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 CH_4, toxic combustion gases such as CO, agents for stratospheric O_3 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 O_2 and O_3. These oxidants have large bond energies and are hence relatively unreactive except toward radicals (O_2 only toward highly unstable radicals). With a few exceptions, oxidation of non-radical atmospheric species by O_2 or O_3 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 H_2O. Production of OH is by reaction of water vapor with $O(^1D)$ (section 10.2.1):

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \tag{R1}$$

$$O(^1D) + M \rightarrow O + M \tag{R2}$$

$$O(^1D) + H_2O \rightarrow 2OH \tag{R3}$$
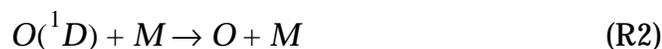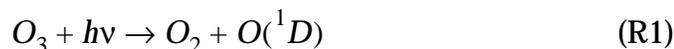
We saw in chapter 10 how OH oxidizes a number of trace gases in the stratosphere. A simple expression for the source P_{OH} of OH from reactions *(R1)-(R3)* can be obtained by assuming steady state for $O(^1D)$. Laboratory studies show that *(R2)* is much faster than *(R3)* at the H_2O mixing ratios found in the atmosphere, allowing for simplification:

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

$$\approx \frac{2k_1k_3}{k_2[M]}[O_3][H_2O] \tag{11.1}$$

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 O_3 column overhead. It was thought that oxidation of species emitted from the Earth's surface, such as CO and CH_4, required transport to the stratosphere followed by reaction with OH in the stratosphere:

$$CO + OH \rightarrow CO_2 + H \qquad\qquad (R4)$$
$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad\qquad (R5)$$

This mechanism implied long atmospheric lifetimes for CO and CH_4 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 CH_4 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 O_3, 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 O_3. 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 H_2O mixing ratios in the troposphere (10^2-10^3 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 10^6 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%.
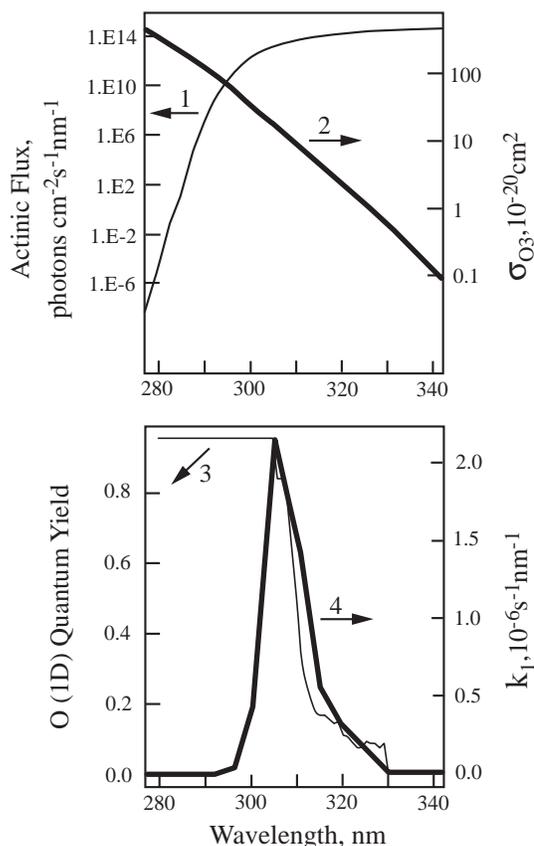
Figure 11-1. Computation of the rate constant k_1 for photolysis of O_3 to $O(^1D)$ in the troposphere as a function of wavelength. (1) Solar actinic flux at sea level for 30° solar zenith angle and a typical O_3 column overhead; (2) Absorption cross-section of O_3 at 273 K; (3) $O(^1D)$ quantum yield 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

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

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 CH_4 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.
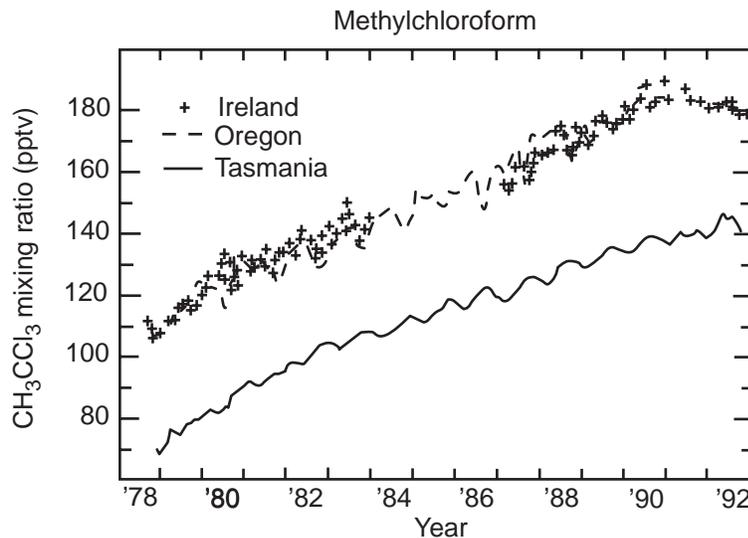
Figure 11-2 Atmospheric distribution and trend of methylchloroform. From *Scientific Assessment of Ozone Depletion: 1994,* WMO, 1995.

In the late 1970s it was discovered that the industrial solvent methylchloroform (CH_3CCl_3) could be used to estimate the global mean OH concentration. The source of CH_3CCl_3 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 CH_3CCl_3 in surface air has been measured continuously since 1978 at a worldwide network of sites (Figure 11-2). Rapid increase of CH_3CCl_3 was observed in the 1970s and 1980s due to rising industrial emissions, but concentrations began to decline in the 1990s because CH_3CCl_3 was one of the gases banned by the Montreal protocol to protect the O_3 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:

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

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

$$L_{trop} = \int_{trop} k(T)Cn_a[OH]dV \qquad (11.4)$$

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

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

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:

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

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 $\overline{[OH]}$ = 1.2×10^6 molecules cm^{-3}.

This empirical estimate of $\overline{[OH]}$ is useful because it can be used to estimate the lifetime $\tau_i = 1 / (k_i \overline{[OH]})$ 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 CH_4 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 CH_4

	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 CH_4 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 CH_4 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 $1\text{-}2\text{x}10^{13}$ 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 $2F = 2\text{-}4\text{x}10^{13}$ moles yr^{-1}. In comparison, the global source of CO to the atmosphere is $6\text{-}10\text{x}10^{13}$ moles yr^{-1} (Table 11-1) and the global source of CH_4 is about $3\text{x}10^{13}$ 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 ($NO_x \equiv NO + NO_2$) 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:

$$CO + OH \rightarrow CO_2 + H \tag{R4}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{R6}$$

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

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{R7}$$
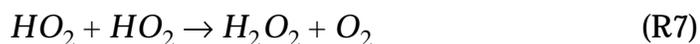
Hydrogen peroxide is highly soluble in water and is removed from the atmosphere by deposition on a time scale of a week. It can also photolyze or react with OH:

$$H_2O_2 + h\nu \rightarrow 2OH \tag{R8}$$

$$H_2O_2 + OH \rightarrow HO_2 + H_2O \tag{R9}$$
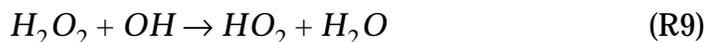
Reaction *(R8)* regenerates OH while *(R9)* consumes additional OH. Problem *11. 3* examines the implication of these different H_2O_2 loss pathways for the oxidizing power of the atmosphere.

