The atmosphere of the earth is in a state of dynamic equilibrium which hopefully is sufficiently stable to endure the impact of anthropogenic emissions. Nevertheless, predictions about the influence of emissions upon the local air quality or even upon the climate on a global scale are only possible, if the physical and chemical processes controlling the equilibrium are understood. Towards this objective, the chemistry of trace gases as well as some of the chemical cycles involved in the degradation of compounds in air
are examined in terms of presently accepted reaction schemes. Physical processes such as transport and deposition which affect trace gas mixing ratios are omitted from discussion. Emphasis is placed on homogeneous gas phase reactions. Heterogeneous processes will only be briefly mentioned as they are more thoroughly discussed by Parlar and Kotzias in Section 2.4.

Sunlight is the major driving force behind most processes in the atmosphere. Radiant energy produces excited or reactive species which often have lifetimes sufficiently long as to react further with other constituents of air. Most trace substances are thereby decomposed either directly or indirectly and their degradation products eventually disappear from the atmosphere or are added to one of the major reservoirs of atmospheric gases.

In 'background' air direct photolysis and oxidation by ozone and OH radical reactions are the most important mechanisms of degradation for many substances (Weinstock, 1969; Levy, 1971). However, intense anthropogenic emissions alter the local air composition to such an extent that other chemical processes may become important. For example, other oxidizing species like O\(_2\)\(^{(3P)}\), O\(_2\)\(^{(1D)}\), O\(_2\)\(^{3\Sigma^+}\), O\(_3\), and NO\(_3\) become reactive, and heterogeneous processes on aerosol surfaces appear to be rate determining for the degradation of certain compounds.

### 2.2.2 DESCRIPTION OF THE ATMOSPHERE

The structure of the atmosphere is determined by energy transport which dissipates the radiant energy received from the sun. Figure 2.2.1 depicts graphically the intensity of solar radiation as a function of wavelength. The intensity maximum lies at 540 nm corresponding to a black body radiation of 6000 K. The light reaching the earth's surface has been attenuated by the cooler gas clouds around the sun and by the earth's atmosphere. Below 240 nm by short wave absorption oxygen leads to the formation of ozone which itself absorbs light more strongly at longer wavelengths causing a cutoff at 290 nm. In the stratosphere where the main bulk of ozone is situated, the strong energy absorption by ozone gives rise to a temperature increase. Despite the small share of total sun emission found in the wavelength region between 290 and 400 nm, this radiation is mainly responsible for the initiation of photochemical processes and for direct degradation of air constituents. Besides radiation intensity, temperature is also of importance for chemical reactions.

The vertical temperature distribution for the atmosphere (Figure 2.2.2) reaches a minimum at the tropopause. This inversion separates the main bulk of air into the stratosphere, extending to about 50 km above the inversion and the troposphere below. The circulation time for an exchange of air between the two spheres is of the order of several years.

Symmetrical circulation cells at the equator in both hemispheres, caused by
the intense insolation, restrict interhemispherical mixing to about one to two years. Within a hemisphere transport is rather fast. While latitudinal mixing is in the order of months, the longitudinal and vertical exchanges occur in a couple of weeks. These times can be compared with the 1000 years needed for the exchange of deep ocean water.

The main chemical processes in the atmospheric compartments often differ widely according to temperature, insolation and initial chemical composition. Gradients in mixing ratios can be observed for compounds which are rapidly degraded relative to their transport in a single compartment. This phenomenon is a common feature between compartments where exchange is still further reduced. For example, the mixing ratio of methane diminishes with increasing height in the stratosphere because its lifetime becomes shorter and upward transport is too slow to compensate for the loss (Ehhalt, 1979). Similar behaviour is observed for nitrous oxide (Figure 2.2.3).

The composition of the troposphere is determined by available sources and sinks. Under the steady state conditions established between the atmosphere, the land masses and the oceans, most gases are cycled through at widely
Figure 2.2.2 Temperature variation with altitude

Figure 2.2.3 Vertical distribution of CO₂, CH₄ and N₂O
differing rates. In those cycles biological and chemical as well as transport phenomena are important (Korte, 1978).

Species which have long lifetimes compared with their transport time, or short-lived compounds which have extended and evenly distributed sources and sinks throughout the troposphere, show little variation in their mixing ratio. However, most substances are emitted from the surface into a well mixed layer which stretches up to the first inversion layer, not higher than 1 to

*Table 2.2.1 Composition of the background atmosphere (northern hemisphere) and of polluted air near the earth surface 25 °C*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Background atmosphere (p.p.b. mol basis)</th>
<th>Los Angeles Basin (noon time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>7.8 x 10⁶</td>
<td>2000 Calvert (1976)</td>
</tr>
<tr>
<td>O₂</td>
<td>2.1 x 10⁶</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>1.3 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>Rare gases</td>
<td>1.0 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>3.3 x 10⁴</td>
<td></td>
</tr>
<tr>
<td>N₂O</td>
<td>Connell <em>et al.</em> (1980) 300</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>Ehhalt (1979) 1600</td>
<td>2000 Calvert (1976)</td>
</tr>
<tr>
<td></td>
<td>Reichle and Condon (1979)</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>Seller (1974) 150</td>
<td>100 Finlayson-Pitts and Pitts (1977)</td>
</tr>
<tr>
<td>NO₂</td>
<td>Noxon (1975) 0.1</td>
<td></td>
</tr>
<tr>
<td>CH₂O</td>
<td>Platt <em>et al.</em> (1980) 0.2</td>
<td>30 Tuazon <em>et al.</em> (1980)</td>
</tr>
<tr>
<td>O₃</td>
<td>40</td>
<td>2000 Finlayson-Pitts and Pitts (1977)</td>
</tr>
<tr>
<td>PAN</td>
<td></td>
<td>15 Tuazon <em>et al.</em> (1978)</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>Rudolph <em>et al.</em> (1981 a, b.) 2.0</td>
<td>49 Calvert (1976)</td>
</tr>
<tr>
<td>C₂H₄</td>
<td></td>
<td>43 Calvert (1976)</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>Whitby and Altwicker (1968) 0.2</td>
<td>38 Calvert (1976)</td>
</tr>
<tr>
<td>C₃H₈</td>
<td></td>
<td>37 Calvert (1976)</td>
</tr>
<tr>
<td>C₃H₆</td>
<td></td>
<td>9 Calvert (1976)</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td></td>
<td>37 Calvert (1976)</td>
</tr>
<tr>
<td>iso-C₄H₁₂</td>
<td></td>
<td>44 Calvert (1976)</td>
</tr>
<tr>
<td>n-C₅H₁₂</td>
<td></td>
<td>16 Calvert (1976)</td>
</tr>
<tr>
<td>l-C₅H₁₀</td>
<td></td>
<td>4 Calvert (1976)</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td></td>
<td>11 Calvert (1976)</td>
</tr>
<tr>
<td>C₆H₆</td>
<td></td>
<td>8 Calvert (1976)</td>
</tr>
<tr>
<td>n-C₆H₁₄</td>
<td></td>
<td>4 Calvert (1976)</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td>20 Calvert (1976)</td>
</tr>
<tr>
<td>Et-C₆H₆</td>
<td></td>
<td>4 Calvert (1976)</td>
</tr>
<tr>
<td>p, m-Xylenes</td>
<td></td>
<td>14 Calvert (1976)</td>
</tr>
<tr>
<td>o-Xylene</td>
<td></td>
<td>6 Calvert (1976)</td>
</tr>
</tbody>
</table>
2 km. Chemical processes are especially intense in this so-called planetary boundary layer. In addition anthropogenic emissions are retained in this layer for an extended time. Consequently, a larger part of the emissions can be chemically degraded within the boundary layer.

Besides the primary constituents \( \text{O}_2, \text{N}_2, \text{water and CO}_2 \), a large number of trace gases are found in air. The chemically important substances for tropospheric reactions are listed in Table 2.2.1. Background concentrations are given together with a typical example of levels found in polluted air. In order to properly assess the degradation process, the mechanisms of the various possible reaction pathways should be known. The source strength for these compounds can be used to cross-check estimates.

### 2.2.2.1 Hydrocarbons

Methane, the most abundant hydrocarbon, has a source strength of \((2.2 \text{ to } 3.5) \times 10^{37} \text{ molecules y}^{-1}\) (equivalent to 5.9 to 9.3 Mtons per year) and a tropospheric lifetime of about 8 years. It is emitted from the earth surface, like all hydrocarbons and reaches a uniform distribution throughout the troposphere. Methane's long lifetime is the result of its slow rate of reaction with OH, which is the principal pathway of degradation (Ehhalt, 1979) (Figure 2.2.3).

