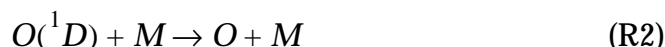
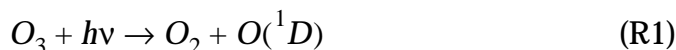


CHAPTER 11. OXIDIZING POWER OF THE TROPOSPHERE

The atmosphere is an oxidizing medium. Many environmentally important trace gases are removed from the atmosphere mainly by oxidation: greenhouse gases such as CH₄, toxic combustion gases such as CO, agents for stratospheric O₃ depletion such as HCFCs, and others. Oxidation in the troposphere is of key importance because the troposphere contains the bulk of atmospheric mass (85%, see section 2.3) and because gases are generally emitted at the surface.

The most abundant oxidants in the Earth's atmosphere are O₂ and O₃. These oxidants have large bond energies and are hence relatively unreactive except toward radicals (O₂ only toward highly unstable radicals). With a few exceptions, oxidation of non-radical atmospheric species by O₂ or O₃ is negligibly slow. Work in the 1950s first identified the OH radical as a strong oxidant in the stratosphere. OH reacts rapidly with most reduced non-radical species, and is particularly reactive toward H-containing molecules due to H-abstraction reactions converting OH to H₂O. Production of OH is by reaction of water vapor with O(¹D) (section 10.2.1):

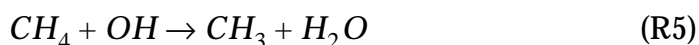


We saw in chapter 10 how OH oxidizes a number of trace gases in the stratosphere. A simple expression for the source P_{OH} of OH from reactions (R1)-(R3) can be obtained by assuming steady state for O(¹D). Laboratory studies show that (R2) is much faster than (R3) at the H₂O mixing ratios found in the atmosphere, allowing for simplification:

$$P_{OH} = 2k_3[O(^1D)][H_2O] = \frac{2k_1k_3}{k_2[M] + k_3[H_2O]}[O_3][H_2O] \quad (11.1)$$

$$\approx \frac{2k_1k_3}{k_2[M]}[O_3][H_2O]$$

Critical to the generation of OH is the production of O(¹D) atoms by (R1). Until 1970 it was assumed that production of O(¹D) would be negligible in the troposphere because of near-total absorption of UV radiation by the O₃ column overhead. It was thought that oxidation of species emitted from the Earth's surface, such as CO and CH₄, required transport to the stratosphere followed by reaction with OH in the stratosphere:



This mechanism implied long atmospheric lifetimes for CO and CH₄ because air takes on average 5-10 years to travel from the troposphere to the stratosphere (section 4.4.4) and the stratosphere accounts for only 15% of total atmospheric mass. In the 1960s, concern emerged that accumulation of CO emitted by fossil fuel combustion would soon represent a global air pollution problem.

11.1 THE HYDROXYL RADICAL

11.1.1 Tropospheric production of OH

A major discovery in the early 1970s was that sufficient OH is in fact produced in the troposphere by reactions (R1)-(R3) to allow for oxidation of species such as CO and CH₄ within the troposphere. A calculation of the rate constant for (R1) at sea level is shown in Figure 11-1 as the product of the solar actinic flux, the absorption cross-section for O₃, and the O(¹D) quantum yield. Tropospheric production of O(¹D) takes place in a narrow wavelength band between 300 and 320 nm; radiation of shorter wavelengths does not penetrate into the troposphere, while radiation of longer wavelengths is not absorbed by O₃. Although the production of O(¹D) in the troposphere is considerably slower than in the stratosphere, this is compensated in terms of OH production by the larger H₂O mixing ratios in the troposphere (10²-10³ times higher than in the stratosphere). Model calculations in the 1970s accounting for the penetration of UV radiation at 300-320 nm found tropospheric OH concentrations of the order of 10⁶ molecules cm⁻³, resulting in a tropospheric lifetime for CO of only a few months and allaying concerns that CO could accumulate to toxic levels. Crude measurements of OH concentrations in the 1970s confirmed

this order of magnitude and hence the importance of OH as an oxidant in the troposphere; further confirmation came from long-lived proxies (section 11.1.2). The accurate measurement of OH turned out to be an extremely difficult problem because of the low concentrations, and only in the past decade have instruments been developed that can claim an accuracy of better than 50%.

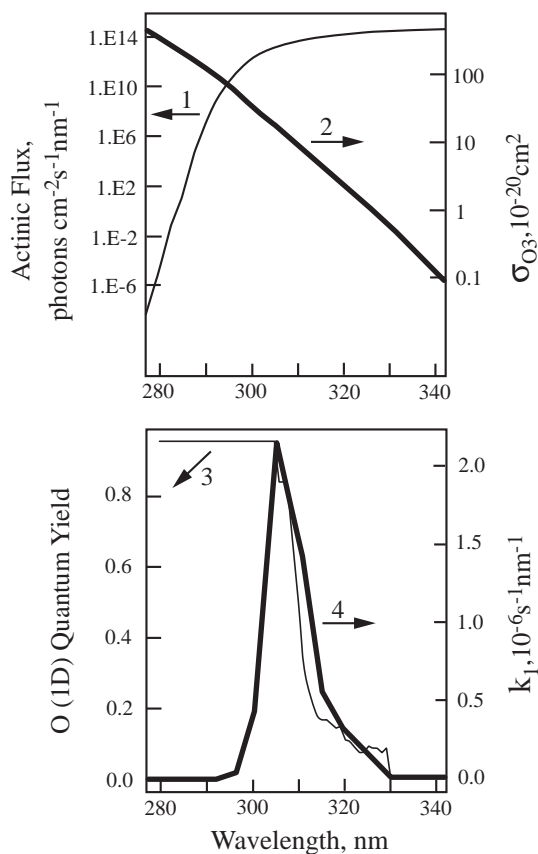


Figure 11-1. Computation of the rate constant k_1 for photolysis of O_3 to $O(^1D)$ in the troposphere as a function of wavelength. (1) Solar actinic flux at sea level for 30° solar zenith angle and a typical O_3 column overhead; (2) Absorption cross-section of O_3 at 273 K; (3) $O(^1D)$ quantum yield at 273 K; and (4) rate constant k_1 calculated as the product of (1), (2), and (3).

