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The role of fixed nitrogen in atmospheric photochemistry

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Among the N compounds released to the atmosphere, NH_3 and the oxides N_2O, NO and NO_2 are most important. Various microbial and human activities constitute the main sources of these compounds. NH_3 strongly influences precipitation chemistry, but its role in atmospheric photochemistry is probably not very important. The oxides of N, however, must be regarded as key compounds. N_2O seems to be inert in the troposphere, but its oxidation is the main source of NO in the stratosphere. The more reactive NO and NO_2 act as catalysts in various photochemical reaction chains which affect the residence times of many carbon, sulphur and halogen compounds in the atmosphere through the role that they play in the ozone balance of the atmosphere. The atmospheric abundance of N_2O, NO, NO_2 and a variety of halogen compounds is increasingly influenced by man. As one of the consequences one may expect changes in the abundance of atmospheric ozone, perhaps leading to increased intensity of ultraviolet radiation at ground level or climatic changes.

INTRODUCTION

The composition of the natural atmosphere is to a considerable degree determined by biological processes, and a substantial fraction of the gases containing C, N and S is of biological origin. This is particularly true for N. The atmosphere constitutes the largest reservoir of N, and atmospheric photochemistry and the cycling of other elements through the atmosphere are markedly influenced by N compounds, predominantly by oxides of N.

Released to the atmosphere in lower oxidation states, N is further oxidized and transformed by photochemical reactions to nitric acid and nitrates. These compounds are very soluble in water and, therefore, removed from the atmosphere by precipitation scavenging and redeposition on the Earth's surface. After redeposition, nitric acid and nitrates enter the biogeochemical cycles in soil and water bodies supplying oxygen for redox processes in anoxic environments. The portion of the fixed N that is lost as N_2 is compensated for by biological N_2 fixation and by its production in the shock-waves created by electrical discharges in the atmosphere (lightning). The production of fixed N by industrial activities substantially disturbs this balance.

The atmospheric part of the global nitrogen cycle is dominated by fixed N in the form of ammonia (NH_3), nitrous oxide (N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2), nitric acid (HNO_3), and various organic N compounds. Among the N compounds released to the atmosphere as a result of microbiological and human activities, N_2O, NO and NO_2 are of particular importance. Acting as catalysts for various reaction chains, both in the troposphere and in the stratosphere, NO and NO_2 control the distribution of atmospheric ozone (O_3) to a high degree. The less reactive N_2O does not appear to participate in any gas-phase photochemical reactions in the troposphere, but it forms the main source of NO in the stratosphere.

Together with water vapour and carbon dioxide, ozone plays an essential role in the radiation budget of the Earth's atmosphere. This is due to its radiative properties in the ultraviolet and in the infrared. The absorption of u.v. radiation prevents harmful effects on the biosphere. As a result of the absorption of u.v. light by ozone, electronically excited $O(^1D)$ atoms are formed which react with water molecules to give hydroxyl radicals (OH). Many trace gases which otherwise would be inert in the troposphere, such as carbon monoxide (CO), hydrocarbons and chlorinated hydrocarbons, are attacked by OH. In the absence of tropospheric OH, the abundances of such gases would be much larger than observed, in many cases by orders of magnitude. The importance of atmospheric ozone for the average vertical temperature profile is well established. Reductions in the total abundance of atmospheric O_3 allow penetration of more solar radiation to the Earth's surface, resulting in higher surface temperatures. However, the decrease in downward long-wave radiation, emitted by CO_2, O_3 and H_2O from a possibly cooler lower stratosphere, containing less O_3, would actually produce a decrease in surface temperatures (Ramanathan *et al.* 1976). The climatic impact of changes in the composition of the stratospheric gas mixture was discussed by Liu *et al.* (1976*a*) and Ramanathan & Coakley (1978). Besides CO_2, H_2O and O_3, N_2O also absorbs significantly in the infrared. Therefore, any changes in the atmospheric abundance of N_2O are of interest for the terrestrial radiation budget (Wang *et al.* 1976). Recent work in the field of theoretical dynamic meteorology has shown the important role of stratospheric thermal stability in controlling the vertical transfer of wave energy between the troposphere and the stratosphere (Bates 1977; Lindzen & Tung 1978). As Bates (1977) pointed out, substantial reductions in upper stratospheric temperatures due to industrial activities could indirectly lead to marked changes in the horizontal heat flux by ultra-long planetary waves in the troposphere.

As a result of human activities, increasing amounts of oxidized gases are emitted into the atmosphere. The total global fluxes of man-made fixed N in the form of NO and of man-made fixed sulphur in the form of SO_2 into the atmosphere are now comparable with the biogenic fluxes of these elements. In contrast to biogenic emissions, industrial emissions are mainly from point sources, so that the atmospheric concentrations of various pollutants are highly non-uniformly distributed and often strongly correlated. Consequently, photochemical interactions between emitted gases are most important in polluted air masses.

The effects of additions of NO to the stratosphere, resulting from a number of human activities, especially the effect on stratospheric O_3, have been the subject of considerable concern and have led to intense research activities during the last decade on the distribution and chemistry of oxides of N in the stratosphere. Such NO emissions may be due to emission of exhaust gases of high-flying aircraft, particularly of large fleets of supersonic aircraft cruising between 16 and 20 km altitude (Johnston 1971; Crutzen 1971), and to increases in atmospheric N_2O, leading in turn to more stratospheric NO. In this article, we review only briefly the potential consequences of increased atmospheric N_2O levels. Various views on this subject have been published elsewhere (Crutzen 1976; McElroy *et al.* 1976, 1977; Crutzen & Ehhalt 1977; Liu *et al.* 1976*b*, 1977; Sze & Rice 1976; Pratt *et al.* 1977; Hahn & Junge 1977; N.A.S. 1978; Hahn 1979). Before the role of fixed N in the photochemistry of the troposphere and stratosphere is discussed, a brief summary of what is known about the atmospheric cycle of fixed N is in order.

Table 1. Oxidized N species in the atmosphere: sources, removal processes, lifetimes and diffusion distances in east–west, south–north, and vertical directions over which concentrations are reduced to 30% by chemical reactions

(Calculated with $[OH] = 7 \times 10^5$ cm^{-3}.)

species	source		annual emission rate	removal by	mean atmospheric lifetime	transfer distances
	primary	secondary	10^{12} g N			Δx, Δy, Δz/km
$NO+NO_2$	combustion		10–20	OH	1.5 days	1500, 400, 1
	jet aircraft		0.25	dry deposition		
	biomass burning		10–40			
	lightning		3–4			
	soils		0–15			
		oxidation of N_2O	0.3–0.8			
HNO_3		NO_2+OH	22–80	rain	*ca.* 3 days	3000, 600, 1.5
N_2O	combustion		1.8	photolysis in stratosphere	*ca.* 100 years	global
	biomass burning		1–2			
	oceans		1–10			
	soils, natural		0.7–7			
	soils, manipulated		1.5–3			
	N fertilizer application		0.4–4	other sinks?		