None-methane hydrocarbons (NMHC) are also released to the atmosphere in large quantities. Their source strengths are less well known. Rasmussen and Went (1965) estimated the global emission to be \(2 \times 10^{37} \text{ C-atoms y}^{-1}\), while Zimmerman et al. (1978) estimated concentrations for isoprenes and terpenes to be \(3.5 \times 10^{37} \text{ C-atoms y}^{-1}\). The alkanes and alkenes are primarily decomposed by reaction with OH and have relatively short lifetimes in the atmosphere. Their concentration profiles depend upon the OH-concentration, \([\text{OH}]\), and upon the distribution of their sources.

Recent measurements of hydrocarbons in the atmosphere have been reported by Robinson (1978); Singh et al. (1979); Eichmann et al. (1979, 1980); Rudolph et al. (1981); Rudolph and Ehhalt (1981).

### 2.2.2.2 Carbon Monoxide and Carbon Dioxide

Most CO is formed during oxidation of hydrocarbons (Seiler, 1974; Hanst et al., 1980). However, due to the different source strength of non-methane hydrocarbons in the two hemispheres, emission of CO into the northern hemisphere is larger as is the mixing ratio (Table 2.2.1). The lifetime of CO, which is mainly determined by its reaction with OH (1), is of the order of several months.

\[
\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2 \quad (1)
\]
A nearly homogeneous distribution of CO is reached within each hemisphere. Total source strengths are estimated to be $2.4 \times 10^{37}$ molecules y$^{-1}$ and $1.1 \times 10^{37}$ molecules y$^{-1}$ for the northern and southern hemisphere respectively (Hanst et al., 1980). Volz et al. (1981) determined a global source strength of $(4$ to $8) \times 10^{37}$ molecules y$^{-1}$.

The present mixing ratio of CO$_2$ (Figure 2.2.3) is 330 p.p.m. (by volume) and is slowly being increased by 1.3 p.p.m. y$^{-1}$ due to the use of fossil fuel and reduction of plant matter (Keeling et al., 1976). The tropospheric lifetime of CO$_2$ is dependent upon its equilibrium with the deep ocean water and therefore is of the order of 1000 years.

2.2.2.3 Radical Producing Compounds

The processes which lead to reactive free radicals are especially important. A number of atmospheric constituents yield radicals upon photolysis. These compounds include ozone, formaldehyde, hydrogen peroxide, nitrous acid and nitrogen oxides. Their lifetimes are generally long enough so that they can serve as primary radical sources even during periods when photolytic reactions are greatly reduced or non-existent.

_Ozone_, besides being the major work-horse, may be at times an indicator for chemical activity in the atmosphere. In the stratosphere ozone mixing ratios of several p.p.m. are maintained. The ozone shields the earth's surface and is responsible for the compartment stratosphere through the radiation absorption. Moreover, ozone is transported from the stratosphere into the troposphere (Junge, 1962). Fabian and Pruchniewicz (1977) estimated a flux of $(3$ to $7) \times 10^{10}$ molecules cm$^{-2}$ sec$^{-1}$ exchange for the northern hemisphere. This ozone mixing represents the largest primary radical source for initiation of chemical cycles. Extended ozone measurements have been made throughout the world (for a review see Dütsch, 1974). Figure 2.2.4 shows a typical ozone distribution in the troposphere.

In background air, ozone levels are 20 to 50 p.p.b. at ground level (Chatfield and Harrison, 1977). Its apparent lifetime is around one to two months. Photolysis during daylight quickly decomposes ozone (2) and (3):

$$
O_3 + hv \rightarrow O^1D + O_2^1\Delta_g \leq 310 \text{ nm} \quad (2)
$$

$$
O_3 + hv \rightarrow O^3P + O_2^3\Sigma_g^+ > 310 \text{ nm} \quad (3)
$$

and would lead to a half-life of 20 min if the ozone was not restored by the recombination reaction (6):

$$
O^3P + O_2 \xrightarrow{M} O_3 \quad (6)
$$
However, part of the O³D atoms (2) are not deactivated by reactions (4, 5) and react with water (about 14% in the presence of 26 mbar water and normal air pressure) to produce OH radicals (7).

\[
\text{O}^3\text{D} + \text{H}_2\text{O} \rightarrow 2\text{OH}
\]  

(7)

This set of reactions causes a net destruction of ozone and limits its lifetime in the lower tropical boundary layer to one week.

In order to produce a tropospheric ozone profile as given by Chatfield and Harrison (1977), the ozone injection from the stratosphere has to be about \(1.5 \times 10^{11}\) molecules cm\(^{-2}\) sec\(^{-1}\) which is much larger than estimated above (Fishman and Crutzen, 1977; Chameides and Stedman, 1977). However, this discrepancy is minimized if the photochemical oxidation cycles of hydrocarbons and CO are included in estimating the ozone profile (Chameides and Walker, 1973; Stewart et al., 1977; Fishman and Crutzen, 1978; Chameides, 1978; Fishman et al., 1979; Crutzen, 1979). While ozone is consumed by reaction (7) it produces OH radicals which can again react with ozone (8). In the absence of NO\(_x\) (the sum of NO and NO\(_2\)) the chain reactions (8) and (9) will cause an additional but minor depletion of ozone.

\[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2
\]  

(8)

\[
\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2
\]  

(9)

However, in the presence of sufficient NO\(_x\), ozone can be produced via reactions (10), (11) and (6).
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\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]  \hspace{1cm} (10)

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \]  \hspace{1cm} (11)

Obviously the ozone is a product of NO$_2$-photolysis and its production depends critically upon the global NO$_2$ distribution (Fishman et al., 1979) and oxidation rate of CO and hydrocarbons. The most recent evaluation of the tropospheric ozone source using NO$_2$-profiles by Kley et al. (1981) showed ozone production exceeding the flux from the stratosphere by a factor of more than three (Liu et al., 1980).

Besides yielding reactive species, ozone’s reactions with NO$_2$ and with unsaturated hydrocarbons (ozonolysis) are most important for the degradation process. The products from these reactions can initiate or maintain chemical degradation processes even at night, though the intensity of daytime processes may not be reached.

Reaction (12) is an important reaction in polluted air when large NO$_2$ and O$_3$ mixing ratios are present. NO$_3$ represents a powerful oxidizing agent.

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]  \hspace{1cm} (12)

During the day most of the ozone is reformed through NO$_3$ photolysis as shown in reactions (13a, b).

\[ \text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O} \]  \hspace{1cm} (13a)

\[ \text{NO}_3 + h\nu \rightarrow \text{NO} + \text{O}_2 \]  \hspace{1cm} (13b)

During the night, however, NO$_3$ in reactions (14), (15) and (16) leads to a net destruction of ozone.

\[ \text{NO}_3 + \text{NO}_3 \rightarrow 2\text{NO}_2 + \text{O}_2 \]  \hspace{1cm} (14)

\[ \text{NO}_3 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2 \]  \hspace{1cm} (15)

\[ \text{NO}_3 \xrightarrow{\text{aerosol}} \text{NO}_2 \]  \hspace{1cm} (16)

Formaldehyde. Carbonyl compounds are one class of intermediate products formed during photochemical degradation of hydrocarbons in the atmosphere. Formaldehyde, the simplest aldehyde, is formed during most oxidation reactions with hydrocarbons. Therefore it is not surprising that 40–60% of the total aldehydes found in air is formaldehyde (Altshuller and McPherson, 1963).

Formaldehyde is produced, for example, in the methane oxidation cycle.

\[ \text{CH}_4 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3 \]  \hspace{1cm} (17)

\[ \text{CH}_3 + \text{O}_2 \rightarrow \text{M} \rightarrow \text{CH}_3\text{O}_2 \]  \hspace{1cm} (18)
Higher alkanes have to undergo carbon bond scission for its production. Ketones are the probable intermediate species (see Section 2.2.3.3). Ozonolysis of alkenes is another important CH₂O source which does not depend on sunlight (see Section 2.2.3.6).

Background mixing ratios of formaldehyde are reported from <0.1 to 0.2 p.p.b. (Platt et al., 1979; Platt and Perner, 1980; Lowe et al., 1980; Neitzert and Seiler, 1981). Fushimi and Miyake (1980) reported from 0.8 to a few p.p.b. for the air above the open ocean surface of the western North Pacific and the Indian Oceans. In Central Europe an average concentration of 2 p.p.b. was found in slightly polluted areas (Platt et al., 1979; Lowe et al., 1980). The highest concentrations are observed in heavily polluted areas. The first spectroscopic study of CH₂O showed concentrations up to 16 p.p.b. (Tuazon et al., 1978), while the highest level reported was 160 p.p.b. and was measured by chromotropic acid (Altshuller and McPherson, 1963). The highest level found spectroscopically was around 40 p.p.b. in Los Angeles basin (Tuazon et al., 1980) and in Köln (Perner and Kessler, unpublished results). With increasing altitude a rapid decrease in formaldehyde concentration was found (Schmidt and Lowe, 1981). The level reached at 7 km was less than 0.1 p.p.b.

