

THE ROLE OF NO AND NO₂ IN THE CHEMISTRY OF THE TROPOSPHERE AND STRATOSPHERE *10120

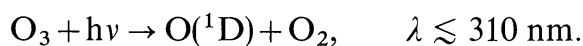
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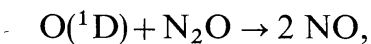
INTRODUCTION

The main importance of the oxides of nitrogen (NO, NO₂) in atmospheric chemistry is their role in the determination of the earth's ozone distribution. In the stratosphere (≈ 10 –50 km) nitric oxide (NO) is formed mainly by the oxidation of nitrous oxide (N₂O). Nitric oxide and its oxidation product nitrogen dioxide (NO₂) then participate in an important set of catalytic reactions which transfer ozone (O₃) to molecular oxygen and which are effective especially above about 24 km. Surprisingly, however, at lower altitudes nitric oxide acts catalytically to produce ozone by natural “smog” reactions. Although the effects of such reactions are clearly observable during photochemical smog episodes near urban centers (see, for example, the discussion by Altshuller & Bufalini 1971), there is no reason to assume that they are restricted to such environments. Analogous reactions should occur also outside the urban boundary layer during the oxidation of carbon monoxide and natural hydrocarbons (especially methane, isoprene, and the terpenes) in the presence of nitric oxide (Crutzen 1973, Zimmerman et al 1978).

Like water vapor and carbon dioxide, ozone plays an essential role in the radiation budget of the earth's atmosphere below about 80 km. This is because of its radiative properties in the ultraviolet and in the infrared. The absorption of ultraviolet radiation protects the biosphere from harmful radiation. In this process electronically excited O(¹D) atoms are generated:



In contrast to ground state atomic oxygen, excited oxygen atoms react rapidly with several minor gaseous constituents in the atmosphere, such as nitrous oxide and water vapor (H_2O), leading to the formation of nitric oxide and hydroxyl (OH):



The hydroxyl radical reacts with many gases which otherwise would be inert in the troposphere, such as carbon monoxide (CO), hydrocarbons (Levy 1971, 1974), and chlorinated hydrocarbons. If no OH were present in the troposphere, the atmospheric abundances of these gases would be much larger than observed in the atmosphere, in many cases by orders of magnitude. One of the most important tasks in atmospheric chemistry is to establish the origin of tropospheric ozone, because ozone affects the chemical composition and thermal characteristics of the atmosphere in decisive ways.

According to classical views, tropospheric ozone emanates from the stratosphere and is destroyed at the earth's surface (Junge 1962, 1963, Mohnen et al 1977, Danielsen & Mohnen 1977). It is clear, however, that the production of ozone in the troposphere under the influence of man's activities and involving catalysis by NO and NO_2 should be substantial. Consequently, this is one of the issues that we review.

The effects of additions of nitric oxide to the stratosphere under the influence of a number of human activities and the effect on stratospheric ozone have been a subject of considerable concern, stimulating intense research activities during the last decade on the chemistry and distribution of the oxides of nitrogen in the stratosphere. Such additions may occur due to emissions in the exhaust gases of high-flying aircraft, especially large fleets of supersonic aircraft cruising between 16 and 20 km (Johnston 1971, Crutzen 1971). Since nitrous oxide is produced in the soils and waters by microbiological processes (Pratt et al 1977), increased agricultural activities, in particular the use of nitrogen fertilizer, may well lead to an accumulation of N_2O in the atmosphere. In addition, nitrous oxide is produced by combustion (Weiss & Craig 1976, Pierotti & Rasmussen 1976). Because the oxidation of N_2O by $\text{O}({}^1\text{D})$ leads to production of NO in the stratosphere, the concentrations of ozone will be affected (Crutzen 1974a, McElroy 1976). In this article we only briefly review the potential consequences of an increase in N_2O mixing ratios in the atmosphere. Discussions of the factors influencing increased N_2O release from soils and the different views on this subject have been presented elsewhere (Crutzen 1976, McElroy et al 1976, 1977, Crutzen & Ehhalt 1977, Liu et al 1976a, 1977, Sze & Rice 1976, Pratt et al 1977, Hahn &

Junge 1977). A thorough study of current knowledge on the effects of nitrates in the environment, including a review of the nitrogen fertilizer-ozone problem, has just been published (NAS 1978).

The importance of ozone, and therefore of the oxides of nitrogen, for the terrestrial radiation budget and average vertical temperature profile is now well recognized. Although reductions in the total abundance of atmospheric ozone allow more solar radiation to penetrate to ground level, and tend to produce higher surface temperatures, the decrease in the downward longwave radiation emitted by CO₂, O₃, and H₂O from a cooler lower stratosphere containing less ozone would actually cause a decrease in surface temperatures. Using radiative-convective models Manabe & Wetherald (1967) and Ramanathan et al (1976) have calculated lower surface temperatures for atmospheres containing less than standard ozone concentrations throughout the atmosphere. Global surface temperatures would be lower by about 1.5–3°C in an atmosphere containing no ozone at all. For situations in which ozone is removed at higher levels (≈ 24 km) and increased at lower levels (as will occur for NO_x injections), the effects are probably opposite. The climatological aspects of stratospheric composition changes are discussed by Liu et al (1976b) and by Ramanathan & Coakley (1978). Since nitrous oxide itself is a significant absorber of infrared radiation of atmospheric and terrestrial origin, the direct effects of atmospheric nitrous oxide increases on the terrestrial radiation budget are also of interest (Wang et al 1976). Recent research in theoretical dynamic meteorology indicates the important role of stratospheric thermal stability in controlling the vertical transfer of wave energy between the troposphere and stratosphere (Bates 1977, Lindzen & Tung 1978). According to Bates (1977) substantial reductions in upper stratospheric temperatures by 10 K, as a consequence of industrial activities, could indirectly lead to marked changes in the horizontal heat flux by ultra-long planetary waves in the troposphere.

Nitric oxide is produced in very large amounts in the upper atmosphere, mostly in polar regions, from the action of ultraviolet and X-ray radiation, from precipitating solar electrons in auroras (above 100 km), from solar protons in the upper stratosphere and mesosphere, and from galactic cosmic rays in the lower stratosphere. All these emissions are in some way dependent on solar activity, especially in the upper layers of the atmosphere. Correlations between solar activity and climate have been shown to exist on long time scales (Eddy 1976, 1977) and may be due to variations in the solar energy output. However, solar activity could also influence climate and the dynamics of the atmosphere through the previously discussed chain of effects (NO_x → O₃ → static stability → planetary wave reflections).

Table 1 Abbreviations of groups of chemical constituents of importance, especially to the ozone budget of the stratosphere. The symbols within parentheses denote densities in molecules per cubic centimeter.

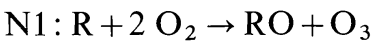
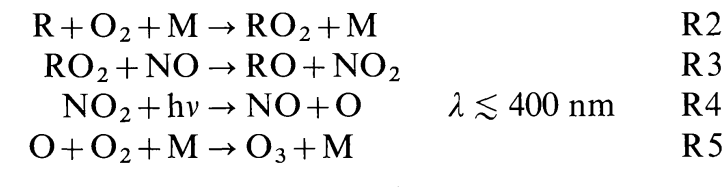
$O_x = O + O_3$ (odd oxygen)
$NO_x = N + NO + NO_2$ (active nitrogen)
$HNO_x = HNO + HONO + HONO_2 + HO_2NO_2$
$NOX = NO_3 + NO_2NO_3 + HNO_x + ClONO_2 + PAN + \dots$
$(NOX) = (NO_3) + 2(N_2O_5) + (HNO_x) + (ClONO_2) + (PAN) + \dots$
$NX = NO_x + NOX$ (odd nitrogen oxides, odd nitrogen)
$ClO_x = Cl + ClO$ (active chlorine)
$CIX = ClO_x + HCl + ClOH + ClONO_2$ (odd chlorine)
$HO_x = H + OH + HO_2$ (active hydrogen)
$HX = HO_x + HNO_x + HOOH$ (odd hydrogen)
$(HX) = (HO_x) + (HNO_x) + 2(H_2O_2)$

This article concentrates on the important role played by the oxides of nitrogen in the chemistry of the global atmosphere. Among the nitrogen oxides, NO and NO₂ are by far the most important because of their ability to affect ozone through catalytic reactions. Chemical interactions with several other atmospheric gases produce a great number of species of oxides of nitrogen. The terminology adopted in this discussion is presented in Table 1. Unfortunately, a generally accepted terminology does not exist and occasionally one encounters terms like Cl_x, NO_x, and NO_y defined differently by different authors. The most recent compilation of reaction rate coefficients can be found in the review by Hampson & Garvin (1977).