Table 2. Reduced N in the atmosphere: sources, removal processes, lifetimes and diffusion distances in east–west, south–north, and vertical directions over which concentrations are reduced to 30% by chemical reactions

(Calculated with $[OH] = 7 \times 10^5$ cm^{-3}.)

species	source		annual emission rate	removal by	mean atmospheric lifetime	transfer distances
	primary	secondary	10^{12} g N			Δx, Δy, Δz/km
NH_3	domestic animals		10–20	rain dry deposition	< 9 days	< 9000, 1000, 3
	wild animals		2–6			
	biomass burning		< 60			
	coal burning		4–12			
	soils, natural		< 30			
	N fertilizer application		< 3			
HCN	biomass burning		< 5	dry deposition	*ca.* 2 years	global

Atmospheric cycle of fixed nitrogen

As was mentioned above, fixed N is released to the atmosphere in various forms. All of these compounds are eventually converted to N_2, which is then turned into fixed N again at the Earth's surface as a result of various microbial and human activities. In addition, some NO is generated in the atmosphere by lightning and subsonic aircraft.

Global emission rates of important N species are compiled in tables 1 and 2. The emission rates are given in teragrams (10^{12} g) N per year. The listed values are based on estimates by Söderlund & Svensson (1976), updated with more recent data and assessments. Also given in the two tables are the removal processes, the mean atmospheric lifetimes, and the diffusion distances in east–west, south–north, and vertical directions over which concentrations are reduced to 30% by chemical reactions. The calculation of these distances was carried out assuming a mean OH concentration of $7 \times 10^5\ \mathrm{cm^{-3}}$ (see below). NO and NO_2 are not considered separately, since photochemical reactions establish an equilibrium between the two compounds.

As shown in table 1, there are various sources of atmospheric $NO + NO_2$. One important source is the oxidation of atmospheric N_2 in high-temperature combustion. The estimate of 10–20 Tg N annually is a compromise between the estimates of 8.2–18.5 Tg N by Böttger *et al.* (1980), and the 23 Tg N by Söderlund & Svensson (1976), who extrapolated from the 1965 emission rates of Robinson & Robbins (1968). There is clearly a need to derive up-to-date emission estimates of NO_x, considering its great importance in atmospheric photochemistry.

The emission of NO and NO_2 by subsonic aircraft above 9 km in the Northern Hemisphere was estimated at 0.25 Tg N annually (Liu *et al.* 1980). Considerable attention has recently been given to this source of NO–NO_2, although it is rather small compared with the emission rates of other combustion processes. Liu *et al.* (1980) postulated that, since this NO–NO_2 will reside much longer in the atmosphere (because of less probability of washout) than the NO–NO_2 emitted at low altitudes, aircraft emissions of NO–NO_2 would contribute significantly to the concentration of these two compounds in the upper troposphere together with NO–NO_2 of stratospheric origin. The validity of this argument depends on the efficiency of transfer of man-made NO–NO_2 from the ground to the upper troposphere. Such transport may be significant in occasional events of vigorous overturning of the troposphere during frontal passages and thunderstorms, since both NO and NO_2 are not very soluble in water. The significance of such a transport cannot be assessed by the current one-dimensional and two-dimensional models of the atmosphere, which consider only averaged motions and averaged deviations thereof.

Another major source of atmospheric NO–NO_2 appears to be the burning of biomass in the tropics. In this process, NO–NO_2 is formed mainly as a product of the oxidation of fixed N which comes with the biomass. The global source strength is difficult to assess. From studies by Crutzen *et al.* (1979) and by Seiler & Crutzen (1980), a figure of 20 ± 2 Tg N annually can be derived. Since this flux may represent only 30% of the fixed N contained in the biomass, there remains the possibility of emissions of large quantities of other N compounds. One of these compounds is N_2O. Other possible candidates are, e.g., NH_3, amines, HCN and maybe other nitriles (Schmeltz & Hoffmann 1977).

Lightning as a source of atmospheric NO–NO_2 was once estimated to be as large as 40 Tg N annually (see, for example, Chameides *et al.* 1977). Recent estimates are much lower. According to Hill *et al.* (1980) and Dawson (1979), this source produces only 3–4 Tg NO–NO_2-N annually.

The soil as a source of atmospheric NO–NO_2 still awaits careful evaluation. Laboratory studies have shown that the emission of NO is very dependent on soil acidity (Nelson & Bremner 1970). Söderlund & Svensson (1976) gave a range of 1–14 Tg N for the global annual emission of NO from soil. Galbally & Roy (1978) proposed 10 Tg N as the global annual emission rate extrapolating from results obtained from box measurements on some Australian soils. With so little information available, we propose a global annual production of 0–15 Tg N, which includes the possibility of no appreciable emission at all.

In the stratosphere, NO is produced by the reaction of N_2O with electronically excited atomic oxygen, $O(^1D)$:

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

$$N_2O + O(^1D) \rightarrow 2\,NO. \tag{2}$$

This source probably dominates any other sources of stratospheric NO–NO_2. Many estimates are available for the source strength, depending on the assumptions made about the stratospheric distribution of N_2O, of which there are far too few measurements. Especially critical in making these estimates are the assumptions about the vertical N_2O distribution in the tropics. From the analysis of one balloon flight at 9° N and several observations at other latitudes, Schmeltekopf *et al.* (1977) derived an average annual global vertically integrated production rate of 1.4 Tg N. The measured vertical N_2O profiles showing high stratospheric N_2O concentrations have been confirmed by three other flights near the equator by the same group (Goldan *et al.* 1980). The value of the NO_x production by Schmeltekopf *et al.* (1977) is, however, two times too high as the calculations were done for 24 h of sunlight. Model calculations indicate an annual production rate of NO from the oxidation of N_2O of 0.4 Tg N. Thus, the annual amount should be somewhere between 0.3 and 0.8 Tg NO-N.

Although difficult to assess, the possibility of some significant contribution to the stratospheric NO–NO_2 budget from higher altitudes cannot be ruled out. At high altitudes, huge quantities of NO are produced by ionization by short-wave u.v. radiation (200–400 Tg N annually) and by auroral activity at solar maximum (20 Tg N annually). By far the most NO produced in this way is removed by photochemical reactions above 50 km in the atmosphere. But even a small leakage would give a significant flux of NO into the stratosphere.