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

$$HO_2 + NO \rightarrow OH + NO_2 \tag{R10}$$
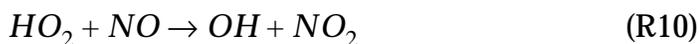
which regenerates OH, and also produces NO_2 which goes on to photolyze as we have already seen for the stratosphere (section 10.2.2):

$$NO_2 + h\nu \overset{O_2}{\rightarrow} NO + O_3 \tag{R11}$$
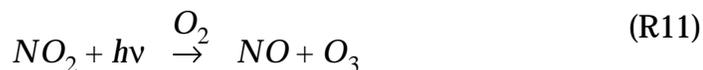
Reaction *(R11)* regenerates NO and produces an O_3 molecule, which can then go on to photolyze by reactions *(R1)-(R3)* to produce two additional OH molecules. Reaction *(R10)* thus yields up to three OH molecules, boosting the oxidizing power of the

atmosphere. The sequence of reactions *(R4)+(R6)+(R10)+(R11)* is a *chain mechanism* for O_3 production in which the oxidation of CO by O_2 is catalyzed by the HO_x chemical family ($HO_x \equiv H + OH + HO_2$) and by NO_x:

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2 \qquad \text{(R4+R6)}$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad \text{(R10)}$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3 \qquad \text{(R11)}$$
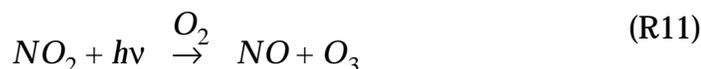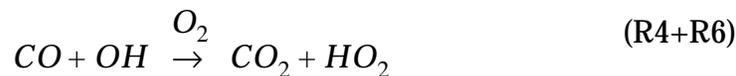
The resulting net reaction is

$$\text{net:} \quad CO + 2O_2 \rightarrow CO_2 + O_3$$

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 O_3, HO_x, and NO_x cycles is shown in Figure 11-3.
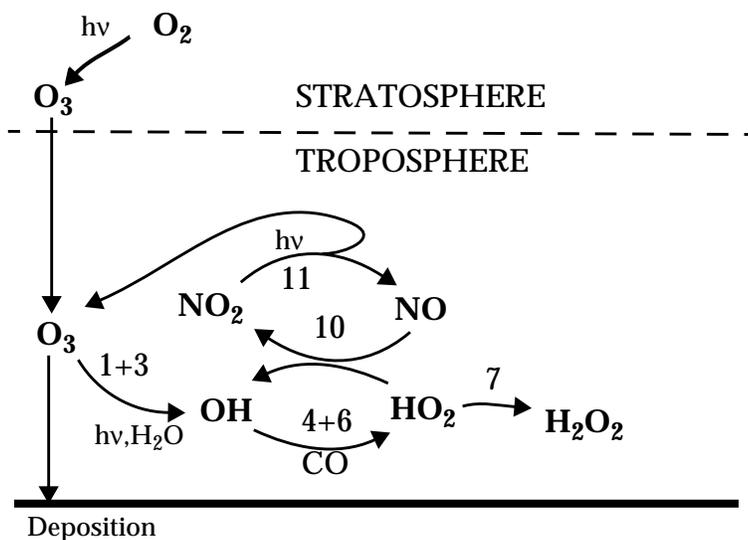
Figure 11-3 Mechanism for O_3-HO_x-NO_x-CO chemistry in the troposphere

Remarkably, HO_x and NO_x catalyze O_3 *production* in the troposphere and O_3 *destruction* in the stratosphere. Recall the catalytic HO_x and NO_x cycles for O_3 loss in the stratosphere (section 10.2):

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad \text{(R12)}$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad \text{(R13)}$$

and

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \text{(R14)}$$

$$NO_2 + O \rightarrow NO + O_2 \qquad \text{(R15)}$$
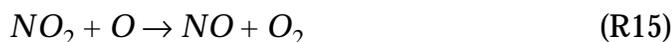
The key difference between the troposphere and the stratosphere is that O_3 and O concentrations are much lower in the troposphere. The difference is particularly large for O atom, whose concentrations vary as $[O_3]/n_a^2$ (equation *(10.4)*). In the troposphere, reaction *(R12)* is much slower than 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:

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad \text{(R5)}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad \text{(R16)}$$
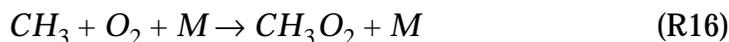
The methylperoxy radical (CH_3O_2) is analogous to HO_2 and is considered part of the HO_x family. Its main sinks are reaction with HO_2 and NO:

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \qquad \text{(R17)}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad \text{(R18)}$$

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:

$$CH_3OOH + OH \rightarrow CH_2O + OH + H_2O \qquad \text{(R19)}$$

$$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O \qquad \text{(R20)}$$

$$CH_3OOH + h\nu \rightarrow CH_3O + OH \qquad \text{(R21)}$$
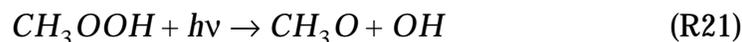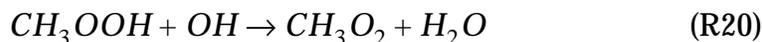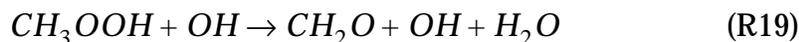
The methoxy radical (CH_3O) produced by reactions *(R18)* and *(R21)* goes on to react rapidly with O_2:

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad \text{(R22)}$$

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):

$$CH_2O + OH \rightarrow CHO + H_2O \qquad \text{(R23)}$$

$$CH_2O + h\nu \quad \overset{O_2}{\rightarrow} \quad CHO + HO_2$$
$$\text{(R24)}$$

$$CH_2O + h\nu \rightarrow CO + H_2 \qquad \text{(R25)}$$
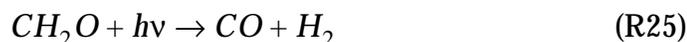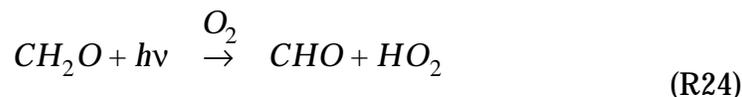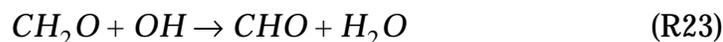
Reactions *(R23)* and *(R24)* produce the CHO radical, which reacts rapidly with O_2 to yield CO and HO_2:

$$CHO + O_2 \rightarrow CO + HO_2 \qquad \text{(R26)}$$

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:

$$\text{net:} \quad CH_4 + 10\,O_2 \rightarrow CO_2 + H_2O + 5\,O_3 + 2\,OH$$

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:

$$\text{net:} \quad CH_4 + 3\,OH + 2\,O_2 \rightarrow CO_2 + 3\,H_2O + HO_2$$
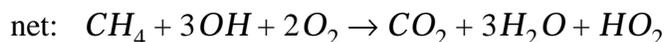
so that no O_3 is produced and two HO_x molecules are consumed. This result emphasizes again the critical role of NO_x for maintaining O_3 and OH concentrations in the troposphere.