The lifetime of formaldehyde is determined by photolysis (23), (24) and reaction with OH (25).

\[
\begin{align*}
\text{CH}_2\text{O} + h\nu & \longrightarrow \text{H}_2 + \text{CO} \\
\text{CH}_2\text{O} + h\nu & \longrightarrow \text{H} + \text{HCO} \quad \leq 355 \text{ nm} \\
\text{CH}_2\text{O} + \text{OH} & \longrightarrow \text{H}_2\text{O} + \text{HCO}
\end{align*}
\]

In air with \([\text{OH}] > 4 \times 10^6 \text{ cm}^{-3}\) the reaction with OH will be rate determining, however, in polluted air with often reduced \([\text{OH}]\), photolysis can prevail. Formaldehyde’s minimum lifetime is a couple of hours. Aldehyde photolysis yields radicals (24) and molecular products (23) like CO. The radicals react further with oxygen (26), (27)

\[
\begin{align*}
\text{H} + \text{O}_2 & \xrightarrow{M} \text{HO}_2 \\
\text{HCO} + \text{O}_2 & \longrightarrow \text{HO}_2 + \text{CO}
\end{align*}
\]
and yield HO₂ which may be converted to OH by reactions (9) and (10).

\[
\begin{align*}
    \text{HO}_2 + \text{O}_3 & \rightarrow \text{OH} + 2\text{O}_2 \\
    \text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2
\end{align*}
\]

Other reactions of HO₂ are (20) and (28)

\[
\begin{align*}
    \text{HO}_2 + \text{CH}_3\text{O}_2 & \rightarrow \text{CH}_3\text{OOH} + \text{O}_2 \\
    \text{HO}_2 + \text{HO}_2 & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\end{align*}
\]

whereby the formation of hydrogen peroxide and methylhydrogen peroxide through the radical termination reaction (28) is of special importance because they represent a reservoir of radicals.

**Hydrogen peroxide.** Measurements of hydrogen peroxide in the atmosphere are scarce. It is produced during the photochemical oxidation cycles from HO₂ reaction (28). Its concentration was detected in medium polluted air at Boulder, Colorado using a chemiluminescent method (Kelly et al., 1979) and seemed to increase with NOₓ.

In another polluted area (Riverside), 10–20 p.p.b. H₂O₂ have been reported (Bufalini et al., 1972). Similar values were found by Kok et al. (1978). Unfortunately a simultaneous measurement by long path Fourier-transform-IR spectroscopy did not detect H₂O₂ due to the method's lack of sensitivity (Tuazon et al., 1980).

These results contain an apparent discrepancy. The production of H₂O₂ according to reaction (28) depends on [HO₂]. This concentration, however, is controlled by the reaction of NO with HO₂ (10). In the presence of large [NO], reaction (28) should be negligible. Therefore, an increase in NO should be followed by a decrease in H₂O₂ if there is a concurrent [NO] increase as is expected from NO₂ photolysis. An explanation for this discrepancy could be that estimated NO concentrations are smaller than expected (see Section 2.2.4.2). There are some experimental indications of this possibility.

OH radicals are produced directly from photolysis of H₂O₂ (29) which itself reacts also with OH (30).

\[
\begin{align*}
    \text{H}_2\text{O}_2 + h\nu & \rightarrow 2\text{OH} \\
    \text{H}_2\text{O}_2 + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{HO}_2
\end{align*}
\]

The lifetime of hydrogen peroxide in background air is limited by reaction (30) to about 20 h during daylight. In polluted air, small [OH] suggest the greater importance of photolysis reaction (29) which allows an even longer lifetime (for H₂O₂). Under these conditions other processes such as deposition to soil and water and heterogeneous interaction with aerosols are
probably determinant of the lifetime for H$_2$O$_2$. The heterogeneous oxidation of SO$_2$ by H$_2$O$_2$ on wet aerosols has been reported by Penkett et al. (1979). The H$_2$O$_2$ concentration is an indicator of HO$_2$ in the atmosphere and is therefore of considerable interest to atmospheric chemists.

*Nitrous acid* yields OH radicals directly by photolysis (31).

\[
\text{HNO}_2 + h\nu \rightarrow \text{OH} + \text{NO}
\] (31)

While HNO$_2$ is not detected in clean air (Platt and Perner, 1980), it is often observed in polluted air (Perner and Platt, 1979; Platt et al., 1980b; Perner, 1980; Harris et al., 1982). HNO$_2$ accumulates during the dark hours and up to 8 p.p.b. HNO$_2$ have been observed at Los Angeles in the presence of 100 p.p.b. NO and 100 p.p.b. NO$_2$ (Harris et al., 1982).

HNO$_2$ seems to be formed in heterogeneous processes as first described by Ten Brink et al. (1978). Direct emissions from Otto engines are negligible, while the contribution from diesels is about 1% of the NO$_x$ (Kessler et al., submitted). HNO$_2$ is always observed in the presence of haze when high mixing ratios of NO$_2$ or of NO and NO$_2$ are found. Therefore, reactions (32) and (33) are probably producing the HNO$_2$.

\[
\text{NO}_2 + \text{NO}_2 + \text{H}_2\text{O}_{\text{liq}} \rightarrow \text{HNO}_2 + \text{HNO}_3
\] (32)

\[
\text{NO} + \text{NO}_2 + \text{H}_2\text{O}_{\text{liq}} \rightarrow 2\text{HNO}_2
\] (33)

HNO$_2$ will diffuse out of the liquid layer especially at low pH and enter the gas phase. An equilibrium exists which is controlled by the heterogeneous destruction of HNO$_2$ (34a, b).

\[
2\text{HNO}_2 \xrightarrow{\text{aerosol}} \text{NO} + \text{NO}_2 + \text{H}_2\text{O}
\] (34a)

\[
3\text{HNO}_2 \xrightarrow{\text{aerosol}} \text{HNO}_3 + 2\text{NO}_2 + \text{H}_2\text{O}
\] (34b)

HNO$_2$ is quickly destroyed by photolysis in the morning at sunrise (Platt et al., 1980b) and represents often the largest OH source during this time, initiating other photochemical processes (Harris et al., 1982).

The combination of OH with NO (35) also yields HNO$_2$ and can be used to monitor the steady state concentration of OH (Kessler et al., submitted).

\[
\text{OH} + \text{NO} \xrightarrow{\text{M}} \text{HNO}_2
\] (35)

However, in the free atmosphere the NO mixing ratios often seem to be so low that HNO$_2$ concentrations remained below the detection limit. Under photostationary conditions HNO$_2$ does not represent an OH-reservoir of important strength.

Recently Martin et al. (1981) observed oxidation of SO$_2$ to SO$_4^{2-}$ by nitrite ions which are then reduced to N$_2$O (36) in the liquid phase at low pH values.
2.2.2.4 Nitrogen Oxides

As already mentioned, nitrogen oxides (NO$_x$) are active in atmospheric trace gas cycles (Crutzen, 1979) because of their free radical structure. The background concentrations of NO$_x$ are low. Noxon (1975; 1978; 1980) found ~0.1 p.p.b. NO$_2$. Helas and Warneck (1981) reported 0.04 to 0.09 p.p.b. NO$_2$ for maritime air while NO was found to be below its detection limit of 10 p.p.t. McFarland et al. (1979) found 3 p.p.t NO over the Pacific ocean. Kley et al. (1981) observed more than 100 p.p.t. NO$_x$ in the upper troposphere with decreasing mixing ratios at lower altitudes. They estimated a stratospheric source of about $3 \times 10^8$ cm$^{-2}$ sec$^{-1}$ and half of this may be emissions from high flying subsonic aircraft (Liu et al., 1980). By far the largest source of NO$_x$ is anthropogenic emissions. Another is nitrogen fixation by lightning. The strength of this latter source was estimated to be $1.2 \times 10^9$ and $8 \times 10^8$ cm$^{-2}$ sec$^{-1}$ by Hill et al. (1980) and Dawson (1980), respectively. These estimates should be regarded as upper limits. A survey of global NO$_x$ sources was given by Böttger et al. (1978).

