_2O(ads) \rightarrow 2HONO(g). \quad (12)$$

There have been numerous laboratory kinetic investigations of these reactions (England and Corcoran, 1974; Sakamaki et al., 1983; Pitts et al., 1984; Svensson et al., 1987; Jenkin et al., 1988). These studies indicate that reaction (11) is probably more important than reaction (12), but that the measured rates in laboratory reactors are typically too slow to explain the HONO concentrations observed in the atmosphere (Jenkin et al., 1988; Lammel and Cape, 1996). More recent studies have demonstrated, however, that carbonaceous surfaces (e.g. soot aerosols) are particularly reactive, and may represent an important substrate for HONO formation (Ammann et al., 1998; Kalberer et al., 1999).

Atmospheric observations are also mainly consistent with HONO formation by reaction (11) on land or aerosol surfaces. Kessler and Platt (1984) derived a conversion rate of NO_2 to HONO of ca. 0.6% h^{-1} in the urban boundary layer, from nighttime measurements in Juelich, Germany. Kitto and Harrison (1992) have confirmed that there is a surface source of nitrous acid by reaction of NO_2, and Harrison et al. (1996) have derived an effective rate coefficient of $5.6\times10^{-6}\times100/h\,s^{-1}$ (where h is the mixing height in m) for reaction (11) in the suburban boundary layer.

2.3. The formation and removal of organic nitrates

The reactions of the organic peroxy radicals (RO_2) with NO, in addition to converting NO to NO_2 as described above (reaction (6a)), also have minor channels leading to the production of organic nitrates ($RONO_2$):

$$RO_2 + NO(+M) \rightarrow RONO_2(+M). \quad (6b)$$

The majority of information available for these reactions is for simple alkyl peroxy radicals derived from the oxidation of alkanes which have been studied in some detail, and for the corresponding alkyl nitrate products (Carter and

Atkinson, 1989; Roberts, 1990; Atkinson, 1990; Lightfoot et al., 1992). Reaction channel (6b) is extremely minor for small peroxy radicals such as CH_3O_2 ($< 0.5\%$) and $C_2H_5O_2$ ($< 1.4\%$), but increases with radical size up to ca. 35% of the overall reaction for the secondary $C_8H_{17}O_2$ isomers under boundary layer conditions (Carter and Atkinson, 1989; Lightfoot et al., 1992). Reaction (6b) has been shown to be more important for secondary alkyl peroxy radicals than for isomeric primary radicals, but there is currently insufficient information to draw any firm conclusions for tertiary radicals. The limited information available for peroxy radicals containing oxygenated functional groups also suggests that the formation of $RONO_2$ species is less efficient than for the corresponding unsubstituted alkyl peroxy radicals (Lightfoot et al., 1992; Muthuramu et al., 1993; Atkinson, 1994; Eberhard et al., 1995).

Alkyl nitrates have been routinely detected in the atmosphere in numerous field studies over the past decade (e.g., Buhr et al., 1990; Flocke et al., 1991, 1998; Atlas et al., 1992; Shepson et al., 1993; Williams, 1994; O'Brien et al., 1995, 1997). For example, a series of nine C_1–C_5 alkyl nitrates has been detected, both in the boundary layer over southern England, and at various altitudes at locations over the North Atlantic (Williams, 1994). Although these measurements have shown the alkyl nitrates to be present at comparatively low levels in the springtime boundary layer (typically in the range 10–20 pptv for each of methyl, ethyl, 1 and 2 propyl and 2-butyl nitrate), the data also indicate that the compounds are comparatively stable under tropospheric conditions, persisting at a similar level in aged boundary layer air masses and being transported into the background troposphere. Laboratory studies have established that alkyl nitrates are insoluble in water, and do not readily transfer to the particulate phase (Roberts, 1990; Kames and Schurath, 1992), which indicates that they are ultimately degraded either by reaction with OH or by photolysis. For small alkyl nitrates, the major loss process is photolysis (Yang et al., 1993; Talukdar et al., 1997a; Zhu and Ding, 1997; Zhu and Kellis, 1997), which occurs on the timescale of about 2–4 weeks during spring and summer at northern mid-latitudes (Luke et al., 1989; Roberts and Fajer, 1989; Turberg et al., 1990; Clemitshaw et al., 1997b). For the larger compounds, however, attack of OH on the carbon skeleton becomes important (Atkinson, 1990,1994; Roberts, 1990). Consequently, for butyl and pentyl nitrates, removal by reaction with OH is competitive with photolysis, and the tropospheric lifetimes of the compounds become progressively shorter as the size of the carbon skeleton increases $> C_5$, owing to more rapid removal by reaction with OH. Although photolysis is known to release NO_x in the form of NO_2 (Roberts, 1990; Yang et al., 1993; Talukdar et al., 1997a; Zhu and Ding, 1997; Zhu and Kellis, 1997), and measurements of rate coefficients for OH radical reactions have been carried out (Roberts, 1990; Shallcross et al., 1997; Talukdar et al., 1997b), there

are currently no reported studies of the products of the reactions of OH with alkyl nitrates.

Ambient measurements of a series of organic nitrates containing hydroxy groups in the position β to the nitrate group (i.e., β-nitrooxy alcohols) have also been reported (O'Brien et al., 1995, 1997). Under the photochemical episodic conditions of those field studies, the nitrates were believed to be formed exclusively from the reactions of β-hydroxy peroxy radicals with NO (reaction (6b)). Such peroxy radicals are generated predominantly from the OH-initiated oxidation of alkenes, and the observations confirmed their significant participation in regional scale O_3 formation downwind of major population centres (Toronto and Vancouver). It should be noted, however, that β-nitrooxy alcohols and other bifunctional organic nitrates may also be generated from the NO_3 radical initiated oxidation of alkenes, which occurs predominantly at night-time (as discussed further in Section 4.2).

There is only limited information available on the further oxidation of bifunctional oxidised organic nitrogen compounds in general, and this relates solely to the rate of removal (e.g. Roberts and Fajer, 1989; Zhu et al., 1991; Barnes et al., 1993). It is probable that β-nitrooxy alcohols will be removed predominantly by reaction with OH. This may ultimately re-release NO_x, if the oxidation occurs in the gas phase. However, as the further oxidation is likely to generate intermediate products containing a large number of polar substituent groups (e.g., $-ONO_2$, –OH, –CHO), uptake into aqueous droplets may also be particularly important (Kames and Schurath, 1992).

2.4. The formation and removal of organic peroxy nitrates

The reactions of NO_2 with organic peroxy radicals (RO_2) lead to the production of compounds most commonly referred to as *organic peroxy nitrates* (RO_2NO_2), although such compounds are also (more correctly) called *peroxycarboxylic nitric anhydrides* by some authors (see discussion in Roberts, 1990):

$$RO_2 + NO_2(+M) \rightleftharpoons RO_2NO_2(+M). \qquad (13)$$

Conversion of NO_2 to organic peroxy nitrates by reaction (13) occurs only about an order of magnitude more slowly than photolysis (reaction (3)). The thermal stability of peroxy nitrates is, however, strongly dependent on the structure of the organic group "R", as shown in Table 1. Simple alkyl peroxy derivatives, such as $CH_3O_2NO_2$, are unstable and decompose on the timescale of about 1 s under typical boundary layer conditions. Consequently, the equilibrium (13) is rapidly established, with only a very small amount of NO_x sequestered in the form of the peroxy nitrate. The presence of electron-withdrawing substituents in the organic group, however, tends to increase the

Table 1. Thermal decomposition rates (k_{-13}) and lifetimes (τ) for a series of peroxy nitrates (RO_2NO_2) at 298 K and 760 Torr

RO_2NO_2 (+M) $\rightarrow$ $RO_2 + NO_2$ (+M)		
R	k_{-13} s^{-1}	τ
H	0.076[a]	13 s
CH_3	1.6[b]	0.61 s
C_2H_5	4.0[b]	0.25 s
CH_3CO	0.00033[b]	50 min
CH_2=CH(CH_3)CO	0.00035[c]	48 min

[a]Based on parameters recommended by Atkinson et al. (1997b).
[b]Based on parameters recommended by Atkinson et al. (1997a).
[c]Roberts and Bertman (1992).

thermal stability of the compounds (Lightfoot et al., 1992). Thus, a carbonyl (C=O) group adjacent to the peroxy radical centre has a particularly marked effect on the strength of the OO–NO_2 bond, and the resultant *peroxy acyl nitrates* are significantly more stable than the alkyl peroxy derivatives. The simplest example of this class of compound, peroxy acetyl nitrate or PAN ($CH_3C(O)OONO_2$), was first detected in the atmosphere about thirty years ago (Stevens, 1969), and subsequent field measurements have established that PAN often makes a significant contribution to NO_z in the boundary layer, particularly at high northern latitudes (e.g., Singh et al., 1992; Bottenheim et al., 1993; Solberg et al., 1997). Furthermore, PAN is invariably more abundant in ambient air than its higher homologues (Singh and Salas, 1989; Walega et al., 1992; Singh et al., 1993; Altschuller, 1993). This is mainly because the precursor peroxy radical, $CH_3C(O)O_2$, is potentially produced from the degradation of a large number of organic compounds $\geqslant C_2$, whereas the abundance of potential source compounds systematically diminishes for the larger $RC(O)O_2$ radicals.

Whereas PAN itself is potentially generated from many organic compounds (e.g., Derwent et al., 1998; Jenkin et al., 1999), other peroxy acyl nitrates may be generated from only a limited number of organic precursors. This is particularly true for those peroxy acyl nitrates which contain other specific functional groups. One such compound which has received particular interest (e.g., Bertman and Roberts, 1991; Williams et al., 1997), is peroxy methacroyl nitrate or MPAN (CH_2=C(CH_3)C(O)OONO$_2$). The only known source of MPAN is the degradation of methacrolein which, in turn, is only believed to be generated significantly from the abundant natural hydrocarbon isoprene. Consequently, MPAN represents a unique marker for isoprene degradation, and is generally present at about 10% of the PAN concentration under conditions where isoprene represents the dominant local hydrocarbon emis-

Table 2. Thermal decompostion lifetimes (τ) of PAN as a function altitude at mid latitudes[a,b]

$CH_3C(O)OONO_2$ (+M) $\rightarrow$ $CH_3C(O)O_2 + NO_2$ (+M)			
Approx. altitude/km	T (K)	P (Torr)	τ
0	288	760	4.2 hr
2.5	273	540	2.4 day
5.0	258	390	46 day
7.5	243	280	3.4 yr
10.0	228	200	144 yr

[a]Based on parameters recommended by Atkinson et al. (1997a).
[b]The increase of τ with altitude is almost entirely due to the decrease in temperature.

sion (Williams et al., 1997). Interestingly, however, current knowledge of isoprene degradation is also consistent with significant generation of other peroxy acyl nitrates containing additional hydroxy functionalities (Jenkin et al., 1999), namely $HOCH_2C(O)OONO_2$, $HOCH_2C(CH_3)=CHC(O)OONO_2$ and $HOCH_2CH=C(CH_3)C(O)OONO_2$, and such compounds are represented in some detailed chemical mechanisms (e.g., Jenkin et al., 1997a; Saunders et al., 1997). Indeed there are almost certainly many unidentified peroxy acyl nitrates containing additional oxygenated functionalities present in the atmosphere which are difficult to detect with established techniques.

