2

Atmospheric Chemistry

Air quality, the health of the ozone layer, and the earth's global climate are closely tied to the composition of the atmosphere and the chemical transformation of natural and anthropogenic trace gases. Although the purpose of this book is not to cover the full breadth of atmospheric chemistry, this chapter provides a short introduction into this topic, with the intent to motivate and clarify the applications of the differential optical absorption spectroscopy (DOAS) technique. Key elements of the contemporary understanding of atmospheric chemistry and ongoing research efforts are presented. This chapter is mostly restricted to chemical reactions occurring between gas molecules, although a few surface reactions are also presented. It should be noted that much of our knowledge of atmospheric chemistry comes from studies employing sophisticated instrumentation for the detection of atmospheric trace gases, including the DOAS technique.

Much of the motivation to study atmospheric chemistry and the composition of the atmosphere is based on various man-made environmental problems that have emerged over the past two centuries. Human activities have upset the natural balance of the atmosphere by influencing the trace gas and aerosol composition on local, regional, and even global scales. The following list names the most significant atmospheric environmental problems:

- 'London Type' smog was first recognised as an environmental problem in the 19th century (Brimblecombe and Heymann, 1998). The emission of soot particles and the formation of aerosols consisting of sulphuric acid, which were produced from photochemical oxidation of SO_2 emitted from combustion sources, had a severe impact on human health. During the so-called 'London Killer Smog', approximately 4000 excess deaths were counted in London during a 4-day period. It should be noted that the term 'Smog' was coined to describe the interaction of Smoke and Fog (Smog) that formed the strong haze observed in London during winter time.

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- Crop damage and human discomfort were the first indication of high levels of oxidants during sunny and hot days in Los Angeles (Haagen-Smit, 1952; Haagen-Smit and Fox, 1954; Finlayson-Pitts and Pitts, 2000). The formation of this ‘Los Angeles Type’ smog was found to be primarily due to photochemical formation of large amounts of ozone, carbonyl compounds, and organic aerosol from car exhaust and industrial emissions of nitrogen oxides, carbon monoxide, and volatile organic compounds (VOCs) (Haagen-Smit, 1952; Finlayson-Pitts and Pitts 2000). Despite many decades of research and mitigation activities, Los Angeles type smog remains one of the most common air pollution problems in urban areas today.
- Forest decline and lake acidification were signs of another man-made environmental problem. Increased emissions of sulphur dioxide and nitrogen oxides, followed by their gas and aqueous phase oxidation to sulphuric and nitric acid, lead to ‘Acid rain’ that lead to the deposition of these acids to various ecosystems (Charlson and Rhode, 1982). While acid rain has successfully been reduced in Europe and the United States, it remains a problem in many developing countries.
- The health of the atmospheric ozone layer has always been a concern of atmospheric scientists. In 1971, Johnston (1971) predicted the loss of stratospheric ozone due to emission of oxides of nitrogen by a planned fleet of supersonic passenger aircraft. Molina and Rowland (1974) warned of a gradual loss of stratospheric ozone due to catalysed ozone destruction processes by halogen species transported to the stratosphere in the form of extremely stable halogen-containing compounds, so called chlorofluorocarbons (CFCs), used as coolants or spray can propellants. Their predictions became reality in 1985, when Farman et al. (1985) discovered the stratospheric ‘ozone hole’ over Antarctica. This recurring phenomenon reduces the thickness of the stratospheric ozone layer over Antarctica to less than one third of its normal level every Antarctic Spring (e.g. Farman et al., 1985; Solomon, 1999). While steps have been taken to stop the emissions of CFCs, it is estimated that it will take another three decades before the ozone hole will close again.
- One of the most serious environmental problems is the impact of human activities on the climate of our planet. The potential of global warming caused by IR-active ‘greenhouse’ gases such as CO_2, CH_4, N_2O, O_3, CFCs (e.g. $CFCl_3$ and CF_2Cl_2), and the direct and indirect effects of chemically generated aerosol, have been known for some time (e.g. Arrhenius, 1896; Rhode et al., 1997; IPCC, 2002). Human activities, and thus the emission of the various greenhouse gases, over the past century have reached levels where an impact on global surface temperatures, the global water cycle, ocean levels, etc. has become very likely. Today, many signs point at the beginning of a global climate change which will have a severe impact on our earth. The global increase of tropospheric ozone, which apparently started in the middle of the 19th century, also contributes to this phenomenon. It is thought to be caused by catalytic ozone production due to wide-spread

emission of oxides of nitrogen and hydrocarbons (HC) (Volz and Kley, 1988; Staehelin et al. 1994).

Many of these phenomena are closely related to the atmospheric chemistry presented in this chapter.

Environmental conditions, such as temperature, pressure, and the solar spectrum, change with altitude and several altitude regimes of atmospheric chemistry can be distinguished. These properties of the atmosphere relevant for atmospheric chemistry will be presented in Sect. 2.1. The composition of the atmosphere is influenced by emissions of natural and man-made species. A short overview over these emission and their sources is given in Sect. 2.2. Tropospheric chemistry is dominated by ozone and other oxidants, i.e. hydroxyl/peroxy radicals, nitrogen oxides, and volatile organic carbons. While their chemistry is closely linked, we will discuss the chemistry of each class of species in Sects. 2.4–2.7. Sulphur chemistry (Sect. 2.8) also plays an important role as it aids in the formation of atmospheric acid and is also crucial for the formation of particles in the atmosphere. The chemistry of reactive halogen species (RHS) in the troposphere, which is suspected to influence ozone levels on a global scale, is presented in Sect. 2.9. The various radical species in the troposphere also play a crucial role for the 'self-cleaning' power of the atmosphere (Sect. 2.11). The atmospheric region between 15 and 50 km height, the stratosphere, hosts the ozone layer, which protects the earth surface from solar UV radiation. Consequently, stratospheric chemistry (Sect. 2.10) revolves around the formation and destruction pathways of ozone, as well as the chemical mechanisms leading to the destruction of ozone over Antarctica in spring, the so-called ozone hole.

2.1 Atmospheric Structure and Composition

For practical purposes, air can be viewed as an ideal gas. The relationship between pressure p, absolute temperature T, and volume V for a given number of moles n (1 mole is equal to $\mathrm{N_A} = 6.023 \times 10^{23}$ molecules of air) is given by the ideal gas law:

$$pV = nRT \tag{2.1}$$

where $R = 8.315\,\mathrm{J\,mole^{-1}K^{-1}}$ denotes the universal gas constant.

At standard sea-level pressure, $p_0 = 1.013 \times 10^5\,\mathrm{Nm^{-2}}$ and temperature $T_0 = 273.15\,\mathrm{K}$ (or 0.0° Celsius), each cubic centimetre ($\mathrm{cm^3}$) of air contains 2.69×10^{19} molecules. At higher altitudes, z, the atmospheric pressure, $p(z)$ drops exponentially from its value at sea level:

$$p\,(z) = p_0 e^{-\frac{Mgz}{RT}} = p_0 e^{-\frac{z}{z_S}} \tag{2.2}$$

where $M = 0.02897\,\mathrm{kg\,mole^{-1}}$ is the mean molar mass of air, $\mathrm{g} = 9.81$ is the acceleration of gravity, and $z_\mathrm{S} = \frac{RT}{Mg} \approx 7 \pm 1\,\mathrm{km}$ denotes the 'scale height' of the atmosphere.

While there is a monotonic drop in pressure with altitude, the vertical temperature profile shows distinct variations, with several maxima and minima. The variation of temperature, type of chemical processes, and mixing mechanisms at different altitudes leads to a division of the atmosphere into a number of distinct compartments (see Fig. 2.1):

The *troposphere* is the lowest layer of the atmosphere, and is relatively well mixed. It extends from the surface to about 8 km altitude at the poles, and from the surface to about 18 km at the equator. The troposphere can be further subdivided into:

- The atmospheric boundary layer (BL), which roughly covers the lowest 1–2 km of the atmosphere. Air movement and mixing in the BL are influenced by friction on the earth's surface.
- The free troposphere, which extends from the top of the BL to the tropopause.

The *stratosphere* is a poorly mixed layer extending above the troposphere to about 50 km altitude. Common subdivisions of the stratosphere include:

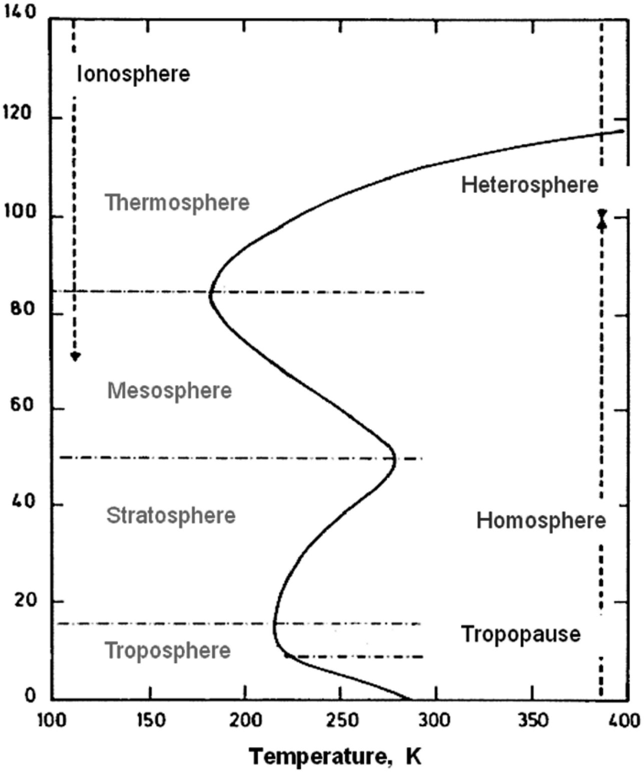


Fig. 2.1. The layers of the atmosphere, divided according to temperature, mixing mechanism, and degree of ionisation (from Brasseur and Solomon, 1986)

- The tropical tropopause layer
- The lower and middle stratosphere
- The upper stratosphere

The *upper atmosphere* extending above the stratopause is subdivided into the mesosphere, thermosphere, and exosphere.

Despite the vertical temperature and pressure variation up to about 100 km altitude, the composition of the atmosphere is fairly constant with respect to its main components. The three most abundant species, which constitute more than 99.9% of dry air (see Table 2.1), are molecular nitrogen and oxygen, as well as the noble gas argon. In addition, the atmosphere contains water vapour between $10^{-4}\%$ and a few % (by volume). Other species with comparable abundances are carbon dioxide, and all remaining nobel gases. With the exception of water vapour and carbon dioxide, the species listed in Table 2.1 have atmospheric residence times in excess of 1000 years, and are therefore referred to as 'permanent' constituents. In addition to the above species, the atmosphere contains a multitude of other species at much lower abundance. They are called 'trace gases' and include methane (CH_4, $\approx 0.00017\%$), molecular hydrogen (H_2, $\approx 0.00005\%$), and nitrous oxide (N_2O, $\approx 0.00003\%$) among others.

2.1.1 Trace Species in the Atmosphere

In addition to the main gaseous constituents (Table 2.1), the atmosphere contains a large number of trace gases. Only a few trace species (e.g. CH_4) exceed a mixing ratio of one molecule in a million air molecules. However, a very large number of species (e.g. ozone, carbonyl sulphide, difluoro–dichloro–methane, methyl chloride, and methyl bromide) are present at mixing ratios around or below one molecule in a billion air molecules. Atmospheric chemistry

Table 2.1. The main constituents of the (unpolluted), dry atmosphere

Gas	Chemical formula	Mixing ratio by volume	Mixing ratio vol. %
Nitrogen	N_2	0.7808	78.08
Oxygen	O_2	0.2095	20.95
Argon	Ar	$9.3 \cdot 10^{-3}$	0.93
Carbon dioxide	CO_2	$0.37 \cdot 10^{-3}$	0.037
Neon	Ne	$18 \cdot 10^{-6}$	0.0018
Helium	He	$5.2 \cdot 10^{-6}$	0.00052
Methane	CH_4	$1.7 \cdot 10^{-6}$	0.00017
Krypton	Kr	$1.1 \cdot 10^{-6}$	0.00011
Xenon	Xe	$0.9 \cdot 10^{-6}$	0.00009
Hydrogen	H_2	$0.5 \cdot 10^{-6}$	0.00005
Dinitrogen oxide	N_2O	$0.3 \cdot 10^{-6}$	0.00003

is predominately concerned with the fate of these trace species, which, despite their low concentration, have a very noticeable impact on our atmosphere.

Another very important class of components in the atmosphere, which is not gaseous, is small particles of liquid or solid matter dispersed and suspended in air, the *aerosol*. The literal translation of the word aerosol is ‘solution in air’. Since a solution includes both a solvent and a solute, one might insist that the term aerosol should only be used to denote the entire system, including both the suspended particles and the carrier gas. Usually, however, the term aerosol is used in the literature synonymously with ‘suspended particles’, excluding the carrier gas.

An important property of a solution is that it is a stable system. Applying a similar criterion to aerosol particles means that only those particles which remain suspended in air for a sufficiently long time to be transported by the wind over reasonably long distances can be part of an aerosol. The atmospheric residence time of large aerosol particles is limited by their settling velocity, which is the cause of sedimentation. The settling velocity varies approximately with the square of the particle radius, and therefore the upper limit for the size of aerosol particles is relatively sharp. Particles with radii much larger than about $10\,\mu\text{m}$ have too large settling velocities to behave like true aerosol particles, and are thus classified as ‘coarse dust particles’. (A spherical particle of $10\,\mu\text{m}$ diameter has a settling velocity of about $2.42\,\text{cm}\,\text{s}^{-1}$, or $87\,\text{m}\,\text{h}^{-1}$, and thus will be rapidly removed from the atmosphere by sedimentation).

Defining the lower limit for the existence range of aerosol particles is more difficult. Clearly, aerosol particles must exceed the size of individual molecules, which have radii in the range of fractions of a nanometre (e.g. the gas kinetic radius of N_2 or O_2 is $\approx 0.2\,\text{nm}$). Nucleation theory teaches us that clusters composed of several condensable molecules (e.g. a mixture of sulphuric acid and water molecules) can only be stable when they exceed a certain critical size. Before reaching that critical size, the clusters tend to evaporate again. It appears attractive to use that critical size as a lower limit for the definition range of aerosol particles in the atmosphere. However, the critical size is not uniquely defined, but depends on atmospheric conditions, in particular on temperature, relative humidity, and the oxidation rate of SO_2, which yields the condensable sulphuric acid molecules. Very often the critical size of these so-called ‘secondary aerosols’ is in the range of 1 nm.

2.1.2 Quantification of Gas Abundances

The amount of trace gases present in the atmosphere can be quantified by using two different descriptions. First, we define the **concentration** of a trace gas as the amount of trace gas per volume of air (at a given temperature):

$$c = \frac{\text{Amount of trace gas}}{\text{Volume of air}} \tag{2.3}$$

where ‘amount’ refers to either mass (c_m), number of molecules (c_n), or number of moles (c_M). Examples for units of concentration are micrograms per

m^3 or molecules per cm^3. The latter is also known as 'number density' of a gas. The partial pressure of a species is also a measure of its concentration.

Second, we can define the *mixing ratio* of a trace gas as the ratio of the amount of a trace gas to the amount of air, including the trace gas:

$$x = \frac{\text{Amount of trace gas}}{\text{Amount of air + Trace gas}} \approx \frac{\text{Amount of trace gas}}{\text{Amount of air}} \tag{2.4}$$

At typical atmospheric trace gas mixing ratios of $<10^{-6}$, the distinction between the 'amount of air' and 'amount of air + trace gas' is so small that it can be neglected for practical purposes. It is necessary to distinguish whether the 'amount' is in volume, number of moles, number of molecules, or mass.

An example of a mixing ratio is parts per million (ppm) by volume:

$$x_\mathrm{V} = \frac{\text{Unit volume of trace gas}}{10^6\,\text{unit volumes of}\,(\text{air} + \text{trace gas})}\text{ppm}$$

For smaller trace gas mixing ratios, x_V is given as parts per billion (ppb) and parts per trillion (ppt), which are analogously defined as:

$$x_\mathrm{V} = \frac{\text{Unit volume of trace gas}}{10^9\,\text{unit volumes of}\,(\text{air} + \text{trace gas})}\text{ppb}$$

$$x_\mathrm{V} = \frac{\text{Unit volume of trace gas}}{10^{12}\,\text{unit volumes of}\,(\text{air} + \text{trace gas})}\text{ppt}$$

While mixing ratios could also be given by mass, this is rarely done in atmospheric chemistry. Nevertheless, in the literature the terms ppmv, ppbv, and pptv are sometimes used to stress the fact that volume mixing ratios are understood. Similar to volume mixing ratios are molar mixing ratios:

$$x_\mathrm{M} = \frac{\text{Moles of trace gas}}{\text{Mole of}\,(\text{air} + \text{trace gas})} \tag{2.5}$$

It should be noted that x_M is the new SI unit for mixing ratios. Since air under ambient conditions can be regarded in good approximation as an ideal gas, for practical purposes a mixing ratio x_M specified in moles per mole equals the mixing ratio x_V. Thus, the terms micromole per mole, nanomole per mole, and picomole per mole are essentially equivalent to ppm, ppb, and ppt by volume, respectively.

A common problem in atmospheric chemistry is the conversion of units of the amounts of trace gases. For example, for trace gas i we obtain the following conversion between the number density c_n (in molecules per cm^3) and mass concentration c_m (in grams per cm^3):

$$(c_\mathrm{m})_i = \frac{c_\mathrm{n} \cdot M_i}{N_\mathrm{A}} \tag{2.6}$$

where M_i denotes the molecular mass of the species i in g per mole and N_A is Avogadro's number with $N_\mathrm{A} = 6.0221420 \times 10^{23}$ molecules mole^{-1}. Thus, the conversion between number density and mass concentration is different for species with different molecular (atomic) mass.

The conversion of number density c_n (in molecules per cm^3) into the corresponding (volume) mixing ratio is given by:

$$x_\mathrm{V} = c_\mathrm{n} \frac{V_0}{N_\mathrm{A}} \text{ or } c_\mathrm{n} = x_\mathrm{V} \cdot \frac{N_\mathrm{A}}{V_0} \tag{2.7}$$

where V_0 denotes the molar volume in cm^3 for the pressure p and temperature T at which the number density c_n was measured. For standard conditions ($p_0 = 101325\,\mathrm{Pa} = 1$ Atmosphere, $T = 273.15\mathrm{K}$) the molar volume is $V_0 = 22414.00\,\mathrm{cm}^3\,\mathrm{mole}^{-1}$. For arbitrary temperature and pressure conditions, we can use:

$$x_\mathrm{V} = c_\mathrm{n} \frac{1}{N_\mathrm{A}} \frac{T}{p} \frac{p_0}{T_0} V_0 = c_\mathrm{n} \frac{1}{N_\mathrm{A}} \cdot \frac{RT}{p} = c_\mathrm{m} \frac{1}{M_i} \cdot \frac{RT}{p} \tag{2.8}$$

or

$$c_\mathrm{m} = x_\mathrm{V} \cdot M_i \cdot \frac{p}{RT} \tag{2.9}$$

Table 2.2 gives a few examples for the conversion of the different units in which the abundance of trace gases is customarily expressed.

It should be noted that mixing ratios, x_V and x_M, are independent of temperature and pressure. Consequently, they are conserved during vertical transport in the atmosphere. In contrast, the concentration c depends on both parameters and change when air is transported. However, trace gas concentrations are relevant for the calculation of chemical reaction rates and radiative properties (such as UV absorption) of the atmosphere. Spectroscopic measurement techniques (including DOAS) also give results in number density or concentration, not mixing ratios.

Table 2.2. The different units for the abundance of atmospheric trace gases ($T = 293.15\mathrm{K}$, $p = 101325\,\mathrm{Pa}$)

Trace gas	Molecular mass g/mole	Mixing ratio x_V ppb	Number density c_n molec. cm^{-3}	Concentration c_m µg m^3
O_3	48.00	1.000	$2.503 \cdot 10^{10}$	1.995
		0.501	$1.254 \cdot 10^{10}$	1.000
SO_2	64.06	1.000	$2.503 \cdot 10^{10}$	2.662
		0.376	$0.941 \cdot 10^{10}$	1.000
NO	30.01	1.000	$2.503 \cdot 10^{10}$	1.251
		0.799	$2.000 \cdot 10^{10}$	1.000
NO_2	46.01	1.000	$2.503 \cdot 10^{10}$	1.912
		0.532	$1.33 \cdot 10^{10}$	1.000
CH_4	16.04	1.000	$2.503 \cdot 10^{10}$	0.667
		1.500	$3.755 \cdot 10^{10}$	1.000
CH_2O	30.03	1.000	$2.503 \cdot 10^{10}$	1.248
		0.801	$2.005 \cdot 10^{10}$	1.000
CO	28.01	1.000	$2.503 \cdot 10^{10}$	1.164
		0.859	$2.150 \cdot 10^{10}$	1.000

Thus both types of units are useful and must be converted into each other as needed. Atmospheric trace gas profiles might look quite different when viewed in terms of mixing ratios or concentrations, as illustrated by the example of the atmospheric ozone profile in Fig. 2.2. The concentration (in molecules per cm^3) has a noticeable, essentially constant level in the troposphere, and a maximum at about 22 km in the lower stratosphere. In contrast, tropospheric mixing ratios (in ppm or µmole per mole) are very low and peak at about 36 km.

Another category for specifying trace gas abundances is the column density S, which is defined as the integral of the number density along a certain path in the atmosphere:

$$S = S_\mathrm{n} = \int_\mathrm{Path} c_\mathrm{n}(s)\, ds \tag{2.10}$$

The unit of S_n, and column densities in general, is molecules per cm^2. In analogy to the mass mixing ratio c_m, the mass column density S_m can be defined as:

$$S_\mathrm{m} = \int_\mathrm{Path} c_\mathrm{m}(s)\, ds \tag{2.11}$$

Typical units for mass column densities are µg/cm^2. The conversion between S_n and S_m is analogous to the conversion between c_n and c_m.