11.1.2 Global mean OH concentration

The lifetime of OH in an air parcel is given by

$$\tau_{OH} = \frac{1}{\sum_i k_i n_i} \quad (11.2)$$

where n_i is the number density of species i reacting with OH, k_i is the corresponding rate constant, and the sum is over all reactants in the air parcel. One finds that CO is the dominant sink of OH in most of the troposphere, and that CH₄ is next in importance. The resulting OH lifetime is of the order of one second. Because of this short lifetime, atmospheric concentrations of OH are highly variable; they respond rapidly to changes in the sources or sinks.

Calculating the atmospheric lifetimes of gases against oxidation by OH requires a knowledge of OH concentrations averaged appropriately over time and space. This averaging cannot be done from direct OH measurements because OH concentrations are so variable. An impossibly dense measurement network would be required.

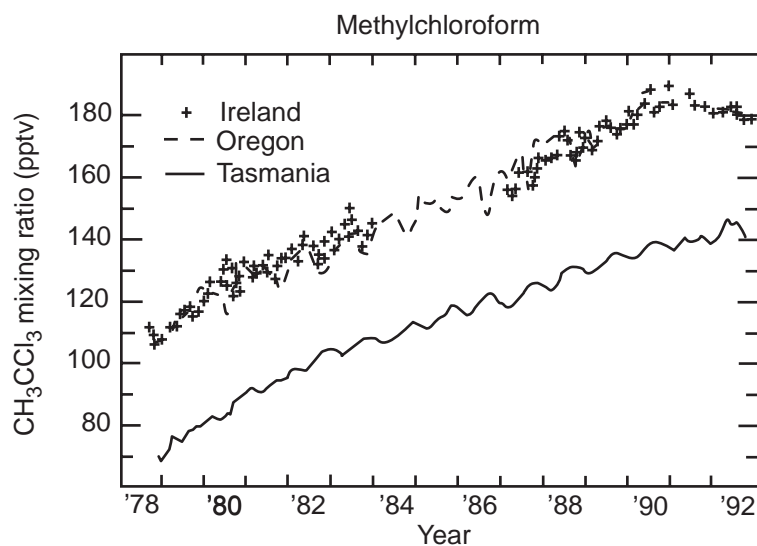


Figure 11-2 Atmospheric distribution and trend of methylchloroform. From *Scientific Assessment of Ozone Depletion: 1994*, WMO, 1995.

In the late 1970s it was discovered that the industrial solvent methylchloroform (CH₃CCl₃) could be used to estimate the global mean OH concentration. The source of CH₃CCl₃ to the atmosphere is exclusively anthropogenic. The main sink is oxidation by OH in the troposphere (oxidation and photolysis in the stratosphere, and uptake by the oceans, provide small additional sinks). The concentration of CH₃CCl₃ in surface air has been measured continuously since 1978 at a worldwide network of sites (Figure 11-2). Rapid increase of CH₃CCl₃ was observed in the 1970s and 1980s due to rising industrial emissions, but concentrations began to decline in the 1990s because CH₃CCl₃ was one of the gases banned by the Montreal protocol to protect the O₃ layer. Although

only a small fraction of CH_3CCl_3 is oxidized or photolyzed in the stratosphere, the resulting Cl radical source was sufficient to motivate the ban.

Industry statistics provide a reliable historical record of the global production rate P (moles yr^{-1}) of CH_3CCl_3 , and it is well-established that essentially all of this production is volatilized to the atmosphere within a few years. The global mass balance equation for CH_3CCl_3 in the troposphere is:

$$\frac{dN}{dt} = P - L_{trop} - L_{strat} - L_{ocean} \quad (11.3)$$

where N is the number of moles of CH_3CCl_3 in the troposphere, L_{trop} is the loss rate of CH_3CCl_3 in the troposphere, and L_{strat} and L_{ocean} are the minor loss rates of CH_3CCl_3 in the stratosphere and to the ocean. We calculate L_{trop} as

$$L_{trop} = \int_{trop} k(T) C n_a [\text{OH}] dV \quad (11.4)$$

where $k(T)$ is the temperature-dependent rate constant for the oxidation of CH_3CCl_3 by OH, C is the mixing ratio of CH_3CCl_3 , n_a is the air density, and the integral is over the tropospheric volume. We define the global mean OH concentration in the troposphere as

$$\overline{[\text{OH}]} = \frac{\int_{trop} k(T) n_a [\text{OH}] dV}{\int_{trop} k(T) n_a dV} \quad (11.5)$$

where $k(T)n_a$ is an *averaging kernel* (or weighting factor) for the computation of the mean. Replacing (11.3) and (11.4) into (11.5) yields:

$$\overline{[\text{OH}]} \approx \frac{P - \frac{dN}{dt}}{C \int_{trop} k(T) n_a dV} \quad (11.6)$$

where we have assumed C to be uniform in the troposphere (Figure 11-2) and neglected the minor terms L_{strat} and L_{ocean} . All terms on

the right-hand side of (11.6) are known. The values of C and dN/dt can be inferred from atmospheric observations (Figure 11-2). The integral $\int_{trop} k(T)n_a dV$ can be calculated from laboratory measurements of $k(T)$ and climatological data for tropospheric temperatures. Substituting numerical values we obtain $[\overline{\text{OH}}] = 1.2 \times 10^6 \text{ molecules cm}^{-3}$.