Laboratory studies have established that PAN (and other peroxy acyl nitrates) typically has a lifetime of the order of hours with respect to thermal decomposition at temperatures characteristic of the planetary boundary layer (e.g., Lightfoot et al., 1992; Wallington et al., 1992; Roberts and Bertman, 1992; Grosjean et al., 1994a,b). As shown in Table 2, however, the stability of PAN is strongly dependent on temperature, its lifetime increasing dramatically as the temperature is lowered. Consequently, under meteorological conditions characterised by rapid vertical transport accompanied by rapid decrease in temperature, PAN and other peroxy acyl nitrates become stable molecules which may only be degraded to release NO_x on much longer timescales, either by reaction with OH radicals, or by photolysis (e.g., Talukdar et al., 1997a,b). At higher altitudes, concentrations of PAN have been shown to exceed those of the NO_x species (Singh et al., 1992, 1993). Consequently, the long-range transport of peroxy acyl nitrates (and possibly the organic nitrates referred to in Section 2.3) is believed to provide a major source of NO_x in the background troposphere (Singh et al., 1992; Horowitz et al., 1998; Thakur et al., 1999).

3. The role of volatile organic compounds in photochemical ozone formation

3.1. General description

It has been established for some decades (Haagen-Smit and Fox, 1954, 1956; Leighton, 1961) that the formation of O_3 in the troposphere is promoted by the presence of volatile organic compounds (VOCs), NO_x and sunlight, and the mechanism by which this occurs is now well understood (e.g., Atkinson, 1990, 1994, 1998a,b). The sunlight initiates the process by providing near ultra-violet radiation which dissociates certain stable molecules, leading to the formation of hydrogen-containing free radicals (HO_x). In the presence of NO_x, these free radicals catalyse the oxidation of VOCs, ultimately to carbon dioxide and water vapour. Partially oxidised organic species such as aldehydes, ketones and carbon monoxide are produced as intermediate oxidation products, with O_3 formed as a by-product. An enormous variety of VOC classes may be emitted from numerous anthropogenic and biogenic sources (e.g. Rudd, 1995; Guenther et al., 1995) and, depending on location, either or both categories can make a major contribution to photochemical ozone formation (e.g., Sillman, 1999, and references therein).

The details of the chemistry are shown schematically in Fig. 2 for the oxidation of a generic saturated hydrocarbon, RH (i.e., an alkane), into its first generation oxidised products. In common with the tropospheric oxidation of most organic compounds, the oxidation is initiated by reaction with the hydroxyl radical (OH), leading to the following rapid sequence of reactions:

$$OH + RH \rightarrow R + H_2O, \tag{14}$$

$$R + O_2(+M) \rightarrow RO_2(+M), \tag{15}$$

$$RO_2 + NO \rightarrow RO + NO_2, \tag{6a}$$

$$RO \rightarrow\rightarrow \text{carbonyl product(s)} + HO_2, \tag{16}$$

$$HO_2 + NO \rightarrow OH + NO_2. \tag{5}$$

Since OH is regenerated, this mechanism is a catalytic cycle with OH, R (alkyl radical), RO_2, RO (alkoxy radical) and HO_2 acting as chain propagating radicals. Reactions (5) and (6a), involving the peroxy radicals, play a key role in O_3 formation by oxidising NO to NO_2. As discussed in Section 2.1, NO_2 is efficiently photodissociated by near ultra-violet and visible radiation to generate O_3 by reactions (3) and (4).

The abbreviated reaction (16) shows that the RO radical is converted into HO_2 as part of the chain propagating process leading to the regeneration of

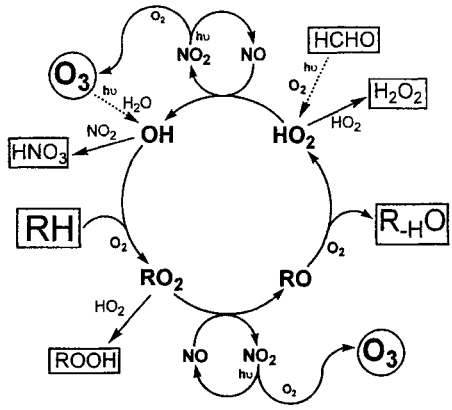

Figure 2. Schematic representation of the free radical-catalysed oxidation of a generic saturated hydrocarbon, RH, to its first generation oxidised product, $R_{-H}O$. The key role played by the NO_x species in the chain-propagating process is also illustrated, which leads to the generation of O_3 as a by-product. The major sources and sinks of the free radicals are also shown (detailed discussion is given in the text).

OH. The mechanism of reaction (16) is strongly dependent on the structure of RO, and therefore on the structure of the parent organic compound. For small alkoxy radicals (e.g., CH_3O), conversion to HO_2 is achieved in a single step by reaction with O_2, also yielding an aldehyde or ketone oxidation product $R_{-H}O$ (e.g., in the case of CH_3O, the product is formaldehyde, HCHO):

$$RO + O_2 \rightarrow R_{-H}O + HO_2. \tag{16}$$

Larger or more complex RO radicals may also thermally decompose or isomerise (if they contain a carbon chain $\geqslant C_4$). In these cases, the mechanism is frequently multi-step, possibly involving further peroxy and oxy radical intermediates but, in the majority of cases, still ultimately yielding HO_2. Assuming reaction (16′) is the fate of RO, the overall chemistry of the oxidation of RH into its first generation product $R_{-H}O$ (i.e., one cycle in Fig. 2) is given by the following overall equation:

$$RH + 4O_2 \rightarrow R_{-H}O + H_2O + 2O_3.$$

Thus, the oxidation of one molecule of RH to $R_{-H}O$ (catalysed by HO_x and NO_x) is accompanied by the generation of two molecules of O_3. As discussed in the next section and shown in the figure, O_3 photolysis is a major source of HO_x radicals. It may therefore be regarded as an autocatalyst, since it stimulates its own production via the chemistry described above.

The further oxidation of the first generation product, $R_{-H}O$, also follows the same general pattern (i.e. generating O_3), and subsequent organic products are, in turn, oxidised until CO_2 is eventually produced. The penultimate oxidised product is commonly CO, for which the atmospheric oxidation of organic compounds is therefore the major global source. Its oxidation to CO_2 (achieved by reaction with OH radicals) also generates HO_2, and therefore O_3 by the chemistry described above:

$$OH + CO \rightarrow H + CO_2, \tag{17a}$$

$$H + O_2(+M) \rightarrow HO_2(+M), \tag{18}$$

$$OH + CO(+M) \rightarrow HOCO(+M), \tag{17b}$$

$$HOCO + O_2 \rightarrow HO_2 + CO_2. \tag{19}$$

In the polluted troposphere, direct emissions of CO as a result of combustion processes are often the major local source, and therefore make some contribution to O_3 production in the boundary layer.

The chemistry outlined above specifically describes the oxidation of an alkane. The OH radical initiated oxidation of other VOCs (and of the oxygenated products of alkane degradation referred to above) generally occurs by very similar mechanisms, the details of which are reasonably well understood. For many small VOCs (e.g., methane, ethane, ethene, methanol, *t*-butanol, acetaldehyde, acetone and dimethyl ether), the rates and products of the elementary reactions involved in their oxidation have received a great deal of attention, and the mechanisms are well established (see, for example, Atkinson, 1994, 1997; Atkinson et al., 1997a; Jenkin et al., 1997a). For many other VOCs, oxidation mechanisms defined by analogy are fully consistent with available experimental data, and it is also possible to predict with reasonable confidence oxidation mechanisms for some compounds for which little or no experimental data exist, by use of structure–reactivity correlations (e.g., Atkinson, 1987; Dagaut et al., 1989; Kwok and Atkinson, 1995; Jenkin et al., 1997a; Porter et al., 1997). In view of the very large number of VOCs emitted into the atmosphere, the use of such correlations is essential in mechanism construction. There are, however, still significant uncertainties in the oxidation mechanisms of some common complex VOCs, such as aromatic hydrocarbons and terpenes, although new data are constantly emerging (Kwok et al., 1997; Atkinson and Arey, 1998; Barnes et al., 1998; BIOVOC, 1998; Calogirou et al., 1999).

The rate of oxidation of VOCs (and therefore production of O_3) is governed by the ambient concentration of the catalytic HO_x radicals, which is controlled by a balance between production and removal routes. In the subsections which follow, the major sources and sinks of HO_x radicals are described.

3.2. *Sources of HO_x radicals*

HO_x radicals are generated by the photolysis of certain atmospheric trace species. A strict definition of HO_x radicals would include only OH and HO_2. For the purposes of the present discussion, however, organic radicals are also classed as HO_x since (as described above and shown in Fig. 2), they are readily converted to OH and HO_2 under atmospheric conditions.

The incident sunlight which penetrates to the lower layers of the atmosphere is almost entirely at wavelengths longer than ca. 290 nm, and potential radical precursors are therefore those species which absorb light at these wavelengths. A further requirement is that the energy of the absorbed radiation is sufficient to break the weakest bond in the molecule. Major photolytic sources of HO_x radicals, listed in Table 3, are the photolysis of O_3 and aldehydes. In global terms, the most important tropospheric source of free radicals results from the photolysis of O_3 in its near ultra-violet band (e.g., Meier et al., 1997):

$$O_3 + h\nu \rightarrow O(^1D) + O_2, \tag{20}$$

$$O(^1D) + H_2O \rightarrow 2OH. \tag{21}$$

However, the required wavelengths are near the atmospheric cut-off at ca. 290 nm, where both the O_3 absorption cross-section and the quantum yield for $O(^1D)$ formation are wavelength dependent, decreasing with increasing wavelength (e.g. see discussion in Ravishankara et al., 1998). Consequently, the photolysis rate J_{20} varies strongly with the changes in the atmospheric pathlength which accompany variations in altitude, latitude and season, and other sources of free radicals may be more important under specific conditions. A further influence on the production rate of OH results from competing "quenching" reactions for the electronically excited $O(^1D)$ atom:

$$O(^1D)(+M) \rightarrow O(^3P)(+M), \tag{22}$$

$$O(^3P) + O_2(+M) \rightarrow O_3(+M). \tag{4}$$

Available kinetic data for reactions (21) and (22) (Atkinson et al., 1997b) suggest that the fractional conversion, f, of $O(^1D)$ into OH is given approximately by the expression

$$f = P_{H_2O}/(P_{H_2O} + 0.13(P - P_{H_2O})) \tag{vi}$$

where P_{H_2O} is the partial pressure of water vapour and P is the total pressure. Thus, this factor has to be taken into consideration when comparing the relative importance of photolysis reactions as free radical sources.

