

THE OXIDIZING POWER OF THE ATMOSPHERE

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Chapter for the *Handbook of Weather, Climate and Water*, ed. by T. Potter, B. Colman, and J. Fishman, Mc-Graw Hill (in press)

Revised: January 2000

1. INTRODUCTION

The atmosphere is an oxidizing medium. Many environmentally important trace gases are removed from the atmosphere by oxidation including methane and other organic compounds, carbon monoxide, nitrogen oxides, and sulfur gases (Table 1). Understanding the processes and rates by which species are oxidized in the atmosphere, i.e., the oxidizing power of the atmosphere, is crucial to our knowledge of atmospheric composition. Changes in the oxidizing power of the atmosphere would have a wide range of implications for air pollution, aerosol formation, greenhouse radiative forcing, and stratospheric ozone depletion [Thompson, 1992].

The most abundant oxidants in the Earth's atmosphere are O_2 and O_3 . They have large bond energies and are hence relatively unreactive. With a few exceptions, oxidation of non-radical atmospheric species by O_2 or O_3 is negligibly slow. Photochemical modeling of stratospheric chemistry in the 1950s first implicated the strong radical oxidants O and OH, generated from photolysis of O_3 and H_2O , in the oxidation of CO and CH_4 [Bates and Witherspoon, 1952]. The importance of photochemically generated radicals in the chain oxidation of hydrocarbons leading to urban O_3 smog was also recognized in the 1950s [Leighton, 1961]. Smog models of that time hypothesized that O atoms produced in urban air from the photolysis of NO_2 and O_3 would provide the main pathway for hydrocarbon oxidation [Altshuller and Bufalini, 1965, 1971]. This mechanism was thought unimportant outside of urban areas, because of low O_3 and NO_2 concentrations, and transport to the stratosphere was viewed as necessary for oxidation of CO, CH_4 , and other gases present in the global troposphere [Cadle and Allen, 1970]. Long atmospheric lifetimes for these gases were implied because of the 10-year residence time of air in the troposphere.

This view of a chemically inert troposphere was first challenged by Weinstock [1969] who found from ^{14}CO measurements that the atmospheric lifetime of CO is only ~0.1 years, requiring a dominant sink in the troposphere. Levy [1971] then presented photochemical model calculations for the unpolluted troposphere showing that high concentrations of OH could be generated from photolysis of O_3 in the presence of water vapor and account for the missing sink

of CO in the Weinstock [1969] analysis. Further work in the early 1970s confirmed the importance of tropospheric oxidation by OH as the main sink of CO and CH₄ [McConnell et al., 1971; Weinstock and Niki, 1972; Levy et al., 1973] and further showed that OH, not O, is the main oxidant of hydrocarbons in urban air [Heicklen, 1971; Kerr et al., 1972; Demerjian et al., 1974]. Considerable evidence over the past three decades supports the view that tropospheric OH is the main oxidant for non-radical species in the atmosphere.

Table 1 Atmospheric lifetimes of selected species

| Species | Lifetime ^a | Reference |
|---------------------------------------|----------------------------|-----------------------------|
| CH ₃ CCl ₃ | 4.8 y (5.7 y) | WMO [1999] |
| CH ₄ | 8.4 y (8.9 y) | <i>ibid.</i> |
| CHF ₂ Cl | 11.8 y (12.3 y) | <i>ibid.</i> |
| CH ₃ Br | 0.7 y (1.7 y) | <i>ibid.</i> |
| Isoprene ^b | ~ 1 h (~ 1 h) | Jacob et al. [1989] |
| CO | 2 mo (2 mo) | Logan et al. [1981] |
| NO _x (NO+NO ₂) | ~ 1 d (~1 d) ^c | Dentener and Crutzen [1993] |
| SO ₂ | ~ 1 d (2 wks) ^d | Chin et al. [1996] |
| (CH ₃) ₂ S | ~ 1 d (~1 d) | <i>ibid.</i> |

- a. The atmospheric lifetime of a species is defined as the average time that a molecule of the species remains in the atmosphere before it is removed by one of its sinks. It can be calculated as the atmospheric mass of the species divided by the species loss rate. The first number given for each entry in the column is the mean atmospheric lifetime, and the second number in parentheses is the mean atmospheric lifetime against oxidation by OH.
- b. CH=C(CH₃)-CH=CH₂, a major hydrocarbon emitted by vegetation.
- c. Loss of NO_x in summer and in the tropics is mostly by reaction of NO₂ with OH; loss in winter at extratropical latitudes is mostly by a non-photochemical pathway involving formation of N₂O₅ and hydrolysis to HNO₃. The sum of these two processes results in a lifetime of NO_x of the order of a day.
- d. The principal SO₂ sinks are deposition and in-cloud oxidation by H₂O₂(aq).