The atmospheric lifetime of NO–NO_2 is determined by the reaction of NO_2 with OH radicals:

$$NO_2 + OH + M \rightarrow HNO_3 + M. \tag{3a}$$

Since this reaction is fast, the mean atmospheric lifetime of NO–NO_2 is only 1.5 days. The resulting nitric acid (22–80 Tg HNO_3-N annually) is removed from the atmosphere by washout and rainout processes, which are probably very efficient owing to the high solubility of HNO_3 and nitrates in water. Nitric acid is almost certainly not photolysed back to NO_2 in the troposphere, since the mean atmospheric lifetime of HNO_3 (and nitrates) must be shorter than that of a water molecule, which is about 9 days. This is much shorter than the time span of 2 months needed for HNO_3 to photolyse back to OH and NO_2:

$$HNO_3 + h\nu \rightarrow OH + NO_2. \tag{3b}$$

Since the publication of the first N_2O balances of the atmosphere (Söderlund & Svensson 1976; Hahn & Junge 1977), the data on the N_2O distribution in the atmosphere and on N_2O emissions from various soils, both fertilized and unfertilized, have considerably increased. The new data strongly indicate that the total global source of atmospheric N_2O must be smaller than previously estimated. It now appears possible that photochemical reactions in the stratosphere represent the main sink of atmospheric N_2O. This sink is still not very well known because of remaining uncertainties about the vertical distribution of N_2O in the stratosphere, especially in the tropical stratosphere. The annual loss rate of 15 Tg N_2O-N estimated by Schmeltekopf *et al.* (1977) is probably an upper limit. With this loss rate, the mean atmospheric lifetime of N_2O is about 100 years. Whether there are other sinks of atmospheric N_2O or not is still an open question.

Virtually all known sources of atmospheric N_2O are found at the Earth's surface. Some N_2O is produced during the combustion of fossil fuels. Weiss & Craig (1976) estimated an annual release of 1.6 Tg N_2O-N due to industrial combustion processes. To this emission must be added about 0.15 Tg N_2O-N annually from the burning of natural gas as estimated by Pierotti & Rasmussen (1976). This brings the annual amount to about 1.8 Tg N, a figure that must be expected to grow at a rate of 3.5% per year. The increase of this combustion source is nearly sufficient to account for the observed worldwide increase in atmospheric N_2O of about 0.2% per year, as reported by Weiss (1981). Additionally, a potentially important production of N_2O may result from the use of catalysts in combustion engines to reduce NO emissions (Weiss & Craig 1976; Pierotti & Rasmussen 1976). Weiss & Craig (1976) estimated a potential annual N_2O emission of as much as 2.1 Tg N if all 1976 automobiles were to be equipped with Pt converters.

N_2O is also produced during biomass burning. This source was estimated to 8 Tg N annually by Crutzen *et al.* (1979). More recent data (unpublished) indicate, however, a lower global annual emission rate of 1–2 Tg N.

Assuming bacterial nitrification as the main source, the annual N_2O release of oceans and estuaries to the atmosphere was estimated as 1–10 Tg N (Cohen & Gordon 1979). Recently, lower oceanic N_2O releases were proposed (W. Seiler and R. F. Weiss, personal communications). Therefore, a marine source of 1–10 Tg N annually was included in table 1.

According to estimates by Bohn (1977) and Wilson (1978), the average annual worldwide loss of organic carbon due to soil manipulation during the past century was 1–2 Pg ($\text{Pg} = 10^{15}$ g) carbon. With an average C:N ratio of 10–20 (Delwiche & Likens 1977), the annual loss of fixed N from these soils has amounted to 50–100 Tg N. In a recent study, Terry *et al.* (1980) reported that from the drained cultivated soils of southern Florida, 2.7% of the fixed N that is lost appeared in the form of N_2O. If similar ratios apply to other ecosystems which lose fixed N owing to soil manipulation, the annual global source of N_2O would be 1.5–3 Tg N.

The annual rate of biological N_2 fixation on the continents was estimated as 140 Tg N (Burns & Hardy 1975). To this must be added an annual 70–80 Tg N of fixed N, including 55 Tg N in the form of industrial N fertilizers, 3 Tg N in the form of other industrial N compounds, and 15–25 Tg N from the combustion of fossil fuels, lightning and return of stratospheric fixed N (see above). The man-made contribution has thus reached almost 50% of the terrestrial biological N_2 fixation rate. The 15–25 Tg N annually from the combustion of fossil fuels, lightning and return of stratospheric fixed N are released to or produced in the atmosphere in the form of NO and NO_2, but are then converted to nitrate, which is scavenged by precipitation and carried into the various ecosystems at the Earth's surface. Most of the nitrate ends up in terrestrial ecosystems.

The yield factor A (Hahn & Junge 1977; Hahn 1979), i.e. the fraction of the fixed N that is returned to the atmosphere in the form of N_2O as a result of microbial activities, was overestimated in earlier studies. The highest values for A observed in recent studies of soil emissions are close to 0.05 (Bremner & Blackmer 1980), the lowest close to 10^{-4} (Bremner & Blackmer 1978; Conrad & Seiler 1980; Hutchinson & Mosier 1979). Largest emissions of N_2O occurred when soils were treated with anhydrous NH_3. The A values given above apply, however, only to the direct release of N_2O from soil. They do not take into consideration the production of N_2O by microbial processes that utilize the fixed N contained in the various excreta resulting from the consumption and digestion of N-rich plant products by domestic animals and man. There are not sufficient data available to estimate a global value for A. Therefore, we assume a range of 0.005–0.05. With this range of A values, one obtains an annual rate of N_2O release from both natural and agricultural soils of between 1 and 11 Tg N_2O-N, of which 0.7–7.0 Tg N may be assigned to the release of N_2O from natural soils and 0.4–4.0 Tg N to the contribution of fixed N from industrial N fertilizers. With such a wide range of uncertainties, it is clear that the impact of the increased use of N fertilizers on atmospheric N_2O release and stratospheric ozone remains an unanswered question. Fortunately, the rather slow increase of N_2O by 0.2 % per year (Weiss 1981) will allow enough time to conduct successful research efforts on all possible sources of N_2O.

The global figures for the emission of NH_3 to the atmosphere are compiled in table 2. Ammonia is the form in which most fixed N seems to be circulated through the atmosphere (McConnell 1973). Depending on the ecological conditions, NH_3 can be released or taken up by microorganisms and higher plants so that the flux pattern is very complex and therefore poorly understood. It seems that NH_3 is not participating in any significant homogeneous gas-phase reactions (see below). The emission of NH_3 from the land surface to the atmosphere appears to be much larger than that from the oceans, and it is not yet clear whether or not the oceans contribute significantly to the atmospheric NH_3 levels observed in marine air. Over land, there is normally a very marked drop of the NH_3 mixing ratio with height.

NH_3 is released from the excretions of animals. Healy *et al.* (1970) listed animal urea excretion rates for most important domestic animals in the U.K. From this information and statistics on the population of domestic animals, one can extrapolate to an annual urea production of about 50 Tg in the developed world.