This empirical estimate of $[\overline{\text{OH}}]$ is useful because it can be used to estimate the lifetime $\tau_i = 1/(k_i[\overline{\text{OH}}])$ of any long-lived gas i against oxidation by OH in the troposphere. For example, one infers a lifetime of 9 years for CH_4 and a lifetime of 2.0 years for CH_3Br (problem 6. 4). One can also determine the atmospheric lifetimes of different hydrochlorofluorocarbon (HCFC) species and hence the fractions of these species that penetrate into the stratosphere to destroy O_3 (problem 3. 3).

11.2 GLOBAL BUDGETS OF CO AND METHANE

Carbon monoxide and methane are the principal sinks for OH in most of the troposphere. These two gases play therefore a critical role in controlling OH concentrations and more generally in driving radical chemistry in the troposphere.

Table 11-1 Present-day global budget of CO

	Range of estimates (Tg CO yr ⁻¹)
SOURCES	1800-2700
Fossil fuel combustion / industry	300-550
Biomass burning	300-700
Vegetation	60-160
Oceans	20-200
Oxidation of methane	400-1000
Oxidation of other hydrocarbons	200-600
SINKS	2100-3000
Tropospheric oxidation by OH	1400-2600
Stratosphere	~100
Soil uptake	250-640

Table 11-1 gives a global budget of CO for the present-day atmosphere. Fossil fuel combustion and biomass burning (principally associated with tropical agriculture) are large anthropogenic sources, and oxidation of CH₄ is another major source (problem 11. 1). Most of the CO in the present-day troposphere is anthropogenic. The main sink of CO is oxidation by OH and results in a 2-month mean lifetime; because of this relatively short lifetime, CO is not well-mixed in the troposphere. Concentrations are 50-150 ppbv in remote parts of the world, 100-300 ppbv in rural regions of the United States, and up to several ppmv in urban areas where CO is considered a hazard to human health.

Table 11-2 Present-day global budget of CH₄

	Rate, Tg CH ₄ yr ⁻¹ ; best estimate and range of uncertainty
SOURCES, natural	160 (75-290)
Wetlands	115 (55-150)
Termites	20 (10-50)
Other	25 (10-90)
SOURCES, anthropogenic	375 (210-550)
Natural gas	40 (25-50)
Livestock (ruminants)	85 (65-100)
Rice paddies	60 (20-100)
Other	190 (100-300)
SINKS	515 (430-600)
tropospheric oxidation by OH	445 (360-530)
stratosphere	40 (30-50)
soils	30 (15-45)
ACCUMULATION IN ATMOSPHERE	37 (35-40)

Atmospheric concentrations of CH₄ have increased from 800 to 1700 ppbv since preindustrial times (Figure 7-1). The reasons are not well understood. A present-day global budget for CH₄ is given

in Table 11-2. There are a number of anthropogenic sources, some combination of which could have accounted for the observed CH_4 increase. One must also consider the possible role of changing OH concentrations. Oxidation by OH in the troposphere provides 85% of the global CH_4 sink (uptake by soils and oxidation in the stratosphere provide small additional sinks; see problem 4. 8). A decrease in OH concentrations since pre-industrial times would also have caused CH_4 concentrations to increase. Long-term trends in OH concentrations will be discussed in section 11.5.

11.3 CYCLING OF HO_x AND PRODUCTION OF OZONE

11.3.1 OH titration

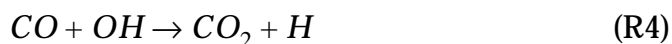
In the early 1970s when the importance of OH as a tropospheric oxidant was first realized, it was thought that the O_3 molecules necessary for OH production would be supplied by transport from the stratosphere. As we saw in section 10.1.2, the chemical lifetime of O_3 in the lower stratosphere is several years, sufficiently long to allow transport of O_3 to the troposphere. The transport rate F of O_3 across the tropopause is estimated to be in the range $1\text{-}2 \times 10^{13}$ moles yr^{-1} (section 11.5 and problem 11. 2). One can make a simple argument that this supply of O_3 from the stratosphere is in fact far from sufficient to maintain tropospheric OH levels. Each O_3 molecule crossing the tropopause can yield at most two OH molecules in the troposphere by reactions (R1)+(R3) (some of the O_3 is consumed by other reactions in the troposphere, and some is deposited at the Earth's surface). The resulting maximum source of OH is $2F = 2\text{-}4 \times 10^{13}$ moles yr^{-1} . In comparison, the global source of CO to the atmosphere is $6\text{-}10 \times 10^{13}$ moles yr^{-1} (Table 11-1) and the global source of CH_4 is about 3×10^{13} moles yr^{-1} (Table 11-2). There are therefore more molecules of CO and CH_4 emitted to the atmosphere each year than can be oxidized by OH molecules originating from O_3 transported across the tropopause. In the absence of additional sources OH would be *titrated*; CO, CH_4 , HCFCs, and other gases would accumulate to very high levels in the troposphere, with catastrophic environmental implications.

A key factor preventing this catastrophe is the presence in the troposphere of trace levels of NO_x ($\text{NO}_x \equiv \text{NO} + \text{NO}_2$) originating from combustion, lightning, and soils. The sources and sinks of NO_x will be discussed in Section 11.4. As we first show here, the

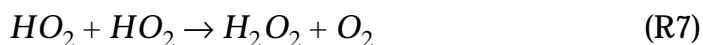
presence of NO_x allows the regeneration of OH consumed in the oxidation of CO and hydrocarbons, and concurrently provides a major source of O_3 in the troposphere to generate additional OH.

