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Recent Developments in the Chemistry of the Stratosphere

B. A. Thrush

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Recent developments in the chemistry of the stratosphere

By B. A. Thrush, F.R.S.

Department of Physical Chemistry, University of Cambridge, Lensfield Road,
Cambridge CB2 1EP, U.K.

The recognition in the 1970s that Man's activities could affect significantly stratospheric ozone led to much activity in atmospheric measurements and in laboratory studies of relevant chemical reactions. The latter has led to the realization that the rates of some apparently bimolecular reactions involving such important atmospheric species as HO and HO_2 have unexpected and unexplained pressure dependences. It has also been recognized that relatively unstable molecules such as chlorine nitrate, pernitric acid and hypochlorous acid may persist long enough in the stratosphere to reduce the rate of ozone destruction. Attempts to verify the role of these species by direct or indirect determination of their abundancies in the stratosphere are discussed.

Introduction

The realization in the 1970s that Man's activities might affect the integrity of stratospheric ozone provided a powerful stimulus to research on the chemistry of the stratosphere. At the time when fears were being expressed about ozone destruction by nitrogen oxides released directly into the stratosphere by the predicted large fleets of supersonic aircraft (Johnston 1971), the natural abundance of nitrogen oxides in the stratosphere was unknown (Crutzen 1970).

It was next pointed out that the relatively stable chlorofluoromethanes that are accumulating in the lower atmosphere would be transported up to the stratosphere where their breakdown would yield chlorine radicals that effectively catalyse the destruction of ozone (Molina & Rowland 1974). Here, independent calculations of the effect of continued release of chlorofluoromethanes at the 1973 rates predicted eventual steady-state ozone depletions close to 10%. However, it was soon realized (National Academy of Sciences 1976) that these calculations were all based on similar assumptions as to the rates of vertical transport in the atmosphere and as to the rate coefficients of the chemical processes involved, many of which were highly uncertain.

The subsequent decade has therefore been spent in refining our understanding of atmospheric chemistry by improving laboratory measurements of reaction rates, in identifying significant species and reactions that had been omitted from the models, in improving the models and, most important of all, in attempting to validate the models by comparing measured and calculated concentrations of trace species. As the models often incorporate about 100 chemical reactions, the rates of which are unlikely to be known at stratospheric temperatures to better than 20%, it is clear that modelling alone cannot provide a precise answer to our question.

Basic atmospheric chemistry

Ten years ago, most of the dominant processes in the chemistry of stratospheric ozone had been identified. These can be summarized as follows.

Formation of 'odd oxygen' $O_2+h\nu = O+O,$ (1)

interconversion of 'odd oxygen' species $O+O_2+M = O_3+M,$ (2)

interconversion of 'odd oxygen' species $O_3+h\nu = O_2+O,$ (3)

destruction of 'odd oxygen' $O+O_3 = O_2+O_2.$ (4)

Catalytic cycles destroying odd oxygen generally have the form

$$\begin{array}{lll} X+O_3 = XO+O_2 & & (5) \\ \underline{XO+O = X+O_2}, & \text{where } X = NO, H, HO, Cl. & (6) \\ O+O_3 = O_2+O_2, & & \end{array}$$

Formation and removal of nitrogen oxides and hydrogen radicals

$$\begin{align} N_2O+h\nu &= N_2+O, \tag{7}\\ O(^1D)+N_2O &= NO+NO, \tag{8}\\ &= N_2+O_2, \tag{9}\\ HO+NO_2+M &= HNO_3+M, \tag{10}\\ HO+HNO_3 &= H_2O+NO_3, \tag{11}\\ HNO_3+h\nu &= HO+NO_2, \tag{12}\\ NO_2+h\nu &= NO+O, \tag{13}\\ O(^1D)+H_2O &= HO+HO, \tag{14}\\ HO+HO_2 &= H_2O+O_2, \tag{15}\\ HO_2+HO_2 &= H_2O_2+O_2, \tag{16}\\ HO+CH_4 &= H_2O+CH_3, \tag{17}\\ CH_3+O_2 &\rightarrow HO_2, \text{ etc.}, \tag{18} \end{align}$$

where the number of excited oxygen atoms $(O(^1D))$ is governed by the processes

$$\begin{align} O_3+h\nu\ (\lambda < 310\ \text{nm}) &= O_2+O(^1D), \tag{19}\\ O(^1D)+N_2, O_2 &= O(^3P)+N_2, O_2. \tag{20} \end{align}$$

