The Chemistry of the Stratosphere

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The chemistry of the stratosphere

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The chemistry of the stratosphere is dominated by the processes that remove the 'odd oxygen' (atomic oxygen and ozone) generated by the photolysis of molecular oxygen. In recent years it has been established that the Chapman reaction, $O + O_3 = O_2 + O_2$, cannot account for all the observed destruction of odd oxygen. Catalytic cycles involving nitrogen oxides (NO, NO_2), hydrogen radicals (H, HO, HO_2) and chlorine species (Cl, ClO) have been shown to be important and it is now realized that these catalytic cycles are closely linked to each other. Measurements of these trace species, their precursors (e.g. N_2O, H_2O, CH_4) and their reaction products (e.g. HNO_3, HCl) in the stratosphere are essential to understanding its chemistry. The natural variability of the stratosphere places a premium on simultaneous measurements of those trace species that are interconverted by rapid chemical reactions.

INTRODUCTION

The stratosphere is a dry, cloudless region of the Earth's atmosphere which extends from the temperature minimum of the tropopause at an altitude of 10–16 km to the temperature maximum of the stratopause at an altitude of about 50 km (figure 1). It is a region of temperature inversion, this being produced by absorption of visible and ultraviolet light by the few parts per million of ozone that are present in this region (figure 2). The stratosphere contains about one tenth of the Earth's atmosphere by mass, and, apart from the presence of ozone and smaller amounts of other trace species discussed below, its chemical composition is close to that of the troposphere. An exception to this statement is water vapour, which is only present in a few parts per million because the tropopause, where the temperature can be as low as 200 K, acts as a cold trap for water rising from the troposphere, and only small amounts of water are generated in the stratosphere by the photo-oxidation of methane.

Although current concern about pollution problems has led people to speak of an 'ozone layer' as though this were synonymous with the stratosphere where the bulk of the atmospheric ozone resides, the total vertical column of ozone in the Earth's atmosphere corresponds to a layer of pure gaseous ozone only 3 mm thick at ground level.

The stratosphere contains relatively few aerosol particles (about $1/cm^3$) or ions and these play no significant role in its chemistry, which is dominated by the chemical reactions of free atoms and free radicals. Solar radiation with wavelengths below 180 nm is completely absorbed by O_2, N_2 and O, and the photochemical processes that occur in the stratosphere therefore generate atoms and free radicals but not ions (figure 3).

Transport of gases in the stratosphere occurs much more rapidly by movement of air masses than it would by molecular diffusion. These processes are discussed in the papers by Murgatroyd & O'Neill (1979, this symposium) and by Harwood (1979, this symposium) and are not considered further here. However, it should be noted that the amounts of various trace species (e.g. ozone, water vapour or nitrogen oxides) in a sample of air depend on its past history as well as on such parameters as altitude, latitude, intensity of solar irradiation and temperature. In general, chemical conversion processes are more rapid than transport in the upper stratosphere (above 35 km), whereas transport processes can be dominant for some species in the lower stratosphere.

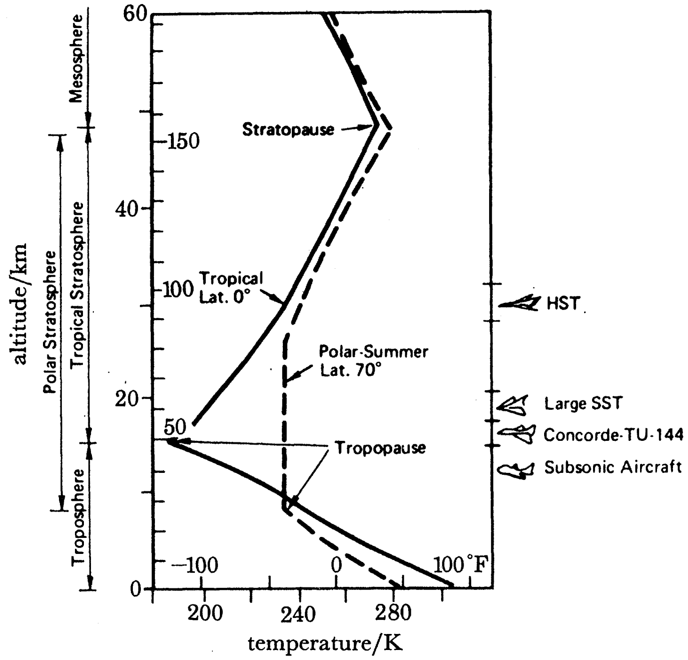

Figure 1. Variation of temperature with altitude in the Earth's atmosphere.