The main sinks for NO$_x$ in the troposphere are the reactions of NO$_2$ with OH (37) and of N$_2$O$_5$ with liquid water (38).

\[
\begin{align*}
\text{OH} + \text{NO}_2 & \rightarrow \text{M} \rightarrow \text{HNO}_3 & (37) \\
\text{N}_2\text{O}_5 + \text{H}_2\text{O}_{\text{liq}} & \rightarrow 2\text{HNO}_3 & (38)
\end{align*}
\]

Transport of NO$_x$ from the lower troposphere to greater altitudes can be greatly reduced by the fast reaction (38) in clouds. The lifetime of NO$_3$ which in turn controls the lifetime of N$_2$O$_5$ (see Section 2.2.2.3) is ~5 sec. This period is long compared with time between collisions of N$_2$O$_5$ and cloud droplets ~0.3 sec (see Section 2.2.2.5).

However, nitrogen oxides can be transported by other nitrogen containing products. For example, peroxyacetyl nitrates are formed during photochemical cycles in air. The most important of these substances, peroxyacetyl nitrate (PAN), was identified for the first time in polluted air (Stephens, 1969) and since has been found in remote areas as well (Lovelock and Penkett, 1974; Penkett et al., 1975).

PAN is formed by the combination of NO$_2$ with peroxyacetyl radicals (39) which are produced during photo-oxidation of hydrocarbons. Reaction (40) is strongly temperature dependent so that its lifetime increases from about one hour at ground-level to about a year at 10 km.

\[
\begin{align*}
\text{CH}_3\text{COOO} + \text{NO}_2 & \rightarrow \text{CH}_3\text{COOONO}_2 & (39) \\
\text{CH}_3\text{COOONO}_2 & \rightarrow \text{CH}_3\text{COOO} + \text{NO}_2 & (40)
\end{align*}
\]
2.2.2.5 Aerosols

The effect of aerosols on the degradation of organic chemicals in air is less well understood than degradation via homogeneous gas phase reactions. The processes of photo-degradation of organic materials in the adsorbed state have been known for some time. Such processes may be very important in polluted air (see Sections 2.4 and 2.5). The physical characteristics (size and numbers) of aerosols have been well investigated (Jaenicke, 1975; 1978) but their composition is less well known. The chemical interactions of trace gases with aerosols are still largely unidentified.

Aerosols can be described in terms of a trimodal size distribution (Figure 2.2.5). Coarse particles (2 to 100 μm) are generated by the dispersion of dust or sea-water and their relative short lifetime in the atmosphere is determined by sedimentation. Condensate is often formed by chemical reactions and gives rise to primary nuclei (Aitken particles, 0.001 to 0.1 μm). These particles coalesce quickly into large aerosols (accumulation mode, 0.1 to 1 μm) which have a longer residence time before being washed out. For an average urban aerosol, the characteristic number, surface and mass are affiliated with one particular mode (Figure 2.2.5). The largest surface area of the aerosol is found within the accumulation mode. World-wide this combined surface area equals that of the earth and may exceed the corresponding soil surface by an order of magnitude in polluted regions.

The collision frequency of air molecules with aerosols and their reaction efficiency (or collision efficiency) are essential parameters for estimating reaction rates. Warnecke (1974) calculated collision frequencies at different altitudes (Table 2.2.2). In the stratosphere the collision frequency is about $10^{-5}$ sec$^{-1}$ and it is increased with increasing aerosol content to about $10^{-2}$ sec$^{-1}$ in background and maritime air, and to 1 sec$^{-1}$ or greater in polluted regions. In principle, therefore, heterogeneous reactions are rapid enough to compete with homogeneous reactions under polluted conditions (Graedel, 1979; Schiavone and Graedel, 1981). However, collision efficiencies are difficult to estimate and can vary dramatically with changes in aerosol composition. For example, such changes would be expected when variations in relative humidity influence the water content of aerosols.

Baldwin and Golden (1979) measured collision efficiencies for the interaction of several gases with surfaces of concentrated sulfuric acid. They obtained values for $\gamma$ of $>10^{-5}$, $7.8 \times 10^{-4}$ and $3.8 \times 10^{-3}$ for NH$_3$, H$_2$O$_2$ and N$_2$O$_5$, respectively. The reaction of ammonia proceeds very quickly with sulfuric acid while N$_2$O$_5$ reacts quite slowly. These rates would certainly change at higher pH values where the collision efficiency of N$_2$O$_5$ would be expected to increase. Similar studies of the collision efficiencies of SO$_2$ with solids were conducted by Judeikis et al. (1978). In atmospheric chemistry very few aerosol–gas interactions are well understood. The oxidation of SO$_2$ by
Figure 2.2.5 Average urban aerosol: (a) number distribution, (b) surface distribution, (c) volume distribution (Whitby and Sverdrup, 1980)

\[ \frac{\Delta W}{\Delta \log D} \text{ vs. } D, \mu m \]

\[ \frac{\Delta S}{\Delta \log D} \text{ vs. } D, \mu m^2/\text{cm}^3 \]

\[ \frac{\Delta V}{\Delta \log D} \text{ vs. } D, \mu m^3/\text{cm}^3 \]

Table 2.2.2 Collision frequencies (sec\(^{-1}\)) of air molecules with aerosols (Warneck, 1974)

<table>
<thead>
<tr>
<th>Type of aerosol</th>
<th>Altitude (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Background</td>
<td>0.011</td>
</tr>
<tr>
<td>Continent</td>
<td>0.12</td>
</tr>
<tr>
<td>Clouds</td>
<td>3.5</td>
</tr>
</tbody>
</table>
H₂O₂ in clouds (Penkett et al., 1979), and the formation of HNO₂ (Ten Brink et al., 1978; Platt et al., 1980b) have received the most attention.

The influence of aerosols on tropospheric radical cycles was discussed by Warneck (1974). He pointed out that the OH concentration was influenced by aerosol scavenging of HO₂. Likewise, Farrow et al. (1975) showed that [HO₂] and [NO₃] in urban air are controlled by aerosol interactions. An NO₃/aerosol interaction was also reported by Platt et al. (1981).

2.2.3 MECHANISMS CONTROLLING THE CONCENTRATION OF ORGANIC CHEMICALS IN THE ATMOSPHERE

The depletion of a substance S in air is governed by the physico-chemical interaction R, by deposition D (dry deposition on the earth surface, washout) and by dilution T during transport. It can be represented by a pseudo first-order equation (41).

\[- \frac{dS}{dr} = [S](R + D + T)\]  (41)

In this section only the physico-chemical interaction R will be considered. These include photolysis J₀, homogeneous gas reactions kₙ[y] and heterogeneous processes with aerosols A₀. The process that determines chemical lifetime will depend on several parameters and even in a single air mass may be altered with changing conditions.

\[ R = J₀ + kₙ[y] + A₀ \]  (42)

In equation (42) J₀ (sec⁻¹) is the photo-dissociation rate, kₙ (cm³/sec⁻¹) the rate constant for reaction of S with compound y, and A₀ (sec⁻¹) the rate of destruction through aerosol interactions.

Chemical processes change with altitude in the atmosphere due to three effects: (1) the temperature decreases with altitude according to the dry adiabatic lapse rate of 0.7 K/100 m, (2) the gas concentration decreases with a scale height of about 5 km, and (3) the water mixing ratio decreases even faster with height due to the strong dependence of vapor pressure on temperature. In the following sections the processes governing the physico-chemical interactions are discussed in greater detail.

2.2.3.1 Photolysis

The photo-dissociation or excitation rate J₀ of a compound is given by

\[ J₀ = \int \sigma(\lambda) \Phi_{\lambda}j₀(\lambda) d\lambda \]  (43)

where \( \sigma(\lambda) \) (cm²) is the photoabsorption cross-section, \( \Phi_{\lambda} \) the quantum yield.
of photo-dissociation and $j_0(\lambda)$ the omnidirectional flux (photons cm$^{-2}$ sec$^{-1}$ nm$^{-1}$) for wavelength $\lambda$ (nm).

The spectral intensity distribution of sunlight is given in Figure 2.2.1. The light flux density depends on attenuation of the light by scattering (Mie scattering, Rayleigh scattering), absorption (aerosols, below 330 nm the stratospheric ozone layer becomes extremely important), and cloud coverage. The actinic irradiance will also be influenced by the albedo. The influence of the zenith angle is indirect via the path-length of the light in the various layers of air.