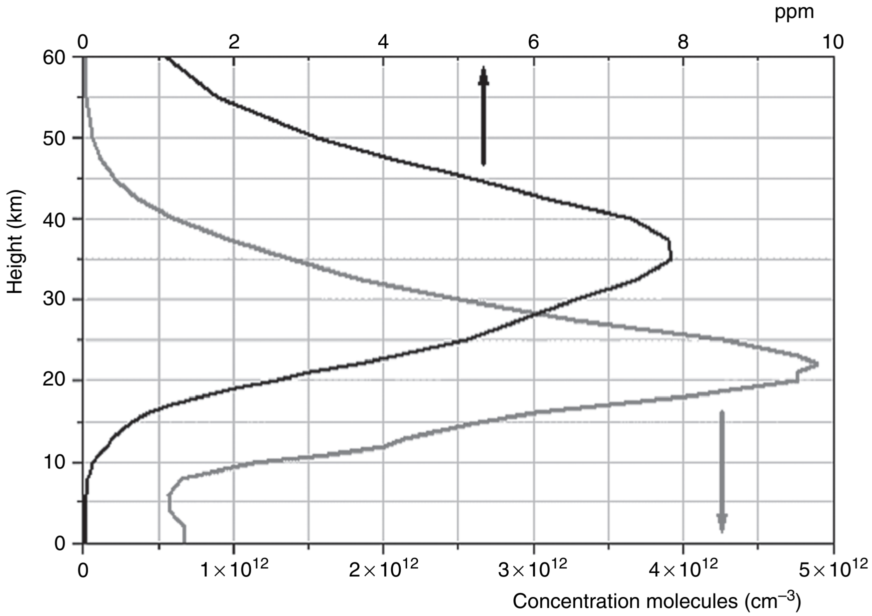


Fig. 2.2. Vertical profile of ozone in troposphere and stratosphere (US Standard Atmosphere), both in mixing ratio (in ppm or µmole per mole), peaking at about 36 km and concentration (molecules per cm^3), peaking at about 22 km

A frequently used path is the total (vertical) atmospheric column density V, where the concentration is integrated vertically from the surface to infinity:

$$V = \int_0^\infty c_\mathrm{n}(z)\, dz \tag{2.12}$$

2.1.3 Lifetime of Trace Gases in the Atmosphere

The atmosphere is not a static system with respect to its components. Rather, gases are released to the atmosphere or formed by chemical transformations, and removed again by chemical degradation or deposition on the ground. A useful quantity in this context is the steady-state (average) lifetime, or residence time, of a species in the atmosphere.

If the concentration of a species has reached a steady-state value, i.e. its rate of production P equals its rate of destruction D, its lifetime can be defined as the ratio:

$$\tau = \frac{c}{D} = \frac{c}{P} \tag{2.13}$$

Assuming the production P to be constant and the destruction D to be proportional to c, i.e. $D = c/\tau$ with the constant of proportionality $1/\tau$, we obtain:

$$c(t) = P \cdot \tau \cdot \left(1 - e^{-\frac{t}{\tau}}\right) \xrightarrow[\tau \to \infty]{} P \cdot \tau \tag{2.14}$$

The constant τ becomes clear by calculating $c(\tau) = 1 - 1/e \approx 63.2\%$ of the final value $c(\infty) = c(t \to \infty) = P \cdot \tau$. In other words, the lifetime τ is the time constant with which the trace gas concentration approaches its steady state.

Figure 2.3 gives approximate lifetimes of atmospheric trace constituents. The abundance of atmospheric constituents frequently is in a stationary state which depends on the lifetime of the particular gas. The variation of the concentration of a gas in space and time also depends on its lifetime. For instance, the long-lived components such as N_2, O_2, or noble gases, with lifetimes of thousands of years, show very little variation, whereas the concentrations of short-lived species may vary considerably with time and location. A quantitative relationship of residence time and variation of the mixing ratio of a gas was first established by Junge (1963).

2.2 Direct Emission of Trace Gases to the Atmosphere

As described above (Sect. 2.1.3), most gaseous (and particulate) components of our atmosphere are in a balance between continuous addition to

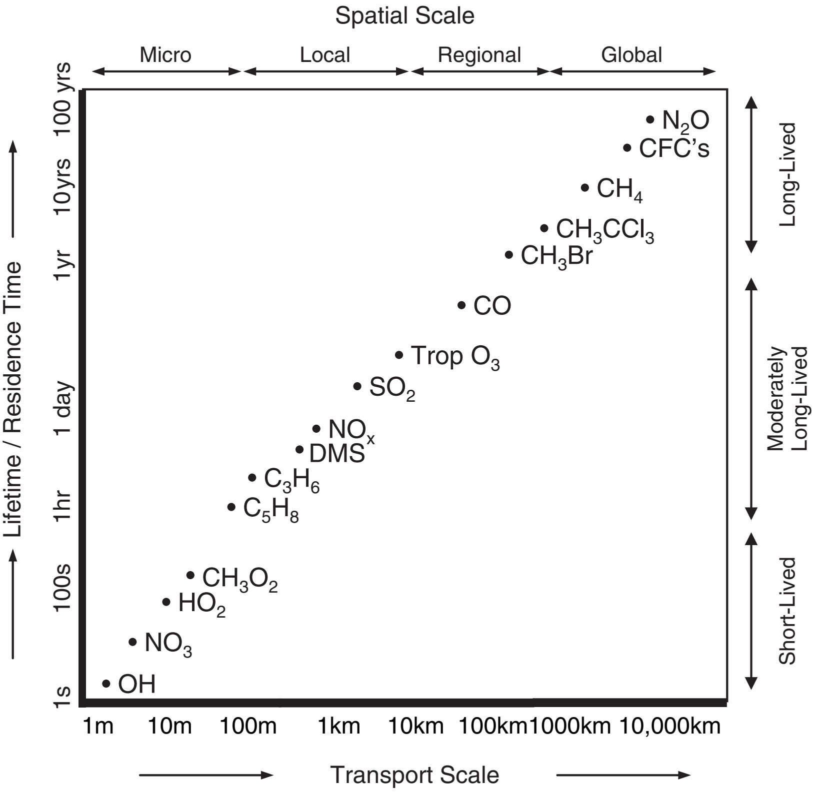


Fig. 2.3. Average lifetimes (residence times) of gases in the atmosphere range from seconds (and below) to millennia. Accordingly, transport can occur on scales reaching from a few meters to the global scale (adapted from Seinfeld and Pandis, 1998)

the atmosphere and removal from it. To understand the levels of trace gases in the atmosphere and their chemistry, it is important to study their sources or, in the case of gases which are formed chemically, the sources of their precursors. In particular with respect to air pollution, this is an important issue since human activities have added new trace gas sources over the past centuries. These sources have to be compared with natural emission sources in order to assess their impact on the composition of the atmosphere. While this section only gives a very brief overview of trace gas sources, which is limited to the gases that are of interest in this book, it should be noted that the accurate determination of emissions is a crucial aspect of atmospheric chemistry.

Emission sources are typically subdivided into natural and anthropogenic processes. The following list gives examples of the types of sources found in the atmosphere:

Natural emission of gases includes the following processes:

- Emission of gases from soil (e.g. methane, oxides of nitrogen NO and N_2O)
- Emission of gases by vegetation (primarily volatile organic compounds (VOC))
- Emission by biomass burning (VOCs, CO, NOx, etc.)
- Marine emissions [Dimethyl sulphide (DMS) and sea salt aerosol]
- Volcanic emissions (CO_2, SO_2, HCl, BrO, etc.)
- Formation in thunderstorms (NO)

Anthropogenic emissions are due to a series of human activities, primarily traffic, heating, and industrial processes, and also agricultural activities. The latter include emission from bare, or fertilised soils, flooded areas (e.g. for rice growing), or biomass burning. Anthropogenic emissions include:

- Emission during combustion processes (e.g. cars, power stations, and industry). The emitted gases include oxides of nitrogen (NO and NO_2), carbon monoxide, and VOCs
- Emission by industrial processes

Some anthropogenic emissions occur through the same processes as natural emission:

- Impact on gas emissions from soil due to agriculture: oxides of nitrogen (NO and N_2O)
- Emission by biomass burning (VOCs, CO, and NO_X)
- Emission of gases, by vegetation (primarily VOC)

We will briefly discuss the source and sink strengths, as well as average mixing ratios and lifetimes (residence times), of a series of important atmospheric trace gases, which have their dominant sources at the surface. The discussion is subdivided into nitrogen, sulphur, and carbon-containing species.

2.2.1 Nitrogen Species

Fixed nitrogen species play an important role in the chemistry and the climate of the atmosphere. We will focus here on the three most nitrogen important species that are emitted into the atmosphere – nitrous oxide (N_2O), nitrogen oxides (NO and NO_2), and ammonia (NH_3).

N_2O

Nitrous oxide is an important greenhouse gas and also the dominant source of reactive nitrogen in the stratosphere. N_2O is naturally emitted by bacteria in the soil and the ocean during the nitrogen fixation process (Table 2.3). Human activities have lead to an increase of these sources, predominantly due to the intensivation and expansion of agriculture. As a consequence, N_2O mixing ratios have increased from ∼275 ppb before the year 1800 to over 310 ppb today.

Table 2.3. Tropospheric sources, sinks, and mixing ratios of nitrogen species [Source strength in million tons of fixed nitrogen (Tg N) per year (from Lee et al., 1997, Ehhalt 1999)]

Species	Mixing ratio, ppb	Major sources	Average source strength Tg/year	Major Sinks	Sink strength Tg/year	Atm. life time
Nitrous oxide, N_2O	310	Soil emission Ocean emission Anthropogenic	10 6 9	Loss to stratosphere	25	110 a
Nitrogen oxides, NO, NO_2	0.03–5	Fossil fuel combustion Biomass burning Soil emission/microbial production Thunderstorms Aircraft emissions	21 8 10 5 0.8	Oxidation by OH and O_3 to HNO_3	44	2d
Ammonia, NH_3	0.1 marine 5 continent	Domestic animals Emission from vegetation Ocean emission Fertilizer use	26 6 9 8	Dry deposition Conversion to NH_4+ aerosol	17 36	5d

h = hour, d = day, a = year.

NO_X ($NO + NO_2$)

The significance of nitrogen oxides will be discussed in detail in Sect. 2.5. Oxides of nitrogen, NO and NO_2, are produced in a large number of natural and anthropogenic processes. Particularly important are those where air is heated to high temperatures, such as in combustion processes (in internal combustion engines), forest fires, or lightning strikes. Natural sources of nitrogen oxides produce globally about 13–31 million tons of nitrogen fixed as NO_X per year (Table 2.3). The largest natural contributions come from brush and forest fires, lightning storms, and emission from the soil. Smaller contributions come from diffusion from the stratosphere and oxidation of ammonia (Ehhalt and Drummond, 1982; Lee et al., 1997).

Anthropogenic NO_X emissions can be grouped into three categories that essentially all originate from combustion processes. Thus, the largest source is the stationary combustion of fossil fuel (power stations, industry, and home heating). A further important – and growing – source is emission by automobiles. This emission additionally occurs in densely populated areas at very low emission height. Finally, part of the NO_X emission from forest fires and from soil is due to anthropogenic influence (intentional forest fires and artificial fertilisation).

In Table 2.3, the contributions of the various NO_X sources are summarised. On a global scale, the contributions of natural and anthropogenic NO_X sources are about equal in magnitude. The spatial distribution of strong NO_X sources, as derived from satellite-based DOAS measurements, is shown in Figs. 11.45 and 11.46 (Leue et al., 2001; Beirle et al., 2004a,c).

It should, however, be considered that the natural NO_X sources are much more equally distributed over the surface of the earth than the anthropogenic sources, which are concentrated on a very small fraction of the earth's surface (see also Fig. 11.45). For instance, in Germany [NO_X emission 2000: 0.9 million tons nitrogen, as N (Schmölling, 1983; Fricke and Beilke, 1993)], the natural contribution to the total NO_X emission is small.

NH_3

Ammonia plays a crucial role in the atmosphere as it is the only significant atmospheric base neutralising acids such as sulphuric and nitric acids. The ammonium ion, which is formed upon the uptake of ammonia on particles, is an important part of the aerosol. Ammonia is emitted predominately by livestock wastes and fertilised soils. Emissions from the ocean and vegetation also play a role (Table 2.3). Modern cars with catalytic converters also emit ammonia.

2.2.2 Sulphur Species

The increase of sulphur emissions since the onset of industrialisation has led to numerous environmental problems, such as London-type smog and acid rain. Naturally sulphur is emitted through biological processes in the soil and the ocean in its reduced form as carbonyl sulphide (COS), hydrogen sulphide (H_2S), and DMS (CH_3SCH_3). Volcano eruptions can also contribute to the natural sulphur emissions, in the form of sulphur dioxide, SO_2 (Table 2.4). Of the natural emissions, those of DMS dominate and are particularly important for the global sulfur budget (Sect. 2.7).

Anthropogenic emissions of SO_2 originate primarily from fossil fuel combustion. Over the past 200 years, sulphur emissions have sharply increased. As a response to the growing acid rain problem, the emission of sulphur has been greatly reduced in industrialised countries since 1975 (see also Fig. 2.4). This is due to stack gas desulphurisation measures, and also to the change of the economies in the eastern European countries. On a global scale, however, there is an expected increase of sulphur emission, due to enhanced coal combustion in Asian countries (Fig. 2.4).

The sulphur species that are most important in the atmosphere, their typical concentrations and atmospheric residence times, and their degradation mechanisms are summarised in Table 2.4.

2.2.3 Carbon-Containing Species

A very large number of carbon-containing trace species are present in the atmosphere. The most important carbon-containing species is carbon dioxide (CO_2). While CO_2 plays a crucial role as a greenhouse gas, it undergoes little chemistry in the atmosphere, and its sources will not be a topic of this section. The second most abundant carbon species is methane (CH_4), which, as will be discussed in Sect. 2.4, is chemically degraded in the atmosphere, directly participating in the formation of tropospheric ozone. Methane is also a greenhouse gas. It is difficult to distinguish natural and anthropogenic sources of methane as the emissions predominately stem from animals, including farm livestock, and wetlands, which includes rice paddies (Table 2.5). Fossil fuel consumption also contributes to today's methane emissions. The expansion of agriculture over the past two centuries has led to an increase of methane sources and a rise of methane mixing ratios from $\sim$750 ppb to over 1700 ppb today. Carbon monoxide (CO) is a product of incomplete combustion of natural material, for example forest fires, and fossil fuels. In addition, CO is a product of the chemical degradation of methane and volatile organic carbon (VOC) species in the atmosphere. Because CO is toxic and participates in the formation of photochemical smog, various measures have been taken to reduce its emissions from combustion sources. The most prominent example is the catalytic converter of automobiles, which was primarily designed to reduce CO emissions.

Hydrocrabons – often the term non-methane hydrocarbons (NMHC) is used to exclude CH_4 from this group – constitute a large class of carbon-containing species in the atmosphere. The number of different species is very large and we will consider only the most important members of this group

Table 2.4. Tropospheric sources, sinks, and mixing ratios of sulphur species [Source strength in million tons of sulphur (Tg S) per year (from Ehhalt 1999)]

Species	Mixing ratio, ppb	Major sources	Source strength Tg/year	Major sinks	Sink strength Tg/year	Atm. life time
Carbonyl sulphide, COS	0.5	Soil emission	0.3	Uptake by vegetation	0.4	7 a
		Ocean emission	0.3	Flux to stratosphere	0.15	
		CS_2 + DMS ox.	0.5			
Hydrogen sulphide, H_2S	0.005–0.09	Soil emission	0.5	Reaction with OH	2.7	3 d
		Vegetation	1.2			
		Volcanoes	1			
Dimethyl sulphide, DMS, CH_3SCH_3	0.005–0.1	Ocean emission	68	Reaction with OH, NO_3, BrO	70	2 d
		Soil emission	2			
Sulphur dioxide, SO_2	0.02–0.09 (marine), 0.1–5 cont.	Fossil fuel burning	160	Dry deposition, reaction with OH, liquid phase	100	4 d
		Volcanoes	14	Oxidation to $SO_4^=$ + Wet deposition	140	
		Sulphide oxidation	70			

h = hour, d = day, a = year.

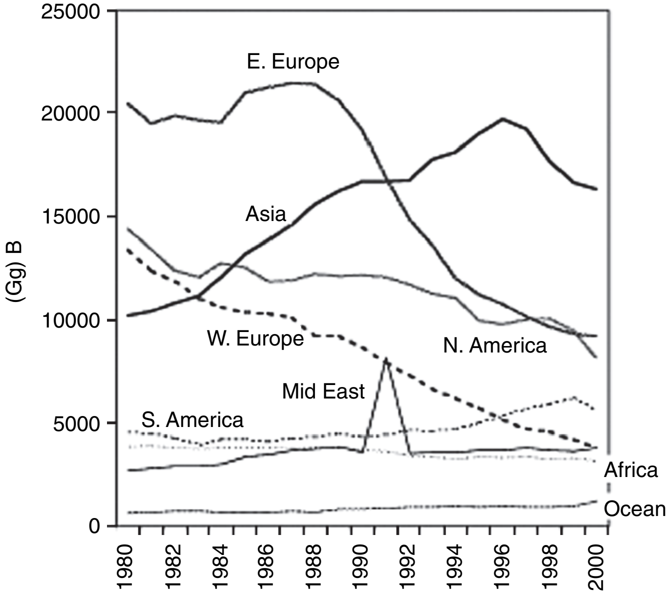


Fig. 2.4. Regional trends of global sulphur emissions (in giga-grams of sulphur per year) during the past two decades (from Stern, 2005, Copyright Elsevier, 2005)

here. On a global scale, the emission by vegetation of isoprene, C_5H_8, and to a lesser extent, terpenes, $C_{10}H_{16}$, dominate the emissions of VOC. These species are highly reactive in the atmosphere and participate in the formation of ozone and particles. Globally, natural emissions of other species are of lesser importance. Anthropogenic (and natural) emissions of VOC are an essential part of Los Angeles-type smog. A complex mixture of different trace gases is emitted by fossil fuel consumption, both through incomplete combustion and the loss of VOC vapours before combustion, industrial processes, refining of oil, solvents, etc. The emitted mixture, which contains alkanes (ethane, propane, etc.), alkenes (ethane, propene, etc.), alkynes and aromatics (benzene, toluene, etc.), and a variety of oxidised VOC (formaldehyde, acetaldehyde, etc.), depends on the emissions signatures of the different sources, as well as the distribution of these sources. For details on urban VOC emissions, we refer the reader to atmospheric chemistry textbooks, such as Finalyson-Pitts and Pitts (2000).

2.3 Ozone in the Troposphere

Ozone is a key compound in the chemistry of the atmosphere. In the troposphere it is a component of smog, poisonous to humans, animals and plants, as well as a precursor to cleansing agents (such as the OH radical, see Sect. 2.4.1). Tropospheric ozone is also an important greenhouse gas.

Table 2.5. Important organic trace gases, approximate mixing ratio, emission to the atmosphere, removal from the atmosphere, and average lifetime (residence time) τ in the atmosphere [see (2.14)]

Species	Mixing ratio, ppb	Major sources	Source strength Tg/year	Major Sinks	Sink strength Tg/year	Atm. life time
Methane, CH_4	1700	Rice fields	75	Reaction with OH	490	8 a.
		Domestic animals	100	Export to stratosphere	40	
		Swamps/marshes	200	Soil uptake	30	
		Biomass burning	40			
		Fossil fuel	100			
Carbon monoxide, CO	200 (NH) 50 (SH)	Anthropogenic emission	440	Reaction with OH	2400	0.2 a
		Biomass burning	770	Flux to stratosphere	100	
		CH_4 oxidation	860	Soil uptake	400	
		O_x. of natural VOC	610			
Isoprene, C_5H_8	0.6–2.5	Emission from deciduous trees	570	Reaction with OH, ozonolysis	570	0.2 d
Terpenes, $C_{10}H_{16}$	0.03–2	Emission from coniferous trees	140	Reaction with OH, ozonolysis	140	0.4 d
Total VOC		Fossil fuel	65	Reaction with OH	850	
		Biomass burning	35			
		Foliar emission	744			
		Ocean emission	6			

The table is based on Ehhalt (1999), but has been extended.
h = hour, d = day, a = year.

Ozone is formed by two distinctly different mechanisms in the troposphere and stratosphere. In the stratosphere, O_2 molecules are split by short-wave UV radiation into O-atoms, which combine with O_2 to form O_3. This process is the core of the 'Chapman Cycle' (Chapman, 1930; see Sect. 2.10.1). Until the late 1960s, it was believed that tropospheric ozone originated from the stratosphere. Today we know that large amounts of O_3 are formed and destroyed in the troposphere. Influx of O_3 from the stratosphere is only a minor contribution to the tropospheric ozone budget. Recent model calculations (IPCC, 2002) put the cross tropopause flux of O_3 at 390–1440 Mt a^{-1} (very recent investigations indicate that values near the lower boundary of the range are more likely), while they derive ozone formation rates in the troposphere at 2830–4320 Mt a^{-1}. The formation is largely balanced by photochemical destruction in the troposphere amounting to 2510–4070 Mt a^{-1}. Another, relatively small contribution to the O_3 loss is deposition to the ground, modelled at 530–900 Mt a^{-1}.

2.3.1 Mechanism of Tropospheric Ozone Formation

In the early 1950s, it became clear that under certain conditions in the atmosphere near the ground high concentrations of ozone are formed (e.g. Haagen-Smit, 1952). In fact, it could be shown in 'smog-chamber' experiments that large amounts of ozone are formed when mixtures of NO_X ($NO + NO_2$) and VOC are exposed to solar UV radiation. While the phenomenon of ozone formation as a function of VOC and NO_X in illuminated mixtures was empirically found in the 1960s, the exact mechanism only became clear much later, due to the work of Weinstock (1969), Crutzen (1970), and Levy et al. (1971). Ozone formation in the troposphere is initiated by the production of $O(^3P)$ from NO_2 photolysis (indicated by the term hν, see Chap. 3).

Under clear sky conditions at noontime, the average lifetime of the NO_2 molecule is only on the order of 2 min [$j_{NO2} = j_2 \approx 8 \times 10^{-3} s^{-1}$; e.g. Junkermann et al. (1989)]:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \quad \text{(R2.1)}$$

This reaction is followed by the rapid recombination of O with O_2:

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad \text{(R2.2)}$$

Where M denotes any atmospheric molecule. At high pressure (and thus M and O_2 concentrations) in the troposphere, other reactions of $O(^3P)$, in particular its reaction with O_3, are negligible. Therefore, for each photolysed NO_2 molecule, an ozone molecule is formed. Reactions R2.1 and R2.2 are essentially the only source of ozone in the troposphere. However, ozone is often rapidly oxidised by NO to back NO_2:

$$O_3 + NO \rightarrow NO_2 + O_2 \quad \text{(R2.3)}$$

Reactions R2.1–R2.3 lead to a 'photo-stationary' state between O_3, NO, and NO_2. The relation between the three species can be expressed by the *Leighton Relationship* (Leighton, 1961):

$$\frac{[\mathrm{NO}]}{[\mathrm{NO_2}]} = \frac{j_{2.1}}{k_{2.3} \cdot [\mathrm{O_3}]} \tag{2.15}$$

where $j_{2.1}$ denotes the photolysis frequency of NO_2 and $k_{2.2}$ denotes the rate constant for the reaction of ozone with NO. For typical ozone mixing ratios of 30 ppb (1 ppb $\approx 10^{-9}$ mixing ratio), the $[NO]/[NO_2]$ ratio during daytime near the ground is on the order of unity. The reaction cycle formed by R2.1–R2.3 does not lead to a net formation of ozone. However, any reaction that converts NO into NO_2 without converting an O_3 molecule interferes with this cycle and leads to net ozone production. The key factor in tropospheric O_3 formation is, thus, the chemical conversion of NO to NO_2.