Indirect estimates of global mean OH concentrations have been made since the 1970s using a number of proxies, the most useful of which has been CH₃CCl₃, a long-lived gas emitted by industry and removed from the atmosphere by

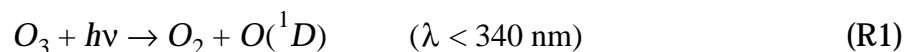
oxidation by OH [Lovelock, 1977; Singh, 1977]. The most recent analyses of CH_3CCl_3 data, based on observations at a worldwide network of sites [Prinn et al., 1995], imply a global mean OH concentration in the troposphere of $(1.1 \pm 0.1) \times 10^6$ molecules cm^{-3} [Krol et al., 1998; Spivakovsky et al., 2000]. Techniques for direct measurement of tropospheric OH were first developed in the 1970s but suffered from interferences or poor sensitivity. Only in the 1990s have reliable techniques been developed and successfully intercompared [special issue of *Journal of the Atmospheric Sciences*, October 1995; Crosley, 1997]. Direct measurements provide the means to test our understanding of the local processes controlling OH concentrations [e.g., McKeen et al., 1997; Jaeglé et al., 1997, 2000; Frost et al., 1999]. By simulating these processes in global models, one can assess the sensitivity of the oxidizing power of the atmosphere to different anthropogenic perturbations [Wang and Jacob, 1998].

This chapter reviews current understanding of the factors controlling abundances and long-term trends of OH. It also briefly reviews (section 3) other atmospheric oxidants which are important in certain environments or for certain non-radical molecules. It does not cover the oxidation of short-lived radical species, which often involves reaction with O_2 or O_3 [Atkinson, 1990]. It does not cover either oxidation in the stratosphere, whose importance as a sink for species emitted at the surface is limited by the long time for transfer of air from the troposphere to the stratosphere.

2. THE HYDROXYL RADICAL OH

2.1 Processes controlling OH concentrations

A detailed and still fairly current discussion of OH chemistry in the troposphere is given by Logan et al. [1981]. The primary source of OH is the photolysis of O_3 to produce an excited state of atomic oxygen, $\text{O}(^1\text{D})$, which then reacts with water vapor:



Here M is an inert molecule (N_2 or O_2). Only ~1% of the $\text{O}(^1\text{D})$ atoms produced by (R1) react with H_2O ; most are deactivated to the ground state $\text{O}(^3\text{P})$ and recombine with O_2 to return O_3 . Photolysis of O_3 to $\text{O}(^1\text{D})$ in the troposphere is determined by a narrow band of radiation in the 290-330 nm range, reflecting the combined wavelength dependences of the actinic flux, O_3 absorption

cross-section, and $O(^1D)$ quantum yield (Figure 1). Radiation in this wavelength range is strongly absorbed by overhead O_3 and hence the production of $O(^1D)$ is strongly dependent on the thickness of the stratospheric O_3 layer [Madronich and Granier, 1992].

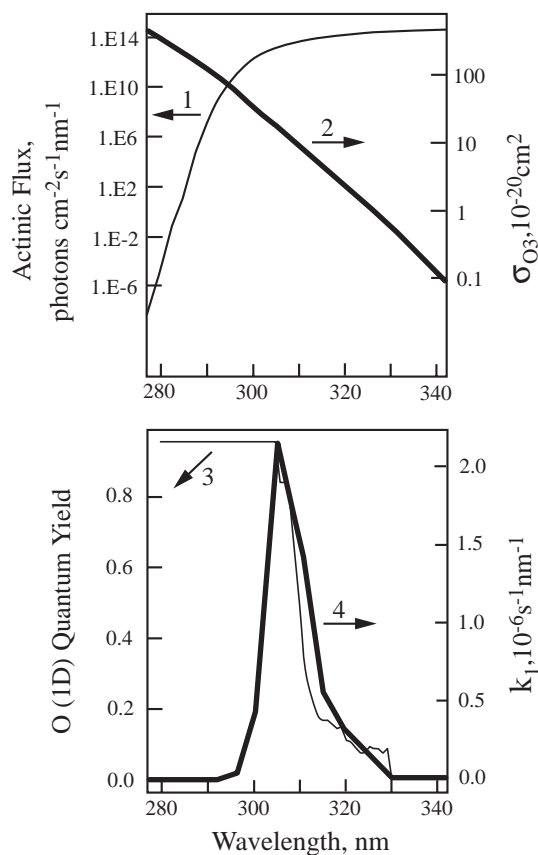


Figure 1. Computation of the rate constant k_1 for photolysis of O_3 to $O(^1D)$ in the troposphere as a function of wavelength. (1) Solar actinic flux at sea level for 30° solar zenith angle and a typical O_3 column overhead [DeMore et al., 1997]; (2) Absorption cross-section of O_3 at 273 K [DeMore et al., 1997]; (3) $O(^1D)$ quantum yield at 273 K [Talukdar et al., 1998]; and (4) rate constant k_1 calculated as the product of (1), (2), and (3). From Jacob [1999].