In the developing world the food intake per head is, however, only 30–60 % of that in the developed world, so that urea production per animal should be about half as large as in the developed countries. With the statistics available for the developing world, one may then calculate an additional urea production of 20 Tg per year. The total worldwide urea production by domestic animals adds up to about 70 Tg or 35 Tg N per year. Healy *et al.* (1970) assumed that 10 % of the N in the urea would volatilize to NH_3. This release estimate is, however, very low in comparison with the results of field studies obtained by Denmead *et al.* (1976) and especially Porter (1975), which indicate a relative volatilization loss of 30 %. Adopting this ratio as representative, the global annual production of NH_3 from urea would be about 10 Tg N. To this must be added the contribution from faeces, which may double the release of NH_3 to 20 Tg N (Böttger *et al.* 1980). This estimate is somewhat smaller than those derived by Söderlund & Svensson (1976) and Böttger *et al.* (1980). For the release of NH_3 from wild animals we shall accept the relatively small annual source of 2–6 Tg N as given by Söderlund & Svensson (1976).

The loss of NH_3 from fertilized soils is estimated to be about 5 %. With an annual fertilizer application rate of almost 60 Tg N, the release of NH_3 is equal to about 3 Tg N per year.

The NH_3 release from natural soils is a large unknown. Dawson (1977) made a detailed analysis of biomass decomposition and proposed a soil–atmosphere exchange model with an annual NH_3 source of 27 Tg N, with maximum emissions at temperate latitudes. Even if this rate were roughly correct, reabsorption of NH_3 by living vegetation is going to take place as in the study by Denmead *et al.* (1974) in the ungrazed pasture. Böttger *et al.* (1980) actually rule out significant release from natural soils on the basis of a few quoted measurements on NH_3 release from soils, and Söderlund & Svensson (1976) do not even discuss it. Here we shall consider the value of Dawson (1977) as an upper limit. In particular, we may expect substantial releases of NH_3 during early spring when the new vegetation is not well developed and dead material on the ground is abundant. When the soil is warmed up by solar radiation much release of NH_3 to the atmosphere should indeed occur.

Regarding the NH_3 emission during biomass burning, we may not rule out an annual volatilization of NH_3 of up to 60 Tg N taking place, especially in the tropics. This requires, of course, that much of the NH_3 is not oxidized in fires. Söderlund & Svensson (1976) already mentioned that NH_3 is a surprisingly stable gas in combustion systems. It is clearly important to identify the major fixed N compounds that are emitted in vegetation fires. For example, HCN has recently been discovered in the atmosphere with a volume mixing ratio of 0.16 $\mathrm{nl\,l^{-1}}$ (Coffey *et al.* 1981 *b*). Biomass burning was proposed by Crutzen *et al.* (1979) to be an important source of HCN, and the presence of HCN in the atmosphere was consequently predicted by those authors. This gas reacts only slowly with OH (Fritz *et al.* 1981), so that only about 0.1 Tg of NO_x can be formed annually from HCN oxidation in the atmosphere. The solubility of HCN in rainwater is also not sufficiently high for it to be affected significantly by rainout and washout (Landolt-Börnstein 1962). Because of its long residence time in the atmosphere (*ca.* 2 years) it seems most likely that HCN is deposited on land and ocean surfaces. For the latter, the model of Liss & Slater (1974) would predict a deposition velocity of less than 0.5 $\mathrm{cm\,s^{-1}}$. Similar deposition velocities may apply to vegetation-covered surface areas. Adopting this sketchy analysis, a maximum transfer of about 5 Tg N of fixed N as HCN may occur through the atmosphere, which may not be totally negligible for some ecosystems. For the NH_3 emission from coal burning, we refer to the estimate by Söderlund & Svensson (1976), who proposed 4–12 Tg N as the global source.

Atmospheric photochemistry

The most important N species in atmospheric photochemistry are NO and NO_2. They act as catalysts in many atmospheric reaction chains and control the distribution of atmospheric ozone. In the stratosphere, NO is formed by oxidation of N_2O, as explained above. NO and its oxidation product NO_2 then participate in a complex set of catalytic reactions that convert O_3 to O_2. These reactions are especially effective in altitudes above 24 km. At lower altitudes, however, NO acts catalytically to *produce* O_3 by natural 'smog' reactions. The effects of such reactions are clearly observable during photochemical smog episodes in urban areas. But there is no reason to assume that they are restricted to such situations. Analogous reactions should occur also in rural and remote areas during the oxidation of CO and natural hydrocarbons, especially methane, isoprene and the terpenes, in the presence of NO.

TROPOSPHERIC PHOTOCHEMISTRY

Although only about 10% of all atmospheric ozone is located in the troposphere, the lowest 10–17 km of the atmosphere, this small amount of ozone is nevertheless of fundamental importance for the composition of the Earth's atmosphere. The reason for this is the production of the highly reactive hydroxyl radical (OH) by the two reactions

$$O_3 + h\nu\ (< 310\ \text{nm}) \rightarrow O(^1D) + O_2; \tag{1}$$

$$O(^1D) + H_2O \rightarrow 2\ OH. \tag{4}$$

It is the attack by OH that initiates the oxidation of many reduced gases in the atmosphere. In the background troposphere, about 70% of the OH radicals react with CO, and about 30% with CH_4. Smaller fractions react with other trace gases, leading to their loss from the atmosphere.

The average concentration of hydroxyl in the atmosphere is now estimated to be $5–7 \times 10^5$ molecules cm^{-3} (Derwent & Eggleton 1981; Crutzen *et al.* 1978), agreeing with the global observations of methylchloroform, which is removed from the atmosphere by reactions with OH and has no atmospheric sources other than the well known industrial emissions. Most hydroxyl is found in equatorial regions, where the intensity of ultraviolet radiation is at a maximum (Crutzen *et al.* 1978). The calculated OH distribution also explains quite well most of the features of the $C^{14}O$ observations in the troposphere (Volz *et al.* 1979). The reactions of OH with carbon monoxide and methane, however, do not necessarily lead to removal of hydroxyl from the atmosphere, because hydroxyl may merely act as a catalyst. In the presence of sufficient concentrations of another catalyst, nitric oxide, such reactions will lead to the formation of tropospheric ozone, as follows:

$$CO + OH \rightarrow H + CO_2 \tag{5}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{6}$$

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

$$NO_2 + h\nu\ (< 400\ \text{nm}) \rightarrow NO + O \tag{8}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{9}$$

