



Heterogeneous chemistry and tropospheric ozone

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Abstract

Ozone is produced in the troposphere by gas-phase oxidation of hydrocarbons and CO catalyzed by hydrogen oxide radicals ($\text{HO}_x \equiv \text{OH} + \text{H}$ + peroxy radicals) and nitrogen oxide radicals ($\text{NO}_x \equiv \text{NO} + \text{NO}_2$). Heterogeneous chemistry involving reactions in aerosol particles and cloud droplets may affect O_3 concentrations in a number of ways including production and loss of HO_x and NO_x , direct loss of O_3 , and production of halogen radicals. Current knowledge and hypotheses regarding these processes are reviewed. It is recommended that standard O_3 models include in their chemical mechanisms the following reaction probability parameterizations for reactive uptake of gases by aqueous aerosols and clouds: $\gamma_{\text{HO}_2} = 0.2$ (range 0.1–1) for $\text{HO}_2 \rightarrow 0.5 \text{H}_2\text{O}_2$, $\gamma_{\text{NO}_2} = 10^{-4}$ (10^{-6} – 10^{-3}) for $\text{NO}_2 \rightarrow 0.5 \text{HONO} + 0.5 \text{HNO}_3$, $\gamma_{\text{NO}_3} = 10^{-3}$ (2×10^{-4} – 10^{-2}) for $\text{NO}_3 \rightarrow \text{HNO}_3$, and $\gamma_{\text{N}_2\text{O}_5} = 0.1$ (0.01–1) for $\text{N}_2\text{O}_5 \rightarrow 2 \text{HNO}_3$. Current knowledge does not appear to warrant a more detailed approach. Hypotheses regarding fast O_3 loss on soot or in clouds, fast reduction of HNO_3 to NO_x in aerosols, or heterogeneous loss of CH_2O are not supported by evidence. Halogen radical chemistry could possibly be significant in the marine boundary layer but more evidence is needed. Recommendations for future research are presented. They include among others (1) improved characterization of the phase and composition of atmospheric aerosols, in particular the organic component; (2) aircraft and ship studies of marine boundary layer chemistry; (3) measurements of HONO vertical profiles in urban boundary layers, and of the resulting HO_x source at sunrise; (4) laboratory studies of the mechanisms for reactions of peroxy radicals, NO_2 , and HNO_3 on surfaces representative of atmospheric aerosol; and (4) laboratory studies of O_3 reactivity on organic aerosols and mineral dust. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ozone is produced in the troposphere by oxidation of hydrocarbons and CO catalyzed by hydrogen oxide radicals ($\text{HO}_x \equiv \text{OH} + \text{H}$ + peroxy radicals) and nitrogen oxide radicals ($\text{NO}_x \equiv \text{NO} + \text{NO}_2$). In polluted regions with large sources of NO_x and hydrocarbons, high concentrations of O_3 in surface air represent a major air pollution problem. Tropospheric O_3 is also of global interest as the primary source of OH (the main atmospheric oxidant) and as a greenhouse gas. Successive

generations of models have been developed over the past decades to understand the factors controlling tropospheric O_3 and to formulate emission control strategies (National Research Council (NRC), 1991; World Meteorological Organization (WMO), 1995). These models have still only limited success in reproducing observed concentrations of O_3 and its precursors (HO_x , NO_x , hydrocarbons). Uncertainties in emission inventories, transport, and chemical mechanisms may all contribute to the model deficiencies. A long-standing concern has been the role of heterogeneous chemistry.

It is common practice in the atmospheric chemistry literature to refer to “heterogeneous chemistry” as the ensemble of chemical processes involving aerosol phases (liquid and solid particles) in the atmosphere. It is also common practice to reserve the term “aerosol” to the

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suspension of solid and concentrated liquid particles present ubiquitously in the atmosphere, as distinct from the dilute water droplets and ice crystals found in clouds. Aerosols and clouds occupy a minute fraction of atmospheric volume (at most 10^{-6} cm³ per cm³ of air in dense clouds) but allow for chemistry that would not take place in the gas phase, such as ionic and surface reactions. The importance of heterogeneous chemistry in the atmosphere was first recognized in the late 1970s for the production of H₂SO₄ and HNO₃ in acid rain (Calvert, 1984). Its critical role for the depletion of stratospheric O₃ was recognized in the late 1980s (WMO, 1995). Compared to these two issues, the effect of heterogeneous chemistry on tropospheric O₃ has been much less studied. There is however a growing body of literature on the subject, and a review appears timely in the context of the North American Research Strategy on Tropospheric Ozone (NARSTO). Although the prime motivation for this review is to examine how heterogeneous chemistry affects O₃ pollution in North America, it would be artificial to restrict the scope geographically or to the polluted troposphere. I will endeavor to examine heterogeneous processes affecting O₃ over the range of tropospheric conditions from urban to remote.

I will not cover wet deposition processes. The effect of wet deposition on O₃ is indirect and rather peripheral, involving mainly the scavenging of HNO₃ and H₂O₂ which are reservoirs for NO_x and HO_x. It could be argued that a simple rainout parameterization for HNO₃ and H₂O₂ (Giorgi and Chameides, 1985) is sufficient to describe wet deposition in O₃ models. Lawrence and Crutzen (1998) have suggested that cirrus precipitation could be an important sink of HNO₃ in the upper troposphere. A useful discussion of wet deposition would require extending the review to include physical processes of scavenging, and this would detract from my focus.

Much of the literature on heterogeneous chemistry in the troposphere has focused on clouds, in part because of historical interest in acid rain, and in part because of the applicability of standard water chemistry models to cloud droplets. However, clouds represent only about 7% of tropospheric volume (Lelieveld et al., 1989; Prupacher and Jaenicke, 1995). An air parcel in the lower troposphere typically flows through a cloud on the order of once a day, with an in-cloud residence time τ of a few hours (Lelieveld and Crutzen, 1990). This frequency of cloud processing is an important consideration for species that have lifetimes much longer than τ outside of cloud and much shorter than τ in cloud. Such is the case for SO₂, the precursor of H₂SO₄ (Daum et al., 1984), but such is not the case for O₃, NO_x, or HO_x radicals. It appears therefore that the effect of cloud chemistry on O₃ is limited intrinsically by the small fraction of atmospheric volume occupied by clouds, and that most of this review should focus on non-cloud aerosols. Nevertheless, because much of our understanding of heterogeneous

processes originates from cloud chemistry studies, I will discuss them at some length.

I begin the review (Section 2) with a brief overview of gas-phase O₃ chemistry as is necessary for subsequent discussion of heterogeneous processes. In Section 3 I summarize the chemical properties of aerosols and clouds, and discuss gas-particle mass transfer. The reaction probability formulation for reactive uptake of gases by aerosols and clouds is presented in Section 4. Evidence for heterogeneous chemistry from field observations is examined in Section 5. Mechanisms for production and loss of HO_x, production and loss of NO_x, loss of O₃, and generation of halogen radicals are reviewed in Sections 6–10. Model studies examining the sensitivity of O₃ concentrations to heterogeneous chemistry are discussed in Section 11. Specific recommendations for including heterogeneous chemistry in 3-dimensional O₃ models are presented in Section 12. Recommendations for future research are in Section 13.

2. Gas-phase chemistry of tropospheric ozone

Fig. 1 is a schematic of gas-phase O₃ chemistry in the troposphere emphasizing the coupling between the cycles of O₃, HO_x, and NO_x. Ozone is supplied to the troposphere by transport from the stratosphere, is removed by deposition to the surface, and is produced and consumed chemically within the troposphere. Chemical production and loss are the dominant terms in most of the troposphere (Hauglustaine et al., 1998; Wang et al., 1998c).

2.1. HO_x-catalyzed chain mechanism

Production of O₃ in the troposphere can be described as a HO_x-catalyzed chain oxidation of CO and

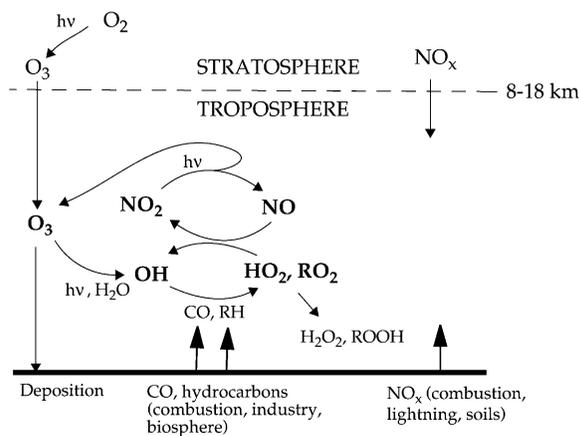
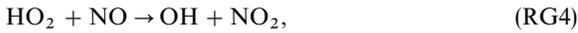
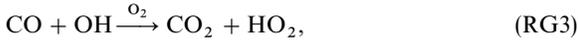


Fig. 1. Schematic of tropospheric O₃ chemistry illustrating the coupling between the chemical cycles of ozone, HO_x, and NO_x. RO₂ refers to the ensemble of organic peroxy radicals.

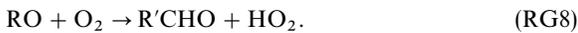
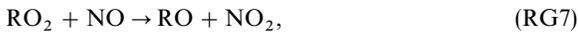
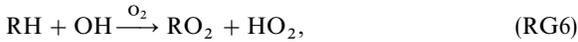
hydrocarbons in the presence of NO_x . The chain is initiated by production of HO_x , principally from



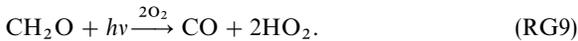
The chain is then propagated by the cycling of HO_x between its OH and peroxy forms. The simplest case involves oxidation of CO:



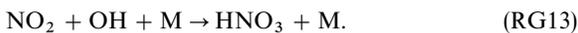
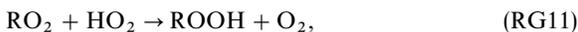
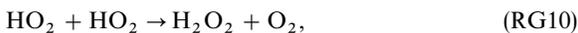
Oxidation of hydrocarbons (RH) proceeds by a similar mechanism involving organic peroxy radicals (RO_2). A generic reaction sequence is



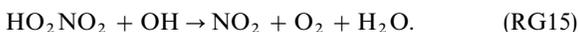
followed by (RG 4)–(RG 5). Carbonyl compounds (here $\text{R}'\text{CHO}$) go on to react with OH, producing additional O_3 . They may also photolyze to produce additional HO_x and branch the chain, as in the case of CH_2O :



The chain is terminated by loss of HO_x , which takes place mainly by



The peroxides and HNO_3 may photolyze to recycle HO_x ; alternatively, they may react with OH or be removed by deposition. In the upper troposphere, reaction of HO_2NO_2 with OH is also an important sink for HO_x :



2.2. Budgets of ozone and NO_x

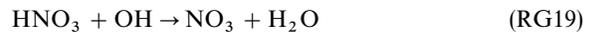
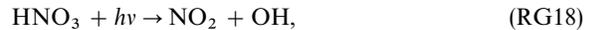
The budget of O_3 in the troposphere is commonly defined as that of the odd oxygen chemical family ($\text{O}_x \equiv \text{O}_3 + \text{O} + \text{NO}_2 + \text{HO}_2\text{NO}_2 + (2x)\text{NO}_3 + (3x)$

N_2O_5) to account for rapid interconversion within the family (Wang et al., 1998a). Ozone accounts typically for over 90% of O_x so that the budgets of O_3 and O_x can be viewed as equivalent. Production of O_x is by the peroxy + NO reactions (RG 4) and (RG 7). Loss of O_x is principally by (RG 2) and by



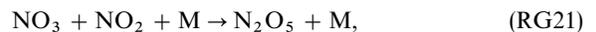
The chemical lifetime of O_x ranges from about a week in the tropical lower troposphere to several months in the upper troposphere and in extratropical winter.

Liu et al. (1987) defined the ozone production efficiency ε as the total number of O_x molecules produced per molecule of NO_x oxidized to HNO_3 . The idea is that a NO molecule emitted to the atmosphere undergoes a number ε of peroxy + NO reactions, producing O_3 , before being oxidized to HNO_3 . The lifetime of HNO_3 against photochemical recycling to NO_x by



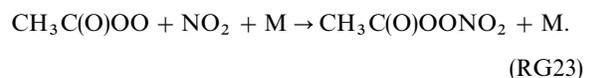
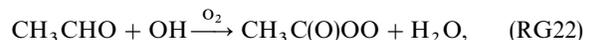
is about two weeks in the tropics and longer at midlatitudes. Deposition provides the dominant sink for HNO_3 in most of the troposphere. Values of ε typically range from ~ 1 in polluted urban air to ~ 100 in the remote troposphere (Liu et al., 1987).

The oxidation of NO_x to HNO_3 takes place by (RG 13) and also by nighttime hydrolysis of N_2O_5 :

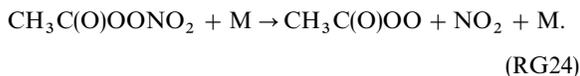


This pathway is ineffective in the daytime because NO_3 photolyzes back to NO_2 on a time scale of the order of 10 s. Hydrolysis of N_2O_5 has often been included in models as a gas-phase reaction with a rate constant specified from an upper limit estimate (Lurmann et al., 1986). However, it is now well established that the reaction proceeds in hydrated aerosols rather than in the gas phase (DeMore et al., 1997).

Formation of $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ (peroxyacetyl nitrate, abbreviated as PAN) is another sink for NO_x in hydrocarbon-rich environments. It takes place for example by oxidation of acetaldehyde:



The main sink for PAN in most of the troposphere is thermolysis, regenerating NO_x :



The lifetime of PAN against thermolysis is about 1 h at 295 K but several months at 240 K. PAN is an important contributor to total NO_y (sum of NO_x and its oxidation products) in polluted regions such as the eastern United States (Parrish et al., 1993). Long-range transport of PAN at high altitude (low temperature) is a major source of NO_x in the remote troposphere (Moxim et al., 1996).