Table 3. Comparison of boundary layer photolytic radical sources for various scenarios under midsummer and midwinter conditions

Reaction	Photolysis rate[a] (10^{-6} s^{-1})	Precursor concentration (10^9 molecule cm^{-3})	Radical production rate (10^4 molecule cm^{-3}s^{-1})
Midsummer			
(a) Rural average			
$O_3 \rightarrow O(^1D) + O_2$	12.8	981 (40.0 ppbv)[b]	252[c]
$HCHO \rightarrow H + HCO$	15.7	41.0 (1.67 ppbv)[d]	129
$RCHO \rightarrow R + HCO$	9.53[e]	20.4 (0.83 ppbv)[d]	38.9
(b) Rural episode			
$O_3 \rightarrow O(^1D) + O_2$	12.8	2450 (100 ppbv)[f]	651[c]
$HCHO \rightarrow H + HCO$	15.7	94.0 (3.83 ppbv)[g]	295
$RCHO \rightarrow R + HCO$	9.53[e]	39.5 (1.61 ppbv)[g]	75.3
(c) Urban average			
$O_3 \rightarrow O(^1D) + O_2$	12.8	613 (25 ppbv)[h]	157[c]
$HCHO \rightarrow H + HCO$	15.7	245 (10 ppbv)[i]	769
$RCHO \rightarrow R + HCO$	9.53[e]	123 (5 ppbv)[i]	234
Midwinter			
(a) Rural average			
$O_3 \rightarrow O(^1D) + O_2$	0.486	794 (30 ppbv)[b]	7.73[c]
$HCHO \rightarrow H + HCO$	2.42	22.8 (0.86 ppbv)[k]	11.0
$RCHO \rightarrow R + HCO$	1.46[e]	17.5 (0.66 ppbv)[k]	5.11
(b) Urban average			
$O_3 \rightarrow O(^1D) + O_2$	0.486	397 (15 ppbv)[h]	3.87[c]
$HCHO \rightarrow H + HCO$	2.42	397 (15 ppbv)[i]	192[j]
$RCHO \rightarrow R + HCO$	1.46[e]	199 (7.5 ppbv)[i]	58.1

[a]Daylight average, 50° Lat., calculated using parameters reported by Jenkin et al. (1997b).
[b]Typical daytime concentrations at rural sites in the southern UK (PORG, 1997).
[c]Calculated assuming 11 Torr water vapour.
[d]Mean of data measured at Harwell, UK April–September 1993–1997 (Solberg, 1999; Dollard and Jenkin, 1999).
[e]Using propanal (propionaldehyde) as a representative.
[f]Typical level during photochemical pollution episode in the southern UK (PORG, 1997).
[g]Simulated concentration for southern UK under episodic conditions (Dollard and Jenkin, 1999).
[h]Typical daytime concentrations at urban centre sites in the UK (PORG, 1997).
[i]Typical seasonal average for European cities (Dollard and Jenkin, 1999).
[j]Harrison et al., 1996.
[k]Mean of data measured at Harwell, UK October–March 1993–1997 (Solberg, 1999; Dollard and Jenkin, 1999).

As shown in Table 3, the photolysis of HCHO (reaction (23)) makes an important contribution to free radical production at the concentrations observed in the rural UK, and dominates radical production under urban conditions, when the concentration of O_3 tends to be suppressed to a certain extent by reaction

with NO (reaction (2)), and the concentration of HCHO is elevated due to high local emissions or production rates from hydrocarbon oxidation (see above):

$$\mathrm{HCHO} + h\nu \rightarrow \mathrm{H} + \mathrm{HCO}, \tag{23}$$

$$\mathrm{RCHO} + h\nu \rightarrow \mathrm{R} + \mathrm{HCO}, \tag{24}$$

$$\mathrm{H} + \mathrm{O_2}(+\mathrm{M}) \rightarrow \mathrm{HO_2}(+\mathrm{M}), \tag{18}$$

$$\mathrm{R} + \mathrm{O_2}(+\mathrm{M}) \rightarrow \mathrm{RO_2}(+\mathrm{M}), \tag{15}$$

$$\mathrm{HCO} + \mathrm{O_2} \rightarrow \mathrm{HO_2} + \mathrm{CO}. \tag{25}$$

Similarly, the photolysis of other aldehydes (reaction (24)) can collectively make a significant contribution to radical production, particularly in polluted regions. Clearly, the photolysis of HCHO, and to a lesser extent RCHO, can play an important role in the initiation of summertime pollution at urban locations, when O_3 concentrations may initially be significantly suppressed.

Also worthy of note is the photolysis of HONO (reaction 10), which is very efficient under both summertime and wintertime conditions, and is a potentially important free radical source, despite being present at very low concentrations during daylight hours. On the basis of a daytime concentration of 100 pptv, typically observed in urban locations (Kitto and Harrison, 1992; Harrison et al., 1996; Andres Hernandez et al., 1996), and typical mid-latitude photolysis rates of ca. $10^{-3}\ s^{-1}$, HONO photolysis potentially makes a major contribution to free radical production compared with the reactions shown in Table 3. However, since a large proportion of the observed daytime HONO is derived from the reaction of OH with NO, particularly under summertime conditions,

$$\mathrm{OH} + \mathrm{NO}(+\mathrm{M}) \rightarrow \mathrm{HONO}(+\mathrm{M}) \tag{9}$$

the net radical source is invariably substantially lower than the actual flux through the photolysis reaction. Thus, only HONO generated from alternative sources (e.g., thermal heterogeneous reactions of NO_x and water vapour as described in Section 2.2, or direct emission in vehicle exhaust) leads to net radical production upon photolysis. This is particularly significant immediately after sunrise, when observed concentrations of HONO are generally at their highest owing to its nighttime generation from thermal reactions, and accumulation in the absence of sunlight (Harris et al., 1982; Kessler and Platt, 1984; Kitto and Harrison, 1992; Harrison et al., 1996). Consequently, HONO photolysis potentially provides a pulse of free radical production in the early morning when the photolysis rate of O_3 and aldehydes is very slow owing to the long atmospheric pathlength. This has been confirmed by boundary layer model calculations (Harris et al., 1982; Jenkin et al., 1988) which have demonstrated a

substantial enhancement of early morning OH radical production, following the photolysis of HONO, and increased O_3 generation.

As discussed further in Section 3.5, another significant source of HO_x radicals throughout the diurnal cycle results from the reactions of O_3 with alkenes. Paulson and Orlando (1996) have demonstrated that these reactions are possibly major daytime sources of HO_x under some urban settings, even exceeding radical production rates from the photolysis reactions discussed above.

3.3. Sinks and reservoirs for HO_x radicals

HO_x radicals are removed from the atmosphere by a variety of termination reactions. The molecular products of these reactions are usually termed reservoirs, since the possibility of HO_x regeneration through thermal decomposition or photolysis often exists. The lifetimes of reservoirs with respect to these processes are very variable, and even for a given reservoir, may be a strong function of time and location (i.e., temperature, pressure, solar intensity). If a reservoir is short-lived, it has only a minor effect on HO_x (e.g., the formation and thermal decomposition of HO_2NO_2 in the boundary layer, reaction (8)). If the reservoir is comparatively stable with respect to thermal decomposition or photolysis, however, it is likely that its removal by either physical processes (e.g., dry deposition) or chemical ones (e.g., reaction with OH radicals) becomes competitive or even dominant. Since this precludes the quantitative regeneration of HO_x radicals, the formation of the reservoir represents a sink for HO_x radicals. In addition, the formation and transport of reservoirs with intermediate thermal lifetimes in the boundary layer (in particular PAN), can lead to significant net radical removal locally (e.g., Sillman and Samson, 1995), with the possibility of subsequent radical regeneration.

On the basis of measured rate coefficients (Atkinson et al., 1997a,b; DeMore et al., 1997), the most significant tropospheric sinks for HO_x radicals involve either the mutual termination of two HO_x species,

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2, \tag{26}$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2, \tag{27}$$

$$OH + HO_2 \rightarrow H_2O + O_2, \tag{28}$$

or the removal of HO_x by reaction with the NO_x species by the following reactions:

$$OH + NO_2(+M) \rightarrow HNO_3(+M), \tag{7}$$

$$RO_2 + NO(+M) \rightarrow RONO_2(+M). \tag{6b}$$

Table 4. Illustrative comparison of boundary layer HO_x radical removal rates from major sink reactions in the southern UK[a]

Midsummer, 50° Lat		Urban[b]	Rural[c]	Rural episode[d]
$HO_x + HO_x$ reactions				
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	(26)	42	42	260
$RO_2 + HO_2 \rightarrow ROOH + O_2$	(27)	28	28	320
$OH + HO_2 \rightarrow H_2O + O_2$	(28)	7.0	7.0	94
$HO_x + NO_x$ reactions				
$OH + NO_2 (+M) \rightarrow HNO_3 (+M)$	(7)	1300	280	1100
$RO_2 + NO (+M) \rightarrow RONO_2 (+M)$	(6b)	470	23	48

[a]Units 10^4 molecule cm^{-3} s^{-1}. The figures given are based on illustrative midday reactant concentrations, inferred from ambient measurements and modelling studies appropriate to the southern UK, as given in the following notes.

[b]Urban conditions, $[OH] = 1.6\times10^6$ molecule cm^{-3}; $[HO_2] = 2.0\times10^8$ molecule cm^{-3}; $[RO_2] = 1.0\times10^8$ molecule cm^{-3}; $[NO] = [NO_2] = 6.2\times10^{11}$ molecule cm^{-3} (ca. 25 ppbv).

[c]Rural conditions, $[OH] = 1.6\times10^6$ molecule cm^{-3}; $[HO_2] = 2.0\times10^8$ molecule cm^{-3}; $[RO_2] = 1.0\times10^8$ molecule cm^{-3}; $[NO] = 3.0\times10^{10}$ molecule cm^{-3} (ca. 1.2 ppbv) $[NO_2] = 1.3\times10^{11}$ molecule cm^{-3} (ca. 5 ppbv).

[d]Rural episode conditions, $[OH] = 8.5\times10^6$ molecule cm^{-3}; $[HO_2] = 5.0\times10^8$ molecule cm^{-3}; $[RO_2] = 4.5\times10^8$ molecule cm^{-3}; $[NO] = 1.4\times10^{10}$ molecule cm^{-3} (ca. 0.6 ppbv) $[NO_2] = 9.5\times10^{10}$ molecule cm^{-3} (ca. 3.9 ppbv).