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

Similar reactions which lead to the production of ozone in the troposphere may take place during the oxidation of methane and other hydrocarbon gases (Crutzen 1973; Zimmerman *et al.* 1978). The oxidation of CO and hydrocarbon gases does not always lead to ozone production in the troposphere. A competing chain of reactions,

$$CO + OH \rightarrow H + CO_2 \tag{5}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{6}$$

$$HO_2 + O_3 \rightarrow OH + 2\ O_2 \tag{10}$$

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

takes place whenever the ratio of the atmospheric concentrations of NO and O_3 is less than 2×10^{-4}. With ozone volume mixing ratios increasing from about 20×10^{-9} (20 nl l^{-1}) at ground level to 100 nl l^{-1} at the tropopause, the break-even point is attained at NO volume mixing ratios of 4×10^{-12} (4 pl l^{-1}) at ground level and 20 pl l^{-1} at the tropopause. These are indeed very low concentrations, but they may nevertheless not be reached in extensive regions of the troposphere because of the very short residence times of the NO and NO_2 owing to the rapid formation of highly water-soluble nitric acid by the reactions

$$NO + O_3 \rightarrow NO_2 + O_2; \qquad (11)$$

$$NO_2 + OH(+M) \rightarrow HNO_3(+M). \qquad (3a)$$

McFarland *et al.* (1979) have indeed indicated the possibility of very low background concentrations of NO by the measurements of volume mixing ratios of less than 10 pl l^{-1} in the marine boundary layer of the tropical Pacific. There are, unfortunately, far too few measurements to derive a typical distribution of NO in the troposphere, so that it is not possible to make a good estimate of the sources and sinks of tropospheric ozone. The only term that can be estimated with reasonable reliability is the global ozone loss by reactions (1) and (4), amounting to about 8×10^{10} molecules $cm^{-2}\,s^{-1}$ (Fishman *et al.* 1979). This ozone loss may be compared with the estimated downward transport of about 6×10^{10} molecules $cm^{-2}\,s^{-1}$ of stratospheric ozone by meteorological processes (Fabian & Pruchniewiecz 1977). Tropospheric photochemistry should therefore play an important role in defining the concentrations of ozone in the troposphere, which in turn determines the tropospheric OH concentrations.

It is informative to estimate an upper limit to potential ozone production rates in the troposphere by assuming that there is always enough NO present in the atmosphere so that during the oxidation of a hydrocarbon molecule to CO there is a production of 2–3 ozone molecules per carbon atom (Crutzen 1973; Fishman *et al.* 1979). The further oxidation of CO to CO_2 could subsequently add another ozone molecule to the atmosphere. Making use of the information on the same sources of CO, CH_4 and non-methane hydrocarbons, a maximum global tropospheric production potential of ozone of 2×10^{12} molecules $cm^{-2}\,s^{-1}$ can be calculated. The real ozone production in the troposphere at present is probably only between 1 and 10 % of this maximum yield, indicating that much oxidation of hydrocarbons takes place without the production of ozone. One may guess that this is so because in most of the troposphere NO is present at only very low concentrations. Further expansions of anthropogenic activities may therefore have significant implications for the tropospheric ozone distribution. It should be mentioned that NO may likewise be of much importance for the efficiency of CO production from hydrocarbon oxidation.

As CO is the main reactant of OH, an increase in the atmospheric CO content could lead to lower tropospheric concentrations of OH and thereby cause an increase in the tropospheric abundances of those gases that are mainly removed by reactions with OH (Wofsy 1978). This could have further chemical and climatological consequences, for instance a larger transfer of gases to the stratosphere with possible effects on ozone. It is likely, however, that a rise in the tropospheric CO abundance by anthropogenic activities will be accompanied by a simultaneous increase in the tropospheric NO abundance. This would lead to higher ozone concentrations. The increases in NO and O_3 would lead to higher OH concentrations through reactions (4) and (7).

Methane oxidation is not only a potentially significant source of CO, but the atmospheric concentrations of OH may be largely determined by the particular reaction paths that are followed during the oxidation of methane. Again, nitric oxide may well play an important role in this. With enough NO present (more than 10 pl l^{-1}) the reaction path, leading to formaldehyde, is as follows:

$$CH_4 + OH \rightarrow CH_3 + H_2O \tag{12}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{13}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{14}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{15}$$

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

$$NO_2 + h\nu\ (< 400\ \text{nm}) \rightarrow NO + O,\ 2\times \tag{8}$$

$$O + O_2 + M \rightarrow O_3 + M,\ 2\times \tag{9}$$

$$\text{net: } CH_4 + 4\,O_2 \rightarrow CH_2O + H_2O + 2\,O_3.$$

Further reactions of CH_2O towards CO lead then to a net gain of hydroxyl (Levy 1971). With little NO present, the oxidation path is:

$$CH_4 + OH \rightarrow CH_3 + H_2O \tag{12}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{13}$$

$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \tag{16}$$

$$CH_3O_2H + h\nu \rightarrow CH_3O + OH \tag{17}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{15}$$

$$\text{net: } CH_4 + O_2 \rightarrow CH_2O + H_2O.$$

The photodissociation of CH_3O_2H is, however, slow, allowing a residence time of 1 week for this compound, so that the methyl hydroperoxide may be rained out of the atmosphere or react with the Earth's surface or aerosol particles. If this is so, the oxidation of CH_4 will lead to a loss of two odd-hydrogen radicals (OH and HO_2). Likewise, no formation of CO would then occur in the atmosphere. It should be emphasized that the problems related to methane oxidation in the atmosphere are far from resolved. More intricate questions will have to be answered regarding the oxidation of higher hydrocarbons.

An interesting, and potentially important, interaction between carbon and N gases in the atmosphere occurs through the formation of certain organic nitrate molecules during the oxidation of hydrocarbons, the most important of which are probably the peroxyacyl nitrates, especially peroxyacetyl nitrate (PAN) with the chemical formula $CH_3C(O)O_2NO_2$. This pollutant, which causes eye irritation at high concentrations, has now been observed in many urban environments in the U.S. (Stephens 1969; Lonneman *et al.* 1976; Tuazon *et al.* 1981; Spicer 1977) and in Europe (Nieboer & van Ham 1976; Penkett *et al.* 1977). PAN is thermally decomposed via the reactions

$$CH_3C(O)O_2NO_2 \rightleftharpoons CH_3C(O)O_2 + NO_2;$$

$$CH_3C(O)O_2 + NO \rightarrow CH_3 + CO_2 + NO_2;$$

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)O_2H + O_2;$$

$$CH_3C(O)O_2H + h\nu \rightarrow CH_3 + CO_2 + OH.$$

Using the kinetic information of Hendry & Kenley (1977), we compute the following values for the atmospheric residence time of PAN against photochemical destruction as a function of altitude, adopting temperature tabulations in the U.S. standard atmosphere: at $z = 0$ km and $T = 288$ K, τ (PAN) $= 2.9$ days; at $z = 4$ km and $T = 262$K, τ(PAN) $= 28$ days; at $z = 6$ km and $T = 249$ K, τ(PAN) 1 year; at $z = 8$ km and $T = 235$ K, τ(PAN) $= 15$ years.

