ATMOSPHERIC CHEMISTRY: A REVIEW OF PROGRESS IN THE PAST DECADE

R. A. COX

Environmental and Medical Sciences Division, Atomic Energy Research Establishment, Harwell, Didcot, Oxon. OX11 0RA (Gt. Britain)

(Received February 6, 1984)

During the past decade considerable attention has been directed towards research in atmospheric chemistry with emphasis on the gas phase reactions of ozone (O_3) and important hydrogen, nitrogen, carbon, halogen and sulphur species. This increased interest in atmospheric chemistry has been stimulated by a recognition that man's activities could lead to significant changes in the chemical composition of the atmosphere on a global scale. Such a danger has been recognized for the stratosphere (the 15 - 50 km altitude region) because of the input of NO_x and halogen-containing compounds, but global effects on the troposphere (the lowest 10 - 15 km of the atmosphere) due to man's activities can likewise be identified [1].

Increasing amounts of pollutant gases are being directly emitted to the atmosphere by man's activities. The total global anthropogenic sources of NO_x and SO_2 to the atmosphere are now comparable with or larger than the natural sources of these gases. Although these emissions occur mainly in highly industrial regions, photochemical pollution, for example, has been observed over distances of 1000 km adjacent to source regions [2]. Because of the increased burden of these pollutants and their reaction products in the atmosphere, there is much concern about the effects not only on humans, but also on large-scale ecological systems. In particular, attention has been directed to the effects of increased acidity of precipitation from sulphuric and nitric acids [3].
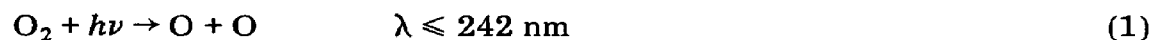
The composition of the natural atmosphere is to a considerable degree determined by the functioning of the biosphere in soils, vegetation and waters. A typical life cycle of a trace element consists of release at the Earth's surface in the form of a reduced gas (often bonded to hydrogen), photochemically induced oxidation in the atmosphere and removal from the atmosphere by precipitation, scavenging and/or by direct uptake at land and water surfaces. Important examples of reduced gases of biological origin include CH_4, C_5H_8 (isoprene), $C_{10}H_{16}$ (terpenes), CO, N_2O, NH_3, CH_3Cl, H_2S and organic sulphides. These compounds are photo-oxidized in the atmosphere to compounds such as aldehydes, peroxides, CO, CO_2, NO, SO_2 etc. The aim of research in atmospheric chemistry has been to

gain a quantitative understanding of the chemical pathways and budgets in these trace gas cycles so that the importance of man-made perturbations can be assessed objectively and with greater confidence.

Atmospheric trace gases are only present in a very low molecular concentration and, in order that the chemical changes proceed at significant rates, energy to overcome the kinetic activation barrier, in a broad sense of the term, is required. This energy is provided by absorption of solar photons in the visible and UV spectral region by several key photochemically active molecules such as O_2, O_3 and NO_2, leading to labile photofragments of high chemical reactivity. Photochemistry therefore plays a fundamental role in atmospheric chemistry and consequently the field has received considerable stimulation from the increased interest in atmospheric science.

In the following paragraphs a brief summary of some of the key photochemically driven reaction mechanisms is given, emphasizing their role in the cycling of oxygen, hydrogen, carbon, halogen and sulphur compounds. In this discussion the chemistry of the stratosphere and the troposphere is treated separately since these regions have quite distinct properties in chemical terms, resulting from the different physical environments pertaining.