The OH radical is consumed on a time scale of ~ 1 s by oxidation of a large number of reduced atmospheric species. Its main sinks in the troposphere are CO and CH_4 . Non-methane hydrocarbons (NMHCs) are also important sinks in the lower troposphere over continents. Oxidation of CO or hydrocarbons by OH propagates a radical reaction chain initiated by the generation of OH radicals from (R4). The simplest case is oxidation of CO:



The HO₂ radicals may self-react to produce H₂O₂ (hydrogen peroxide):



or they may regenerate OH by reaction with NO or O₃:



Hydrogen peroxide produced by (R7) is removed from the atmosphere by deposition. It may also photolyze, regenerating OH,



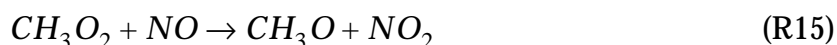
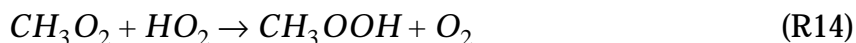
or react itself with OH:



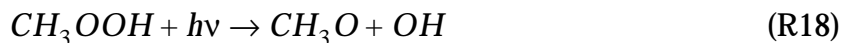
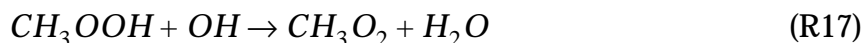
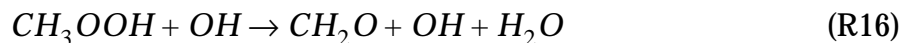
The same type of chain mechanism applies to the oxidation of hydrocarbons, but the complexity increases rapidly as the size of the hydrocarbon molecule increases. The mechanism for CH₄ is described here. It begins by



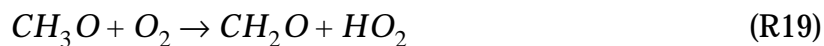
The CH₃O₂ molecule (methylperoxy radical) is analogous to HO₂. Its dominant sinks in the atmosphere are reactions with HO₂ and NO:



Similarly to H₂O₂, methylhydroperoxide (CH₃OOH) may either react with OH or photolyze:

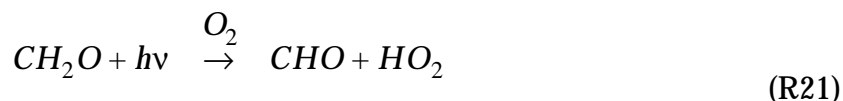


The methoxy radical CH₃O produced by (R15) and (R18) reacts rapidly with O₂:



Formaldehyde produced by (R16) and (R19) may either react with OH or

photolyze (two photolysis branches):



Reactions (R20) and (R21) produce the CHO radical, which reacts rapidly with O_2 to yield CO:



In this overall sequence the C(-IV) atom in CH_4 is gradually oxidized to C(-II) in CH_3OOH , C(0) in CH_2O , C(+II) in CO, and C(+IV) in CO_2 (highest oxidation state for carbon).

The regeneration of OH radicals by (R8) plays a critical role in maintaining OH concentrations in the troposphere. The main sink for NO_2 produced by (R8) and (R15) is photolysis, regenerating NO and producing O_3 :



This O_3 may then photolyze to yield additional OH by (R1)+(R4). Although reaction (R9) also recycles OH, it consumes in the process an O_3 molecule which could have otherwise photolyzed to produce OH. Therefore it is not effective for maintaining OH concentrations.