We note that the lifetime of PAN against decomposition increases rapidly with altitude, becoming longer than 1 year above 5 km. Photolysis of PAN in the troposphere is probably negligible (Stephens 1969), while reaction with OH also seems to be slow (Atkinson *et al.* 1979). It may be that PAN formation will be favoured during the cold winter months (Hendry & Kenley 1977). Concentrations of PAN comparable with those of nitric acid and typically 10–20% of those of NO_x have been measured in contaminated air close to major U.S. urban centres (Lonneman *et al.* 1976; Tuazon *et al.* 1981; Spicer *et al.* 1976). In this air, conversion of NO_x to HNO_3 and to PAN will not go to completion. According to Spicer *et al.* (1976) and to Spicer (1977), on average about 80% of the NO and NO_2 removed from the polluted air could well end up as PAN. This would agree with results of smog chamber experiments and theoretical calculations (Spicer *et al.* 1976; Hendry & Kenley 1977), which indicate a buildup of PAN to concentrations larger than NO_2 in the later phases of photochemical smog episodes. The hydrocarbons that operate in the transformation of NO to PAN near urban centres no doubt come overwhelmingly from automotive exhaust. In the middle and upper troposphere the production of PAN from NO_x may be driven by long-lived hydrocarbons and their oxidation products, as recently postulated by Singh & Hanst (1981) for C_2H_6. Clearly, then, it is important to consider the role of PAN and other vapour-phase organic nitrates in global air chemistry. This is important as PAN is lost surprisingly slowly from the atmosphere by wet removal. A laboratory study by Garland & Penkett (1976) gave a deposition rate of PAN on water surfaces slower than that of ozone. Global transport of PAN will therefore occur in the middle and upper troposphere. When PAN is transported to the lower half of the troposphere, it will decompose thermally and release its NO_x content to the atmosphere. The formation of PAN may thus affect long-range transport of NO_x through the atmosphere by a considerable lengthening of the atmospheric residence time of NO_x (Crutzen 1979).

The foregoing reactions are of critical importance in tropospheric photochemistry, because of their role in determining the concentrations of tropospheric OH. Most other homogeneous gas-phase photochemistry of the troposphere derives from this. After the initial attack by hydroxyl, the reduced sulphur gases H_2S, $(CH_3)S$ and CH_3SH are probably converted rapidly to SO_2, but detailed reaction steps are unknown, especially for those extensive parts of the atmosphere that contain little NO, as is probably true of remote oceanic areas (McFarland *et al.* 1979). The further oxidation of SO_2 in the presence of NO likewise involves an initial reaction with hydroxyl, leading to the reaction sequence (Calvert *et al.* 1978)

$$SO_2 + OH(+M) \rightarrow HSO_3(+M); \tag{18}$$

$$HSO_3 + O_2(+M) \rightarrow HSO_5(+M); \tag{19}$$

$$HSO_5 + NO \rightarrow HSO_4 + NO_2; \tag{20}$$

$$HSO_4 + HO_2 \rightarrow H_2SO_4 + O_2. \tag{21}$$

At low NO concentrations the oxidation steps are more uncertain, although possibilities have been identified (Davis *et al.* 1976). Although heterogeneous reactions may be at least as important as homogeneous reactions for the oxidation of SO_2 to H_2SO_4 (see, for example, Shaw

& Rodhe 1981), we must point out an interesting possible influence that NO_x might exert on the SO_2 oxidation cycle in industrial air masses (Rodhe *et al.* 1981). Because reaction (3*a*) between OH and NO_2 is about ten times faster than reaction (18), HNO_3 formation may act as a sink for OH, when the mixing ratio of NO_x is of the order of a few nanolitres per litre or more. Under situations when photochemical oxidation is important, the oxidation of SO_2 may, therefore, be delayed until the concentrations of NO_2 become smaller than about 1 $\mathrm{nl\,l^{-1}}$. When this is so, the production of H_2O_2 from

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{22}$$

is also strongly affected, because of a decrease in HO_2 concentration by reaction (7). As H_2O_2 may be an important oxidant of SO_2 in water droplets, the oxidation of SO_2 in cloud water may likewise be substantially delayed.

As mentioned above, NO_2 is removed from the atmosphere by its reaction with hydroxyl to produce HNO_3, most of which is not photolysed back to NO_2 because rainout and washout will probably be efficient in removing it from the atmosphere. This reaction is very important as it prevents, to a large degree, the upward transport of NO and NO_2 to the stratosphere because HNO_3 is so highly soluble in water.

It remains of interest, however, to explore the possibility of some leakage of NO and NO_2 (and other pollutant gases such as SO_2) through the tropospheric water vapour and cloud filter to higher altitudes (middle and upper troposphere, lower stratosphere), e.g. at high latitudes during winter when little or no OH is produced by reaction (4) between $O(^1D)$ and H_2O and when, furthermore, precipitation occurs in rather small amounts as snow, which may be less efficient than rain in scavenging some trace gases. This possibility of global NO and NO_2 transport is speculative, though not entirely unreasonable, judging from the findings of Rahn and colleagues of considerable pollution levels in Arctic regions in winter (see Kerr 1979). Nevertheless, it seems certain that, globally averaged, the transfer of NO to the stratosphere is significantly smaller than the formation of NO in the stratosphere through reaction (2). Observations of HNO_3, by Lazrus and coworkers (Huebert & Lazrus 1978; Lazrus & Gandrud 1974) and of NO_2 by Noxon (1978, 1979) in areas remote from pollution sources, have shown volume mixing ratios of NO_2 and HNO_3 that are substantially larger in the stratosphere than in the troposphere.

We should also briefly address the issue of whether photochemical reactions may affect NH_3, for which both uptake and release by microbiological processes should be considered in order to establish the overall net source of atmospheric NH_3. The only homogeneous gas-phase reaction of NH_3 is again a reaction with OH:

$$OH + NH_3 \rightarrow NH_2 + H_2O. \tag{23}$$

This reaction is, however, rather slow ($k_{22} = 1.5 \times 10^{-13}\ \mathrm{cm^3\,mol^{-1}\,s^{-1}}$), so that with an average $[OH] \approx 7 \times 10^5\ \mathrm{cm^{-3}}$, NH_3 would remain in the atmosphere for a season, if reaction (23) represented the only process of atmospheric loss. In reality, NH_3 will be removed from the atmosphere on average in about 9 days, which represents the average residence time of water vapour in the atmosphere. This means that at most only a fraction of atmospheric NH_3, perhaps 10–20%, could react with OH. The NH_2 radical reacts only very slowly with O_2, so that reactions with minor constituents are important, e.g. with HO_2,

$$NH_2 + HO_2 \rightarrow NH_3 + H_2O, \tag{24}$$

providing a pathway back to NH_3. It has also been debated whether NH_3 oxidation would represent a source or a sink for atmospheric NO_x through reactions such as

$$NH_2+NO \rightarrow N_2+H_2O; \tag{25}$$

$$NH_2+NO_2 \rightarrow N_2O+H_2O; \tag{26}$$

$$NH_2+O_3 \rightarrow NH_2O+O_2; \tag{27}$$

where further oxidation of NH_2O may lead to NO_x probably via HNO formation. The break-even point between reactions (25)+(26) and (27) occurs at about 60 pl NO_x l^{-1}. Such mixing ratios of NO_x can indeed be reached in continental, agricultural areas, where most atmospheric NH_3 is probably located. It may therefore be that NH_3 oxidation implies a small sink for atmospheric NO_x and a source for N_2O.