A good example for the importance of photolysis is the degradation of nitrous oxide in the stratosphere (Figure 2.2.3). The fluorochloromethanes, which have raised world-wide attention due to their potential influence upon stratospheric ozone, show similar photolytic behaviour (Hudson and Reed, 1979). Photolysis not only decomposes molecules but more importantly produces reactive free radicals which in turn initiate other degradation processes. Especially important in this respect is the photolysis of ozone, nitrogen dioxide, carbonyl compounds (formaldehyde), hydrogen peroxide and nitrous acid which produces $O_3^P$, OH and HO$_2$ radicals.

### 2.2.3.2 Oxygen Species

Substances which are especially more reactive than ground-state oxygen molecules towards air constituents will be discussed. Their importance to the degradation of trace substances depends on their concentration and the specific constant for the reaction.

$O^1D$ is formed during ozone photolysis (2).

$$O_3 + h\nu \rightarrow O^1D + O_2^1\Delta_g \quad 310 \text{ nm}$$

(2)

The lifetime of $O^1D$ is about $8 \times 10^{-10}$ sec due to quenching by oxygen and nitrogen (4, 5).

$$O^1D + O_2(N_2) \rightarrow O_3^P + O_2(N_2)$$

(4, 5)

A steady state concentration of 0.018 $O^1D$ cm$^{-3}$ near the earth’s surface is sufficient to produce most of the OH radicals in the remote atmosphere through reactions with water (7).

$$O^1D + H_2O \rightarrow 2OH$$

(7)

The rate of reaction for $O^1D$ with some other molecules is also very fast but these reactions are of significance only in the stratosphere (Figure 2.2.3).

$O^3P$ atoms. The photolytic cycles of ozone (3) and (2) combined with
reactions (4), (5) (see above) and the photolysis of nitrogen dioxide (11) yields most of the tropospheric $O^3P$.

$$O_3 + h\nu \rightarrow O^3P + O_2 \quad (3)$$

$$NO_2 + h\nu \rightarrow O^3P + NO \quad (11)$$

The combination of $O^3P$ with oxygen (6) produces ozone.

$$O^3P + O_2 \rightarrow O_3 \quad (6)$$

$O^3P$ reaches a noon-time concentration of about $5 \times 10^3 \text{ cm}^{-3}$ in the remote atmosphere. The steady state concentration increases slightly with altitude, because reaction (6) is pressure dependent. In polluted areas in the presence of 200 p.p.b. $NO_x$ the steady state concentration of $O^3P$ increases a hundredfold and can become comparable to the OH concentration. In smog chamber experiments, when large $NO_x$ concentrations are used, special attention must be given to $O^3P$ reactions.

$O_2^1\Delta_g$, Leighton (1961) first considered the possibility that singlet molecular oxygen could play a role in photochemical reactions. However, he observed as well, that no photochemical reaction on exposure of hydrocarbon–oxygen mixtures to visible light at room temperature had ever been reported.

The excitation energy of $O_2^1\Delta_g$ is 22.4 kcal/mol and its radiative lifetime 3900 sec (Badger et al., 1965). At normal pressure, quenching by $O_2$ and $N_2$ limits the lifetime to $8.5 \times 10^{-2}$ sec. Several sources of $O_2^1\Delta_g$ exist in air. It is certainly formed in reaction (2) (Kummler et al., 1969). Its production rate is $4.7 \times 10^7 \text{ cm}^{-3} \text{ sec}^{-1}$ if in addition reaction (4) is considered.

$$O^1D + O_2 \rightarrow O^3P + O_2^1\Delta_g \quad (4)$$

Reaction (3a) as proposed by Moreels and Megie (1977) may also be an appreciable source.

$$O_3 + h\nu \rightarrow O^3P + O_2^1\Delta_1 \quad \lambda \approx 611 \text{ nm} \quad (3a)$$

The direct production rate through excitation of oxygen by sunlight can be estimated to be $10^7 \text{ cm}^{-3} \text{ sec}^{-1}$ as compared to the estimated $^1\Sigma_g^+$ production rate reported by Leighton (1961).

Pitts et al. (1969), considering energy transfer from electronically excited organic molecules, derived an upper limit of $2.4 \times 10^9 \text{ cm}^{-3} \text{ sec}^{-1}$ as the production rate of singlet oxygen in polluted air. A similar energy transfer from excited $NO_2$ (44) may also play a role.

$$NO_2^* + O_2 \rightarrow NO_2 + O_2^1\Delta_g \quad (44)$$

From these reactions, a steady state concentration is estimated which varies from $5 \times 10^6$ to $10^9 \text{ cm}^{-3}$. Reaction rate constants for $O_2^1\Delta_g$ with
molecules are generally small and therefore this species is of minor importance under normal circumstances. However, under conditions of low $O^3P$ and OH concentrations, reactions of $O_2^1\Delta_g$ may become comparatively important. Specific reactions of $O_2^1\Delta_g$ and organic chemicals in the atmosphere were reviewed previously by Korte (1978).

$O_2^1\Sigma_g^+$. The excitation energy of the $O_2^1\Sigma_g^+$ is 37.4 kcal/mol and its radiative lifetime 12 sec (Wallace and Hunten, 1968). However, quenching by air is very efficient. Therefore, at normal pressures the lifetime is only $2.5 \times 10^{-5}$ sec. The main source for $O_2^1\Sigma_g^+$ production is direct radiant excitation of oxygen. Assuming a production rate of $1.2 \times 10^9$ cm$^{-3}$ sec$^{-1}$ (Leighton, 1961), the steady state concentration would be about $3 \times 10^3$ cm$^{-3}$ sec$^{-1}$ which is too low to be of significance for tropospheric photochemical processes.

Excited ($O_2$)$_2$. The van der Waals molecule ($O_2$)$_2$ in air gives rise to atmospheric absorption bands (Krupenie, 1972). Its excited states correspond to combined electronically excited oxygen molecules with energies of 44.8 kcal/mol ($^1\Delta_g + ^1\Delta_g$), 59.8 kcal/mol ($^1\Delta_g + ^1\Sigma_g^+$) and 76.8 kcal/mole ($^1\Sigma_g^+ + ^1\Sigma_g^+$). Considering their large excitation energies, these molecules could play a role in the photochemistry of the lower atmosphere if their concentrations as well as the rate constants for the reactions with atmospheric constituents were appreciable. However, only the rates of formation from the measured absorptions have been calculated (Perner and Platt, 1980) and only the radiative lifetime for ($O_2$)$_2$ ($^1\Delta_g + ^1\Delta_g$), $1.2 \times 10^{-3}$ sec, is known. The possible roles of ground-state van der Waals molecules in atmospheric processes were discussed recently by Calo and Narcisi (1980).

2.2.3.3 OH-radical

The hydroxyl radical, OH, has been identified as playing a central role in the chemical transformation processes in the atmosphere because of its ubiquitous production (Levy, 1971; McConnell et al., 1971). The multitude of production pathways for OH, HO$_2$, etc. makes estimates of their concentrations very difficult. A number of compounds yield radicals which start photochemical cycles. In the course of these cycles, radical species are preserved and even multiplied. Only a detailed model calculation could assess the relative importance of the different reaction channels and unfortunately some of the mechanisms are not yet precisely known.

Over the years, measurements of OH reactivity with almost every component possibly present in the atmosphere have been made. Because of this, atmospheric lifetimes for those compounds can be readily estimated if the OH radical concentration or rather its distribution is determined.
Ozone, which is always available from the stratosphere, is a prime source of OH-production via reactions (2) and (7).

\[
\begin{align*}
O_3 + h\nu & \rightarrow O^1D + O_2^3\Delta_g & \leq 310 \text{ nm} \\
O^1D + H_2O & \rightarrow 2OH
\end{align*}
\]  

(2)  

(7)  

A production rate of $10^7$ OH cm$^{-3}$ sec$^{-1}$ may be reached with 30 p.p.b. ozone and 20 Torr water in the tropics. However, in complex chemical cycles other products like formaldehyde, $H_2O_2$, alkylhydrogen peroxides, nitrous acid and nitric acid are continuously formed and can act as additional OH sources. Their long lifetimes often make them the primary OH sources during the day, especially in the morning.