In the troposphere, the conversion of NO to NO_2 without O_3 occurs through a combination of the reaction cycles of hydroxyl HO_X ($OH + HO_2$), peroxy radicals, and NO_X (Fig. 2.5). In these cycles, OH radicals are converted to HO_2 or RO_2 radicals, through their reaction with CO or HC. HO_2 and RO_2, on the other hand, react with NO to reform OH, thus closing the HO_X/RO_X cycle. This reaction also converts NO to NO_2 (see also Sect. 2.5.1), which is then photolysed back to NO (R2.1). The oxygen atom formed in the NO_2 photolysis then reacts with O_2 to form ozone (R2.2). The process, shown in Fig. 2.5, therefore acts like a machine that, in the presence of NOx and sunlight, converts the 'fuel' CO and HC into CO_2, water, and ozone. Because, HO_X and NO_X are recycled, this catalytic ozone formation can

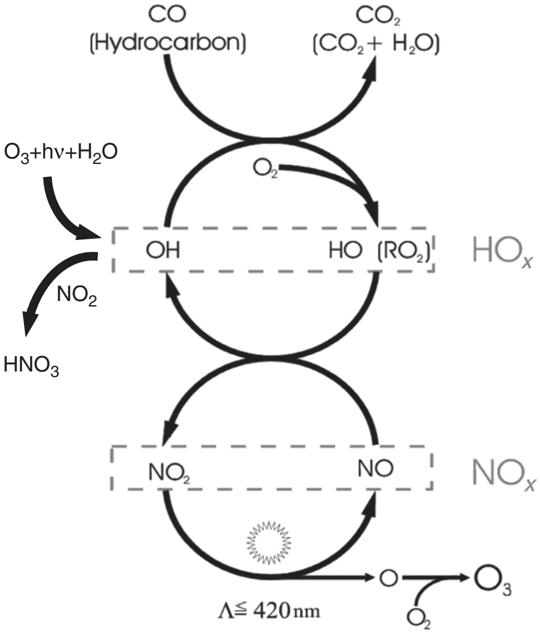


Fig. 2.5. Ozone formation in the troposphere is catalysed by hydrogen radicals ($OH + HO_2 = HO_X$), peroxy radicals, and NO_X

be quite efficient (Crutzen, 1970). HO_X radicals are always present in the sunlit atmosphere (see Sect. 2.4); they are, for example, formed through the photolysis of ozone in the presence of water vapour. The cycles are only interrupted if either a NO_X or a HO_X is removed from the respective cycles, for example by the reaction of OH with NO_2, or the self-reactions of HO_2 and RO_2.

In background air, fuel for ozone formation is always present in the form of methane (mixing ratio of ∼1.7 ppm) and CO, which is formed as a degradation product of CH_4 (Sect. 2.4.1). However, in clean air, the NO_X level might be very low, and thus insufficient to act as catalyst. This effect is outlined in more detail in Sect. 2.5.1.

2.3.2 Ozone Formation in Urban Centres and Downwind

In many urban centres, car exhaust dominates as a source of pollution. Emissions from home heating and industry can also contribute considerably. These sources emit large amounts of NO_X (mostly in the form of NO) and VOC, the main ingredients of ozone formation. As a consequence, ozone formation rates can be orders of magnitude higher than in slightly polluted air outside urban centres. On the other hand, in urban centres there are also effective ozone sinks:

- Reaction of O_3 with freshly emitted NO
- Reaction of O_3 with olefins.

Overall, the ozone lifetime can be quite short (on the order of a few hours) in urban areas. Therefore, there are usually large diurnal variations of the O_3 level in these regions. In fact, in urban centres the ozone level near the ground frequently reaches zero a few hours after sunset and remains at zero for the rest of the night. After sunrise, enhanced vertical mixing replenishes some O_3 from higher layers, thus initiating radical chemistry again (see Fig. 2.8). In addition, photolysis of formaldehyde and nitrous acid (see Sects. 2.4.1 and 2.5.1) can considerably speed up radical processes, and thus growth of the O_3 mixing ratio in the morning.

In a series of experiments where the concentrations of NO_X and VOC were independently varied, the ozone formation after a fixed time was found to vary with the initial levels of both groups of species in a characteristic way: At a given initial level of NO_X, the O_3 increases linearly with the initially present level of VOC. In other experiments with higher initial VOC levels, the amount of O_3 levels off. Increasing initial VOC even further does not lead to higher O_3 production. This regime is called 'NO_X limited'. Conversely, at a given initial level of VOC, the O_3 increases linearly with the initially present level of NO_X. At higher initial NO_X levels, the amount of O_3 levels off. Increasing initial NO_X even further in this 'VOC limited' regime does

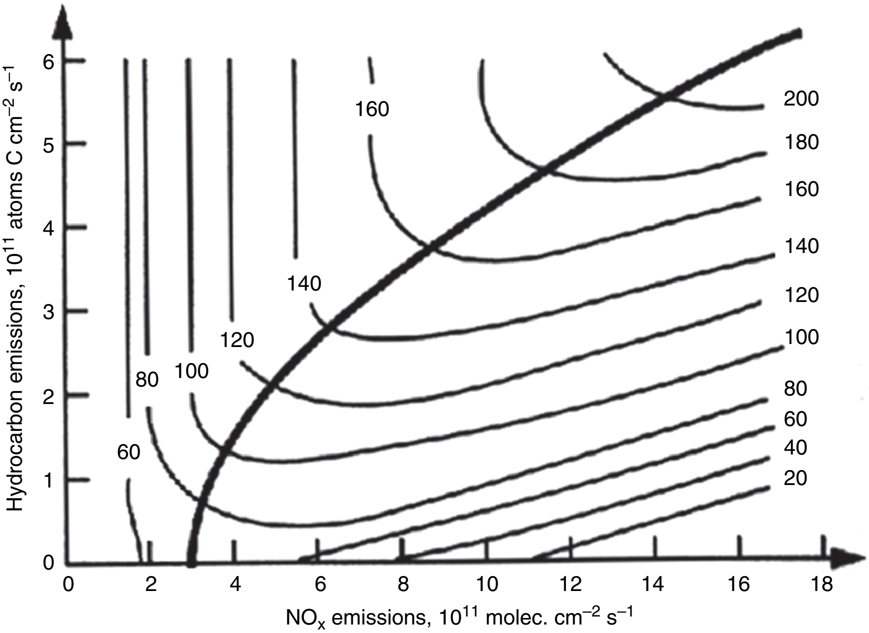


Fig. 2.6. Ozone concentrations simulated by a regional photochemical model as a function of NO_X and hydrocarbon (VOC) emissions. The thick line separates the NO_X limited regime (top left) from the VOC limited regime (bottom right) (from Sillman et al., 1990)

not lead to higher O_3 production. In fact, due to removal of OH by reaction with NO_2 (Fig. 2.5), O_3 formation will be reduced. Figure 2.6 illustrates this relationship. The lines of constant ozone formation as function of the VOC and NO_X composition of the initial mixture (or VOC and NO_X emission) are called ozone isopleths. Measurements in the open atmosphere also illustrate this dependence of the ozone production on the NO_X level (an example is shown in Fig. 2.7).

When considering which 'mixture' of HC (VOC) and NO_X is most effective in ozone production (at a given level of solar UV), it turns out that NO_X and VOC must be present in a certain ratio $R_{X0} = [NO_X]/[VOC]$, indicated by the ridge line in Fig. 2.6. Often this maximum is not reached in urban centres, where the primary emissions occur. Because the atmospheric lifetimes of VOC and NO_X are different, R_{X0} for an air-mass changes with time. In addition, it takes several hours for high ozone levels to be formed. Consequently, the highest O_3 levels are often found downwind of urban centres. This is illustrated in Fig. 2.8 which shows the diurnal variation of ozone levels in different types of air masses at a rural site (Forest, Weltzheimer Wald, Germany), and in a city (Heilbronn, southern Germany).

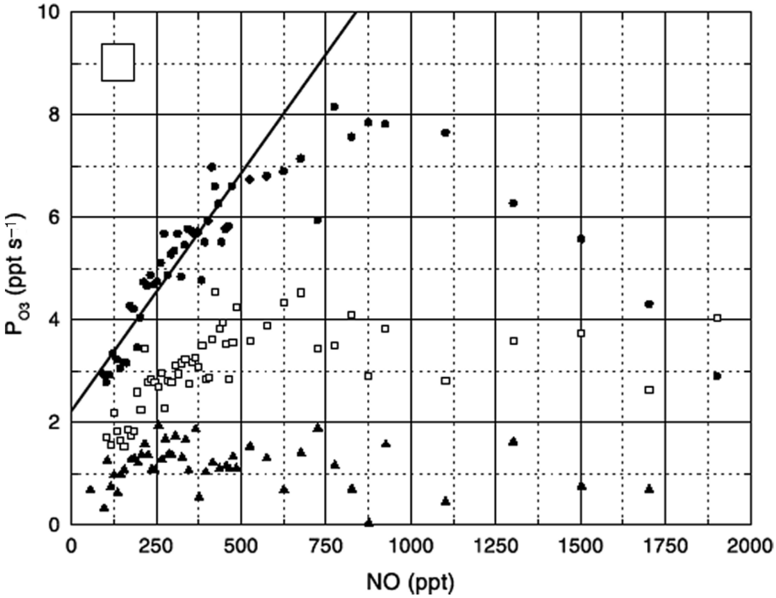


Fig. 2.7. Ozone production rates (P_{O3}) calculated from simultaneous observations of NO, NO_2, O_3, OH, HO_2, H_2CO, actinic flux, and temperature during the 1999 'Southern Oxidant Study' (June 15 to July 15) at Cornelia Fort Airpark, Nashville, Tennessee. Averaged P_{O3} is plotted as a function of the NO mixing ratio. The data were placed into three P_{HOx} bins: high ($0.5 < P_{HOx} < 0.7\,\text{ppt}\,\text{s}^{-1}$, circles), moderate ($0.2 < P_{HOx} < 0.3\,\text{ppt}\,\text{s}^{-1}$, squares), and low ($0.03 < P_{HOx} < 0.07\,\text{ppt}\,\text{s}^{-1}$, triangles), and then averaged as a function of NO. All three P_{HOx} regimes demonstrate the expected generic dependence on NO. P_{O3} increases linearly with NO for low NO (<600 ppt NO), and then P_{O3} becomes independent of NO for high NO (>600 ppt NO). The crossover point between NO_X-limited and NO_X-saturated O_3 production occurs at different levels of NO in the three P_{HOx} regimes (from Thornton et al., 2002, Copyright by American Geophysical Union (AGU), reproduced by permission of AGU).

2.4 Radical Processes in the Atmosphere

Free radicals are the driving force for most chemical processes in the atmosphere. Since the pioneering work of Weinstock (1969) and Levy (1971), photochemically generated HO_X radicals (hydrogen radicals, $OH + HO_2$) have been recognised to play a key role in tropospheric chemistry. In particular, hydrogen radicals:

- initiate the degradation and thus the removal of most oxidisable trace gases emitted into the atmosphere
- give rise to the formation of strongly oxidising agents (mostly in the troposphere), such as ozone or hydrogen peroxide
- catalytically destroy stratospheric ozone (see Sect. 2.10)

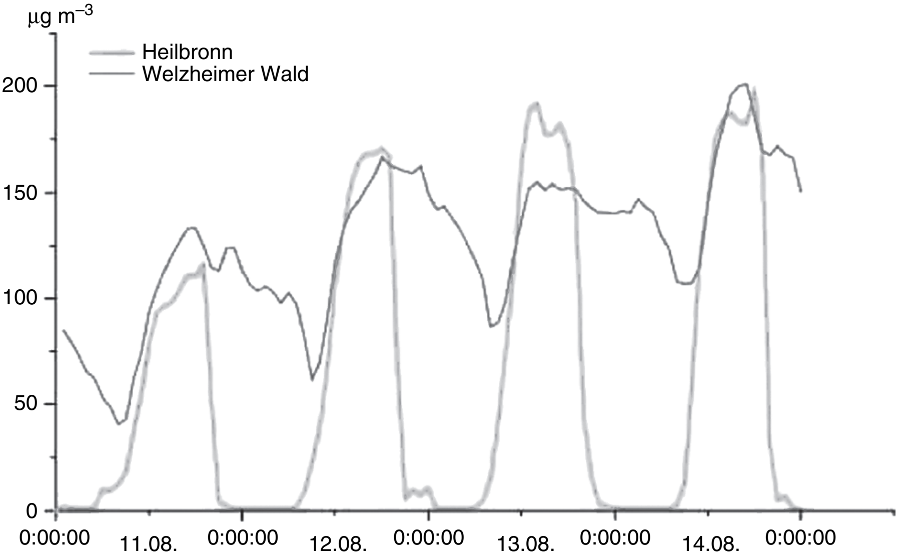


Fig. 2.8. Diurnal variation of ozone levels in different types of air masses during August 11–14, 2000: Forest (Weltzheimer Wald, Germany) and city of Heilbronn (southern Germany).
Source: Landesanstalt für Umweltschutz Baden-Württemberg and UMEG

- are difficult to remove once they are generated, since radical-molecule reactions tend to regenerate radicals.

Today we have an enormous amount of direct and indirect evidence of the presence of HO_X radicals (see, for example, Ehhalt et al., 1991; Wennberg et al. 1998; Platt et al., 2002), and the importance of HO_X for atmospheric chemistry can be assumed to be proved beyond reasonable doubt. Nevertheless, the possible role of other radicals, beginning with the (historical) idea of the impact of oxygen atoms $O(^3P)$ or excited oxygen molecules $O_2(^1\Delta)$ has been the topic of past and current investigations. In particular, the nitrate radical, NO_3, (see Sect. 2.5.2) and the halogen atoms and halogen oxide radicals BrO, IO, and ClO (Sect. 2.8) can make a considerable contribution to the oxidising capacity of the troposphere. For instance, reaction with NO_3 or BrO can be an important sink of DMS in marine environments. In addition, night-time reactions of nitrate radicals with organic species and NOx play an important role for the removal of these species. NO_3 chemistry can also be a source of peroxy radicals (such as HO_2 or CH_3O_2), and even OH radicals (Sect. 2.5.2). Table 2.6 shows an overview of the most important radical species in the troposphere and their significance for atmospheric chemistry. The details of the chemistry of NO_3 and halogen oxides will be discussed in the following sections. Here, we will concentrate on the tropospheric chemistry of hydroxyl radicals.

Table 2.6. Free radical cycles pertinent to tropospheric chemistry, and key processes influenced or driven by reaction of those radicals

	Species	Significance
HO_X cycle	OH	Degradation of most volatile organic compounds (VOC) Key intermediate in O_3 formation $NO_X \Rightarrow NO_Y$ conversion
	HO_2	Intermediate in O_3 formation Intermediate in H_2O_2 formation
	RO_2	Intermediate in ROOR' formation Aldehyde precursor PAN precursor Intermediate in O_3 formation
NO_3 cycle	NO_3	Degradation of certain VOC (olefins, aromatics, DMS, etc.) $NO_X \Rightarrow NO_Y$ conversion (via N_2O_5 or DMS-reactions) RO_2 precursor (night-time radical formation)
XO_X cycle	XO (X = Cl, Br, I)	Catalytic O_3 destruction (cause of 'Polar Trop. Ozone Hole') Degradation of DMS (BrO) Change of the NO_2/NO (Leighton) ratio
	X	Degradation of (most) VOC (Cl) Initiates O_3 formation RO_2 precursor Initiates particle formation (IO_X)

2.4.1 Sources of Hydrogen Radicals (OH and HO_2)

Hydroxyl radicals are probably the most important free radicals in the atmosphere. The degradation of most (but not all) oxidisable trace gases (such as HC or CO) is initiated by OH reaction (cf. Platt, 1999). OH radicals are therefore sometimes called the 'cleansing agent' of the atmosphere. Figure 2.9 shows a simplified outline of the HO_X ($OH + HO_2$) and RO_2 cycle.

Several primary OH production mechanisms are known:

(a) Globally, the most important process forming OH is initiated by UV photolysis of ozone to form electronically excited oxygen atoms:

$$O_3 + h\nu(\lambda < 320\,\mathrm{nm}) \rightarrow O(^1D) + O_2(^1\Delta) \qquad \text{(R2.4a)}$$

Recent research shows that photolysis of vibrationally excited ozone can considerably enhance the rate of reaction (R2.4a). In addition, some contribution comes from the channel:

$$O_3 + h\nu(\lambda < 420\,\mathrm{nm}) \rightarrow O(^1D) + O_2(^3\Sigma) \qquad \text{(R2.4b)}$$

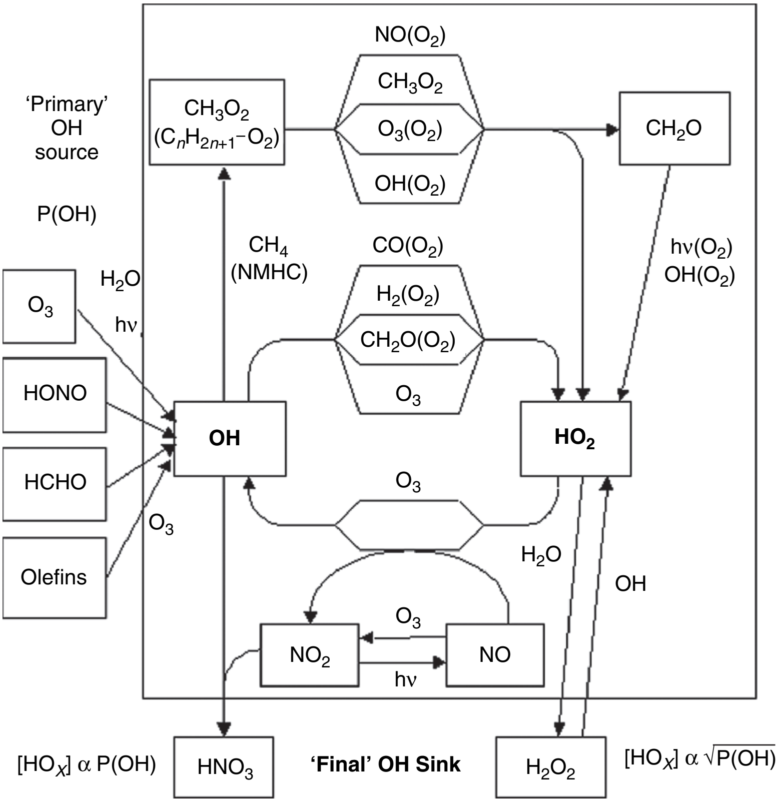


Fig. 2.9. A simplified outline of the $HO_X(OH + HO_2)$ and RO_2 cycles in the troposphere. The very reactive OH attacks most oxidiseable species (e.g. CO, hydrocarbons). Typical OH lifetimes are therefore below 1 s. Consequently, noontime concentrations only reach 10^6–10^7 cm^{-3} (0.04–0.4 ppt). These reactions usually lead to the formation of HO_2 or RO_2, which, in turn, can be reconverted to OH by reaction with NO or O_3, thus preserving HO_X. Alternatively HO_X is destroyed by self-reaction of HO_2, producing H_2O_2. The only other 'final' HO_X, sink of importance is the $OH + NO_2$ recombination. In a very simplified picture, one can imagine the HO_X reservoir to be fed by R2.4 followed by R2.6 (rate of OH production = P_{OH}) and drained by either HO_2 self-reaction (if NO_X is low) or $OH + NO_2$ recombination (at high NO_X). All other reactions (inside the box) only interconvert OH and HO_2 (partly via RO_2). Note that $[HO_X] \propto \sqrt{P_{OH}}$ at low NO_X and $[HO_X] \propto P_{OH}$ at high NO_X (i.e. $NO_X > 1$ ppb)

(see e.g. Talukdar et al., 1998). The excited oxygen atoms $O(^1D)$ from (R2.4) can be deactivated by collision with N_2, O_2, or H_2O (i.e. any molecule 'M'):

$$O(^1D) + M \rightarrow O(^3P) + M \tag{R2.5}$$

A certain fraction X of the excited oxygen atoms, however, will react according to:

$$\mathrm{O(^1D) + H_2O \rightarrow OH + OH} \tag{R2.6}$$

Assuming $k_{2.5\mathrm{a}}$ and $k_{2.5\mathrm{b}}$ denote the rate constants of the reaction of $\mathrm{O(^1D)}$ with N_2 or O_2, respectively, and $k_{2.6}$ the rate constant of reaction (R2.6), we obtain for X:

$$X = \frac{k_3 \cdot [\mathrm{H_2O}]}{k_{2.5\mathrm{a}} \cdot [\mathrm{N_2}] + k_{2.5\mathrm{b}} \cdot [\mathrm{O_2}] + k_{2.6} \cdot [\mathrm{H_2O}]} \tag{2.16}$$

(Chemical symbols in square brackets denote the concentration of the particular species in the atmosphere.) In the lower troposphere, X is typically in the range of 0.05–0.1. At very high relative humidity, up to 20% can be reached. The production rate of OH radicals, $P(\mathrm{OH})$, is accordingly calculated from the O_3-concentration and the photolysis frequency [see (2.18) below] for the above process (R2.4a):

$$\frac{d}{dt}\left[O(^1D)\right] = [O_3] \cdot J_1 \tag{2.17}$$

$$P(\mathrm{OH}) = \frac{d}{dt}[\mathrm{OH}] = 2 \cdot X \cdot [\mathrm{O_3}] \cdot J_1 \tag{2.18}$$

(b) Another important source of OH is the reaction of HO_2 radicals with NO:

$$\mathrm{HO_2 + NO \rightarrow OH + NO_2} \tag{2.19}$$

An analogous reaction of HO_2 with ozone (R2.18) also yields OH. HO_2 radicals are largely formed by OH reactions. The consequences of this 'radical recycling' will be analysed below. In addition, the photolysis of aldehydes forms HO_2. This process is particularly significant in urban areas, where the oxidation of VOC and direct emissions lead to high aldehyde levels. A number of non-photochemical mechanisms also produce HO_2 radicals. Among these, reactions of NO_3 radicals with certain organic species, such as olefins, phenols, or DMS, are particularly important (e.g. Platt et al. 1990, 2002; Geyer et al., 2003a; Geyer and Stutz, 2004; see Sect. 2.5.2).

(c) A further OH source is the photolysis of HONO (nitrous acid, see Sect. 2.5.3):

$$\mathrm{HONO + h\nu \rightarrow OH + NO} \tag{R2.8}$$

This OH source is only of importance in polluted air, where HONO is formed by heterogeneous processes, i.e. chemical reactions on surfaces e.g. of building walls or aerosol particles (see, e.g. Platt 1986, Alicke et al. 2002, 2003 Sect. 2.5).

(d) The ozonolysis of olefins also produces OH radicals (Atkinson et al., 1992; Atkinson and Aschmann, 1993; Paulson et al., 1997, 1999):

$$\text{Olefin} + O_3 \rightarrow OH + \text{products} \tag{R2.9}$$

An ozone molecule adds across the C=C double bond to form a primary ozonide, which decomposes to form vibrationally excited carbonyl oxide and carbonyl products. The subsequent chemistry in the gas phase is still not completely understood. For a recent publication, see e.g. (Finlayson-Pitts and Pitts, 2000; Paulson et al., 1999). The OH production yields of these reactions vary from 7% to 100%, depending on the structure and size of the alkene (Paulson et al., 1997; 1999). Note that this source (though usually weak when compared with others) is independent of the light, and thus also provides radicals at night.