Stratospheric photochemistry

The temperature structure and the dynamic processes in the stratosphere are determined, to a major degree, by the absorption of solar ultraviolet energy by ozone. The total amount of ozone in the stratosphere is nevertheless rather small; it corresponds to about the number of air molecules contained in a layer 3 mm thick at standard temperature and pressure (as we have noted, the troposphere contains only 10% of the atmospheric ozone). Atmospheric ozone also plays an important ecological role. Most ultraviolet solar radiation between about 210 and 310 nm is filtered out by atmospheric ozone. However, penetration of u.v. radiation starts at about 300 nm and increases by orders of magnitude within the next 20 nm. It is this radiation that may be biologically harmful. Its penetration to the ground is significantly enhanced by a decrease in the overlying ozone column.

Since the beginning of the 1970s it has become increasingly clear that a number of human activities can lead to global changes in the amount of stratospheric ozone. Following suggestions by Johnston (1971) and Crutzen (1971), initial attention was directed to pollution of the stratosphere by direct injections of NO from high-flying aircraft. Earlier, Crutzen (1970) had proposed that NO_x $(NO+NO_2)$ would catalyse the destruction of ozone and limit its stratospheric abundance by a simple set of photochemical reactions:

$$O_3+h\nu\ (<1140\text{ nm}) \rightarrow O+O_2 \tag{28}$$

$$O+NO_2 \rightarrow NO+O_2 \tag{29}$$

$$\underline{NO+O_3 \rightarrow NO_2+O_2} \tag{30}$$

$$\text{net: } 2\ O_3 \rightarrow 3\ O_2.$$

This catalytic chain of reactions largely balances the formation of ozone in the stratosphere through the reaction sequence

$$O_2+h\nu\ (<240\text{ nm}) \rightarrow 2\ O \tag{31}$$

$$\underline{O+O_2+M \rightarrow O_3+M\ (2\times)} \tag{9}$$

$$\text{net: } 3\ O_2 \rightarrow 2\ O_3.$$

The main source of NO_x in the stratosphere is most likely to be the oxidation of nitrous oxide

(N_2O) via two reactions (Crutzen 1971; Nicolet & Vergison 1971; McElroy & McConnell 1971):

$$O_3 + h\nu\ (< 310\ \text{nm}) \rightarrow O(^1D) + O_2; \tag{1}$$

$$O(^1D) + N_2O \rightarrow 2\ NO. \tag{2}$$

Stratospheric ozone is especially affected by compounds that have a low solubility in water and do not react with OH and solar radiation, and are inert in the troposphere (e.g. N_2O and several chlorocarbon gases, such as natural CH_3Cl and industrially produced $CFCl_3$, CF_2Cl_2, CCl_4 and CH_3CCl_3). Another way to influence stratospheric chemistry is by direct injection of material into the upper troposphere and stratosphere well above most atmospheric water and water vapour (e.g. volcanic eruptions, meteoritic impacts and emissions from aircraft in the stratosphere).

The oxides of N, NO_x, play a remarkable role in the ozone balance, particularly in the stratosphere. Above about 25 km the net effect of NO_x additions to the stratosphere is ozone destruction by the set of reactions presented earlier (28–30). At lower altitudes in the stratosphere, NO_x may actually protect ozone from some destruction. An important reason for this is a generalized set of reactions:

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

$$NO_2 + h\nu\ (< 400\ \text{nm}) \rightarrow NO + O \tag{8}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{9}$$

$$\text{net: } HO_2 + O_2 \rightarrow OH + O_3.$$

As we have shown before, this reaction set is also basically the cause of ozone production that takes place in the troposphere. In the lower stratosphere, the chain of reactions (7–9) tends to counteract the destruction of ozone by the catalytic reaction pair:

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{31}$$

$$HO_2 + O_3 \rightarrow OH + 2\,O_2 \tag{10}$$

$$\text{net: } 2\,O_3 \rightarrow 3\,O_2,$$

by deflecting it into the chain:

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{31}$$

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

$$NO_2 + h\nu \rightarrow NO + O \tag{8}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{9}$$

(No net chemical effect.)

An additional important role of NO_x ($NO + NO_2$) in the stratosphere occurs through interactions with Cl and ClO. As with NO_x, Cl and ClO participate in an effective catalytic chain of reactions, which converts ozone back to molecular oxygen. This cycle operates as follows:

$$O_3 + h\nu \rightarrow O + O_2 \tag{28}$$

$$O + ClO \rightarrow Cl + O_2 \tag{32}$$

$$Cl + O_3 \rightarrow ClO + O_2 \tag{33}$$

$$\text{net: } 2\,O_3 \rightarrow 3\,O_2.$$

At altitudes lower than about 25 km in the stratosphere, where the ozone destruction catalysis chain (28–30) (involving NO and NO_2) becomes less efficient because of lower concentrations of atomic oxygen, the reaction

$$NO + ClO \rightarrow Cl + NO_2 \tag{34}$$

interferes with the ozone-destroying reaction-set (28) + (32) + (33), yielding a catalytic cycle that does not destroy ozone. More important, chlorine atoms produced by reaction (34) react with CH_4 to yield HCl, which does not react photochemically with ozone. Furthermore, since the reaction

$$ClO + NO_2 + M \rightarrow ClNO_3 + M \tag{35}$$

ties both some ClO and some NO_2 as non-reactive $ClNO_3$, it is clear that ozone removal by NO_x additions to the stratosphere is mitigated by the NO_x interactions with the Cl–ClO catalytic ozone-destroying cycle.

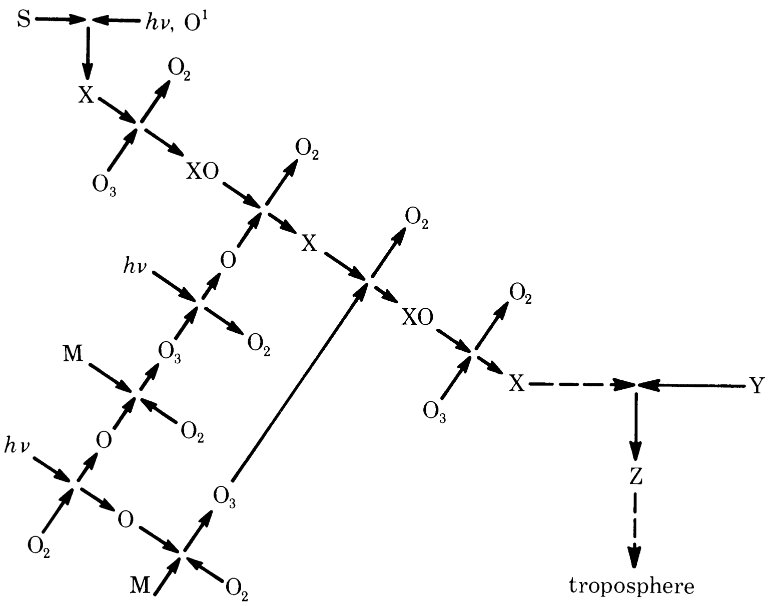

FIGURE 1. Simplified schematic flow diagram showing the main features of the atmospheric photochemistry that controls the ozone balance in the upper stratosphere. (M symbolizes some neutral particle; O^1 stands for $O(^1D)$ atomic oxygen. S = N_2O, RCl, H_2O; X = NO, Cl, OH; Y = OX, CH_4; Z = HNO_3, HCl, H_2O.)