11.3.2 CO oxidation mechanism

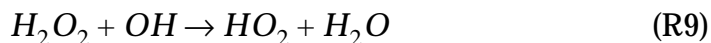
Oxidation of CO by OH produces the H atom, which reacts rapidly with O_2 :



The resulting HO_2 radical can self-react to produce hydrogen peroxide (H_2O_2):

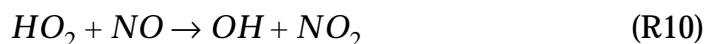


Hydrogen peroxide is highly soluble in water and is removed from the atmosphere by deposition on a time scale of a week. It can also photolyze or react with OH:

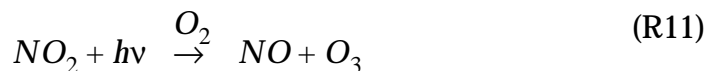


Reaction (R8) regenerates OH while (R9) consumes additional OH. Problem 11.3 examines the implication of these different H_2O_2 loss pathways for the oxidizing power of the atmosphere.

In the presence of NO, an alternate reaction for HO_2 is

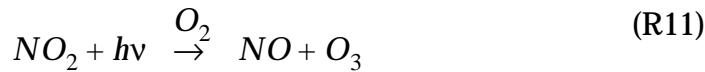
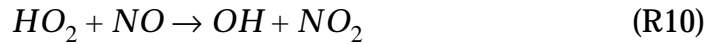
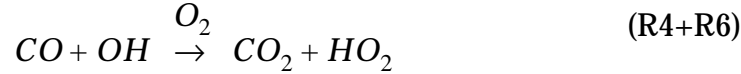


which regenerates OH, and also produces NO_2 which goes on to photolyze as we have already seen for the stratosphere (section 10.2.2):

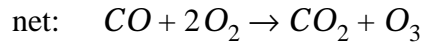


Reaction (R11) regenerates NO and produces an O_3 molecule, which can then go on to photolyze by reactions (R1)-(R3) to produce two additional OH molecules. Reaction (R10) thus yields up to three OH molecules, boosting the oxidizing power of the

atmosphere. The sequence of reactions (R4)+(R6)+(R10)+(R11) is a *chain mechanism* for O₃ production in which the oxidation of CO by O₂ is catalyzed by the HO_x chemical family (HO_x ≡ H + OH + HO₂) and by NO_x:



The resulting net reaction is



The chain is initiated by the source of HO_x from reaction (R3), and is terminated by the loss of the HO_x radicals through (R7). The propagation efficiency of the chain (chain length) is determined by the abundance of NO_x. A diagram of the mechanism emphasizing the coupling between the O₃, HO_x, and NO_x cycles is shown in Figure 11-3.

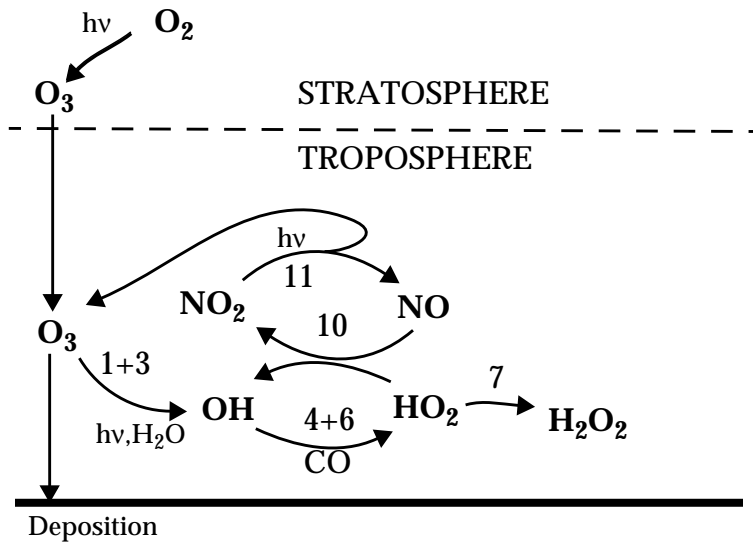


Figure 11-3 Mechanism for O₃-HO_x-NO_x-CO chemistry in the troposphere

Remarkably, HO_x and NO_x catalyze O₃ *production* in the troposphere and O₃ *destruction* in the stratosphere. Recall the catalytic HO_x and NO_x cycles for O₃ loss in the stratosphere (section 10.2):



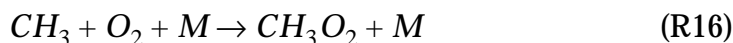
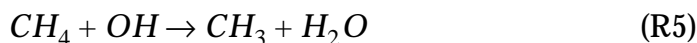
and



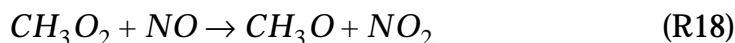
The key difference between the troposphere and the stratosphere is that O_3 and O concentrations are much lower in the troposphere. The difference is particularly large for O atom, whose concentrations vary as $[O_3]/n_a^2$ (equation (10.4)). In the troposphere, reaction (R12) is much slower than reaction (R4), and reaction (R15) is negligibly slow. Ozone loss by the HO_x -catalyzed mechanism (R12)-(R13) can still be important in remote regions of the troposphere where NO concentrations are sufficiently low for (R13) to compete with (R10). Ozone loss by the NO_x -catalyzed mechanism (R14)-(R15) is of no importance anywhere in the troposphere.

11.3.3 Methane oxidation mechanism

The mechanism for oxidation of CH_4 involves many more steps than the oxidation of CO but follows the same schematic. The methyl radical (CH_3) produced from the initial oxidation rapidly adds O_2 :

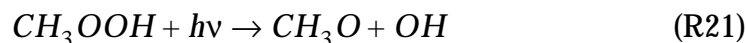
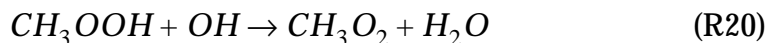
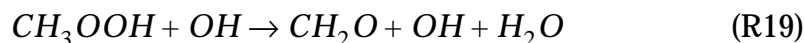


The methylperoxy radical (CH_3O_2) is analogous to HO_2 and is considered part of the HO_x family. Its main sinks are reaction with HO_2 and NO :