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 N_2 produces NO:

$$O_2 \overset{heat}{\Leftrightarrow} O + O \qquad \text{(R27)}$$

$$O + N_2 \Leftrightarrow NO + N \qquad \text{(R28)}$$

$$N + O_2 \Leftrightarrow NO + O \qquad \text{(R29)}$$

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 NH_3 emitted by the biosphere, and transport from the stratosphere of NO_y produced by oxidation of N_2O by $O(^1D)$. Oxidation of N_2O 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 NO_2 takes place in the troposphere on a time scale of a minute in the daytime by *(R10)-(R11)* and by the null cycle:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R14}$$

$$NO_2 + h\nu \overset{O_2}{\rightarrow} NO + O_3 \tag{R11}$$
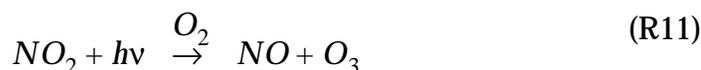
Because of this rapid cycling, it is most appropriate to consider the budget of the NO_x family as a whole, as in the stratosphere (section 10.2.2). At night, NO_x is present exclusively as NO_2 as a result of *(R14)*.

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,

$$NO_2 + OH + M \rightarrow HNO_3 + M \tag{R30}$$

and at night,

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R31}$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \tag{R32}$$

$$N_2O_5 + H_2O \overset{aerosol}{\rightarrow} 2HNO_3 \tag{R33}$$
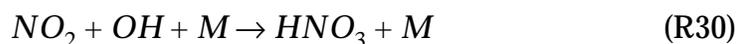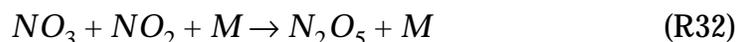
The resulting lifetime of NO_x is approximately one day. In the stratosphere, we saw that HNO_3 is recycled back to NO_x by photolysis and reaction with OH on a time scale of a few weeks. In the troposphere, however, HNO_3 is scavenged by precipitation because of its high solubility in water. The lifetime 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:

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \qquad \text{(R34)}$$

$$CH_3CO + O_2 + M \rightarrow CH_3C(O)OO + M \qquad \text{(R35)}$$

$$CH_3C(O)OO + NO_2 + M \rightarrow PAN + M \qquad \text{(R36)}$$
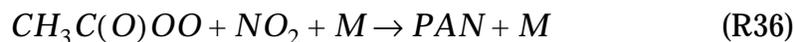
Formation of PAN is generally less important as a sink for NO_x than formation of HNO_3. However, in contrast to HNO_3, PAN is only sparingly soluble in water and is not removed by deposition. Its principal loss is by thermal decomposition, regenerating NO_x:

$$PAN \xrightarrow{heat} CH_3C(O)OO + NO_2 \qquad \text{(R37)}$$

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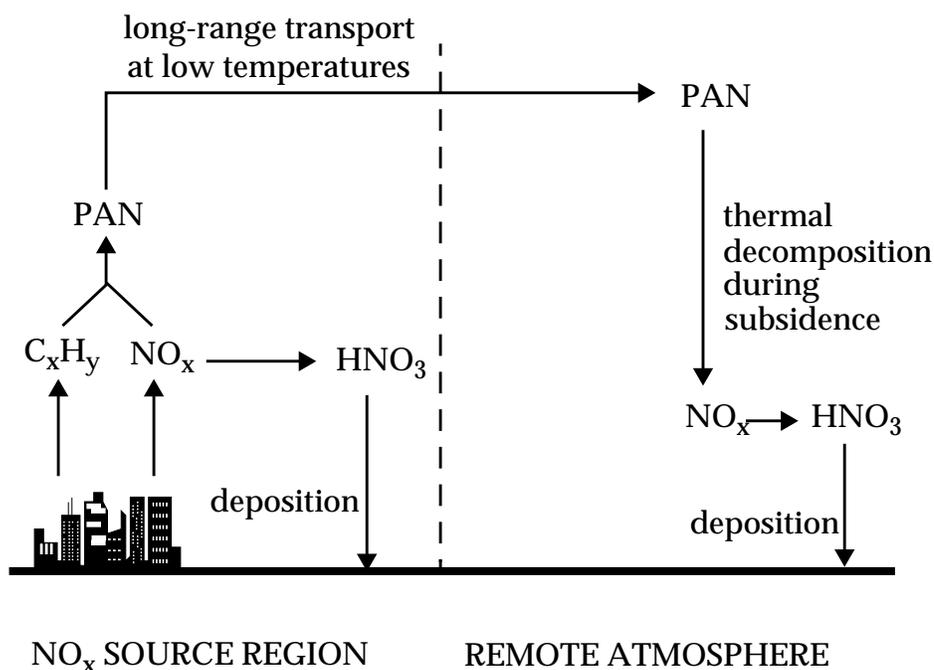
Figure 11-4 PAN as a reservoir for long-range transport of NO_x in the troposphere

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:

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (R10)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad (R18)$$

followed by

$$NO_2 + h\nu \overset{O_2}{\rightarrow} NO + O_3 \qquad (R11)$$
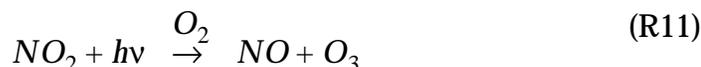
The reactions of NO with peroxy radicals *(R10)-(R18)*, driving O_3 production, compete with the reaction of NO with O_3, driving the null cycle *(R14)-(R11)*. Reactions *(R10)-(R18)* represent therefore the rate-limiting step for O_3 production, and the O_3 production rate P_{O3} is given by

$$P_{O3} = (k_{10}[HO_2] + k_{18}[CH_3O_2])[NO] \qquad (11.7)$$

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 O_3 from the troposphere takes place by photolysis to $O(^1D)$ followed by the reaction of $O(^1D)$ with H_2O. The rate limiting step for O_3 loss is reaction *(R3)* (section 11.1.1):

$$O(^1D) + H_2O \rightarrow 2OH \qquad (R3)$$

Ozone is also consumed by reactions with HO_2 and OH in remote regions of the troposphere (section 11.3.2):