THE TROPOSPHERE

Chemistry of the Oxides of Nitrogen NO and NO₂

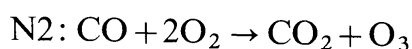
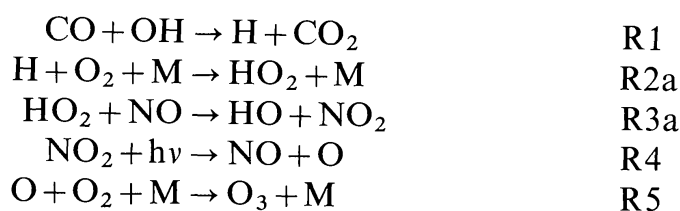
Production of ozone in polluted environments by photochemical oxidation of the unburned hydrocarbons in automobile exhaust gases requires the presence of nitric oxide and nitrogen dioxide as catalysts. The set of reactions responsible for the formation of ozone is basically the following:



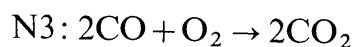
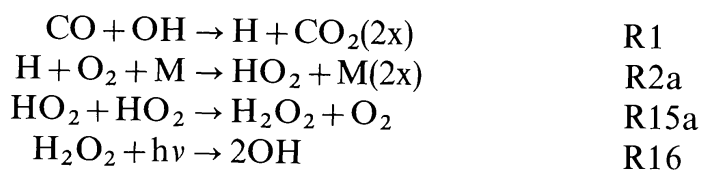
In this set of reactions the symbol R denotes a radical species such as H,

CH₃, and CH₃C(O), which are intermediate products of hydrocarbon and carbon monoxide oxidation in the atmosphere (Altshuller & Bufalini 1971, Demerjian et al 1974). These reactions cause a stepwise dissociation of molecular oxygen, which is a biradical and attaches easily to other radicals. Direct dissociation of O₂ cannot take place in the troposphere because the solar ultraviolet radiation that reaches the troposphere is insufficiently energetic to split the molecule.

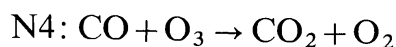
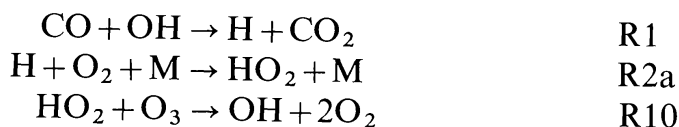
There is no reason to believe that the production of ozone in the troposphere is restricted to polluted urban environments. Ozone should also be produced in the non-urban troposphere, if the necessary photochemical ingredients are present. The oxidation of carbon monoxide (CO) in the presence of nitric oxide provides the simplest mechanism for ozone formation in "clean" air (Crutzen 1973):



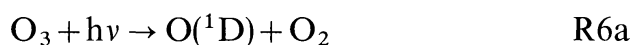
It follows, therefore, that the oxidation of CO in the atmosphere could yield one ozone molecule for each carbon monoxide molecule oxidized in the atmosphere. This set of reactions requires the presence of sufficient NO to insure its occurrence since other reactants compete with NO for the HO₂ radical. Without sufficient NO, one of the following reaction sequences, which do not produce ozone, may occur :



or :



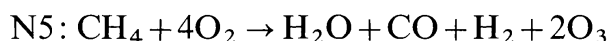
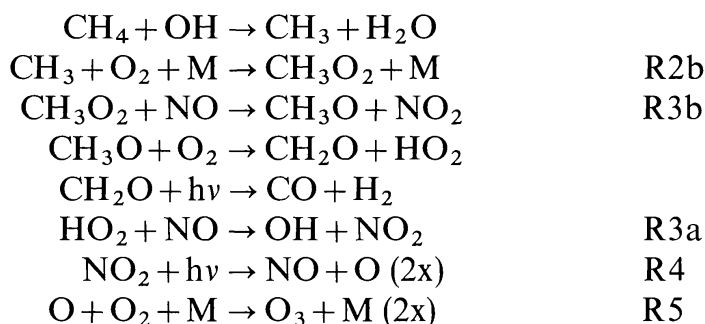
Only recently have the rate coefficients for reaction R3a (Howard & Evenson 1977) and R10 (Zahniser & Howard 1978) been determined satisfactorily, and reaction R3a was shown to be very fast. It is easy to estimate the concentration of nitric oxide required in order for reaction sequence N2 to dominate over N4. Assuming a typical clean air ground level ozone volume mixing ratio of about 20 ppbv (2×10^{-8}), and adopting the rate constants $k_{10} = 1.4 \times 10^{-14} \exp(-580/T)$ and $k_{3a} = 3.3 \times 10^{-12} \exp(254/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, from the work of Howard and co-workers we arrive at a critical volume mixing ratio for NO of 0.005 ppbv. For NO mixing ratios above this very small value, ozone production via the reaction set N2 is larger than its destruction by the reaction set N4. We review the few available measurements of "clean air" NO_x concentrations in the following section, but note here that from available observations, it seems most likely that background concentrations of NO in the troposphere are indeed substantially larger than 0.005 ppbv over the industrialized continental areas in the Northern Hemisphere (N.H.). In the Southern Hemisphere (S.H.) and in unindustrialized areas of the N.H. the situation should be quite different. There is, therefore, a clear possibility that significant in situ photochemical ozone production takes place in the N.H. troposphere by reaction cycle N2, while in the S.H. ozone loss by reaction set N4 may be more important (Fishman & Crutzen 1978). Additional loss of ozone occurs in both hemispheres as reaction R6a is partially ($\lesssim 10\%$) followed by reaction R17



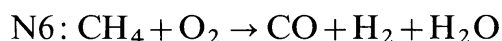
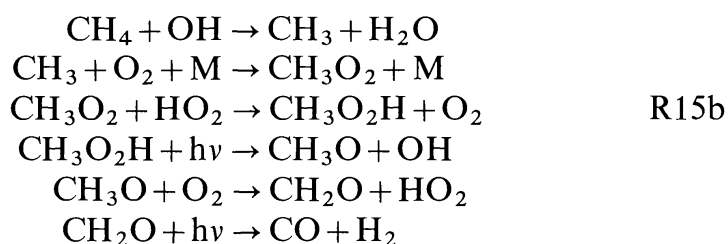
The dominant fate of $\text{O}(^1\text{D})$ atoms in the atmosphere is otherwise deactivation by N_2 and O_2 molecules to yield ground state $\text{O}(^3\text{P})$, which immediately undergoes reaction R5 yielding no net effect on ozone concentrations.

Considerable amounts of tropospheric ozone may also be formed during the photochemical oxidation of industrial and natural hydrocarbons in the presence of NO. Among the natural emissions, isoprene (C_5H_8) and terpenes ($\text{C}_{10}\text{H}_{16}$) are emitted by tree foliage (Zimmerman et al 1978), and methane (CH_4) (Ehhalt 1974) is formed in highly anaerobic environments, especially swamps and marshes, by the decay of organic matter. Carbon monoxide is in all cases an intermediate product of the oxidation of these hydrocarbon gases and the natural atmospheric CO source is probably larger than that provided by the fossil fuel combustion processes (Zimmerman et al 1978). Among possible oxidation sequences leading to

the production of carbon monoxide and molecular hydrogen from methane (CH₄) oxidation is (Levy 1971, 1974):



The efficiency of this set of reactions in producing ozone again depends on the abundance of NO in the atmosphere. A competitive reaction of HO₂ with CH₃O₂ introduces a reaction chain that does not lead to ozone production :