3. Aerosols and clouds

3.1. Aerosol composition

The atmospheric aerosol includes (1) a nucleation mode (particles $< 0.01 \mu\text{m}$ radius) from recent gas-to-aerosol conversion; (2) an accumulation mode (0.01–1 μm) from condensational growth and coagulation of the nucleation mode; and (3) a coarse mode ($> 1 \mu\text{m}$) resulting mostly from direct mechanical generation at the Earth's surface (Seinfeld and Pandis, 1998). Most of the aerosol surface area and mass are in the accumulation and coarse modes, which are hence of most interest for heterogeneous chemistry. The principal components of the fine (accumulation) mode are water, sulfate, nitrate, ammonium, organic compounds, and black carbon soot (Fig. 2). The principal components of the coarse mode are soil dust (including calcium carbonate, silicates, metal oxides) and sea salt.

Sulfuric acid aerosols provide concentrated acid media in the atmosphere and are thus of particular chemical interest. The acidity of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ aerosols is commonly expressed as the weight percent (wt%) of H_2SO_4 . It is about 40 wt % H_2SO_4 at 50% relative humidity (r.h.) and 70 wt % at 10% r.h. (Seinfeld and Pandis, 1998). Relative humidities less than 10% are infrequent in the troposphere. Ammonia partly or totally neutralizes this acidity, forming dry ammonium sulfate salts or $\text{NH}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions depending on r.h. If excess NH_3 is available beyond neutralization of H_2SO_4 , then HNO_3 can condense to form a neutral $\text{NH}_3\text{-H}_2\text{SO}_4\text{-HNO}_3\text{-H}_2\text{O}$ aerosol or a separate NH_4NO_3 aerosol. In concentrated acidic aerosol at tropospheric temperatures, HNO_3 is present only in trace quantities (Carslaw et al., 1995; Tabazadeh and Toon, 1998). For example, in the upper troposphere with a typical temperature of 220 K and a HNO_3 concentration of 100 pptv, a 40 wt% H_2SO_4 aerosol contains only 3×10^{-5} wt% HNO_3 (Zhang et al., 1993).

Measurements at surface sites in the United States indicate that the aerosol is in general fully neutralized,

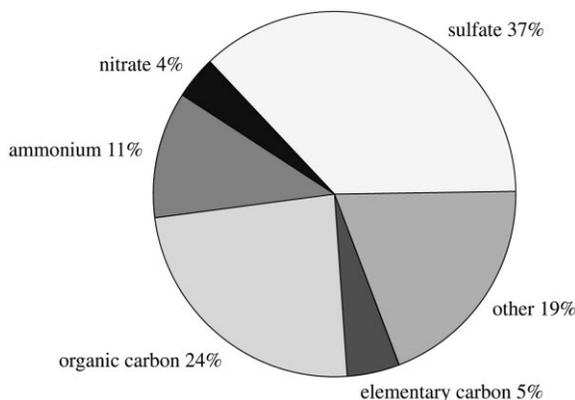


Fig. 2. Typical composition (by mass) of fine continental aerosol, adapted from Heintzenberg (1989).

except in the industrial midwest and the northeast (Altwickler and Johannes, 1987). The principal bases are NH_3 and crustal CaCO_3 . Sulfate aerosol in marine air is usually acidic (Covert, 1988; Vong, 1990). Measurements of aerosol composition in the free troposphere are few. Models suggest that the free tropospheric aerosol should be highly acidic due to efficient wet deposition of NH_3 and soil dust (Adams et al., 1999). However, recent aircraft measurements indicate that the aerosol is frequently neutralized up to the tropopause, with NH_4^+ and Ca_2^+ as the dominant basic cations (Talbot et al., 1998; Schultz et al., 1999b).

Knowledge of whether an aerosol is dry or aqueous is essential for modeling its chemical behavior. A number of laboratory studies have investigated the phase properties of $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-NH}_3\text{-H}_2\text{O}$ aerosols as a function of r.h. Binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ aerosols are aqueous solutions over the range of tropospheric conditions, although sulfuric acid tetrahydrate (SAT) is often the stable phase under cold conditions in the upper troposphere. Deliquescence r.h. of NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, and NH_4NO_3 have been reported by Tabazadeh and Toon (1998) as a function of temperature. Values are respectively 40%, 80%, and 62% r.h. at 298 K, and increase with decreasing temperature. Below the eutectic point (243 K, 254 K, 257 K respectively for the above salts) the stable phase is solid at all r.h. although hydrated solids may form at high r.h. (Xu et al., 1998).

Initially deliquesced aerosols may remain supercooled at r.h. below the deliquescence point because of the energy barrier for nucleation of the solid phase. Imre et al. (1997) report efflorescence (crystallization) points for NH_4HSO_4 aerosols of 20% r.h. at 298 K and 60% r.h. at 240 K. Cziczo et al. (1997) find that aqueous NH_4HSO_4 aerosols remain liquid for r.h. as low as 2% at room temperature. The discrepancy between the two studies may reflect the sizes of the aerosols and hence the ease of

overcoming the nucleation barrier for efflorescence; Imre et al. (1997) used 5–10 μm particles while Czikzo et al. (1997) used submicrometer particles. Czikzo et al. (1997) report an efflorescence point of 33% r.h. for $(\text{NH}_4)_2\text{SO}_4$ at room temperature. No data are available for the efflorescence of NH_4NO_3 . Tabazadeh and Toon (1998) suggest that nucleation of letovicite $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ in acid $\text{NH}_3 : \text{H}_2\text{SO}_4 : \text{H}_2\text{O}$ aerosol in the free troposphere would facilitate the efflorescence process. More generally, solid impurities in aqueous aerosols facilitate efflorescence (Oatis et al., 1998).

Phase equilibrium data for non-sulfate aerosols are few. Sodium chloride aerosols have deliquescence and efflorescence points at room temperature of 75% r.h. and 43% r.h. respectively (Czikzo et al., 1997). Relative humidities in the marine boundary layer are sufficiently high that sea salt aerosols should always be aqueous. Soil dust particles contain little hygroscopic material but may be coated by an aqueous outer layer (Li-Jones et al., 1998).

Organic compounds represent a major fraction of the total aerosol (Fig. 2) but little is known of their composition and hygroscopic properties. A range of water-soluble organic aerosol compounds have been identified in the atmosphere (Saxena and Hildemann, 1996). Single-particle measurements in the upper troposphere from aircraft have revealed an abundance of organic particles internally mixed with sulfate (Murphy et al., 1998). Better characterization of the organic component of the aerosol is needed.

3.2. Cloud composition

Cloud droplets form under supersaturated conditions (r.h. > 100%) by rapid condensation of water vapor on preexisting aerosols. They may remain in a supercooled liquid state down to about 250 K (Pruppacher and Klett, 1978). Most of the cloudwater mass and surface area is in the 5–20 μm size range. Most of the aerosol in a cloud is incorporated into the cloud droplets (ten Brink et al., 1987; Gilliani et al., 1995; Gieray et al., 1997). Gases are absorbed into cloud droplets on the basis of their water solubility and reactivity in the aqueous phase; in particular, HNO_3 and H_2O_2 are efficiently scavenged.

Clouds in different regions of the world typically have pH values in the range 3–6 (Li and Aneja, 1992). A three-year record of observations at a network of mountaintop sites in the eastern United States (Li and Aneja, 1992) indicates mean cloudwater pH values ranging from 3.6 to 4.0 depending on the site, with over 90% of values less than 5.0 and a full range of values extending from 2.3 to 7.3. Fogs forming in urban areas often have higher acidities (Munger et al., 1983) with pH values as low as 1.7 (Jacob et al., 1985).

Individual droplets within a cloud may differ in chemical composition as a result of nucleation on different

aerosol types, or as a result of different histories of nucleation and growth (Ogren and Charlson, 1992; Walcek and Brankov, 1994; Gieray et al., 1997; Schell et al., 1997). Size-fractionated cloudwater samples often show variability in solute concentrations over the cloud droplet size distribution; the variability in pH is in general less than a pH unit (Munger et al., 1989; Keene et al., 1995; Schell et al., 1997) but differences of as much as 2 pH units have been reported in fog (Laj et al., 1998).

3.3. Gas-particle mass transfer

The uptake rate R_{in} (molecules per cm^3 of air per second) of a gas-phase species X by a monodisperse (single-sized) aerosol or cloud composed of particles of radius a is given to a good approximation by (Schwartz, 1986):

$$R_{\text{in}} = \left(\frac{a}{D_{\text{g}}} + \frac{4}{v\alpha} \right)^{-1} An_{\text{X}} \quad (1)$$

and the volatilization rate R_{out} is given by

$$R_{\text{out}} = \left(\frac{a}{D_{\text{g}}} + \frac{4}{v\alpha} \right)^{-1} A \frac{[\text{X}]_{\text{surf}}}{K}. \quad (2)$$

These expressions are readily generalizable to polydisperse aerosols by integrating over the size distribution. Here D_{g} is the gas-phase molecular diffusion coefficient of species X in air, v is the mean molecular speed of X in the gas phase, α is a mass accommodation coefficient representing the probability that a molecule of X impacting the surface will be absorbed in the bulk aqueous phase (Nathanson et al., 1996), A is the aerosol surface area per unit volume of air, and n_{X} is the bulk gas-phase concentration (molecules per cm^3 of air) far from the gas-particle interface. The first term on the right-hand side of Eq. (1) describes uptake by gas-phase diffusion to the particle surface, while the second term describes uptake by free molecular collisions of gas molecules with the surface. Values of α for aqueous surfaces (Table 1) are in the range 0.1–1 for highly soluble gases, decrease with decreasing solubility, and increase with decreasing temperature (Kolb et al., 1995). For $\alpha > 0.05$ and typical tropospheric values of D_{g} ($0.2 \text{ cm}^2 \text{ s}^{-1}$) and v ($3 \times 10^4 \text{ cm s}^{-1}$), uptake of gases by cloud droplets ($a \sim 10 \mu\text{m}$) tends to be diffusion-limited ($R_{\text{in}} \rightarrow D_{\text{g}} An_{\text{X}}/a$). The corresponding time constant $a/D_{\text{g}}A$ is of the order of seconds and shows little dependence on α . In contrast, uptake of gases by non-cloud aerosol ($a \sim 0.1 \mu\text{m}$) tends to be limited by the free molecular collision rate ($R_{\text{in}} \rightarrow v\alpha An_{\text{X}}/4$). The corresponding time constant $4/v\alpha A$ varies inversely with α ; for $\alpha = 0.1$, it is of the order of minutes in the continental lower troposphere and hours to days in the upper troposphere.

Gill et al. (1983) have suggested that organic aerosol surfactants could slow down gas-aerosol transfer rates

Table 1
Henry's Law constants K and mass accommodation coefficients α for selected species in liquid water^a

Species	K_{298} (M atm ⁻¹)	$\Delta H^\circ_{298}/R$ (K)	K^* for pH = 4.5, $T = 280$ K (M atm ⁻¹)	α
O ₃	1.1(–2)	–2400	1.8(–2)	> 2(–3)
OH	2.5(1)	–5300	7.8(1)	> 4(–3)
HO ₂	4.0(3)	–5900	2.4(4) [HO ₂ (aq) + O ₂ ⁻]	> 2(–2)
H ₂ O ₂	8.3(4)	–7400	4.1(5)	1.8(–1)
CH ₃ OOH	3.1(2)	–5200	9.5(2)	9.2(–3) ^b
CH ₂ O	1.7(0) ^c	–3200 ^c	1.4(4) [CH ₂ O(aq) + H ₂ C(OH) ₂ (aq)]	4(–2)
HCOOH	8.9(3)	–6100	2.2(5) [HCOOH(aq) + HCOO ⁻]	1.0(–1)
CH ₃ COOH	5(3)	–6300	3.0(4) [CH ₃ COOH(aq) + CH ₃ COO ⁻]	2(–2) ^d
CH ₃ C(O)OO	< 1(–1) ^e	NA	< 1(–1)	NA
CH ₃ C(O)OONO ₂	2.8(0)	–6500	1.1(1)	> 1(–3) ^d
CH ₃ C(O)CH ₃	3.0(1)	–5500	9.8(1)	1–7(–2)
NO	1.9(–3)	–1500	2.6(–3)	NA
NO ₂	1.2(–2)	NA	1.2(–2)	> 2(–4) ^f
NO ₃	2.0(0)	–2000	3.1(0)	NA
N ₂ O ₅	2(0) ^g	–3400 ^g	∞^h [N ₂ O ₅ (aq) + NO ₃ ⁻]	
HONO	5.0(1)	–4900	1.9(3) [HNO ₂ (aq) + NO ₂ ⁻]	5(–2) ^d
HNO ₃	2.1(5)	–8700	4.3(11) [HNO ₃ (aq) + NO ₃ ⁻]	2(–1)
HO ₂ NO ₂	1.1(4)	NA	1.1(4)	NA

^aNote: 1.1(–2) refers to 1.1×10^{-2} . The Henry's Law constant K at temperature T is $K = K_{298} \exp\left[\frac{-\Delta H^\circ_{298}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$ where $T_0 = 298$ K. Data for K_{298} and ΔH°_{298} are from the compilation by Sander (1999) unless otherwise noted. The effective Henry's Law constant K^* is computed using the sum of aqueous-phase species listed in brackets and aqueous-phase equilibrium constants from Table 2. When no bracketed species are listed, K^* is simply the Henry's Law constant at 280 K. Mass accommodation coefficients α are room temperature values from the compilation of DeMore et al. (1997) unless otherwise noted.

^bMagi et al. (1997).

^cInferred from $K^* = 3.0 \times 10^3$ M atm⁻¹, $\Delta H/R = -7200$ K for the effective Henry's Law equilibrium CH₂O(g) ⇌ H₂C(OH)₂ at 298 K [Betterson and Hoffmann, 1988] and $K_{hyd} = 1.8 \times 10^3$, $\Delta H/R = -4040$ K for the hydration equilibrium CH₂O(aq) ⇌ H₂C(OH)₂ at 298 K (Bell, 1966).

^dSchurath et al. (1996).

^eVillalta et al. (1996).

^fMertes and Wahner (1995).

^gDerived from estimates at 273 K and 230 K by Fried et al. (1994).