Chlorine radicals are generated and removed by the processes

$$\begin{align} CF_2Cl_2, CFCl_3, CCl_4+h\nu &\rightarrow Cl, \text{ etc.}, \tag{21}\\ Cl+CH_4 &= HCl+CH_3, \tag{22}\\ HO+HCl &= H_2O+Cl, \tag{23}\\ NO+ClO &= NO_2+Cl. \tag{24} \end{align}$$

Model validation

Assuming that the rates of the relevant chemical reactions can be measured with sufficient precision in the laboratory to provide reliable data at the temperatures and pressures obtaining in the stratosphere, measurements of trace species in the atmosphere can answer two questions.

(a) Does the model include all the important reactions and trace species?

(b) Does the model incorporate a sufficiently realistic representation of transport processes?

The second question is not considered in detail here, except to note that the vertical profile of a trace species that is not regenerated in the atmosphere is governed by the competition between its transport and its removal processes. For instance, the decrease of $CFCl_3$ or of CF_2Cl_2 with increasing altitude that is shown in figure 1 only provides information about vertical transport rates if the relevant fluxes of ultraviolet light at these altitudes are known reliably. Similarly, the decay of methane at higher altitudes is predominantly by reaction with HO, the concentration of which is not well known, and hence the methane profile cannot provide accurate information about transport in the upper stratosphere.

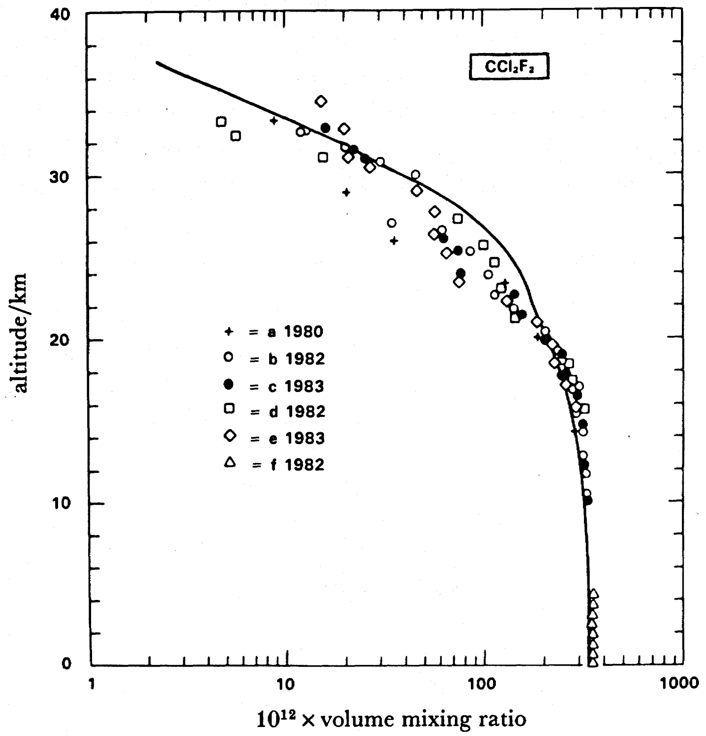


FIGURE 1. Vertical distribution of CCl_2F_2 in northern midlatitudes. (WMO (1986).)