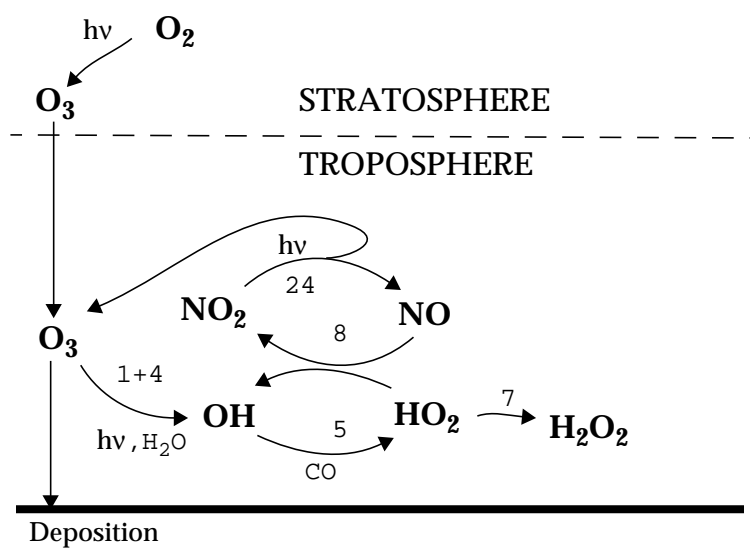


Figure 2. Simplified schematic of O_3 - HO_x - NO_x -CO chemistry in the troposphere

Figure 2 illustrates how tropospheric OH is controlled by chemical cycling of the hydrogen oxide family ($\text{HO}_x \equiv \text{OH} + \text{peroxy radicals}$) and the nitrogen oxide family ($\text{NO}_x \equiv \text{NO} + \text{NO}_2$), for the simple case of CO oxidation. The schematic for hydrocarbon oxidation is similar, except that photolysis of carbonyl compounds as in reaction (R21) provides an additional (generally minor) source of HO_x . The dominant sink for the HO_x family is usually the formation of peroxides. As discussed previously, these peroxides may photolyze to recycle HO_x ; alternatively they may deposit or react with OH, providing a terminal sink for HO_x . Sources of NO_x in the troposphere include combustion, microbial activity in soils, and lightning. Sources of CO and hydrocarbons include combustion, industrial processes, soils, and vegetation.

An analytical expression for the dependence of OH concentrations on chemical variables can be obtained from the simplified O_3 - HO_x - NO_x -CO system of Figure 2 by assuming chemical steady state for the short-lived species $\text{O}(^1\text{D})$, H, OH, and also for the chemical family HO_x . The lifetime of HO_x against formation of peroxides is of the order of minutes, so that the steady state assumption is appropriate. The production rate P_{HO_x} of HO_x from reaction (R4) is given by

$$P_{\text{HO}_x} = 2k_4[\text{O}(^1\text{D})][\text{H}_2\text{O}] \approx 2\frac{k_1k_4}{k_2[M]}[\text{O}_3][\text{H}_2\text{O}] \quad (1)$$

where k_i is the rate constant for reaction (i). In writing equation (1) we have used the approximation (R1) \gg (R4) to simplify the denominator. Steady state for OH is defined by

$$P_{\text{HO}_x} + k_8[\text{HO}_2][\text{NO}] = k_5[\text{CO}][\text{OH}] \quad (2)$$

Loss of HO_x in this system is by (R7). Steady state for HO_x is therefore defined by

$$P_{\text{HO}_x} = 2k_7[\text{HO}_2]^2 \quad (3)$$

from which we derive the following expression for the OH concentration:

$$[\text{OH}] = \frac{P_{\text{HO}_x} + k_8\sqrt{\frac{P_{\text{HO}_x}}{2k_7}}[\text{NO}]}{k_5[\text{CO}]} \quad (4)$$

We see from equation (4) together with equation (1) that OH concentrations depend negatively on CO and positively on water vapor, O_3 , and NO. The dependence on hydrocarbons is more complicated (as hydrocarbons provide both sinks of OH and sources of HO_x) but is generally negative, similar to CO.

One important caveat to this simplified representation of OH chemistry

must be made for high- NO_x environments. When NO_x concentrations exceed a few ppbv, as in urban air, oxidation of NO_2 by OH can become the dominant sink for HO_x :



Under these conditions, OH concentrations decrease with increasing NO_x (as may be derived by repeating the steady-state calculation above) and increase with increasing hydrocarbons. This situation is commonly denoted the NO_x -saturated (or hydrocarbon-limited) regime, as opposed to the NO_x -limited regime normally encountered in the troposphere.

A second caveat applies to the upper troposphere where water vapor concentrations are low (~ 100 ppmv). Under these conditions, reaction (R4) may be less important as a primary source of HO_x than photolysis of acetone originating from the biosphere [Singh et al., 1995] or convective injection of peroxides and aldehydes produced in the lower troposphere [Jaeglé et al., 1997; Prather and Jacob, 1997; Müller and Brasseur, 1999]. Reaction of OH with HO_2 provides in general the dominant HO_x sink in the upper troposphere, which yields a square-root rather than linear dependence of OH concentrations on NO.

