Aspects of the Chemistry of Ozone Depletion [and Discussion]

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Aspects of the chemistry of ozone depletion

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The conversion of stratospheric ozone and atomic oxygen back to molecular oxygen is catalysed by a number of atmospheric trace species such as nitrogen oxides (NO, NO_2), halogen (Cl, ClO) and hydrogen (H, HO, HO_2) radicals. The concentrations of these species are interrelated by a complex series of chemical reactions where those of hydroperoxy (HO_2) are the least well understood. Recent direct laboratory studies of the reactions of HO_2 have a considerable effect on estimates of ozone depletion by anthropogenic nitrogen oxides and halogen compounds.

Introduction

An aspect of atmospheric pollution which has caught the public attention in recent years is depletion of stratospheric ozone. One effect of this would be an increase in the amounts of ultraviolet light between 290 and 320 nm (u.v.-B) reaching ground level. Such light is biologically active and prolonged exposure to it can cause skin cancer in susceptible individuals (Booker 1975). The considerable annual and longer-term fluctuations in the ozone cover make it difficult to observe the relatively slow long-term changes which stratospheric pollutants are expected to produce. For this reason, assessment of the probable impact of stratospheric pollutants is based on modelling calculations. For such calculations we need to know the tropospheric sources and sinks of the species involved; nitrous oxide, which was discussed in the previous paper (Hahn 1979, this volume) is an important example. The problems of modelling the processes which transport the pollutants and their degradation products into and out of the stratosphere have already been discussed by Tuck (1979, this volume). Here, we consider the chemical processes which destroy stratospheric ozone, particularly in relation to the uncertainties of predicting ozone depletions and atmospheric measurements of trace species.

Ozone chemistry

Ozone is thinly distributed over the stratosphere, which is the region of temperature inversion between the tropopause at 10–20 km and the stratopause at 50 km. Its mixing ratio (mole fraction) barely exceeds 10^{-6} and the total amount of ozone in the Earth's atmosphere corresponds to a column height of about 3 mm at s.t.p. (figure 1).

The basic photochemistry of an oxygen atmosphere was established by Chapman in 1930:

$$O_2 + h\nu = O + O, \tag{1}$$

$$O + O_2 + M = O_3 + M, \tag{2}$$

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

$$O + O_3 = O_2 + O_2. \tag{4}$$

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Oxygen is dissociated by light with wavelengths below 242 nm to produce oxygen atoms which combine with molecular oxygen to form ozone. In the stratosphere ozone absorbs sunlight much more strongly than does oxygen. As a result the interconversion of the 'odd oxygen' species O and O_3 by (2) and (3) is orders of magnitude faster than their formation by (1) or removal by (4). Laboratory measurements (Davis *et al.* 1973) of the Arrhenius parameters of (4), $k_4 = 1.9 \times 10^{-11} \exp(-2300/T)$ cm³ s⁻¹, show it to have an unusually low pre-exponential factor and high activation energy for such an exothermic process, making it slow at stratospheric temperatures.
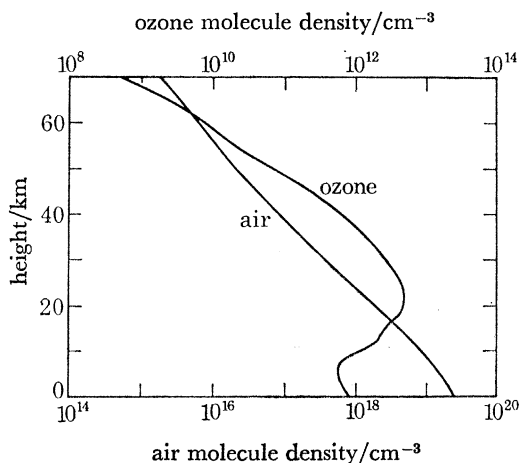

FIGURE 1. Profiles of ozone density and air density in mid-latitudes. Horizontal scales are displaced by a factor of 10^6 to give ozone in parts/10^6 from their separation (Booker 1975).