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad (R13)$$
$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (R12)$$

Additional loss of O_3 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%)
$CH_3O_2 + NO$	(20%)
$RO_2 + NO$	(10%)
Transport from stratosphere	400-1100
SINKS	3400-5700
Chemical loss	3000-4200
$O(^1D) + H_2O$	(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 O_3 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 O_3 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, O_3, and OH simulated with a 3-dimensional model of tropospheric chemistry for present-day conditions.
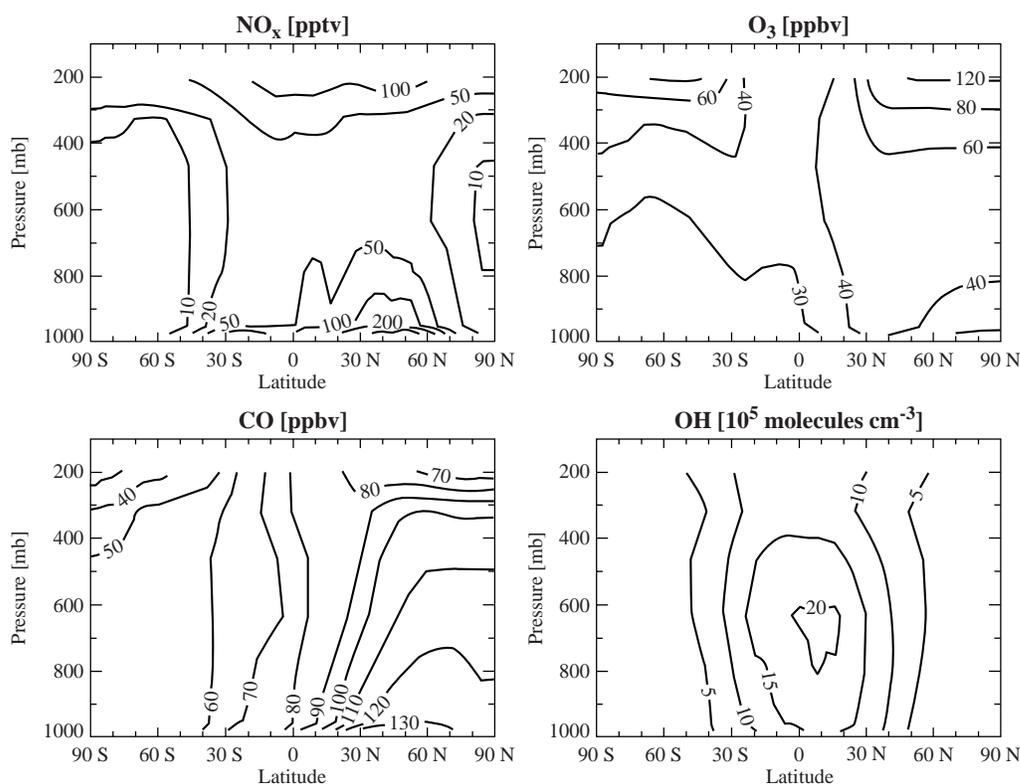
Figure 11-5. Longitudinally averaged concentrations of NO_x, CO, O_3, and OH as a function of latitude and pressure computed with a global 3-dimensional model for the present-day atmosphere. Values are annual averages. Adapted from Wang, Y., and D.J. Jacob, *J. Geophys. Res.*, in press.

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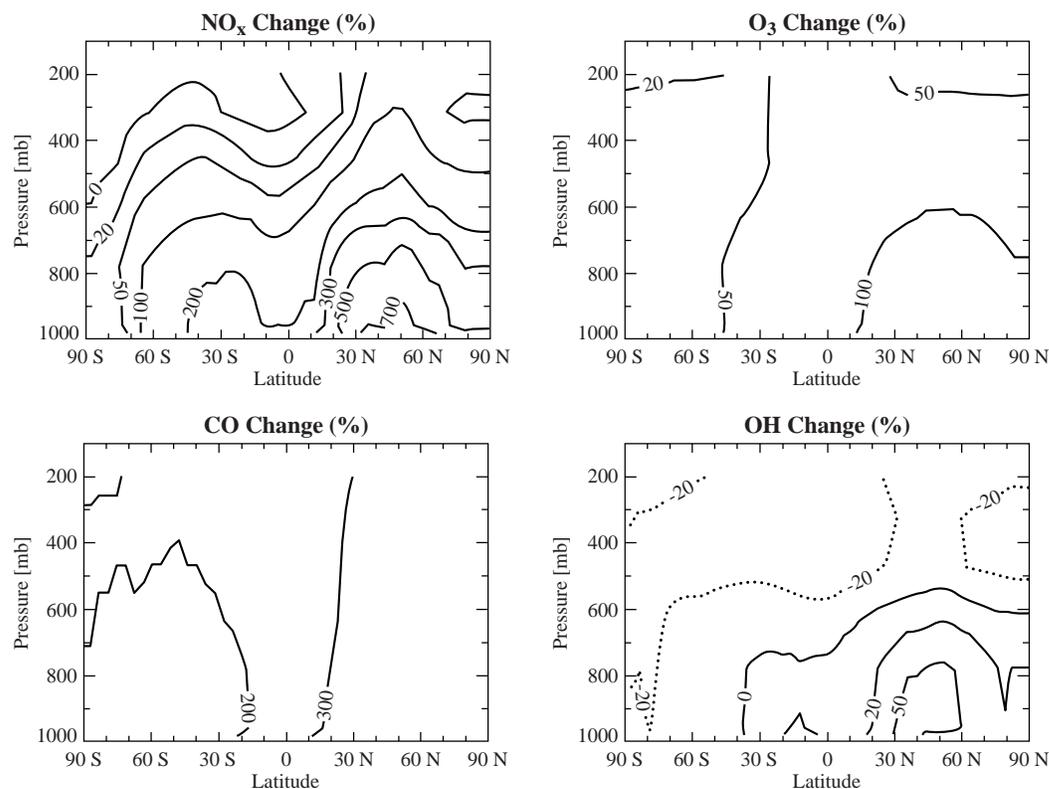
Figure 11-6 Relative enhancements of NO_x, CO, O_3, and OH concentrations from preindustrial times to present, as computed with a global model of tropospheric chemistry. Values are annual longitudinal averages plotted as a function of latitude and pressure. Adapted from Wang, Y., and D.J. Jacob, *J.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

PROBLEMS

11. 1 Sources of CO

The two principal sources of CO to the atmosphere are oxidation of CH_4 and combustion. Mean rate constants for oxidation of CH_4 and CO by OH in the troposphere are $k_1 = 2.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} and $k_2 = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively. Observations indicate mean CO concentrations of 80 ppbv in the northern hemisphere and 50 ppbv in the southern hemisphere, and a globally uniform CH_4 concentration of 1700 ppbv. Calculate the fraction of the CO source in each hemisphere contributed by oxidation of CH_4. Comment on the interhemispheric difference.