Methylhydroperoxide (CH_3OOH) may either react with OH or photolyze. The reaction with OH has two branches because the H-abstraction can take place either at the methyl or at the

hydroperoxy group. The CH_2OOH radical produced in the first branch decomposes rapidly to formaldehyde (CH_2O) and OH:

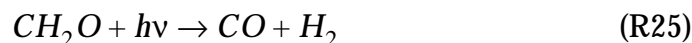
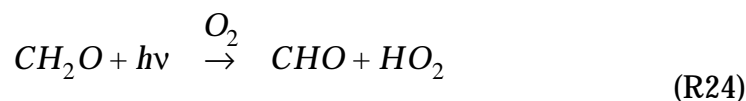
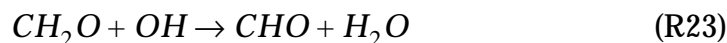


The methoxy radical (CH_3O) produced by reactions (R18) and (R21) goes on to react rapidly with O_2 :

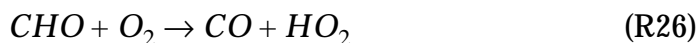


and HO_2 reacts further as described in section 11.3.2.

Formaldehyde produced by (R22) can either react with OH or photolyze (two photolysis branches):



Reactions (R23) and (R24) produce the CHO radical, which reacts rapidly with O_2 to yield CO and HO_2 :



CO is then oxidized to CO_2 by the mechanism described in section 11.3.2.

In this overall reaction sequence the C(-IV) atom in CH_4 (the lowest oxidation state for carbon) is successively oxidized to C(-II) in CH_3OOH , C(0) in CH_2O , C(+II) in CO, and C(+IV) in CO_2 (highest oxidation state for carbon). Ozone production takes place by NO_2 photolysis following the peroxy + NO reactions (R10) and (R18), where the peroxy radicals are generated by reactions (R5)+(R16), (R20), (R22), (R24), (R26), and (R4)+(R6).

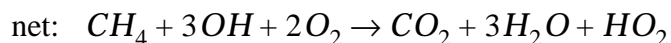
Let us calculate the O_3 and HO_x yields from the oxidation of CH_4 in two extreme cases. Consider first a situation where CH_3O_2 and HO_2 react only by (R18) and (R10) respectively (high- NO_x regime)

and CH_2O is removed solely by (R24). By summing all reactions in the mechanism we arrive at the following net reaction for conversion of CH_4 to CO_2 :



with an overall yield of five O_3 molecules and two HO_x molecules per molecule of CH_4 oxidized. Similarly to CO, the oxidation of CH_4 in this high- NO_x case is a chain mechanism for O_3 production where HO_x and NO_x serve as catalysts. Reaction (R24), which provides the extra source of HO_x as part of the propagation sequence, branches the chain (section 9.4).

In contrast, consider an atmosphere devoid of NO_x so that CH_3O_2 reacts by (R17); further assume that CH_3OOH reacts by (R19) and CH_2O reacts by (R23). Summing all reactions in the mechanism yields the net reaction:



so that no O_3 is produced and two HO_x molecules are consumed. This result emphasizes again the critical role of NO_x for maintaining O_3 and OH concentrations in the troposphere.

Oxidation of larger hydrocarbons follows the same type of chain mechanism as for CH_4 . Complications arise over the multiple fates of the organic peroxy (RO_2) and oxy (RO) radicals, as well as over the structure and fate of the carbonyl compounds and other oxygenated organics produced as intermediates in the oxidation chain. These larger hydrocarbons have smaller global sources than CH_4 and are therefore less important than CH_4 for global tropospheric chemistry. They are however critical for rapid production of O_3 in polluted regions, as we will see in chapter 12, and play also an important role in the long-range transport of NO_x , as discussed below.

11.4 GLOBAL BUDGET OF NITROGEN OXIDES

We now turn to an analysis of the factors controlling NO_x concentrations in the troposphere. Estimated tropospheric sources of NO_x for present-day conditions are shown in Table 11-3. Fossil fuel combustion accounts for about half of the global source.

Biomass burning, mostly from tropical agriculture and deforestation, accounts for another 25%. Part of the combustion source is due to oxidation of the organic nitrogen present in the fuel. An additional source in combustion engines is the thermal decomposition of air supplied to the combustion chamber. At the high temperatures of the combustion chamber (~ 2000 K), oxygen thermolyzes and subsequent reaction of O with N₂ produces NO:

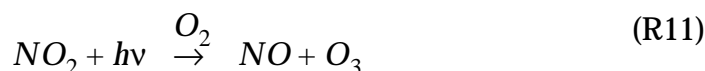


The equilibria (R27)-(R29) are shifted to the right at high temperatures, promoting NO formation. The same thermal mechanism also leads to NO emission from lightning, as the air inside the lightning channel is heated to extremely high temperatures. Other minor sources of NO_x in Table 11-3 include microbial nitrification and denitrification in soils (Section 6.3), oxidation of NH₃ emitted by the biosphere, and transport from the stratosphere of NO_y produced by oxidation of N₂O by O(¹D). Oxidation of N₂O does not take place in the troposphere itself because concentrations of O(¹D) are too low.

Table 11-3 Estimated present-day sources of tropospheric NO_x

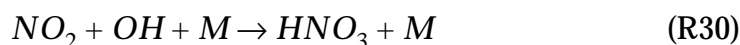
	Source, Tg N yr ⁻¹
Fossil fuel combustion	21
Biomass burning	12
Soils	6
Lightning	3
NH ₃ oxidation	3
Aircraft	0.5
Transport from stratosphere	0.1

Although NO_x is emitted mainly as NO, cycling between NO and NO₂ takes place in the troposphere on a time scale of a minute in the daytime by (R10)-(R11) and by the null cycle:

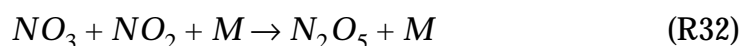
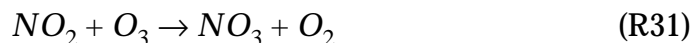


Because of this rapid cycling, it is most appropriate to consider the budget of the NO_x family as a whole, as in the stratosphere (section 10.2.2). At night, NO_x is present exclusively as NO_2 as a result of (R14).