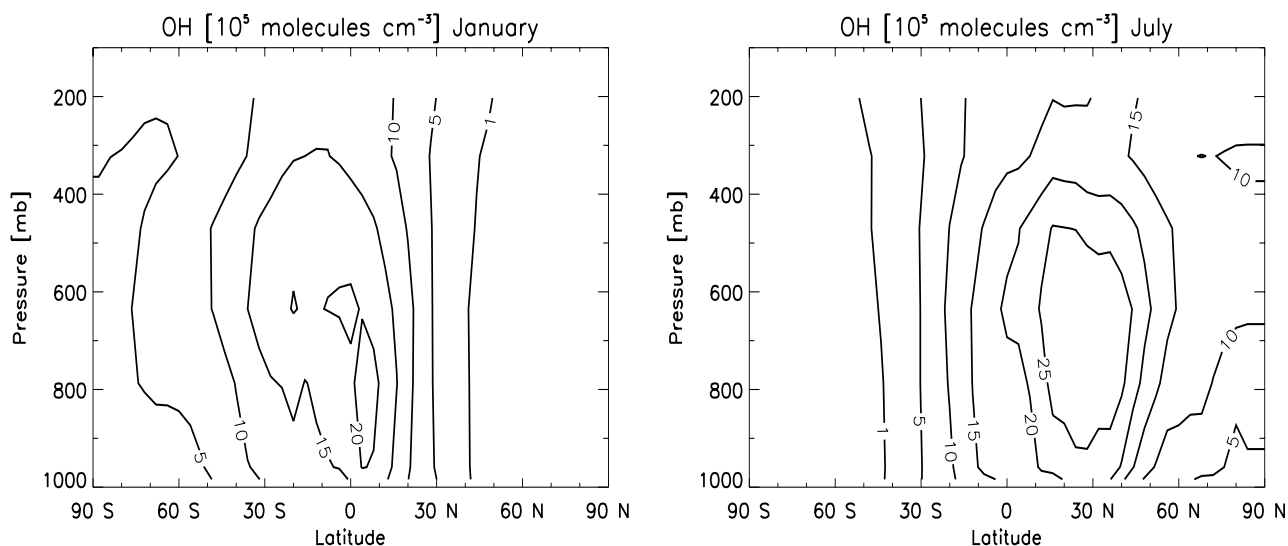


Figure 3. Longitudinally averaged OH concentrations (10^5 molecules cm^{-3}) computed in a global 3-dimensional model of tropospheric O_3 - NO_x -CO-hydrocarbon chemistry for January and July. From Wang et al. [1998b]

Figure 3 shows zonal mean global distributions of OH concentrations computed with a global 3-dimensional model of tropospheric O_3 - NO_x -hydrocarbon chemistry [Wang et al., 1998b]. The highest concentrations (averaging over 2×10^6 molecules cm^{-3}) are in the tropical middle troposphere, reflecting a combination of high UV and high humidity. The large seasonal variation at midlatitudes follows UV radiation. Concentrations tend to be higher

in the northern than in the southern hemisphere, reflecting higher NO_x concentrations.

2.2 Global mean OH concentration

The short lifetime of OH implies that its concentration is highly variable. Deriving the atmospheric lifetimes of gases removed by oxidation by OH requires an estimate of OH concentrations averaged appropriately over time and space. Mass balance arguments for proxy species with known sources can assist for this purpose. The most successful application, first proposed by Singh [1977] and Lovelock [1977], has been the use of the industrial solvent CH_3CCl_3 to estimate the global mean OH concentration. The source of CH_3CCl_3 is exclusively anthropogenic and its historical trend is well known from industrial data. Production of CH_3CCl_3 has been banned since 1996 as part of the Montreal protocol. The dominant sink of CH_3CCl_3 is oxidation by OH in the troposphere (photolysis in the stratosphere and uptake by the oceans are small additional sinks). Tropospheric mixing ratios of CH_3CCl_3 are relatively uniform, so that a mass balance analysis for CH_3CCl_3 yields a global mean OH concentration weighted by atmospheric mass and by the temperature dependence of the $\text{CH}_3\text{CCl}_3 + \text{OH}$ reaction. The global mean OH concentration obtained in this manner can then be used to infer the lifetimes of other long-lived gases removed by reaction with OH, such as CH_4 and hydrogenated halocarbons (HCFCs) [Prather and Spivakovsky, 1990].