(e) Finally, photolysis of hydrogen peroxide produces OH radicals:

$$H_2O_2 + h\nu \rightarrow OH + OH \tag{R2.10}$$

In contrast to processes (b) and (c), the latter source would only be relevant in air masses with very low NO_X pollution, since only under these conditions can significant amounts of H_2O_2 be formed.

2.4.2 Temporal Variation of the HO_X Source Strength

The photolysis frequency $J_{2.4}$, and thus the strength of the main OH source [P(OH)], is given by the expression (e.g. Junkermann et al., 1989): where $I(\lambda)$ denotes the solar intensity (actinic flux), $\sigma(\lambda)$ the ozone absorption cross-section, and $\Phi(\lambda)$ the quantum efficiency of reaction R2.4. Because the solar intensity varies with the time of day, cloudiness, and seasons, the OH source strength is highly variable in the atmosphere. In addition, other environmental variables, such as the water vapour concentration, influence the formation of OH radicals. Figure 2.10, for example, shows the diurnal variation of OH concentrations. The OH levels follow the diurnal behaviour of the O_3 photolysis rate closely. The seasonal dependence of the OH source strength at mid-latitudes is shown in Fig. 2.11.

In polluted air, the diurnal variation of the ozone concentration (with a maximum in the early afternoon) has an additional influence on OH. Since the rate of R2.4 is proportional to the ozone concentration, P(OH) should also be proportional to $[O_3]$. However, a higher O_3 level will shift the NO/NO_2 stationary state towards higher NO_2 (see Sect. 2.5.1), and thus will reduce the OH concentration. The strength of other OH sources (e.g. HONO – photolysis, see Sect. 2.5.1) frequently peak in the morning.

2.4.3 Chemistry of Hydrogen Radicals (OH and HO_2)

Hydroxyl radicals react with most oxidisable gases in the atmosphere, for instance with carbon monoxide:

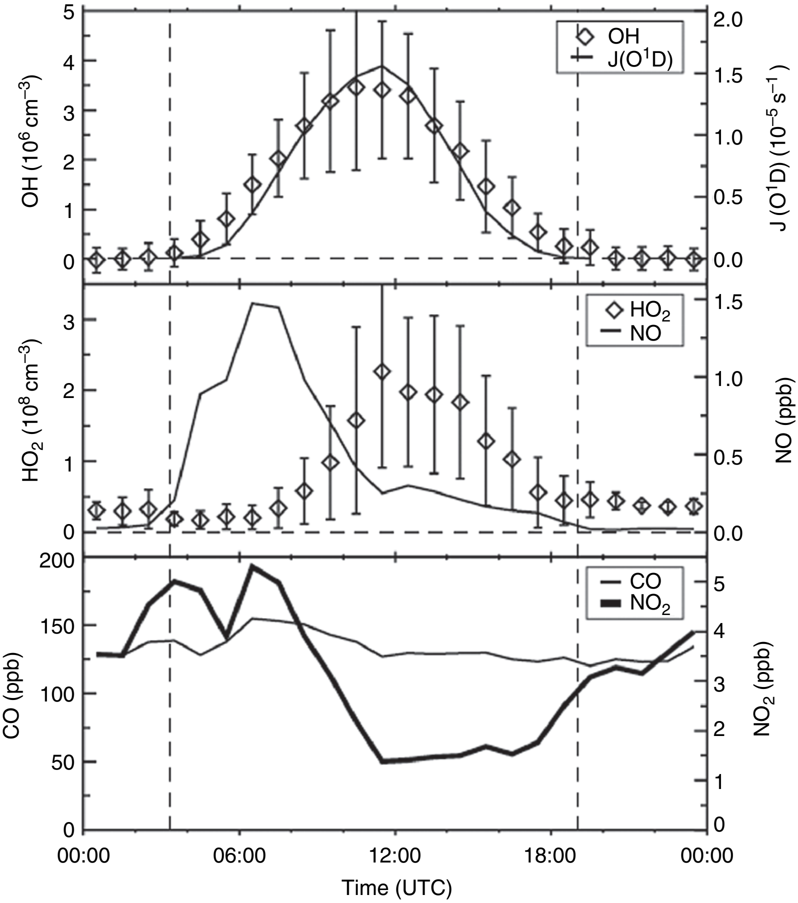


Fig. 2.10. Average diurnal OH, HO_2, and $J(O^1D)$ levels as observed during the BERLIOZ field experiment near Berlin in summer 1998. The OH concentration follows the solar radiation closely, while the levels of HO_2 are also influenced by the concentrations of NO (from Holland et al., 2003, Copyright by American Geophysical Union (AGU), reproduced by permission of AGU).

$$OH + CO \rightarrow CO_2 + H \tag{R2.11}$$

In this reaction, both CO_2 and hydrogen atoms are produced. In the atmosphere, the hydrogen atoms immediately form hydro-peroxy radicals, HO_2:

$$H + O_2 \xrightarrow{M} HO_2 \tag{R2.12}$$

As products of the degradation of VOCs, peroxy radicals are also produced. An example is methane degradation:

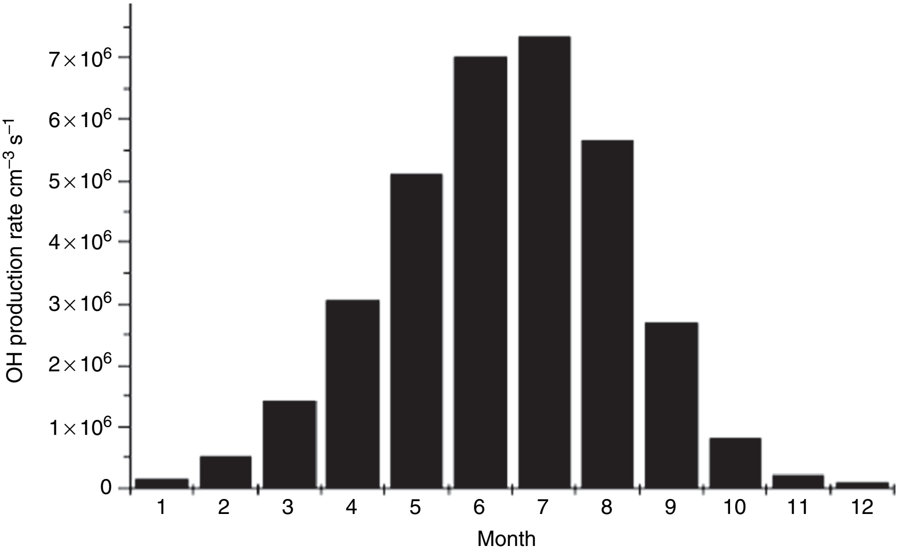


Fig. 2.11. The seasonal variation of the average diurnal OH source strength under cloud-free conditions in mid-latitudes (Germany)

$$OH + CH_4 \rightarrow CH_3 + H_2O \tag{R2.13}$$

$$CH_3 + O_2 \xrightarrow{M} CH_3O_2 \tag{R2.14}$$

Further important reactions of OH are the oxidation of molecular hydrogen and formaldehyde (and higher aldehydes):

$$OH + H_2 \rightarrow H_2O + H \tag{R2.15}$$

$$OH + CH_2O \rightarrow CHO + H_2O \tag{R2.16}$$

$$CHO + O_2 \rightarrow HO_2 + CO \tag{R2.16a}$$

In these reactions, the primary product is also HO_2 (R2.15 followed by R2.12, or R2.16 followed by R2.16a, respectively)

Thus, in all of the above reactions, and in fact most OH reactions, free radicals (here HO_2 radicals, which are easily converted to OH) are regenerated. An important exception to this rule is the reaction of OH with oxides of nitrogen:

$$OH + NO_2 \xrightarrow{M} HNO_3 \tag{R2.17}$$

The nitric acid produced in this reaction will (in the troposphere) be removed from the gas phase by various processes, such as dry deposition to the ground or rainout. Figure 2.9 shows the simplified reaction scheme of the hydrogen radicals $HO_X(OH + HO_2)$, as outlined above.

The balance between OH sources and sinks determines the levels of OH and HO_2 and their respective lifetimes. Figure 2.12 shows the OH and HO_2 budget as a function of the NO_X ($NO + NO_2$) concentration. The OH concentration shows a non-monotonous behaviour as a function of the NO_X level: At very low NO_X (below e.g. 0.1 ppb) essentially each OH radical reacting with CO (or HC) is converted to HO_2 (or an organic peroxy radical, RO_2). These radicals are, in turn, lost by radical–radical interaction. Thus, the OH concentration remains relatively low. At medium NO_X levels (about 1–2 ppb) most HO_2 and RO_2 radicals react with NO to reform OH. Therefore, OH levels are much higher than in the case of low NO_X. At very high NO_X levels (10 ppb or higher) most of the OH radicals react with NO_2 to form HNO_3, and therefore OH levels are low again.

As a consequence, OH levels show a maximum at around 1 ppb of NO_X, while HO_2 levels drop monotonously with increasing NO_X. This behaviour is illustrated in Fig. 2.13.

Although its concentration (in clean air) can be up to two orders of magnitude larger than that of OH (see Fig. 2.13), the reactivity of the HO_2 radical is much lower than that of the OH radical. However, the HO_2 radical is an important OH reservoir, and it is also the precursor for atmospheric H_2O_2. In addition, there is most likely a direct role of HO_2 in liquid-phase chemistry, for instance in cloud droplets (Chameides and Davis, 1982; Chameides, 1984; Lelieveld and Crutzen, 1990, 1991).

Only four HO_2 reactions play a role in the troposphere. Their significance depends on the levels of NO_x:

(1)

$$HO_2 + NO \rightarrow OH + NO_2 \tag{R2.7}$$

(2)

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{R2.18}$$

(3)

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{R2.19}$$

(4)

$$HO_2 + OH \rightarrow H_2O + O_2 \tag{R2.20}$$

The first two reactions reduce HO_2 radicals to OH. The third and forth reactions can be regarded as ‘final sinks’ for the HO_2 radical (and thus for HO_X). While hydrogen peroxide can be photolysed to yield two OH radicals (R2.10), this is a slow process. Thus rainout and washout of H_2O_2 is much more likely, since it is highly water soluble. A further sink of H_2O_2 is reaction with OH:

$$H_2O_2 + OH \rightarrow H_2O + HO_2 \tag{R2.21}$$

Hydrogen Peroxide is an important oxidant in the liquid phase, e.g. in raindrops, or cloud or haze droplets. Reactions of H_2O_2 in cloud or haze droplets contribute significantly to the oxidation of SO_2 (S(IV)) to sulphate (S(VI)).

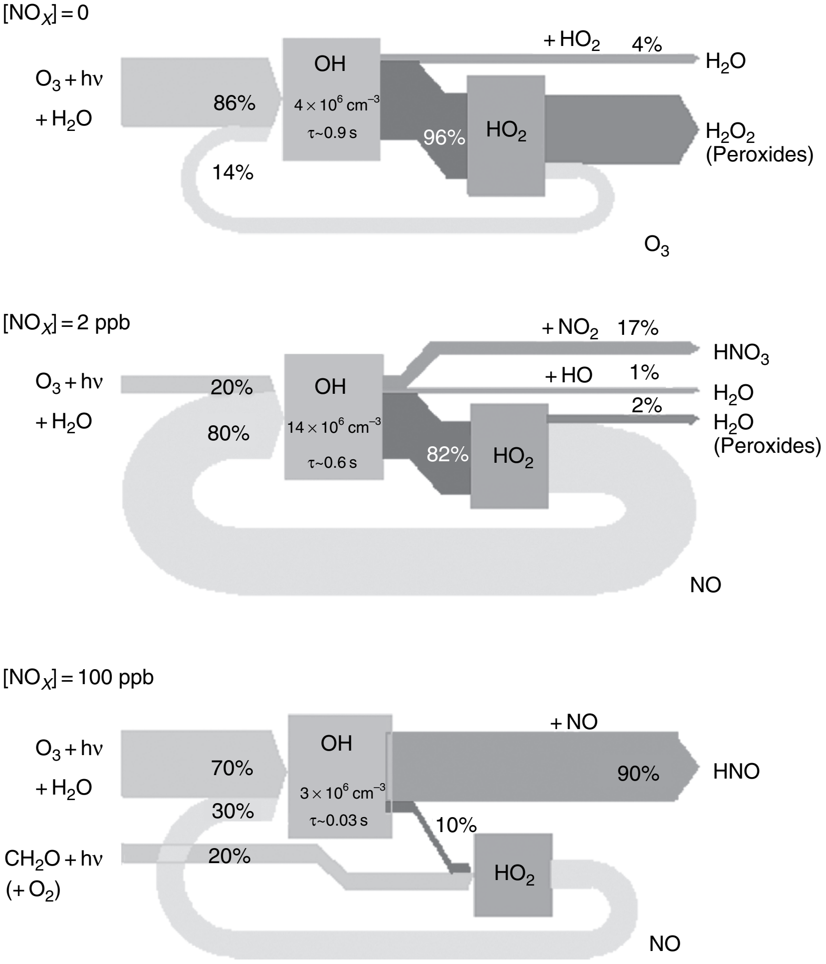


Fig. 2.12. The relative strength of OH sources and sinks, and the resulting OH concentration as a function of the NO$_X$ (NO + NO$_2$) level. Here, three cases are shown: (**a**) At very low NO$_X$, essentially each OH radical reacting with CO (or hydrocarbons) is converted to HO$_2$ (or an organic peroxy radical, RO$_2$). These radicals are, in turn, lost by radical–radical interaction, and thus the OH concentration remains relatively low. (**b**) At medium NO$_X$ levels (about 1 ppb), most HO$_2$ and RO$_2$ radicals react with NO to reform OH. Therefore OH levels are much higher than in case (**a**). (**c**) At very high NO$_X$ levels, most of the OH radicals react with NO$_2$ to form HNO$_3$, and therefore OH levels are low again

Hydrogen peroxide is essentially only formed via reaction R2.19 (i.e. HO$_2$ recombination). A small contribution is assumed to come from the reaction of olefines with ozone (Becker et al., 1990). Assuming reaction R2.19 to be the dominating source, high rates of H$_2$O$_2$ production (and thus usually also high

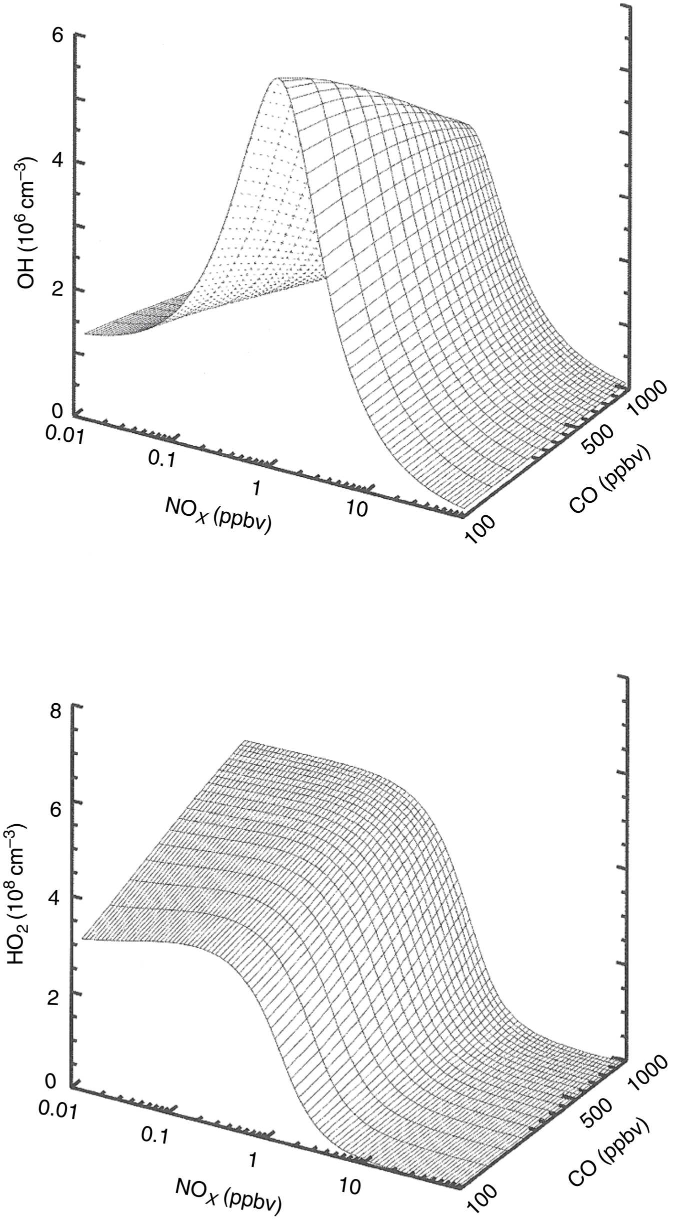


Fig. 2.13. Concentrations of OH (upper panel, units of 10^6 molecules cm$-^3$) and HO_2 (lower panel, units of 10^8 molecules cm^{-3}) as a function of the NO_X ($NO+NO_2$) mixing ratio for typical conditions (37.6 ppb ozone, 88.7 ppb CO, 0.92 ppb CH_2O, $J(O_3 - O^1D) = 3 \times 10^{-5}\,s^{-1}$, $J(NO_2) = 9.1 \times 10^{-3}\,s^{-1}$). The HO_2 concentration, and therefore H_2O_2 production rate, are highest in unpolluted air at NO_X levels below a few 100 ppt (from Enhalt, 1999)

levels) are to be expected under conditions of high HO_2. Thus, in air masses with high humidity and ozone, and low NO, the highest H_2O_2 levels are to be expected.

2.5 Oxides of Nitrogen in the Atmosphere

The oxides of nitrogen, NO and NO_2 (NO_X), are key species in atmospheric chemistry. They regulate many trace gas cycles and influence the degradation of most pollutants in clean air, as well as in polluted regions:

NO_X concentration has a strong influence on the atmospheric level of hydroxyl radicals (OH, see Sect. 2.4.1), which, in turn, are responsible for the oxidation processes of most trace gases. In addition, NO_X is a catalyst for tropospheric ozone production (see Sect. 2.3). Oxides of nitrogen (or acids formed from them) can also react with VOC degradation products to form organic nitrates or nitrites [e.g. peroxy acetyl nitrate (PAN) or methyl nitrite], as well as nitrosamines (Platt et al., 1980b). These species can be much more detrimental to human health than the primary oxides of nitrogen. Finally, the thermodynamically most stable and ultimate degradation product of all atmospheric oxides of nitrogen, nitric acid, is (besides sulphuric acid) the main acidic component in ‘acid rain’.

An overview of the most important oxidised nitrogen species in the atmosphere is given in Fig. 2.14. The main reaction pathways between the various species are indicated by arrows. Oxides of nitrogen are primarily emitted in the form of NO (plus some NO_2) and N_2O. While N_2O is a very inert species and therefore plays no role for the chemical processes in the troposphere, NO reacts rapidly with natural ozone to form NO_2. On the other hand, NO_2 will be destroyed (photolysed) by sunlight during the daytime, and therefore a stationary state between these two NO_X species will be established. NO_2 then further reacts with OH radicals or NO_3, ultimately forming nitric acid (or nitrate aerosol).

The ‘classic’ role of oxides of nitrogen in atmospheric chemistry (see Sect. 2.5.1) has been known since the 1980s. Since then, the importance of this class of species has been underlined by newly obtained results, largely made possible by improved measurement techniques:

- The confirmation of an additional NO_X degradation pathway via heterogeneous and homogeneous hydrolysis of N_2O_5 at night (Heintz et al., 1996; Mentel et al., 1996; Wahner et al., 1998a; Geyer et al., 2001c; Brown et al., 2003; Stutz et al., 2004).
- The non-photochemical production of peroxy radicals (HO_2 and RO_2) via NO_3–VOC reactions as a further consequence of elevated NO_X levels in the atmosphere (Platt et al., 1990; LeBras et al., 1993; Mihelcic et al., 1993; Geyer et al., 1999; Geyer and Stutz, 2004).

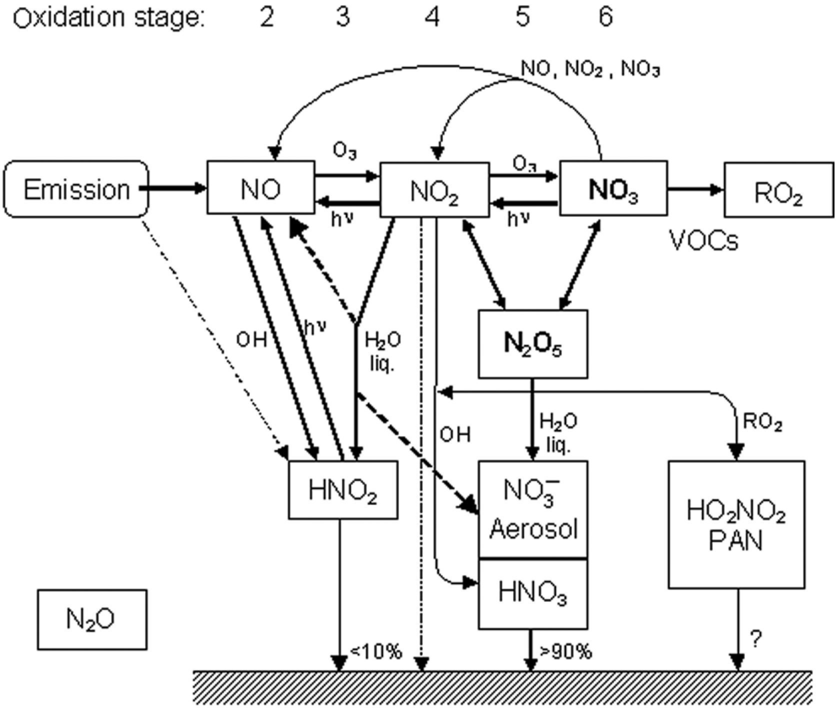


Fig. 2.14. Simplified overview of the NO_X reaction scheme in the atmosphere. Arrows indicate main reaction pathways

- The establishment of HONO photolysis as another significant OH source in polluted air (Perner and Platt, 1979; Harris et al., 1982; Platt, 1986; Harrison et al., 1996; Alicke et al., 2002, 2003).
- Finally, an important role of oxidised nitrogen species is postulated in the mechanisms releasing RHS from sea salt as, for example, observed in the polar BL (Finlayson-Pitts and Johnson, 1988; Finlayson-Pitts et al., 1989, 1990).

The improved knowledge of the cycle of oxidised nitrogen species also has great practical importance: The exact knowledge of the NO_X lifetime allows the estimation of NO_X levels and the health effects of atmospheric NO_X, the amount of long-range transport (and thus, for instance, the amount of acid rain in non-polluted areas), and finally the NO_X level in clean air (and thus the amount of ozone formation there).

2.5.1 Classical Chemistry of Oxides of Nitrogen in the Atmosphere

In this section, we briefly summarise the central aspects of the classical chemistry of oxides of nitrogen in the atmosphere (see also Fig. 2.14 and Table 2.3).

Extensions of our image of the chemical processes related to oxidised nitrogen species are discussed in Sect. 2.5.2.