In remote areas and in the boundary layer these radical sources are minor in comparison to ozone. Formaldehyde is photolysed into radicals (24) which quickly react further to yield $HO_2$ (26), (27).

\[
\begin{align*}
CH_2O + h\nu & \rightarrow H + HCO & 355 \text{ nm} \\
H + O_2 & \rightarrow HO_2 \\
HCO + O_2 & \rightarrow HO_2 + CO
\end{align*}
\]  

(24)  

(26)  

(27)  

The $HO_2$ radical, a common intermediate in many hydrocarbon oxidation cycles, is quickly converted into OH by reactions with ozone (9) and nitric oxide (10).

\[
\begin{align*}
HO_2 + O_3 & \rightarrow OH + 2O_2 \\
HO_2 + NO & \rightarrow OH + NO_2
\end{align*}
\]  

(9)  

(10)  

The photolysis of $H_2O_2$ (29) yields OH directly.

\[
H_2O_2 + h\nu \rightarrow 2OH
\]  

(29)  

Nitric acid, the final product of NO$_x$ oxidation, photolyses only slowly (45) under tropospheric conditions.

\[
HNO_3 + h\nu \rightarrow OH + NO_2
\]  

(45)  

In polluted air the photolysis of HNO$_2$ (31) becomes an important OH source during the morning (Perner and Platt, 1979; Platt et al., 1980b; Perner, 1980).

\[
HNO_2 + h\nu \rightarrow OH + NO & \leq 390 \text{ nm}
\]  

(31)  

This OH source does not depend on foregoing chemical cycles involving ozone. It is an independent source resulting from high NO$_x$ mixing ratios.

The formation of OH via reactions (9) and (10) of the short-lived $HO_2$ radical seems to be extremely important. $HO_2$ can be formed in many ways during atmospheric oxidation processes, such as when H atoms are produced.
as in the reaction of OH and CO (25) and by the photolysis of carbonyls (24). Alkoxy radicals formed in hydrocarbon oxidation cycles yield $\text{HO}_2$ as in the oxidation cycle of methane (17)-(22).

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2
\]  

(22)

While ethane reacts analogously to methane, the higher alkanes undergo preferential secondary hydrogen abstraction and yield ketones and $\text{HO}_2$ (46), (47), (48) and (49).

\[
\begin{align*}
\text{R'}-\text{CH}_2-\text{R}'' + \text{OH} & \rightarrow \text{R'}-\text{CH}-\text{R}'' + \text{H}_2\text{O} \\
\text{R'}-\text{CH}-\text{R}'' + \text{O}_2 & \xrightarrow{M} \text{R'}-\text{CHO} - \text{R}'' \\
\text{R'}-\text{CHOO} - \text{R}'' + \text{NO} & \rightarrow \text{R'}-\text{CHO} - \text{R}'' + \text{NO}_2 \\
\text{R'}-\text{CHO} - \text{R}'' + \text{O}_2 & \rightarrow \text{HO}_2 + \text{RCOR}''
\end{align*}
\]

(46), (47), (48) and (49)

The ketones finally are photolysed or react with OH.

In general, reactions of OH radicals with organics follow three different modes:

1. Abstraction of hydrogen from a carbon-hydrogen bond is the exclusive path for reactions with alkanes (17) (46). Olefins show abstractions at CH$_2$ bonds and of allylic hydrogen.

2. The primary reaction of OH with olefins is addition to the double bond (50).

\[
\text{OH} + \text{C} = \text{C} \rightarrow \text{C} - \text{C} - \text{OH}
\]  

(50)

3. A similar reaction occurs with aromatic rings (51), which leads to ring cleavage and gives rise to the production of multifunctional compounds resembling those found in aerosols.

\[
\text{OH} + \text{C}_{\text{ar}} \rightarrow \text{C} - \text{C} - \text{OH}
\]  

(51)

In all three oxidation modes the loss of an OH radical is followed by the production of one HO$_2$ radical. In certain instances, as in the case of C-C bond scission, even more radicals may be produced. Therefore, these oxidation processes must be known in detail in order to avoid serious errors in the calculation of OH concentrations.

Sink reactions of OH are those reactions which lead to a loss of radicals. Reaction (52) is a representative sink reaction because two radicals are lost and the products do not yield radicals by thermal or photolytic decay in the troposphere.
The same holds for the reaction of OH with HNO₂ (53) and HNO₃ (54).

\[
\begin{align*}
OH + HNO₂ & \rightarrow H₂O + NO₂ \\
OH + HNO₃ & \rightarrow H₂O + NO₃
\end{align*}
\]

However, these reactions (52)–(54) are relatively unimportant. The principal reactions of OH in the unpolluted atmosphere are with CO (1) and with hydrocarbons.

\[
OH + CO \rightarrow H + CO₂
\]

These recycle and may even lead to a net gain in radicals. HO₂ radicals formed in (26) and (49) disappear mainly through disproportionation (20) (28).

\[
\begin{align*}
HO₂ + CH₃O₂ & \rightarrow CH₃OOH + O₂ \\
HO₂ + HO₂ & \rightarrow H₂O₂ + O₂
\end{align*}
\]

The products CH₃OOH and H₂O₂ are still potential radical sources. Only removal of these compounds by deposition or washout renders them to radical sinks. However, the more important radical sink reactions are those of OH with those potential radical sources such as (25) and (30).

\[
\begin{align*}
OH + CH₂O & \rightarrow H₂O + HCO \\
OH + H₂O₂ & \rightarrow H₂O + HO₂
\end{align*}
\]

Note though radicals are actually recycled, this is a net depletion of radicals. In polluted air other reactions like (37) become dominant OH sinks.

\[
OH + NO₂ \rightarrow HNO₃
\]

Boundary layer lifetimes for OH are less than 1 sec in background air and as low as 10⁻² sec in polluted air. Calculations of OH concentrations are hampered by the uncertainty of specific reaction mechanisms and by imprecise rate constants. For example, the rate constants of (1), (9) and (10) have been substantially revised within the last few years. Therefore, at present, the accurate measurement of tropospheric OH levels is an urgent need in order to validate proposed reaction schemes and estimates of tropospheric lifetimes for those molecules reacting with OH. Currently, concentrations of OH are estimated by measuring conversion rates of certain compounds reacting with OH or by direct sonding using physical techniques.

*Indirect measurements.* OH concentrations may be obtained from the steady-state relationship derived from reactions (41) and (42). The tracer is presumably removed by reaction with OH at the rate constant \( k \).
In a similar approach, the source strength can be replaced by the rate of disappearance of a compound. This latter approach makes possible the determination of [OH] using appropriate tracers within a shorter time scale.

The steady-state approach for the measurement of average tropospheric [OH] using naturally produced $^{14}$CO as a tracer was introduced by Weinstock (1969) and further elaborated by Weinstock and Niki (1972) and Weinstock and Chang (1974). Volz et al. (1979, 1981) made extensive measurements using this method and were able to distinguish seasonal variations. They obtained a yearly average value of $4.5 \times 10^4$ to $9.5 \times 10^5$ OH cm$^{-3}$ in the northern hemisphere. Similar results were found by several authors using methylchloroform as tracer. Values of $(3 \text{ to } 5) \times 10^5$ and $(0.8 \text{ to } 2) \times 10^6$ OH cm$^{-3}$ were obtained for the northern and southern hemisphere, respectively (Lovelock, 1977; Singh, 1977a, 1977b; Neely and Plonka, 1978). The reported discrepancy between results for the northern hemisphere derived from the $^{14}$CO and CH$_3$CCl$_3$ techniques was resolved through the use of a revised rate constant for the reaction of OH with the CH$_3$CCl$_3$ (Derwent and Eggleton, 1981). Hanst et al. (1980) re-estimated the global CO budget and found a reasonable source-sink balance assuming $4 \times 10^5$ OH cm$^{-3}$ as an average global value.

Atmospheric OH concentrations will vary widely according to air composition and other parameters; therefore, suitable compounds for mass balance considerations will enable estimating of OH concentrations to be better defined with respect to location and time. Calvert (1976) estimated the hydrocarbon consumption in the Los Angeles basin to be equivalent to $(2 \pm 1.8) \times 10^6$ OH cm$^{-3}$ for the morning hours. The apparent OH concentration depended on the type of compound. For example, the very reactive C$_3$H$_8$ and 1-butene yielded an apparent OH-concentration of only $7 \times 10^3$ OH cm$^{-3}$. This unexpected behaviour may indicate the competition of other processes. Campbell et al. (1979) determined OH-concentrations of $3 \times 10^3$ to $3.5 \times 10^6$ cm$^{-3}$ by measuring the local CO oxidation rate by a $^{14}$CO tracer method. The maximum OH concentration for moderately polluted sites was $2 \times 10^5$ OH cm$^{-3}$.

Direct measurements. Exact information as to the importance of OH for tropospheric oxidation processes can only be gained from physical methods. Unfortunately, the interpretation of results reported so far seem to have been hampered by experimental difficulties. Groups often measure OH directly by two physical methods, e.g. optical fluorescence or absorption. While the fluorescence method is compact, it seemed to suffer from cross-sensitivities caused mainly by the action of high flux density laser light. On the contrary,
the absorption method is less versatile because it uses a 3–10 km light path but it offers today the possibility of unambiguous identification and quantitative determination of OH concentrations and interference by the sounding laser beam is negligible.