The stratosphere is characterized by low temperature (220 - 260 K), slow vertical mixing and strong UV radiation flux at wavelengths of less than 300 nm. Chemically it is characterized by high concentrations of O_3 and low water vapour abundance. Until the 1960s most studies of stratospheric O_3 only considered the Chapman reactions [4] in order to explain its distribution:

$$O_2 + h\nu \to O + O \qquad \lambda \leqslant 242 \text{ nm} \tag{1}$$

$$O + O_2 + M \to O_3 + M \tag{2}$$

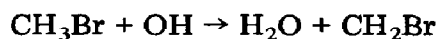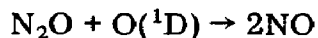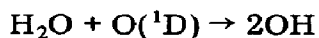$$O_3 + h\nu \to O + O_2 \tag{3}$$

$$O + O_3 \to 2O_2 \tag{4}$$

In this mechanism the production and loss of odd oxygen O and O_3 is controlled by reactions (1) and (4) respectively, whilst reactions (2) and (3) partition the odd-oxygen species between O and O_3. It was subsequently recognized that other O_3 destruction mechanisms had to be introduced in order to explain the observed abundance of stratospheric O_3, since the slow rate of reaction (4) was insufficient to balance the rate of photodissociation of O_2 in the known solar flux. Work in the last decade has established fairly firmly that additional O_3 destruction occurs through the following simple catalytic cycle:

$$X + O_3 \to XO + O_2 \tag{5}$$

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

$$O + O_3 \to 2O_2 \qquad \text{(net)}$$
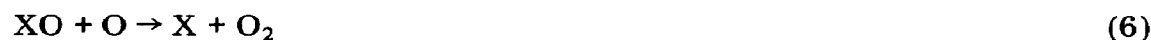
The species X can be H, OH [5], NO [6], Cl [7] or Br [8], which fulfil the role of catalyst with varying degrees of efficiency depending on the appro-

priate rate coefficients for reactions (5) and (6) and the local abundance of the radical species, X and XO. The amount and distribution of radical species depend on their sources and sinks. The main natural sources of the species mentioned above are as follows:

$$H_2O + O(^1D) \rightarrow 2OH$$

$$N_2O + O(^1D) \rightarrow 2NO$$

$$CH_3Cl + OH \rightarrow H_2O + CH_2Cl$$

$$CH_3Br + OH \rightarrow H_2O + CH_2Br$$

The CH_2Cl and CH_2Br radicals undergo subsequent reactions to yield Cl (and ClO) and Br (and BrO) respectively. The excited oxygen atom is produced by photolysis of O_3 by UV solar radiation at $\lambda < 320$ nm:

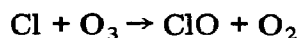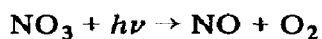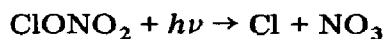$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad \lambda < 320 \text{ nm}$$
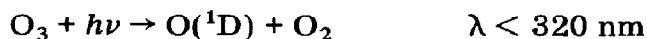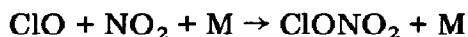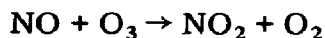
Interest in the role of NO_x in the catalytic cycle increased when it was suggested that a substantial reduction in stratospheric O_3 might result from direct injections of nitric oxide from the exhaust gases of supersonic aircraft [7]. Similarly the potential for significant destruction of O_3 by ClO_x radicals was recognized when it was suggested [9] that an important source of stratospheric chlorine would result from the photolysis of the chlorofluoromethanes CF_2Cl_2 and $CFCl_3$, which have exclusively man-made sources in their usage as aerosol propellants and refrigerants. Their low chemical reactivity ensures that they can be transported to the stratosphere where they are photolysed by short wavelength UV solar radiation.

The catalytically active radicals are removed by conversion to product molecules such as H_2O, HNO_3, HCl etc. which are stable towards radical or photochemical decomposition and are eventually transported out of the stratosphere:

$$OH + HO_2 \rightarrow H_2O + O_2$$

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

$$Cl + CH_4 \rightarrow HCl + CH_3$$
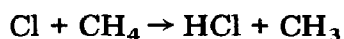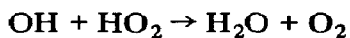
In addition to these "sink" processes, the radicals may form temporary reservoir species such as H_2O_2, N_2O_5 and $ClONO_2$, which do not directly participate in odd-oxygen destruction catalytic cycles. This route serves to reduce the active radical concentration but the overall role of temporary reservoirs may inhibit or enhance the catalytic destruction of O_3, depending on the reactions involved. For example, photolysis of $ClONO_2$ can provide a sink for odd oxygen:

$$ClONO_2 + h\nu \rightarrow Cl + NO_3$$

$$NO_3 + h\nu \rightarrow NO + O_2$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$ClO + NO_2 + M \rightarrow ClONO_2 + M$$

$$2O_3 + 2h\nu \rightarrow 3O_2 \qquad \text{(net)}$$

It is clear from this summary that the stratosphere is a highly complex and coupled system involving a large number of elementary chemical and photochemical reactions. The consensus view of the importance of these interactions has changed as knowledge of the rate coefficients, absorption cross sections and photolysis quantum yields has improved. As the understanding of stratospheric chemistry has evolved, the predicted O_3 depletion due to increases in stratospheric NO_x and Cl_x has changed significantly. This has been an important factor in determining internationally agreed guidelines for protection of the integrity of the O_3 layer [10].
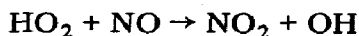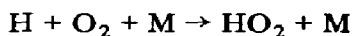
The troposphere is characterized by rapid vertical mixing, an abundance of water vapour and the absence of short wavelength UV radiation (less than 300 nm). Although only about 10% of all atmospheric O_3 is located in this region, its presence is of fundamental importance for atmospheric composition. This arises from the production of the hydroxyl radical [11] by the two reactions:

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$
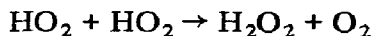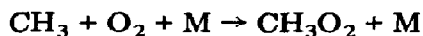
$$H_2O + O(^1D) \rightarrow 2OH$$
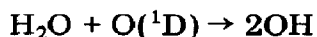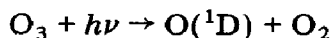
It is attack by OH that initiates the oxidation of many gases in the atmosphere including hydrocarbons, halogen-containing organics, organosulphur compounds and many inorganic gases such as CO, NO_2, H_2S and SO_2. In this way OH acts as a scavenging agent, preventing build-up of these pollutant gases in the atmosphere. In the unpolluted troposphere about 70% of the OH radicals react with CO and 30% with CH_4:

$$OH + CO \rightarrow H + CO_2$$

$$OH + CH_4 \rightarrow H_2O + CH_3$$
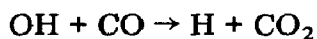
The subsequent reactions of H and CH_3 can either regenerate OH by the reactions

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow NO_2 + OH$$

or lead to removal of radicals, *e.g.*

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$
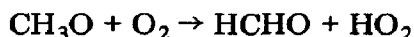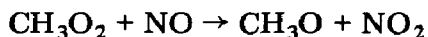
The resultant steady state of OH depends on the relative importance of the chain-carrying reaction involving NO and the radical termination reactions. The important role of NO in tropospheric chemistry is therefore apparent.

Oxidation of CH_3O_2 via reaction with NO subsequently leads to formaldehyde (HCHO) formation:

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$CH_3O + O_2 \rightarrow HCHO + HO_2$

Photodissociation of HCHO then provides an additional source of radicals:

$HCHO + h\nu \rightarrow HCO + H$ $\qquad \lambda \leqslant 340$ nm

The $RO_2 + NO$ reactions in which NO is oxidized to NO_2 are additionally important in that they provide a net source of O_3 through NO_2 photodissociation:

$RO_2 + NO \rightarrow NO_2 + RO$

$NO_2 + h\nu \rightarrow NO + O$

$O + O_2 + M \rightarrow O_3 + M$
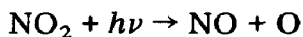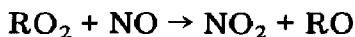
Net production of O_3 from this route occurs at all altitudes below 15 km but is particularly important in the lower troposphere where, in polluted air containing high hydrocarbon levels and consequent enhanced RO_2 concentration, it leads to photochemical smog formation. Hydrocarbon oxidation is also initiated by attack by OH.

NO concentrations are critical for photochemical O_3 formation in the troposphere since the alternative radical removal reactions lead to net loss of O_3. Observations [12] indicate that NO_x concentrations are very low in extensive regions of the troposphere because of the short residence times of NO and NO_2 through the reactions

$NO + O_3 \rightarrow NO_2 + O_2$

$OH + NO_2 + M \rightarrow HNO_3 + M$

followed by rain-out of HNO_3.