Because the reaction $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$ is very fast, nitric oxide plays an important role in determining the concentration of perhydroxyl radical (HO₂). Lower concentrations of NO, therefore, allow higher concentrations of HO₂. If we adopt similar rate coefficients for reactions R3b and R15b, as for R3a and R15a respectively, we can again estimate that reaction with nitric oxide and subsequent ozone formation (chain N5) will be more important than the chain which does not produce ozone (N6) for nitric oxide volume mixing ratio larger than about 0.005 ppbv. For much lower volume mixing ratios we do not expect significant ozone production from methane oxidation in the troposphere. We note also that species like CH₃O₂H (methyl-hydroperoxide), other organic hydroperoxides, as well as H₂O₂ (hydrogen peroxide), are quite soluble in water and may be removed from the atmosphere in rainwater before photodissociation occurs, so that production of CO in reaction cycle N6 is in no way guaranteed. The photodissociation probability of CH₃O₂H is not

known, but is normally assumed to be close to that of H_2O_2 , which has a tropospheric lifetime against photolysis of a few days. The oxidative power of the peroxides in rainwater may strongly influence the oxidation of SO_2 to H_2SO_4 as hypothesized by Crutzen (1975) and convincingly shown in the laboratory by Penkett et al (1978). Through the combined effect of reactions R3 and R15, the probability of photochemical gas phase formation of the peroxides (RO_2H) is inversely proportional to the square of the nitric oxide concentrations. Consequently, the conversion of SO_2 to H_2SO_4 in cloud droplets by H_2O_2 could strongly depend on the concentrations of NO_x in the air. Thus the contribution of HNO_3 to precipitation acidification via the reaction $\text{OH} + \text{NO}_2 (+\text{M}) \rightarrow \text{HNO}_3 (+\text{M})$ may be favored over that of H_2SO_4 in regions close to pollution sources, where NO concentrations are high. If this hypothesis is indeed correct, it would follow that increasing additions of NO_x to the atmosphere would have the effect of pushing the oxidation zone of SO_2 to H_2SO_4 further away from the pollution source areas.

The oxidation schemes of isoprene and the terpenes in the atmosphere are more complicated than those of CH_4 , but ozone production occurs much faster than during the oxidation of methane, if NO is present (Zimmerman et al 1978). In these cases, the abundance of nitric oxide is again of great importance in defining the oxidation paths and products, and the possibility of a substantial removal of the peroxides and other oxygenated hydrocarbon intermediates should be considered, if insufficient nitric oxide ($\lesssim 0.005$ ppbv) is present. Little information is presently available to allow estimations of the importance of homogeneous versus heterogeneous reactions in the troposphere and much of the present discussion is, therefore, rather descriptive.

The exact magnitude of carbon monoxide and ozone production in the troposphere for the moment must remain quite uncertain. Some rough estimates of maximum production rates of carbon monoxide in the troposphere can be made, however, by assuming that each carbon atom emitted into the atmosphere as isoprene and methane will yield one molecule of carbon monoxide.

Adopting the estimated worldwide production rates of methane of $400\text{--}620 \times 10^{12}$ g C/yr (Ehhalt 1974) and 830×10^{12} g C/yr for terpenes and isoprene (Zimmerman et al 1978), we arrive at a maximum average global CO column production rate of about 4×10^{11} mol $\text{cm}^{-2} \text{ s}^{-1}$ due to the oxidation of methane and isoprene/terpenes, if all oxidations lead to CO. In comparison, the industrial input of carbon monoxide from incomplete combustion amounts on the average to about 9×10^{10} mol $\text{cm}^{-2} \text{ s}^{-1}$ (Seiler 1974). NO and CO are emitted together in industrial and automotive emissions, so that these CO emissions are most likely to

yield ozone by reaction sequence N2. As we will see, the atmospheric residence time of NO_x must be very short, so that the presence of enough NO_x to produce ozone during natural hydrocarbon oxidation is not certain.

We have seen that during the oxidation of CH₄ to CO, there is a production of two ozone molecules (mechanism N5). Similar results apply to the oxidation of other hydrocarbons (Zimmerman et al 1978). If the oxidation of all organic compounds (including that of CO) were to yield only two ozone molecules per carbon atom emitted, then the average global yield of ozone would already be about $10^{12} \text{ mol cm}^{-2} \text{ s}^{-1}$, compared to an estimated average flux of ozone out of the stratosphere into the troposphere in the N.H. of less than $10^{11} \text{ mol cm}^{-2} \text{ s}^{-1}$ (Mohnen et al 1977, Danielsen & Mohnen 1977) and a ground level average global ozone destruction rate of $4\text{--}7.6 \times 10^{10} \text{ mol cm}^{-2} \text{ s}^{-1}$ (Fabian & Junge 1970). Such an ozone column production rate is clearly too large; the sink of ozone provided by the sequence of reaction R6a followed by R17 is an order of magnitude smaller (Fishman & Crutzen 1978). Consequently, there are probably large portions in the troposphere where the NO volume mixing ratio is less than 0.005 ppbv. This would also imply a substantial removal of organics from the atmosphere in rainfall and the existence of quite large concentrations of peroxides, alcohols, and aldehydes in air with low NO concentrations.

A substantial fraction of the ozone molecules in the troposphere has probably been produced in situ (especially in the N.H.) and is not of stratospheric origin. We should note that the stratospheric flux of ozone into the troposphere occurs in bursts over restricted geographical areas in the vicinity of tropopause breaks. Such meteorological processes are clearly much more easily observable than the in situ ozone formation and destruction processes taking place virtually everywhere on a time scale of weeks. In view of the important chemical role played by tropospheric ozone, a careful examination of the origin of tropospheric ozone is necessary. This requires a much better and more extensive data base on the worldwide tropospheric and lower-stratospheric ozone distribution than is presently available, especially in the S.H. The issue is clearly of substantial importance for the prediction of future changes in the distribution of some photochemically and radiatively active minor constituents in the earth's atmosphere, which are affected by OH radical attack. The observed ozone distributions in the N.H. and S.H., taking into account differences in stratosphere-troposphere exchange and the much larger destruction rates of ozone on soil than on sea water, require a four-fold larger annual flux of ozone from the stratosphere to the troposphere in the N.H. than in the S.H. (Fishman & Crutzen 1978). Meteorological parameters which,

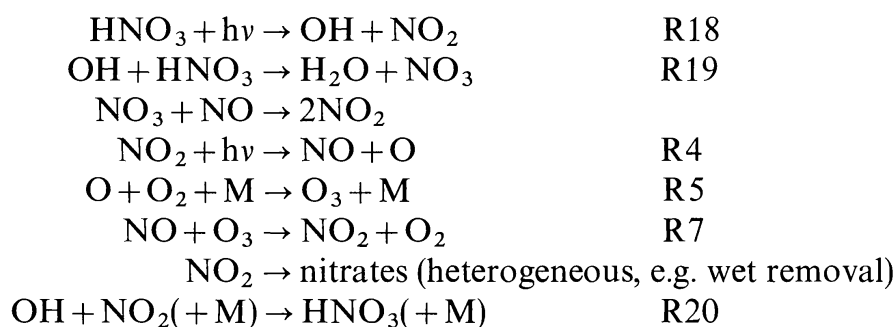
indirectly, should be indicative of stratosphere-troposphere exchange do not suggest such a large difference in meteorological behavior between hemispheres. However, insufficient meteorological data in the S.H. make this study rather tentative. Nevertheless, we should seriously consider the hypothesis of substantial ozone production in the N.H. and ozone destruction in the S.H. The concentration of NO is one of the most important, and least known, photochemical parameters in this regard. Some rate coefficients of essential reactions may still not be well enough known for tropospheric applications. For instance, the reaction coefficients determined for some reactions involving HO_2 at low pressure probably need to be adjusted for applications at tropospheric conditions. In addition, an increase in the rates of the reactions $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$ and $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ has been observed following water vapor additions in laboratory systems (Hamilton 1975, Hamilton & Naleway 1976, Cox 1978). Similar complications could prove to be the case with other reactions involving HO_2 .