An assessment of the total rate of formation of odd oxygen in the atmosphere and its removal by (4) and by slow transport to the surface based on the observed ozone distribution shows that these processes can only account for **ab**out 20 % of the actual rate of removal of odd oxygen (ozone) (Johnston 1974). Other chemical processes must therefore account for the bulk of ozone destruction and their basic mechanisms can be simplistically represented by a chain mechanism which achieves the same result as reaction (4):
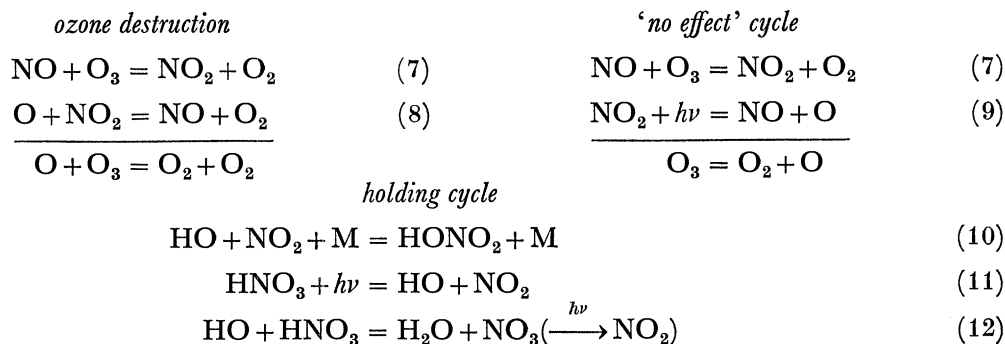
$$X + O_3 = XO + O_2 \tag{5}$$

$$XO + O = X + O_2 \tag{6}$$

$$\overline{}$$

$$O + O_3 = O_2 + O_2.$$
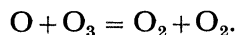
The condition that both (5) and (6) should be exothermic is

$$100 \text{ kJ mol}^{-1} < D(X-O) < 485 \text{ kJ mol}^{-1}$$

which is clearly satisfied by many gaseous species X. The most important of these, particularly in the lower stratosphere, involves X = NO (Crutzen 1970; Johnston 1971), while in the upper stratosphere and mesosphere, cycles with X = HO and X = H contribute significantly.
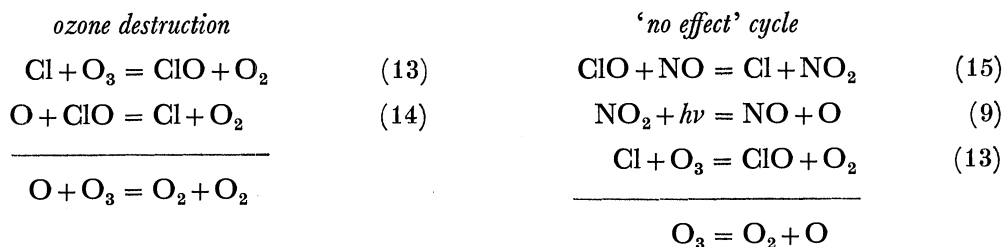
Halogen atoms can also play the rôle of X, as has been shown by recent concern over the fate of chlorine liberated in the decomposition of aerosol propellants and halogenated solvents released into the atmosphere.