Human activity is clearly a major source of NO_x in the troposphere, but quantifying the global extent of human influence on NO_x concentrations is difficult because the lifetime of NO_x is short. The principal sink of NO_x is oxidation to HNO_3 , as in the stratosphere; in the daytime,



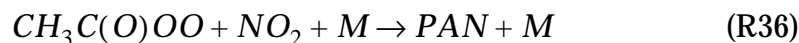
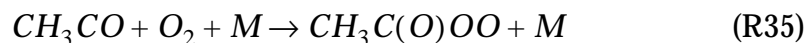
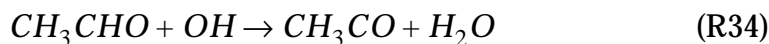
and at night,



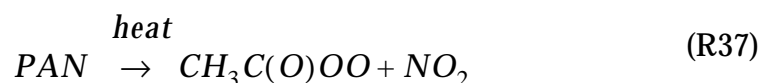
The resulting lifetime of NO_x is approximately one day. In the stratosphere, we saw that HNO_3 is recycled back to NO_x by photolysis and reaction with OH on a time scale of a few weeks. In the troposphere, however, HNO_3 is scavenged by precipitation because of its high solubility in water. The lifetime of water-soluble species against deposition is typically a few days in the lower troposphere and a few weeks in the upper troposphere (problem 8.1). We conclude that HNO_3 in the troposphere is removed principally by deposition and is not an effective reservoir for NO_x .

Research over the past decade has shown that a more efficient mechanism for long-range transport of anthropogenic NO_x to the global troposphere is through the formation of another reservoir species, peroxyacetylnitrate ($CH_3C(O)OONO_2$). Peroxyacetylnitrate (called PAN for short) is produced in the troposphere by photochemical oxidation of carbonyl compounds in the presence of NO_x . These carbonyls are produced by

photochemical oxidation of hydrocarbons emitted from a variety of biogenic and anthropogenic sources. In the simplest case of acetaldehyde (CH_3CHO), the formation of PAN proceeds by:



Formation of PAN is generally less important as a sink for NO_x than formation of HNO_3 . However, in contrast to HNO_3 , PAN is only sparingly soluble in water and is not removed by deposition. Its principal loss is by thermal decomposition, regenerating NO_x :



The lifetime of PAN against (R37) is 1 hour at 295 K and several months at 250 K; note the strong dependence on temperature. In the lower troposphere, NO_x and PAN are typically near chemical equilibrium. In the middle and upper troposphere, however, PAN can be transported over long distances and decompose to release NO_x far from its source, as illustrated in Figure 11-4.

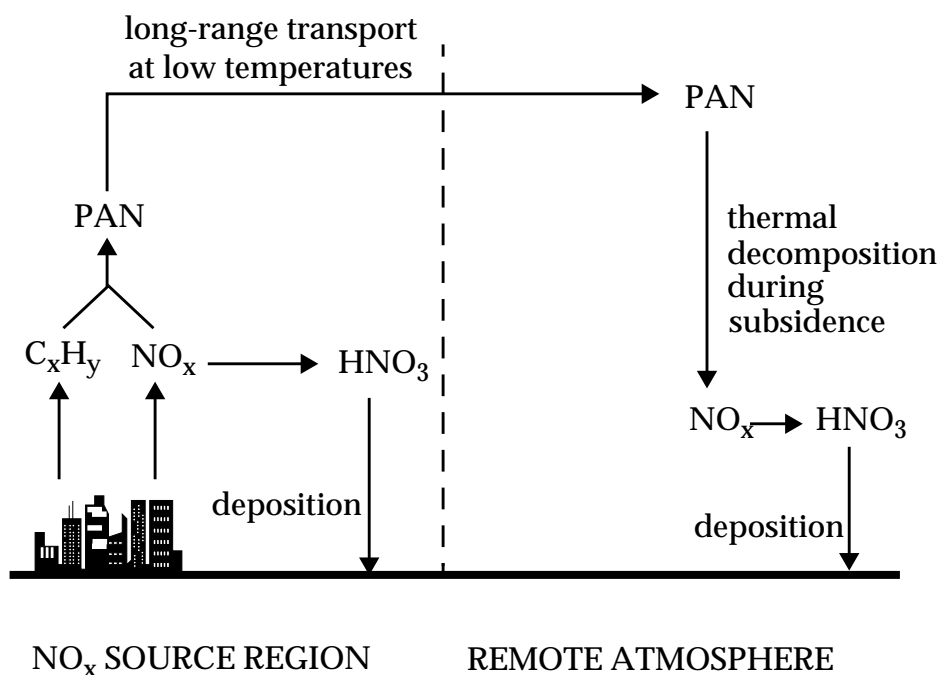
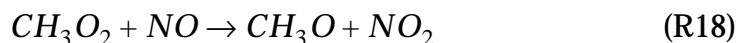
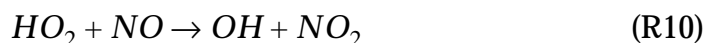


Figure 11-4 PAN as a reservoir for long-range transport of NO_x in the troposphere

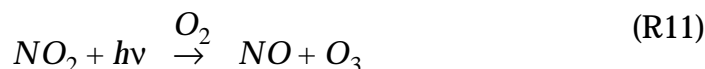
Measurements of PAN and NO_x concentrations in the remote troposphere over the past decade support the view that long-range transport of PAN at high altitude plays a critical role in allowing anthropogenic sources to affect tropospheric NO_x (and hence O_3 and OH) on a global scale. Although PAN is only one of many organic nitrates produced during the oxidation of hydrocarbons in the presence of NO_x , it seems to be by far the most important as a NO_x reservoir. Other organic nitrates either are not produced at sufficiently high rates or do not have sufficiently long lifetimes.