If we turn to trace species that are important in the destruction of stratospheric ozone, or its equivalent 'odd oxygen', the rate-determining processes in the removal of odd oxygen by nitrogen oxides and chlorine radicals are

$$O+NO_2 = NO+O_2, \tag{25}$$

$$O+ClO = Cl+O_2. \tag{26}$$

It is possible to measure O, NO_2 and ClO simultaneously in the stratosphere (Anderson 1979) and hence to evaluate the contribution of nitrogen oxides and chlorine radicals to ozone destruction. However, the measurement of NO_2 or of ClO does not provide a particularly useful test of our understanding of the chemistry of the stratosphere because the measured value is governed not only by the reactions that interconvert nitrogen oxides (chlorine radicals) but also by the transport of precursors into the stratosphere (sources) and the rate of removal from the stratosphere (sinks).

A more useful approach is to divide the problem into sections. For instance, reactions (5), (6) (X = NO), (13) and (24) interconvert NO and NO_2 on a timescale of minutes, whereas other processes involving these species such as their formation from N_2O and removal from the stratosphere occur on much longer timescales. Simultaneous measurements of the ratio of NO and NO_2 can (and broadly do) establish that our picture of their interconversion is essentially correct. Similarly, the ratio of NO_2 to HNO_3 is determined by the rates of the somewhat slower processes (10), (11) and (12); however, this is more useful as a method for estimating the stratospheric concentration of HO, which is hard to measure directly (Pyle *et al.*, this symposium).

In fact, the lack of extensive and reliable direct measurements of HO in the stratosphere is the longest standing major uncertainty in the atmospheric chemistry. Its importance stems from the fact that HO converts the nitrogen oxides that catalyse ozone destruction to inactive nitric acid but converts inactive hydrogen chloride to reactive chlorine radicals. The points in figure 2 are measurements of hydroxyl-radical concentration based on ultraviolet (UV) fluorescence techniques (Anderson 1976; Heaps & McGee 1983, 1985) whereas the lines are deduced from satellite measurements by using either the ratio of HNO_3 to NO_2 mentioned above, or calculations of the sources and sinks of HO (Pyle & Zavody 1985; Jackman *et al.* 1986).

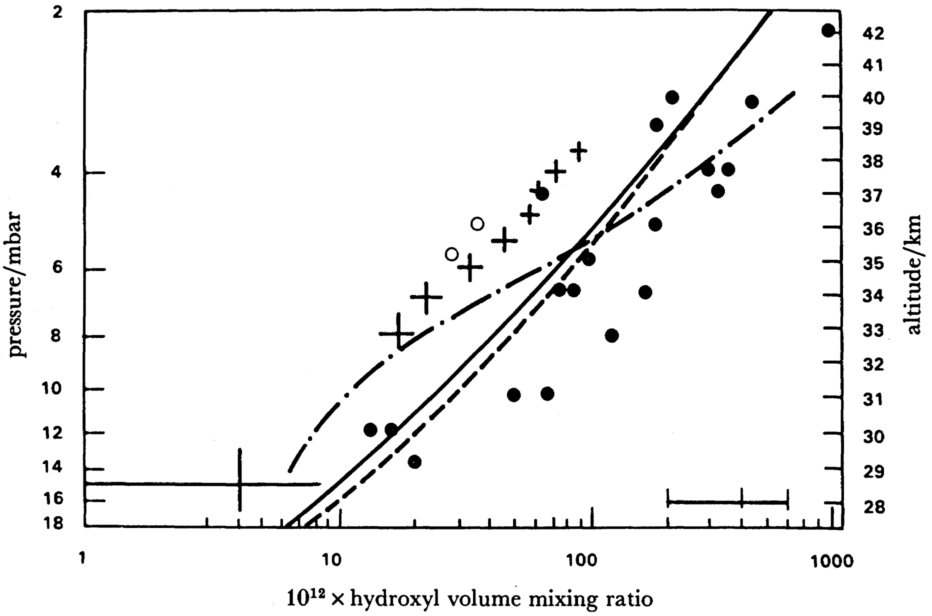
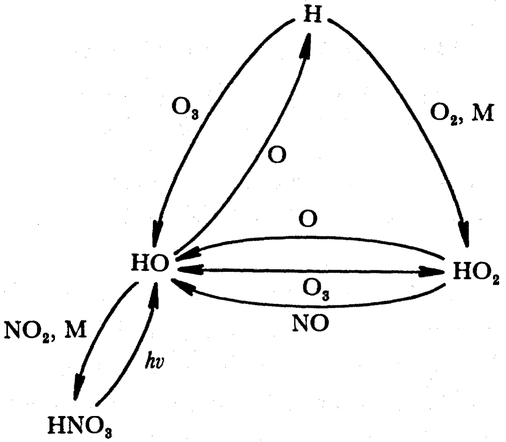