OXYGEN ATMOSPHERE

Historically, the basic mechanism for the formation and removal of ozone was proposed by Chapman in 1930. Molecular oxygen is dissociated by light with wavelengths less than 242 nm. This is a slow process because light that is strongly absorbed by O_2 has been filtered out at higher altitudes.

$$O_2 + h\nu\ (\lambda < 242\ \text{nm}) = O + O \quad \text{(slow)}, \tag{1}$$

$$O + O + M = O_2 + M \quad \text{(slow)}, \tag{2}$$

$$O + O_2 + M = O_3 + M \quad \text{(quick)}, \tag{3}$$

$$O_3 + h\nu = O_2 + O \quad \text{(quick)}, \tag{4}$$

$$O + O_3 = O_2 + O_2 \quad \text{(slow)}. \tag{5}$$

Of the subsequent processes, (2) is only significant in the mesosphere (above the stratosphere) where the lower density of oxygen limits the rate of formation of ozone by reaction (3). The ozone formed in reaction (3) absorbs light very strongly below 300 nm and is also dissociated by visible light, the timescale of its decomposition by process (4) being about 1 min by day. However, this process and reaction (3) merely interconvert the 'odd oxygen' species formed by process (1). In contrast, reaction (5) converts the odd oxygen species O and O_3

back to O_2 which can be regarded as even oxygen; this process is unusually slow for a highly exothermic reaction ($\Delta H = -390$ kJ mol^{-1}) involving a free atom. Only in the last decade have laboratory measurements of the rates of these processes become accurate enough to show that reaction (5) accounts for the removal of only about one-fifth of the 'odd oxygen' generated in the atmosphere by the photolysis of molecular oxygen. Rate coefficients for individual reaction processes will not be quoted here, since a compendium has recently been published by the U.S. National Bureau of Standards (1978).

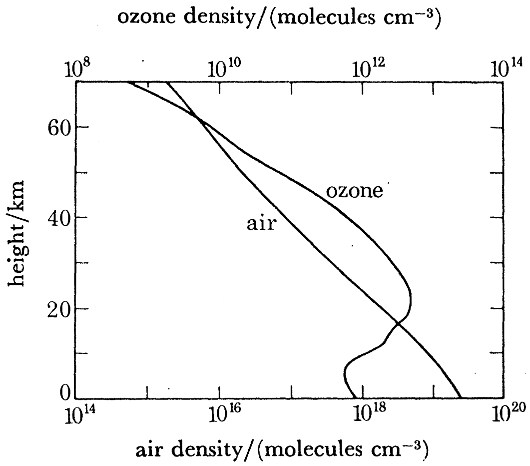

FIGURE 2. The density of air and of ozone in mid-latitudes as a function of altitude. Note that the density scales differ by a factor of 10^6 so that the curves intersect at 1 part/10^6 of ozone.

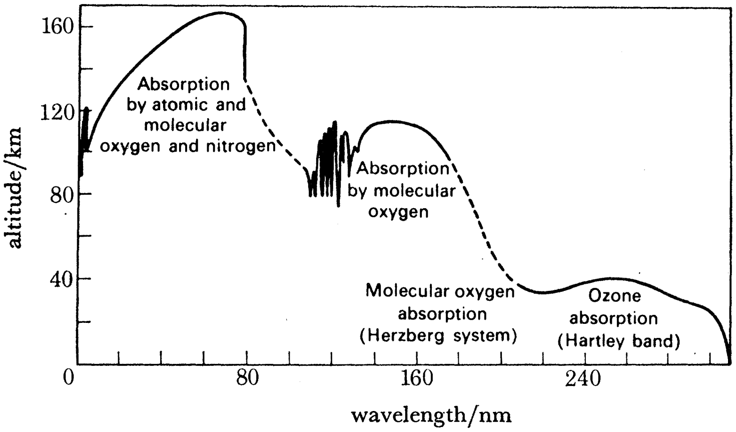

FIGURE 3. Altitudes of maximum light absorption as a function of wavelength for overhead sun.