11.5 GLOBAL BUDGET OF TROPOSPHERIC OZONE

Tropospheric ozone is the precursor of OH by (R1)-(R3) and plays therefore a key role in maintaining the oxidizing power of the troposphere. It is also of environmental importance as a greenhouse gas (chapter 7) and as a toxic pollutant in surface air (chapter 12). We saw in section 11.3 that O_3 is supplied to the troposphere by transport from the stratosphere, and is also produced within the troposphere by cycling of NO_x involving reactions of peroxy radicals with NO:



followed by



The reactions of NO with peroxy radicals (R10)-(R18), driving O_3 production, compete with the reaction of NO with O_3 , driving the null cycle (R14)-(R11). Reactions (R10)-(R18) represent therefore the rate-limiting step for O_3 production, and the O_3 production rate P_{O_3} is given by

$$P_{\text{O}_3} = (k_{10}[\text{HO}_2] + k_{18}[\text{CH}_3\text{O}_2])[\text{NO}] \quad (11.7)$$

Other organic peroxy radicals RO_2 produced from the oxidation of nonmethane hydrocarbons also contribute to O_3 production but are less important than HO_2 and CH_3O_2 except in continental regions with high hydrocarbon emissions (chapter 12).

Loss of O₃ from the troposphere takes place by photolysis to O(¹D) followed by the reaction of O(¹D) with H₂O. The rate limiting step for O₃ loss is reaction (R3) (section 11.1.1):



Ozone is also consumed by reactions with HO₂ and OH in remote regions of the troposphere (section 11.3.2):



Additional loss of O₃ takes place by reaction with organic materials at the Earth's surface (*dry deposition*).

Table 11-4 Present-day global budget of tropospheric ozone

	Tg O ₃ yr ⁻¹
SOURCES	3400-5700
Chemical production	3000-4600
HO ₂ + NO	(70%)
CH ₃ O ₂ + NO	(20%)
RO ₂ + NO	(10%)
Transport from stratosphere	400-1100
SINKS	3400-5700
Chemical loss	3000-4200
O(¹ D) + H ₂ O	(40%)
HO ₂ + O ₃	(40%)
OH + O ₃	(10%)
others	(10%)
Dry deposition	500-1500

Global models of tropospheric chemistry which integrate HO_x-NO_x-CO-hydrocarbon chemical mechanisms in a

3-dimensional framework (chapter 5) have been used to estimate the importance of these different sources and sinks in the tropospheric O₃ budget. Table 11-4 gives the range of results from the current generation of models. It is now fairly well established that the abundance of tropospheric O₃ is largely controlled by chemical production and loss within the troposphere. Transport from the stratosphere and dry deposition are relatively minor terms.

11.6 ANTHROPOGENIC INFLUENCE ON OZONE AND OH

Figure 11-5 shows the global mean distributions of NO_x, CO, O₃, and OH simulated with a 3-dimensional model of tropospheric chemistry for present-day conditions.

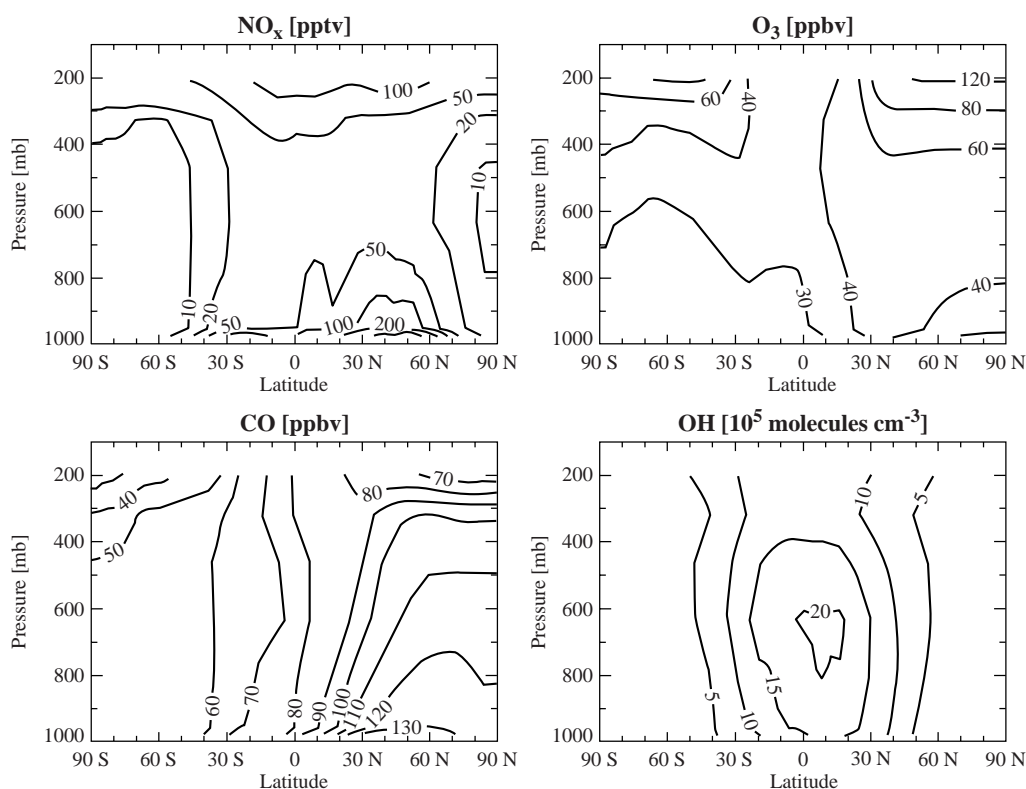


Figure 11-5. Longitudinally averaged concentrations of NO_x, CO, O₃, and OH as a function of latitude and pressure computed with a global 3-dimensional model for the present-day atmosphere. Values are annual averages. Adapted from Wang, Y., and D.J. Jacob, *J. Geophys. Res.*, in press.