Nitrogen Oxide Observations

There are few reliable observations of the concentrations of the oxides of nitrogen NO, NO_2 , and HNO_3 in the non-urban troposphere. The optical measurements of Noxon (1978, 1979) clearly show that most of the vertical column mass of NO_2 (and therefore NO) is located in the stratosphere, when observations are made in relatively unpolluted air masses. During such conditions, the total NO_2 abundance in the troposphere is mostly well below 10^{15} cm^{-2} , even in the industrial eastern United States. This normally applies if measurements are made at a distance of more than 50 km from urban centers outside the urban plume. Assuming a scale height of 2 km for the NO_2 mixing ratio, the average volume mixing ratio of NO_2 is less than 0.25 ppbv. Near cities, higher tropospheric NO_2 concentrations on the order of 100 ppbv or more are typically found (Trijonis 1978). Noxon's measurements of background, continental, NO_x concentrations, which are much below 1 ppbv, cast considerable doubt on the value of the often quoted literature estimates of Robinson & Robbins (1971), which were based on older and presumably less reliable techniques. Subsequent measurements include those of Lodge et al (1974) in the humid tropics in Panama (0.1–0.3 ppbv), Drummond (1977) near Laramie, Wyoming (0.1–0.4 ppbv of NO_x), and Moore (1974), who measured 0.1–0.3 ppbv of NO_2 near Boulder, Colorado. Ritter et al (1978) report NO_x volume mixing ratios between 0.3 and 0.5 ppbv during "clean air" conditions in northern Michigan and an average of 0.2 ppbv at a station in the Rocky Mountains at a 3-km altitude 30 km northeast of

Denver. Measurements over Colorado and Wyoming in December by Kley et al (1978) give ground level mixing ratios of about 1 ppbv for NO_x and a fall-off to 0.15 ppbv above 6 km. Ground level observations by the same researchers at the same Rocky Mountain station give NO_x volume mixing ratios between 0.02 and 0.2 ppbv. Considering Noxon's low background tropospheric NO₂ concentration determinations ($\lesssim 0.25$ ppbv) and the high urban concentrations of about 100 ppbv (Trijonis 1978), clearly the residence time of NO_x in the troposphere must be remarkably short, maybe less than one day.

The most extensive tropospheric measurement of nitric acid (HNO₃) in the "clean" troposphere has been conducted by Huebert & Lazrus (1978, 1979) during the worldwide chemistry expeditions "GAMETAG" (an acronym for Global Atmospheric Measurement Experiment of Tropospheric Aerosols and Gases). These measurements were made on board the NCAR Electra aircraft in 1977 and 1978. These observations show average nitric acid volume ratios between about 0.2 and 0.8 ppbv over continental mid-latitudes (US and Canada), while at all other locations (mostly over the Pacific) measured mixing ratios were lower, <0.03–0.15 ppbv in the lowest two kilometers and <0.03–0.3 ppbv in the middle troposphere. From these data we can, for the sake of discussion, make some rough estimates of the background volume mixing ratios of NO_x. To a first approximation the reactions affecting the concentrations of NO_x in the unpolluted troposphere are



Note that in this set of reactions the photolysis of nitric acid provides a source of NO₂ and, therefore, of NO_x as reactions R3, R4, and R7 will immediately establish a steady state ratio between the concentrations of NO and NO₂. Neglecting heterogeneous removal and assuming that there are no other atmospheric sources of NO_x than HNO₃ decomposition, and stationary state conditions for NO_x, we can derive the upper limit to the concentration of NO_x from the equation

$$(\text{NO}_2) < \frac{[J_{18} + k_{19}(\text{OH})](\text{HNO}_3)}{k_{20}(\text{OH})}$$

Assuming tropospheric global daytime concentrations of OH to be near 10^6 mol cm^{-3} (Perner et al 1976, Davis et al 1976) and adopting appropriate values for the reaction coefficients and the dissociation probability of nitric acid, we arrive at $(\text{NO}) \lesssim 4 \times 10^{-2} (\text{HNO}_3)$, since $(\text{NO}) \approx (\text{NO}_2)$ in the lower “clean” troposphere. This leads to NO volume mixing ratios over continental mid-latitudes of $8\text{--}32 \times 10^{-12}$ to less than 6×10^{-12} over non-continental areas. The calculated concentrations over continental areas are generally smaller than those obtained by direct measurements of NO. Therefore in the following section of this paper we explore possible sources of NO_x in the free troposphere other than from photolysis of nitric acid.

Sources and Sinks of Tropospheric NO_x

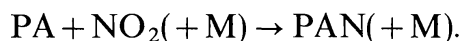
The input of nitric oxide into the troposphere consists of an anthropogenic source of about $20 \times 10^{12} \text{ g N/yr}$ from combustion engines (Pratt et al 1977), a contribution by lightning of $8\text{--}40 \times 10^{12} \text{ g N/yr}$ (Noxon 1978, Chameides et al 1977), and a possible production of 10^{13} g N/yr in soils (Galbally & Roy 1978). Adopting the known rate constants for the reaction $\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O}$ and assuming an average OH concentration of 10^6 cm^{-3} , we estimate a tropospheric lifetime of NH_3 against gas phase destruction of about 3 months. Because this is so long, it seems likely that most ammonia emitted into the atmosphere is removed by processes other than gas phase destruction. Furthermore, since it is not certain that NH_2 will oxidize to NO_x , the production of NO_x from NH_3 oxidation should be less than about 8 Tg N/yr . This estimate is based on a total ammonia source of $73\text{--}100 \text{ Tg N/yr}$ (Söderlund & Svensson 1976, Dawson 1977) and an average tropospheric lifetime of less than one week. Soils were previously thought to release NO into the atmosphere (see e.g. Robinson & Robbins 1971) in amounts much larger than the industrial input. This view is unacceptable in view of the global atmospheric NO_x observations and estimated residence times.

For the reaction $\text{NO}_2 + \text{OH} (+\text{M}) \rightarrow \text{HNO}_3 (+\text{M})$ to provide an NO_x residence time of one day, average daytime OH concentrations must be about $2.5 \times 10^6 \text{ mol cm}^{-3}$. From observations, average global mid-latitude molecular densities of hydroxyl are probably about 10^6 cm^{-3} or larger (Perner et al 1976, Davis et al 1976, Crutzen & Fishman 1977). Most of the industrial input of NO_x , together with copious amounts of other pollutants, such as reactive hydrocarbons, occurs, however, in or near urban centers. In such environments the hydroxyl concentrations in the planetary boundary layer are expected to be substantially higher than in the “clean” troposphere, so that reaction with OH may provide the required efficient sink for NO_x . The nitric acid formed in this conversion

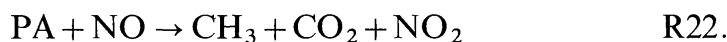
should then be removed on a time scale of less than one month to explain the measurements of Huebert & Lazrus (1978, 1979). Some of the nitric acid formed in the polluted boundary layer may, however, be converted back to NO_x after dispersion into the background troposphere as the equilibrium value of the ratio (HNO₃)/(NO₂) decreases from 100 to 25 to 3 for OH concentrations of respectively 10⁷, 10⁶, and 10⁵ cm⁻³. It is possible that gaseous organic nitrates play a substantial role as a sink for urban NO_x and a global source of NO_x for outside industrial areas, and provide another source of NO_x in the "clean" troposphere.

Organic peroxy-nitrates are produced by recombination reactions $\text{RO}_2 + \text{NO}_2 (+\text{M}) \rightarrow \text{RO}_2\text{NO}_2 (+\text{M})$. In smog chamber experiments (see Demerjian et al 1974) the observed peroxy-nitrates originated only from the peroxy-acyl radicals $\text{CH}_3\text{C}(=\text{O})\text{O}_2$, $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{O}_2$, and their higher homologues, and not from the peroxy-alkyl radicals, such as CH_3O_2 , $\text{C}_2\text{H}_5\text{O}_2$, etc, indicating that the peroxy-alkyl nitrates are less stable than the peroxy-acyl nitrates. This experimental finding has now been confirmed by a review of kinetic and thermochemical studies on the thermal stability and kinetics of $\text{CH}_3\text{C}(=\text{O})\text{O}_2\text{NO}_2$ (PAN), $\text{CH}_3\text{O}_2\text{NO}_2$, and HO_2NO_2 (Cox & Roffey 1977, Hendry & Kenley 1977, 1979, Cox 1978, Graham et al 1977).

Among the peroxy-acyl nitrates the most important species, both in smog chamber experiments and in the atmosphere, seems to be peroxy-acetyl nitrate (PAN), which is formed from the peroxy-acetyl (PA) radical, $\text{CH}_3\text{C}(=\text{O})\text{O}_2$, by the reaction



PAN is not stable in the atmosphere, but is decomposed according to the following chain



These reactions yield the following formula for the photochemical lifetime of PAN during daytime when NO is present :

$$\tau_{\text{PAN}} = \frac{1}{k_{21a}} \left\{ 1 + \frac{k_{21b}(\text{NO}_2)}{k_{22}(\text{NO})} \right\}$$

with

$$k_{21a} = (7.9 \times 10^{14}) \exp \left(\frac{-12540}{T} \right)$$

and with $k_{21b} = 1.4 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{22} = 2.4 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Cox & Roffey 1977).