^hMeasurements in 40–80 wt % H₂SO₄ solutions indicate that irreversible hydrolysis of N₂O₅(aq) to NO₃⁻ proceeds with a rate constant of order 10⁸–10¹¹ s⁻¹ (Fried et al., 1994).

considerably, and Capel et al. (1990) observed an organic surfactant phase in urban fog sampled in Switzerland. Further investigation of this surfactant effect is needed.

The volatilization rate R_{out} in Eq. (2) depends on the equilibrium constant $K = [X]_{surf}/n_{X,surf}$, where $[X]_{surf}$ and $n_{X,surf}$ are respectively the aerosol- and gas-phase concentrations at the particle surface. For a dilute aqueous aerosol K is the Henry's Law constant (Table 1). When uptake and volatilization are in balance

($R_{in} = R_{out}$) there is no net flux of gas at the surface so that $n_{X,surf} = n_X$ and $K = [X]_{surf}/n_X$. If in addition the chemical lifetime of X in the aerosol phase is long relative to the time scale for internal mixing of the particles, then $[X]_{surf}$ is equal to the bulk aerosol-phase concentration $[X]$ and the bulk concentrations in the gas and aerosol phases are related by $[X] = Kn_X$.

For highly reactive species in the aerosol, mass transfer limitations may prevent equilibrium between the bulk

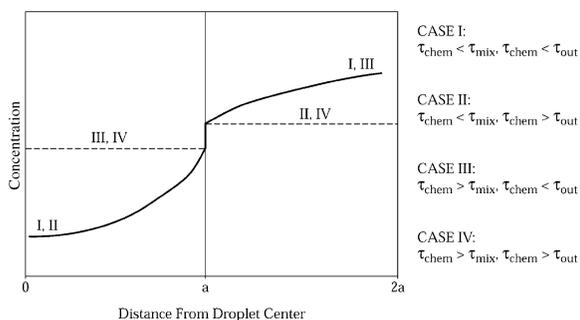
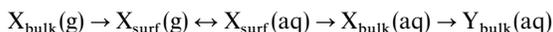


Fig. 3. Schematic concentration profiles across a gas-droplet interface. Cases I–IV represent different regimes of mass transfer limitation. In a cloud Case I applies to OH, Case II applies to O₃ and NO₃, Case III applies to HO₂, Case IV applies to most other species.

gas and aerosol phases (Schwartz and Freiberg, 1981; Schwartz, 1986,1988; Shi and Seinfeld, 1992; Kolb et al., 1995). Consider a species with a first-order rate constant k_{chem} (s⁻¹) for reaction in the aerosol phase; the corresponding lifetime of the species in the aerosol is $\tau_{\text{chem}} = 1/k_{\text{chem}}$. A first type of mass transfer limitation applies if this chemical loss is sufficiently rapid to compete with volatilization (R_{out}), in which case $R_{\text{out}} < R_{\text{in}}$ and $n_{\text{X,surf}} < n_{\text{X}}$. The characteristic time τ_{out} for volatilization is of the order of a few seconds in the limit $K \rightarrow \infty$ and decreases as the Henry's Law constant decreases (Jacob, 1985). If $\tau_{\text{chem}} < \tau_{\text{out}}$, mass transfer limitation produces a gas-phase concentration gradient in the vicinity of the surface.

A second type of mass transfer limitation applies for liquid particles when τ_{chem} is short relative to the characteristic time $\tau_{\text{mix}} = a^2/(\pi^2 D_1)$ for internal mixing of the droplet. Here D_1 is the molecular diffusion coefficient in the liquid phase. For aqueous solutions, $D_1 \sim 10^{-5}$ cm² s⁻¹ and the resulting τ_{mix} for cloud droplets ($a \sim 10$ μm) is of the order of 10^{-2} s.

Jacob (1986) described how these two types of mass transfer limitations can be accounted for quantitatively in cloud chemistry models. There are four general cases, illustrated in Fig. 3 for the reaction schematic



- Case I ($\tau_{\text{chem}} < \tau_{\text{mix}}, \tau_{\text{chem}} < \tau_{\text{out}}$). Mass transfer limitations in both the gas and aqueous phase prevent achievement of Henry's Law equilibrium between the bulk phases; concentration gradients within the droplets must be accounted for in chemical rate calculations.
- Case II ($\tau_{\text{chem}} < \tau_{\text{mix}}, \tau_{\text{chem}} > \tau_{\text{out}}$). Mass transfer limitation in the aqueous phase prevents achievement of Henry's Law equilibrium between the bulk phases;

concentration gradients within the droplets must be accounted for in chemical rate calculations.

- Case III ($\tau_{\text{chem}} > \tau_{\text{mix}}, \tau_{\text{chem}} < \tau_{\text{out}}$). Mass transfer limitation in the gas phase prevents achievement of Henry's Law equilibrium between the bulk phases, but species is well mixed in the aqueous phase.
- Case IV ($\tau_{\text{chem}} > \tau_{\text{mix}}, \tau_{\text{chem}} > \tau_{\text{out}}$). Species is well mixed in the aqueous phase and Henry's Law is achieved between the bulk phases.

In clouds Case I applies to OH, Case II applies to O₃ and NO₃, Case III applies to HO₂, and Case IV applies to most other species of interest. Cloud chemistry models generally account for mass transfer limitation in the gas phase, which is easily formulated by Eqs. (1) and (2), but often ignore mass transfer limitation in the aqueous phase. Neglecting the latter may cause a 20% overestimate of OH(aq) (Jacob, 1986) and over a factor of 2 overestimate of NO₃(aq) (Rudich et al., 1998).

For species sufficiently long-lived (Case IV), the fractionation between the bulk gas and aqueous phases is given by the Henry's Law constant $K = [X(\text{aq})]/P_{\text{X}}$ where P_{X} is the partial pressure of X in the gas phase (Table 1). Species undergoing rapid hydration, acid-base dissociation, or complexation can be taken up by the aqueous phase in excess of K ; one accounts for this enhancement by defining an effective equilibrium constant $K^* = \Sigma[X(\text{aq})]/P_{\text{X}}$ where $\Sigma[X(\text{aq})]$ refers to the sum of concentrations for the ensemble of aqueous-phase species in equilibrium. The equilibrium fractionation $f = \Sigma[X(\text{aq})]/[X(\text{g})]$ (dimensionless) of a species between the gas and the aqueous phase is

$$f = K^* L R T \quad (3)$$

where L (cm³ water per cm³ of air) is the liquid water content, R is the gas constant, and T is temperature. Effective Henry's Law constants K^* for a typical cloud environment are given in Table 1. Over the range of typical values for L in cloud (10^{-8} – 10^{-6} cm³ cm⁻³), a species is dominantly in the gas phase if $K^* < 10^4$ M atm⁻¹ and dominantly in the cloudwater if $K^* > 10^6$ M atm⁻¹. We see from Table 1 that HNO₃, H₂O₂, and HCOOH partition preferentially in the aqueous phase in cloud, while other species partition preferentially in the gas phase. For a non-cloud aqueous aerosol ($L < 10^{-9}$ cm³ cm⁻³), only HNO₃ still partitions preferentially in the aqueous phase and then only if excess base is available; in the absence of acid-neutralizing capacity, HNO₃ uptake is limited by acidification of the aerosol phase.

4. Reaction probability formulation

Models investigating chemical processes in aqueous aerosols and clouds generally include detailed gas-phase

Table 2
Selected aqueous-phase equilibrium constants^a

Equilibrium	K_{298} (M^n)	$\Delta H^\circ_{298}/R$ (K)
$\text{HO}_2 \rightleftharpoons \text{H}^+ + \text{O}_2^-$	2.1(–5)	0
$\text{HONO} \rightleftharpoons \text{H}^+ + \text{NO}_2^-$	5.1(–4)	1250
$\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^-$	1(1)	NA
$\text{CH}_2\text{O} \rightleftharpoons \text{H}_2\text{C}(\text{OH})_2$	1.8(3)	–4040
$\text{HCOOH} \rightleftharpoons \text{H}^+ + \text{HCOO}^-$	1.8(–4)	150
$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$	1.7(–5)	–50
$\text{HO}_2\text{NO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_4^-$	1.4(–6) ^b	NA
$\text{Fe}^{2+} + \text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})^+$	3.2(4)	NA
$\text{Fe}^{3+} + \text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})^{2+}$	6.3(11)	–3200
$\text{Fe}^{3+} + 2\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_2^+$	2.0(22)	–2300
$\text{Fe}^{3+} + 3\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_3(\text{s})$	1.3(37) ^c	–10400

^aNote: Read 2.1(–5) as 2.1×10^{-5} . Data are from the compilations of Jacob (1986) and Jacob et al. (1989) unless otherwise noted. The equilibrium constant K at temperature T is

$$K = K_{298} \exp\left[\frac{-\Delta H^\circ_{298}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \text{ where } T_0 = 298 \text{ K.}$$

^bLogager and Sehested (1993).

^cPrecipitation constant $K = 1/([\text{Fe}^{3+}][\text{OH}^-]^3)$.

and aqueous-phase chemical mechanisms coupled by gas-droplet transfer (Chameides and Davis, 1982; Jacob, 1986; Pandis and Seinfeld, 1989; Lelieveld and Crutzen, 1991; Chameides and Stelson, 1992; Sander and Crutzen, 1996). Data for important aqueous-phase equilibria and reactions are listed in Tables 2 and 3. Such mechanisms are computationally expensive to integrate in 3-dimensional models (Jacobson and Turco, 1994), and their usefulness may be limited by insufficient characterization of the condensed phase. A simpler approach is to describe the reactive uptake of a gas by an aerosol as the reaction probability γ that a molecule impacting the aerosol surface undergoes reaction (Ravishankara, 1997). From the definition of γ , it follows that the net loss rate $-dn_X/dt$ of a gas due to reaction in the aerosol is given by Eq. (1) with γ replacing α and with $-dn_X/dt = R_{\text{in}} - R_{\text{out}}$ replacing R_{in} :

$$-\frac{dn_X}{dt} = \left(\frac{a}{D_g} + \frac{4^{-1}}{v\gamma}\right) An_X. \quad (4)$$

The concept of reaction probability is applicable to both solid and liquid aerosols. Values of γ measured in the laboratory for a bulk liquid phase and a planar gas-liquid interface (γ_{bulk}) convolve processes of mass accommodation into the liquid phase, diffusion within the liquid phase, and chemical loss. In the case of first-order chemical loss in the liquid phase (rate constant k_{chem}), γ_{bulk} is given by (Kolb et al., 1995):

$$\gamma_{\text{bulk}} = \left[\frac{1}{\alpha} + \frac{v}{4K^*RT\sqrt{D_a k_{\text{chem}}}}\right]^{-1}. \quad (5)$$

For atmospheric applications involving uptake by spherical particles of radius a , values of γ_{bulk} measured in the laboratory must be corrected for saturation of the liquid phase (Hanson et al., 1994):

$$\gamma_{\text{aerosol}} = \left[\frac{1}{\alpha} + \frac{v}{4K^*RT\sqrt{D_a k_{\text{chem}}}} \cdot \frac{1}{f(q)}\right]^{-1}. \quad (6)$$

where

$$f(q) = \coth q - \frac{1}{q} \quad (7)$$

and $q = a(k_{\text{chem}}/D_a)^{1/2}$ is the diffuso-reactive parameter (Schwartz and Freiberg, 1981). For a fast liquid-phase reaction ($q \rightarrow \infty$), $f(q) \rightarrow 1$, while for a slow reaction ($q \rightarrow 0$), $f(q) \rightarrow q/3$; if $\gamma \ll \alpha$, these two limiting cases correspond to $\gamma \sim k_{\text{chem}}^{1/2}$ and $\gamma \sim k_{\text{chem}}$ respectively.

The reaction probability γ for gas uptake by a liquid aerosol thus depends on the aerosol composition (which affects α , K^* , D_a , k_{chem}) and on the aerosol size distribution (which affects q). These data are often not available in 3-dimensional O_3 models. Even if the aerosol composition were known, there is often enough uncertainty in k_{chem} that Eq. (6) cannot be reliably applied to a given atmospheric situation. In addition, Eq. (6) is applicable only to first-order loss processes.

With these considerations in mind, it appears that the most appropriate approach for parameterizing heterogeneous chemistry in 3-dimensional O_3 models is to use the reaction probability formulation (4) with order-of-magnitude estimates for γ . The first-order rate constant k for heterogeneous loss of a gas to the aerosol is then given by

$$k = \left(\frac{a}{D_g} + \frac{4}{v\gamma}\right)^{-1} A \quad (8)$$

which can be integrated over the aerosol size distribution (if this information is available) or applied to estimated values of A and effective values of a for rough calculations. Fig. 4 (from Dentener and Crutzen, 1993) shows values of k calculated with a global 3-dimensional model for reactive uptake of a gas with $\gamma = 0.1$ by sulfate and sea salt aerosols in different regions of the troposphere. The corresponding time constants for uptake range from less than one hour in the polluted lower troposphere to about a day in the upper troposphere. For submicrometer aerosols these time constants are roughly inversely proportional to γ (Section 3.3).

5. Field evidence for heterogeneous chemistry

Before discussing condensed-phase chemical mechanisms in detail, I first review the available evidence for heterogeneous chemistry from field observations. Some of this evidence is solid while some is highly speculative.