However, an estimate of the rate of ozone removal depends not merely on the laboratory determination of the rates of (5) and (6) for various species X. It also depends on the rates of the processes forming and removing X or XO in the stratosphere (chemistry and transport) and on processes which interconvert X and XO without ozone removal. These are well illustrated for the NO_x and ClX cycles by figure 2. For the former we can distinguish three types of cycle:

ozone destruction

$$NO + O_3 = NO_2 + O_2 \qquad (7)$$
$$O + NO_2 = NO + O_2 \qquad (8)$$
$$\overline{O + O_3 = O_2 + O_2}$$

'no effect' cycle

$$NO + O_3 = NO_2 + O_2 \qquad (7)$$
$$NO_2 + h\nu = NO + O \qquad (9)$$
$$\overline{O_3 = O_2 + O}$$

holding cycle

$$HO + NO_2 + M = HONO_2 + M \qquad (10)$$
$$HNO_3 + h\nu = HO + NO_2 \qquad (11)$$
$$HO + HNO_3 = H_2O + NO_3(\xrightarrow{h\nu} NO_2) \qquad (12)$$

Here (8) controls the rate of odd oxygen destruction because it competes with the 'no effect' process (9) and with (10) which results in the formation of the relatively long-lived nitric acid molecule.

For ClX the 'no effect' cycle involves nitrogen oxides:

ozone destruction

$$Cl + O_3 = ClO + O_2 \qquad (13)$$
$$O + ClO = Cl + O_2 \qquad (14)$$
$$\overline{O + O_3 = O_2 + O_2}$$

'no effect' cycle

$$ClO + NO = Cl + NO_2 \qquad (15)$$
$$NO_2 + h\nu = NO + O \qquad (9)$$
$$Cl + O_3 = ClO + O_2 \qquad (13)$$
$$\overline{O_3 = O_2 + O}$$

and two holding processes have been identified, the main one involving HO,

$$Cl + CH_4 = CH_3 + HCl, \qquad (16)$$
$$HO + HCl = H_2O + Cl, \qquad (17)$$

the other involving nitrogen oxides,

$$ClO + NO_2 + M = ClONO_2 + M, \qquad (18)$$

although chlorine nitrate has not yet been detected in the stratosphere.

Thus the rates of destruction of odd oxygen by the rate-determining processes (8) and (14) are governed by the proportions of NO_x (NO, NO_2, HNO_3) and ClX (Cl, ClO, HCl) which are present as NO_2 and ClO respectively. In particular, HO plays a crucial rôle in both systems, where it forms the holding species HNO_3 but removes the holding species HCl. The reactions which form, interconvert and remove the HO_x species H, HO and HO_2 are illustrated by a Nicolet diagram in figure 3. Although the rate of production of HO_x species by the reactions with water, methane and hydrogen of the excited oxygen atoms, $O(^1D)$, produced by ozone photolysis is comparatively well known, the rates of interconversion of H, HO and HO_2 and their removal, principally by the reaction
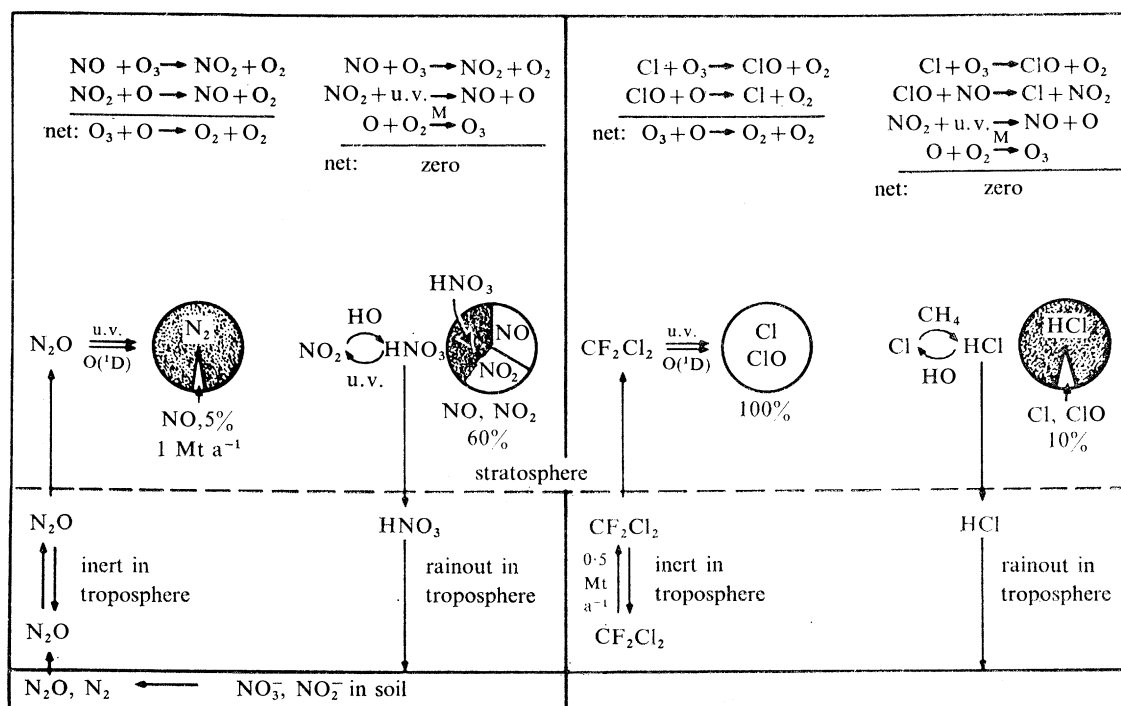
$$HO + HO_2 = H_2O + O_2, \qquad (19)$$