The transformation pathways between the atmospheric nitrogen reservoir are closely coupled to the reactions of ozone (as discussed in Sect. 2.3) and to the cycles of hydrogen radicals (OH and HO_2). An important question in this context is: Are NO_X reactions sources or sinks for ozone? The simple system described by reactions R2.1–R2.3 (Sect. 2.3) neither destroys nor produces ozone. However, in the atmosphere there are additional reactions oxidising NO to NO_2 without consuming ozone. Thus, the NO_X level ultimately determines whether there is net ozone formation or destruction. In the unpolluted (background) atmosphere, the processes oxidising NO to NO_2 without consuming O_3 (and thus producing O_3 via reactions R2.1 and R2.2) are reactions of NO with peroxy radicals (HO_2, CH_3O_2, and higher RO_2). In the simple case of HO_2, we have:

$$NO + HO_2 \rightarrow NO_2 + OH \tag{R2.7}$$

The HO_2 radicals are produced, for example, by reaction of OH radicals with CO (R2.11, followed by R2.12). At the same time, the reactions R2.7, R2.11, and R2.12 facilitate another stationary state in the atmospheric concentration ratio of the hydrogen radicals OH and HO_2, (HO_X). Since ozone also reacts with HO_2 radicals (but not with other peroxy radicals), the HO_X system also destroys ozone:

$$O_3 + HO_2 \rightarrow OH + 2O_2 \tag{R2.18}$$

Whether the above-described interplay of the NO_X and HO_X systems leads to net ozone formation (as shown in Fig. 2.7) or O_3 destruction depends on the relative rates of the reactions R2.7 and R2.18, and thus on the NO concentration. At a NO concentration around 1/3000 of the O_3 concentration (i.e. $[NO] \approx 0.01\,\text{ppb}$ at $30\,\text{ppb}$ O_3), the rates of both reaction pathways are equal. In other words, ozone formation equals ozone destruction. At higher NO_X (and thus NO) levels net O_3 formation occurs, while at lower NO levels O_3 is photochemically destroyed. In regions influenced by industrial activities, where NO levels can reach many ppb, O_3 formation by far exceeds destruction. This can also be seen from the observation that ozone levels in the (more industrialised) northern hemisphere exceed those in the southern hemisphere by about 50%. Figure 2.7 shows model calculated and observed ozone formation rates as a function of the NO level.

Oxides of nitrogen influence the concentrations of OH and HO_2 radicals in the atmosphere by several mechanisms. The most important removal process for OH radicals is their recombination with NO_2. This reaction (R2.6) leads to final removal of OH from the radical chain. Consequently, the OH concentration is reduced by high levels of NO_X (and thus NO_2). On the other hand, the reaction of NO with HO_2 radicals reduces the stationary state $[HO_2]/[OH]$ ratio (reactions R2.7, R2.11, and R2.12), and consequently leads to higher OH radical concentrations. This relationship is illustrated in Figs. 2.12 and 2.13.

The crucial step initiating the eventual removal of nitrogen oxides from the atmosphere is their conversion to nitric acid (HNO_3), which is subsequently removed from the atmosphere by dry and wet deposition (see also Table 2.3). The direct (dry) deposition of nitrogen oxides to the ground is of minor importance in comparison (<10%). On the other hand, re-conversion of nitric acid to NO_X is negligible in the troposphere. Nitric acid is formed in reactions of NO_2:

- Directly by reaction with OH (R2.17).
- Indirectly by reaction of NO_2 with O_3, leading to NO_3 (R2.22), which can either abstract a hydrogen atom (e.g. from DMS) or further react with NO_2 to form N_2O_5, (R2.26) the anhydride of nitric acid, which in turn is converted to HNO_3 by reaction with gas-phase or liquid water (R2.27).

2.5.2 Tropospheric Chemistry of Nitrate Radicals, NO_3

At night, when levels of OH radicals are low, other oxidants play an important role in the troposphere. Among those, the NO_3 radical plays an important role for the budget of NO_X and for the concentrations of certain organic compounds. Nitrate radicals are formed by reaction of NO_2 with ozone (see also Fig. 2.14)

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R2.22}$$

which constitutes the only relevant source of NO_3 in the troposphere. The rate of NO_3 production, P_{NO3}, can be calculated from the concentration of NO_2 and O_3:

$$\frac{d\,[NO_3]}{dt} = [NO_2] \cdot [O_3] \cdot k_1 = P_{NO3} \tag{2.20}$$

During the daytime, NO_3 radicals are effectively destroyed by photolysis:

$$NO_3 + h\nu \rightarrow NO + O_2 \tag{J2.23a}$$

$$\rightarrow NO_2 + O \tag{J2.23b}$$

(photolytic lifetime is about 5 s), and rapid reaction with NO ($k_{2.24} = 2.6 \times 10^{-11}\,cm^3 s^{-1}$ at 293K):

$$NO_3 + NO \rightarrow NO_2 + NO_2 \tag{R2.24}$$

At night, when photolysis is unimportant and NO levels are usually low, the NO_3 loss rate is much smaller and thus its concentration is larger. Loss of NO_3 due to gas-phase reaction with nitrogen dioxide or the NO_3 self-reaction is slow. Similarly, the unimolecular decomposition of NO_3 is probably of minor importance in the atmosphere (Johnston et al., 1986; Russel et al., 1986). Gas-phase reaction of NO_3 with water vapour is endothermic.

Main destruction mechanisms are thus reaction with organic species (see Table 2.7) or heterogeneous loss (i.e. reaction at the ground or at the surface of aerosol or cloud particles) of either NO_3 or N_2O_5.

Table 2.7. Reaction of OH, NO_3, O_3, and Cl with VOC (at 25°C) (from Atkinson, 1994)

Species	Reaction rate constant 10^{15} cm^3 $molec.^{-1}$ s^{-1}			
	With OH	With NO_3	With Ozone	With Cl
Alkanes				
Methane	6.14	<0.001	<0.00001	100
Ethane	254	0.0014	<0.00001	59000
Propane	1120	0.017	<0.00001	137000
n-Butane	2190	0.046	<0.00001	205000
n-Pentane	4000	0.04	<0.00001	280000
Alkenes				
Ethene	8520	0.21	0.0017	99000
Propene	26300	9.4	0.013	230000
1-Butene	31400	12	0.011	220000
2-Methyl-2-Butene	68900	9300	0.423	
2,3-Dimethyl-2-Butene	110000	57000	1.16	
Alkynes				
Ethyne	5100	0.0082	<0.00001	
Aromatics				
Benzene	1230	<0.03	<0.00001	
Toluene	5960	0.068	<0.00001	
Phenol	26300	3780		
o-Cresol	42000	13700	0.00026	
m-Cresol	64000	9740	0.00019	
p-Cresol	47000	10700	0.00047	
Benzaldehyde	12900	2.6	No data	
Isoprene	101000	678	0.013	460000
Terpenes				
α - Pinene	53700	6160	0.0866	480000
β - Pinene	78900	2510	0.015	
3-Carene	88000	9100	≈0.037	
Limonene	171000	12200	≈0.2	
Sabinene	117000	10000	≈0.086	
α - Terpinene	363000	180000	8.47	
Myrcene	215000	11000	0.47	
Aldehydes				
Formaldehyde	9370	0.6	<0.00001	73000
Acetaldehyde	15800	2.7	<0.00001	79000

NO_3 + VOC Reactions

NO_3 reacts with a variety of organic compounds in the atmosphere. In particular, reactions with biogenic VOC, such as isoprene and terpenes, as well as the reactions with DMS, are of significance.

NO_3 reactions with alkanes and aldehydes proceeds via H abstraction (Atkinson, 1990):

$$NO_3 + RH \rightarrow R + HNO_3 \tag{R2.25}$$

The alkyl radicals produced in reaction R2.25 are transformed to peroxy radicals (RO_2) by reaction with O_2.

Reactions with alkenes (including isoprene and terpenes) proceed via NO_3 addition to a $C = C$ double bond. Further reaction steps are O_2 addition, followed by either reaction with other peroxy radicals or NO_2. Reasonably stable end products are organic nitrates and peroxy radicals (Atkinson, 1990).

Reactions with aromatic compounds are also important. While reaction with benzene is quite slow (rate constant on the order of $10^{-17}\,\mathrm{cm^3 molec.^{-1} s^{-1}}$), hydroxy-substituted benzenes react very fast, with reaction rate constants on the order of $10^{-12}\,\mathrm{cm^3\,molec.^{-1}\,s^{-1}}$ (furane and phenol) to $10^{-11}\,\mathrm{cm^3\,molec.^{-1}\,s^{-1}}$ (cresols).

Finally, NO_3 radicals react rapidly with DMS (reaction rate constant $10^{-12}\,\mathrm{cm^3\,s^{-1}}$). This can be significant for the budgets of both DMS and NO_3, in particular in the marine atmosphere. The exact reaction mechanism is still subject to investigations. Recent investigations show that the primary step is probably H abstraction. Thus, nitric acid and peroxy radicals should be the dominant products (Butkovskaya and LeBras, 1994; Platt and LeBras, 1997).

Heterogeneous Loss of NO_3 and N_2O_5

In the atmosphere, NO_3 and NO_2 are in a chemical equilibrium with N_2O_5:

$$NO_2 + NO_3 \overset{M}{\longleftrightarrow} N_2O_5 \tag{R2.26}$$

The equilibrium concentration of N_2O_5 is given by:

$$[N_2O_5] = K \cdot [NO_2] \cdot [NO_3] \tag{2.21}$$

Under ‘moderately polluted’ conditions (NO_2 mixing ratio of about 1 ppb) typical for rural areas in industrialised countries, NO_3 and N_2O_5 concentrations are roughly equal (293K) (e.g. Wängberg et al., 1997). While homogeneous reactions of N_2O_5 with water vapour and other atmospheric trace gases are believed to be extremely slow (Mentel et al., 1996), heterogeneous reaction with water contained in aerosol or cloud particles will convert N_2O_5 to nitric acid:

$$N_2O_5 + H_2O \xrightarrow{het} HNO_3 \tag{R2.27}$$

Accommodation coefficients γ for N_2O_5 and NO_3 on water (droplet) surfaces are in the range of 0.04–0.1 (the higher values applying to water containing

H_2SO_4) (Van Doren et al., 1990; Mozurkewich and Calvert, 1988; Mentel et al., 1996; Wahner et al., 1998; Hallquist et al., 2003), and >0.0025 (Thomas et al., 1993), respectively. If reaction R2.27 leads to accumulation of nitrate in the liquid phase, the accommodation coefficients can be considerably (by about one order of magnitude) reduced. For instance, Wahner et al. (1998) find γ in the range of 0.002–0.023 at relative humidities of 48–88% for the accommodation of N_2O_5 on sodium nitrate aerosol.

NO_3 Lifetime

From measured concentrations of O_3, NO_2, and NO_3, the atmospheric lifetime of NO_3 (τ_{NO3}, see Sect. 2.1.3), limited by the combination of any first-order loss process, can be calculated (Heintz et al., 1996; Geyer et al., 2001a,b,c, 2002; Brown et al., 2003; Geyer and Stutz, 2004):

$$NO_3 + Z \rightarrow \text{products} \tag{R2.28}$$

Assuming pseudo stationary state conditions with respect to NO_3, τ_{NO3} becomes

$$\tau_{NO3} = \frac{[NO_3]}{P_{NO3}} = \frac{[NO_3]}{[NO_2] \cdot [O_3] \cdot k_1} \tag{2.22}$$

Since $k_{2.22}$ is known from laboratory measurements, and the concentrations of O_3, NO_2, and NO_3 can be simultaneously measured (for instance, by the DOAS technique), τ_{NO3} can readily be calculated for various atmospheric conditions. It must be emphasised that the steady-state assumption is an approximation, which is quite good for most atmospheric situations. The NO_3 lifetime can also be limited by any irreversible loss of N_2O_5 (for instance $k_{2.27} > 0$), because both species are in a rapidly established thermodynamic equilibrium (R2.28, the time constant to reach equilibrium, is on the order of 1 min at ambient temperatures). Under conditions where both NO_3 and N_2O_5 are lost, the observed NO_3 lifetime τ_{NO3} is given by:

$$\tau_{NO3} = \frac{1}{\dfrac{1}{\tau'_{NO3}} + \dfrac{[NO_2]}{K} \cdot \dfrac{1}{\tau_{N2O5}}} \tag{2.23}$$

Of course, in the case of negligible loss of $N_2O_5(\tau_{N2O5} \rightarrow \infty)$, $\tau'_{NO3} = \tau_{NO3}$. For conditions where direct loss of NO_3 molecules can be neglected ($\tau'_{NO3} \rightarrow \infty$), (2.23) reduces to:

$$\tau_{NO3} = \frac{K}{[NO_2]} \cdot \tau_{N2O5} \tag{2.24}$$

The simple stationary state assumption predicts an observed NO_3 lifetime τ_{NO3} inversely proportional to the NO_2 concentration in cases where only

N_2O_5 is lost. Since NO_3 formation is proportional to $[NO_2]$ (R2.20), $[NO_3]$ should become independent of the NO_2 concentration under such conditions.

Formation of Hydrogen Radicals by NO_3 + VOC Reactions

Since most of the above reactions of NO_3 with organic species appear to lead to the formation of peroxy radicals, an interesting consequence of the nighttime reaction of NO_3 with organic species is a considerable contribution to the HO_X budget (Platt et al., 1990; Mihelcic et al., 1993; Carslaw et al., 1997; Geyer et al., 2001; Geyer and Stutz, 2004).

In circumstances where NO levels are very low, peroxy radicals undergo reactions with other RO_2 radicals, O_3, or NO_3:

$$RO_2 + NO_3 \rightarrow RO + NO_2 + O_2 \qquad (R2.29)$$

In urban areas, where ubiquitous NO emissions and vertical transport can lead to an active mixing of NO_3, N_2O_5, and NO, the likely fate of RO_2 radicals is reaction with NO (Geyer and Stutz, 2004):

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (R2.30)$$

This gives rise to a radical chemistry which is similar to that during the day. However, the region in which NO_3 and NO can coexist is often shallow and it moves vertically throughout depending on the NO emission strength and vertical stability (Geyer and Stutz, 2004).

2.5.3 Nitrous Acid, HONO in the Atmosphere

The photolysis of nitrous acid, HONO, is an important source for OH radicals in the polluted urban atmosphere (Perner and Platt, 1979; Platt et al., 1980b; Kessler et al., 1981; Harris et al., 1982; Alicke et al., 2002, 2003; Zhou et al., 2002; Aumont et al., 2003; Ren et al., 2003; Kleffmann et al., 2005), and the polar BL (Li, 1994; Zhou et al., 2001). In addition, HONO is toxic (Beckett et al., 1995) and its chemistry leads to the formation of carcinogenic nitrosamines, (Shapley, 1976; Famy and Famy, 1976; Pitts, 1983). HONO formation at chamber walls is a candidate for an intrinsic ‘chamber dependent’ radical formation, which is observed in most smog chamber experiments (e.g. Gleason and Dunker, 1989; Rohrer et al., 2004).

The photolysis of HONO, which absorbs in the wavelength range from 300 to 405 nm, leads to a formation of an OH radical and NO (Stockwell and Calvert, 1978; Stutz et al., 2000):

$$HONO + h\nu \rightarrow OH + NO \ \ (300\,\text{nm} < \lambda < 405\,\text{nm}) \qquad (R2.8)$$

The photolysis of HONO begins early in the morning, when HONO concentrations are typically highest. The combination of elevated HONO concentrations at sunrise and fast photolysis results in a peak in the production of OH which surpasses other HO_X sources, such as O_3 and HCHO photolysis (Alicke et al., 2002).

Nitrous acid was first identified and quantified in the atmosphere by DOAS (Perner and Platt, 1979; Platt and Perner, 1980). Typical HONO mixing ratios are in the range of 0 – 15 ppb (see Calvert et al., 1994; Lammel and Cape, 1996; or Alicke, 2000 for reviews). Generally, nitrous acid concentrations scale with the NO_2 concentration, and therefore approximately with the degree of pollution. The diurnal variation of the mixing ratio of HONO is dominated by its photolysis, which leads to lower levels during the day. During the night concentrations increase, often reaching a constant value in the early morning. The amount of HONO formed is often correlated with the stability of the nocturnal BL, as inferred for example from radon data (Febo et al., 1996).

Several studies have discussed the importance of HONO photolysis as an OH source (e.g. Platt et al., 1980b; Harrison et al., 1996; Stutz et al., 2002; Alicke et al., 2002, 2003). Alicke et al. (2002) showed OH production rates of up to 3×10^7 molecules $cm^{-3}\,s^{-1}$ in Milan, Italy. Other observations confirm these results (Harris et al., 1982; Sjödin, 1988). Model studies (e.g. Harris et al., 1982) show that HONO photolyis can lead to an increase in the maximum daytime ozone concentration of up to 55%, if 4% of the initial NO_X is present as HONO (Los Angeles case, initial NO_x: 0.24 ppm), compared with a calculation without nitrous acid. Jenkin et al. (1988) showed HONO photolysis can account for a fivefold increase in OH at 6:00 AM, a 14% increase in OH present at the daily maximum (noon), and a 16% increase in net photochemical ozone production. In addition, the formation of ozone begins earlier in the day due to the HONO photolysis in the morning.

HONO is formed through various chemical mechanisms in the atmosphere. The only important gas-phase reaction forming nitrous acid is 2.31 (Stuhl and Niki, 1972; Pagsberg et al., 1997; Zabarnick, 1993; Nguyen et al., 1998):

$$OH + NO(+M) \rightarrow HONO(+M) \qquad (R2.31)$$

Gas-phase nitrous acid producing pathways, such as the reaction of NO_2 with HO_2, have been reported to be of minor importance (e.g. Howard, 1977; Tyndall et al., 1995). The bulk of urban HONO is suspected to be formed from either of the mechanisms summarised in reaction R2.32 or R2.33, involving only NO_X and water vapour (Perner and Platt, 1979; Kessler and Platt, 1984; Platt, 1986).

$$NO_2 + NO + H_2O \Leftrightarrow 2\,HONO \qquad (R2.32)$$

$$2NO_2 + H_2O \Leftrightarrow HONO + HNO_3 \qquad (R2.33)$$

These reactions (and their reverse reactions) appear to proceed heterogeneously on surfaces (Kessler, 1984; Kessler et al., 1981; Sakamaki et al., 1983; Lammel and Perner, 1988; Notholt et al., 1991, 1992; Junkermann and Ibusuki, 1992; Ammann et al., 1998; Calvert et al., 1994; Longfellow et al., 1998; Goodman et al., 1999; Kalberer et al., 1999; Veitel, 2002; Veitel et al., 2002). A number of laboratory studies (Sakamaki et al., 1983; Pitts et al., 1984b; Jenkin et al., 1988; Svensson et al., 1987; Kleffmann et al., 1998) have shown reaction R2.32 to be insignificant. Several field observations, where the presence of high ozone at night excluded NO, or low NO was documented, confirm this result (e.g. Kessler and Platt, 1984; Harrison and Kitto, 1994).

The exact mechanism of the heterogeneous formation of HONO summarised in reaction R2.33 is unknown, but several studies (Svensson et al., 1987; Jenkin et al., 1988; Kleffmann et al., 1998; Finlayson-Pitts et al., 2003) have shown that it is first order in NO_2 and water. Neither the reaction rate constants nor the nature of the surface is known, which makes calculation of the OH production by models difficult. In addition, reactions on 'urban surfaces' like organic aerosols or soot aerosols were suggested (e.g. Gutzwiller et al., 2002; Bröske et al., 2003). In fact reactions of NO_2 on asphalt or roof tile surfaces appear to be sufficiently rapid to explain observations (Trick, 2004).

The most important gas-phase chemical removal process for HONO, besides photoloysis, is reaction R2.34. A few percent of HONO is expected to be destroyed by OH radicals:

$$\mathrm{OH} + \mathrm{HONO} \rightarrow .\mathrm{H_2O} + \mathrm{NO_2} \tag{R2.34}$$

Several studies have been carried out to estimate the strength of direct emission of nitrous acid from combustion processes (Kessler and Platt, 1984; Pitts et al., 1984a; Kirchstetter et al., 1996; Ackermann, 2000; Winer and Biermann, 1994). Up to 1% of the emitted NO_X was found as nitrous acid, making this source important, especially in heavily polluted areas with high amounts of traffic. (Kirchstetter et al., 1996) report a HONO/NO_X emission ratio of 0.35% for a north-American car fleet, while (Ackermann, 2000; Kurtenbach et al., 2002) found 0.65% of NO_X emitted as HONO in a traffic tunnel in Germany.

2.6 Tropospheric Chemistry of VOCs

Organic compounds are an extremely large class of chemicals that play a significant role in the atmosphere. As discussed in Sect. 2.3, they provide the fuel for ozone formation. In addition, chemical reactions with organic carbons can lead to the formation of particles, so called secondary organic aerosol. They also impact radical budgets (see Sect. 2.4) and thus influence radical chemistry.

The chemistry of volatile organic carbon compounds (VOCs) is a complex topic which, by far, exceeds the scope of this book. Here, we will only briefly discuss typical levels of organics in the atmosphere, and in particular in urban areas, and their initial reactions with various radical species. VOCs can be subdivided into a number of different classes encompassing hydrocarbons (HC) and oxidised species (Table 2.7):

- alkanes, with the overall formula C_nH_{2n+2}
- alkenes (or olefins), with the overall formula C_nH_{2n} (mono-olefins)
- alkynes, with the overall formula C_nH_{2n-2}
- aromatics, which contain one or more benzene rings (C_6H_6)
- isoprene and terpenes
- oxidised species: aldehydes, ketones, alcohols, and organic acids

Members of each class often undergo similar chemistry. We will therefore discuss their initial reactions steps in a general way.

Alkanes are molecules containing carbon and hydrogen molecules, whereas the carbon molecules are held together by single molecular bonds. Consequently, the degradation of alkanes by OH proceeds by abstraction of one hydrogen atom, in analogy to the reaction of methane (R2.35 and R2.36):

$$\mathrm{OH + RH \rightarrow\ R + H_2O} \tag{R2.35}$$

where R denotes an alkyl radical (C_nH_{2n+1}), e.g. C_2H_5. The rate constants for some alkane–OH reactions are given in Table 2.7.

Analogous to CH_3 (see Sect. 2.4.1), alkyl radicals immediately react with molecular oxygen to form organic peroxy radicals:

$$\mathrm{R + O_2 \xrightarrow{M} RO_2} \tag{R2.36}$$

The fate of peroxy radicals in the atmosphere are self-reaction (forming peroxides), reaction with O_3, and, mostly in polluted areas, reaction with NO:

$$\mathrm{RO_2 + NO \rightarrow\ RO + NO_2} \tag{R2.37}$$

Alkoxy radicals RO react with O_2 to form aldehydes and HO_2 radicals:

$$\mathrm{RO + O_2 \rightarrow\ R'CHO + HO_2} \tag{R2.38}$$

where R′ denotes an alkyl radical with one less C atom ($C_{n-1}H_{2n-1}$).

Initial reactions of alkanes with NO_3 radicals and Cl atoms also proceed by hydrogen abstraction, followed by reactions R2.36–R2.38 (Table 2.7). Ozone only reacts very slowly with alkanes and its ractions are unimportant in the atmosphere (Table 2.7).