Not counting earlier measurements by Wang and Davis (1974) which showed excessively high OH concentrations, probably due to experimental interferences (Wang and Davis, 1975), two groups reported $\sim 10^7$ OH cm$^{-3}$ under various conditions using laser fluorescence. Wang et al. (1975) reported up to $5 \times 10^7$ OH cm$^{-3}$ near the ground while Davis et al. (1976) found $8 \times 10^6$ OH cm$^{-3}$ at 7 km and $5 \times 10^6$ at 11.5 km. These values seem to be very high in view of the results from indirect estimation techniques (foregoing section) and from the present state of understanding of atmospheric chemistry. A possible explanation of the high OH estimates may be the interference of O1D atoms produced from ozone by laser light photolysis (Ortgies et al., 1980). However, there are absorption bands of other air constituents in the same spectral region and misinterpretation of SO$_2$ absorptions as OH cannot be entirely excluded. A boundary layer measurement of OH has shown levels to be $1 \times 10^7$ OH cm$^{-3}$ in the vicinity of a power plant plume (Davis et al., 1979) and $3 \times 10^6$ OH cm$^{-3}$ above the Rocky Mountains at 6.9 km altitude. The self-induced signal by the laser pulse was 50% (Davis et al., 1981). Philen et al. (1978) found a large difference in [OH] within the boundary layer ($1.5 \times 10^7$ OH cm$^{-3}$) and above ($1.4 \times 10^6$ OH cm$^{-3}$). Perner et al. (1976) reported OH radical concentrations of up to $1.1 \times 10^7$ OH cm$^{-3}$ from long path light absorption measurements. (The concentrations of OH listed in Table 1 in that earlier report should be multiplied by 1.5 for consistency with revised thermal distribution and oscillator strength.) Results with an improved machine showed an average OH concentration in Jülich of $(1.6 \pm 0.5) \times 10^6$ OH cm$^{-3}$ for most sunny days (12–4 p.m.) from March to September 1979 (Hübner et al., 1982).

These latter results agree in general with the findings of Campbell et al. (1979). In Section 2.2.4.2 these results will be compared with model calculations.

2.2.3.4 HO$_2$-radical

The hydrogen peroxy radical is produced in a number of reactions during the oxidation of hydrocarbons from alkoxy radicals (49), from H-atoms (26) and from HCO (27).

$$
R'\text{-CHO} - R'' + O_2 \rightarrow \text{HO}_2 + R'\text{-CO} - R'' \quad (49)
$$

$$
H + O_2 \xrightarrow{M} \text{HO}_2 \quad (26)
$$

$$
HCO + O_2 \rightarrow \text{HO}_2 + \text{CO} \quad (27)
$$
The H-atoms are produced in reaction (1) and by photolysis of aldehydes (24). The HCO stems from formaldehyde (24) (25). The reactions of HO₂ are slower than those of OH and therefore [HO₂] usually exceeds that of [OH]. The reactions restricting lifetime of HO₂ in background air are those with radicals (28) and (56) while the reactions with O₃ (9), NO (10), and OH (52) are of lesser importance.

\[
\begin{align*}
\text{HO₂} + \text{HO₂} & \rightarrow \text{H₂O₂} + \text{O₂} \\
\text{HO₂} + \text{RCH}_2\text{O₂} & \rightarrow \text{RCH}_2\text{OOH} + \text{O₂}
\end{align*}
\]

In polluted air the reaction with NO (10) becomes predominant so that [HO₂] is reduced and the production channels of alkylhydrogen peroxides (56) and hydrogen peroxide (28) are less important. However, field measurements of H₂O₂ seem to contradict this assumption (see Section 2.2.2.3). In polluted air HO₂ also reacts quickly with NO (57) to yield HNO₄, a reservoir for HO₂, which is small at room temperature where HNO₄ is thermally unstable. Even in heavily polluted areas, reaction (57) will only be of significance if HNO₄ reacts very rapidly or at low temperature. Graham et al. (1977) found reaction (58) to be of no importance in this reaction scheme.

\[
\begin{align*}
\text{HO₂} + \text{NO₂} & \overset{M}{\rightarrow} \text{HNO₄} \\
\text{HNO₄} & \overset{M}{\rightarrow} \text{HNO₂} + \text{O₂} \\
\text{HNO₄} & \overset{M}{\rightarrow} \text{HO₂} + \text{NO₂}
\end{align*}
\]

No direct measurements of HO₂ in the troposphere have been reported so far. However, matrix isolation studies have shown strongly variable peroxy radical concentrations (Mihelcic, private communication).

Aerosols could interfere with HO₂ (Warneck, 1974). The collision frequency of molecules with aerosol in polluted air may be greater than 1 sec⁻¹. Under those circumstances the lifetime of HO₂ could be determined by aerosol collisions and the rate of formation of OH (9) (10) as well as [H₂O₂] (28) could be considerably reduced.

**2.2.3.5 NO₃**

The reaction of NO₂ with ozone (12) produces NO₃ radicals which react much faster with certain substances than with ozone.

\[
\text{NO₂} + \text{O}_3 \rightarrow \text{NO₃} + \text{O}_2
\]

NO₃ has been detected in polluted air in the presence of largely varying NO₂ mixing ratios (Platt et al., 1980a; Noxon et al., 1980; Platt et al., 1981). It has not been detected in the absence of ozone and its lifetime based on the production rate (12) ranges from 0.1 to 30 min. The maximum mixing ratios
observed were 200–300 p.p.t. (based on $\varepsilon_{662} = 4500$ M$^{-1}$ cm$^{-1}$ by Graham and Johnston, 1978). The longest lifetimes were observed in remote areas. Presently no satisfactory explanation for the observed lifetimes can be given. Apparently NO$_3$ is often decomposed without permanent loss of NO$_2$ (Platt et al., 1980a, 1981). NO$_3$ and NO$_2$ are in equilibrium with N$_2$O$_5$ (60, 61).

$$\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5 \quad (60)$$

$$\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3 \quad (61)$$

The equilibrium constant $K_{eq}$ was found to be $2 \times 10^{10}$ cm$^{-3}$ at 10°C (Platt et al., 1981). Therefore, the N$_2$O$_5$ concentration usually exceeds the NO$_3$ concentration.

The depletion of NO$_3$ can take place via NO$_3$-reactions or via reactions of N$_2$O$_5$. Probably both reactions occur in connection with aerosols. While the reaction of NO$_3$ with dry aerosols seems not to remove NO$_3$ from the air, under the condition of developing fog, a drastic lowering of the NO$_3$ mixing ratio has been observed (Platt et al., 1981). Unfortunately, the behaviour of NO$_2$ could not be followed. The likely reaction of N$_2$O$_5$ with the water droplets (38) can lead to a deposition of NO$_3$ through nitric acid formation.

$$\text{N}_2\text{O}_5 + \text{H}_2\text{O}_{\text{aq}} \rightarrow 2\text{HNO}_3_{\text{aq}} \quad (38)$$

In Central Europe, NO$_3$ is observed very rarely, which suggests that reactions like (38) are of general importance and may also occur in clouds (see Section 2.2.2.4).

The lifetimes for NO$_3$ depletion with aerosols are in accordance with the collision frequency of $10^{-1}$ sec$^{-1}$ in continental air and about 1–10 sec$^{-1}$ in polluted regions, if collision efficiencies of $10^{-2}$ to $10^{-3}$ are assumed for the dry aerosols and higher values for wet aerosols.

### 2.2.3.6 Ozone Reactions

While ozone is more or less inert against reaction with many air constituents, it reacts efficiently with olefins. Such oxidation reactions may be further accelerated through the action of NO$_3$ (Carter et al., 1981). These reactions may be of importance in the atmosphere at night in the absence of photochemical processes.

As a typical example, the ozone/ethene reaction mechanism, as recently investigated with Fourier-Transform-Infrared-Spectroscopy (FTIR) by Su et al. (1980), is described.