Other processes removing odd oxygen from the stratosphere can be visualized in terms of a catalytic cycle in which the interconversion of two species X and XO achieves the same effect as reaction (5) and continues to destroy odd oxygen until X or XO is removed by some other process.

$$X + O_3 = XO + O_2, \tag{6}$$

$$XO + O = X + O_2 \tag{7}$$

$$O + O_3 = O_2 + O_2 \qquad (6) + (7)$$

The condition that both these processes should be exothermic is only that the dissociation energy of the X–O bond should lie between the wide limits of 100 and 490 kJ mol^{-1}. There are many free radical species, all of them species with a single unpaired electron for which both reactions (6) and (7) are rapid. The importance of atmospheric cycles involving X = H, HO, NO and Cl has been recognized and these are discussed separately below. The actual position is, however, more complicated than this because these free radical species can undergo rapid reactions with each other as well as with ozone and atomic oxygen, thereby giving cycles that interconvert free radicals X and XO without removing odd oxygen.

A reasonably full description of the chemistry of the stratosphere involves about one hundred chemical and photochemical processes of which nearly half play a significant role. These can be classified into the processes that form the free radicals mentioned above, the balancing removal processes for these radicals and the much more rapid processes by which these radicals are interconverted.

HYDROGEN SPECIES (HO_x)

Bates & Nicolet (1950) recognized early the importance in the atmosphere of the free radicals H, HO and HO_2 (cumulatively called HO_x). The strongest feature of the airglow at night is the Meinel band emission from the mesosphere, due to vibrationally excited hydroxyl radicals produced in the reaction

$$H + O_3 = HO + O_2. \tag{8}$$

The main source of HO_x in the stratosphere is the rapid reaction of excited oxygen atoms ($O(^1D)$) with water vapour and to some extent with methane transported upwards from the troposphere. $O(^1D)$ is produced by the photolysis of ozone at wavelengths below about 310 nm and is removed mainly by quenching by N_2 and O_2, which occurs with a collisional efficiency of about one quarter.

$$O_3 + h\nu\ (\lambda < 310\ \text{nm}) = O_2 + O(^1D), \tag{9}$$

$$O(^1D) + N_2, O_2 = O(^3P) + N_2, O_2, \tag{10}$$

$$O(^1D) + H_2O = HO + HO, \tag{11}$$

$$O(^1D) + CH_4 = CH_3 + HO. \tag{12}$$

Oxidation of the methyl radicals proceeds by the mechanism

$$CH_3 + O_2(+M) = CH_3O_2\ (+M), \tag{13}$$

$$CH_3O_2 + NO = CH_3O + NO_2, \tag{14}$$

$$CH_3O + O_2 = CH_2O + HO_2, \tag{15}$$

$$HO + CH_2O = H_2O + HCO, \tag{16}$$

$$CH_2O + h\nu = HCO + H, \tag{17}$$

$$HCO + O_2 = CO + HO_2. \tag{18}$$

In the stratosphere, methane is also converted to methyl radicals by the reaction

$$HO + CH_4 = H_2O + CH_3. \tag{19}$$

This is overall a source of HO_x when the formaldehyde produced is decomposed photochemically (reaction (17)) rather than by HO (reaction (16)).

In the upper stratosphere the cycle

$$\mathrm{HO+O_3 = HO_2+O_2}, \tag{20}$$

$$\underline{\mathrm{HO_2+O = HO+O_2}}, \tag{21}$$

$$\mathrm{O+O_3 = O_2+O_2}, \tag*{(20)+(21)}$$

is an important removal process for odd oxygen, while the corresponding cycle in the lower stratosphere is

$$\mathrm{HO+O_3 = HO_2+O_2}, \tag{20}$$

$$\underline{\mathrm{HO_2+O_3 = HO+O_2+O_2}}, \tag{22}$$

$$\mathrm{O_3+O_3 = O_2+O_2+O_2}. \tag*{(20)+(22)}$$

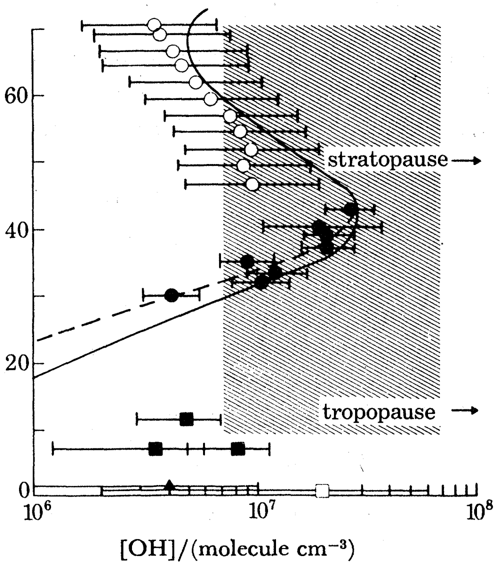

FIGURE 4. Calculated and observed profiles of HO (Hudson 1977).