As illustrated in Table 4, the relative importance of these reactions depends strongly on ambient conditions. Reactions (26)–(28) show a second order (quadratic) dependence on the concentration of HO_x and therefore vary greatly with time of day, location and season. Reactions (6b) and (7) involving NO_x are clearly much more important in the boundary layer over populated areas than in remote tropospheric environments, owing to the higher levels of NO_x. As discussed in Section 2.3, the efficiency of reaction (6b) relative to the alternative channel (6a) is a strong function of the size and structure of the RO_2 radical. Consequently the importance of reaction (6b) as a radical sink is influenced by the precise composition of the peroxy radical population. The data presented in Table 4 were calculated assuming reaction channel (6b) accounts for 1% of the overall reaction, which is consistent with the major contribution to the RO_2 radical population being made by small peroxy radicals such as CH_3O_2 and $C_2H_5O_2$, and oxygenated peroxy radicals such as $HOCH_2CH_2O_2$ and $CH_3C(O)O_2$.

The data presented in Table 4 provide an illustrative comparison, and clearly only consider selected boundary layer conditions. Nevertheless, the data demonstrate that reaction (7) tends to be the major radical sink for conditions appropriate to the boundary layer in the UK and other populated regions.

This reaction totally dominates radical removal at urban levels of NO_2, and also makes the main contribution under representative rural conditions. At the elevated radical concentrations consistent with a photochemical episode in the southern UK, however, reactions (26) and (27) compete with reaction (7), owing to their second-order dependence on $[HO_x]$. At other locations with lower levels of NO_x, or high local emissions of natural hydrocarbons (in particular, isoprene), reactions (26) and (27) are often the dominant radical removal processes.

Since reactions (7), (26) and (27) are collectively the major radical sinks, the overall removal rate of HO_x (φ) is given by the following equation, to a first approximation:

$$\varphi = k_7[OH][NO_2] + 2k_{26}[HO_2]^2 + 2k_{27}[HO_2][RO_2]. \qquad \text{(vii)}$$

An additional contribution to radical removal is made by reactions (6b) and (28). However, reaction (6b), involving NO_x, is generally minor in comparison with reaction (7), and the second order reaction (28) is minor in comparison with reactions (26) and (27), although it does gain in significance in the middle and upper troposphere.

In addition to being an important radical sink, the self-reaction of HO_2 (reaction (26)) is the major source of hydrogen peroxide (H_2O_2) in the atmosphere. Consequently, H_2O_2 is a further indicator of free-radical driven photochemical processes (e.g., Kleinman, 1986; Ayers et al., 1992), and it is routinely measured in the polluted and remote planetary boundary layer (e.g., Dollard et al., 1991; Slemr and Tremmel, 1994). Similarly, reaction (27) for a variety of organic peroxy radicals leads to the generation of analogous organic hydroperoxides (ROOH), which have been detected in numerous field studies (e.g., Hellpointer and Gab, 1989; Hewitt and Kok, 1991; Slemr and Tremmel, 1994; Jackson and Hewitt, 1996; Staffelbach et al., 1996; Ayers et al., 1996). H_2O_2 readily transfers to the aqueous phase, and is particularly important as an oxidant for sulphur dioxide (e.g., Penkett et al., 1979; Martin and Damschen, 1981; Chandler et al., 1988; Gervat et al., 1988).

3.4. Sensitivity of O_3 formation chemistry to changes in NO_x and VOC concentration

The production of O_3 from the ultra-violet irradiation of mixtures of VOCs and NO_x in air was first demonstrated in the smog chamber studies of Haagen-Smit and coworkers (e.g., Haagen-Smit and Fox, 1954,1956). The peak O_3 concentrations generated from various initial concentrations of NO_x and VOCs were usually presented as an O_3 isopleth diagram of the form shown in Fig. 3, in

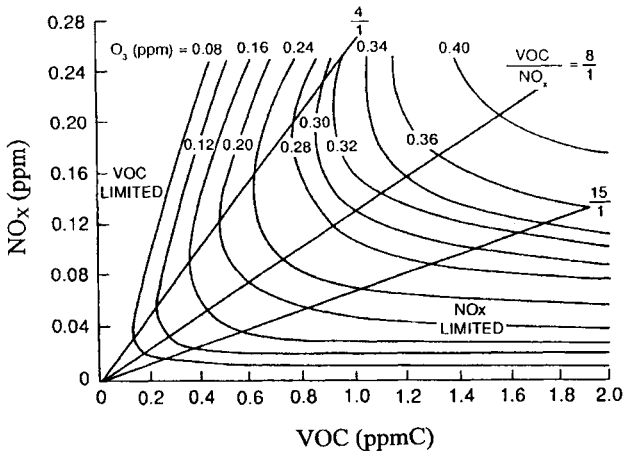

Figure 3. Example of an isopleth diagram illustrating calculated peak O_3 concentrations generated from various initial concentrations of NO_x and a specified VOC mixture using the US EPA empirical kinetic modelling approach (diagram adapted from Dodge, 1977). Although the methodology was originally developed for highly polluted scenarios, and the reagent concentrations on the axes are thus significantly greater than typically observed in the boundary layer, the characteristic shape of the O_3 isopleths as a function of VOC/NO_x ratio also applies to lower reagent concentrations (detailed discussion is given in the text).

which initial mixture compositions giving rise to the same peak O_3 concentration are connected by the appropriate isopleth. Although such diagrams were originally defined by experiment, the detailed chemistry leading to O_3 formation is now well understood, and isopleth diagrams can be generated from modelling studies using validated chemical mechanisms. In this way, diagrams can be generated for different VOCs (or VOC mixtures) and for different levels of solar intensity. Such diagrams are sometimes used to assess the effect on O_3 which would result from NO_x and VOC emissions control strategies (e.g., Dodge, 1977; NRC, 1991). It is clear from Fig. 3 that the influence of changing the concentration of NO_x or VOCs on the production of O_3 is strongly dependent on the ambient conditions (in particular on the relative concentrations of NO_x and VOCs). In this subsection, some features of the isopleth diagram are explained in terms of the chemistry described in the preceding subsections, with the species RH as a representative VOC.

The propensity for O_3 formation in a given air mass is essentially proportional to the number of free radical-propagated cycles (in Fig. 2) which can occur before radical removal. This is usually referred to as the chain-length for O_3 formation. Thus, when considering the influence of changing the concentration of NO_x or VOC on the production of O_3, it is the effect of such a change on the chain-length which is important. This is determined primarily

by the effect the change has on the rate of the chain terminating reactions (i.e., the radical sinks) compared with the competing chain propagating reactions.

Let us first consider the situation when the relative concentration $[NO_x]/[VOC]$ is high, the condition usually referred to as VOC limited. As indicated in the previous subsection, the dominant chain terminating reaction under these circumstances is reaction (7). As shown in Fig. 2, the competing chain propagating reaction is reaction (14), which leads to O_3 formation:

$$OH + RH \rightarrow R + H_2O, \tag{14}$$

$$OH + NO_2(+M) \rightarrow HNO_3(+M). \tag{7}$$

Clearly, a decrease in the concentration of RH, which might result from VOC emission controls, would decrease the chain length and hence the rate of O_3 formation. In contrast, a decrease in the concentration of NO_2, which might result from NO_x emission controls, would increase the chain length and hence the rate of O_3 formation unless a simultaneous reduction in the concentration of RH occurs. Thus, under VOC-limited conditions, O_3 formation correlates positively with the ratio $[VOC]/[NO_x]$, and the O_3 isopleths tend towards lines which pass though the origin (i.e., lines of constant $[VOC]/[NO_x]$) in this region of the diagram.

At high $[VOC]/[NO_x]$ ratios, or NO_x-limited conditions, the dominant chain-terminating reactions are (26) and (27). As discussed in the previous subsection, this circumstance is more readily achieved at higher total radical concentrations, so that the $[VOC]/[NO_x]$ ratio required for NO_x-limited conditions to prevail is also influenced by the solar intensity. As presented schematically in Fig. 2, the ozone formation chain length under these conditions is determined by a competition between reactions (5) and (26),

$$HO_2 + NO \rightarrow OH + NO_2, \tag{5}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2, \tag{26}$$

and between reactions (6a) and (27):

$$RO_2 + NO \rightarrow RO + NO_2, \tag{6a}$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2. \tag{27}$$

In contrast to the VOC-limited conditions, the key chain propagating reactions (5) and (6a) involve NO_x and, consequently any reduction in NO_x decreases the O_3 formation chain length. Since RH is not itself directly involved in these competitions, the O_3 formation chain length is insensitive to changes

in the level of RH which might result from VOC emission control. Thus, under NO_x-limited conditions, O_3 formation correlates positively with $[NO_x]$, and the O_3 isopleths tend towards lines which run parallel with the VOC axis (i.e., lines of constant $[NO_x]$) in this region of the diagram. It should be noted, however, that variation of the concentration of some VOCs has an effect on O_3 formation under NO_x-limited conditions, resulting from an indirect influence on the ambient concentration of NO_x. This arises because the degradation of some VOCs can lead to the significant removal of NO_x as organic nitrates and peroxy nitrates (see Sections 2.3 and 2.4).

Fig. 3 clearly demonstrates that reduction of ozone formation is best achieved by a decrease in the VOC concentration under VOC-limited conditions, and by a reduction of NO_x concentration under NO_x-limited conditions. It is apparent from the above discussion, however, that VOC-limited conditions correspond to when the dominant radical sink is reaction (7), and that NO_x-limited conditions correspond to when reactions (26) and (27) are the major sinks. Indeed, the use of the ratio of the products of reactions (26) and (7), $[H_2O_2]/[HNO_3]$, as an indicator for VOC or NO_x limitation is well established and documented (e.g., Sillman, 1995,1999; Sillman et al., 1998). As implied by the illustration in Table 4, the conditions encountered in the boundary layer (particularly over Europe) tend to be intermediate to these extremes, or possibly varying between them for a given air mass trajectory. Consequently, a thorough appraisal of the influence of reductions of VOC and NO_x emissions on O_3 production is often achieved by use of suitable boundary layer airshed or trajectory models incorporating the precursor emissions and appropriate chemical mechanisms (e.g., Derwent and Davies, 1994). Such models are also used to consider the relative contributions to ozone formation made by many different emitted VOCs, recognising that the contribution (per unit mass emission) can vary from one compound to another by virtue of differences in reactivity and structure (e.g., Carter, 1991,1994; Derwent and Jenkin, 1991; Andersson-Skold et al., 1992; Simpson, 1995; Derwent et al., 1998). This has given rise to the definition of scales of so-called *reactivity* or *ozone formation potential* of which the most widely publicised and applied are the Maximum Incremental Reactivity (MIR) scale, developed by Carter and co-workers to assess ozone formation over periods of up to a day in urban scenarios in the USA (e.g., Carter, 1994,1995; Carter et al., 1995), and the Photochemical Ozone Creation Potential (POCP) scale, developed by Derwent and co-workers to investigate regional scale ozone formation over periods of up to five days in northwest Europe (e.g., Derwent and Jenkin, 1991; Derwent et al., 1996,1998; Jenkin and Hayman, 1999).