Alkenes are HC which contain one or more carbon double bonds. While hydrogen abstraction can still occur, the predominant first step in alkene+OH reactions is the addition of the OH radical to the double bond, followed by addition of O_2 to the resulting peroxy radical:

$$\mathrm{OH + RCH_2CH_2 \xrightarrow{M} RCH_2CH_2OH} \tag{R2.39}$$

$$\mathrm{RCH_2CH_2OH + O_2 \xrightarrow{M} O_2RCH_2CH_2OH} \tag{R2.40}$$

Alkenes with aliphatic chains can also (though less likely) react by hydrogen abstraction from the aliphatic chain. The rate constants for some of the more abundant alkenes with OH radicals are listed in Table 2.7. Similar to the alkane reaction chain, the $O_2RCH_2CH_2OH$ radical can react with NO forming a β-hydroxyalkoxy radical:

$$O_2RCH_2CH_2OH + NO \xrightarrow{M} ORCH_2CH_2OH \qquad \text{(R2.41)}$$

The $ORCH_2CH_2OH$ radical then further decays into hydroxyl or alkoxy radicals and aldehydes.

Reactions of alkenes with NO_3 radicals proceed primarily through the addition of NO_3 to the double bond. The radical formed in the NO_3 addition reacts further with O_2 to form a β-nitratoalkyl peroxy radical, which can then react with NO to form nitrates, hydroxyl radicals, and other products. Alkenes can also react with O_3. Although these reactions are slower than those of OH, they can be important at night, when OH levels are low. Their significance also stems from the fact that OH radicals are formed from the reaction of ozone and larger alkenes (Paulson et al., 1999). Cl atom reactions

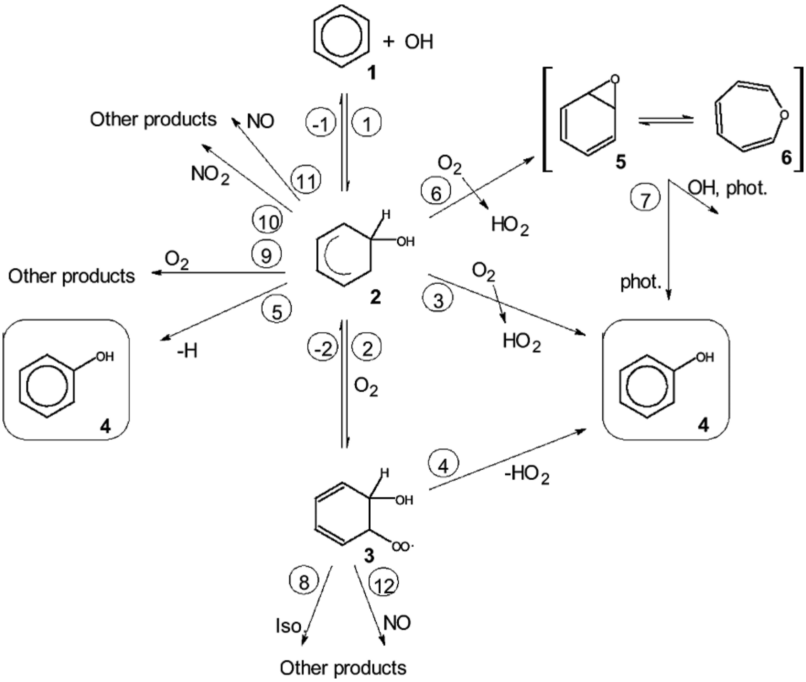


Fig. 2.15. The initial steps in the OH initiated oxidation of benzene (1) Currently proposed loss processes of the aromatic-OH adduct (2) and the peroxy radical (3) (which are in rapidly established equilibrium) are shown that lead in part to the formation of phenol (4) Intermediate species are indicated by bold numbers. Similar schemes for the phenol forming pathways can also be drawn for the alkyl-substituted aromatics (from R. Volkamer, 2001)

also proceed through Cl addition to the double bond. Details of the reaction chains for individual alkenes can, for example, be found in Finlayson-Pitts and Pitts (2000).

Alkynes contain carbon triple bonds. Their reactions proceed in similar ways as those of alkenes. An important product of these reactions is glyoxal (CHOCHO).

For monocyclic *aromatics* the primary reaction pathway is also OH addition. The resulting radical can either lose a hydrogen atom (through HO_2 formation) and form a phenol, or the ring can open leading to rapid degradation of the products (see Fig. 2.15) (Volkamer et al., 2002). In the latter case, glyoxal was found to be an important product (Volkamer et al., 2001).

Isoprene and terpenes are olefins with more than one double bond; they are very reactive towards OH, NO_3, O_3, and Cl, with reaction rate constants towards OH radicals approaching the collision limit. Because these molecules have a complex chemical structure, their reactions mechanisms are quite complex, and beyond the scope of this book. The reader is referred to a review by Atkinson and Arey (1998).

Aldehydes, such as formaldehyde and acetaldehyde, react with OH, NO_3, and Cl by abstraction of the weakly bond aldehydic hydrogen (see for example R2.16). The radical formed in this reaction then reacts with O_2, similar to the reactions described above. Ketones react by abstraction of the H atom from the alkyl chains, similar to the reactions of alkanes.

2.7 Tropospheric Chemistry of Sulphur Species

Sulphur compounds play an important role in the atmosphere, in clean air as well as in polluted areas (e.g. Rotstayn and Lohmann, 2002). In particular, sulphur species with low vapour pressure (such as sulphuric acid or methane sulphonic acid) have a large influence on particle formation in the atmosphere. The legendary London Smog largely consisted of sulphuric acid aerosol. The most important atmospheric sulphur species, their typical mixing ratios, residence times, and degradation pathways are summarised in Table 2.8. In this section we will briefly discuss the chemistry of these species and the impact of sulphur chemistry on the climate.

2.7.1 Sulphur Dioxide – SO_2

Sulphur dioxide is oxidised in the gas phase and, owing to its relatively high solubility in water, by reactions in atmospheric liquid water, such as cloud, fog, or aerosol (see Fig. 2.16)

The most important gas-phase reaction is oxidation, which is initiated by OH addition:

Table 2.8. Sulphur compounds in the atmosphere

Species	Chemical formula	Typ. mixing ratio ppb	Atmospheric life-time	Degraded by reaction with
Sulphur dioxide	SO_2	$10–10^5$	1–9 days	OH, liquid-phase oxidation
Hydrogen sulphide	H_2S	0–300	~3 days	OH
Methyl mercaptan	CH_3SH		0.2 days	OH
Dimethyl sulphide (DMS)	CH_3SCH_3	0.01–1	0.3–3 days	OH, NO_3, BrO
Dimethyl disulphide	CH_3SSCH_3		~1day	Like DMS
Dimethyl sulphoxide (DMSO)	CH_3SOCH_3	0–0.02	Days	OH, deposition
Methansulphonic acid (MSA)	CH_3SO_3H	0–0.06		OH, gas–particle conv.
Carbon Disulphide	CS_2	25 ± 10	12 days	OH
Carbonyl sulphide	COS	510 ± 70	≈6 years	OH, O
Sulphurous acid	H_2SO_3			Liquid phase
Sulphuric acid	H_2SO_4	$10^{-4}–10^{-3}$	0.01 day	Gas to particle conversion
Sulphates, e.g. Ammonium sulphate	$(NH_4)SO_4$ Aerosol		2–8 days	Deposition
Sulphur hexafluoride	SF_6	0.002	>1000 years	Ion reactions
Short lived intermediates				
Sulphur trioxide	SO_3	10^{-5}	10^{-6} s	H_2O
SH-radicals	SH		Seconds	O_3, O_2
SO-radicals	SO		<3 ms	O_2

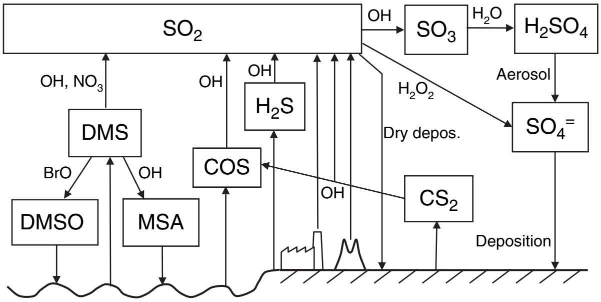


Fig. 2.16. Overview of the cycles of sulphur species in the atmosphere. The surface ocean (lower left corner) is relevant as source of atmospheric sulphur compounds

$$SO_2 + OH \xrightarrow{M} HSO_3 \tag{R2.42}$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \tag{R2.43}$$

$$SO_3 + H_2O \xrightarrow{M} H_2SO_4 \tag{R2.44}$$

In this reaction sequence, discovered by Stockwell and Calvert (1983), the number of HO_X radicals is conserved, as in many other OH-initiated oxidation processes. Overall, OH oxidation of SO_2 facilitates about one third of the total SO_2 degradation.

The oxidation of SO_2 in the liquid phase also plays an important role (see Sect. 2.4.1). Gaseous SO_2 is in an equilibrium with aqueous SO_3^-:

$$SO_{2(g)} + H_2O_{(liq)} \leftrightarrow SO_2 \cdot H_2O_{(liq)} \tag{R2.45}$$

$$SO_2 \cdot H_2O_{(liq)} \leftrightarrow HSO^-_{3\,(liq)} + H^+_{(liq)} \tag{R2.46}$$

$$HSO_3^- \leftrightarrow SO_3^- + H^+ \tag{R2.47}$$

${HSO_3}^-$ and ${SO_3}^-$ can be further oxidised to H_2SO_4 or sulphate, for example by hydrogen peroxide. This oxidation mechanism can be summarised as:

$${HSO_3}^- \rightarrow \ldots \rightarrow {SO_4}^= \tag{R2.48}$$

The sulphate formed is eventually transported to the ground together with the (cloud or fog) droplets, thus contributing to ‘acid rain’ or ‘acid haze’.

Finally, SO_2 can also react directly with the ground. This process is termed dry deposition (in contrast to processes where precipitation events play a role). About 30–50% of the SO_2 is removed from the atmosphere by dry deposition.

2.7.2 Reduced Sulphur Species: DMS, COS, CS_2, H_2S

Most sulphur compounds, with the exception of SO_2, are emitted in a reduced form and are rapidly oxidised in the atmosphere. With the exception of volcanic SO_2 all natural sulphur emissions are in the form of the following species:

Hydrogen Sulphide (H_2S) is present at mixing ratios of up to 300 ppb in the atmosphere. It is a by-product of the degradation of proteins and smells like rotten eggs. The oxidation of H_2S is initiated by reaction with OH:

$$H_2S + OH \rightarrow H_2O + SH \tag{R2.49}$$

The reaction pathways of the SH radical are currently unclear. While an analogy to the OH radical should exist, (cf. sulphur ↔ oxygen), analogous reactions of SH with methane and CO are endothermic (Becker et al., 1975b). The reaction of SH with molecular oxygen is assumed to be very slow. However, SH reacts with ozone, forming SO radicals. The SO radicals finally react with O_2 or ozone to form SO_2.

Carbonyl Sulphide is, to a large extent, produced by the photolysis of sulphur-containing organic species (e.g. of amino acids) in the surface layer of the ocean (e.g. Ulshöfer and Andreae, 1998). Once released to the water, the majority of COS is degraded by hydrolysis to H_2S (timescale of about 10–12 h). The remaining COS is emitted to the atmosphere. In addition, there is some emission from soils and marshes (Ulshöfer, 1995). In addition to the direct emission, degradation of DMS and CS_2 by OH radicals is a source of COS (Chin and Davis, 1993):

$$CS_2 + OH \rightarrow SCSOH \tag{R2.50}$$

$$SCSOH \rightarrow COS + SO_2 + H \tag{R2.51}$$

Carbonyl sulphide is removed from the atmosphere by plant uptake and reaction with OH. The lifetime of COS in the troposphere is on the order of 2–3 years, and thus only small deviations from its average mixing ratio of 500 ppt are found (Ulshöfer, 1995).

Vertical transport of COS plays an important role as a sulphur source in the stratosphere (much like N_2O for the transport of oxidised nitrogen, CFCs for chlorine, and halons for Bromine, see Sect. 2.10.2). The degradation of COS in the stratosphere partially sustains the stratospheric sulphate – aerosol layer [named after its discoverer Christian Junge, 'Junge-layer' (Junge et al., 1961)].

Carbon Disulphide (CS_2) is naturally released via volcanoes, the ocean, marshes and forests, and industrial activities (Watts, 2000). Atmospheric mixing ratios are on the order of 15–35 ppt. Recently, CS_2 was found by DOAS in the city of Shanghai at levels up to 1.2 ppb (Yu et al., 2004). CS_2 is degraded in the atmosphere by OH oxidation (R2.50).

Dimethyl Sulphide (CH_3SCH_3) is produced by biological processes in the ocean (Andreae et al., 1985). Besides sporadic volcanic eruptions, oceanic DMS emissions are the largest natural source of sulphur in the atmosphere. Due to the important role of sulphur in the formation of aerosol particles and cloud condensation nuclei (CCN) DMS has received considerable attention (see also Sect. 2.7.3).

The degradation mechanisms of this species are not fully elucidated to date. Reactions of free radicals are probably largely responsible for its degradation. A role of OH in the degradation is likely. The first step in OH initiated degradation of DMS is OH abstraction from one of the methyl groups, or OH addition to the sulphur atom (Yin et al., 1990a,b).

$$OH + CH_3SCH_3 \rightarrow H_2O + CH_3SCH_2 \tag{R2.52}$$

$$OH + CH_3SCH_3 + M \rightarrow CH_3S(OH)CH_3 + M \tag{R2.53}$$

Intermediate products in this reaction chain are dimethyl sulphoxide (DMSO), CH_3SOCH_3, and $CH_3SO_2CH_3$. Stable end products are sulphuric acid and methane sulphonic acid (CH_3SO_3H). The involvement of NO_3 radicals has also been suggested (Winer et al., 1984; Platt and Le Bras, 1997), where the H abstraction channel appears to be predominant (Butkovskaya and Le Bras, 1994):

$$NO_3 + CH_3SCH_3 \rightarrow HNO_3 + CH_3SCH_2 \qquad \text{(R2.54)}$$

In addition, there are several reports of a possible role of halogen oxide radicals, in particular of BrO (Toumi, 1994). The product of the BrO–DMS reaction is DMSO:

$$BrO + CH_3SCH_3 \rightarrow Br + CH_3SOCH_2 \qquad \text{(R2.55)}$$

While sulphuric acid and methane sulphuric acid form particles, DMSO does not. Thus, the fraction of DMS degraded by BrO may determine the efficiency of particle formation in marine areas, as discussed by von Glasow et al. (2004).

2.7.3 Influence of Sulphur Species on the Climate, the CLAW Hypothesis

The low vapour pressure sulphur compounds, H_2SO_4 and methane sulphonic acid, will quickly condense after their formation in the gas phase (e.g. by reaction R2.44). In this process, small particles are formed, which can act, under appropriate conditions, as cloud condensation nuclei (CCN) and thus impact cloud formation. Therefore, biological emission of sulphur species could affect cloud formation and thus our climate. This theory was proposed in 1987 by Charlson, Lovelock, Andreae and Warren (referred to as the CLAW hypothesis after the authors, initials) (Charlson et al., 1987; Bates et al., 1987). The authors postulate the following mechanism: Due to microbiological activities in the ocean, volatile sulphur species (essentially DMS) are released. DMS is oxidised by photochemical processes in the atmosphere to sulphuric acid or methane sulphonic acid. Due to their low vapour pressure, these species condense to form small particles (mean radius $\sim 0.07\,\mu m$), which can act as CCN.

In large areas of the worlds oceans, the supply of CCN is so small that cloud formation can be limited by CCN availability and not by the water vapour supply (about $200\,\text{CCN}\,\text{cm}^{-3}$ are required, corresponding to a DMS mixing ratio of less than 100 ppt). The extent of cloud cover now feeds back on the insulation and thus the ocean surface temperature. If the biological DMS formation is positively correlated with the ocean surface temperature, which is likely, this process could form a biological negative feedback loop which effectively stabilises the surface temperature of earth [see also Gaia Hypothesis (Lovelock, 1979)]. Since its publication, the CLAW hypothesis has been under intense debate. For instance, Schwartz (1988) argued that the emission of gaseous sulphur species in the northern hemisphere (but not in the southern hemisphere) largely increased during the last 100 years due to anthropogenic activities (in fact the present anthropogenic S emission exceeds the DMS source in the northern hemisphere), without major change in cloud albedo or temperature (Schwartz, 1988).

2.8 Chemistry of Halogen Radicals in the Troposphere

During the last decade, significant amounts of the halogen oxides BrO, IO, OIO, and ClO were detected in the tropospheric BL by DOAS (Table 2.9). Direct and indirect evidence for Cl and Br atoms, as well as for Br_2 and BrCl, was also found under certain conditions. In addition, there is growing evidence for a BrO 'background' in the free troposphere. Observations were made at a variety of sites (see also Table 2.9 and Fig. 2.17):

The presence of these RHS in the troposphere has many consequences. Elevated RHS levels are associated with ozone destruction, which can lead to complete loss of BL ozone in the Arctic. This 'Polar Tropospheric Ozone Hole' was the first hint for tropospheric halogen chemistry (Oltmans and Komhyr, 1986; Bottenheim et al., 1986, 1990; Barrie et al., 1988; Platt and Lehrer, 1997; Barrie and Platt, 1997; Platt and Hönninger, 2003). In addition, other disturbances of tropospheric chemistry can occur, as detailed in Sect. 2.8.3.

2.8.1 Tropospheric Sources of Inorganic Halogen Species

The sources of RHS (X, X_2, XY, XO, HOX, $XONO_2$, HX, where X = Cl, Br, I) in the troposphere are the degradation of organic halogen compounds and the volatilisation of halogen ions (X^-) from sea salt aerosol or surface salt deposits.

Fully halogenated compounds (such as CF_2Cl_2 or CF_2ClBr), which are the main source of RHS in the stratosphere, are photolytically stable in the troposphere. RHS can therefore only be released from less stable precursors (Cauer, 1939), such as partially halogenated organic compounds like CH_3Br, or polyhalogenated species, such as $CHBr_3$, CH_2Br_2, CH_2I_2, CH_2BrI (Cicerone, 1981; Schall and Heumann, 1993; Khalil et al., 1993; Schauffler et al., 1998; Carpenter et al., 1999, 2001), or even I_2 (Saiz-Lopez et al., 2004b; Peters, 2004; Peters et al., 2005). While some of these species, such as CH_3Br, are emitted by up to 50% from anthropogenic sources, most of them, and in particular polyhalogenated species, are only emitted from biological sources predominately in the ocean or in coastal areas.

The atmospheric lifetime of halogenated organics varies widely. The lifetime of methyl bromide, CH_3Br, is on the order of 1 year, bromoform, $CHBr_3$, has a lifetime of several days, while diiodo methane CH_2I_2 is photodegraded in minutes. (Wayne et al., 1995; Yvon and Butler, 1996; Davis et al., 1996; Carpenter et al., 1999). It is possible that even less stable halocarbon species are emitted, which, probably due to their instability, have escaped detection (Carpenter et al., 1999).

The release of inorganic halogen species from sea salt (e.g. sea salt aerosol or sea salt deposits), appears to proceed by three main pathways:

(1) Strong acids can release HCl (but not HBr) from sea-salt halides. Under certain conditions (see below), HX can be heterogeneously converted to RHS.

Table 2.9. Observation of reactive halogen species in the troposphere and their probable source mechanism

Species	Measurement site	Technique	Conc. level	Reference
Br	Arctic BL	Hydrocarbon Clock	$(1\text{–}10) \cdot 10^7\,\mathrm{cm}^{-3}$	Jobson et al. (1994), Ramacher et al. (1997, 1999)
BrO	Arctic and Antarctic BL	DOAS (ground based)	Up to 30 ppt	Hausmann and Platt (1994), Tuckermann et al. (1997), Hegels et al. (1998), Martínez et al. (1999), Hönninger and Platt (2002), Frieß et al. (2004a), Hönninger et al. (2004c)
BrO	Arctic and Antarctic BL	DOAS (satellite)	Around 30 ppt (assuming 1000 m layer)	Wagner and Platt (1998), Richter et al. (1998), Hegels et al. (1998), Martinez et al. (1999), Wagner et al. (2001b), Hollwedel et al. (2004)
BrO	Salt lakes (Dead Sea, Salt Lake City, Caspian Sea, Salar de Uyuni)	Active DOAS, MAX-DOAS	Up to 176 ppt	Hebestreit et al. (1999), Matveev et al. (2001), Stutz et al. (2002), Wagner et al. (2001b), Hönninger et al. (2004b)
BrO	Mid-Lat. Marine BL	MAX-DOAS	Up to 2 ppt	Leser et al. (2002), Saiz-Lopez (2004a)
BrO	Mid-Lat. Free Troposphere	DOAS (difference)	1–2 ppt	Frieß et al. (1999), van Roozendael et al. (2002), Pundt et al. (2002)
BrO	Polar free Troposphere	Airborne DOAS	0–20 ppt	McElroy et al. (1999)

BrO	Volcanic plumes	MAX-DOAS	Up to 1000 ppt	Bobrowski et al. (2003), Bobrowski (2005)
HOCl/Cl_2	Marine BL	Mist Chamber	up to 254 ppt	Pszenny et al. (1993)
Cl	Arctic BL	Hydrocarbon Clock	$(1–10) \cdot 10^4\,cm^{-3}$	Jobson et al. (1994), Ramacher et al. (1997, 1999)
Cl	Arctic BL	$^{12}C/^{13}C$ in CO	$(1–10) \cdot 10^4\,cm^{-3}$	Röckmann et al. (1999)
Cl	Remote Marine BL	Hydrocarbon Clock	$(1–15) \cdot 10^3\,cm^{-3}$	Wingenter et al. (1996)
Cl	Extra-tropical S. hemisphere	$^{12}C/^{13}C$ in CH_4	$2.6-18 \times 10^3$	Platt et al. (2004)
ClO	Salt Lake City	DOAS	Up to 15 ppt	Stutz et al. (2002)
ClO	Volcanic plumes	MAX-DOAS		
Br_2, BrCl	Arctic BL	APCIMS	Up to 30 ppt	Foster et al. (2001), Spicer et al. (1998, 2002)
I_2	Mid-Lat. Marine BL	Active DOAS	Up to 90 ppt	Saiz-Lopez (2004b), Peters (2004), Peters et al. (2005)
Cl_2/HOCl	Arctic BL		$Cl_X \leq 100$	Impey et al. (1999)
Br_2/HOBr			$Br_X \leq 38$ ppt	
IO, OIO	Coastal Areas	DOAS	Up to 6 ppt ($\approx$0.2 ppb h^{-1})	Alicke et al. (1999), Allan et al. (2005a), Wittrock et al. (2000a), Frieß et al. (2001), Saiz-Lopez et al. (2005), Zingler and Platt (2005)

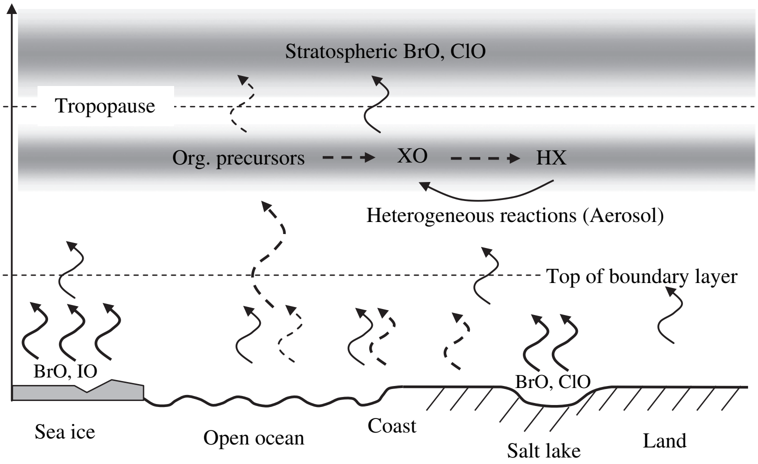


Fig. 2.17. The occurrence of reactive halogen species (XO, X = Cl, Br, I) in the atmosphere: BrO is found above polar sea ice during springtime, IO (and BrO) are present at most coastal areas. It is suspected that there is a layer of BrO in the free troposphere (see von Glasow et al., 2004). *Drawn arrows*: emission of RHS, *dashed arrows*: emission of organohalogens

(2) Oxidising agents may convert Br^- or Cl^- to gaseous Br_2 or BrCl. In particular, HOX (i.e. HOBr and HOCl) is such an oxidant. Direct photochemical (Oum et al., 1998a) or non-photochemical oxidation of halides by O_3 may also occur (Oum et al., 1998b; Hirokawa et al., 1998), though probably quite slowly.