Table 3
Kinetic data for selected aqueous-phase reactions

Reaction	k_{298} (M^ns^{-1})	E_a/R (K)
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	8.6(5)	2400
$HO_2 + O_2^- \xrightarrow{H_2O} H_2O_2 + O_2 + OH^-$	1.0(8)	NA
$O_2^- + O_2^- \xrightarrow{2H_2O} H_2O_2 + O_2 + 2OH^-$	< 3(-1)	NA
$HO_2 + O_3 \rightarrow OH + 2O_2$	< 1(4)	NA
$O_2^- + O_3 \xrightarrow{H_2O} OH + 2O_2 + OH^-$	1.5(9)	NA
$H_2C(OH)_2 + OH \xrightarrow{O_2} HCOOH + HO_2 + H_2O$	7.7(8) ^a	NA
$HCOOH + OH \xrightarrow{O_2} CO_2 + HO_2 + H_2O$	2.(8)	NA
$HCOO^- + OH \xrightarrow{O_2} CO_2 + HO_2 + OH^-$	2.5(9)	NA
$CH_3C(O)OO + H_2O \rightarrow CH_3C(O)OH + HO_2$	> 7.(5) ^b	NA
$PAN + H_2O \rightarrow CH_3COOH + HNO_3$	1.7(-5) ^c	6600 ^c
$NO_3 + H_2O \rightarrow NO_3^- + OH + H^+$	6.0(0) ^d	4500 ^d
$NO_3 + Cl^- \rightarrow NO_3^- + Cl$	1.0(7) ^e	4300 ^e
$NO_3 + HCOO^- \xrightarrow{O_2} NO_3^- + CO_2 + HO_2$	5.0(7) ^f	2200 ^f
$NO_3 + HCOOH \xrightarrow{O_2} NO_3^- + CO_2 + HO_2 + H^+$	3.3(5) ^f	3400 ^f
$Fe^{2+} + HO_2 \xrightarrow{H_2O} Fe^{3+} + H_2O_2 + OH^-$	1.2(6)	NA
$Fe^{2+} + O_2^- \xrightarrow{2H_2O} Fe^{3+} + H_2O_2 + 2OH^-$	1.0(7)	NA
$Fe(OH)^+ + H_2O_2 \rightarrow Fe(OH)^{2+} + OH + OH^-$	1.9(6)	6200
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$	4.2(1)	NA
$Fe^{2+} + O_3 \xrightarrow{H_2O} Fe^{3+} + OH + OH^- + O_2$	5.7(5) ^g	NA
$Fe(OH)^{2+} + HO_2 \rightarrow Fe^{2+} + H_2O + O_2$	2.0(4)	NA
$Fe(OH)^{2+} + O_2^- \rightarrow Fe^{2+} + OH^- + O_2$	1.5(8)	NA
$Fe(SO_4)^+ + O_2^- \rightarrow Fe^{2+} + SO_4^{2-} + O_2$	1.5(8)	NA
$Fe(OH)^{2+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+} + OH^-$	2.1(7) ^h	NA
$Cu^+ + HO_2 \xrightarrow{H_2O} Cu^{2+} + H_2O_2 + OH^-$	1.5(9)	NA
$Cu^+ + O_2^- \xrightarrow{2H_2O} Cu^{2+} + H_2O_2 + 2OH^-$	9.4(9) ⁱ	NA
$Cu^{2+} + HO_2 \rightarrow Cu^+ + O_2 + H^+$	1.(8)	NA
$Cu^{2+} + O_2^- \rightarrow Cu^+ + O_2$	8.0(9) ⁱ	NA

Note: Data are from the compilations by Jacob (1986) and Jacob et al. (1989) unless otherwise noted. The rate constant k at temperature T is $k = k_{298} \exp(-E_a/RT)$.

^aChin and Wine (1994).

^bVillalta et al. (1996).

^cKames et al. (1991).

^dRudich et al. (1996).

^eExner et al. (1992).

^fExner et al. (1994).

^gLogager et al. (1992).

^hSedlak and Hoigne (1993).

ⁱvon Piechowski et al. (1993).

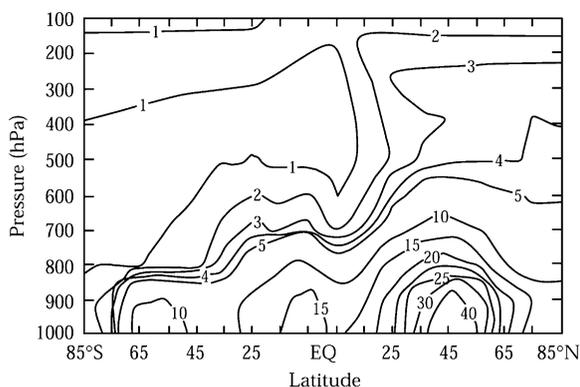


Fig. 4. Rate constant k (10^{-5} s^{-1}) for reactive uptake of a gas by sulfate and sea salt aerosols with $\gamma = 0.1$. Values are zonal and yearly means computed with a global 3-dimensional model. From Dentener and Crutzen (1993)

5.1. HO_x chemistry

Field observations offer some evidence for uptake of HO_2 by atmospheric aerosols. Cantrell et al. (1996a,b) measured total peroxy radical concentrations ($\text{HO}_2 + \text{RO}_2$) at Mauna Loa Observatory, Hawaii using a chemical amplifier method with an estimated accuracy of $\pm 30\%$. Comparison with results from a gas-phase photochemical model showed a mean model overestimate of 10–40%. The overestimates were worse when aerosol concentrations were high. The problem could be corrected by including in the model a loss of peroxy radicals to aerosols with a reaction probability $\gamma_{\text{HO}_2 + \text{RO}_2} \sim 0.1$ –1. Plummer et al. (1996) similarly found that ($\text{HO}_2 + \text{RO}_2$) concentrations at a rural site in Ontario were less than half the values they computed with a gas-phase model, and that the discrepancy could be resolved by assuming uptake by aerosols with $\gamma_{\text{HO}_2 + \text{RO}_2} \sim 1$. Recent aircraft observations of HO_2 , OH , and H_2O_2 in the upper troposphere show an imbalance in the H_2O_2 chemical budget which can be corrected by accounting for conversion of HO_2 to H_2O_2 in aerosols with $\gamma_{\text{HO}_2} = 0.2$ (Jaeglé et al., 1999). The few measurements of HO_2 in fogs, clouds, and cirrus show concentrations much lower than in clear sky (Cantrell et al., 1984; Cantrell, personal communication, 1998; Brune et al., 1999).

There is also some field evidence for OH uptake by clouds. In-cloud measurements of gas-phase OH concentrations by Mauldin et al. (1997) show a chemical depletion of OH by a factor of 2–3, and imply direct uptake of OH by cloud droplets with an effective rate constant of about 0.5 s^{-1} . Heterogeneous chemistry of OH is unimportant outside of clouds because of the short chemical lifetime of OH in the gas phase ($\sim 1 \text{ s}$) relative to the time scale for uptake by the aerosol (minutes).

There is ample evidence that photolysis of HONO produced heterogeneously at night provides a major early-morning source of HO_x in high- NO_x environments (Harrison et al., 1996). Observations in urban air show that HONO often accumulates to several ppbv over the course of the night (Harris et al., 1982; Calvert et al., 1994). A number of field and chamber studies reviewed by Calvert et al. (1994) indicate that the nighttime production of HONO must involve a heterogeneous process converting NO_x at a rate of the order of $0.5\% \text{ h}^{-1}$. The importance of nighttime HONO formation may not be limited to urban air. An analysis of aircraft observations in the free troposphere (Jaeglé et al., 1999) suggests that photolysis of HONO produced heterogeneously at night might help to explain observations of high HO_x at sunrise.

5.2. Formaldehyde

Concentrations of CH_2O measured in the remote troposphere are often lower and show considerably more variability than values computed from standard photochemical models (Liu et al., 1992; Zhou et al., 1996; Jacob et al., 1996; Ayers et al., 1997; Jaeglé et al., 1999). Some model studies have proposed that heterogeneous chemistry in aerosols and clouds could provide a fast sink for CH_2O (Chatfield, 1994; Lelieveld and Crutzen, 1990) though field observations offer no support for this hypothesis. Measurements of CH_2O gas-aerosol partitioning in surface air (Klippel and Warneck, 1980) indicate that only a small fraction of CH_2O is present in the aerosol. Observations in fogs and clouds show no evidence of CH_2O depletion relative to clear sky (Facchini et al., 1992; Keene et al., 1995; Munger et al., 1995).

5.3. NO_x chemistry

There is clear evidence from field observations that nighttime hydrolysis of N_2O_5 in aerosols is a major atmospheric sink of NO_x . The evidence includes nighttime measurements of NO_3 behavior (Platt et al., 1984), Lagrangian field experiments (Colville et al., 1994), and diel trends of NO_x and HNO_3 concentrations at rural sites (Li et al., 1993; Munger et al., 1998). In addition, hydrolysis of N_2O_5 in aerosols offers an explanation for the weak seasonal variation in nitrate deposition over Europe and North America (Dentener and Crutzen, 1993; Munger et al., 1998) and for the low NO_x concentrations observed at high latitudes in winter (Munger et al., 1998).

Measurements of the NO/HNO_3 concentration ratio in the free troposphere often indicate values several times higher than computed from photochemical steady-state models (Liu et al., 1992; Jacob et al., 1996; Keim et al., 1999; Schultz et al., 1999b). Rapid recycling of HNO_3 to NO_x in aerosols has been proposed as an explanation

(Chatfield, 1994; Fan et al., 1994; Hauglustaine et al., 1996; Lary et al., 1997), but this is speculative. Other possible explanations include long-range transport of primary NO_x (Wang et al., 1998b), precipitation of HNO_3 in cirrus (Lawrence and Crutzen, 1998), and suppression of N_2O_5 hydrolysis when the aerosol is dry (McKeen et al., 1997a; Schultz et al., 1999b). No such problem is apparent in the lower troposphere; measurements of the chemical partitioning of NO_y are consistent with gas-phase models including N_2O_5 hydrolysis in aerosols, both for the United States (Trainer et al., 1991; Parrish et al., 1993; Horowitz et al., 1998) and for remote regions (Jacob et al., 1992; Fan et al., 1994; Schultz et al., 1999a).

5.4. Ozone loss

Direct inference of O_3 chemical loss from observations is difficult because of the long lifetime of O_x (Section 2). Acker et al. (1995) reported an anticorrelation between O_3 concentrations and cloud occurrence at a mountain-top site in Germany which they attributed to cloud chemistry, but it is hard to separate chemical from dynamical factors behind such a correlation. The authors proposed that the fast reaction of $\text{O}_3(\text{aq})$ with SO_3^{2-} originating from the acid-base dissociation of SO_2 would be a major sink for O_3 in the clouds they sampled, but their computed O_3 loss rates from this reaction (10^{-9} M s^{-1} in cloudwater, corresponding to $0.01\text{--}0.1 \text{ ppbv h}^{-1}$) are in fact negligibly slow. Reichardt et al. (1996) reported ozonesonde measurements of O_3 -depleted layers (less than 10 ppbv) in the upper troposphere associated with cirrus, and argued that cloud chemistry was responsible for the O_3 depletion. However, a dynamical explanation seems more likely for such observations (Davies et al., 1998). Data from aircraft missions show no obvious evidence of O_3 depletion in cirrus (A. Weinheimer, personal communication, 1998).

Kawa and Pearson (1989) used eddy correlation flux measurements from an aircraft flying at different altitudes to derive O_3 budgets in the marine boundary layer (MBL) off the California coast. Data from ten flights indicated net O_3 loss rates consistent with values expected from gas-phase photochemical models. There was no apparent correlation with the presence of stratus or with wind speed (a proxy for sea salt aerosol concentrations). More recently, Heikes et al. (1996) used vertical profiles of O_3 and its precursors measured from aircraft over the south tropical Atlantic to construct an ozone budget for the cloud-topped MBL. They found that gas-phase photochemistry could explain the budget to within the uncertainty on the entrainment velocity at MBL top. These observations argue against a rapid loss of O_3 from aqueous-phase chemistry in cloud.

The only well-documented case of O_3 loss driven by heterogeneous chemistry is in surface air in arctic spring,

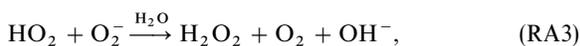
where events of depleted O_3 ($< 5 \text{ ppbv}$) are correlated with high BrO (up to 17 pptv) driving a fast cycle for O_3 loss catalyzed by BrO_x radicals ($\text{BrO}_x \equiv \text{Br} + \text{BrO}$) (Barrie et al., 1988; Haussmann and Platt, 1994). The BrO_x radicals are presumably generated by a heterogeneous process involving sea salt aerosols deposited on snow or sea ice (Mozurkewich, 1995; Tang and McConnell, 1996; Oum et al., 1998a; Impey et al., 1999).

Observations of sea salt debromination and of large diurnal cycles for O_3 in the marine boundary layer (MBL) offer some circumstantial evidence that significant Br radical chemistry could take place in that environment (Ayers et al., 1999; Dickerson et al., 1999). Dickerson et al. (1999) point out that a BrO concentration of $\sim 5 \text{ pptv}$ in the MBL would result in a major O_3 loss pathway from BrO_x catalysis. Measurements of BrO in the MBL by B.J. Allan and J.M.C. Plane (personal communication, 1999) have so far shown no instances of concentrations above their detection limit of 5 pptv.

6. HO_x chemistry in cloud

6.1. Cycling of HO_x in cloud

Much of our present understanding of heterogeneous HO_x chemistry is from cloud chemistry models (Chameides and Davis, 1982; Graedel and Goldberg, 1983; Schwartz, 1984; Graedel et al., 1986; Jacob, 1986; Lelieveld and Crutzen, 1991). Fig. 5 summarizes the major processes. The HO_2 radical is efficiently scavenged by cloud droplets because of acid-base dissociation $\text{HO}_2(\text{aq})/\text{O}_2^-$ ($pK_a = 4.7$) followed by electron transfer from O_2^- to $\text{HO}_2(\text{aq})$ to produce H_2O_2 :



Reaction (RA3) is considerably faster than the corresponding reaction (RG10) in the gas phase. Model calculations indicate that $\text{HO}_2(\text{g})$ concentrations should be depleted by 70% in a cloud of pH 4 relative to clear sky; in a cloud of pH 5 the depletion is 90% (Jacob, 1986). Even larger depletion is expected if (RA3) is catalyzed by trace metals, as discussed in Section 6.3.

Depletion of $\text{HO}_2(\text{g})$ suppresses O_3 production by the $\text{HO}_2 + \text{NO}$ reaction (RG4). In contrast to HO_2 , NO is not significantly soluble in cloud so that the $\text{HO}_2 + \text{NO}$ reaction does not proceed in the aqueous phase. The decrease of O_3 production due to HO_2 scavenging is partly compensated by an increase in the NO/NO_x ratio, as (RG4) is a significant pathway converting NO to NO_2 in the gas phase.