Although reaction (8) has a rate coefficient many times that of reaction (20) or reaction (22), the cycle

$$\mathrm{H+O_3 = HO+O_2}, \tag{8}$$

$$\mathrm{HO+O = H+O_2}, \tag{23}$$

is not important in the stratosphere because the reaction

$$\mathrm{H+O_2+M = HO_2+M}, \tag{24}$$

which has a rate coefficient about one hundred times greater than that of reaction (3), maintains a very high ratio of $[\mathrm{HO_2}]$ to [H], particularly in the lower stratosphere where the densities of O_2 and of M are higher.

Recombination of the hydrogen radicals occurs mainly by the processes

$$\mathrm{HO+HO_2 = H_2O+O_2}, \tag{25}$$

$$\mathrm{HO_2+HO_2 = H_2O_2+O_2}. \tag{26}$$

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The latter is more important in the lower stratosphere, although the H_2O_2 yielded by the latter has not yet been detected in the atmosphere.

Figure 4 shows that the measured concentrations of HO (and HO_2) in the stratosphere are around 10^7 cm^{-3}, in moderate agreement with the predicted values.

NITROGEN OXIDES (NO_x)

Nitric oxide (NO) and nitrogen dioxide (NO_2), which are present in the stratosphere at the parts in 10^8 level, are formed predominantly by the reaction of excited oxygen atoms with nitrous oxide (N_2O), a process that has two rapid and equally probable paths:

$$O(^1D) + N_2O = NO + NO, \tag{27}$$

$$O(^1D) + N_2O = N_2 + O_2. \tag{28}$$

Nitrous oxide, which is derived from terrestrial denitrification processes, is mainly removed from the stratosphere by photolysis to yield $N_2 + O$ and only 1–2 % generates NO by reaction (27). Lesser amounts of nitric oxide are generated in the mesosphere where photoionization processes can occur

$$N_2 + h\nu = 2N(^4S, {}^2D), \tag{29}$$

$$N(^2D) + O_2 = NO + O, \tag{30}$$

$$NO + h\nu = NO^+ + e, \tag{31}$$

$$NO^+ + e = N(^2D) + O. \tag{32}$$

By day, the NO_x catalysed odd oxygen removal cycle

$$NO + O_3 = NO_2 + O_2, \tag{33}$$

$$\underline{O + NO_2 = NO + O_2,} \tag{34}$$

$$O + O_3 = O_2 + O_2, \tag*{(33) + (34)}$$

is partly neutralized by efficient photolysis of NO_2 by ultraviolet light, which initiates the 'no-effect' cycle (Crutzen 1970; Johnston 1971).

$$NO_2 + h\nu\ (\lambda < 400\ \text{nm}) = NO + O, \tag{35}$$

$$O + O_2 + M = O_3 + M, \tag{3}$$

$$NO + O_3 = NO_2 + O_2. \tag{33}$$

In addition, recent laboratory measurements (Howard & Evenson 1977; Thrush 1979) have shown that reaction (36) is many times faster than had been believed. This means that the mixed cycle

$$HO_2 + NO = HO + NO_2, \tag{36}$$

$$NO_2 + h\nu = NO + O, \tag{35}$$

$$O + O_2 + M = O_3 + M, \tag{3}$$

$$HO + O_3 = HO_2 + O_2, \tag{20}$$

which does not destroy odd oxygen, is an important process by day in the lower stratosphere.