FIGURE 2. Vertical profile of HO. The points are observations by fluorescence techniques. The lines are inferred values (see text) –·–·–, HNO_3/NO_2 ratio; ----, sources and sinks (Pyle & Zavody 1985); ——, sources and sinks (Jackman *et al.* 1986). (WMO 1985.) (1 mbar = 10^2 Pa.)

It is unfortunate that HO_2, which as figure 3 shows has chemistry closely coupled to that of HO, is also very difficult to measure. The ingenious use of cryotrapping and electron spin resonance (ESR) spectroscopy by the Julich group (Helten *et al.* 1984) yields results that are

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

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



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

Figure 3. Relation between the hydrogen radicals.

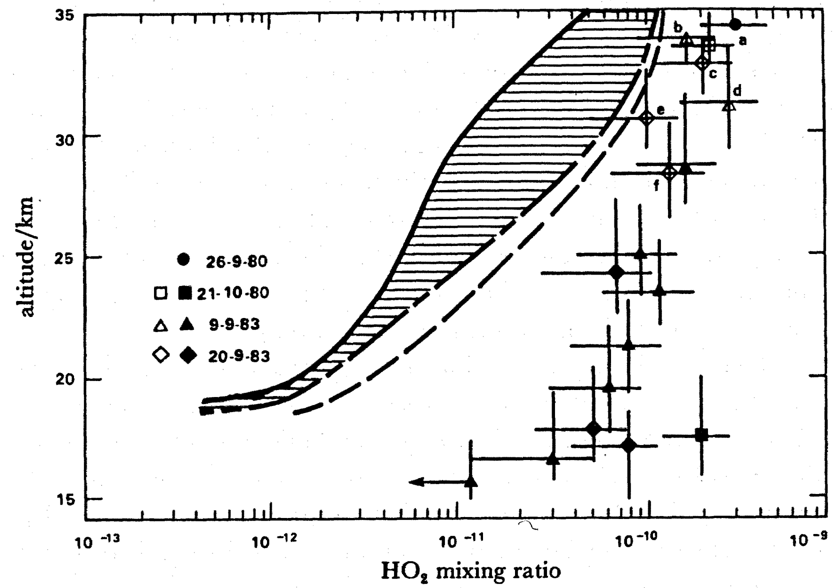


Figure 4. Measurements of HO_2 by matrix isolation compared with profiles calculated by two-dimensional and one-dimensional models (broken line) (Helten *et al.* 1984). The shaded area shows the two-dimensional model for the range summer to winter, daytime average. (WMO (1986).)

higher than predicted by the models (figure 4), a surprising result in view of the possible losses in sampling.

In practice, the recognition of the need to add extra chemical reactions and species to the basic list has come from laboratory experiments rather than from atmospheric measurements. The additional species whose presence has been postulated are molecules that have limited stability in the laboratory but can have a lifetime of hours under the low-temperature and highly oxidizing conditions that exist in the lower stratosphere. Such species would build up at night and be protected by ozone from rapid photolysis at dawn. They are formed by the combination of radical species

$$ClO + NO_2 + M = ClONO_2 + M, \tag{27}$$

$$HO_2 + NO_2 + M = HO_2NO_2 + M, \tag{28}$$

$$ClO + HO_2 = HOCl + O_2. \tag{29}$$

Their presence would therefore reduce the rate of destruction of odd oxygen by simultaneously tying up the radicals involved in two of the catalytic cycles represented by reactions (5) and (6).