The most recent use of CH_3CCl_3 observations to constrain the global mean OH concentration has been by Krol et al. [1998] and Spivakovsky et al. [2000]. These authors derive a CH_3CCl_3 lifetime of 5.5 years in the troposphere against oxidation by OH, corresponding to a global mean OH concentration of $(1.1 \pm 0.2) \times 10^6$ molecules cm^{-3} . Spivakovsky et al. [2000] point out that the magnitude of the CH_3CCl_3 interhemispheric gradient implies that the difference between the mean OH concentrations in the northern and southern hemispheres is no more than 50%. Mass balance arguments for other chemical tracers oxidized by OH including ^{14}CO , CHF_2Cl , CH_2Cl_2 , and hydrocarbons have been used to confirm the above estimate of the global mean OH concentration and to provide additional constraints on the geographical and seasonal distribution of OH [Volz et al., 1981; Mak et al., 1992; Goldstein et al., 1995; Spivakovsky et al., 2000].

Simulation of the CH_3CCl_3 lifetime has long been a standard test for evaluating the global mean OH concentration computed in tropospheric chemistry models, starting from the work of Crutzen and Fishman [1977]. In these models, the OH concentrations are computed from a global simulation of O_3 - NO_x -CO-hydrocarbon chemistry that treats emissions, transport, chemistry, and deposition in a self-consistent way [e.g., Wang et al., 1998a]. The current generation of models reproduces the atmospheric lifetime of CH_3CCl_3 to within

typically 25%.

2.3 Measurements of OH concentrations and comparisons to models

The past few years have seen the development of a number of methods for direct measurement of tropospheric OH [special issue of *J. Atmos. Sci.*, October 1995]. Two of these methods, a long-path absorption (LPA) instrument [Mount, 1992] and a Chemical Ionization Mass Spectrometry (CIMS) instrument [Eisele and Tanner, 1991] were intercompared formally at a mountain site in Colorado during the Tropospheric OH Photochemistry Experiment (TOHPE). Under well-mixed atmospheric conditions where the local OH measurement from CIMS could be compared to the long-path average from LPA, the intercomparison demonstrated a good correlation between the two instruments down to concentrations of less than 1×10^6 molecules cm^{-3} , with no significant bias [Crosley, 1997].

A number of ancillary chemical measurements were made during TOHPE which McKeen et al. [1997] used to compare the observed OH concentrations to values computed from a standard photochemical model. The model overestimated OH concentrations by a factor of 1.3 on average. It captured 48% of the variance in the CIMS instrument, although much of that variance was driven by the diurnal cycle. It was not correlated with the LPA instrument, which may reflect the non-local nature of the latter measurement.

The model overestimate of OH in TOHPE is consistent with other model-measurement comparisons conducted at continental sites [Poppe et al., 1995; Thompson, 1995; George et al., 1999]. As discussed by McKeen et al. [1997], possible causes include inadequate model representation of hydrocarbon chemistry or of uptake of HO_x by aerosols. Eisele et al. [1996] conducted a model-measurement comparison using the CIMS instrument at Mauna Loa Observatory, Hawaii (3.4 km altitude); they found good agreement when subsiding motions brought free tropospheric air to the site but a factor of 2 model overestimate under upslope flow, supporting the view that biogenic hydrocarbons may provide important sinks for OH. Frost et al. [1999] found a median model overestimate of 32% in simulation of aircraft observations for clean marine air.

An important aspect of these model-measurement comparisons has been to examine the ability of models to reproduce the dependence of OH concentrations on chemical and meteorological variables. Poppe et al. [1995] found that their model could capture successfully the observed correlations of OH concentrations with UV intensity, temperature, humidity, and CO concentration. Measurements in TOHPE showed OH concentrations increasing with increasing NO_x up to about 2 ppbv NO_x and then decreasing, consistent with model calculations of NO_x - vs. hydrocarbon-limited chemistry [Eisele et al., 1997; McKeen et al., 1997].

Aircraft measurements of OH and HO_2 concentrations in the upper troposphere have been reported by Brune et al. [1998, 1999] and Wennberg et al. [1998]. The measured OH/ HO_2 ratios and their variances agree with model

values to within the uncertainties of the relevant rate constants, implying a good understanding of the cycling of HO_x [Jaeglé et al., 2000]. The observed HO_x concentrations are often several times lower than would be predicted solely from the O(¹D)+H₂O source (R4) and support the presence of other primary HO_x sources in the upper troposphere including acetone, peroxides, and aldehydes.

2.4 Long-term trends in atmospheric OH

Assessing human influence on the oxidizing power of the atmosphere is intricate. On the one hand, anthropogenic emissions of CO and hydrocarbon emissions act to deplete OH; on the other hand, anthropogenic emissions of NO_x and the thinning of the stratospheric O₃ layer act to boost OH. Human-induced changes in the Earth's climate (temperature, cloudiness, circulation) add to the complication. Large regional differences may be expected in the response of OH to human activity, depending on the relative importance and coupling of the above factors.