The main removal process for NO_x also involves an HO_x species:

$$HO+NO_2+M = HNO_3+M. \tag{37}$$

The nitric acid formed is transported downwards to the tropopause, where it is rained out. During this process, NO_x can be regenerated by the reactions

$$HNO_3+h\nu = HO+NO_2, \tag{38}$$

$$HO+HNO_3 = H_2O+NO_3, \tag{39}$$

$$NO_3+h\nu = NO_2+O \text{ (predominantly)}, \tag{40}$$

$$NO_2+h\nu = NO+O. \tag{35}$$

It should be noted that the rapid reaction (36) assists the removal of NO_x by generating both active species for the formation of nitric acid in reaction (37). Thus reaction (36) followed by the above sequence of (37), (39), (40) and (35) removes $HO+HO_2$ from the stratosphere, but unlike their direct reaction (25) generates two oxygen atoms in the process. The recognition of this reaction sequence and of the competition between the odd oxygen destruction cycle (22)+(20) and the no-effect cycle (36), (35), (3)+(20) has led to a drastic reduction in the estimated effects on ozone of the nitrogen oxides released directly into the stratosphere from the engine exhausts of such aircraft as Concorde and the Boeing SP747. The much more uncertain estimates of the effects of increased atmospheric N_2O due to increased use of nitrogenous fertilizers are similarly reduced.

Chlorine compounds (ClX)

The ability of chlorine compounds to catalyse ozone removal was not considered until the besign of the U.S. Space Shuttle, which incorporates solid fuel rockets based on ammonium perchlorate and aluminium powder. Stolarski & Cicerone (1974) showed that the amounts of hydrogen chloride thereby released directly into the stratosphere would have a negligible effect on ozone. Soon afterwards, Molina & Rowland (1974) and Rowland & Molina (1975) pointed out that the transport upwards to the stratosphere of F-11 ($CFCl_3$) and F-12 (CF_2Cl_2), which are accumulating in the atmosphere owing to their extensive use as aerosol propellants, refrigerants and foam-blowing agents, would eventually provide a much larger source of reactive chlorine species in the stratosphere.

F-11 and F-12 have no known tropospheric sinks and are removed from the atmosphere by transport upwards to altitudes of 25–30 km where they are photolysed, to yield chlorine atoms, by light of wavelength between 180 nm and 220 nm in the 'solar window' between the strong absorptions by O_2 and by O_3 (figure 3). This process and the parallel but less important decomposition of F-11 and F-12 by $O(^1D)$ will produce a stratospheric burden of reactive chlorine species (Cl, ClO, HCl) of about 5 parts/10^9 on a timescale of about 50 years. The current burden is 2–3 parts/10^9 and is thought to be partly derived from the attack of HO radicals on CH_3Cl, which is produced by marine algae and by slash-and-burn agriculture and is the main chlorine species in the troposphere (Lovelock 1975). Other contributors are CCl_4 (origin uncertain), F-11, F-12, volcanic activity and sea spray. CH_3CCl_3, which finds increasing use as a cleaning agent, may prove a significant source in the future.

The cycle for the chlorine catalysed decomposition of ozone is

$$\begin{aligned} \mathrm{Cl+O_3} &= \mathrm{ClO+O_2}, && (41)\\ \mathrm{ClO+O} &= \mathrm{Cl+O_2}, && (42)\\ \hline \mathrm{O+O_3} &= \mathrm{O_2+O_2}. && (41)+(42) \end{aligned}$$

This removal process occurs mainly in the 30–50 km altitude range, and, particularly at lower altitudes, there is a no-effect cycle

$$\mathrm{ClO+NO} = \mathrm{Cl+NO_2}, \tag{43}$$

$$\mathrm{NO_2}+h\nu = \mathrm{NO+O}, \tag{35}$$

$$\mathrm{O+O_2+M} = \mathrm{O_3+M}, \tag{3}$$

$$\mathrm{Cl+O_3} = \mathrm{ClO+O_2}. \tag{41}$$

This is strictly analogous to the cycle (36), (35), (3) + (20) discussed above and it is interesting to note that the parallel behaviour of reactions of Cl and HO, which is familiar in laboratory studies of chemical kinetics, extends to the atmospheric reactions of the analogous species ClO and $\mathrm{HO_2}$. A further example is provided by the similar rate coefficients for the formation of chlorine nitrate and pernitric acid:

$$\mathrm{ClO+NO_2+M} = \mathrm{ClONO_2+M}, \tag{44}$$

$$\mathrm{HO_2+NO_2+M} = \mathrm{HO_2NO_2+M}. \tag{45}$$

Although these molecules have limited thermal stability and are decomposed by sunlight and by free radical attack in a matter of hours, they should be present in the stratosphere in detectable quantities.