With $(\text{NO}_2) \approx (\text{NO})$ during daytime and no PAN loss at night, because (NO) disappears, 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 US standard atmosphere: at $z = 0$ km, $T = 288$ K, $\tau(\text{PAN}) = 0.4$ days; $z = 2$ km, $T = 275$ K, $\tau(\text{PAN}) = 2.9$ days; $z = 4$ km, $T = 262$ K, $\tau(\text{PAN}) = 28$ days; $z = 6$ km, $T = 249$ K, $\tau(\text{PAN}) \approx 1$ yr; $z = 8$ km, $T = 235$ K, $\tau(\text{PAN}) = 15$ yr.

We note that the lifetime of PAN against photochemical destruction increases rapidly with altitude, becoming longer than one year above 5 km. Photolysis of PAN below this altitude is probably negligible (E. R. Stephens, personal communication). Above 5 km PAN is probably slowly decomposed by OH radical attack and maybe by photolysis. No information on either of these processes is currently available. It is clear that PAN formation will be favored during the cold winter months (Hendry & Kenley 1979). Concentrations of PAN similar to or larger than those of nitric acid have been measured in contaminated air in West Covina near Los Angeles. According to Spicer et al (1976) and Spicer (1977), on the average about 80% of the NO_x removed from the polluted air ended up as PAN (average daily volume mixing ratio ≈ 12 ppbv against nitric acid ≈ 3 ppbv). Only a little particulate nitrate (≈ 1 ppbv) was formed. From an extensive series of measurements in St. Louis, Missouri, and West Covina, California, the ratio $(\text{PAN} + \text{HNO}_3)/(\text{NO} + \text{NO}_2 + \text{PAN} + \text{HNO}_3)$ in the afternoon was shown to range between 0 and 76% in St. Louis and between 2 and 54% in West Covina, with an average value of about 11% in both cities (Spicer et al 1976). As these measurements were conducted at sites continuously supplied with fresh automotive NO_x and hydrocarbon emissions, the observations were clearly made in air masses in which transformations of NO_x to PAN and HNO_3 were still taking place. In fact, both smog chamber experiments and theoretical calculations (Spicer et al 1976, Hendry & Kenley 1979) indicate a buildup of PAN to concentrations larger than NO_2 in the later phases of photochemical smog formation. The hydrocarbons which operate in the transformation of NO_x to PAN in St. Louis and West Covina no doubt come overwhelmingly from automotive exhaust. In rural environments, especially near forests, hydrocarbon emissions consist mainly of isoprene and terpenes from tree foliage. Clearly then, it is not only important to consider nitric acid, but also and possibly more importantly PAN and other vapor phase organic nitrates as precursors to NO_x in the global atmosphere. This is important as PAN is surprisingly slowly lost 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 NO_x may, therefore, occur in the manner shown in

Figure 1. Whether or not PAN can indeed be a "hiding place" for NO_x has to be determined from measurements of NO_x and PAN in the unpolluted troposphere far from urban centers. Fortunately, good techniques to make low concentration measurements of these gases are now becoming available.

In considering non-photochemical removal rates of NO, NO₂, and their oxidation products from the atmosphere, we must consider the role of rainout and washout (wet removal) in the atmosphere. According to Rodhe & Grandell (1973) the efficiency of this process is to an important degree determined by the frequency of precipitation, and can at the fastest lead to a removal time of a few days (2–4 days for Stockholm, Sweden). This time is about equal to the estimated residence time of nitric acid, but seems to be too long to explain the residence time of NO_x. Gas phase reactions must, therefore, be more important.

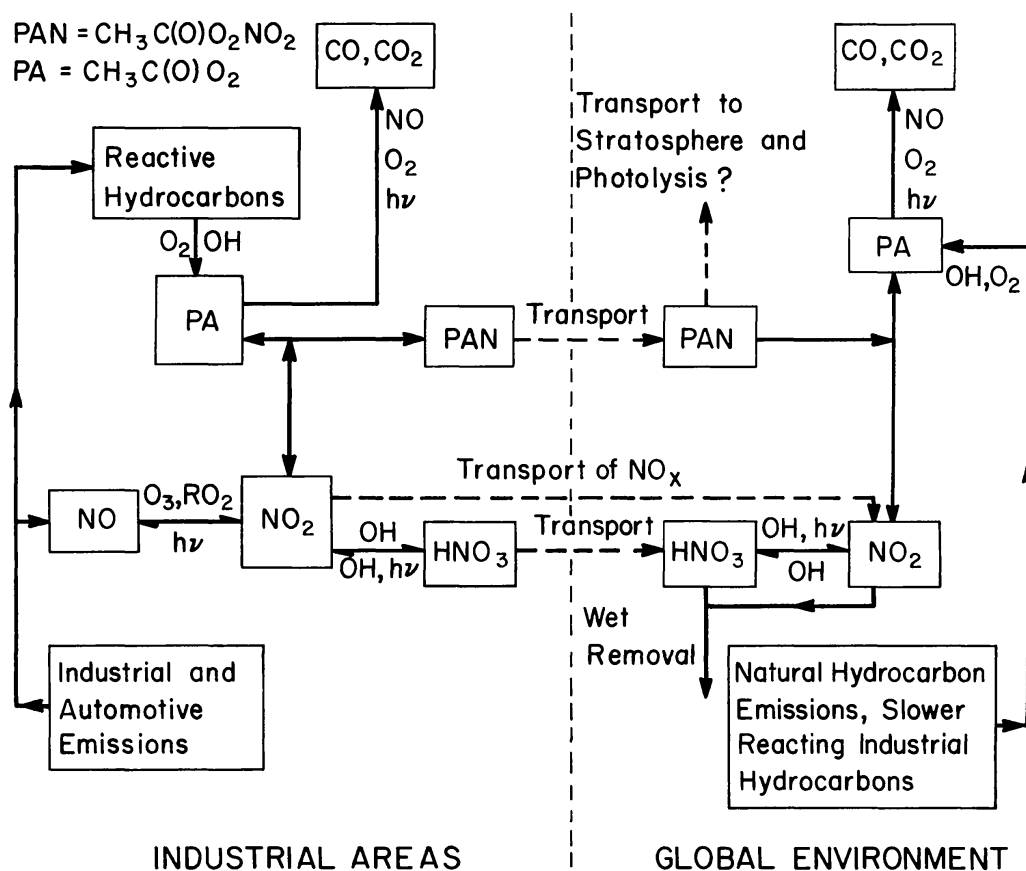


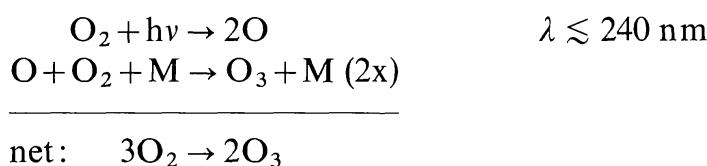
Figure 1 Transport of NO_x, HNO₃, and CH₃C(O)O₂NO₂ (= PAN) from urban centers to the "clean" troposphere. PAN has a long lifetime in the middle or upper troposphere and may deliver NO_x in the warmer lower troposphere at large distances from the urban centers in which PAN was initially formed. Likewise, nitric acid formed in polluted environments may supply NO_x to the "clean" troposphere.

Finally, we must also consider the effects of “dry” deposition. Hill (1971) observed a deposition velocity of 2 cm/s of NO₂ on an alfalfa canopy with an NO₂ volume mixing ratio of 50 ppbv (the deposition velocity of NO was only 0.1 cm/s). Similar removal rates were determined by Tingey (1968) on alfalfa and oats. With a deposition velocity of the order of 2 cm/s, soils, vegetation, and water surfaces may provide a significant sink for tropospheric NO_x (and presumably nitric acid) yielding a residence time in the lower atmosphere of a few days.