11. 2 Sources of tropospheric ozone

1. Ozone is supplied to the troposphere by transport from the stratosphere. We estimate here the magnitude of this source by using the two-box model for stratosphere-troposphere exchange introduced in problem 3. 3, where $k_{ST} = 0.7$ yr^{-1} is the transfer rate constant of air from the stratosphere to the troposphere and $k_{TS} = 0.14$ yr^{-1} is the reverse transfer rate constant from the troposphere to the stratosphere. Observations indicate that the atmosphere contains 5×10^{13} moles of O_3 and that 90% of that total is in the stratosphere (the remaining 10% is in the troposphere). Calculate the net source of tropospheric O_3 contributed by transport from the stratosphere.

2. Ozone is also produced within the troposphere by oxidation of CO and hydrocarbons (principally CH_4) in the presence of NO_x. One of the earliest estimates of the global source of ozone in the troposphere was done by scaling the emission inventories of CH_4 and CO.   We repeat this calculation here. Consider the following mechanism for oxidation of CH_4 and CO to CO_2 under high-NO_x conditions:

$$CH_4 + OH \xrightarrow{O_2} CH_3O_2 + H_2O$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$
$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$
$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$CH_2O + OH \rightarrow CHO + H_2O$$

$$CHO + O_2 \rightarrow CO + HO_2$$
$$O_2$$
$$CO + OH \rightarrow CO_2 + HO_2$$
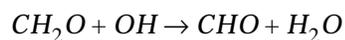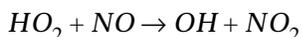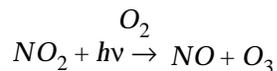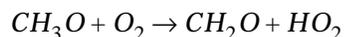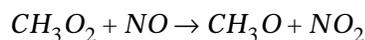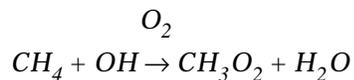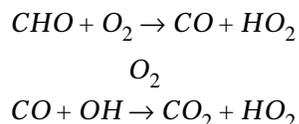
2.1 Write a net reaction for the oxidation of CO to CO_2 by the above mechanism. Do the same for the oxidation of CH_4 to CO_2 (some of the reactions may proceed more than once). How many O_3 molecules are produced per molecule of CO oxidized? per molecule of CH_4 oxidized?

2.2 Present-day global emission estimates are 3×10^{13} moles yr^{-1} for CH_4 and 4×10^{13} moles yr^{-1} for CO. Using your results from question 2.1, estimate the global production rate of ozone in the troposphere.

2.3 The range of estimates for the global chemical production rate of ozone in the troposphere, as derived from 3-dimensional models of tropospheric chemistry, is $6\text{-}10 \times 10^{13}$ moles yr^{-1}. Explain how the approach you used in question 2.2 might be expected to overestimate the production rate of ozone.

2.4 Conclude as to the relative importance of transport from the stratosphere and production within the troposphere as sources of tropospheric ozone.

11. 3 Oxidizing power of the atmosphere

1. Consider the mechanism for oxidation of CH_4 to CO_2:

$$CH_4 + OH \xrightarrow{O_2} CH_3O_2 + H_2O \tag{1}$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \tag{2a}$$

$$CH_3O_2 + NO \xrightarrow{O_2} CH_2O + NO_2 \tag{2b}$$

$$CH_3OOH + h\nu \xrightarrow{O_2} CH_2O + HO_2 + OH \tag{3a}$$

$$CH_3OOH + OH \rightarrow CH_2O + OH + H_2O \tag{3b}$$

$$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O \tag{3c}$$

$$CH_2O + h\nu \xrightarrow{O_2} CO + 2HO_2 \tag{4a}$$

$$CH_2O + h\nu \rightarrow CO + H_2 \tag{4b}$$

$$CH_2O + OH \xrightarrow{O_2} CO + HO_2 + H_2O \qquad (4c)$$

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2 \qquad (5)$$
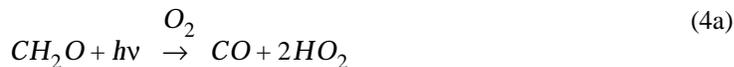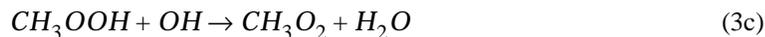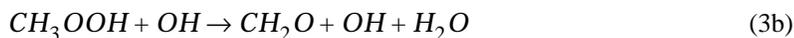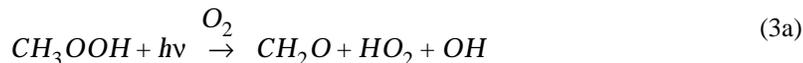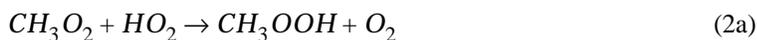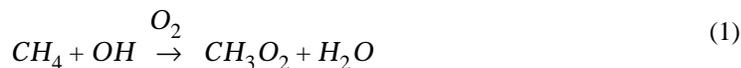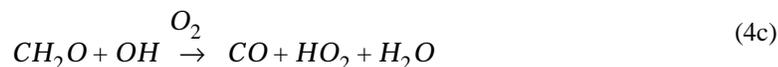
Assume the following branching ratios: (2:1) for loss of CH_3O_2 by (2a:2b), (1:1:1) for loss of CH_3OOH by (3a:3b:3c), (2:1:1) for loss of CH_2O by (4a:4b:4c). These ratios are typical of lower tropospheric air in the tropics.

1.1 Show that $9/7 = 1.29$ molecules of CH_3O_2 are produced in the oxidation of one molecule of methane to CO_2. (1st hint: Reaction (3c) recycles CH_3O_2. 2nd hint: $1/(1-x) = 1 + x + x^2 + ...$).

1.2. Which reactions in the mechanism consume OH? Which reactions produce OH? What is the net number of OH molecules consumed in the oxidation of one molecule of methane to CO_2?

1.3. What is the net number of HO_2 molecules produced in the oxidation of one molecule of methane to CO_2?

1.4. What is the net number of HO_x molecules consumed in the oxidation of one molecule of methane to CO_2? Could modifications in the branching ratios of (2), (3), (4) turn the oxidation of methane into a net source of HO_x? How so? How would it be possible to modify the branching ratios?

2. We go on to examine the efficiency with which the HO_2 produced from methane oxidation is recycled back to OH. The following reactions are important:

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (6a)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad (6b)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (6c)$$

$$H_2O_2 + h\nu \rightarrow 2OH \qquad (7a)$$

$$H_2O_2 + OH \rightarrow HO_2 + H_2O \qquad (7b)$$

Assume branching ratios (1:1:2) for loss of HO_2 by (6a:6b:6c) and (1:1) for loss of H_2O_2 by (7a:7b).