(3) Oxidised nitrogen species, in particular N_2O_5 and NO_3, and perhaps even NO_2, can react with sea-salt bromide or chloride to release HBr, HCl, or photolabile species, in particular $ClNO_2$ and $BrNO_2$ (Finlayson-Pitts and Johnson, 1988; Finlayson-Pitts et al., 1990; Behnke et al., 1993, 1997; Rudich et al., 1996; Schweitzer et al., 1999; Gershenzon et al., 1999).

Because these mechanisms are closely linked to the atmospheric cycling of RHS, we will discuss their details in the next section.

2.8.2 Tropospheric Cycles of Inorganic Halogen Species

In this section, we review the reaction cycles of inorganic halogen species in the troposphere (see Fig. 2.18), (see Wayne et al., 1995; Platt and Janssen, 1996; Platt and Lehrer, 1997; Lary et al., 1996; Platt and Hönninger, 2003; von Glasow Crutzen, 2003).

Following release, inorganic and organic halogen species are photolysed to form halogen atoms which then predominately react with ozone:

$$X + O_3 \rightarrow XO + O_2 \qquad \text{(R2.56)}$$

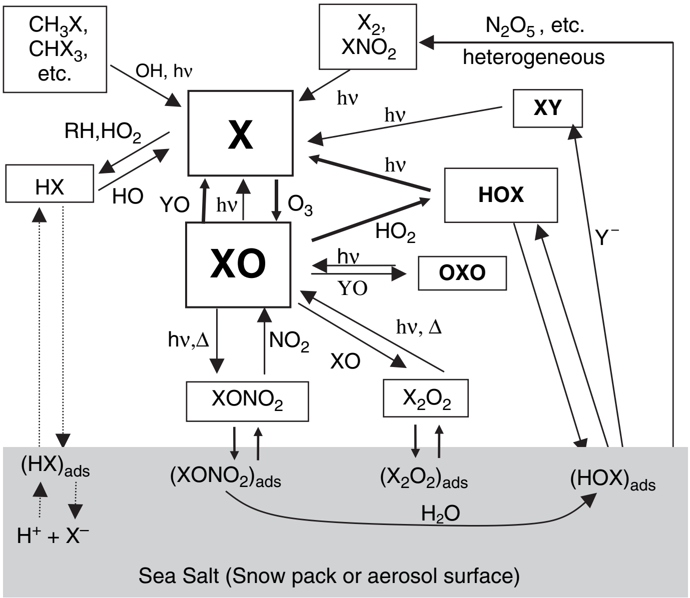


Fig. 2.18. Reaction cycles of reactive halogen species in the troposphere

Typical lifetimes of halogen atoms (X) due to R2.56 at tropospheric background O_3 levels are around 0.1 s for Cl, and on the order of 1 s, for Br and I. Halogen atoms are regenerated in a series of reactions including photolysis of XO, which is of importance for X = I, Br, and, to a minor extent, Cl:

$$\mathrm{XO} + h\nu \rightarrow \mathrm{X} + \mathrm{O} \tag{R2.57}$$

where $J_{2.57} \approx 3 \times 10^{-5}\,\mathrm{s}^{-1}$, $4 \times 10^{-2}\mathrm{s}^{-1}$, $0.2\mathrm{s}^{-1}$ for X = Cl, Br, and I, respectively. The reaction of XO with NO also recycles halogen atoms:

$$\mathrm{XO} + \mathrm{NO} \rightarrow \mathrm{X} + \mathrm{NO_2} \tag{R2.58}$$

This reaction leads to a shift of the NO/NO_2 photostationary state in the atmosphere, by providing a shortcut in the normal $NO/NO_2/O_3$ cycle (R2.1/R2.2/R2.3). This has consequences for the photochemistry in the troposphere and, in particular, ozone formation (Stutz et al., 1999).

The self-reactions of XO (or reaction with another halogen oxide YO) also play a role:

$$\mathrm{XO} + \mathrm{YO} \rightarrow \mathrm{X} + \mathrm{Y} + \mathrm{O_2} \tag{R2.59a}$$

$$\mathrm{XO} + \mathrm{YO} \rightarrow \mathrm{XY} + \mathrm{O_2} \tag{R2.59b}$$

$$\mathrm{XO} + \mathrm{YO} \rightarrow \mathrm{OXO} + \mathrm{O} \tag{R2.59c}$$

$$\mathrm{XO} + \mathrm{YO} \xrightarrow{\mathrm{M}} \mathrm{X_2O_2} \tag{R2.59d}$$

Reactions R2.56, R2.59a,b,d, and the photolysis of the halogen molecules formed in R2.59 constitute a catalytic cycle which destroys ozone in the troposphere. The efficiency of this cycle is determined by the amount of RHS present and the rates of R2.59a,b,d. This type of halogen-catalysed ozone destruction has been identified as the prime cause of polar BL ozone destruction (Oltmanns and Komhyr, 1986; Barrie et al., 1988; Barrie and Platt, 1997).

Halogen atoms can also react with saturated (Cl) or unsaturated HC (Cl and Br) to form hydrogen halides, e.g.:

$$\mathrm{RH} + \mathrm{Cl} \rightarrow \mathrm{R} + \mathrm{HCl} \tag{R2.60}$$

Here, R denotes an organic radical. An alternative is the reaction of halogen atoms with formaldehyde (or higher aldehydes) or HO_2, also leading to the conversion of halogen atoms to hydrogen halides:

$$\mathrm{X} + \mathrm{HO_2} \rightarrow \mathrm{HX} + \mathrm{O_2} \tag{R2.61}$$

$$\mathrm{X} + \mathrm{HCHO} \rightarrow \mathrm{HX} + \mathrm{CHO} \tag{R2.62}$$

The former reaction occurs for $X = Cl, Br, I$, the latter only for $X = Cl, Br$. In particular, Cl is a very strong oxidant and a Cl concentration of $10^4\,\mathrm{cm}^{-3}$ can already considerably contribute to the oxidation capacity of the troposphere.

The main loss of RHS is their conversion to hydrogen halides which are highly water soluble, and can thus be easily lost from the atmosphere by wet or dry deposition. The only relevant gas-phase 'reactivation' mechanism of HX is reaction with OH:

$$\mathrm{HX} + \mathrm{OH} \rightarrow \mathrm{X} + \mathrm{H_2O} \tag{R2.63}$$

Only at high HO concentration and in the absence of deposition processes, such as in the free troposphere, does this reaction play a role. HX can also be recycled through the aerosol phase, as we will discuss below.

Other important inorganic halogen species are HOX and $XONO_2$. HOX is formed via the reaction of peroxy radicals with XO (Canosa-Mas et al., 1999):

$$\mathrm{XO} + \mathrm{HO_2} \rightarrow \mathrm{HOX} + \mathrm{O_2} \tag{R2.64}$$

Formation of HOX is followed by its photolysis:

$$\mathrm{HOX} + h\nu \rightarrow \mathrm{X} + \mathrm{OH} \tag{R2.65}$$

Reactions R2.56, R2.64, and R2.65 form another catalytic cycle that destroys ozone during the day. This cycle dominates at low RHS levels, such as those found in the marine BL. The catalytic ozone destruction cycle through R2.59 is important at higher RHS levels, such as those found in polar regions. Reactions R2.64 and R2.65 also lead to a shift in the HO_2/OH ratio in the troposphere, and thus directly influence the oxidising capacity of the troposphere (Bloss et al., 2005).

Another important reaction cycle involving HOBr is the liberation of gaseous bromine species (and to a lesser extent chlorine species) from (sea-salt) halides (Fan and Jacob, 1992; Tang and McConnel, 1996; Vogt et al., 1996):

$$\mathrm{HOBr} + (\mathrm{Br}^-)_{\mathrm{Surface}} + \mathrm{H}^+ \rightarrow .\mathrm{Br}_2 + \mathrm{H_2O} \tag{R2.66}$$

The required H^+ [the reaction appears to occur at appreciable rates only at $pH < 6.5$ (Fickert et al., 1999)] can be supplied by strong acids, such as H_2SO_4 and HNO_3 from anthropogenic or natural sources. Reaction R2.66, together with R2.64, R2.56, and the photolysis of Br_2, form a cycle where Br^-, for example, in sea ice or the aerosol, is volatilised. Because the uptake of one HOBr molecule leads to the formation of two Br atoms, which, ignoring any Br loss, can form two HOBr molecules (R2.64), this cycle is autocatalytic. The explosion-like behaviour of this cycle has lead to the term 'Bromine Explosion' for this cycle, which is believed to be responsible for the high reactive bromine levels found in the Arctic (Platt and Lehrer, 1995; Platt and Janssen, 1996; Wennberg, 1999).

The reaction of halogen oxides with NO_2 forms halogen nitrate, $XONO_2$:

$$\mathrm{XO} + \mathrm{NO_2} \xrightarrow{\mathrm{M}} \mathrm{XONO_2} \tag{R2.67}$$

Bromine nitrate is assumed to be quite stable against thermal decay, but is readily photolysed and may be converted to HOX by heterogeneous hydrolysis (van Glasow et al., 2002):

$$\mathrm{XONO_2} + \mathrm{H_2O} \xrightarrow{\mathrm{M}} \mathrm{HNO_3} + \mathrm{HOX} \tag{R2.68}$$

or to Br_2 or BrCl by heterogeneous reaction with HY:

$$\mathrm{XONO_2} + \mathrm{HY} \xrightarrow{\mathrm{Surface}} \mathrm{HNO_3} + \mathrm{XY} \tag{R2.69}$$

Overall, $XONO_2$ is probably of minor importance at the low NO_X levels typically found in the free troposphere, but it can play an important role in polluted air, for instance at polluted coastlines. There $XONO_2$ can be an important source of HOX, thus in particular $BrONO_2$ might contribute to bromine explosion events.

Under conditions of high NO_X, halogen release can also occur via the reactions:

$$\mathrm{N_2O_5(g)} + \mathrm{NaX(s)} \rightarrow \mathrm{NaNO_3(s)} + \mathrm{XNO_2(g)} \tag{R2.70}$$

(e.g. Finlayson-Pitts et al., 1989). The XNO_2 formed in the above reaction may photolyse to release a halogen atom, or possibly further react with sea salt (Schweitzer et al., 1999):

$$\mathrm{XNO_2(g)} + \mathrm{NaX(s)} \rightarrow \mathrm{NaNO_2(s)} + \mathrm{X_2(g)} \tag{R2.71}$$

The above reaction sequence would constitute a dark source of halogen molecules. The direct reaction of NO_3 on salt surface can also release reactive halogens, for example in the form of halogen atoms:

$$NO_3(g) + NaX(s) \rightarrow NaNO_3(s) + X(s) \tag{R2.72}$$

(Seisel et al., 1997; Gershenzon et al., 1999). The uptake coefficient of NO_3 by aqueous solutions of NaBr and NaCl was found by Rudich et al. (1996) to be near 0.01 for sea water, while Seisel et al. (1997) found up to 0.05 for dry NaCl.

2.8.3 Potential Impact of Inorganic Halogen Species on Tropospheric Chemistry

The role of reactive halogens in the troposphere has been a controversial issue and remains a poorly understood aspect of atmospheric chemistry. However, it is becoming clear that the RHS are present in many parts of the troposphere (Table 2.9). At the levels shown in Table 2.9, RHS can have a noticeable effect on several aspects of tropospheric chemistry. These include:

(1) RHS, and in particular reactive bromine and iodine can readily destroy tropospheric ozone through catalytic cycles (Solomon et al., 1994b; Platt and Janssen, 1996; Davis et al., 1996; Sander et al., 2003; von Glasow et al., 2004). This has consequences for atmospheric chemistry and, considering that ozone is a greenhouse gas, also the global climate (e.g. Roscoe et al., 2001).
(2) Reactions R2.64, and J2.65 will lead to the conversion of HO_2 to OH, and thus reduce the HO_2/OH ratio, with consequences for the atmospheric oxidation capacity and thus indirectly for the lifetime of methane, another important greenhouse gas.
(3) The presence of highly reactive chlorine atoms, and to a lesser extent bromine atoms, has a direct impact on the oxidation capacity of the troposphere.
(4) The reaction of BrO with DMS might be important in the unpolluted remote marine BL, where the only other sink for DMS is the reaction with OH radicals (Toumi, 1994; von Glasow and Crutzen, 2003, 2004). It may thus have an impact on cloud formation as explained in Sect. 2.8.3.
(5) Deposition of mercury was found to be enhanced by the presence of reactive bromine species, in particular in polar regions (e.g. Barrie and Platt, 1997; Schroeder et al., 1998). This process appears to be one of the most important pathways for toxic mercury compounds to enter the arctic (Lindberg et al., 2002), and possibly also other ecosystems.
(6) Iodine species might be involved in particle formation in the marine BL (Hoffmann et al., 2001; O'Dowd et al., 2002; Jimenez et al., 2003; Burkholder et al., 2004).

At present, more measurements are needed to ascertain the distribution and levels of RHS in the troposphere and to assess the significance of RHS on local, regional, and global atmospheric chemistry and our climate.

2.9 Oxidation Capacity of the Atmosphere

The term oxidation capacity, sometimes also called oxidative power, refers to the capability of the atmosphere (or rather a part thereof) to oxidise (or otherwise degrade) trace species emitted into it. This ability is crucial for the removal of trace species, such as the greenhouse gas methane, and is thus often also referred to as the 'self-cleaning' capacity of the atmosphere. Although there is no general definition, the oxidation capacity is frequently associated with the abundance of OH. However, as explained above, many other oxidants (including O_2 and O_3), as well as free radicals other than OH, can contribute to the oxidation capacity of the atmosphere. While the oxidation capacity is quite a popular concept, it is nevertheless difficult to define.

One difficulty in defining the term oxidation capacity lies in the fact that a given agent (e.g. OH radicals) might act quite differently on various pollutants. Perhaps the best definition for the oxidation capacity C_i of a radical R_i (e.g. $\mathrm{R}_i = \mathrm{NO_3}$, OH, O_3, Cl) with the atmospheric abundance (concentration) $[R]$, with respect to the degradation (oxidation) of species X_j (e.g. volatile organic species, CO, and NO_X), oxidised by the molecule (per second and cm^{-3}), might be a sum such as:

$$C_i = \sum_j [\mathrm{X}_j] \cdot [\mathrm{R}_i] \cdot k_{ij} \qquad \text{(R2.73)}$$

where $[\mathrm{R}_i]$ denotes the concentration of radical species i with the reaction rate constant k_{ij} towards species X_j (Geyer et al., 2001; Platt et al., 2002). Frequently 24-h average values of the oxidation capacity are calculated.

Table 2.10 summarises typical and maximum tropospheric concentrations of the radicals discussed, and shows minimum and typical fractional lifetimes of key VOCs against degradation by the various free radicals.

As an example, the relative contribution of the atmospheric oxidants OH, NO_3, and ozone to the 24 h average of the degradation of organic species in the atmosphere, as observed during the BERLIOZ 1998 campaign at Papstthum near Berlin, Germany, is shown in Fig. 2.19. When all VOCs (including CH_4 and CO) are considered, OH reactions constitute about three quarters of the oxidation capacity. For NMHC, NO_3 contributes almost one third of the oxidation capacity (Geyer et al., 2001).

Open questions include the role of heterogeneous reactions in radical cycles. While the contribution of heterogeneous reactions to HO_X chemistry is unclear to date, it is likely that heterogeneous reactions play an important role in the atmospheric cycles of most other radicals. Another interesting question

Table 2.10. Estimated lifetime (hours) for selected VOC

Species	OH (av.)	OH (peak)	NO_3 (av.)	NO_3 (peak)	ClO (av.)	ClO (peak)	Cl (av.)	Cl (peak)	BrO (av.)	Br (av)
Conc. molec. cm^{-3}	6×10^5	1×10^7	1.5×10^8	1×10^{10}	10^6	10^8	10^3	10^5	10^8	5×10^6
DMS	110	6.3	1.7	0.03	3×10^4	280	870	8.7	10^{c}	26
n-Butane	190	11	2.8×10^4	430	–		1400	14		
C_2H_4	56	3.4	1×10^4	160			2800	28		
Isoprene	4.6	0.3	1.9	0.03	–		<1100	<11		0.9
Toluene	77	4.6	3.1×10^4	460	–					
CH_4	7×10^4	4×10^3	$>5 \times 10^4$	>700	$>7 \times 10^7$	$>7 \times 10^5$	3×10^6	3×10^4		

is whether the effect of several oxidising species is additive. In fact, it is possible that the presence of halogen oxides may reduce the OH concentration due to an increase in the photo-stationary state NO_2/NO ratio. In addition, it is well possible that there are other, yet unrecognised, mechanisms involving the above or other free radicals.

2.10 Stratospheric Ozone Layer

The role of atmospheric ozone as a filter for the Sun's harmful UV radiation has lead to an early interest in ozone chemistry in the investigation of the chemistry of the atmosphere. Spectroscopic measurements by Gordon Miller Bourne Dobson in 1925 showed an ozone column density larger than expected from assuming the O_3 mixing ratio found near the surface to be constant throughout the atmosphere (e.g. Dobson and Harrison, 1926; Dobson, 1968). Subsequent spectroscopic measurements using the so-called 'Umkehr' effect by Paul Götz proved the theory of an ozone layer and determined the altitude of its maximum at 25 km (Götz et al., 1934). This stratospheric ozone layer contains 90% of the atmosphere's ozone and is thus responsible for the majority of the absorption of solar UV radiation.

2.10.1 Stratospheric Ozone Formation: The Chapman Cycle

In the late 1920s, Sidney Chapman proposed a reaction scheme which explained the observed vertical profile of ozone, with relatively low mixing ratios in the troposphere and a maximum around 25 km altitude, the 'Chapman Mechanism' (Chapman, 1930). The initial process is the photolysis of oxygen molecules to form two oxygen atoms in their ground state (indicated by the spectroscopic notation (^{3}P), see Chap. 3). In the stratosphere, sufficiently energetic UV light (i.e. light with wavelengths below 242 nm) is available to photolyse oxygen molecules:

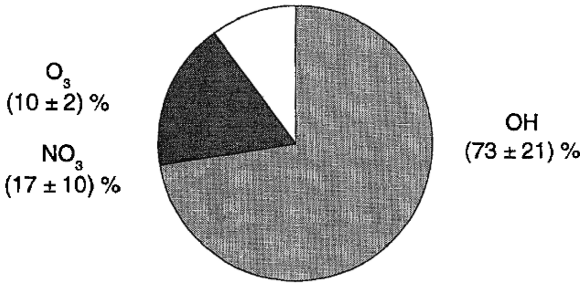
$$O_2 + h\nu(\lambda < 242\,\mathrm{nm}) \rightarrow O(^3P) + O(^3P) \qquad \text{(R2.74)}$$

The oxygen atoms can react in three ways: (1) Recombine with an oxygen molecule to form ozone. Since two particles (O and O_2) combine to make one (O_3), collision with a third body (M, likely N_2 or O_2,) is required to facilitate simultaneous conservation of energy and momentum. The reaction is therefore pressure dependent:

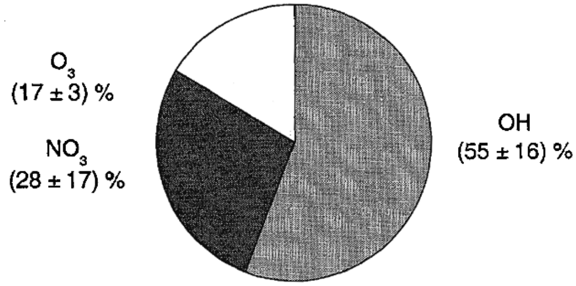
$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad \text{(R2.2)}$$

Alternatively, (2) the oxygen atom can react with an existing ozone molecule:

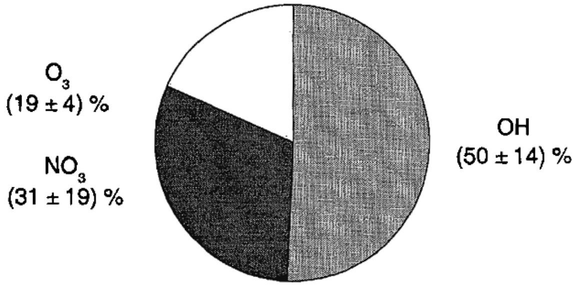
$$O(^3P) + O_3 \rightarrow O_2 + O_2 \qquad \text{(R2.74)}$$



a) Oxidation of VOCs, CO, and CH_4



b) Oxidation of VOCs



c) Oxidation of olefinic VOCs

Fig. 2.19. The relative contribution of the atmospheric oxidants OH, NO_3, and ozone to the degradation of organic species in the atmosphere on a 24-h basis. Case study during the BERLIOZ 1998 campaign at Papstthum near Berlin, Germany. (**a**) VOCs including CH_4 and CO, (**b**) non-methane VOCs, (**c**) alkenes only (from Geyer et al., 2001, Copyright by American Geophysical Union (AGU), reproduced by permission of AGU)

Finally, (3) the recombination of two oxygen atoms to form molecular oxygen is possible but largely unimportant in the stratosphere:

$$O(^3P) + O(^3P) + M \rightarrow O_2 + M \qquad \text{(R2.75)}$$

In addition to the ‘primary’ production of O atoms by the photolysis of O_2, the photolysis of O_3 also provides ‘secondary’ O atoms. In fact, photolysis of ozone molecules occurs at a much higher rate than that of oxygen molecules:

$$O_3 + h\nu(\lambda < 612\,\mathrm{nm}) \rightarrow O(^3P) + O_2 \tag{R2.76}$$

In summary, the above reactions, also known as the ‘Chapman Reactions’, lead to a steady-state O_3 level in the stratosphere, in which the O atom production via reactions R2.74 and R2.76 is in balance with their destruction via recombination with O_2 and reaction with O_3. The above set of reactions explains the formation of a layer of ozone with a maximum concentration in the lower stratosphere. In the lower stratosphere and troposphere, the rate of O_2 photolysis, and thus the ozone formation rate, becomes extremely low (despite the much higher O_2 concentration there). However, O_3 destruction still occurs via O_3 photolysis, which takes place at much longer wavelengths, and the reaction of $O + O_3$. This explains why the ozone concentration should increase with height (in fact the Chapman mechanism predicts zero O_3 formation in the troposphere). On the other hand, in the upper part of the stratosphere the recombination of $O + O_2$ (reaction R2.2) becomes slower, since the concentration of air molecules necessary as a ‘third body’ (M) in the recombination of $O + O_2$ (reaction R2.2) reduces proportionally to the atmospheric pressure. Thus, despite increasing levels of UV radiation, the O_3 concentration (and also the mixing ratio) will eventually decrease with altitude. Figure 2.20 depicts the ozone profile predicted by the Chapman cycle.