Ozone adds to the olefin and yields an ozonide (62) which fragments into a carbonyl compound and a reactive species known as Criegee intermediate (63).
The Criegee intermediate is partly stabilized as free CH$_2$O$_2$ radical (66) and partly converted into excited formic acid (65) which decomposes (67) (68) or is partly stabilized (69).

\[
\text{CH}_2\text{OO} \xrightarrow{\text{M}} \text{H}_2\text{C}=\text{O}^* \\
\text{H}_2\text{C}=\text{O}^* \xrightarrow{\text{M}} \text{CH}_2\text{O}_2 \\
\text{HCO}_2\text{H}^* \xrightarrow{\text{M}} \text{CO} + \text{H}_2\text{O} \\
\text{CO}_2 + \text{H}_2 \{ \\
\text{CO}_2 + 2\text{H} \} \\
\text{HCO}_2\text{H} \xrightarrow{\text{M}} \text{H}_2\text{C}=\text{O} \\
\]

The CH$_2$O$_2$ takes part in secondary bimolecular reactions for example with CH$_2$O (70), CH$_3$CHO, CO and SO$_2$. The reaction with formaldehyde yields formic acid anhydride (72) via an unidentified precursor $X$ (71).

\[
\text{CH}_2\text{O}_2 + \text{CH}_2\text{O} \xrightarrow{\text{M}} \text{H}_2\text{C} = \text{O} \quad \text{(70)} \\
\text{H}_2\text{C} = \text{O} \quad \text{(X)} \\
\text{OHCH}_2\text{OCH} \quad \text{(71)} \\
\text{OHCH}_2\text{OCH} \xrightarrow{\text{M}} (\text{CHO})_2\text{O} + \text{H}_2 \\
\]

The ozonide produced in reaction (70) was not observed spectroscopically; however, the corresponding propylene ozonide is found when formaldehyde is replaced by acetaldehyde.
Cox and Penkett (1972) found that butene and higher alkenes react with ozone to create a species which oxidizes SO$_2$ rapidly and forms an aerosol. Su et al. (1980) found that products from CH$_3$O$_2$ were quenched by SO$_2$.

2.2.3.7 Aerosols

The active participation of aerosols in the formation or destruction of gaseous compounds (Judeikis and Siegel, 1973) has probably not been fully accounted for in atmospheric models. In Section 2.2.2.5 a few examples have been given. In situ photolysis of nitrous acid formed on aerosols from NO$_x$ could provide a certain [OH] at the aerosol and may lead to an efficient depletion of air constituents. It could be expected that the relative reactivities of trace gases under this regime will differ from those of homogeneous gas-phase OH reactions. Also, an increase in aerosol size is expected as they may profit from reaction products.

Both phenomena seem to be actually observed. Calvert (1976) and Singh et al. (1981) had to assume different steady state OH concentrations for alkene and alkane depletion when they interpreted the hydrocarbon consumption in polluted air by homogeneous OH reactions. Photochemical activity is often accompanied by aerosol formation which is especially expressed during smog formation and causes a sometimes rapid visibility reduction.

2.2.4 MODEL CALCULATIONS

The discussion of the individual species showed already the interconnection of the atmospheric constituents often through a number of cycles or reactions. These complex systems of simultaneous processes can best be followed by model calculations. The behaviour of chemicals in the atmosphere represents essentially a three-dimensional, time dependent problem. The present models, however, are simplifications in order to investigate specific questions in an economic but yet reasonably accurate manner. These models normally consider homogeneous gas-phase reactions only.

For example, a large number of model studies were undertaken to explain the hydrocarbon and CO oxidation processes in air on the basis of OH as primary species. At first stationary state photochemical models were used (Levy, 1971, 1974). Then, the methane chemistry was treated by coupling such a model to one-dimensional eddy diffusion (McConnell et al., 1971). Later, more sophisticated models were developed in order to include an increasing number of atmospheric parameters (Fishman and Crutzen, 1978; Derwent and Curtis, 1977). Models have also been used to predict future climatic changes with regard to increasing CO$_2$ mixing ratios (Manabe and Wetherald, 1980; Wetherald and Manabe, 1980).

Singular aspects such as the production of ozone in the oxidation cycles of
hydrocarbons and CO have been examined (Fishman and Crutzen, 1977, 1978; Chameides and Stedman, 1977; Chameides, 1978). When homogeneous gas-phase reactions are considered, the OH radical becomes the important reactive species in almost every reaction cycle. Many model calculations have been made on this assumption.

Recently, a review by Logan et al. (1981) dealt with most of the important aspects of tropospheric chemistry.

2.2.4.1 Clean Air

Global OH distributions have been calculated by several groups as a function of season and daytime. In this section [OH] values for summer and noontime are compared. Crutzen and Fishman (1977) obtained \((3 \text{ to } 1) \times 10^6 \text{ OH cm}^{-3}\) for 0–60° latitude at the ground. Duewer et al. (1977) cited a range of \((3 \text{ to } 10) \times 10^6 \text{ OH cm}^{-3}\) in a sensitivity study of rate constants. However, in both papers the rate constant for reaction (10) of HO₂ with NO was under-estimated. Logan et al. (1981) obtained \((5 \text{ to } 2) \times 10^6 \text{ OH cm}^{-3}\) from 0 to 50 °N and found little variation of [OH] with altitude. It has to be pointed out that OH is very sensitive to the water content of the atmosphere (Weinstock et al., 1980) and also to the NO₂ mixing ratio (Hameed et al., 1979; Fishman et al., 1979; Weinstock et al., 1980; Logan et al., 1981). According to a straightforward consideration, the [OH] should decrease at higher altitude because of the rapidly diminishing water vapour pressure if OH is solely produced via reactions (2) and (7). However, the importance of OH sources may shift. For example, the OH source from photolysis of H₂O₂ will become comparable to the O₃/H₂O source (Logan et al., 1981).

In Figure 2.2.6 the major chemical cycles are considered for the case of no NO₃ which comes close to approximately the NO mixing ratio of about 3 p.p.t. reported by McFarland et al. (1979). The OH concentration for maximum light flux \((J_2 = 5 \times 10^5 \text{ sec}^{-1})\) is \(5 \times 10^6 \text{ OH cm}^{-3}\). This value is lower than some of the directly measured concentrations (see Section 2.2.3.3). However, the values found by Campbell et al. (1979) and Hübler et al. (1982) are of the same order of magnitude.

2.2.4.2 Polluted Air

Hov and Isaksen (1979) calculated radical concentrations for urban atmospheres and obtained a maximum OH-concentration of \(~10^7 \text{ OH cm}^{-3}\) at noon during summer. Derwent and Hov (1980) determined a maximum concentration of \(7 \times 10^6 \text{ OH cm}^{-3}\) for a photochemical episode in London. It is the presence of substantial amounts of NO which causes the increase of OH. The RHO₂ and HO₂ radicals are more efficiently recycled leading to an increase of the OH radical concentration. The maximum [OH] is reached
Figure 2.2.6 OH-cycle in the absence of NO₂ for overhead sun conditions. RH is produced by reaction of peroxyradicals RHO₂.
Figure 2.2.7  OH-cycle with NO\textsubscript{2} when NO\textsubscript{2} mixing ratio is chosen to yield about maximum [OH]. The ratio NO/NO\textsubscript{2} is assumed to be determined by NO\textsubscript{2} photolysis and by reactions of NO with ozone, HO\textsubscript{2} and RHO\textsubscript{2} as shown. RHO is exclusively produced by reaction of peroxyradicals with NO.
when with increasing NO, the rate for OH consumption (37) nearly equals the primary OH production rate.

\[
\text{NO}_2 + \text{OH} \xrightarrow{M} \text{HNO}_3 \tag{37}
\]

At still higher NO, concentrations, reaction (37) causes [OH] to drop to lower values (Hameed et al., 1979; Weinstock et al., 1980; Logan et al., 1981). Figure 2.2.7 shows the same cycles as Figure 2.2.6 but with the amount of NO, necessary to reach maximum [OH]. The hydrocarbon reaction rate with OH was set equal to that with CO. An important assumption is that the ratio NO/NO, is controlled by reactions (11) and (73) as well as by the additional oxidation of NO by peroxides (10) (21).

\[
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \tag{11}
\]

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \tag{73}
\]

In background air, Kelly (1980) found low NO/NO, ratios which show substantial oxidation rates for NO by reactions other than (73). Similar data are found in experiments with polluted air. The combined oxidation rate of NO in Figure 2.2.7 by peroxides is 20% of the rate of reaction (73) so that the NO/NO, ratio is not strongly affected by the peroxides from those cycles. The direct measurements of [OH] at Jülich by Hübler et al. (1982) showed often smaller concentrations than expected from pollution models. This may indicate too high NO, or SO, concentrations or the existence of interferences not yet included in the models.

### 2.2.5 CONCLUSIONS

The presently accepted approach of atmospheric chemists using homogeneous gas-phase reactions is probably adequate to describe processes in the background atmosphere, where during the daylight the OH radical is the main reactive species. In strongly polluted regions, other species such as O³P atoms or other excited oxygen species become important reactants. There are also indications that heterogeneous reactions gain in importance and become rate determining under conditions of high levels of complex organic contaminants in the atmosphere.

### 2.2.6 REFERENCES


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