The main removal process for ClX species is the reaction of chlorine atoms with methane to yield hydrogen chloride, which is transported downwards to the troposphere where it is rained out:

$$\mathrm{Cl+CH_4} = \mathrm{HCl+CH_3}. \tag{46}$$

Sufficient formaldehyde may be present as an intermediate in the stratospheric oxidation of methane for reaction (47), which has a much higher rate coefficient than reaction (46), to contribute significantly to HCl formation:

$$\mathrm{Cl+CH_2O} = \mathrm{HCl+HCO}. \tag{47}$$

Unlike the NO_x system, where HO radicals react to form the stable nitric acid, here the action of HO radicals is to regenerate Cl atoms from hydrogen chloride:

$$\mathrm{HO+HCl} = \mathrm{H_2O+Cl}. \tag{48}$$

Recent measurements by three groups have shown that the reaction

$$\mathrm{ClO+HO_2} = \mathrm{HOCl+O_2} \tag{49}$$

can remove significant amounts of ClO. The importance of this process in stratospheric chemistry depends on the lifetime of the HOCl formed. There is considerable controversy as to the form and strength of the spectrum of HOCl above 280 nm, but present evidence strongly suggests that HOCl is rapidly photolysed to yield the active species HO and Cl.

Figure 5 brings out the similarities and differences in the stratospheric cycles of nitrogen oxides and chlorine compounds. A particular point of interest is the differing proportions of the active species X and XO in the two cases.

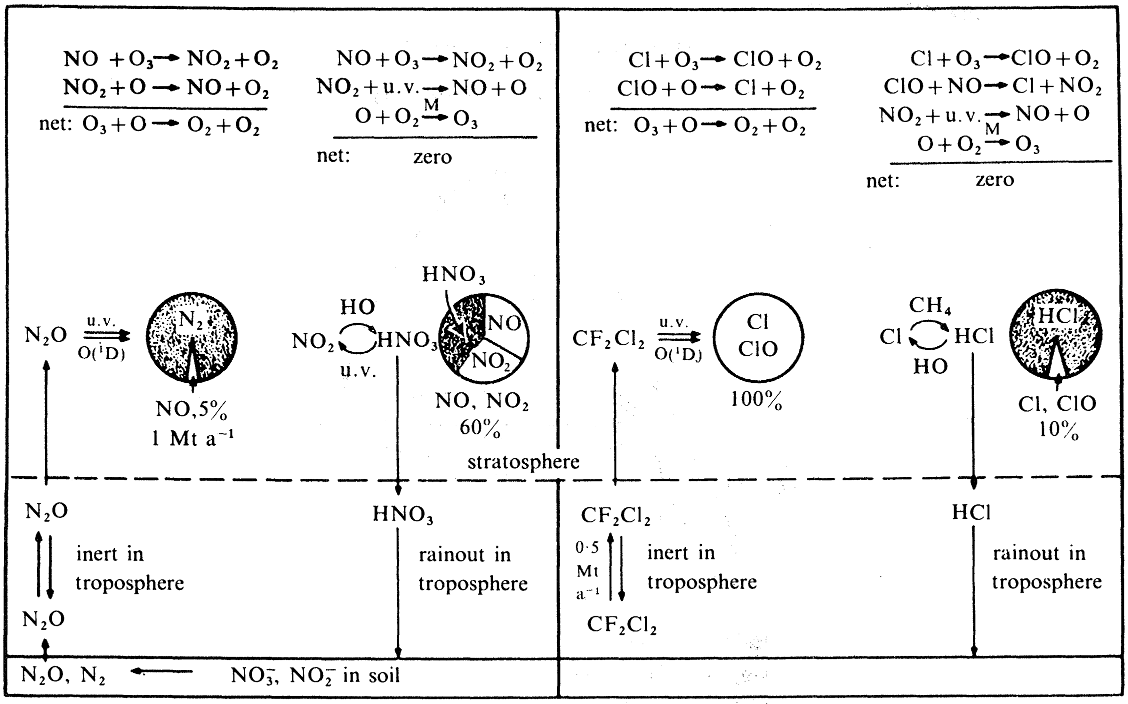


FIGURE 5. The ClX and NO_x cycles in the atmosphere showing the average proportions of the various reactive species (Johnston 1975).