Of these the most important and interesting species is chlorine nitrate ($ClONO_2$), which is predicted to have an abundance close to 1 part in 10^9 by volume (1 p.p.b.) in the lower stratosphere, where it would represent a significant fraction of the chlorine present, the dominant chlorine species being HCl with much smaller amounts of ClO and Cl. The inclusion of chlorine nitrate in modelling calculations significantly reduces the estimates of ozone destruction due to release of chlorofluoromethanes because the chlorine released into the stratosphere would tie up significant amounts of nitrogen oxides. However, this effect could disappear for stratospheric chlorine contents exceeding about 12 p.p.b. for which ozone depletions are predicted to rise again sharply (Prather *et al.* 1984).

For these reasons, the verification of the predicted chlorine nitrate amounts in the stratosphere is very important. Because it is a heavy 'floppy' molecule its infrared spectrum has few of the strong, sharp features needed for its detection with the required sensitivity (better than 10^{-9}). Preliminary measurements by Murcray's group (1979) have now been confirmed by the detection of another band by members of the same group (Rinsland *et al.* 1985). Chlorine nitrate has also been detected in the ATMOS experiment from the Space Shuttle.

The presence of chlorine nitrate in roughly the predicted amounts can also be inferred from ground-based (Solomon *et al.* 1984) and balloon-borne (Waters *et al.* 1981) millimetre-wave measurements of the diurnal variation of ClO, illustrated in figure 5 by the slow rise of ClO after dawn when chlorine nitrate is photolysed over a period of hours.

However, the modelled abundances of chlorine nitrate are such that there should be a distinct hollow in the HCl profile between 20 and 35 km because a significant fraction of the chlorine in this range would be present as chlorine nitrate. Such a hollow is not normally observed and the measured vertical profiles of HCl closely resemble those of HF, which, like HCl, is formed by breakdown of halogenated hydrocarbons in the stratosphere and is removed by rain-out in the troposphere. HF provides an ideal comparison because once formed it is completely stable chemically in the stratosphere, unlike HCl, which can be converted to chlorine nitrate by the reaction sequence.

$$HCl \xrightarrow{HO} Cl \xrightarrow{O_3} ClO \xrightarrow{NO_2, M} ClONO_2.$$

Figure 6 shows an early measurement of the HF/HCl ratio by Farmer & Raper (1977) that does not exhibit the predicted bulge due to the presence of a significant proportion of the chlorine nitrate in the lower stratosphere. Further measurements of this ratio which should be unaffected by the vagaries of transport in the lower stratosphere are clearly needed to see if the ratio HF/HCl does imply a low concentration of $ClONO_2$ or the presence of some unknown chemistry.