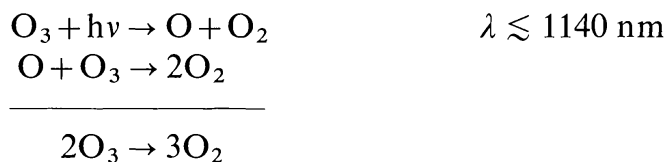
OXIDES OF NITROGEN IN THE STRATOSPHERE

At the end of the last decade our knowledge of stratospheric photochemistry was truly rudimentary. Considering the supreme importance of ozone to the atmosphere and the biosphere, the slow evolution of knowledge up to that time seems most remarkable. It was then still commonly accepted that the photochemical processes affecting ozone in the stratosphere, as proposed by Chapman (1930), were adequately explained by

(a) formation through photolysis of O₂ :



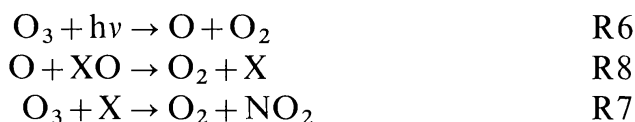
(b) removal through the reactions :



Regarding the troposphere, it was believed that ozone was essentially inert when transported below about 25 km and only destroyed by contact with the earth's surface. During the last decade, the progress in our knowledge of the photochemistry of atmospheric ozone has been truly revolutionary. Indeed, comparing the present literature with that written before 1970 one wonders whether it describes the chemistry of the same planet.

Now it is clear that the oxides of nitrogen play an important role in defining the abundance and distribution of stratospheric ozone. Interest in the stratospheric role of the oxides of nitrogen started with the recognition that NO and NO₂ could catalyze the destruction of ozone in the stratosphere and that human activities could lead to significant increases

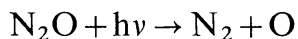
in the stratospheric abundance of NO_x (Johnston 1971, Crutzen 1970). Ozone destruction was postulated to occur, with X = NO, via the cycle of reactions :



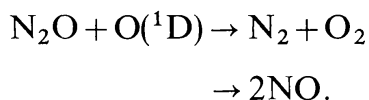
The existence of an effect from the catalytic cycle involving nitric oxide and leading to ozone destruction in the stratosphere below 45 km was clearly demonstrated by the observations of a sudden decrease in ozone concentrations lasting for several weeks immediately following the huge solar proton event of August, 1972 (Heath et al 1977). The detected decrease in ozone was very close to that earlier calculated through use of a two-dimensional, photochemical model of the atmosphere (Heath et al 1977).

We may infer from the preceding discussion that direct transfer of NO_x and HNO₃ from the troposphere to the stratosphere must be essentially forbidden by the very short tropospheric residence time of NO_x of the order of one day. Observational support of this contention is provided by the global distribution measurements of nitric acid by Huebert & Lazrus (1978, 1979) in which nitric acid was shown to be present in the middle troposphere at volume mixing ratios ranging from less than 0.03 to 0.3 ppbv. In contrast, stratospheric nitric acid volume mixing ratios are, on the average, close to 5 ppbv (Lazrus & Gandrud 1974). In addition, in the previous section we referred to the observations of Noxon (1978), which show that most of the atmospheric NO₂ is likewise located in the stratosphere.

Less reactive and less water soluble oxides of nitrogen do, however, penetrate the tropopause. There may possibly be some upward transfer of organic nitrate molecules (in particular PAN). There is, however, little doubt about the importance of nitrous oxide (N₂O). This gas seems very inert in the troposphere and is photochemically destroyed in the stratosphere (Bates & Hays 1967), mainly through the photolysis reaction



with smaller contributions coming from the reactions



Although only about 10% of the nitrous oxide that enters the stratosphere is removed by the latter reaction (Johnston et al 1978), this reaction is of substantial importance because it provides an important, and probably a dominant, source of nitric oxide in the ozone layer (Nicolet & Vergison 1971, Crutzen 1971, McElroy & McConnell 1971).

Other natural sources of stratospheric nitric oxide are provided by the action of galactic cosmic rays at high geomagnetic latitudes especially in the lower stratosphere (Nicolet 1975) and by sporadic outbursts of solar protons following some solar flares, the so-called solar proton events (SPE) or polar cap absorption events (PCA) (Crutzen et al 1975). Very large amounts of NO_x are produced above 100 km by EUV radiation and in auroras by the ionizing and dissociative action of energetic electrons of solar origin. Using a one-dimensional photochemical model, Strobel et al (1970) and Strobel (1971) estimated that only a negligible fraction of the nitric oxide produced at high altitudes could reach the stratosphere. This is due to the efficient reactions (Cieslik & Nicolet 1974), $(\text{NO} + h\nu \rightarrow \text{N} + \text{O}) + (\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}) = 2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$, which occur, however, only in the sunlit atmosphere above 45 km (Nicolet 1975). In darkness, no nitrogen atoms are formed and those present are transformed into nitric oxide by reactions with molecular oxygen and ozone. During the long polar night conditions NO may be transported downwards into the stratosphere by the general circulation of the upper atmosphere (Murgatroyd & Singleton 1961, Geisler & Dickinson 1968, Crutzen 1972). This idea is supported by some modern developments in the theory of the large scale, Lagrangian-formulated, dynamics of the upper atmosphere (McIntyre 1977, Matsuno & Nakamura 1978, Dunkerton 1978). According to Offerman (personal communication, 1978) downward transport of NO near the mesopause (≈ 80 km) does apparently also occur at middle and high latitudes during periods of enhanced D-region radio wave absorption (D-region winter anomalies). Such downward transport, if it occurred to a significant degree, would be of special interest, as NO production in the high atmosphere is large and related to solar activity (Strobel et al 1970, Crutzen 1970).

Table 2 shows estimates of the gross NO_x production rates in the atmosphere above 100 km. Stolarski et al (1975) show that the absorbed solar EUV energy ($\lambda < 1025 \text{ \AA}$) is about equally split between photoelectrons and ion pair production that becomes stored as chemical energy. Photoelectron impact dissociates N_2 into $\text{N}(^2\text{D})$ and $\text{N}(^4\text{S})$ and in the global mean about $2.5 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ dissociations occur above 100 km. The gross global NO_x production rate is, thus, $2.7 \times 10^{29} \text{ s}^{-1}$ above 100 km. This source can vary by a factor of two as the solar EUV output varies over the solar cycle. $\text{N}(^4\text{S})$ and $\text{N}(^2\text{D})$ are produced not only by

Table 2 Sources of atmospheric NO_x (1 Tg = 10¹² g)

<u>Troposphere</u>	
Lightning :	8–40 Tg N/yr (Noxon 1978, Chameides et al 1977)
Combustion :	20 Tg N/yr (Söderlund & Svensson 1976)
Soil exhalations :	10 Tg N/yr (Galbally & Roy 1978)
Ammonia oxidation :	< 8 Tg N/yr (this review)
<u>Stratosphere</u>	
N ₂ O oxidation :	1 Tg N/yr (Johnston et al 1978)
Galactic cosmic rays :	0.024–0.036 Tg N/yr (Nicolet 1975); solar maximum-minimum
Solar proton event :	0.12 Tg N (1972 maximum, Crutzen et al 1975)
Nuclear bombs :	0.024 Tg N per megaton TNT (Johnston et al 1973)
<u>Thermosphere</u>	
Meteoroids :	0.17 Tg N/yr (Park & Menees 1978)
Solar EUV :	200–400 Tg N/yr; solar minimum-maximum

photoelectron dissociation but also by ion chemistry as discussed by Strobel et al (1970), Strobel (1971), Rusch et al (1975), and Roble et al (1978).

At high latitudes, the aurora is a source of NO through electron dissociation by N₂ into N(⁴S) and N(²D) and ion chemistry. The global production rate by auroral processes is highly variable and difficult to estimate. Akasofu (1976) using satellite photographs of auroral structure estimated the total area in the polar cap that was subjected to auroral particle bombardment to vary between 4×10^5 and 1.8×10^7 km² for geomagnetic quiet and intense auroral substorm conditions. Using the particle data measured by the Atmospheric Explorer satellite, Torr & Torr (1976) determined the latitude distribution of the auroral energy deposition and mean particle spectrum. Above about 60° geomagnetic latitude the energy input was about 2 ergs cm⁻² s⁻¹ with an electron particle spectrum that peaked about 1.5 keV. The total dissociation rate of N₂ by auroral electrons for this energy input and spectrum is about 1.7×10^{10} cm⁻² s⁻¹ above 100 km with peak production at an altitude of 115 km. These values were calculated using the aurora model of Roble & Rees (1977). This is a lower limit of the production rate and the actual rate could be a factor of four larger, since one must also consider the complex ion chemistry. If the production rate is multiplied by the total area of auroral emissions as evaluated by Akasofu then the global auroral NO_x production rate (considering magnetically conjugate auroral zones) exceeds 6×10^{26} s⁻¹ for geomagnetic quiet periods and 2.5×10^{28} s⁻¹ for intense auroral substorm conditions. Although these rates are smaller than the global EUV production rates, they may be important because

of the probability of downward transport at high latitudes during winter. It follows clearly from a comparison of the NO_x production rates in Table 2 that a very small leakage of thermospheric NO_x into the stratosphere may have important consequences for the photochemistry of the stratosphere.