2.1. What net fraction of HO_2 molecules is recycled to OH?

2.2. Taking into account this recycling, how many OH molecules are actually lost in the oxidation of one molecule of methane to CO_2? How many OH molecules are actually lost in the oxidation of one molecule of CO to CO_2?

2.3. The global average CH_4 and CO emission fluxes are estimated to be 1.2 and 1.9×10^{11} molecules cm^{-2} s^{-1}, respectively. Assume a fixed global average OH source from O_3 photolysis of 2.9×10^{11} molecules cm^{-2} s^{-1} in the troposphere, and fixed branching ratios taken from above for all reactions in the mechanism. Based on the mechanism, would OH be titrated if CH_4 emissions doubled? If CO emissions doubled?

2.4. In fact the branching ratios would change if OH concentrations changed. How could these changes help in providing stability to OH? Which branching ratio is most critical for ensuring OH stability?

11. 4 OH concentrations in the past

There has been interest in using Greenland ice core measurements of methane (CH_4) and formaldehyde (CH_2O) to derive OH concentrations in the past.

1. The main sink for CH_2O in the Arctic is photolysis, with a mean rate constant $k = 1 \times 10^{-5}$ s^{-1}. Oxidation of CH_4 is the only significant source of CH_2O. Show that the steady-state concentration of CH_2O is given by

$$[CH_2O] = \frac{k'}{k}[CH_4][OH]$$

where $k' = 2.0 \times 10^{-12}$ exp(-1700/T) cm^3 molecule^{-1} s^{-1} is the rate constant for oxidation of methane by OH.

2. The Table below shows the concentrations (ppbv) of CH_2O and CH_4 in Greenland for three historical periods: present, pre-industrial (1600 A.D.), and last glaciation (18,000 B.C.).

	$[CH_4]$	$[CH_2O]$	T, K
Present	1700	0.10	260
Preindustrial	740	0.050	260
Glacial	410	0.010	250

2.1. Compute the OH concentration (molecules cm^{-3}) over Greenland for each period.

2.2. How do you interpret the difference in OH concentrations between pre-industrial times and today?

2.3. One possible explanation for the difference in OH concentrations between glacial and pre-industrial times is that stratospheric ozone concentrations were higher in glacial times. Why would that be? How would that affect OH concentrations?

[Source: Staffelbach, T., et al., Formaldehyde in polar ice cores: a possibility to characterize the atmospheric sink of methane in the past?, *Nature, 349*, 603-605, 1991.]

11. 5 Acetone in the upper troposphere

Recent measurements have revealed the ubiquitous presence of high concentrations of acetone in the upper troposphere, raising interest in the possible implications for tropospheric O_3. Acetone is emitted to the atmosphere by both biogenic and anthropogenic sources, and is removed from the atmosphere mainly by photolysis (λ < 360 nm).   Consider the following mechanism for complete oxidation of acetone to CO_2 in the atmosphere:

$$CH_3C(O)CH_3 + h\nu \xrightarrow{2O_2} CH_3C(O)OO + CH_3O_2 \qquad (1)$$

$$CH_3C(O)OO + NO \xrightarrow{O_2} CH_3O_2 + CO_2 + NO_2 \qquad (2)$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3 \qquad (3)$$

$$CH_3O_2 + NO \xrightarrow{O_2} CH_2O + HO_2 + NO_2 \qquad (4)$$

$$CH_2O + h\nu \xrightarrow{2O_2} CO + 2HO_2 \qquad (5)$$

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2 \qquad (6)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (7)$$
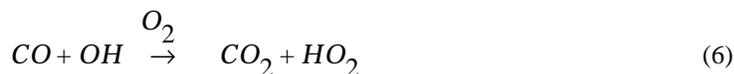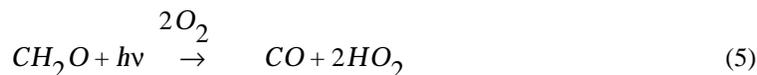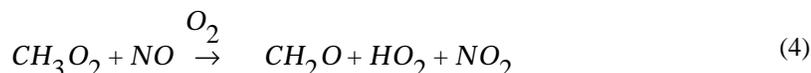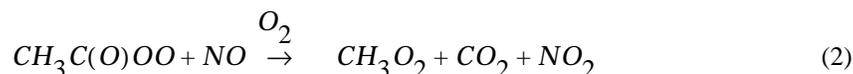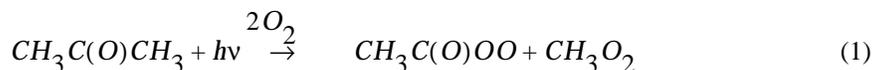
We assume in this problem a typical lifetime of 1 month for acetone ($k_1 = 3.7\text{x}10^{-7}$ s^{-1}).

1. How many O_3 molecules and how many HO_x molecules are produced in the complete oxidation of one molecule of acetone to CO_2 by reactions (1)-(7)? (note that some of the reactions may proceed more than once)

2. The source of HO_x from photolysis of acetone can be compared to the source from photolysis of O_3:

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \tag{8}$$

$$O(^1D) + M \rightarrow O + M \tag{9}$$

$$O(^1D) + H_2O \rightarrow 2OH \tag{10}$$

with rate constants $k_8 = 1.0 \times 10^{-5}$ s^{-1}, $k_9 = 3.6 \times 10^{-11}$ cm^{-3} molecule^{-1} s^{-1}, $k_{10} = 2.2 \times 10^{-10}$ cm^{-3} molecule^{-1} s^{-1}. For typical conditions at 10 km altitude with 67 ppmv H_2O, 50 ppbv O_3, 0.5 ppbv acetone, and an air density [M] = 8×10^{18} molecules cm^{-3}, compare the source of HO_x from reaction (10) to that from conversion of acetone to CO_2.

3. You should have found in question 2 that photolysis of acetone is an important source of HO_x in the upper troposphere. One finds by contrast that it is a negligible source of HO_x in the lower troposphere or in the stratosphere. Why?

4. The upper troposphere also contains 100 ppbv CO. The lifetime of CO against oxidation by OH is estimated to be 3 months.

4.1. How many molecules of O_3 and of HO_x are produced in the oxidation of one molecule of CO to CO_2?

4.2. Compare the O_3 production rates resulting from the oxidation of CO and from the photolysis of acetone. Do you conclude that O_3 production in the upper troposphere is insensitive to changes in the concentration of acetone? Briefly explain.

[To know more: McKeen, S.A., et al., The photochemistry of acetone in the upper troposphere: a source of odd-hydrogen radicals, *Geophys. Res. Lett., 24,* 3177-3180, 1997.]

11. 6 Transport, rainout, and chemistry in the marine upper troposphere

We consider a simple dynamical model for the upper troposphere over the tropical oceans where direct transfer from the lower troposphere to the upper troposphere by deep convective clouds is balanced by large-scale subsidence. Let k_{ij} represent the first-order rate constant for transfer of air from layer i to layer j.