FIGURE 2. Comparison of the nitrogen oxide and chlorine cycles for ozone removal, illustrating the relative proportions of active and inactive species (Johnston 1975).
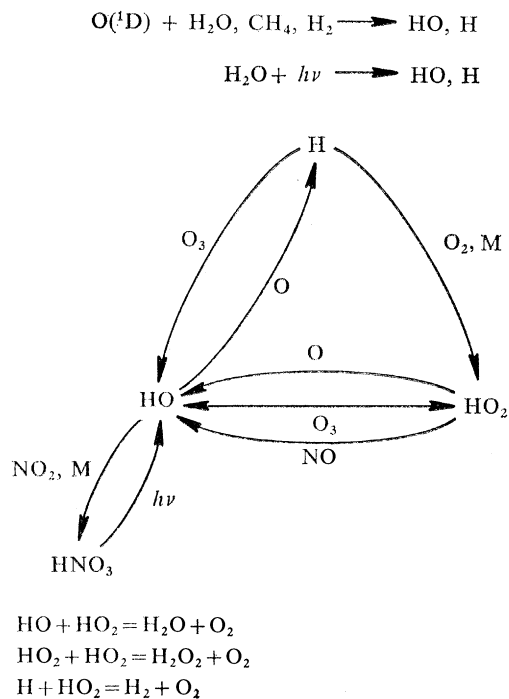
$$O(^1D) + H_2O, CH_4, H_2 \longrightarrow HO, H$$

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

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

FIGURE 3. Sources, dominant interconversion processes and removal processes of hydrogen radicals (H, HO, HO$_2$) in the stratosphere.

contain major uncertainties, largely associated with the difficulty of making direct laboratory studies of the reactions of HO_2. Some recent investigations of these reactions and their consequences in atmospheric chemistry are considered below.

REACTIONS OF HYDROPEROXY (HO_2)