A further parameter of interest is the number of molecules of O_3 generated for every molecule of NO_x oxidised (e.g., to HNO_3), which is sometimes referred to as the *ozone production efficiency*, OPE. On the basis of the above

discussion, the OPE would be expected to vary with ambient conditions. Under VOC-limited conditions, when the cyclic mechanism is terminated by reaction (7) (i.e., converting NO_2 to HNO_3), the OPE is essentially equal to the chain length (i.e., the number of O_3 molecules generated by the free radical-propagated mechanism before termination occurs). Thus, as described above, the precise value depends on the VOC/NO_x ratio. Values of the OPE inferred from ambient measurements, or calculated using boundary layer models, are consistent with values in the region of 1–5 under comparatively polluted conditions in the boundary layer over the US (Ryerson et al., 1998; Sillman et al., 1998; Nunnermacker et al., 1998) and Europe (Derwent et al., 1994; Derwent and Davies, 1994). Under NO_x-limited conditions, when reactions (24) and (25) are the dominant termination reactions, the O_3 formation mechanism is less efficient at oxidising NO_x and the OPE is potentially much greater. However, the minor participation of reaction (7), and the additional removal of NO_x as organic nitrates and peroxy nitrates tends to place an upper limit on the values which may be achieved. Available ambient measurements at rural sites in the US and Canada are consistent with OPE values of approximately 10 (Liu et al., 1987; Trainer et al., 1993; Olszyna et al., 1994), although calculations indicate that this is likely to increase dramatically as NO_x is further reduced (Lin et al., 1988), and values approaching 100 may be possible in the remote boundary layer and the free troposphere (e.g., Collins et al., 1995). It should also be noted that the observed yield of O_3 relative to the oxidation of NO_x is also influenced by the night-time oxidation of NO_x by thermal reactions, which leads to the removal of O_3 (i.e., the OPE is effectively negative at night). The chemistry involved is discussed further below in Section 4.

The HO_X species, OH and HO_2, also react directly with O_3. Consequently, VOC oxidation can lead to the removal of O_3 at very low levels of NO_x, mainly as a result of the reaction of HO_2 with O_3 (reaction (29)):

$$HO_2 + O_3 \rightarrow OH + 2O_2, \tag{29}$$

$$HO_2 + NO \rightarrow OH + NO_2. \tag{5}$$

The competition between reactions (5) and (29) therefore effectively determines whether net O_3 production or removal occurs. Assuming a background concentration of O_3 of ca. 30 ppbv, the available rate coefficients for reactions (5) and (29) (Atkinson et al., 1997b) indicate that only ca. 7 pptv NO is required for O_3 production from reaction (5) to balance the destruction from reaction (29). At higher levels of NO, the photochemical oxidation of VOCs leads to net O_3 production by the mechanism described above.

3.5. VOC oxidation initiated by reaction with O_3

Unsaturated VOCs such as alkenes dienes and monoterpenes, in addition to reacting rapidly with OH, may also be oxidised by reaction with O_3 (e.g., Atkinson and Carter, 1984; Atkinson, 1997). The importance of reaction with OH and O_3 for a series of VOCs detected at rural locations in the UK is compared in Table 5. It is clear that O_3-initiated oxidation makes an important contribution, in particular for the more alkyl-substituted alkenes such as the 2-butene isomers and 2-methyl 2-butene.

Although the details of the oxidation mechanisms are less well known than for those following OH attack, the main features are reasonably well established (Atkinson, 1997). The mechanism proceeds *via* addition of O_3 to the double bond, leading initially to formation of an energy rich ozonide. This ozonide decomposes rapidly by two possible channels, each forming a carbonyl compound and a Criegee biradical which also possesses excess energy (denoted by ‡). For example, in the case of 2-methyl-2-butene, this may be represented as follows:

$$O_3 + CH_3C{=}C(CH_3)_2 \rightarrow CH_3CHO + [(CH_3)_2COO]^{\ddagger} \quad (30a)$$

$$\rightarrow CH_3C(O)CH_3 + [CH_3CHOO]^{\ddagger}. \quad (30b)$$

The energy rich Criegee biradicals are either collisionally stabilised, or decompose to yield a series of radical and molecular products. For $[CH_3CHOO]^{\ddagger}$, the following have been postulated as being the probable major reaction channels (Atkinson, 1997):

$$[CH_3CHOO]^{\ddagger}(+M) \rightarrow CH_3CHOO(+M), \quad (31)$$

$$[CH_3CHOO]^{\ddagger} \rightarrow CH_2CHO + OH, \quad \text{or } CH_3 + CO + OH, \quad (32a)$$

$$\rightarrow CH_3 + CO_2 + H, \quad (32b)$$

$$\rightarrow CH_4 + CO_2. \quad (32c)$$

The predominant reaction for the stabilised biradicals (such as CH_3CHOO formed in reaction (31)) under tropospheric conditions is believed to be the reaction with water vapour, which can lead to the formation of carboxylic acids, hydroxyalkyl hydroperoxides and H_2O_2 (see Atkinson, 1997, and references therein), e.g.:

$$CH_3CHOO + H_2O \rightarrow CH_3C(O)OH + H_2O \quad (33a)$$

$$\rightarrow CH_3CH(OH)OOH \quad (33b)$$

$$\rightarrow CH_3CHO + H_2O_2. \quad (33c)$$

Table 5. Comparison of chemical lifetimes of selected VOC detected at UK rural sites with respect to reaction with OH, O_3 and NO_3 at assumed ambient levels

VOC	OH[a]	O_3[a]	NO_3[a]
Alkanes			
Ethane	29 d		91 yr
Propane	6.3 d		7.8 yr
Butane	2.9 d		2.7 yr
2-Methyl propane	3.1 d		1.5 yr
Pentane	1.8 d		1.5 yr
2-Methyl butane	1.9 d		1.3 yr
Alkenes			
Ethene	20 h	9.7 d	7.3 month
Propene	6.6 h	1.5 d	4.9 d
1-Butene	5.5 h	1.6 d	3.5 d
2-Butene	2.9 h	2.4 h	2.9 h
2-Methyl propene	3.4 h	1.4 d	3.4 h
1-Pentene	5.5 h	1.5 d	3.5 d[b]
2-Pentene	2.6 h	2.4 h[b]	2.9 h[b]
2-Methyl 1-butene	2.8 h	1.4 d[b]	3.4 h[b]
3-Methyl 1-butene	5.5 h	1.6 d[b]	3.5 d[b]
2-Methyl 2-butene	2.0 h	55 min	7.1 min
1,3-Butadiene	2.6 h	2.4 d	11 h
Isoprene	1.7 h	1.2 d	1.7 h
Aldehydes			
Formaldehyde	18 h		2.7 month
Acetaldehyde	11 h		17 d
Aromatics			
Benzene	5.7 d		
Toluene	1.2 d		1.8 yr
Ethyl benzene	23 h		
o-Xylene	12 h		4.1 month
m-Xylene	7.1 h		6.6 month
p-Xylene	12 h		3.4 month
Sulpur-containing organics			
Dimethyl sulphide	1.5 d		1.0 h
Dimethyl disulphide	46 min		1.5 h

[a]Concentrations used in calculations: $[OH] = 1.6\times10^6$ molecule cm^{-3} (ca. 0.06 pptv), $[O_3] = 7.5\times10^{11}$ molecule cm^{-3} (ca. 30 ppbv), $[NO_3] = 2.5\times10^8$ molecule cm^{-3} (ca. 10 pptv); 1/e lifetimes calculated using rate coefficients taken from the evaluations of Atkinson (1991,1994) except where indicated.

[b]Rate coefficient estimated by analogy.

However, they may also play a minor role in the oxidation of trace atmospheric species, for example SO_2 (Cox and Penkett, 1971,1972):

$$CH_3CHOO + SO_2 \rightarrow CH_3CHO + SO_3. \quad (34)$$

Reactions (32a) and (32b) show that the production of free radicals from the O_3-initiated oxidation of unsaturated VOCs can occur. Since free radicals catalyse the formation of O_3, as described above, it is apparent that the reactions of O_3 with unsaturated VOCs do not necessarily constitute a sink for O_3 in the troposphere. Most attention has been given to the generation of OH, which has been observed in significant yield from the reactions of O_3 with more than 20 alkenes, dienes and monoterpenes (e.g., Niki et al., 1987; Atkinson and Aschmann, 1993; Paulson et al., 1997; Paulson et al., 1998; Marston et al., 1998; Pfeiffer et al., 1998; Donahue et al., 1998). These laboratory studies indicate that the OH yield increases with alkyl substitution of the double bond, for example from ca. 30% for propene to ca. 60% and 90% for trans-2-butene and 2-methyl-2-butene respectively. The more substituted alkenes also tend to have an increased reactivity towards O_3 and (as shown in Table 5) are therefore those most likely to react with O_3 under tropospheric conditions. Consequently the tropospheric reactions of O_3 with alkenes potentially lead to significant radical formation (e.g., see Paulson and Orlando, 1996) and, depending on the ambient conditions, possible net O_3 production. It is also clear that these reactions can generate radicals at night, as will be discussed further below in Section 4.3.

4. Nighttime chemistry

Although the major oxidation processes in the troposphere are initiated by the presence of sunlight, there are potentially significant chemical processes which can occur during the night. These processes cannot generate O_3 (indeed, they lead to O_3 removal), but potentially do produce a series of secondary pollutants, including H_2O_2. The chemistry also oxidises NO_x and VOCs which, as described above, are precursors to the formation of O_3 and other secondary photochemical pollutants during daylight. In this section, current understanding of nighttime chemistry is summarised, with particular emphasis placed on the role of the nitrate radical, NO_3.

4.1. The formation of NO_3 and N_2O_5

Throughout the diurnal cycle, NO_2 is slowly converted into NO_3 by reaction with O_3, which occurs on the timescale of ca. 12 h at a typical boundary layer

O_3 concentration of 30 ppbv:

$$NO_2 + O_3 \rightarrow NO_3 + O_2. \tag{35}$$

During daylight, however, NO_3 is photolysed extremely efficiently (on the timescale of a few seconds), leading mainly to the regeneration of both NO_2 and O_3:

$$NO_3 + h\nu \rightarrow NO_2 + O(^3P), \tag{36}$$

$$O(^3P) + O_2(+M) \rightarrow O_3(+M). \tag{4}$$

NO_3 also reacts rapidly with NO, leading to the regeneration of NO_2:

$$NO_3 + NO \rightarrow 2NO_2. \tag{37}$$

Consequently, the importance of NO_3 in daytime chemistry is severely limited. At night, however, the chemistry of both NO_3 and NO_x differs from the daytime behaviour. In addition to the absence of sunlight itself, the concentration of the OH radical is significantly suppressed, since it is produced mainly from the photolysis of stable molecules. Thus, once formed from reaction (2), NO_2 cannot be photolysed to regenerate NO, or removed at a significant rate by reaction with OH (reaction (7)). Provided the ambient concentration of O_3 is sufficiently high, therefore, NO is rapidly converted to NO_2 (reaction (2)), which in turn is slowly converted to NO_3 by reaction (35), as shown schematically in Fig. 4. Reaction (37) is therefore generally unimportant at night, because NO is only present in significant concentrations close to points of emission where O_3 has been completely titrated, and NO_3 cannot be formed. The principle reaction of NO_3 at night is often with NO_2:

$$NO_3 + NO_2(+M) \rightleftharpoons N_2O_5(+M). \tag{38}$$

The lifetime of NO_3 with respect to this reaction is about 2 s for an ambient [NO_2] of ca. 10 ppbv (Atkinson et al., 1997b). However, since the product N_2O_5 is thermally unstable and decomposes on a similar timescale (ca. 15 s at 298 K), equilibrium (38) is readily established with NO_3 and N_2O_5 present in comparable concentrations. As a result, their behaviour is strongly coupled and any process removing one of the species is also a sink for the other. Thus, at sunrise both species rapidly fall to very low concentrations due to the efficient photolysis of NO_3.