A number of global tropospheric chemistry model studies, reviewed by Thompson [1992], have examined the changes in OH concentrations since preindustrial times as driven by trends in emissions of CO, hydrocarbons, and NO_x. These studies report 10-30% decreases in the global mean OH concentration from preindustrial times to today, a relatively small effect considering that emissions of CO, CH₄, and NO_x increased several-fold over that period (Table 2). The global 3-dimensional model study of Wang and Jacob [1998] indicates a 9% decrease in the global mean OH concentration since pre-industrial times and suggests that the OH trend should follow roughly the trend of the $S_{\text{NO}}/S_{\text{C}}^{3/2}$ ratio, where S_{NO} is the global source of NO and S_{C} is the global source of CO and hydrocarbons; the parallel changes in S_{NO} and S_{C} over the past century would thus have had nearly canceling effects on OH concentrations. This study points out that estimates of past and future trends in OH are highly sensitive to assumed trends in tropical biomass burning, because NO_x emitted in the tropics is particularly efficient for generating O₃ and OH.

Observational constraints on long-term OH trends are largely limited to the CH₃CCl₃ record since 1978. An analysis of this record by Krol et al. [1998] indicates a 0.5% yr⁻¹ increase in global mean OH concentrations over the 1978-1993 period. This result is consistent with radiative transfer model calculations by Madronich and Granier [1992] which indicate a 0.4% yr⁻¹ increase in OH concentrations over the 1979-1989 decade as a result of stratospheric O₃ depletion.

Table 2 Comparison of present and preindustrial atmospheres^a

| | Emission | | | | O ₃ source ^b (Tg O ₃ yr ⁻¹) | [OH] ^c (molecules cm ⁻³) |
|---------------|---|--|---------------------------------|---|---|---|
| | CH ₄ (Tg CH ₄ yr ⁻¹) | Nonmethane hydrocarbons (Tg C yr ⁻¹) | CO (Tg CO yr ⁻¹) | NO _x (Tg N yr ⁻¹) | | |
| Preindustrial | 160 | 610 ^d | 50 | 9 | 2300 | 1.15x10 ⁶ |
| Present | 460 | 710 | 1040 | 42 | 4500 | 1.04x10 ⁶ |

- Global data from the 3-dimensional model study of Wang and Jacob [1998].
- Tropospheric O₃ source including transport from the stratosphere (400 Tg O₃ yr⁻¹ in both preindustrial and present cases) and chemical production within the troposphere.
- Global mean tropospheric concentration weighted by atmospheric mass.
- Biogenic isoprene and acetone.

Estimates of OH trends since pre-industrial and glacial times have been made using polar ice core records of CH₂O and H₂O₂. Interpretation of these records is complicated by post-depositional exchange with the atmosphere and reactions within the ice [Neftel et al. 1995]. Also, since CH₂O and H₂O₂ have atmospheric lifetimes of about a day, they can only diagnose trends in polar OH, which may be different from global tropospheric trends. Analysis of the CH₂O/CH₄ ratio in a Greenland ice core [Staffelbach et al., 1991] suggests that OH concentrations were 30% higher in the pre-industrial atmosphere than today, and 2-4 times lower in the last glacial maximum (LGM) than today. Such depletion of OH in the LGM is not consistent with results from tropospheric chemistry models, which indicate higher OH concentrations in glacial than interglacial periods due to lower emissions of CH₄ [Thompson, 1992]. Staffelbach et al. [1991] suggested that a thicker stratospheric O₃ layer could be responsible for low OH levels during glacial periods.

Data for H₂O₂ in Greenland ice going back to 1300 A.D. show constant concentrations until about 1970, and a doubling of concentrations since then [Sigg and Neftel, 1991; Anklin and Bales, 1997]. Although the rise in H₂O₂ would imply a rise in HO_x, the CH₃CCl₃ record shows no large trend in global mean OH concentrations during that same period.

3. OTHER ATMOSPHERIC OXIDANTS

Other atmospheric oxidants besides OH may also be important in some environments and for some species. They are reviewed briefly below.