Most laboratory studies of reactions of stratospheric importance use either discharge flow systems or flash photolysis with highly sensitive specific methods for determining the concentrations of active species such as chemiluminescence (O, NO), resonance fluorescence (H, O, Cl, HO) absorption spectroscopy (ClO, O_3) or mass spectrometry (O, Cl, ClO, etc.). Unfortunately, HO_2 cannot be detected by chemiluminescence. Its electronic spectrum consists of weak bands near 1.2 μm and featureless continuous absorption around 200 nm where many other species absorb.
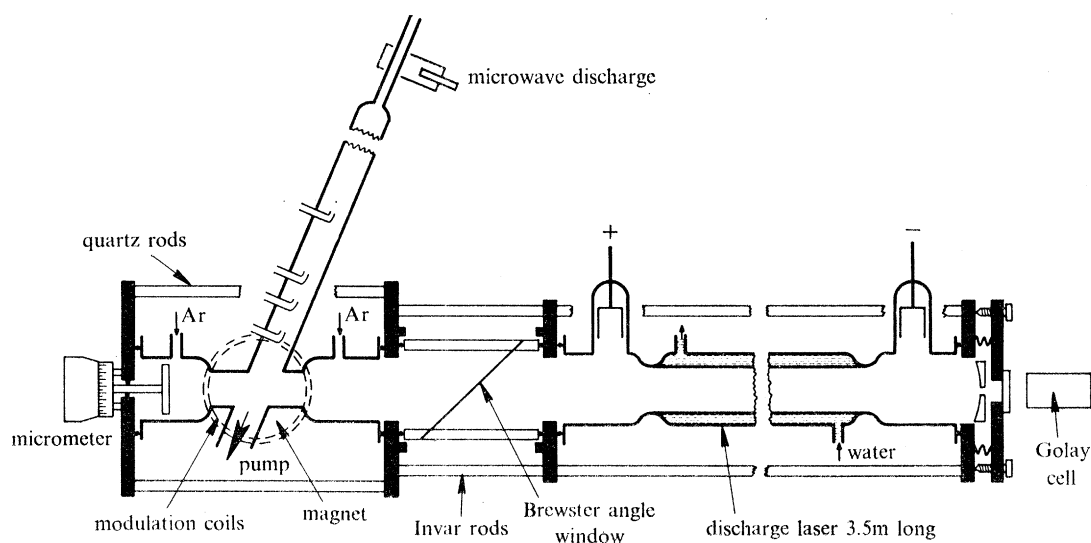

FIGURE 4. Laser magnetic resonance spectrometer for free radical studies (Burrows *et al.* 1977).

These spectra are unsuitable for resonance fluorescence and cause difficulties in attribution of absorption measurements. With mass spectrometry, calibration can cause difficulties particularly as the ion HO_2^+ is readily formed from other species. Recently, laser magnetic resonance spectroscopy in which a strong magnetic field is used to bring Zeeman components of the rotational transitions of a free radical into resonance with a far infrared laser has provided a highly specific method for the detection and study of such radicals as HO_2. Furthermore, the problem of calibration is minimized because the intensity of the spectrum depends directly on the square of the dipole moment of the species rather than on the dipole moment derivative (vibration spectrum) or an electronic transition moment.

Figure 4 shows the basic arrangement of a discharge-flow system for studying atomic and free radical reactions coupled to a laser magnetic resonance spectrometer based on the 118.6 μm water vapour line with which it is possible to detect HO_2, HO and NO_2. With this apparatus we have been able to make the first measurement of the rate of the reaction.

$$O + HO_2 = HO + O_2, \qquad (20)$$

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and the first direct measurement of the rate of coefficient of

$$HO + HO_2 = H_2O + O_2. \tag{19}$$

Both these rate coefficients (Burrows *et al.* 1977) were fairly close to values used by atmospheric modellers but a more recent determination of the rate of the reaction

$$HO_2 + NO = HO + NO_2, \tag{21}$$

in which nitric oxide was added to HO_2 radicals produced by a Tesla discharge through hydrogen peroxide (figure 5), yielded