A major removal process for N_2O_5 (and therefore NO_3) at night is the reaction of N_2O_5 with water:

$$N_2O_5 + H_2O \rightarrow 2HNO_3. \tag{39}$$

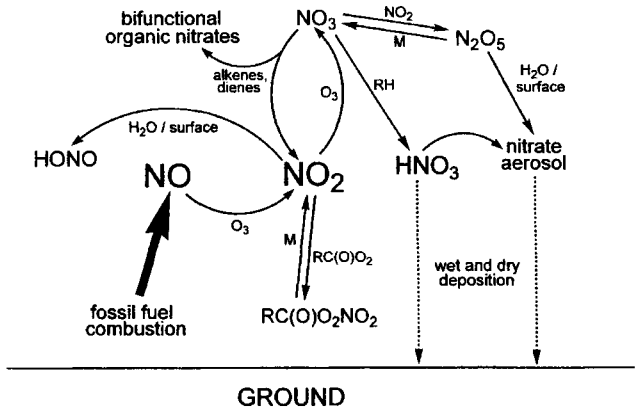

Figure 4. Nighttime interconversions of oxidised nitrogen compounds in the troposphere.

Laboratory studies of this reaction have shown it to occur extremely slowly in the gas phase (Mentel et al., 1996; Atkinson et al., 1997b). In the troposphere it is believed to occur predominantly in cloud water and on the surface of particulate, presumably involving the charge transfer, or ionic, intermediate $NO_2^+NO_3^-$, with the product being nitrate aerosol rather than gaseous HNO_3. Laboratory studies have also established that N_2O_5 uptake is efficient on water droplets, and on aerosols of sulphuric acid or ammonium sulphate (Mozurkewichz and Calvert, 1988; Van Doren et al., 1990; Hanson and Ravishankara, 1991; Lovejoy and Hanson, 1995), and it is concluded that the heterogeneous hydrolysis of N_2O_5 is an important loss process for tropospheric NO_x. Owing to its heterogeneous nature, however, the precise rate of this reaction is variable and difficult to define under tropospheric conditions. The timescale for removal of N_2O_5 on the tropospheric aerosol is believed to vary from the order of minutes in highly polluted air characterised by high particle densities and surface areas, to several hours in more remote, continental regions (e.g., Dentener and Crutzen, 1993). The heterogenous removal of NO_3 on water droplets may also occur, but it is believed to be much less important than hydrolysis of N_2O_5 (Dentener, 1994).

4.2. The reactions of NO_3 with volatile organic compounds

The reactions of NO_3 with trace organic compounds also potentially contribute to its removal at night. On the basis of available rate coefficients (e.g., see Wayne et al., 1991; Atkinson, 1991,1994), and concentrations of a series of organic compounds observed at rural sites in the UK (PORG, 1997), it is clear that alkenes and sulphur-containing organics are particularly signif-

icant for scavenging NO_3, with minor contributions made by aldehydes, aromatic hydrocarbons and alkanes. From these data it is clear that the sulphur-containing organics are very important for scavenging NO_3 at coastal locations. For example, extensive measurements made on the north Norfolk coast have demonstrated that reaction with dimethyl sulphide (DMS) is the dominant loss process for NO_3 in clean air during spring (Carslaw et al., 1997) and summer (Allan et al., 1997). At other times, and generally at inland rural locations, the most important class of organic compound is the alkenes. In particular, 2-methyl propene (*i*-butene) appears to make a notable contribution to NO_3 removal. Whereas abstraction reactions with other organic compounds convert NO_3 to HNO_3,

$$NO_3 + RH \rightarrow HNO_3 + R \tag{40}$$

the reactions with the alkenes occur by an addition mechanism, initiating a complex chemistry involving nitro-oxy subsitituted organic radicals, which can either regenerate NO_2 or produce comparatively stable bifunctional organic nitrate products (Wayne et al., 1991). For 2-methyl propene, the initial reaction has two channels, as follows:

$$NO_3 + CH_2{=}C(CH_3)_2(+M) \rightarrow CH_2(ONO_2)C(CH_3)_2(+M) \tag{41a}$$

$$\rightarrow CH_2C(ONO_2)(CH_3)_2(+M). \tag{41b}$$

The subsequent reaction mechanism (shown schematically in Fig. 5) is propagated by reactions of nitro-oxy substituted peroxy and oxy radicals, and potentially leads to the production of the bifunctional organic nitrate product 2-nitro-oxy 2-methyl propanal, via the minor reaction channel (41b). As shown in Fig. 5, this reaction sequence also yields HO_2, and is therefore potentially a nighttime source of OH radicals by reactions (29) and (42), and H_2O_2 by reaction (26):

$$HO_2 + NO_3 \rightarrow OH + NO_2 + O_2. \tag{42}$$

However, the major reaction pathway (via channel (41a)) leads to the production of the unsubstituted carbonyl compounds formaldehyde and acetone, and regenerates NO_2. Consequently, the NO_3-initiated oxidation of 2-methyl propene is believed to lead to significant regeneration of NO_x, but is a comparatively minor source of HO_x. Since the same is true for branched alkenes in general, which tend to be the most reactive towards NO_3 (Wayne et al., 1991; Atkinson, 1991,1994), it is probable that, for the most part, the reactions of NO_3 with alkenes lead to significant regeneration of NO_x, thereby inhibiting the conversion of NO_x to nitrate aerosol or HNO_3 at night. The NO_3-initiated oxidation of the less alkyl substituted alkenes (e.g., the 2-butene

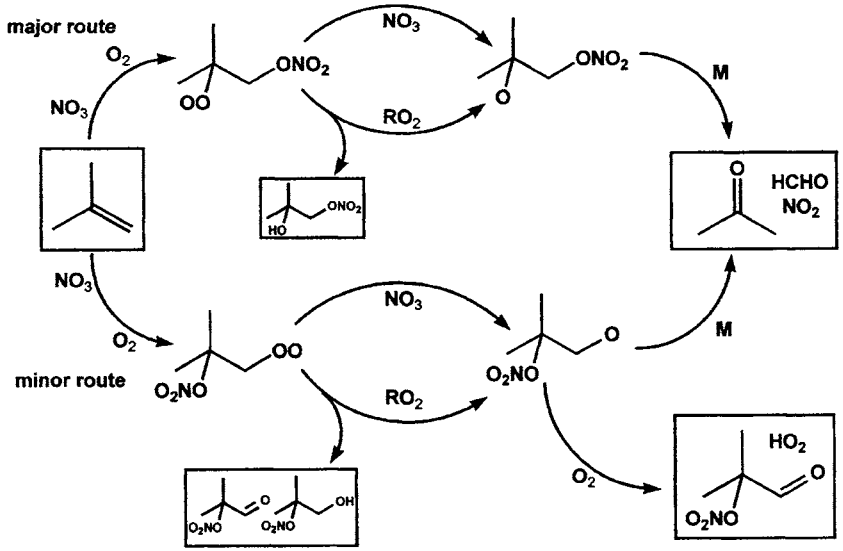

Figure 5. Schematic diagram of the NO_3 radical initiated oxidation of 2-methyl propene (*i*-butene).

isomers) should result in a greater yield of HO_x and bifunctional organic nitrate products, but is also likely to lead to substantial regeneration of NO_x. It should also be noted that terminating reactions of RO_2 and HO_2 with the intermediate nitro-oxy peroxy radicals produced from alkenes in general, can lead to the generation of bifunctional products containing carbonyl, hydroxy or hydroperoxy groups in addition to the nitro-oxy substitution (see Fig. 5), and measurements of such products in ambient air have been reported (e.g., Kastler and Ballschmiter, 1998).

On the basis of the reported concentrations of alkenes and sulphur-containing organics (PORG, 1997), and the likely removal rate of NO_3 via the heterogeneous hydrolysis of N_2O_5, a mean removal rate of NO_3 at night is calculated to be ca. 2×10^{-2} s^{-1}, under UK conditions. This corresponds to a lifetime of ca. 1 min. Assuming ambient concentrations of NO_2 and O_3 of 10 ppbv and 30 ppbv, typical of rural southern UK (PORG, 1997), this implies a mean rural nighttime NO_3 concentration of ca. 10 pptv. Although this is consistent with the limited available UK data (e.g. see Fig. 6), the NO_3 concentration is expected to be strongly dependent on the prevailing ambient conditions (e.g., concentration of NO_x concentration of alkenes, particle density, humidity, temperature).

The above discussion has been concerned primarily with the role of the reactions of NO_3 with organic compounds in sequestering and recycling NO_x. The

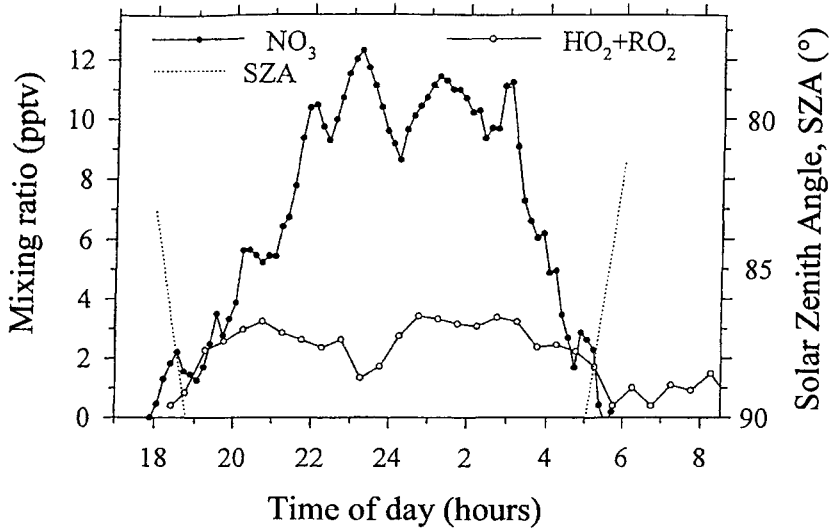

Figure 6. Overnight mixing ratios of NO_3 and peroxy radicals measured at the Weybourne Atmospheric Observatory, Norfolk, UK (15–16th April 1994). The variation of solar zenith angle indicates the times of sunset and sunrise (data taken from Carslaw et al., 1997).

significance of these reactions as removal routes for the organic compounds, in comparison with removal by reactions with OH or O_3 (see Section 3), is also worthy of note. Using the mean nighttime NO_3 concentration calculated above, the lifetimes of a series of organic compounds with respect to reaction with NO_3 can be calculated, as shown in Table 5. Clearly, certain compounds are potentially removed by reaction with NO_3 at a rate which is comparable with, or greater than, the rate of removal by OH and O_3, and these reactions are therefore often included in chemical mechanisms for use in tropospheric models (e.g. Jenkin et al., 1997a; Saunders et al., 1997). However, it should be emphasised that NO_3 initiates, but does not catalyse, the removal of organic compounds. Consequently, its concentration can be substantially suppressed (i.e., to very much lower than the 10 pptv average) by the presence of an organic compound with which it reacts rapidly. Under such circumstances, the lifetimes presented in Table 5 may be significantly underestimated.