100 hPa — Tropopause

Upper troposphere (3)

k_{32}

250 hPa

k_{13}

Middle troposphere (2)

900 hPa

Lower troposphere (1)

1000 hPa — Surface
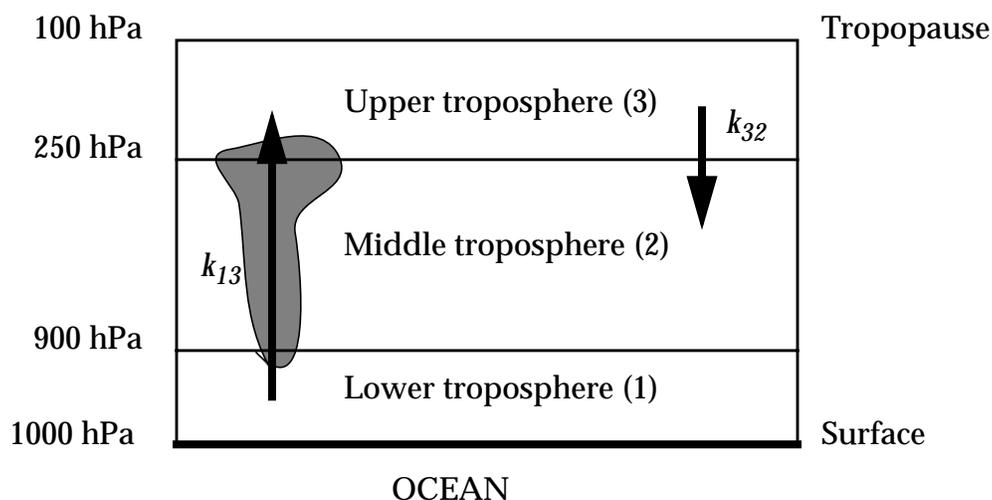
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1. We estimate the residence time of air in the upper troposphere in this model by using methyl iodide (CH_3I) as a tracer of transport. Methyl iodide is emitted from the oceans and has a lifetime of 4 days against photolysis. Mean CH_3I concentrations are 0.36 pptv in the lower troposphere and 0.10 pptv in the upper troposphere. Assuming steady state for CH_3I in the upper troposphere, show that the residence time of air in the upper troposphere is 10 days.

2. Deep convection provides a means for rapid transport of gases from the lower to the upper troposphere, but water-soluble gases are scavenged during transport by precipitation in the deep convective cloud. Consider a gas X with Henry's law constant K_X (M atm^{-1}) in a cloud of liquid water content L (volume of liquid water per volume of air). Show that the dimensionless fractionation f of X between the cloudwater (aq) and the gas phase (g) is given by

$$f = \frac{[X]_{aq}}{[X]_g} = K_X LRT$$

where the concentrations [ ] are moles per unit volume of air, R is the gas constant, and T is temperature.

3. Calculate f for the peroxides H_2O_2 ($K_{H2O2} = 2\times10^5$ M atm^{-1}) and CH_3OOH ($K_{CH3OOH} = 3\times10^3$ M atm^{-1}) for a typical cloud liquid water content $L = 1\times10^{-6}$ m^3 water/m^3 air and temperature $T = 250$ K (be careful with units!). Your results should show that H_2O_2 but not CH_3OOH is efficiently scavenged in deep convection.

4. Observed mean concentrations of CH_3OOH are 1100 pptv in the lower

troposphere and 80 pptv in the upper troposphere. Calculate the net source of CH_3OOH (molecules cm^{-3} s^{-1}) to the upper troposphere associated with deep convection. Use an air density $n_a = 4 \times 10^{18}$ molecules cm^{-3} for the upper troposphere.

5. In the upper troposphere, CH_3OOH photolyzes or reacts with OH, and the resulting CH_2O also photolyzes or reacts with OH:

$$CH_3OOH + h\nu \xrightarrow{O_2} CH_2O + HO_2 + OH \tag{1a}$$

$$CH_3OOH + OH \rightarrow CH_2O + OH + H_2O \tag{1b}$$

$$CH_2O + h\nu \rightarrow CO + H_2 \tag{2a}$$

$$CH_2O + h\nu \xrightarrow{2O_2} CO + 2HO_2 \tag{2b}$$

$$CH_2O + OH \rightarrow CO + HO_2 + H_2O \tag{2c}$$
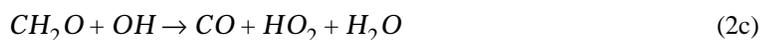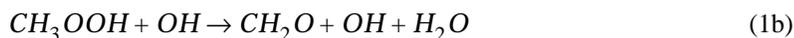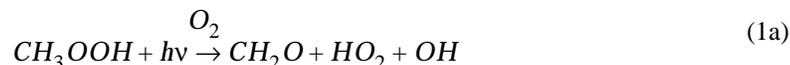
Branching ratios are (1:1) for (1a:1b) and (1:1:1) for (2a:2b:2c). Calculate the yield of HO_x per molecule of CH_3OOH injected to the upper troposphere, and from there the total HO_x source in the upper troposphere resulting from deep convective injection of CH_3OOH. Compare to a typical HO_x source of 1×10^4 molecules cm^{-3} s^{-1} in the upper troposphere from the $O(^1D)+H_2O$ reaction. Is convective injection of CH_3OOH an important source of HO_x in the upper troposphere?

[To know more: Prather, M.J., and D.J. Jacob, A persistent imbalance in HO_x and NO_x photochemistry of the upper troposphere driven by deep tropical convection, *Geophys. Res. Lett., 24,* 3189-3192, 1997.]

11. 7 Bromine chemistry in the troposphere

Events of rapid O_3 depletion are observed in arctic surface air in spring, with concentrations dropping from 40 ppbv (normal) to less than 5 ppbv in just a few days. These O_3 depletion events are associated with elevated bromine which appears to originate from the volatilization of sea salt bromide deposited on the ice pack. In this problem we examine the mechanism for Br-catalyzed O_3 loss thought to operate in arctic surface air. Consider a surface air parcel in the arctic at the onset of an O_3 depletion event. The air parcel contains 40 ppbv O_3, 50 pptv Br_y (sum of Br, BrO, HOBr, and HBr), 10 pptv CH_2O, 3×10^7 molecules cm^{-3} HO_2, and 1×10^5 molecules cm^{-3} OH. The air density in the parcel is 3×10^{19} molecules

cm^{-3}. Bromine chemistry is described by the reactions:

$$Br + O_3 \rightarrow BrO + O_2 \tag{1}$$

$$BrO + h\nu \xrightarrow{O_2} Br + O_3 \tag{2}$$

$$BrO + BrO \rightarrow 2Br + O_2 \tag{3}$$

$$Br + CH_2O \rightarrow HBr + CHO \tag{4}$$

$$BrO + HO_2 \rightarrow HOBr + O_2 \tag{5}$$

$$HBr + OH \rightarrow Br + H_2O \tag{6}$$

$$HOBr + h\nu \rightarrow OH + Br \tag{7}$$
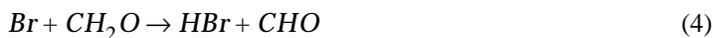
with rate constants $k_1 = 6\text{x}10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, $k_2 = 1\text{x}10^{-2}$ s^{-1}, $k_3 = 3\text{x}10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, $k_4 = 6\text{x}10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, $k_5 = 5\text{x}10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, $k_6 = 1.1\text{x}10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, and $k_7 = 1\text{x}10^{-4}$ s^{-1}.