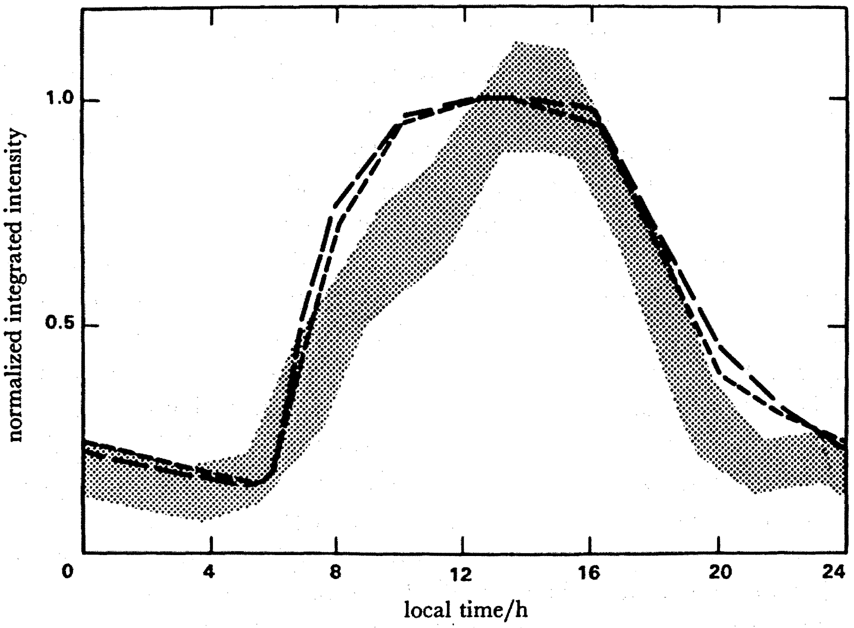


FIGURE 5. Measurements of ClO column above 30 km by ground-based millimetre-wave spectroscopy (stippled area) compared with two model calculations of its diurnal variation. Lines: ——, model of Ko & Sze (1984); ----, model of Froidevaux *et al.* (1985). (WMO (1986).)

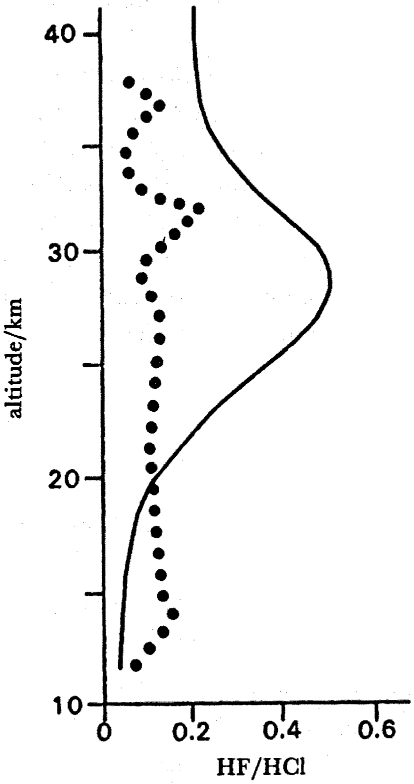


FIGURE 6. Comparison of Farmer & Raper's (1977) measurement of the HF/HCl ratio with a calculated profile showing the predicted maximum due to the presence of $ClONO_2$.

Laboratory kinetics

Because many chemical reactions are included in atmospheric models, their rate coefficients need to be measured in the laboratory with considerable precision. The best achievable accuracy of about 10% has shown that the rate coefficients of many apparently bimolecular reactions such as (11), (15) and (16) increase significantly and unexpectedly over the range of pressures up to 1 atm† (NASA 1985). This group of reactions has the common feature that they involve species capable of forming strong hydrogen bonds (HO, HO_2), and must involve the formation of some intermediate species. However, the magnitude of the observed pressure dependences are greater than can be accounted for by transition-state theories of reaction rates, which assume a free flow of energy between the degrees of freedom in passing through the transition state. There is unfortunately a complete lack of detailed information about the structure of any intermediate species involved. This information is needed to calculate the rates of processes where energy does not flow freely between the degrees of freedom involved.

Until recently, the dominance of one-dimensional models and the limited geographical range of atmospheric measurements concentrated interest on temperature latitudes, particularly around 30 °N (Palestine, Texas). The advent of two-dimensional models and of extensive and reliable satellite measurements of a number of trace species has considerably changed the situation and focused our attention on the need to understand atmospheric chemistry under a wider range of conditions. The severest test of our understanding of atmospheric chemistry is provided by the Antarctic 'ozone hole' (Farman, this symposium) where the ozone in the lower stratosphere decays an order of magnitude faster than in temperature latitudes. It is too early to speculate about detailed mechanisms for the rapid ozone decay, but it should be noted that the stratospheric temperatures down to 190 K encountered in the polar vortex are lower than those that can readily be achieved in laboratory measurements of reaction-rate coefficients. Furthermore, the theoretical basis on which rate coefficients of rapid bimolecular reactions are extrapolated to lower temperatures is not good and lacks predictive power. Heterogeneous processes involving the stratospheric clouds observed in the Antarctic are almost certainly important, and are difficult to study in the laboratory. Finally, it should be noted that the 'ozone hole' and the related behaviour of other species observed in the Antarctic are almost certainly related to the 'polar' cliffs of nitrogen oxides discovered by the late J. F. Noxon.

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† 1 atm = 101325 Pa.

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