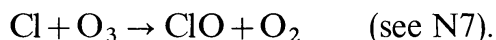
Increased levels of nitric oxide in the stratosphere can be caused in particular by three human activities:

- (a) direct injection of nitric oxide from the exhaust gases of aircraft flying in the stratosphere (Johnston 1971, Crutzen 1971);
- (b) injection of nitric oxide in the fireballs of nuclear explosions (Johnston et al 1973, Goldsmith et al 1973); and
- (c) man's agricultural manipulations, e.g. the increased use of nitrogen fertilizer, leading to the release of nitrous oxide from soils and waters to the atmosphere and thereby increasing the stratospheric levels of nitric oxide (Crutzen 1974a, McElroy 1976).

Many detailed assessment reports have been published over the past years on the stratospheric effects of human activities (NAS 1975, NASA 1977, NAS 1978). We therefore devote our attention only to a brief account of present knowledge of stratospheric photochemistry, an extremely complex subject because of the strong interactions of the oxides of nitrogen with other gases. Photochemically derived species from water vapor and chlorine compounds affect ozone, as does NO_x , by catalytic reactions according to the generalized scheme N7 with $\text{X} = \text{H}$ and OH (Bates & Nicolet 1950, Hampson 1964) and $\text{X} = \text{Cl}$ (Stolarski & Cicerone 1974, Crutzen 1974b, Wofsy & McElroy 1974).

None of these authors foresaw a major role of ClO_x in the stratosphere. A dramatic change took place, however, when Molina & Rowland (1974) discovered the growing production in the stratosphere of the very powerful catalysts Cl and ClO as a result of the photolysis of the chlorofluoromethane gases CFCl_3 and CF_2Cl_2 , by then widely and increasingly used in refrigerators and as propellants in spray cans. With chlorine chemistry taking on great importance in stratospheric photochemistry, the chemical interactions between the ClX , HX , and NX reactant groups became of substantial interest (see Table 1 and Figure 2). If not for these interactions, NO_x , HO_x , and ClO_x would each independently destroy ozone catalytically. It is the interactions between the groups themselves that make the effects of these substances on ozone and on one another much more difficult to predict.

Cl atoms react mainly with O_3 through



Coupling of the NX and ClX groups occurs as follows:



The net effect of these two reactions is to shift the balance from NO to NO₂, thereby enhancing NX catalyzed ozone destruction, when NO₂ reacts with O in reaction R8, but reducing ClX catalyzed destruction, when it dissociates to yield O by reaction R4. The effects of NO_x additions to the stratosphere must, therefore, depend on the ClX concentrations, which at any time are present in the stratosphere. Reaction 23 also shifts the equilibrium between Cl and ClO towards Cl. When more Cl is present, more ClO_x is converted to non-reactive HCl, through the

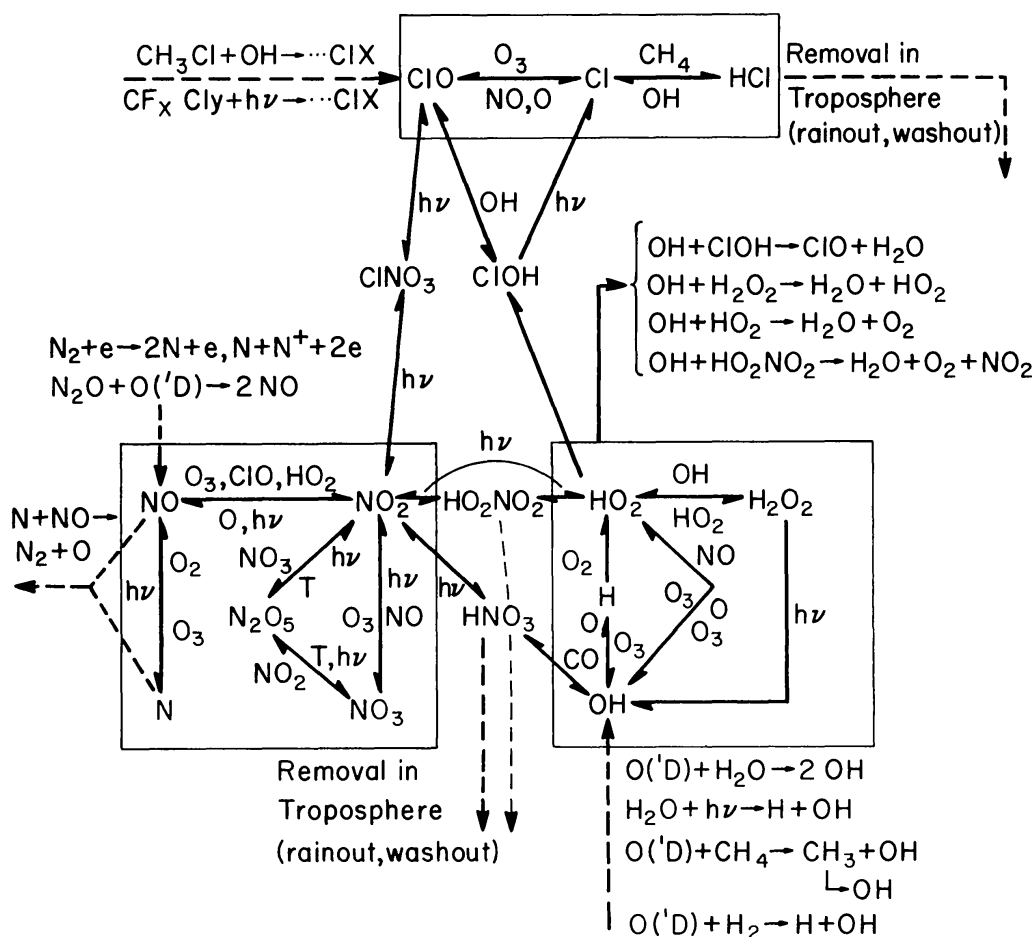
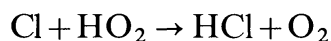
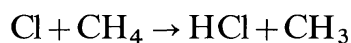


Figure 2 Interactions between the NX, HX, and CIX families of reactants. The transformation reactions within each family of reactants occur generally at much faster rates than the net rates of formation (and destruction) of NX, CIX, and HX. This forms the basis for the “quasi steady state assumption” (QSSA), which is often used with great advantage in time-dependent models. The importance of ClOH and HO₂NO₂ is doubtful.

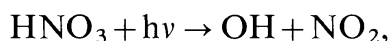
reactions



and thus the ClX-catalyzed destruction of ozone is repressed. However, the HX group is coupled to the NX group via



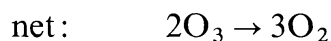
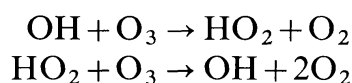
R2a mainly stores active NO_x as HNO_3 (compare HCl, above), thereby protecting ozone from NO_x catalyzed destruction. The reaction that reforms NO_x from HNO_3 ,



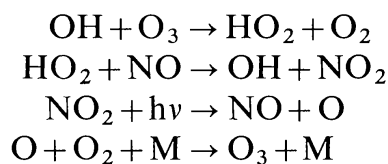
is rather slow below about 30 km.

Reaction R3a is therefore very important below 35 km, since it shifts the equilibrium between HO_2 and OH towards OH, thus enhancing production of HNO_3 via R2a. Reaction R3a has recently been shown to be extremely fast (Howard & Evenson 1977), having the effect of making HNO_3 the predominant NX compound below 30 km.

Reaction R3a also diverts the catalytic, ozone destroying HX reaction set



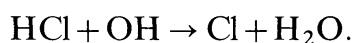
into a “do-nothing” cycle,



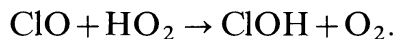
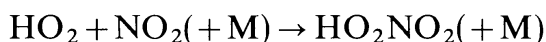
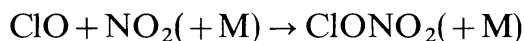
no net chemical effect,

thereby decreasing ozone loss. This will be true under present atmospheric conditions with moderate stratospheric NO_x additions.