If the atmosphere contained significant amounts of bromine, the bromine catalysed cycle corresponding to reactions (41) and (42) would be very important because the weakness of the H–Br bond makes the reactions corresponding to (46) and (47) endothermic and therefore negligibly slow. Formation of the inactive HBr would then have to depend on the reaction of Br with the much less abundant HO_2 radical

$$Br + HO_2 = HBr + O_2, \tag{50}$$

and the proportion of BrX present as HBr would be much smaller than the corresponding fraction for the chlorine case (figure 5).

In contrast, the great stability of the HF formed by the analogue of reaction (46) ensures that the fluorine catalysed decomposition of stratospheric ozone is negligible.

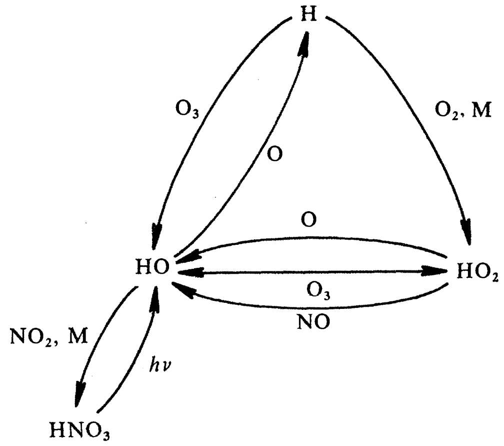
TRACE SPECIES IN THE ATMOSPHERE

The test of our understanding of atmospheric chemistry is the accuracy with which we can use laboratory values for reaction rates and our knowledge of atmospheric circulation to model the profiles of trace species in the atmosphere.

This is a formidably difficult problem since the concentrations of trace species will vary with latitude, solar elevation, season, etc. Although much progress is being made in the measurement of trace species in the stratosphere (Ehhalt 1979, this symposium), only limited data are available on species other than ozone and any deviations between observed and calculated profiles can arise from the chemical inhomogeneity of the stratosphere as well as from the most obvious causes of inadequacies in modelling in laboratory kinetic data or in the observations themselves.

$$O(^1D) + H_2O,\ CH_4,\ H_2 \longrightarrow HO,\ H$$

$$H_2O + h\nu \longrightarrow HO,\ H$$



$HO + HO_2 = H_2O + O_2$
$HO_2 + HO_2 = H_2O_2 + O_2$
$H + HO_2 = H_2 + O_2$

Figure 6. Diagrammatic representation of the formation, interconversion and removal processes for the hydrogen radicals, H, HO and HO_2.

Currently, it is thought that the NO_x cycle is responsible for about half the rate of removal of odd oxygen from the stratosphere, that the HO_x species and reaction (5) between O and O_3 each remove about 20 % and that the ClX cycle removes about 5 %. The rapid interconversion of radicals by processes such as (36) and (43) give rise to mixed cycles which make this partition somewhat arbitrary. For this reason it is wrong to assume that increasing the stratosphere burden of NO_x or ClX by a given factor would produce an ozone depletion that could be estimated from the contribution of that species to ozone removal in the unperturbed stratosphere. This linking of the odd oxygen removal cycles and the 'self-healing' effect, by which a lower ozone concentration at higher altitudes allows the penetration to lower altitudes of the ultraviolet light which generates odd oxygen, both make ozone profiles and total column measurements a relatively insensitive test of our understanding of stratospheric chemistry. This is unfortunate because ozone is by far the best studied reactive trace species.

The vertical profiles of species such as CH_4, N_2O, F-11 and F-12, which are liberated at ground level and removed by chemical reaction and/or photolysis in the stratosphere, provide a measure of the competition between these processes and vertical transport. Such profiles are normally used to provide information about transport rather than to verify calculated reaction rates, although the arguments can be somewhat circular since the reaction rates are derived from a model calculation.

With a short-lived species such as O(^{3}P) or HO, the rate of transport does not govern their transport directly. As figure 6 shows, the concentration of HO is controlled by its rate of formation, by the interconversion reactions of HO_x radicals and by the removal processes for these radicals. Thus, differences between the calculated and observed concentrations (figure 4) can reflect inadequate knowledge of the rates of any of these processes and particularly the rate of the formation reaction (11) since the concentration of water vapour in the stratosphere is somewhat variable. A measurement of the ratios of the concentrations of H, HO and HO_2 would assess our knowledge of the processes for interconversion of these species, which form the centre of figure 6, without being affected by formation, transport and removal processes of the HO_x species as a whole.