$$k_{21} = (8.2 \pm 1.2) \times 10^{-12}\,\mathrm{cm^3\,s^{-1}},$$

which is over twenty times the value normally used in stratospheric modelling (Burrows *et al.* 1978). Howard & Evenson (1977) have obtained a similar value in a variant of the same technique, and unpublished indirect determinations in other laboratories confirm this new value which has a profound effect on our views of the chemistry of atmospheric pollution, since (21) becomes the main process converting HO_2 to HO in the lower stratosphere and in the troposphere.
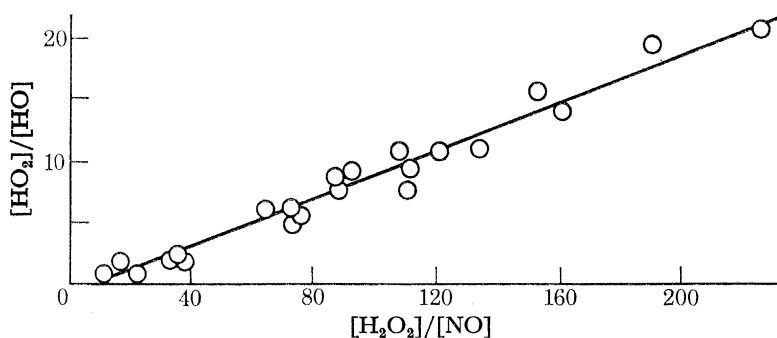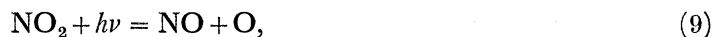

FIGURE 5. Kinetic plot for the reactions $HO_2 + NO = HO + NO_2$ and $HO + H_2O_2 = H_2O + HO_2$.

In particular, interconversion of HO_2 and HO in the lower stratosphere is now believed to be controlled by the 'no effect' cycle,

$$HO_2 + NO = HO + NO_2, \tag{21}$$

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

$$NO_2 + h\nu = NO + O, \tag{9}$$

rather than by the ozone destruction cycle

$$HO_2 + O_3 = HO + O_2 + O_2, \tag{23}$$

$$HO + O_3 = HO_2 + O_2. \tag{22}$$

It also increases the calculated ratio of HO to HO_2 in the upper stratosphere where the corresponding ozone destruction cycle is

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

$$HO + O_3 = HO_2 + O_2. \tag{22}$$

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Ozone depletion

These improvements in our knowledge of reaction rates for HO_2 have considerable effects on estimates of the depletion of stratospheric ozone by various pollutants.

For chlorofluoromethanes and other chlorocarbons, where the maximum ozone depletion is predicted to occur around 30 km altitude, the calculated depletions (National Academy of Sciences (Gutowsky 1976)) are increased by about one half. This arises because increased HO concentrations convert more HCl into active Cl and ClO and because the removal of NO by (21) reduces the rate of (15) which initiates a 'no effect' cycle.
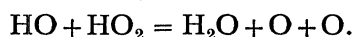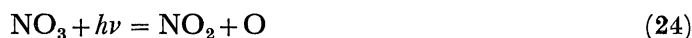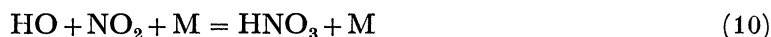
Ozone removal by nitrogen oxides occurs predominantly in the lower stratosphere, and the predicted effect of NO and NO_2 depends on how close to the tropopause they are released. The nitrogen oxides from Concorde and high-altitude subsonic aircraft such as the Boeing 747SP which operate at altitudes up to 18 km are now predicted to enhance ozone slightly. This arises because:

(i) the HO, HO_2 depletion cycle of (22) and (23) is partly replaced by the 'no effect cycle' of (22) (21) and (9);
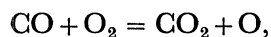
(ii) a higher concentration of HO makes reaction (12) between nitric acid and HO compete significantly with the photolysis of nitric acid in the lower stratosphere. Increases in nitrogen oxide levels then causes HO_x removal by reaction (19),
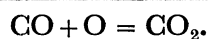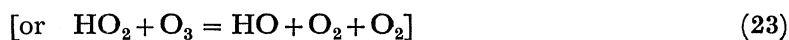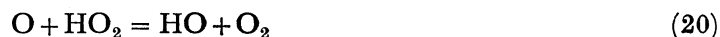
$$HO + HO_2 = H_2O + O_2, \tag{19}$$

to be replaced by the following cycle which generates odd oxygen:

$$HO_2 + NO = HO + NO_2 \tag{21}$$
$$HO + NO_2 + M = HNO_3 + M \tag{10}$$
$$HO + HNO_3 = H_2O + NO_3 \tag{12}$$
$$NO_3 + h\nu = NO_2 + O \tag{24}$$
$$NO_2 + h\nu = NO + O \tag{9}$$
$$\overline{HO + HO_2 = H_2O + O + O.}$$