The main features of the photochemistry controlling the ozone balance in the upper stratosphere are summarized in figure 1. As indicated in this rather simplified scheme, O_3 is formed in two steps: photolysis of an oxygen molecule according to reaction (31) and combination of the resulting atomic oxygen with another oxygen molecule according to reaction (9). The O_3 formed is then eventually photolysed back to molecular oxygen and atomic oxygen. Depending on the wavelength of the photolysing solar radiation, the resulting atomic oxygen occupies two energy levels, the highest being $O(^1D)$ atomic oxygen. $O(^1D)$ is able to convert relatively inert species (S), which diffuse up through the troposphere into the stratosphere, to fast-reacting active species (X) which participate in reaction chains destroying O_3. Some X can also be formed by photolysis of S species. The active X then abstracts one oxygen atom from an O_3 molecule (reactions (30), (31) and (33)) to form XO, which then reacts with one atomic oxygen (from reaction (28)) to give X and molecular oxygen (reactions (29) and (32)). In other words, X acts as a catalyst for the reaction

$$O + O_3 \rightarrow 2\,O_2. \qquad (36)$$

As shown in the flow scheme, for each transformation of X to XO one O_3 molecule is destroyed, whereas each transformation of XO back to X consumes one atomic oxygen. The result of this 'redox' chain, which may be repeated many times, is a considerable lowering of the steady-state concentration of O_3. The steady-state O_3 concentration would be even lower if it were not for the fact that X and XO are temporarily occupied in reactions between X and XO species such as (7), (34) and (35). Finally, X reacts with species Y, which tie it up in more stable products Z. Such reactions are, for example:

$$NO_2 + OH + M \rightarrow M + HNO_3 + M; \qquad (3a)$$

$$ClO + NO_2 + M \rightarrow ClONO_2 + M; \qquad (35)$$

$$Cl + CH_4 \rightarrow CH_3 + HCl; \qquad (37)$$

$$OH + HO_2 \rightarrow H_2O + O_2. \qquad (38)$$

The product Z, although still sensitive to photolysis and attack by OH to some degree, eventually diffuses back into the troposphere, where it is scavenged by precipitation and thus removed from the atmosphere.

The photochemical reaction chains controlling the ozone in the stratosphere are, therefore, complicated. Additions of NO to the low stratosphere tend to increase local ozone concentrations by reducing some of the ozone loss, which would otherwise occur because of the catalytic action of OH and HO_2, and Cl and ClO. The importance of the ozone-producing and ozone-protecting aspects of NO_x catalysis below about 25 km was dramatically emphasized by discoveries by Zahniser & Howard (1979) and Howard & Evenson (1977), who have found reactions (10) and especially (7) to be much faster than had been previously estimated. This finding resulted in substantial downward revisions of estimated total ozone-column decreases due to atmospheric NO_x additions from aircraft (Duewer *et al.* 1977; Crutzen & Howard 1978; Logan *et al.* 1978). As NO_x is produced by the oxidation of N_2O via reaction (2), the same conclusions are also partly valid regarding the possible effects of a future rise in the atmospheric content of nitrous oxide. In this case, however, more of the additional NO_x produced in reaction (2) will reach the upper regions of the stratosphere, where the reaction-set (28–30) is more important. An increase in N_2O may be caused by man's intervention in the nitrogen cycle through the increasing use of synthetic fixed N in agriculture, through changes in the composition of the Earth's soil and vegetation, and through fossil fuel and biomass combustion processes. Without going into details, we briefly review here the sensitivity of stratospheric ozone to N_2O changes and the latest developments in ozone depletion predictions.

In 1974, theoretical predictions (Crutzen 1974) of total ozone reductions, which used the then-recommended rate constants, yielded the following approximate relation between total ozone change (V_3) and a hypothetical increase in the volume mixing ratio of atmospheric nitrous oxide, $\mu(N_2O)$,

$$-\delta V_3/V_3 = \tfrac{1}{5}\delta\mu(N_2O)/\mu(N_2O).$$

A doubling in the atmospheric abundance of N_2O was therefore expected to yield a 20% decrease in total ozone. The rate constants for reactions (5) and (8) subsequently determined by advanced laboratory techniques, first led to substantial downward revisions in the ozone-reduction estimates. Actually, it was consequently estimated that a change of sign in the derived relation could occur. In other words, it was calculated that an increase in the atmospheric N_2O content could result in an increase in total atmospheric ozone content (Crutzen & Howard 1978; Logan *et al.* 1978). At present, it is again calculated, however, that an increase in atmospheric N_2O abundance will lead to a substantial decrease in total ozone. Our calculations indicate a loss in total stratospheric ozone by about 12% for a doubling of N_2O. The reason for this finding is that we now calculate substantially smaller concentrations of OH in the lower stratosphere below about 30 km than in 1978 through new evaluations of the rate coefficients related to the formation and destruction of HO_2NO_2 and HNO_3. In particular the reaction cycles

$$HO_2 + NO_2(+M) \rightarrow HNO_4(+M) \tag{39}$$

$$OH + HNO_4 \rightarrow H_2O + NO_2 + O_2 \tag{40}$$

$$\text{net: } OH + HO_2 \rightarrow H_2O + O_2$$

and

$$OH + NO_2(+M) \rightarrow HNO_3(+M) \tag{3a}$$

$$OH + HNO_3 \rightarrow H_2O + NO_3 \tag{41}$$

$$NO_3 + h\nu \rightarrow NO_2 + O \tag{42}$$

$$\text{net: } 2\,OH \rightarrow H_2O + O,$$

in which NO_2 catalyses the loss of HO_x, lead to much less HNO_3 and more NO_x than was calculated before. The newer calculations are in much better agreement with previous observations (Coffey *et al.* 1981*a*). We thus conclude that the normal ozone balance in the lower stratosphere is substantially affected by NO_x catalysis, i.e. reactions (28–30), so that the compensatory effects of NO_x in the HO_x and ClO_x catalytic cycles in the lower stratosphere, as discussed before, cannot make up for the enhanced loss of ozone due to NO_x catalysis in the entire stratosphere.

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