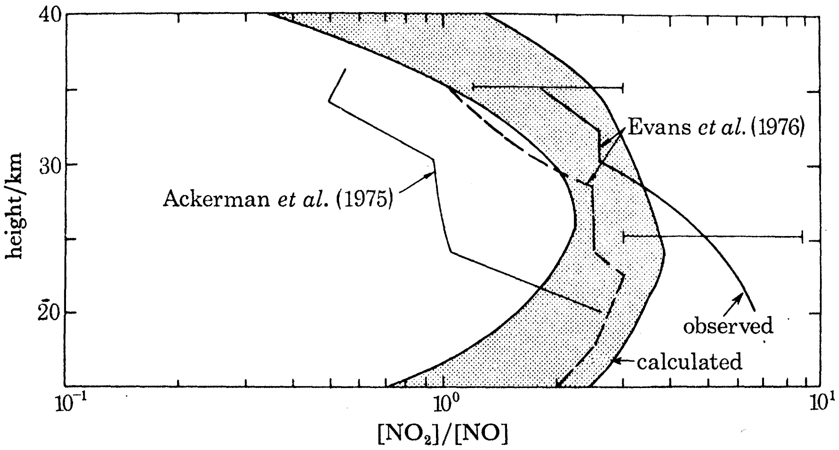


FIGURE 7. Calculated and observed ratios of $[NO_2]$ to [NO] (Hudson 1977).

This approach has been applied most extensively to the nitrogen oxides. Here the ratio of NO to NO_2 at altitudes of 20–25 km is governed by processes (33), (34) and (35)

$$\frac{[NO_2]}{[NO]} = \frac{k_{33}[O_3]}{J_{35}+k_{34}[O]},$$

where the ratio of [O] to $[O_3]$ is determined by processes (3) and (4) (Evans *et al.* 1976). The method can be extended to include HNO_3, which is formed from NO_2 by reaction (37) and converted back to it by process (38) and by reactions (39) and (40). At higher altitudes the ratio of $[NO_2]$ to [NO] is affected by the rapid reactions (36) and (43). Infrared measurements of the ratio of $[NO_2]$ to [NO] agree adequately with the calculated values (figure 7), but extension of this to include HNO_3, which involves the chemistry of HO, produces a significant discrepancy.

Similarly, Anderson *et al.* (1977) find relative values of Cl and ClO in the upper stratosphere that are consistent with the model calculations, but their absolute values do not always agree with the amounts of HCl detected at lower altitudes, which are used to assess total chlorine burdens. Measurement of the ratio of the unreactive HF to the much more reactive HCl as a function of altitude provides a method for estimating the proportion of chlorine present in other forms, e.g. ClO, Cl, $ClONO_2$, HOCl which will vary with altitude (Farmer & Raper 1977).

Thus, measurements of trace species in the atmosphere provide two distinct tests of our understanding of stratospheric chemistry. The neglect or erroneous measurement of the rates of processes interconverting two related trace species will show itself as a disagreement between the observed and calculated ratios of their concentrations. Where species such as HO_2NO_2, N_2O_5 (from $NO_3 + NO_2$), H_2O_2, $ClONO_2$, $HOCl$, etc. are predicted to survive long enough to constitute an appreciable fraction of the NO_x, HO_x or ClX species at a given altitude, these species should be detectable, particularly by long path infrared spectroscopy. Since the rates of formation of these species are relatively well known, continued failure to detect some of them must imply a lack of knowledge of their decomposition rates.

In this connection it is interesting that unpublished measurements at Cambridge by J. P. Burrows, D. I. Cliff, B. A. Thrush and J. P. T. Wilkinson, and at Harwell by J. P. Burrows, R. A. Cox and G. S. Tyndall, have shown that the rate coefficient of reaction (26), which is the dominant source of H_2O_2 in the stratosphere, is pressure dependent. The 'fall-off' from its high pressure value of 3×10^{-12} cm^3 s^{-1} begins at pressures around 25 mbar, and at 1 mbar total pressure k_{26} is less than 1×10^{-12} cm^3 s^{-1}. This new work provides a partial explanation of the failure to detect H_2O_2 in the upper stratosphere.

Although Chapman's work around 1930 provided a secure and accurate basis for our understanding of atmospheric chemistry, the subject has only developed rapidly in the last decade. This has stemmed partly from developments in techniques for laboratory and atmospheric measurements, but largely it has been environmental considerations that have shifted the emphasis from the physics to the chemistry of the atmosphere in recent years.

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