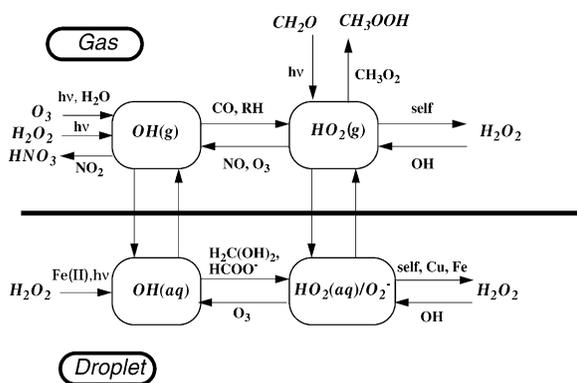
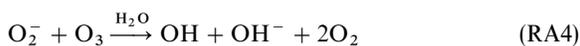


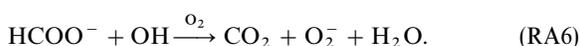
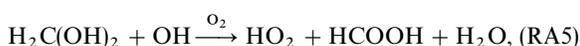
Fig. 5. Chemistry of OH and HO₂ in cloud. Major reaction pathways are indicated.

No data are available for the Henry's Law constant of CH₃O₂, the other major HO_x precursor of O₃. One would expect CH₃O₂ to be far less soluble than HO₂ because of its lower polarity; by analogy, the Henry's Law constant of CH₃OOH is 2–3 orders of magnitude less than that of H₂O₂ (Table 1). Assuming the same ratio for the Henry's Law constants of CH₃O₂ and HO₂, one finds that scavenging of CH₃O₂ by cloud droplets is negligible and that CH₃O₂(g) concentrations may actually increase in cloud due to suppression of the gas-phase sink from reaction (RG11) with HO₂ (Jacob, 1986). In this manner, increase in O₃ production by (RG7) partly compensates for the decrease of (RG4). In continental boundary layers, the hydroxy RO₂ radicals produced from the oxidation of isoprene play an important role in driving O₃ production (Horowitz et al., 1998). One would expect the hydroxy substituent to increase the solubility of the RO₂ radical in water (Berterton, 1992; Shepson et al., 1996), but the fate of the radical in the aqueous phase is unclear.

Scavenging of HO₂ by cloud droplets slows down the gas-phase loss of O₃ from (RG16) but drives fast aqueous-phase loss by the reaction



(in contrast, the aqueous phase reaction of HO₂ with O₃ is negligibly slow; see Table 3). The OH(aq) produced by (RA4) is recycled to HO₂(aq)/O₂⁻ on a time scale of 10⁻⁵ s by oxidation of organic molecules including hydrated formaldehyde and formate (Arakaki and Faust, 1998):



The sequence (RA4)–(RA6) is a HO_x-catalyzed cycle for destruction of O₃ in the aqueous phase (Lelieveld and Crutzen, 1990). The efficiency of the cycle is limited by the aqueous-phase HO_x sink from (RA3). Reaction (RA3) facilitates the scavenging of HO₂ from the gas phase, on the one hand, and thus moderates O₃ production; on the other hand, it competes with (RA4) and moderates O₃ loss. Model calculations based on reactions (RA2)–(RA6) indicate that the HO_x-catalyzed O₃ loss (RA4)–(RA6) is inefficient below pH 5 and only of limited efficiency below pH 6 (Jacob, 1986; Liang and Jacob, 1997). Aqueous-phase loss of HO_x by transition metal chemistry makes the catalytic cycle even less efficient (von Piechowski et al., 1993; Matthijsen et al., 1995).

Cloud chemistry models find that gas-phase OH concentrations in cloud are depleted by ~ 50% relative to clear-sky conditions due to scavenging of both HO₂ and OH (Lelieveld and Crutzen, 1990). The rate constant for uptake of OH(g) by cloud droplets in these models is consistent with the value of 0.5 s⁻¹ estimated by Mauldin et al. (1997) from field observations (Section 5.1). The depletion of OH(g) slows down daytime NO_x oxidation in the gas phase from (RG 13); this reaction is further slowed down by the increase in the NO/NO₂ ratio in cloud due to scavenging of HO₂. Hence NO_x may be preserved in cloud and remain available to produce O₃ after the cloud evaporates (Dentener, 1993).

6.2. Formaldehyde

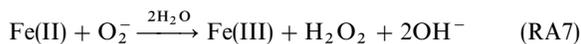
Some model studies have suggested that significant depletion of CH₂O takes place in cloud but this result is probably incorrect. The model calculation by Jacob (1986) indicates a 35% decrease of the CH₂O lifetime in cloud; it used a rate constant $k_{298} = 2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for (RA5), but a more recent measurement by Chin and Wine (1994) gives $k_{298} = 7.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ which makes the effect of cloud formation on CH₂O lifetime negligibly small. The model calculation of Lelieveld and Crutzen (1990) indicates a factor of 3 depletion of CH₂O in cloud, reflecting their assumption that CH₃O₂ is efficiently scavenged by cloud droplets so that CH₂O formation is suppressed. As pointed out above, the solubility of CH₃O₂ in cloud droplets is in fact probably low. The field observations discussed in Section 5 show no evidence of CH₂O depletion in cloud.

6.3. Transition metal chemistry

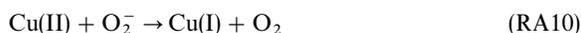
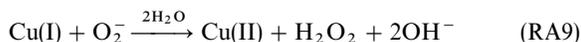
Graedel et al. (1986) and Wechsler et al. (1986) first pointed out the potential importance for in-cloud HO_x chemistry of Fe(II)/Fe(III) and Cu(I)/Cu(II) redox reactions (they also examined Mn(II)/Mn(III), which turns out to be far less important [Jacob et al., 1989]). The transition metals Fe and Cu are ubiquitous components of both crustal and combustion aerosols. Concentrations

in rural air are in the range 0.1–100 $\mu\text{g m}^{-3}$ for Fe and 0.001–0.1 $\mu\text{g m}^{-3}$ for Cu (Schroeder et al., 1987). In cloudwater, a large fraction is dissolved as ions, with typical dissolved concentrations of 0.1–20 μM for Fe and 0.001–0.3 μM for Cu (Anastasio et al., 1994; Sedlak et al., 1997).

The Fe and Cu ions react with O_2^- , catalyzing HO_x destruction:



and

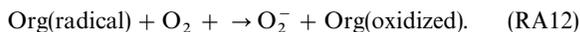
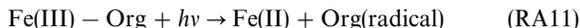


with similar pathways (but much slower rates) for the reactions involving $\text{HO}_2(\text{aq})$ instead of O_2^- (Table 3). Reactions (RA9) and (RA10) have rates approaching the diffusion limit when the Cu ions are in their free forms $\text{Cu}^+/\text{Cu}^{2+}$. For typical cloudwater concentrations of Fe and Cu, the catalytic cycles (RA7)–(RA8) and (RA9)–(RA10) could dominate over (RA3) as sinks for HO_x (von Piechowski et al., 1993). Cloud chemistry model calculations suggest that depletion of HO_x by (RA9)–(RA10) slows down O_3 production significantly in polluted clouds (Matthijssen et al., 1995; Walcek et al., 1997).

However, major uncertainties remain as to the speciation of dissolved Fe and Cu in cloud and aerosol. While most of Fe(II) is thought to be present as the free Fe^{2+} ion, essentially all of Fe(III) is complexed with OH^- , SO_4^{2-} , and organic ions such as oxalate (Faust, 1994). A large fraction of Cu appears to be present as organic complexes (Schroeder et al., 1987; Spokes et al., 1996; Nimmo and Fones, 1997) which are far less reactive towards O_2^- and $\text{HO}_2(\text{aq})$ than the free ions (von Piechowski et al., 1993). Rainwater composition measurements by Spokes et al. (1996) in Great Britain indicate a total Cu concentration of 0.01–0.03 μM but free Cu^{2+} concentrations of only 10^{-11} – 10^{-12} M. At these levels, the free Cu ions play no significant role in HO_x chemistry.

The redox chemistry of iron provides not only a sink but also a source of HO_x in clouds, though the sink effect likely dominates. Wechsler et al. (1986) and Faust and Hoigne (1990) identified photolysis of Fe(OH)^{2+} as a source of $\text{OH}(\text{aq})$, but this source appears to be too slow to be of importance (Jacob et al., 1989; Arakaki and Faust, 1998). Photolysis of FeSO_4^+ is about 50 times slower than photolysis of Fe(OH)^{2+} (Benkelberg and Warneck, 1995). Potentially more important is

the photolysis of Fe(III)-organic complexes such as Fe(III)-oxalates (Zuo and Hoigné, 1992; Faust and Zepp, 1993):



Photolysis of Fe(III)-oxalate complexes is two orders of magnitude faster than that of Fe(OH)^{2+} (Zuo and Hoigné, 1992). Siefert et al. (1996) irradiated aqueous solutions of aerosol samples collected at different sites in the United States and found production of Fe(II) which they attributed to photolysis of Fe(III)-oxalates; based on their Fe(II) production rates they inferred a HO_x source from (RA 11)–(RA 12) of 10^6 – 10^7 molecules $\text{cm}^{-3} \text{s}^{-1}$ for summer noon, which is comparable to typical gas-phase sources of HO_x (McKeen et al., 1991). However, it is possible that some of the Fe(II) production observed by Siefert et al. (1996) was from (RA8) and hence not associated with HO_x production. Direct measurements of HO_x radical formation by irradiation of cloudwater samples collected in the United States (Anastasio et al., 1994) indicate little correlation with Fe, and a wavelength dependence that is not consistent with photolysis of Fe(III)-oxalates.

Zepp et al. (1992) pointed out the potential $\text{OH}(\text{aq})$ source from the Fenton reaction of Fe(II):



A laboratory study by Arakaki and Faust (1998) using cloudwater samples from Whiteface Mountain, New York, shows that cycling of Fe(II)/Fe(III) by (RA11) and (RA13) is a major source of $\text{OH}(\text{aq})$ with a mean daytime rate of about $10 \mu\text{M h}^{-1}$ (3×10^5 molecules $\text{cm}^{-3} \text{s}^{-1}$ gas-phase equivalent for a typical cloud of 0.2 g m^{-3} liquid water content). From an O_3 budget perspective, this source is of interest in that it could drive the catalytic cycle (RA4)–(RA6) for O_3 loss. However, Sedlak et al. (1997) find that for a given amount of Fe the source of $\text{HO}_x(\text{aq})$ from (RA13) is minor compared to the $\text{HO}_x(\text{aq})$ sink from reactions (RA7)–(RA8), so that the net effect of Fe(II)/Fe(III) chemistry is still to suppress the aqueous-phase O_3 loss cycle. Spiking of cloudwater samples with Cu shows no evidence for $\text{OH}(\text{aq})$ formation from a Cu(I)– H_2O_2 Fenton reaction (Arakaki, 1997).

In summary, Fe(II)/Fe(III) and Cu(I)/Cu(II) redox reactions may represent major sinks of HO_x in clouds; they are unlikely to represent significant sources. Key uncertainties are the complexation state of the metals (in particular Cu) and the reaction rate constants involving the metal complexes. By scavenging HO_x , Fe(II)/Fe(III) and Cu(I)/Cu(II) reactions slow down gas-phase O_3 production in cloud but also suppress HO_x -catalyzed O_3 loss in the aqueous phase. From an O_3 budget standpoint, the

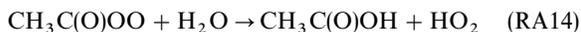
effect is intrinsically limited by the small fraction of time that an air parcel spends in cloud relative to clear sky. Transition metal chemistry in non-cloud aerosols is of more interest and needs further investigation (Section 7.1). The same mechanisms identified for cloud chemistry could also take place in non-cloud aqueous aerosols, with metal speciation and aerosol pH as critical variables.

6.4. Organic chromophores

Faust and Allen (1992,1993) and Anastasio et al. (1994) found that solar irradiation of cloudwater samples produces HO_x and H_2O_2 at a rate correlated with the concentration of total dissolved organic carbon (DOC), and that this process could represent a major source of HO_x and H_2O_2 in the atmosphere. A review of DOC speciation in aerosols (Saxena and Hildemann, 1996) identifies a number of carbonyls and keto-carboxylic acids that could serve as chromophores and lead to HO_x formation. Zuo and Jones (1996) reported the formation of CO from solar irradiation of rainwater samples at a rate correlated with DOC concentrations, supporting the hypothesis of DOC-driven photochemistry in atmospheric water. Most recently, Anastasio et al. (1997) showed that aqueous aromatic carbonyls in the presence of phenols photolyze to form H_2O_2 ; these compounds are abundant in organic aerosols from biomass burning and would also be expected in humic materials attached to windblown dust. More work is needed to quantify the magnitude of the associated source of HO_x and H_2O_2 in the atmosphere, but I doubt that it could be important. Measurements in clouds indicate a depletion rather than an enhancement of HO_2 relative to gas-phase models (Section 5.1). Measurements in continental air show no evidence for a large missing source of HO_x (McKeen et al., 1997b) or H_2O_2 (Horowitz et al., 1998).

6.5. Peroxyacetyl radical

A laboratory study by Villalta et al. (1996) shows irreversible loss of gas-phase $\text{CH}_3\text{C}(\text{O})\text{OO}$ to pure liquid water surfaces with a reaction probability $\gamma = 4.3 \times 10^{-3}$. The uptake is attributed to rapid hydrolysis of $\text{CH}_3\text{C}(\text{O})\text{OO}$ in the aqueous phase,



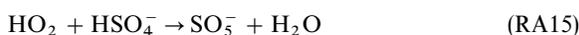
with a rate constant $k > 7 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$. The relatively small value of γ reflects a low Henry's Law constant for $\text{CH}_3\text{C}(\text{O})\text{OO}$ ($K_{\text{H}} < 0.1 \text{ M atm}^{-1}$). Decomposition of PAN followed by (RA14) could represent a small nighttime source of $\text{HO}_x(\text{aq})$ in polluted clouds with elevated PAN; it would be insignificant in the daytime.