With a high value of k_{21}, the oxidation of CO to CO_2 by HO_x species becomes an odd oxygen generating cycle,

$$HO + CO = CO_2 + H \tag{25}$$
$$H + O_2 + M = HO_2 + M \tag{26}$$
$$HO_2 + NO = HO + NO_2 \tag{21}$$
$$NO_2 + h\nu = NO + O \tag{9}$$
$$\overline{CO + O_2 = CO_2 + O,}$$

instead of an odd oxygen removing cycle,

$$HO + CO = CO_2 + H \tag{25}$$
$$H + O_2 + M = HO_2 + M \tag{26}$$
$$O + HO_2 = HO + O_2 \tag{20}$$
$$[or \quad HO_2 + O_3 = HO + O_2 + O_2] \tag{23}$$
$$\overline{CO + O = CO_2.}$$

[43]

Release of NO and NO_2 above $20 \, km$ which might occur from future supersonic aircraft and occurs from the reaction

$$O(^1D) + N_2O = NO + NO, \qquad (27)$$

which is the dominant natural source of stratosphere NO and NO_2, is still predicted to deplete ozone somewhat, as HNO_3 is formed more slowly and photolysed more rapidly at these altitudes. Thus these new results reduce rather than eliminate predictions of ozone depletion by nitrous oxide derived from bacterial denitrification of nitrate fertilizers, the use of which is increasing rapidly. However, as Hahn (1979, this volume) has pointed out, we do not yet know enough about the natural N_2O cycle to predict the increase in atmospheric N_2O due to this source which would be needed to predict any ozone depletion.

Modelling the chemistry of the stratosphere involves about 100 chemical reactions. Although a better knowledge of the rates of many of these processes is unlikely to affect significantly our views on ozone chemistry, future laboratory studies, particularly of the reactions of HO_2, may well yield other surprises. For instance, the rates of (23) and (28),

$$HO_2 + HO_2 = H_2O_2 + O_2, \qquad (28)$$
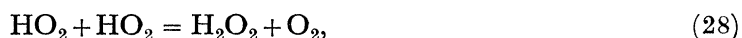
are not well established, and the recent observation of the formation of pernitric acid from the combination of HO_2 and NO_2 (Niki *et al.* 1977) and its attempted detection in the stratosphere by D.G. Murcray (unpublished results) point out directions for future investigations. With the simultaneous measurements of a number of trace species in the stratosphere now being planned in a number of laboratories we should soon have quantitative tests of the accuracy of our predictions of the rates of the various chemical cycles involving stratospheric ozone.

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Discussion

A. F. Tuck (*Meteorological Office, Bracknell, Berkshire, U.K.*). What is your opinion of the possible importance of pernitric acid, HO_2NO_2, and hypochlorous acid, $HOCl$, in stratospheric chemical kinetics?

B. A. Thrush. In the gas phase, Cl and HO normally exhibit very similar reactivities and laboratory studies show that this similarity extends to ClO and HOO, notably in their rapid

reactions with NO and in their three-body combination with NO_2 to form respectively chlorine nitrate ($ClONO_2$) and pernitric acid ($HOONO_2$). The atmospheric photolysis of both these molecules is thought to be slow and their reactivity towards free radicals relatively low. On this basis, one would expect pernitric acid to be more important than chlorine nitrate at the present time.

We cannot assess the rôle of hypochlorous acid (HOCl) until we have more data on its absorption spectrum and reactions. It is closely related chemically and probably spectroscopically to hydrogen peroxide, which has not yet been detected in the stratosphere. As hydrogen peroxide is expected to be more abundant than hypochlorous acid, the relation between its predicted and observed concentrations would be useful in assessing the importance of hypochlorous acid.