Finally, the enhancement of OH through R3a tends to push HCl back to the ozone destroying compounds ClO and Cl via the reaction



Other possible reactions coupling the ClX, NX, and HX groups are the following recombination reactions :



The mixed molecules ClONO₂, HONO₂, HO₂NO₂, and ClOH are all photolyzed effectively at greater heights. The photolysis probabilities of ClOH and HNO₄ and their reaction kinetics are not well known, but it seems most probable that they are sufficiently large that the importance of these compounds in stratospheric chemistry is not great. Stratospheric observations show an upper limit for HO₂NO₂ of less than 10% of the abundance of HNO₃ (Murcray et al 1978), indicating that HO₂NO₂ is probably efficiently removed by photolysis at longer wavelengths than 300 nm. Spectral studies on the absorption cross sections of ClOH also show appreciable absorption at wavelengths longer than 300 nm (Molina & Molina 1978). These experiments are difficult to conduct, however, and the results do not agree with the theoretical calculations by Jaffe & Langhoff (1977). If ClOH photolysis were fast, the impact of ClOH formation would be minor (there is only a slight catalysis of the reaction HO₂ + O₃ → OH + 2O₂). A slow photolysis rate would, however, allow more ClX to be stored as ClOH (which does not react with ozone) and furthermore give rise to a catalytic cycle (ClO + HO₂ → ClOH + O₂) + (ClOH + OH → ClO + H₂O) = (OH + HO₂ → H₂O + O₂), which could influence the odd hydrogen balance of the stratosphere.

The mixed molecules would exist mainly below about 30 km, providing stratospheric ozone protection from otherwise substantially larger destruction. As this complex chemistry occurs in a region of the stratosphere much affected by still badly known transport processes, modeling of the chemistry of the lower stratosphere has become rather complicated. There is also considerable uncertainty about the abundance of gaseous chlorine compounds in the stratosphere. Given the known abundances of natural and anthropogenic organic chlorine compounds (CH₃Cl, CFCl₃, CF₂Cl₂, CH₃CCl₃, CCl₄) in the upper troposphere, the maximum possible volume mixing ratio of ClX in the upper stratosphere should be about 2 ppbv. Available measurements of stratospheric ClO leave the possibility open for far larger concentrations of stratospheric ClX: Anderson et al (1977, 1978) reported mixing ratios larger than 2 ppbv of ClO alone in the 35–50 km altitude region (on one occasion 7 ppbv).

The measurements by Anderson et al (1977, 1978) seem to have been carried out with great care and considerable ingenuity. Nevertheless,

substantial difficulties are connected with such a high concentration of ClO. First, a large enough ClX source to explain these measurements is not presently known. Second, with so much powerful catalyst around, the concentration of ozone should be exceptionally low, or alternatively the large abundance of ClO should be compensated by a very low abundance of NO₂ (ClO reacts about six times faster with O than NO₂ does). The measured volume mixing ratios of ClO at 35–40 km vary widely between 0.6 and 7 ppbv from experiment to experiment, and ozone does not vary that extremely in this altitude range. It would, therefore, be a remarkable coincidence if the ClO and NO₂ volume mixing ratios were exactly anti-correlated such that six times the mixing ratio of ClO and one time that of NO₂ would always add up to approximately the same total number. In favor of the prevalence of lower volume mixing ratios of ClO are the ground and aircraft millimeter-wavelength emission measurements of Waters et al (1978), which show that profile peak ClO volume mixing ratios during their observation period (May–August 1977) cannot have exceeded 1 ppbv.

In general, it now seems from detailed photochemical model calculations that ozone is very sensitive to anthropogenic ClX additions to the stratosphere (NASA 1977). To estimate the influence of anthropogenic additions of NO_x to the stratosphere, knowledge of the background concentration of ClX in the stratosphere is of considerable importance. With a large atmospheric ClX concentration, additions of NO_x tend to reduce ClX destruction of ozone below 35 km by more conversion of active chlorine ClO_x to HCl and by enhanced production of the mixed ClX-NX molecules. NO_x thus affects stratospheric ozone in complex ways and it now seems that the total ozone column density is only slightly dependent on NO_x additions to the stratosphere (Dewer et al 1977, Crutzen & Howard 1978). Specifically, we now expect that NO_x additions to the present stratosphere will lead to smaller ozone concentrations above about 24 km and larger values below 24 km (Crutzen & Howard 1978). It is difficult to predict the effects of stratospheric aircraft and of increased use of nitrogen fertilizer on the stratospheric ozone column, and it is doubtful that a one-dimensional model can be used to estimate these effects. With ozone increases occurring below 24 km, it seems quite possible that the total ozone column will increase at high latitudes (where there is a lot of ozone below 24 km) and decrease at low latitudes (where most ozone is located above 24 km). Because the lower stratosphere is important for climate, the increased heating of this region caused by larger solar ultraviolet radiation penetration into a layer with more ozone can lead to higher tropopause temperatures and more water vapor in the stratosphere (Liu et al 1976b).

It is clear that many years of research are still required to establish the consequences of a number of human activities. It is essential to obtain more measurements of the global distribution of photochemically reactive compounds in the stratosphere. The ClX content of the stratosphere must be measured and more independent observations are clearly necessary. There are now many measurements available of NX compounds (e.g., Ackerman et al 1975, Chaloner et al 1975, Drummond et al 1977, Goldman et al 1970, 1978, Harries 1978, Lazrus & Gandrud 1974, Loewenstein et al 1975, Mason & Horvath 1976, Murcray et al 1973, 1978, Patel et al 1974, Ridley et al 1973, 1975, Toth et al 1973). Although no dramatic disagreement exists here between observations and theoretical model results, agreement is also not sufficiently good (Harries 1978, Crutzen & Howard 1978). Extensive reviews of measurements of stratospheric minor constituents have been given in various assessment studies (NAS 1975, 1976). An extensive study comparing observations with model calculations was performed by Wofsy (1978). The substantial influence of transport processes on the distribution of minor stratospheric constituents was again shown very convincingly by the observational studies of Noxon (1978, 1979), who reported large day-to-day variations in the total column abundance of NO₂, which correlated with the passage of meteorological disturbances in the lower stratosphere. Similar correlations between total ozone recordings and meteorological variations in the lower stratosphere have, of course, been known to exist for many years (Dütsch 1974). A remarkable additional finding of Noxon (1979) is a persistent sharp decline of the total vertical NO₂ column abundance by about a factor of two polewards of 50°N and 50°S during the winter season, when a well-defined polar vortex patterns exists. This "cliff" seems to reflect a sharp gradient in the temperatures below about 30 km and may be explained by the temperature dependence of reaction R7 and stratospheric circulation characteristics. At high latitudes during winter we must further consider the formation of N₂O₅ (Crutzen 1971).

CONCLUSIONS

The oxides of nitrogen, NO and NO₂, are extremely important in atmospheric chemistry, especially because of their role in the radical chemistry and the production and destruction of tropospheric and stratospheric ozone. The role of ozone in tropospheric photochemistry is explained by its role in the formation of the extremely important OH radical, which attacks many otherwise inert gases in the troposphere. In addition, reactions involving OH (and its byproduct H₂O₂) lead to the formation of the acid gases HNO₃ and H₂SO₄. These gases are important in deter-

mining the acidity of precipitation. Because of catalytic ozone-forming reactions, involving NO and NO₂, tropospheric ozone concentrations, especially in the N.H., may be influenced strongly by photochemical in situ production. Anthropogenic activities contribute substantially to the total NO_x source in the atmosphere.

The oxides of nitrogen, NO and NO₂, are removed very efficiently from the lower troposphere. The processes responsible for their fast removal are, however, not well known. Several gaseous organic nitrates, especially PAN, formed in polluted boundary layers, are very stable above about 4 km in the troposphere and may, therefore, carry "captured" NO_x over substantial distances on the globe. After return to the lower, warmer layers of the troposphere PAN will break up, thereby releasing NO₂. This hypothesis of a possible mechanism for long distance transport of NO_x has yet to be tested by observations in "unpolluted" air.

In the stratosphere, NO_x participates in many reactions influencing the equilibria in the ClX and HX photochemical systems in such a way that the total ozone abundance may be relatively insensitive to NO_x additions to the stratosphere. The vertical profile of ozone may, however, be significantly altered with higher ozone concentrations below 24 km and lower concentrations above. Profile changes of this kind may play a role in climatic and dynamical processes.

The large production of NO_x above about 100 km is dependent on solar activity. A small leakage of this NO_x to the stratosphere may have very interesting consequences.

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