7. HO_x chemistry in aerosols

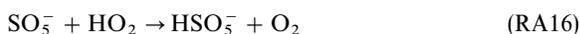
7.1. Uptake of HO_x by aerosols

Outside of clouds, uptake of HO_x species by aerosol takes place on a time scale of a minute or longer because of the lower surface area. Considering that the lifetime of HO_x against gas-phase chemical loss is of the order of a few minutes, aerosol uptake of peroxy radicals (the main component of HO_x) could have a significant effect on HO_x concentrations if $\gamma > 0.1$. Aerosol uptake of OH has no significant effect even with $\gamma = 1$ because the lifetime of OH against gas-phase loss is of the order of a second.

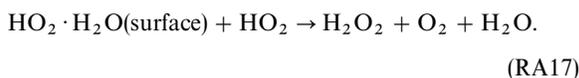
Reaction probabilities γ_{HO_2} in the range 0.1–1 have been measured in the laboratory for uptake of HO_2 by $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ solutions over a range of compositions (Hanson et al., 1992; Gershenson et al., 1995; Cooper and Abbatt, 1996). Hanson et al. (1994) proposed that the fate of $\text{HO}_2(\text{aq})$ is self-reaction to form H_2O_2 but that reaction is relatively slow (Table 3) and second order in $\text{HO}_2(\text{aq})$. Considering that the above-cited experiments used HO_2 concentrations of $10^{10}\text{--}10^{11}$ molecules cm^{-3} , negligibly low γ_{HO_2} would be expected at typical atmospheric HO_2 concentrations (10^8 molecules cm^{-3}) if the mechanism is second order. However, Cooper and Abbatt (1996) found that the uptake is first- rather than second order, implying a mechanism other than self-reaction in the bulk phase. They suggest the reaction



but this reaction would likely be followed by



and titrate sulfate in the atmosphere. An alternate explanation could involve the formation of a hydrated surface complex as the rate-limiting step:



Note that even if (RA15)–(RA16) were only a minor pathway for HO_2 uptake, the resulting source of HSO_5^- could be of great interest for driving halogen radical formation in marine aerosol (Section 10.1).

Free Cu ions in the aerosol enhance the uptake of HO_2 by (RA9)–(RA10). Mozurkewich et al. (1987) reported fast loss of HO_2 ($\gamma_{\text{HO}_2} = 0.4$) in deliquesced NH_4HSO_4 aerosols doped with Cu^{2+} . Ross and Noone (1991) showed that such a high reaction probability, limited by mass accommodation, can be achieved at typical concentrations of aerosol Cu found in rural air and for relative humidities less than 90% (at higher humidities, the rate

of aqueous-phase reaction becomes limiting). If the Cu ions are bound as organic complexes, as discussed above, their reactivity towards HO₂(aq) would be greatly diminished; however, the calculations of Ross and Noone (1991) show that at a relative humidity of 60% the mass accommodation limit for HO₂ uptake is reached even if only 10% of the aerosol Cu is available for reaction.

Reaction probabilities of HO₂ on solid surfaces have been reported by Gershenson et al. (1995) for NaCl, KCl, NH₄NO₃, and (NH₄)₂SO₄ salts (γ_{HO_2} in the range 0.01–0.02) and by Cooper and Abbatt (1996) for ice ($\gamma_{\text{HO}_2} = 0.025$). The latter data imply that HO₂ should be scavenged efficiently by ice clouds such as cirrus (Brune et al., 1999; Jaeglé et al., 1999).

The only data for uptake of organic peroxy radicals by aerosol are those of Gershenson et al. (1995) who observed $\gamma_{\text{CH}_3\text{O}_2} = 3 \times 10^{-3}$ on solid NaCl surfaces, five times lower than the corresponding γ_{HO_2} . One would expect CH₃O₂ to be relatively insoluble in aqueous aerosol but no data are available. In the summertime continental atmosphere, hydroxy-RO₂ radicals produced from isoprene oxidation make an important contribution to the HO_x budget (Horowitz et al., 1998), and these radicals could have a high water solubility owing to the presence of the hydroxy substituent.

In summary, it appears from laboratory studies that uptake of HO₂ by aqueous aerosol takes place with $\gamma_{\text{HO}_2} \sim 0.1$ –1 and represents a significant sink for HO_x in the atmosphere. This aerosol sink is consistent with the field observations reviewed in Section 5.1. The slower uptake on solid surfaces ($\gamma_{\text{HO}_2} \sim 0.01$) would be important only in ice clouds, with little consequence for O₃ in view of the small amount of time spent by air in these clouds. The mechanism for HO₂ uptake is uncertain but H₂O₂ is the likely product. Aerosol uptake of CH₃O₂ is probably negligible but measurements are needed. Aerosol uptake of hydroxy-RO₂ radicals produced from isoprene oxidation could conceivably be important and should be investigated.

7.2. Formation of HONO

It is well established from laboratory studies and field observations (Section 5.1) that heterogeneous conversion of NO_x to HONO at night followed by photolysis of HONO at sunrise can represent a major early-morning source of HO_x. The mechanism for HONO formation is unclear. Production in the bulk aqueous phase by (RA18) or (RA19),

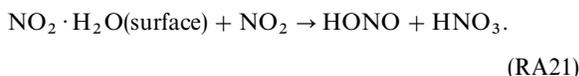


is too slow to be of atmospheric importance even at urban concentrations of NO_x (Lee and Schwartz,

1981a,b). Calvert et al. (1994) proposed the mechanism



to account for the observed correlation of HONO concentrations in nighttime urban air with the product of concentrations [NO][NO₂][H₂O] (see also Notholt et al., 1992). However, laboratory studies using both aqueous and solid surfaces (Jenkin et al., 1988; Bambauer et al., 1994; Mertes and Wahner, 1995) show that the formation of HONO does not involve NO and can be described by a mechanism where formation of the NO₂·H₂O surface complex is the rate-limiting step:



Bambauer et al. (1994) and Harrison and Collins (1998) report a reaction order of unity for NO₂ while Mertes and Wahner (1995) report a reaction order of 1.4. Laboratory studies of NO₂ uptake by aqueous solutions reviewed by DeMore et al. (1997) and also the recent study of Harrison and Collins (1998) indicate γ_{NO_2} in the range of 10^{-4} – 10^{-3} . Another recent study by Kleffmann et al. (1998) indicates much lower values, $\gamma_{\text{NO}_2} = 9 \times 10^{-7}$ in pure water decreasing to 2×10^{-7} for a 60 wt% H₂SO₄ solution. The reason for this difference is unclear. Field studies in urban air suggest a nighttime NO₂ loss rate $\sim 0.5\% \text{ h}^{-1}$ from this mechanism (Section 5.1). Assuming a typical urban aerosol surface area of 10^3 – $10^4 \mu\text{m}^2 \text{ cm}^{-3}$, such a loss rate corresponds to $\gamma_{\text{NO}_2} \sim 10^{-4}$. In the absence of better information, it seems most appropriate for models to use $\gamma_{\text{NO}_2} = 10^{-4}$ (range 10^{-6} – 10^{-3}) for $\text{NO}_2 \rightarrow 0.5\text{HONO} + 0.5\text{HNO}_3$.

7.3. Uptake of CH₂O by aerosols

Although discrepancies between field observations of CH₂O and gas-phase models (Section 5.2) suggest a possible role for heterogeneous chemistry, no mechanism has been identified. Laboratory experiments of CH₂O uptake by H₂SO₄–H₂O solutions show that the effective Henry's Law constant increases above 50 wt% H₂SO₄ due to protonation of H₂C(OH)₂ (Tolbert et al., 1993; Jayne et al., 1996) but such high acidities are rare in the troposphere. Loss of CH₂O by polymerization in concentrated acid solutions proceeds with $\gamma_{\text{CH}_2\text{O}} = 2 \times 10^{-3}$, which is too slow to compete with gas-phase photolysis as an atmospheric sink for CH₂O (Iraci and Tolbert, 1997).

8. Heterogeneous NO_x chemistry

8.1. Loss of NO_x

The importance of N₂O₅ hydrolysis in aqueous aerosols as a sink of NO_x is well established (Section 5.3). The reaction probability $\gamma_{\text{N}_2\text{O}_5}$ measured in the laboratory for aqueous solutions (including concentrated H₂SO₄) is in the range 0.01–1, relatively independent of composition and increasing with decreasing temperature (DeMore et al., 1997). The mechanism is thought to involve decomposition of N₂O₅ in the aqueous phase (Mozurkewich and Calvert, 1988; Wahner et al., 1998):

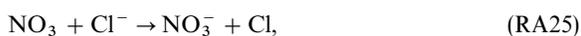


The product is HNO₃ with a yield of two (DeMore et al., 1997; Hu and Abbatt, 1997). An exception is sea salt aerosol where Cl⁻ competes with H₂O for reaction with NO₂⁺, leading to production of ClNO₂ which photolyzes to Cl and NO₂ so that the yield of HNO₃ is only unity (Behnke et al., 1996). In contrast to aqueous aerosols, uptake of N₂O₅ by dry ammonium sulfate aerosols is slow ($\gamma_{\text{N}_2\text{O}_5} < 3 \times 10^{-3}$) (Mozurkewich and Calvert, 1988).

Uptake of NO₃ by aqueous aerosols is limited by its low Henry's Law constant (Table 1). Rudich et al. (1996) measured $\gamma_{\text{NO}_3} = 2 \times 10^{-4}$ for pure water which they attributed to the fast reaction



and further found that γ_{NO_3} can increase to up to 10⁻² in the presence of reactive solutes such as Cl⁻ or HCOO⁻ (Exner et al., 1992,1994):



These values of γ_{NO_3} imply a NO₃ lifetime of the order of hours against uptake by aerosols. Nighttime observations of NO₃ concentrations in continental and marine air indicate a much shorter lifetime (Platt et al., 1984; Carslaw et al., 1997; Allan et al., 1999). Therefore, it appears that uptake by aerosols is a negligible NO₃ sink compared to gas-phase reactions with NO₂ and organic compounds (Russell et al., 1986; Carslaw et al., 1997). Cloud environments might provide an exception as the lifetime of NO₃ against uptake by cloud droplets is of the order of minutes, comparable to gas-phase reaction (Rudich et al., 1998).

Disproportionation of NO₂ to HONO and HNO₃ in aqueous aerosols was discussed previously (Section 7.2). Field observations indicate a NO₂ loss rate constant of ~0.5% h⁻¹ from this reaction (Section 5.1), which is slow compared to other sinks of NO_x. Reaction of NO₂

with dry sea salt surfaces is negligibly slow, with $\gamma \sim 10^{-8}$ (Langer et al., 1997).

8.2. Conversion of HNO₃ to NO_x

The tendency for photochemical equilibrium models to underestimate observed NO/HNO₃ concentration ratios in the free troposphere (Section 5.3) has spurred interest in the possibility that rapid reduction of HNO₃ to NO_x could take place in aerosols. Chatfield (1994) proposed a mechanism involving reaction of CH₂O with HNO₃ in acid aerosols, based on laboratory measurements by Horvath et al. (1988):



The HONO produced in this reaction would volatilize from the aerosol and photolyze to return NO_x. A laboratory study by Iraci and Tolbert (1997) examined this reaction in H₂SO₄-H₂O solutions containing 5 wt% HNO₃ at room temperature. They detected the production of HCOOH, HNO₂, and NO₂ at acidities greater than 35 wt% H₂SO₄; the rate of production increased with increasing acidity. Such high aerosol acidities could conceivably be found in the troposphere under relatively dry conditions and in the absence of NH₃. Iraci and Tolbert (1997) measured $\gamma_{\text{HNO}_3} > 0.01$ for 90 wt% H₂SO₄ with excess CH₂O at 202 K; no determinations were made at lower acidities or higher temperatures where γ_{HNO_3} would be lower. The 5 wt % HNO₃ used in these experiments is orders of magnitude higher than that expected in concentrated H₂SO₄-H₂O aerosols in the troposphere (Carslaw et al., 1995). Further laboratory studies are needed to determine if (RA27) could be significant under conditions representative of the tropospheric aerosol.

Heterogeneous reduction of HNO₃ to NO_x on soot aerosol surfaces in the upper troposphere was investigated in a model study by Lary et al. (1997), assuming $\gamma_{\text{HNO}_3 \rightarrow \text{NO}_2} = 2.1 \times 10^{-2}$ and $\gamma_{\text{HNO}_3 \rightarrow \text{NO}} = 4.2 \times 10^{-3}$ based on laboratory data by Rogaski et al. (1997) for dry carbon black soot. For a typical soot area concentration of 1 μm² cm⁻³ in the upper troposphere, Lary et al. (1997) found that the NO_x/HNO₃ concentration ratio increased by a factor of 5 relative to gas-phase chemical steady state. Model calculations by Hauglustaine et al. (1996) similarly proposed that conversion of HNO₃ to NO_x on soot aerosol could explain the high NO_x/HNO₃ concentration ratios observed at Mauna Loa. However, such a mechanism would be at odds with the fast decay rates of NO_x measured in soot-rich urban plumes (Chang et al., 1979; Spicer, 1982) and biomass burning plumes (Mauzerall et al., 1998). It is not clear that the surface chemistry of soot measured in the laboratory can be assumed to hold in the atmosphere where surfaces are greatly modified and likely hydrated.

8.3. Loss of organic nitrates

Heterogeneous chemistry of PAN appears to be unimportant in the troposphere. Laboratory measurements indicate negligible loss of PAN on dry glass and dry $(\text{NH}_4)\text{HSO}_4$ surfaces (Langer et al., 1992). The effective Henry's Law constant of PAN in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions up to 72 wt % shows little acid dependence and is similar to the low value given in Table 1 for pure water (Kames and Schurath, 1995; Zhang and Leu, 1997). PAN hydrolyzes in aqueous solution on a time scale of a fraction of an hour (Kames et al., 1991), but because of the low Henry's Law constant this process is too slow to represent a significant loss process for PAN. Uptake of $\text{CH}_3\text{C}(\text{O})\text{OO}$ by aqueous aerosols with $\gamma = 4 \times 10^{-3}$ (Villalta et al., 1996) could possibly explain the observation of slow PAN depletion from surface air at night (Shepson et al., 1992), but on a 24-h basis its effect is negligibly slow compared to the gas-phase reaction $\text{CH}_3\text{C}(\text{O})\text{OO} + \text{NO}$.