4.3. Night-time sources of HO_x radicals

Although major sources of HO_x radicals result from photolytic processes (see Section 3.2), generation can also occur from a number of thermal reactions discussed above, namely the reactions of NO_3 with organic compounds (Section 4.2), the reactions of O_3 with alkenes (Section 3.5) and the thermal de-

composition of peroxy acyl nitrates (Section 2.4). These reactions therefore potentially generate HO_x at night, and in the winter months when production by photolysis processes is slow. The reactions of O_3 with alkenes have received particular attention, and can clearly represent significant sources of OH (and other radicals) within the nocturnal boundary layer in rural and semi-polluted environments (Paulson and Orlando, 1996; Bey et al., 1997).

Substantial evidence for nighttime radical generation has been provided by observations of significant peroxy radical concentrations at a variety of locations including north Norfolk, England (Carslaw et al., 1997), Brittany, France (Behmann et al., 1993; Cantrell et al., 1995,1996c), Mace Head, Eire (Carpenter et al., 1997), Hawaii, USA (Cantrell et al., 1997b), Schauinsland, Germany (Mihelcic et al., 1993; Volz-Thomas et al., 1997) and northern Portugal (Kluepfel et al., 1996). In some of these studies, a strong correlation between NO_3 and peroxy radicals has been observed. The data shown in Fig. 6, for example, demonstrate a sharp rise in peroxy radical concentrations from the low values observed at sunset, with a corresponding drop at sunrise (Carslaw et al., 1997). Consequently, this suggests a major role for NO_3 in the chemistry leading to measurable HO_x, which may result both from its reactions with VOCs (as described above), and from its involvement in radical propagation reactions. An example of the latter is the reactions of NO_3 with acyl peroxy radicals, which has been found to be rapid in the case of $CH_3C(O)O_2$ (Canosa-Mas et al., 1996). This can promote the decomposition of peroxy acyl nitrates by competing with the recombination reaction of the acyl peroxy radical with NO_2, e.g., for PAN:

$$CH_3C(O)O_2NO_2(+M) \rightleftharpoons CH_3C(O)O_2 + NO_2(+M), \tag{43}$$

$$CH_3C(O)O_2 + NO_3 \rightarrow CH_3 + CO_2 + NO_2 + O_2, \tag{44}$$

$$CH_3 + O_2(+M) \rightarrow CH_3O_2(+M). \tag{45}$$

Thus, the presence of NO_3 facilitates the conversion of the peroxy radical reservoir, PAN, into methyl peroxy radicals (CH_3O_2) and, subsequently, HO_2 at night. The importance of the reactions of NO_3 with peroxy radicals in general has also been demonstrated in modelling studies (Kirchner and Stockwell, 1996).

A further potential source of free radicals results from the reactions of NO_2 with some reactive conjugated dienes found in vehicle exhaust (Shi and Harrison, 1997; Harrison et al., 1998). Although these reactions may occur throughout the diurnal cycle, they have been postulated as playing an important role in the generation of free radicals under conditions when photochemical sources are inoperative, and concentrations of O_3 and NO_3 are suppressed by high levels of NO (Shi and Harrison, 1997). They have particular significance, there-

fore, to winter-time urban pollution episodes when boundary layer levels of NO_x and hydrocarbons from vehicle exhaust are elevated (Bower et al., 1994). The probable subsequent generation of nitro-substituted peroxy radicals may play a key role in the observed enhanced conversion of NO to NO_2 under such conditions (Harrison et al., 1998).

5. Chemical processes leading to secondary organic aerosol (SOA) formation

The formation of aerosols in the atmosphere has an important influence on visibility, climate and chemical processes, and is of concern since fine particulate matter is inhalable. The reduction of visibility observed in power station plumes and during photochemical episodes is mainly due to the formation and growth of large numbers of particles or droplets, which are able to absorb and scatter radiation. Similarly, the scattering and absorption of incoming solar radiation by aerosols throughout the atmosphere has a direct effect on the Earth's radiative balance (and therefore climate), by influencing the energy reaching ground level. A further indirect effect results from the role of aerosols in cloud formation (i.e., hygroscopic aerosols act as cloud condensation nuclei), since clouds reflect incoming radiation. Both these effects lead to atmospheric cooling (i.e., negative radiative forcing) which offsets the warming influence of radiatively active trace gases such as CO_2 (IPCC, 1995).

Aerosols in the tropospheric boundary layer may be emitted directly, or formed *in situ* as a result of chemical processes. Similarly to gaseous pollutants, therefore, they are usually classified as either primary or secondary respectively. There are numerous sources within these categories, which may either be natural phenomena or as a result of anthropogenic pollution (e.g., see Finlayson-Pitts and Pitts, 1986; Jaenicke, 1993). The sizes (i.e., aerodynamic diameters) of both primary and secondary aerosols may also vary over many orders of magnitude. The complete range of sizes which is usually of interest varies from about 2 nm (the smallest size detectable with a condensation nuclei counter, and effectively a molecular cluster) to about 10 μm. At greater diameters, aerosols are not readily inhaled, and are removed comparatively efficiently from the air by sedimentation.

Secondary aerosols are generated by gas-to-particle conversion, following the formation of products of particularly low-volatility, or high solubility, from gas-phase oxidation processes. Since these processes are often photochemically driven, the resultant aerosol usually falls into the category of secondary photochemical pollutant. A discussion of the chemistry leading to the formation of such products is therefore of relevance to the present review. An essential prerequisite for new particle formation to occur is the presence of a species

in the gas phase at a concentration in excess of its saturation vapour concentration with respect to the condensed phase (i.e., condensable material). This can be achieved by emission of hot gas mixtures into a cool environment (e.g., resulting from combustion processes), with the rapidly formed particulate matter falling into the category of primary aerosol. However, a major contribution to the formation of condensable material in the troposphere results from the significant emission of comparatively volatile trace gases, which are oxidised in the gas phase to yield products of much lower volatility. The subsequently-formed secondary aerosol is generated either by condensation onto existing aerosol, or by nucleation to form new particles or droplets (e.g., see Seinfeld, 1986; Clement and Ford, 1996). The most significant condensable molecule formed in the atmosphere is sulphuric acid (generated from the oxidation of SO_2 and reduced sulphur-containing trace gases, in particular dimethyl sulphide), which has also been long recognised as the most important from the point of view of the nucleation of new particles (e.g., Jaenicke, 1993; Clement and Ford, 1999a,b). However, increasing attention in recent years has been given to the contribution to secondary aerosol formation made by organic material. The main aim of the present section is to give an overview of the gas-phase chemical processes leading to low-volatility organic oxygenates, which can contribute to the formation of secondary organic aerosol (SOA).

5.1. The formation of organic oxygenates

Numerous studies in recent years have established that the production of condensable material from the tropospheric oxidation of emitted VOCs leads to the formation of SOA (e.g., Simoneit, 1986; Pandis et al., 1993; Saxena et al., 1995; Kavouras et al., 1998). This can occur, for example, during photochemical smog episodes (i.e., driven by anthropogenic pollution), but also as a natural phenomenon resulting from the rapid oxidation of some biogenic hydrocarbons (e.g. monoterpenes).

As described in Section 3, the gas-phase oxidation of VOCs proceeds by complex mechanisms, leading initially to the production of a variety of first generation oxidised organic products. These products are either of the same carbon number as the parent VOC, or of a lower carbon number if a fragmentation process has occurred. Those of the same carbon number are invariably less volatile than the parent VOC, since they are of higher molecular weight and contain one or more polar functional groups. Key functional groups which tend to reduce the volatility of a product are, in particular, carboxylic acid (–C(=O)OH), but also aldehyde (–C(=O)H), ketone (–C(=O)–), alcohol (–OH) and nitrate ($–ONO_2$). The possible transfer of oxidised products to the condensed phase occurs in competition with further oxidation in the gas phase which, once again, can either generate even less volatile multi-functional prod-

ucts of the same carbon number, or products of lower carbon number following fragmentation steps.

For all classes of VOC, the propensity for aerosol formation increases as the size of the VOC is increased. This arises partially because the reactivity of larger organic molecules in a given class is generally greater than that of smaller ones (i.e., the rate of accumulation of oxidised products increases with the size of the VOC), and partially because the volatility of the oxidation products of larger VOCs is lower. Consequently, the oxidation of larger VOCs is more likely to generate oxidised products at concentrations in excess of the saturation vapour concentration.

For many VOCs known to be emitted, the fractional conversion to aerosol under typical tropospheric conditions is estimated to be very low indeed (Grosjean and Seinfeld, 1989). However, it is also clear that certain classes of VOC are more likely to lead to aerosol formation by virtue of their general high reactivity and types of oxidation product formed. Of particular significance are cyclic compounds, since the products of fragmentation (i.e., ring opening) processes are often of the same (or similar) carbon number as the parent compound. Furthermore, in the cases of cycloalkenes, aromatic compounds and terpenes, oxidation occurs predominantly by an addition mechanism, so that the first generation products contain two polar functional groups. Consequently the oxidation of these classes of compound is more likely to lead to the generation of aerosol than the oxidation of similar sized compounds in other classes. For cycloalkenes and terpenes, oxidation by reaction with O_3 is potentially very important, with the possibility of the generation of low volatility bifunctional carboxylic acids as first generation products (e.g., Hoffmann et al., 1997; Christoffersen et al., 1998; Glasius et al., 1999).

The ability of monoterpenes to generate condensable material, and therefore SOA, has received particular attention in recent years, owing to the magnitude of their global emissions (Guenther et al., 1995), and their is a growing body of information on their formation and composition, both in enviromental chambers and the troposphere. The available chamber studies (e.g. Pandis et al., 1991; Odum et al., 1996; Hoffmann et al., 1997; Hallquist et al., 1999; Jang and Kamens, 1999) have demonstrated that aerosol yields are very variable, depending on the identity and starting concentration of the terpene, and on the experimental conditions (e.g. whether oxidation is initiated predominantly by O_3, OH or NO_3). In particular, these studies have confirmed that dark ozonolysis experiments tend to lead to the largest aerosol yields (Hoffmann et al., 1997), and that the fractional yields in all experiments generally depend on the organic aerosol mass concentration, commonly denoted M_0 (Odum et al., 1996; Hoffmann et al., 1997).