B. J. Mason, Treas.R.S. (*Meteorological Office, Bracknell, Berkshire, U.K.*). The running of a complex three-dimensional dynamical model of the stratosphere, such as that developed in the Meteorological office and incorporating the full ozone photochemistry, would be very expensive in computer time. In view of the present uncertainties concerning the concentrations of key species and the rate constants of many of the reactions, I should like to ask Dr Thrush whether, in his opinion, such computations are justified at present. My own inclination would be to support Dr Tuck in incorporating the essential transport properties culled from the three-dimensional meteorological model into a one-dimensional model of the 'full' photochemistry and use this to test the sensitivity of ozone production and destruction to changes in the concentrations of the important species, to variations in reaction rates, and to the inclusion of new reactions.

B. A. Thrush. The total cost of the laboratory determination of the rate coefficient for a reaction of HO_2 is about £10 000 and until more rate coefficients are accurately known, I believe it is more appropriate to work on improving techniques for chemical modelling than to undertake very large computations on stratospheric chemistry at present. An important intermediate stage is the simultaneous measurement of concentrations of related trace species under conditions where their relative concentrations are determined by chemical processes and not by transport. Such measurements will test the adequacy and accuracy of the chemical model employed.

T. M. Sugden, F.R.S. What is the state of our knowledge of the total flux of chlorine to the stratosphere?

B. A. Thrush. The measured vertical profiles for F-11 and F-12 agree well with the calculated ones indicating that their fluxes into the stratosphere can be predicted with reasonable accuracy. However, the dominant chlorine species in the troposphere is methyl chloride for which Lovelock has suggested that tropical slash-and-burn agriculture is a major source. As much of the transport from the troposphere into the stratosphere is believed to occur via tropical storms which penetrate the tropopause, the flux in methyl chloride into the stratosphere must be highly uncertain.

Although Anderson's recent measurements of ClO at altitudes between 25 and 40 km give vertical profiles which agree well with modelling calculations, they correspond to total chlorine concentrations of 5 parts/10^9 by volume or more, whereas the more numerous measurements of HCl mainly at lower altitudes correspond to values around 2 parts/10^9. There is no obvious flaw in Anderson's measurements, but they are hard to reconcile with the observed ozone concentrations and with the measured amounts of chlorine compounds at lower altitudes. However, they may point to a lack of understanding of the stratospheric chlorine cycle.

G. Diprose (*I.C.I. Limited, Mond Division, Winnington, Northwich CW8 4DJ, U.K.*). Our knowledge and understanding of fluxes and concentration profiles of chlorinated species in the stratosphere is still very far from complete and there are a number of anomalies such as the decrease in HCl concentration measured above 35 km and the very high measurements of ClO reported by Anderson still to be explained. In addition we have the possibility that HOCl may be a stratospheric species of importance and that there may be other species still awaiting recognition.

All this puts at a premium a reliable method for the determination of total chlorine in the stratosphere. Comparison of such measurements with simultaneous determinations of individual chlorinated species can act as a check on the measurements themselves and can give some indication if there is a hitherto unrecognized species of importance in the stratosphere and also help to put the relative fluxes of natural and man-made chlorine-containing compounds into their correct perspective.

Concluding remarks

B. A. Thrush. My paper stressed the importance to stratospheric pollution of knowing the concentrations of hydroxyl radicals in the stratosphere. Greater concentrations would decrease ozone removal by nitrogen oxides but increase ozone removal by halogen compounds. Dr Swift-Hook and others have pointed out the need for measurement of free radical concentrations in the troposphere, and in the case of hydroxyl this is particularly important, since this species plays a large rôle in photochemical smog, in oxidizing sulphur dioxide, in converting carbon monoxide to carbon dioxide, and in removing methyl chloride and other partly halogenated hydrocarbons. It is interesting to note that the concentration of this important scavenger is much higher in urban than in rural atmospheres.