The atmospheric cycles of many trace gases are determined by the OH distribution. For instance natural sulphur compounds are oxidized by OH attack, mainly to SO_2. A fraction of the SO_2 in the atmosphere is converted to H_2SO_4 by gas phase oxidation, the first step being accomplished by reaction with OH [13]:

$OH + SO_2 + M \rightarrow HSO_3 + M$

Detailed oxidation mechanisms of the sulphur compounds are not well known, however. Oxidation of SO_2 in atmospheric rain drops is also important, and this reaction probably also occurs through oxidizing agents (OH, HO_2, O_3, H_2O_2) present in solution, which are ultimately derived from gas phase photochemistry [14].

Chlorine chemistry in the troposphere is largely governed by OH attack followed by conversion of the chlorine constituent of the resultant radical to HCl or $COCl_2$, which are removed mainly by precipitation. The tropospheric chemistry of bromine and iodine is less well understood. Since HBr and HI are much more reactive than HCl with OH and are also less

readily formed from atomic bromine and iodine, it seems probable that the chemical behaviour of iodine and bromine differs from that of chlorine species.

In summary, it can be concluded that considerable advances in knowledge of the gas phase chemistry of minor constituents of the atmosphere have occurred in the past decade. The resulting picture provides a sound framework with which to approach new problems. This progress has resulted from a fruitful dialogue between chemists working in the laboratory and atmospheric scientists concerned with measurements of trace gases and modelling of the atmosphere. Photochemistry plays a central role in the problems that have been addressed and photochemists have made a considerable contribution to the detailed understanding of atmospheric behaviour. Evidence for this will be found in the titles published in the *Journal of Photochemistry* over the past decade.

References

1 R. D. Hudson and E. I. Reed (eds.), The stratosphere — present and future, *NASA Ref. Publ. 1049*, 1979 (National Aeronautics and Space Administration).
2 R. A. Cox, A. E. J. Eggleton, R. G. Derwent, J. E. Lovelock and D. H. Pack, *Nature (London)*, *255* (1975) 118 - 121.
3 National Academy of Sciences, *Acid Deposition — Atmospheric Processes in Eastern North America*, National Academy Press, Washington, DC, 1983.
4 S. Chapman, *Philos. Mag.*, *10* (1930) 369.
5 D. R. Bates and M. Nicolet, *J. Geophys. Res.*, *55* (1950) 301.
  B. G. Hunt, *J. Geophys. Res.*, *71* (1966) 1385.
6 P. J. Crutzen, *Q. Rev. R. Meteorol. Soc.*, *96* (1970) 320.
  H. S. Johnston, *Science*, *173* (1971) 517.
7 R. S. Stolarski and R. J. Cicerone, *Can. J. Chem.*, *52* (1974) 1610.
  S. C. Wofsy and M. B. McElroy, *Can. J. Chem.*, *52* (1974) 1582.
8 S. C. Wofsy, M. B. McElroy and Y. L. Yung, *Geophys. Res. Lett.*, *2* (1975) 215.
  Y. L. Yung, J. Pinto, R. T. Watson and S. P. Sander, *J. Atmos. Sci.*, *37* (1980) 339.
9 M. J. Molina and F. S. Rowland, *Nature (London)*, *249* (1974) 810.
10 Environmental assessment of ozone depletion and its impact, *Bull. 7*, January 1982 (United Nations Environment Programme).
11 H. Levy, *Science*, *173* (1971) 141.
   H. Levy, *Planet. Space Sci.*, *20* (1972) 919.
12 M. McFarland, D. Kley, J. W. Drummond, A. L. Schmeltekopf and R. H. Winkler, *Geophys. Res. Lett.*, *6* (1979) 605.
13 R. A. Cox, *J. Photochem.*, *3* (1974) 291.
14 S. A. Penkett, B. M. R. Jones, K. A. Brice and A. E. J. Eggleton, *Atmos. Environ.*, *13* (1979) 123.