Concentrations of NO_x and CO are highest in the lower troposphere at northern midlatitudes, reflecting the large source from fossil fuel combustion. Lightning is also a major source of

NO_x in the upper troposphere. Recycling of NO_x through PAN maintains NO_x concentrations in the range of 10-50 pptv throughout the remote troposphere. Ozone concentrations generally increase with altitude, mainly because of the lack of chemical loss in the upper troposphere (water vapor and hence HO_x concentrations are low). Higher O_3 concentrations are found in the northern than in the southern hemisphere, reflecting the abundance of NO_x . Concentrations of OH are highest in the tropics where water vapor and UV radiation are high, and peak in the middle troposphere because of opposite vertical trends of water vapor (decreasing with altitude) and UV radiation (increasing with altitude). Concentrations of OH tend to be higher in the northern than in the southern hemisphere because of higher O_3 and NO_x , stimulating OH production; this effect compensates for the faster loss of OH in the northern hemisphere due to elevated CO.

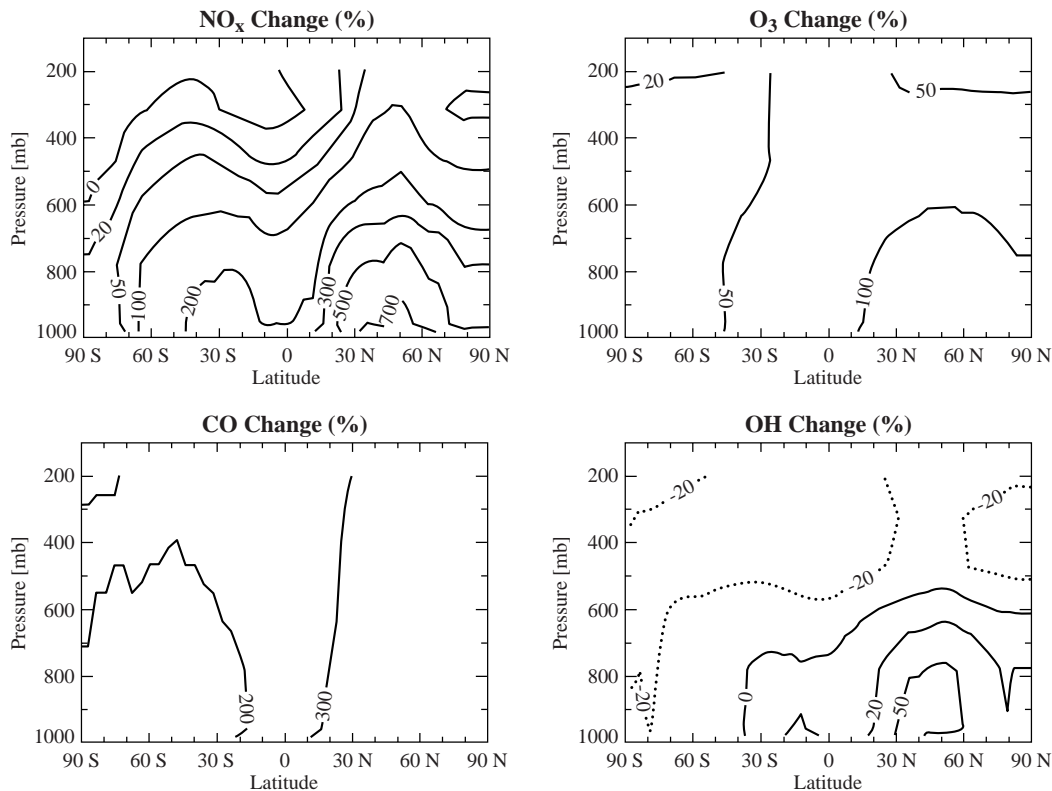


Figure 11-6 Relative enhancements of NO_x , CO, O_3 , and OH concentrations from preindustrial times to present, as computed with a global model of tropospheric chemistry. Values are annual longitudinal averages plotted as a function of latitude and pressure. Adapted from Wang, Y., and D.J. Jacob, *J. Geophys. Res.*, in press.

Figure 11-6 shows the relative enhancements of NO_x , CO, O_3 , and OH computed with the same model from preindustrial times to

today. The preindustrial simulation assumes no emission from fossil fuel combustion and a much reduced emission from biomass burning. Results suggest that anthropogenic emissions have increased NO_x and CO concentrations in most of the troposphere by factors of 2-8 (NO_x) and 3-4 (CO). Ozone concentrations have increased by 50-100% in most of the troposphere, the largest increases being at low altitudes in the northern hemisphere.

The anthropogenic influence on OH is more complicated. Increasing NO_x and O_3 act to increase OH, while increasing CO and hydrocarbons act to deplete OH (section 11.3). Because CO and CH_4 have longer lifetimes than NO_x and O_3 , their anthropogenic enhancements are more evenly distributed in the troposphere. It is thus found in the model that the net effect of human activity is to increase OH in most of the lower troposphere and to decrease OH in the upper troposphere and in the remote southern hemisphere (Figure 11-6). There is compensation on the global scale so that the global mean OH concentration as defined by (11.5) decreases by only 7% since preindustrial times (other models find decreases in the range 5-20%). The relative constancy of OH since preindustrial times is remarkable in view of the several-fold increases of NO_x , CO, and CH_4 . There remain large uncertainties in these model analyses. From the CH_3CCl_3 observational record, which started in 1978, we do know that there has been no significant global change in OH concentrations for the past 20 years.

Further reading:

Intergovernmental Panel on Climate Change, *Climate Change 1994*, Cambridge University Press, 1995. Global budgets of tropospheric gases.

World Meteorological Organization, *Scientific assessment of ozone depletion: 1998*, WMO, Geneva, 1999. Models and long-term trends of tropospheric O_3 .