2.10.2 Stratospheric Ozone Chemistry: Extension of the Chapman Cycle

The Chapman mechanism gave a satisfactory explanation for the occurrence of an ozone layer. However, detailed investigation during the 1960s of the elementary reactions and photolysis processes involved revealed that quantitatively the mechanism overestimates the O_3 levels by about a factor of three, see Figure 2.20. It subsequently became clear that there are many other trace gas cycles affecting stratospheric O_3 levels. In particular, a group of reactions were found to catalyse the elementary reaction of $O + O_3$ (reaction R2.74 above). These reaction sequences follow the general scheme:

$$O_3 + Z \rightarrow ZO + O_2 \tag{R2.77}$$

$$ZO + O(^3P) \rightarrow Z + O_2 \tag{R2.78}$$

With the net result,

$$O(^3P) + O_3 \xrightarrow{Z} O_2 + O_2 \tag{R2.79}$$

where Z (and ZO) denotes a species acting as catalyst Z for reaction R2.75. In the stratosphere, the following species are active (see Table 2.11): Cl (ClO),

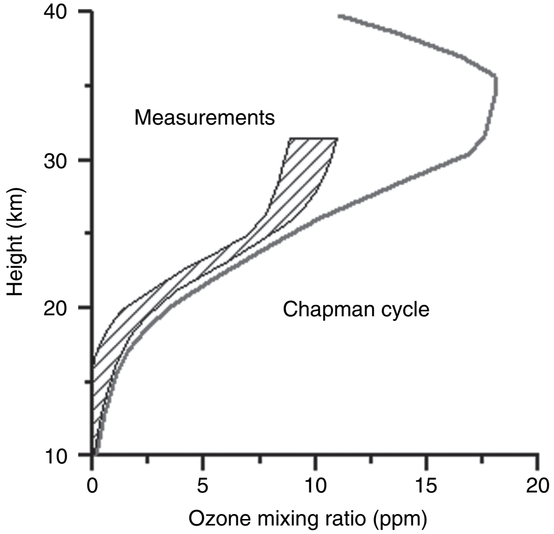


Fig. 2.20. The stratospheric ozone profile according to the Chapman Mechanism, compared to observations (figure adapted from Roth, 1994)

Br (BrO), NO (NO_2), or OH (HO_2). Inclusion of these reactions brings observations and model calculations in very good agreement. Figure 2.21 illustrates the contribution to the ozone destruction of each of the catalysts at different altitudes.

All species listed in Table 2.11 play an important role in stratospheric chemistry. The *oxides of nitrogen* (NO, NO_2, see Sect. 2.5) are formed in the stratosphere by reaction of excited oxygen atoms $O(^1D)$ with N_2O (which can be regarded as a 'transport species' for oxidised nitrogen into the stratosphere):

$$\begin{aligned} N_2O + O(^1D) &\rightarrow NO + NO \\ &\rightarrow N_2 + O_2 \end{aligned} \tag{R2.80}$$

Table 2.11. 'Catalysts' destroying stratospheric ozone

Catalyst Z	ZO	Stratospheric source
NO	NO_2	Degradation of N_2O from the troposphere
OH	HO_2	$O^1D + H_2O$
Cl	ClO	Degradation of (mostly man-made) organo chlorides
Br	BrO	Degradation of CH_3Br, and other organo bromine species

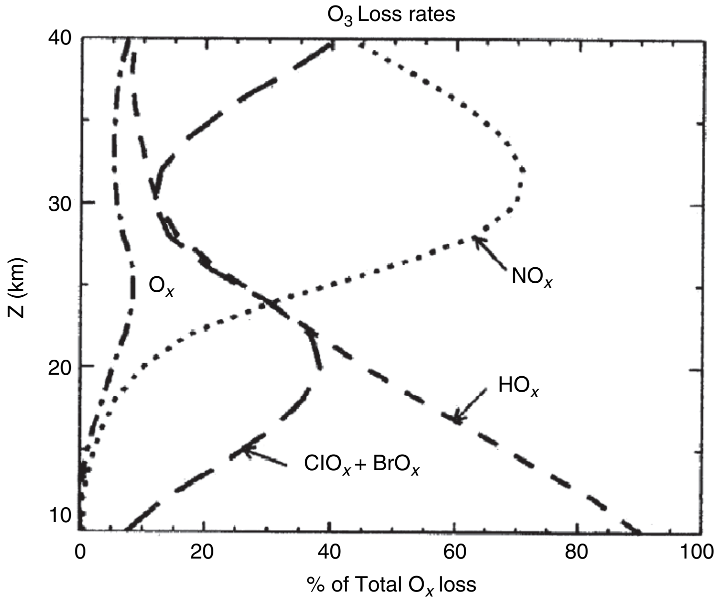


Fig. 2.21. The contribution of the ClO_X, BrO_X, NO_X, and HO_X, catalysed destruction of stratospheric ozone to the original Chapman Mechanism as a function of altitude (from Portmann et al., 1999, Copyright by American Geophysical Union (AGU), reproduced by permission of AGU)

The excited oxygen atoms $O(^1D)$ are formed in the UV photolysis of O_3 by (R2.4). As in the troposphere, a photo-stationary state between NO, NO_2, and O_3 is established and conversion of NO_2 to N_2O_5 will take place. Under 'normal' stratospheric conditions, loss of N_2O_5 occurs due to photolysis, leading to an increase of NO_X during the course of a day (only during polar winter do heterogeneous reactions of N_2O_5, e.g. R2.98 become important).

Halogen atoms are released by the degradation of long-lived halocarbon species (e.g. $CH_3Cl, CFCl_3$, CH_3Br, etc.), which are emitted naturally or anthropogenically in the troposphere and then transported into the stratosphere. Halogen atoms (denoted as X = F, Cl, Br, I), which are released in the degradation processes, react quickly with O_3 to form halogen oxides (see Sect. 2.8). In addition, halogen atoms can react with O_2 by association reactions to form halogen peroxide radicals. These radicals are unstable and dissociate by the reverse of their formation reaction, so that under atmospheric conditions the XO_2 species exists in equilibrium with X and O_2.

$$X + O_2(+M) \rightarrow XO_2(+M) \qquad \text{(R2.81)}$$

The stability of XO_2 decreases in the series $F > Cl > Br > I$. The equilibrium for atmospheric conditions lies in favour of the atom, and XO_2 reactions do not play a significant role in stratospheric chemistry.

A rapid reaction occurs between XO and NO:

$$XO + NO \rightarrow X + NO_2 \qquad (R2.82)$$

NO_2 is rapidly photolysed to produce atomic oxygen, which reforms ozone, and thus the overall effect of this reaction coupled with the $X + O_3$ reaction on ozone is neutral. On the other hand, this reaction will lead to a higher stationary state X/XO ratio, and thus (at least in the case of chlorine) enhance the rate of X → HX conversion by reaction of halogen atoms with HC (i.e. CH_4). Consequently, the presence of nitrogen oxides tends to increase the HX/XO_X ratio, and thus reduce the ozone depletion by halogen radicals.

The chlorine oxide radical undergoes self-reaction to form a dimer, Cl_2O_2 (Cox and Derwent, 1979). The ClO dimer plays a major part in the catalytic destruction of ozone occurring in the polar lower stratosphere during wintertime, which in Antarctica leads to the formation of the ozone hole (see Sect. 2.10.3 below). The relevant cycle is:

$$ClO + ClO + M \rightarrow Cl_2O_2 + M \qquad (R2.83)$$
$$Cl_2O_2 + h\nu \rightarrow Cl + ClO_2 \qquad (R2.84)$$
$$ClO_2 + M \rightarrow Cl + O_2 \qquad (R2.85)$$
$$Cl + O_3 \rightarrow ClO + O_2 \qquad (R2.86)$$

The ClO dimer is relatively unstable, and the cycle is only important at low temperatures ($T \approx 200$K) when the reverse decomposition of Cl_2O_2:

$$Cl_2O_2 + M \rightarrow ClO + ClO + M \qquad (R2.87)$$

is slow compared with its photolysis.

Symmetric chlorine dioxide is formed in the stratosphere from the coupled reaction of BrO with ClO:

$$BrO + ClO \rightarrow OClO + Br \qquad (R2.88a)$$

The discovery of atmospheric OClO using ground-based DOAS spectroscopy at the McMurdo Sound base in Antarctica (Solomon et al., 1987b), was the first positive indication that partitioning of atmospheric chlorine between its active and inactive forms was greatly perturbed in the Antarctic ozone hole. Chlorine dioxide is rapidly photolysed by visible light to yield O atoms

$$OClO + h\nu \rightarrow O + ClO \qquad (R2.89)$$

and thus is not a catalytic agent for O_3 destruction. A consequence of its rapid photolysis are low OClO concentrations during daytime.

Observations of the evolution of stratospheric OClO during sunset allow deduction of information on the BrO concentration in that BrO is an essential ‘catalyst’ for its formation. On the other hand, BrO is lost by BrCl production via reaction:

$$BrO + ClO \rightarrow BrCl + O_2 \tag{R2.88b}$$

while the third channel of reaction R2.88 does not change the XO reservoir, but leads to the destruction of ozone:

$$BrO + ClO \rightarrow Cl + Br + O_2 \tag{R2.88c}$$

Since $k_{2.88b}/(k_{2.88a}+k_{2.88b}+k_{2.88c}) \approx 0.08$, the late night OClO concentration cannot become larger than $1/0.08 \approx 12$ times the daytime BrO concentration (e.g. Wahner and Schiller, 1992).

The behaviour of halogen oxides in the stratosphere is strongly influenced by the chemistry of temporary reservoir species containing chlorine and bromine. Temporary reservoirs are molecules which are formed and broken down at a time scale on the order of 1 day, contain halogens, and are not active in O_3 destruction. For example, chlorine nitrate is an important reservoir for ClO_x. It is formed by the reaction of ClO with NO_2 (R2.67), and active chlorine is released by photolysis; which occurs mainly by the reaction:

$$ClONO_2 + h\nu \rightarrow Cl + NO_3 \tag{R2.90}$$

or

$$ClONO_2 + h\nu \rightarrow ClO + NO_2 \tag{R2.91}$$

The other important temporary reservoir for chlorine is HOCl, formed by reaction of ClO with HO_2:

$$ClO + HO_2 \rightarrow HOCl + O_2 \tag{R2.92}$$

Chlorine is released from HOCl by photolysis. The major channel of this reaction is:

$$HOCl + h\nu \rightarrow HO + Cl \tag{R2.93}$$

In an analogous way ClO may react with CH_3O_2, producing methylhypochlorite CH_3OCl, or other products (Helleis et al., 1993, 1994):

$$ClO + CH_3O_2 \rightarrow CH_3OCl + O_2 \tag{R2.94a}$$

$$\rightarrow Cl + \text{products} \tag{R2.94b}$$

Cycles involving photolytic production of Cl from $ClONO_2$ and HOCl can lead to depletion of ozone in the lower stratosphere, and these may be significant under some circumstances [see for instance Toumi and Bekki, 1993]. Similarly, reaction R2.94a, followed by the photolysis of CH_3OCl or reactions of type R2.94b, could cause ozone loss (Crutzen et al., 1992).

In the polar stratosphere and in circumstances of elevated concentrations of volcanic aerosol, heterogeneous reactions of $ClONO_2$ and HOCl on polar stratospheric clouds (PSCs; particles containing nitric acid trihydrate and/or water ice) lead to gross perturbation of the distribution of ClO_x between inactive reservoirs and active ozone depleting forms. The reactions involved are:

$$ClONO_2 + H_2O(s) \xrightarrow{\text{surface}} HOCl + HNO_3(s) \qquad \text{(R2.95)}$$

$$ClONO_2 + HCl(s) \rightarrow Cl_2 + HNO_3(s) \qquad \text{(R2.96)}$$

$$HOCl + HCl(s) \rightarrow H_2O(s) + Cl_2 \qquad \text{(R2.97)}$$

$$N_2O_5 + HCl(s) \rightarrow ClNO_2 + HNO_3(s) \qquad \text{(R2.98)}$$

Here, (s) refers to the chemical species adsorbed or absorbed in the solid or liquid phase.

As bromine is less tightly bound than chlorine, only a small fraction of the bromine released from bromocarbons is sequestered in the form of HBr and $BrONO_2$, rendering this atom very effective for ozone loss (e.g. Lary, 1995). In particular, the combined Br–Cl catalytic cycles are very efficient in depleting ozone, and can therefore cause equal or even larger ozone destruction than chlorine alone in the lower stratosphere. Although there are significant human sources of bromine, the contemporary abundance of total stratospheric Br is only about 0.5% of that of Cl (e.g. Schauffler et al., 1998; Wamsley et al., 1998). The organic precursor species of inorganic bromine, $= 50\%CH_3Br$, halons, $CHBr_3$, etc. are still increasing. When the precursor species reach the lower stratosphere, they are photolysed and release inorganic bromine (Br_Y = BrO, HBr, HOBr, $BrONO_2$, BrONO, Br, and Br_2). Due to the lower binding energy of HBr compared with HCl, and to the more rapid photolysis of Br_2, BrCl, HOBr, $BrONO_2$ compared with their Cl analogues, BrO is the most abundant bromine species during the daytime and constitutes between 50% and 70% of total Br_Y. In mid-latitude summer with high stratospheric NO_2 levels, BrO is less abundant ($\approx$50% of the total Br_Y), while BrO can amount up to 70% of Br_Y at high latitudes in a denoxified stratosphere. This is because the Br_Y reservoir species $BrONO_2$ is less abundant in a stratosphere with low NO_X loading.

The possible participation of iodine chemistry in stratospheric processes is still under debate. Owing to the much shorter atmospheric lifetimes of iodine-containing compounds (e.g. CH_3I emitted from the oceans) compared with their Cl- and Br-containing analogues, it has generally been assumed that iodine does not reach the stratosphere in significant quantities, and the major focus of studies of iodine photochemistry has been the troposphere, as discussed in detail earlier. However, should iodine reach the stratosphere, its impact on ozone depletion ‘molecule for molecule’ is probably even greater than that of Br. The main reason for this is the inherent instability of potential iodine reservoir species (HI, HOI, or $IONO_2$) compared with their Cl- and Br-containing counterparts (Solomon et al., 1994). In addition, the potential coupling of the chemistry of IO with ClO and BrO may be far more efficient than the XO self-reaction cycles referred to above.

2.10.3 Stratospheric Ozone Hole

In 1985, Farman et al. (1985) observed a decrease of the total ozone column over Antarctica after polar sunrise. Satellite observations revealed that this ozone depletion occurred over the entire Antarctic continent. It soon became clear that, during Antarctic winter, special conditions prevail which lead to the release of reactive chlorine from its 'reservoir compounds' (HCl and $ClNO_3$) by heterogeneous reactions, i.e. chemical processes at the surface of particles in the stratosphere (see reactions R2.95–R2.98) (e.g. Solomon, 1999). This massive activation, bringing the fraction of reactive chlorine from around 1% to near 50%, leads to dramatic ozone losses in the lower stratosphere. A few examples are illustrated in Fig. 2.22, which shows normal ozone profiles recorded in August (Antarctic winter) and disturbed profiles in October (Antarctic spring). There is nearly complete ozone loss in the altitude range from about 14 to 24 km.

A number of factors contribute to the formation of the ozone hole: The primary cause is the increase in stratospheric chlorine and bromine levels due to the release of man-made CFCs, such as CF_3Cl and CF_2Cl_2. These compounds, which have no sinks in the troposphere, have been accumulating since their introduction in the 1930s. Because of their chemical stability, CFCs were widely used as propellants, in refrigerators, as solvents, and in

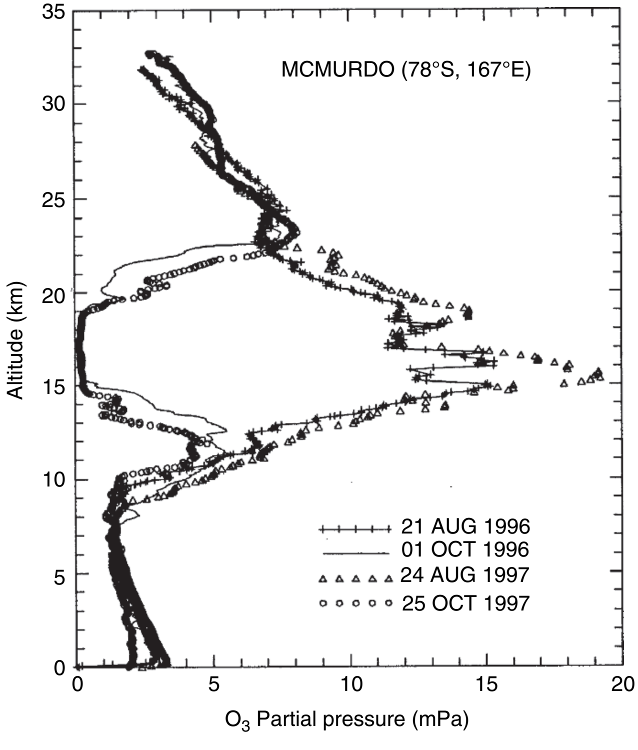


Fig. 2.22. Ozone profiles in August (Antarctic winter) 1996 and October (Antarctic spring) of 1997 (from Nardi et al., 1999, Copyright by American Geophysical Union (AGU), reproduced by permission of AGU)

other industrial applications. Most man-made halocarbons transported to the stratosphere contain more than one halogen atom, and the release of halogen atoms occurs in stages, with intermediate formation of the carbonyl halides (e.g. CFClO). For all halogens, the sink is provided by transport of the most stable (and therefore most abundant) forms (e.g. HX) to the troposphere.

A polar vortex forms in the winter polar stratosphere, which inhibits gas-exchange with lower latitudes. As a consequence, colder polar air cannot mix with warmer lower latitude air, leading to very cold stratospheric temperatures. In addition, ozone from lower latitudes cannot replenish ozone destroyed by halogen catalysed cycles. The polar vortex is very stable over Antarctica, and can exist from June to November. The northern polar vortex is less stable and is typically not stable for more than a few weeks. The more unstable northern vortex is the main reason why the ozone depletion over the north pole has not reached the same extent as that over the south pole.

Very cold stratospheric temperatures develop over Antarctica in winter due to radiative cooling and lack of solar heating. In addition, the lack of air exchange with mid-latitudes also contributes to the low temperature. Once these temperatures fall below a certain value ($\sim$195K), PSCs form. The clouds are made out of nitric acid tri-hydrate and water. PSCs provide a surface on which the chlorine reservoir species, such as HCl and $ClONO_2$ can be converted to Cl_2 (R2.95 and R2.96). In addition, PSC formation removes nitrogen oxides from the gas phase, further increasing the amount of reactive halogens. These heterogeneous processes proceed for several months, as long as PSCs are present.

The rapid photolysis of Cl_2 releases reactive chlorine, in the form of Cl atoms, at polar sunrise. Cl reacts quickly with O_3 forming ClO, which then participates in the catalytic ozone destruction cycles described earlier. ClO is the most important halogen oxide in the stratosphere: its concentration ranges from 10–100 ppt in the undisturbed lower stratosphere to 1–2 ppb under conditions of disturbed stratospheric chemistry, i.e. the ozone hole, where more than 50% of the available chlorine can be present as ClO. Under the conditions of very high ClO levels and low temperatures, the ClO self-reaction to form a dimer, Cl_2O_2 [reaction R2.83 above (Cox and Derwent, 1979; Molina and Molina, 1987)] becomes the dominant catalytic destruction cycle of ozone, leading ultimately to the formation of the ozone hole. It should be noted that cycles involving BrO also contribute to the ozone destruction, although to a lesser extend, since the partitioning between active and reservoir species favours the active forms already in the undisturbed stratosphere.

The break-up of the polar vortex in December marks the disappearance of the ozone hole, as warmer and ozone-rich air masses are transported over Antarctica.

The formation of the ozone hole is a recurring phenomenon, which starts every Antarctic winter.

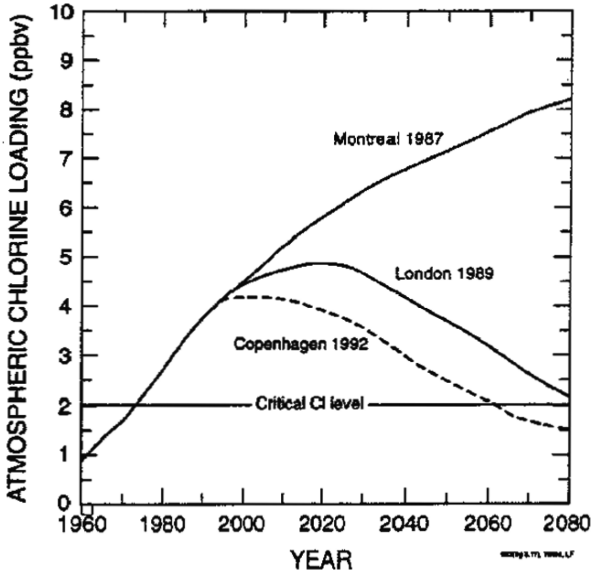


Fig. 2.23. Time series of atmospheric chlorine loading from 1960 – today, with projections to 2080. The expected effect of the treaties for limitation of CFMs is shown (from Brasseur and Solomon 1986)

2.10.4 Recovery of Stratospheric Ozone

Recently, there have been signs of recovery of stratospheric ozone, which is largely due to the successful measures employed to reduce the release of halogen transport species (e.g. CFCs).

Figure 2.23 shows time series of the atmospheric chlorine loading, the total amount of chlorine present as transport, reservoir, and active species from 1960 to 1995 (measured data), and projections to 2080.

The chlorine loading of the troposphere (Montzka et al., 1996) and stratosphere (Rinsland et al., 2003) peaked in 2004, and has begun to decline. The first indication of the expected recovery of stratospheric ozone may already be visible (Newchurch et al., 2003; Bodeker et al., 2005).