3.1 Nitrate radical

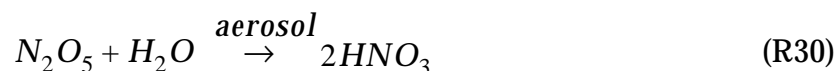
The nitrate radical (NO_3) is a strong radical oxidant formed in the oxidation of NO_2 by O_3 :



A detailed review of its atmospheric chemistry is given by Wayne [1991]. During the daytime, NO_3 photolyzes on a time scale of 1 minute to return NO_2 :



At night the lifetime of NO_3 is much longer. In high- NO_x regions such as the eastern United States, NO_3 accumulates to concentrations of 10-100 pptv during the nighttime hours [Wayne, 1991]. At these concentrations, NO_3 can provide an important sink for some unsaturated hydrocarbons including isoprene and terpenes (O_3 is also an important oxidant for these compounds). Measurements in relatively polluted marine air over the North Sea indicate a mean nighttime NO_3 concentration of about 10 pptv; at this concentration, NO_3 represents a major sink for biogenic dimethylsulfide [Carslaw et al., 1997]. Nighttime accumulation of NO_3 is in general limited by equilibrium with N_2O_5 , followed by hydrolysis of N_2O_5 in aerosols:



At low temperatures ($T < 280 \text{ K}$) the $\text{NO}_3/\text{N}_2\text{O}_5$ equilibrium is shifted far to the right; thus NO_3 is important only in the warm lower troposphere.

3.2 Halogen radical oxidants

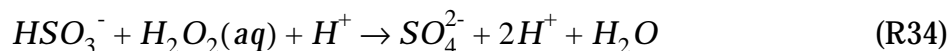
There has been long-standing interest in the possible role of halogen radicals as tropospheric oxidants [Singh and Kasting, 1988; Chatfield and Crutzen, 1990]. The best evidence so far comes from measurements of alkanes and acetylene in Arctic surface air [Jobson et al., 1994] which indicate a sink in April (polar sunrise) consistent with oxidation by Cl atoms present at a concentration $\sim 1 \times 10^4 \text{ atoms cm}^{-3}$. The data also suggest the presence of Br atoms to oxidize acetylene. The source of the halogen oxidants is not well established but likely involves chemical production from sea salt accumulated on the ice over the polar night [Impey et al., 1999].

Generation of halogen oxidants from sea salt would be of little interest for

global tropospheric chemistry if it were confined to Arctic sunrise. However, measurements of hydrocarbons and non-radical Cl species in the marine boundary layer (MBL) at midlatitudes and in the tropics suggest that Cl atoms may be present at least occasionally at concentrations in the range 10^4 - 10^5 atoms cm^{-3} [Keene et al., 1990, 1996; Pszenny et al., 1993; Singh et al., 1996; Spicer et al., 1998]. At such concentrations, oxidation by Cl atoms would provide a major sink for dimethylsulfide and alkanes in the MBL. Even less is known about Br radical chemistry in the MBL, although Toumi [1994] has suggested that BrO could provide an important oxidant for $(\text{CH}_3)_2\text{S}$. Field measurements of the halogen radicals and their reservoirs HOCl and HOBr are needed [Jacob, 2000].

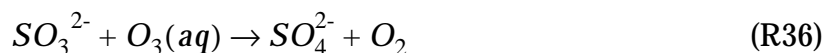
3.3 Cloud and aerosol oxidants

Water-soluble atmospheric species incorporated in cloud droplets and aqueous aerosols may dissociate into ions, and the resulting aqueous-phase redox chemistry provides yet another pathway for oxidation of species in the atmosphere. The importance of this pathway has been established for SO_2 , which dissociates in water to HSO_3^- and SO_3^{2-} ($pK_{a1} = 1.9$, $pK_{a2} = 7.2$). Rapid oxidation of SO_2 by H_2O_2 in cloud was first suggested by Penkett et al. [1979]:



Aircraft measurements by Daum et al. [1984] demonstrated that the reaction is sufficiently fast to titrate either SO_2 or H_2O_2 in cloud (whichever is limiting). It is now well accepted that this mechanism dominates over gas-phase oxidation by OH as a sink for SO_2 in the atmosphere [Chin et al., 1996].

Additional non-radical oxidants may also be important for oxidation of SO_2 in clouds and aqueous aerosols, but their importance is not as well verified as for H_2O_2 . At high pH values ($\text{pH} > 5$), $\text{O}_3(aq)$ reacts rapidly with SO_3^{2-} :



This mechanism, taking place in alkaline sea salt aerosols, could represent a major sink for SO_2 in the marine boundary layer [Chameides and Stelson, 1992]. Additional SO_2 oxidants in sea salt aerosol may include HOCl and HOBr produced by halogen radical chemistry [Vogt et al., 1996]. In polluted clouds, aqueous-phase autoxidation catalyzed by Fe(III) could provide the dominant SO_2

sink [Jacob and Hoffmann, 1983].

ACKNOWLEDGMENT. I thank Clarisa M. Spivakovsky for valuable comments.

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