1. Draw a diagram of the Br_y cycle. Identify a catalytic cycle for O_3 loss consisting of only two reactions, and highlight this cycle in your diagram.

2. Show that reaction (2) is the principal sink for BrO. What is the rate-limiting reaction for O_3 loss in the catalytic mechanism you described in question 1? Briefly explain.

3. Write an equation for the O_3 loss rate $(-d[O_3]/dt)$ in the catalytic mechanism as a function of [BrO]. What would the O_3 loss rate be if BrO were the main contributor to total bromine (that is, if [BrO] $\approx$ 50 ppt)? Would you predict near-total ozone depletion in a few days?

4. Ozone loss can in fact be slowed down by formation of HBr or HOBr.

4.1 Explain briefly why.

4.2 Assuming steady-state for all bromine species, calculate the concentrations of HOBr, HBr, BrO, and Br in the air parcel. How does the resulting O_3 loss rate compare to the value you computed in question 3? Would you still predict near-total O_3 depletion in a few days?

4.3. It has been proposed that O_3 depletion could be enhanced by reaction of HOBr with HBr in the Arctic aerosol followed by photolysis of Br_2:

$$HBr + HOBr \overset{aerosol}{\rightarrow} Br_2 + H_2O$$

$$Br_2 + h\nu \rightarrow 2Br$$
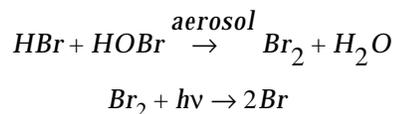
How would these two reactions help to explain the observed O_3 depletion? Draw a parallel to similar reactions occurring in the stratosphere.

[To know more: Haussmann, M., and U. Platt, Spectroscopic measurement of bromine oxide and ozone in the high Arctic during Polar Sunrise Experiment 1992, *J. Geophys. Res., 99,* 25399-25413, 1994]

11. 8 Nighttime oxidation of NO_x

Nighttime loss of NO_x in the lower troposphere proceeds by:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{2}$$

$$NO_2 + NO_3 + M \Leftrightarrow N_2O_5 + M \tag{3}$$

$$N_2O_5 \overset{aerosol, H_2O}{\rightarrow} 2HNO_3 \tag{4}$$

Reaction (3) is viewed as an equilibrium process with constant $K_3 = [N_2O_5]/([NO_3][NO_2]) = 3.6 \times 10^{-10}$ cm^3 molecule^{-1}. Other reactions have rate constants $k_1 = 3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, $k_2 = 2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}, and $k_4 = 3 \times 10^{-4}$ s^{-1}. Consider an air parcel with a temperature of 280 K, pressure of 900 hPa, and constant concentrations of 40 ppbv O_3 and 0.1 ppbv NO_x.

1. The above mechanism for NO_x loss operates only at night. Explain why.

2. At night, almost all of NO_x is present as NO_2 (the NO/NO_x concentration ratio is negligibly small). Explain why.

3. Let NO_3^* represent the chemical family composed of NO_3 and N_2O_5, that is, $[NO_3^*] = [NO_3] + [N_2O_5]$. Calculate the lifetime of NO_3^* at night.

4. Assuming that NO_3^* is in chemical steady state at night (your answer to question 3 should justify this assumption), and that the night lasts 12 hours, calculate the 24-hour average lifetime of NO_x against oxidation to HNO_3 by the above mechanism. Compare to the typical 1-day lifetime of NO_x against oxidation by OH.

[To know more: Dentener, F.J., and P.J. Crutzen, Reaction of N_2O_5 on tropospheric aerosols: impact on the global distributions of NO_x, O_3, and OH, *J. Geophys. Res., 98,* 7149-

11. 9 Peroxyacetylnitrate (PAN) as a reservoir for NO_x

1. Consider an urban atmosphere containing 100 ppbv NO_x and 100 ppbv O_3 with T = 298 K and P = 1000 hPa. Calculate the steady-state concentrations of NO and NO_2 at noon based on the null cycle:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

$$NO_2 + h\nu \overset{O_2}{\rightarrow} NO + O_3 \tag{2}$$

with $k_1 = 2.2 \times 10^{-12}$ exp(-1430/T) cm^3 molecule^{-1} s^{-1}, and $k_2 = 1 \times 10^{-2}$ s^{-1} (noon). How does the $[NO_2]/[NO_x]$ ratio vary with time of day? How would it be affected by the presence of peroxy radicals?

2. Photolysis of acetone ($CH_3C(O)CH_3$) is an important source of PAN. In a high-NO_x atmosphere, the peroxyacetyl radical ($CH_3C(O)OO$) produced by photolysis of acetone reacts with either NO or NO_2:

$$CH_3C(O)CH_3 + h\nu \overset{2O_2}{\rightarrow} CH_3C(O)OO + CH_3O_2 \tag{3}$$

$$CH_3C(O)OO + NO \overset{O_2}{\rightarrow} CH_3O_2 + CO_2 + NO_2 \tag{4a}$$

$$CH_3C(O)OO + NO_2 + M \rightarrow PAN + M \tag{4b}$$

$$PAN \rightarrow CH_3C(O)OO + NO_2 \tag{5}$$
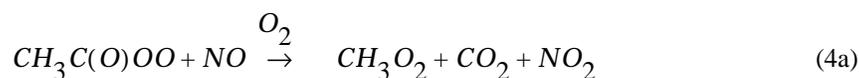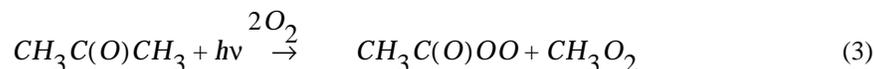
Derive an equation showing that the steady-state concentration of PAN is independent of NO_x but proportional to acetone and O_3. Explain qualitatively this result.

3. Consider an air parcel ventilated from a city at time t = 0 and subsequently transported for 10 days without exchanging air with its surroundings. We wish to examine the fate of NO_x as the air parcel ages. The air parcel contains initially 100 ppbv NO_x, zero PAN, and zero HNO_3. The lifetime of NO_x against conversion to HNO_3 is 1 day. We assume that HNO_3 is removed rapidly by deposition and cannot be recycled back to NO_x. We also assume [NO] << [NO_2] in the air parcel at all times (cf. question 1).