The available results have been simulated reasonably successfully using gas-aerosol partitioning models (e.g. Pankow, 1994a,b; Odum et al., 1996; Hoff-

mann et al., 1997; Kamens et al., 1999), with the methodology gaining further support from measurements of aerosol composition. These studies have shown that, as M_0 increases, a progressively larger proportion of the aerosol mass is made up of comparatively volatile compounds which are present in the gas phase at concentrations significantly below their saturation vapour concentration. Despite this, these compounds are able to partition a proportion of their mass (i.e., "dissolve") into the condensed organic phase (Pankow, 1994a,b). Consequently, at high values of M_0, the major condensed and gas-phase products are often the same species. For example, in the case of the most abundant and well-studied monoterpene, α-pinene, pinonaldehyde (a C_{10} ketoaldehyde) often represents the majority of the aerosol mass in chamber experiments, even though its gas-phase concentration is typically three orders of magnitude below its saturation vapour concentration (i.e., 3.8×10^{-2} Torr at 298 K, corresponding to ca. 50 ppmv at 1 bar; Hallquist et al., 1997). Even at the lower values of M_0 typical of ambient air, pinonaldehyde and nopinone (the major first generation product of β-pinene degradation) have been observed as significant components of secondary organic aerosol (Kavouras et al., 1998).

As indicated above, however, the formation of new aerosol particles requires the production of involatile degradation products which are likely to exceed their saturation vapour concentrations under atmospheric conditions. Recent studies have identified pinic acid (a C_9 dicarboxylic acid) as a promptly formed condensed product of the ozonolysis of both α- and β-pinene (Christoffersen et al., 1998; Kamens et al., 1999; Glasius et al., 1999). On the basis of observed structure–volatility trends for carboxylic acids and dicarboxylic acids (Tao and McMurry, 1989), it is probable that pinic acid is very involatile (its saturation vapour concentration possibly being below 10^{-9} Torr, i.e. ca. 1 pptv at 1 bar), and it is therefore currently believed to be the most likely degradation product of both α- and β-pinene leading to new aerosol formation by nucleation (Christoffersen et al., 1998). At present, however, only speculative mechanisms have been proposed to explain the prompt formation of pinic acid as a first generation product of α- and β-pinene ozonolysis, and further mechanistic information on the formation of condensable products from the oxidation of organics in general is required.

5.2. The hygroscopic properties of SOA

The growth of aerosols by absorption of water, and their ability to act as cloud condensation nuclei, not only has an influence on their interaction with light, but also on their role in chemical processes. The hygroscopic properties of the inorganic acids and salts commonly observed in tropospheric aerosols have been well studied (e.g., Orr et al., 1958; Potukuchi and Wexler, 1995). H_2SO_4, for example, is completely miscible with water, and the quantity absorbed is

proportional to the water vapour pressure. Above a critical relative humidity (known as the deliquescence point), the same is true for soluble inorganic salts such as ammonium sulphate ($(NH_4)_2SO_4$), which deliquesces at ca. 80% relative humidity, and sodium chloride (NaCl) for which the deliquescence point is ca. 75% relative humidity. Consequently, aerosols composed of such inorganic compounds take up water efficiently, and are good cloud condensation nuclei.

The nature of organic aerosols, or aerosols containing organic material, is also of considerable interest, particularly with regard to their hygroscopic properties. A common assumption has been that water absorption by aerosols is due solely to the presence of water soluble inorganic compounds. This would also suggest that the condensation of organic material on to an existing inorganic (e.g., sulphate) core might inhibit its growth by adsorption of water. Although this may be true for condensable hydrocarbons, the same may not be the case for organic oxygenates, since they contain both polar functional groups (which are hydrophilic), and hydrocarbon chains (which are hydrophobic). Indeed, organic compounds have a wide range of aqueous solubilities, and clearly have various possible effects on the water absorption properties of aerosols, and their ability to act as cloud condensation nuclei (CCN).

Observations of particle chemical composition and water content at urban and rural locations in the USA (Saxena et al., 1995), have identified interesting effects of organics on the hygroscopic properties of the particles. The rural data were consistent with an enhanced effect of the organic content on water absorption, whereas the urban data suggested an inhibiting influence. This can be explained in terms of the organic component being dominated by primary organic material (e.g., emitted polycyclic aromatic hydrocarbons) in urban aerosol, but by secondary organic material in rural aerosol. The organic material in primary organic aerosol is likely to be less oxygenated, and therefore more hydrophobic. In contrast, the secondary organic material, formed from hydrocarbon oxidation, contains polar functional groups and is therefore more hydrophilic.

Cruz and Pandis (1997) have recently considered the ability of pure dicarboxylic acid aerosols to act as CCN. As already discussed, such compounds are likely to be important components of secondary organic aerosols. The results indicated that submicron aerosols of glutaric acid (C_5) and adipic acid (C_6) were activated at low supersaturations (1.003 and 1.01 respectively). Furthermore, it was shown that a coating of glutaric acid increased the CCN activation of ammonium sulphate particles. In contrast, aerosols formed from the oxidation of α-pinene, β-pinene and limonene in the EUPHORE smog chamber have been found to be only slightly hygroscopic, with growth factors significantly lower than those of ammonium sulphate (Virkkula et al., 1999). As discussed above, these aerosols are likely to be multi-component, with a significant mass contribution from aldehyde and ketone products, which are likely

to be less hygroscopic than the condensable dicarboxylic acids. Consequently, it is possible that organic aerosols formed under ambient conditions at lower mass concentrations (i.e., predominantly as a result of nucleation/condensation processes) are hygrosopic, but become more hydrophobic at higher mass concentrations when the dicarboxylic acids represent a smaller fraction of the aerosol mass. It is probable, therefore, that CCN activity of secondary organic aerosols is very variable, and further study is clearly required.

6. Conclusions

Considerable progress has been made in identifying chemical processes responsible for the generation of O_3 and other secondary photochemical pollutants in the planetary boundary layer. This has been achieved by a combination of field observations, laboratory investigations and numerical modelling studies. However, further research in all three areas is necessary to improve our quantitative understanding of the impact of the chemical processing of pollutants emitted into the atmosphere.

The general features of O_3 formation from the sunlight-initiated oxidation of VOCs and NO_x are well established, with the rates and mechanisms of the oxidation of numerous VOCs reasonably well characterised and quantified by laboratory study. Clearly it is not feasible to study the complete degradation of all VOCs emitted into the troposphere, and the present database provides a framework for defining oxidation mechanisms for many unstudied VOCs by analogy and with the aid of stucture–reactivity correlations. However, there are certain classes of VOCs for which the detailed oxidation mechanisms are still uncertain (most notably aromatic hydrocarbons, terpenes and sulphur-containing organics), and the degradation of some classes of VOC has received little or no attention. The latter case includes emitted organic compounds containing nitrogen and silicon.

For the aromatic hydrocarbons and terpenes in particular, the remaining uncertainties have repercussions for understanding their role in the generation of both O_3 and SOA. Identifying the detailed chemical processes leading to the generation of products which contribute to the atmospheric burden of SOA (whether by nucleation, condensation or gas-particle partitioning), and establishing the hygroscopic properties of such aerosols, is almost certainly one of the major current challenges in tropospheric chemistry research.

More generally, further information is required on the atmospheric chemistry of specific classes of product formed from VOC oxidation, such as carbonyl compounds, organic hydroperoxides and organic nitrates and peroxy nitrates. For carbonyl compounds, there are comparatively few studies of the UV absorption cross-sections and quantum yields to allow atmospheric photolysis

rates and products to be determined. This is particularly the case for multifunctional compounds containing more that one carbonyl group, or carbonyl groups in addition to other functionalities (e.g., –OH, –OOH, $–ONO_2$). For hydroperoxides, the photolysis and OH reaction has only been studied for CH_3OOH: clearly, additional data for other hydroperoxides would help the assignment of structure–reactivity relationships. For the oxidised organic nitrogen compounds, various aspects of their atmospheric chemistry are incompletely understood, even though their formation, transport and degradation potenially has an impact on the environment and climate in a number of ways, ranging from the inhibition of ozone formation on local/regional scales to influencing the global budget and distribution of NO_x and O_3. For example, there are no reported product studies of the OH initiated degradation of any organic nitrate or peroxy nitrate. Given that the yields of these products can be substantial (e.g., up to 25% from monoterpene oxidation), it is clearly important to establish whether NO_x is ultimately released when they are degraded in the atmosphere. The further development and application of methods of detecting all these classes of oxygenated product in the field, in addition to the HO_x radical intermediates which drive the oxidation mechanisms, is also essential for the validation of our understanding of atmospheric chemical processes, and for pointing out where knowledge is lacking.

In other respects, the chemistry interconverting oxidised nitrogen compounds is reasonably well understood, and explains the formation of a series of inorganic and organic species which can act as reservoirs for NO_x and HO_x. The chemical and photochemical reactions of inorganic oxidised nitrogen species in the gas phase have generally received considerable attention, leading to a large body of evaluated data for these species (Atkinson et al., 1997b; DeMore et al., 1997). Such evaluated data are of clearly invaluable for atmospheric modellers, although there are instances where the evaluations of the two data review panels differ considerably (albeit very few). Most notably, the current recommendations for the reaction of OH with NO_2 (reaction (7)) differ by a factor of ca. 5 at the high pressure limit, such that the recommended values at 298 K and 760 Torr differ by a factor of ca. 1.7. These two different interpretations of the same database is clearly a cause for great concern for a reaction which is a major sink for HO_x and NO_x on local, regional and global scales, and this has stimulated further recent study of the reaction (Dransfield et al., 1999; Brown et al., 1999).

Although not covered in detail in the present review, the role of heterogeneous and multi-phase chemical processes potentially has an important impact on the gas-phase processes leading to the formation of O_3 and other secondary pollutants in the boundary layer. This results not only from the provision of a substrate which allows alternative reactions to occur, but also from an indirect influence on the gas-phase mechanisms through the removal of key species

such as HO_x, NO_x and even O_3 itself. There is still a great deal to be learnt about the role of heterogeneous and multi-phase chemistry in the atmosphere, and this is necessarily an active area of research.

Acknowledgements

MEJ gratefully acknowledges the support of the Department of the Environment, Transport and the Regions, both in the preparation of this review (under contract EPG 1/3/70), and for the some of the work described. KCC gratefully acknowledges financial support from the European Union (under contract ENV4-CT97-0404). Thanks are also due to members of the Photochemical Oxidants Review Group (PORG), in particular Tony Cox (University of Cambridge) and Dick Derwent (UK Meteorological Office) for comments on some of the material presented.

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