Formation of organic hydroxynitrates from the oxidation of biogenic hydrocarbons could be a significant sink for NO_x over the United States in summer (Trainer et al., 1991; Liang et al., 1998; Munger et al., 1998). The fate of these hydroxynitrates is poorly known but the hydroxy group might impart a high solubility in aqueous aerosols (Shepson et al., 1996; Horowitz et al., 1998).

9. Heterogeneous ozone loss

Ozone is a strong aqueous-phase oxidant but its low solubility in water (Table 1) precludes significant uptake by aqueous aerosols under non-cloud conditions. Loss of O_3 in cloud from the reaction $\text{O}_2^- + \text{O}_3(\text{aq})$ was discussed in Section 6.1. Lary et al. (1997) proposed that soot particles could represent an important sink for tropospheric O_3 but this is probably incorrect. Their argument is based on laboratory measurements which indicate $\gamma_{\text{O}_3} \sim 10^{-3}$ on fresh soot surfaces (Stephens et al., 1986; Fendel et al., 1995; Rogaski et al., 1997), independent of solar radiation (Smith and Chughtai, 1997). However, the laboratory studies show a decrease of γ_{O_3} with time which indicates gradual poisoning of the surface (Rogaski et al., 1997). Even more important, the carbon is found to be oxidized in the reaction with O_3 (Smith and Chughtai, 1997). Penner (1995) estimates a global black carbon source of 1.5 Tmol yr^{-1} , which can be compared to estimates of 70–110 Tmol yr^{-1} for loss of tropospheric O_3 from gas-phase chemistry and deposition (Hauglustaine et al., 1998). Fast reaction of O_3 on soot would therefore titrate atmospheric soot without affecting O_3 significantly.

Reduction of NO_2 to NO has been observed on fresh soot surfaces with $\gamma_{\text{NO}_2} = 0.03\text{--}0.11$ (Tabor et al., 1994; Rogaski et al., 1997). Lary et al. (1997) point out the

resulting catalytic cycle for O_3 loss:



Again, the laboratory studies indicate a decrease of γ_{NO_2} with time due to poisoning of the surface. It seems unlikely that the high reaction probabilities measured in the laboratory could apply to the atmosphere.

One possibility in need of exploration is the role of organic carbon aerosols as sinks for O_3 . Unsaturated organic compounds present in the aerosol (Hoffmann et al., 1997) have a high reactivity towards O_3 (de Gouw and Lovejoy, 1998). Penner (1995) estimates a global continental source of $16 \text{ Tmol C yr}^{-1}$ organic carbon aerosol, half anthropogenic and half biogenic. This supply is sufficiently large to possibly provide a significant sink for O_3 in the continental boundary layer.

10. Halogen radical chemistry

10.1. Bromine

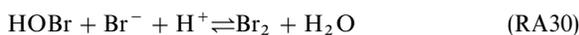
Events of O_3 depletion in surface air in arctic spring are associated with high concentrations of BrO (Section 5.4), driving a fast catalytic cycle for O_3 loss:



The origin of BrO is unclear but a likely precursor is sea salt Br^- , accumulated on the snow pack (Impey et al., 1999). Mozurkewich (1995) proposed an autocatalytic mechanism involving oxidation of Br^- by HSO_5^- ,



followed by acid-catalyzed reaction of HOBr with Br^- (Fan and Jacob, 1992)

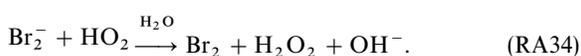
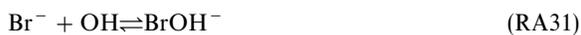


and volatilization of Br_2 . Reaction (RA30) can also take place in the aerosol to recycle HOBr and HBr to Br_2 and thus sustain O_3 loss (Fan and Jacob, 1992). According to Mozurkewich (1995), HSO_5^- would originate from the aqueous-phase radical chain oxidation of SO_2 present at relatively high concentrations in Arctic spring; the HSO_5^- yield from the chain is expected to be high at low temperatures.

Surface O_3 depletion in arctic spring is of limited interest per se but draws attention to the possibility of significant halogen radical chemistry occurring elsewhere in the troposphere, in particular in the marine boundary layer (MBL). Mozurkewich (1995) points out that under

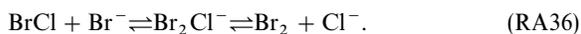
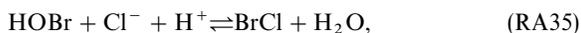
usual MBL conditions the SO₂ concentration is too low, and the yield of HSO₅⁻ from SO₂ oxidation too small, for significant BrO_x production to take place by (RA29)–(RA30). However, as proposed in Section 7.1, the sequence (RA15)–(RA16) for uptake of HO₂ by sulfate aerosols could provide an alternate source of HSO₅⁻ to sustain (RA29).

An alternate mechanism proposed by Mozurkewich (1995) for BrO_x generation in the MBL involves initial oxidation of Br⁻ by OH(aq) in sea salt aerosol:

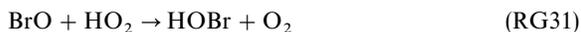


Recent measurements of sea salt aerosol pH by Keene and Savoie (1998) indicate relatively low values (2.5–3.5), which would favor formation of Br atoms by (RA32). A key uncertainty is the supply of OH(aq) to drive (RA31). At low pH the OH(aq) source from (RA4) would be slow.

Yet another mechanism for BrO_x generation in the MBL has been proposed by Vogt et al. (1996). In this mechanism, a small initial source of HSO₅⁻ allows (RA29) to proceed, which then drives an efficient autocatalytic cycle in the sea salt aerosol



Reaction (RA35) also takes place rapidly in concentrated H₂SO₄ – H₂O aerosols (Abbatt and Nowak, 1997). Model calculations by Vogt et al. (1996) suggest that this mechanism can generate up to 35 pptv HOBr in the MBL, and that the resulting gas-phase O₃ loss by the catalytic cycle

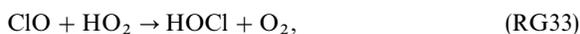


could account for 5–40% of total chemical loss of O₃ in the MBL (see also Dickerson et al., 1999). The mechanism is highly sensitive to aerosol pH (Keene et al., 1998) and to uncertain reaction rate constants.

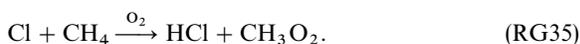
In summary, there is some circumstantial evidence for BrO_x-catalyzed O₃ loss in the MBL, and viable mechanisms have been proposed for the generation of BrO_x radicals. Field measurements of BrO, Br₂, and HOBr are needed for further progress.

10.2. Chlorine

There is indirect evidence from field observations that high concentrations of Cl atoms (10⁴–10⁵ atoms cm⁻³) may sometimes be present in the MBL as a result of the photolysis of chlorine gases such as Cl₂, HOCl, or BrCl volatilized from sea salt aerosol (Keene et al., 1990,1998; Pszenny et al., 1993; Singh et al., 1996). Spicer et al. (1998) observed nighttime Cl₂ concentrations of up to 150 pptv in coastal marine air, which would yield a maximum Cl atom concentration of 1.3 × 10⁵ atoms cm⁻³ shortly after sunrise. Gas-phase cycling of the ClO_x radical family (ClO_x ≡ Cl + ClO) drives a catalytic mechanism for O₃ loss:



but the efficiency of this cycle is low because of competing conversion of Cl atoms to HCl:



Reaction (RG35) actually provides a source of HO_x and hence can lead to O₃ production. Model calculations suggest that the net effect of ClO_x chemistry is to increase O₃ when NO_x is above 20 pptv (Pszenny et al., 1993). The effect of ClO_x chemistry on O₃ becomes significant only for [Cl] ~ 10⁵ atoms cm⁻³ (Keene et al., 1990), at the upper end of values inferred from field observations.

The mechanism for generation of Cl atom precursors from the sea salt aerosol is unclear. Behnke et al. (1996) showed that reaction of N₂O₅ in deliquesced sea salt aerosols produces ClNO₂ which photolyzes to yield Cl atoms, however this source would not be important at the low NO_x levels typically found in marine air. Production of BrCl by (RA35) generates Cl atoms when BrCl volatilizes from the aerosol and photolyzes, but the resulting Cl atom concentrations computed by Vogt et al. (1996) are only in the range 10³–10⁴ atoms cm⁻³.

In a chamber study Oum et al. (1998b) found that Cl₂ is produced rapidly from deliquesced NaCl aerosol in the presence of O₃ and UV radiation, and suggested the following mechanism (Keene et al., 1990):



However, model calculations by Chameides and Stelson (1992) show that this mechanism is negligibly slow under atmospheric conditions, being limited in part by the aerosol surface area available for uptake of OH or HO₂. The NaCl aerosol surface areas used by Oum et al. (1998b) are two orders of magnitude higher than typical marine boundary layer values. In addition, the data of Pszenny et al. (1993) and Spicer et al. (1998) point to nighttime formation of Cl₂ while Oum et al. (1998b) found no Cl₂ generation in their laboratory system in the dark.

In summary, there is evidence for significant ClO_x chemistry taking place in marine air under at least some conditions but the mechanisms for Cl radical generation are unknown. More field measurements of ClO, Cl₂, and HOCl are needed. The effect on O₃ is likely to be marginal.

11. Ozone model studies

A number of model studies have examined how O₃ budgets on global, regional, and urban scales would be affected by heterogeneous chemistry in clouds and aerosols.

11.1. Cloud chemistry

Lelieveld and Crutzen (1990) presented photochemical model calculations of the net production minus loss rate ($P - L$)_{O₃} of O₃ in air parcels subjected to alternating periods of clear and cloudy conditions, for a range of tropospheric environments. They found that including aqueous-phase HO_x chemistry increases the net regional O₃ loss averaged over clear and cloudy conditions by a factor of 1.3 to 2.3 under low-NO_x conditions, and decreases net O₃ production by about 40% under high-NO_x conditions. They concluded that aqueous-phase chemistry represents an important sink for O₃. However, Liang and Jacob (1997) pointed out that a large relative perturbation to ($P - L$)_{O₃} may imply only a small perturbation to O₃ concentrations, considering that P and L are of comparable magnitude in much of the troposphere, and that P is only weakly dependent on the O₃ concentration while L is roughly first order. In addition, the effect of cloud chemistry on O₃ cannot be decoupled from the effect on NO_x; chemical loss of NO_x slows down in cloud due to depletion of HO_x from the gas phase, resulting in enhanced O₃ production after the cloud evaporates (Dentener, 1993).

Liang and Jacob (1997) repeated the air parcel model calculations of Lelieveld and Crutzen (1990) using as diagnostics for the O₃ budget the production efficiency ϵ per unit NO_x (Section 2.2) and the pseudo first-order chemical loss rate constant k for O₃. They concluded that the maximum perturbation to O₃ concentrations from cloud chemistry is less than 3% in the tropics and in

mid-latitudes summer. They showed that a significant effect of cloud chemistry on O₃ concentrations would require a several-fold enhancement of k in cloud relative to clear sky, but there is no known mechanism to achieve such an increase. As pointed out in Section 6.1, catalytic O₃ loss by the O₂⁻ + O₃(aq) reaction appears to be inefficient.

The first application of a coupled chemistry-transport model to assess the effects of cloud chemistry on tropospheric O₃ was by Jonson and Isaksen (1993). They found that including clouds in their 2-D model (longitude–altitude) for northern mid-latitudes, with effects on both chemistry and radiation, decreased O₃ concentrations by up to 20–30% in the middle troposphere. Some of that perturbation was due to the radiation effect. Jonson and Isaksen (1993) assumed an excessively cloudy atmosphere, with one third of the 1–7 km column in cloud at any given time. Dentener (1993) included aqueous-phase HO_x chemistry in a global 3-D model and reported a 7% decrease in the global inventory of tropospheric O₃. Liang and Jacob (1997) argued that even this small effect is an overestimate because Dentener (1993) assumed liquid water abundances in excess of satellite observations and also used a high Henry's Law constant for CH₃O₂.

In summary, there seems to be little justification for including detailed aqueous-phase cloud chemistry in standard O₃ models, particularly in view of the computational cost (Jacobson and Turco, 1994). The importance of cloud chemistry is limited intrinsically by the small atmospheric volume fraction in cloud. Uncertainty in modeling UV actinic fluxes in and around clouds is a far more important concern. The suppression of O₃ production in cloud due to depletion of HO₂ (Walcek et al., 1997) can be parameterized by a simple reaction probability parameterization $\gamma_{\text{HO}_2} \sim 0.1$ for HO₂ → 0.5H₂O₂, as for aqueous aerosols (Section 7.1). Although oversimplified, this parameterization captures the essential result that HO₂ is efficiently scavenged from the gas phase in a cloud.

11.2. Aerosol chemistry

Dentener and Crutzen (1993) used a global 3-D model to investigate the effects of N₂O₅ hydrolysis in aerosols ($\gamma_{\text{N}_2\text{O}_5} = 0.1$) on the global budgets of NO_x and O₃. They found 50% and 9% decreases in the global tropospheric inventories of NO_x and O₃, respectively, relative to a model with gas-phase chemistry only. Decreases of O₃ were as large as 25% in northern midlatitudes in spring. There is no question that N₂O₅ hydrolysis in aqueous aerosols should be included in standard O₃ models. A difficulty lies in diagnosing the phase of the aerosols (Section 3.1). Hydrolysis of N₂O₅ does not proceed at a significant rate on dry aerosols.

A global 3-D model study by Dentener et al. (1996) investigated the potential effects of uptake of O₃, HO₂,

and N_2O_5 by mineral dust. Results showed a 10% decrease of boundary layer O_3 in dusty regions, mostly because of direct uptake of O_3 by the dust; outside dusty regions the effect was negligibly small. The study postulated a reaction probability $\gamma_{\text{O}_3} = 5 \times 10^{-5}$ for O_3 on mineral dust surfaces, based on measured O_3 deposition velocities to sand and bare soil. Although the link between deposition velocities and aerosol reactivity is tenuous, the Dentener et al. (1996) study has the merit of pointing out the sensitivity of O_3 to soil dust aerosols even with a relatively small reaction probability. Measurements of O_3 reactivity on dust particles are needed.

Horowitz et al. (1998) used a continental-scale 3-D model to examine the sensitivity of summertime O_3 concentrations over the United States to uptake of peroxy radicals by sulfate aerosols. They found that irreversible loss of HO_2 to aerosol with $\gamma_{\text{HO}_2} = 1$ causes 10–15% increases in mean NO_x concentrations and 1–3 ppbv decreases in mean O_3 concentrations in surface air over the eastern United States. The small effect on O_3 reflects compensating influences from decreasing HO_2 and increasing NO . Horowitz et al. (1998) also presented a simulation including both $\gamma_{\text{HO}_2} = 1$ and $\gamma_{\text{RO}_2} = 0.1$. In that simulation the mean NO_x concentrations in the eastern United States decreased by 5–10% (due to aerosol uptake of N-containing peroxy radicals) and O_3 concentrations decreased by up to 4 ppbv. As discussed in Section 7.1, there is ample laboratory evidence for uptake of HO_2 by aerosols. Uptake of RO_2 is far more speculative.

The effect on urban O_3 of heterogeneous conversion of NO_2 to HONO at night was investigated by Harris et al. (1982) with a box model simulation for the Los Angeles Basin initialized with 5–10 ppbv HONO at sunrise. These values are at the high end of urban observations reviewed by Calvert et al. (1994). They found that under high NO_x conditions (over 100 ppbv), the HO_x source from HONO photolysis speeds up the morning accumulation of O_3 by about one hour and results in an appreciable increase of integrated O_3 production over the course of the day. By contrast, under moderate NO_x conditions (10 ppbv) the increase in O_3 production is negligible because morning photochemistry is active even without the added HO_x source from HONO photolysis. A nighttime box model simulation by Jenkin et al. (1988) for urban air in London indicates an 8% increase in daily maximum O_3 as a consequence of nighttime HONO production. In contrast, a 3-D urban airshed model study of the Los Angeles Basin by Calvert et al. (1994) shows that nighttime formation of HONO produces less than 1% increase in next-day O_3 concentrations. In that simulation, the HONO concentrations computed in surface air at sunrise were comparable to those of Harris et al. (1982), but decreased rapidly with altitude as the NO_x concentrations decreased. As pointed out by Calvert et al. (1994), the stratification of the atmosphere in early

morning greatly decreases the impact of nighttime HONO on next-day O_3 in a 3-D model as compared to a box model. A.G. Russell (personal communication, 1998) finds in his 3-D urban model that heterogeneous HONO chemistry has typically less than a 1 ppbv effect on next-day peak O_3 concentrations although it can increase O_3 locally by 10–20 ppbv in areas where NO_x is particularly high. In summary, heterogeneous conversion of NO_2 to HONO should be included in standard O_3 models but its effect may often be small.

12. Recommendations for ozone models

The contents of the previous Sections can be summarized into specific recommendations for including heterogeneous chemistry in 3-dimensional O_3 models. Considering the limited state of our knowledge, a detailed treatment of heterogeneous chemistry in these models does not seem justified. As discussed in Section 4, I recommend a simple reaction probability parameterization (Eq. (8)) to describe the reactive uptakes of HO_2 , NO_2 , NO_3 , and N_2O_5 by aqueous aerosols including clouds. The computational overhead of this approach is minimal, as the heterogeneous reactions can be simply added to the gas-phase chemical mechanism of the model without increasing the stiffness of the system or the number of species to be solved. Aerosol surface areas and effective particle sizes (or size distributions) must either be obtained from the model or estimated. An important concern is the phase of the aerosol, since reaction probabilities for the above species on dry particles are at least one order of magnitude smaller than on aqueous particles. In the absence of better information one may assume that the aerosol is aqueous; this assumption should generally be acceptable at least in the lower troposphere due to the energy barrier for efflorescence (Section 3.1). I should stress that the simple recommendations presented here are intended only to ensure that standard O_3 models are consistent with current knowledge of heterogeneous chemistry. Further research on heterogeneous chemistry processes is clearly needed and specific recommendations in that regard are presented in the next Section.

Heterogeneous HO_x chemistry

- Current knowledge does not warrant including an aqueous-phase cloud chemistry mechanism in O_3 models (see Sections 5.4, 11.1). Catalytic O_3 loss driven by the aqueous-phase reaction $\text{O}_2^- + \text{O}_3(\text{aq})$ appears to be inefficient. Aqueous-phase loss of CH_2O in clouds appears to be negligible. The few field investigations of O_3 budgets in cloud-topped boundary layers show no obvious perturbation by aqueous-phase cloud chemistry. Scavenging of HO_2 by clouds

can be acceptably parameterized with $\gamma_{\text{HO}_2} = 0.2$ in the same way as for aqueous aerosols (see next bullet) without accounting for the details of aqueous-phase chemistry. Although this approach may exaggerate HO_2 depletion by not accounting for volatilization of $\text{HO}_2(\text{aq})$ (Schwartz, 1984), concentrations of HO_2 in clouds are low in any case.

- There is strong evidence for uptake of HO_2 in aqueous aerosols though the mechanism is uncertain (Section 7.1). The fate of HO_2 in the aqueous phase is unclear but H_2O_2 is a likely product. On the basis of present knowledge, it seems most appropriate to parameterize HO_2 uptake by a reaction probability $\gamma_{\text{HO}_2} = 0.2$ (range 0.1–1) for $\text{HO}_2 \rightarrow 0.5 \text{H}_2\text{O}_2$.
- Uptake of CH_3O_2 and other organic peroxy radicals by aerosols is probably negligible, with the possible exception of hydroxy- RO_2 radicals produced by oxidation of unsaturated hydrocarbons such as isoprene. The latter possibility can be investigated in sensitivity simulations using $\gamma_{\text{hydroxy-RO}_2} \sim 0.1$ and assuming inert products.
- Hydrolysis of $\text{CH}_3\text{C}(\text{O})\text{OO}$ in aqueous aerosols (RA14) could occasionally have some significance under nighttime conditions when PAN concentrations and aerosol surface areas are high (Section 6.5). It may easily be included in models using $\gamma_{\text{CH}_3\text{C}(\text{O})\text{OO}} = 4 \times 10^{-3}$ with the stoichiometry (RA14).

Heterogeneous NO_x chemistry

- Hydrolysis of N_2O_5 to HNO_3 in aqueous aerosols should be included in models with $\gamma_{\text{N}_2\text{O}_5} = 0.1$ (range 0.01–1), as discussed in Section 8.1.
- Heterogeneous conversion of NO_2 to HONO should be included in models (Sections 5.1 and 7.2). The mechanism is uncertain. I recommend parameterizing this process with $\gamma_{\text{NO}_2} = 10^{-4}$ (range 10^{-6} – 10^{-3}) for $\text{NO}_2 \rightarrow 0.5 \text{HONO} + 0.5 \text{HNO}_3$. Dry and wet deposition of HONO must then be included in the model as sinks for HONO at night. Loss of HONO to aerosols appears to be negligibly slow (Harrison and Collins, 1998).
- There is no evidence for significant heterogeneous PAN chemistry (Section 8.3).
- There is no evidence for significant conversion of HNO_3 to NO_x in aerosols (Sections 5.3 and 8.2).

Heterogeneous ozone loss

- There is no evidence for significant loss of O_3 on aerosol surfaces (Sections 9 and 11).

Halogen radical chemistry

- There is presently little justification for including BrO_x or ClO_x chemistry in standard O_3 models (Section 10).

13. Recommendations for future research

13.1. Improved characterization of aerosol phase and composition

Current knowledge of the phase and composition of tropospheric aerosols is insufficient to assess the atmospheric implications of heterogeneous reaction rates measured in the laboratory. Almost all of the available data on aerosol composition are surface measurements. The value of these measurements is limited by the large vertical gradients of aerosol concentrations, even within the boundary layer. Measurements aloft, from aircraft or balloons, are necessary. Specific measurements should include the size distribution, surface area, and phase of aerosol particles; the size-segregated chemical composition (water, inorganic ions, acidity, speciated transition metals, organic compounds, soot); the chemical composition of individual aerosol particles; the presence of organic surfactants; and the surface properties of solid particles.

13.2. Field study of marine boundary layer (MBL) chemistry

A dedicated aircraft study of the budgets of O_3 , HO_x , NO_x , halogens, and related species in the marine boundary layer (MBL) would improve understanding of the perturbation to O_3 from heterogeneous chemistry in clouds as well as in sea salt and sulfate aerosols. The MBL is an attractive environment for such a study because (1) it is dynamically simple; (2) it has an abundant supply of aqueous aerosols; (3) it allows investigation of halogen chemistry; (4) it is frequently topped by persistent stratus clouds. The subsiding coastal region off southern California would be well-suited because of the frequent occurrence of stratus and because of the range of pollution influences.

A generic flight track, drawing from the field study of Kawa and Pearson (1989), is shown in Fig. 6. The aircraft would be equipped with instrumentation for eddy correlation flux measurements of O_3 and meteorological variables. Additional instruments would measure gas-phase composition (including halogen radicals and their reservoirs), actinic fluxes, aerosol microphysics and chemistry, and cloudwater liquid water content and composition. Successive horizontal flight legs at different altitudes within and above the MBL, and below and above stratus decks, would be used to determine the divergence of the vertical O_3 flux and from there to infer the chemical tendency $(P - L)_{\text{O}_3}$. Using the local measurements of atmospheric composition to constrain photochemical model calculations of O_3 production and loss, it would be possible to diagnose whether the observed values of $(P - L)_{\text{O}_3}$ are consistent

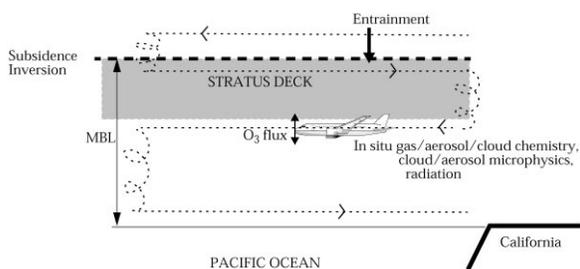


Fig. 6. Flight track for an aircraft mission investigating the effects of cloud, aerosol, and halogen chemistry on the atmospheric budgets of O_3 , HO_x , and NO_x in the marine boundary layer (MBL).

with current understanding and to quantify the role of heterogeneous chemistry. The photochemical model calculations would allow also an examination of the effects of heterogeneous chemistry on the budgets of HO_x and NO_x .

13.3. Marine boundary layer measurements of BrO , $HOBr$, Br_2

Evidence for BrO_x -catalyzed O_3 loss in the MBL is still highly circumstantial (Sections 5.4 and 10.1). It might be important in some regions and not in others. Field measurements of BrO , $HOBr$, or Br_2 over large geographical regions are needed. Of particular interest would be a long-range ship cruise in the Indian Ocean, where observations of a large diel cycle of O_3 concentrations have been attributed tentatively to BrO_x catalysis (Dickerson et al., 1999).

13.4. HONO as a source of HO_x

The only atmospheric measurements of HONO concentrations so far have been in surface air. Measurements of vertical profiles in the boundary layer would provide important information both on the underlying mechanism for HONO formation and on the actual importance of HONO as a source of HO_x driving O_3 formation. Measurements of HONO in the free troposphere would also be of great value but would require a sub-pptv detection limit (Jaeglé et al., 1999). The role of HONO as an early-morning source of HO_x in urban air should be verified by measuring the diel variation of HO_x concentrations together with HONO concentrations and other variables controlling the HO_x budget. The photochemical model calculation of Jenkin et al. (1988) predicts a factor of 5 increase in OH concentration near sunrise as a result of HONO photolysis; such an effect should be readily observable.

13.5. Aerosol sources of HO_x from photolysis of dissolved organic carbon (DOC) and transition metal complexes.

Laboratory studies have suggested a large cloudwater source of HO_x from photolysis of DOC compounds and organic iron complexes (Sections 6.3 and 6.4). The photolyzing compounds would presumably remain in the aerosol under non-cloud conditions. Quantifying the resulting source of HO_x to the gas phase would be of interest. A first step would be to irradiate authentic aerosol samples in the laboratory and measure the volatilization of HO_2 and OH to the gas phase.

13.6. Heterogeneous chemistry of peroxy radicals

Better information is needed on the mechanism and products of HO_2 uptake by aqueous aerosols (Section 7.1). The possible formation of HSO_5^- by (RA15)–(RA16) should be investigated. Laboratory data are needed for the Henry's Law constant of the CH_3O_2 radical and its reactive uptake by different aerosol surfaces. Similar data would also be valuable for the hydroxy- RO_2 radicals produced from the oxidation of isoprene.

13.7. Reduction of HNO_3 to NO_x in aerosols

Rapid reduction of HNO_3 to NO_x has been found to take place on dry black carbon surfaces in the laboratory (Section 8.2) but further investigation of this process is needed using authentic atmospheric soot particles (which may be greatly modified and hydrated). Mechanisms for reduction of HNO_3 to NO_x in acid aerosols, possibly involving NO_2^+ as a strong oxidant (Sampoli et al., 1985), need to be investigated for conditions representative of the troposphere.

13.8. Temperature dependence of aqueous-phase reactions

As can be seen from Table 3, few data are available for the temperature dependences of reaction rate constants in aqueous solutions. There is a general need for such data since atmospheric applications typically involve temperatures much lower than 298 K.

13.9. Compilation of chemical data for modeling atmospheric aqueous-phase chemistry

There is a need for a panel-reviewed compilation of aqueous-phase chemistry data for use in cloud and aerosol chemistry models, following the example of compilations already available for gas-phase chemistry and photochemistry (Atkinson et al., 1997; DeMore et al., 1997). The compilation should contain recommended values and estimated uncertainties for mass accommodation coefficients, Henry's Law constants, reaction probabilities, photochemical data, aqueous-phase equilibrium

constants (including precipitation equilibria), rate constants for chemical reactions, and activity correction factors. The DeMore et al. (1997) compilation already contains data of stratospheric relevance for mass accommodation coefficients, Henry's Law constants, and reaction probabilities.

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