Chemical Events in the Atmosphere and their Impact on Environment
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PHOTOCHEMICAL REACTIONS IN THE ATMOSPHERE

D. PHILLIPS
Davy Faraday Research Laboratory, The Royal Institution
21 Albemarle Street, London WIX 4BS

This review presents both a view of unresolved problems relating to the photochemistry of atmospheric constituents of global importance and some more parochial assessments of problems particular to the U.K.

To begin with the latter, while it is right that there should be concern over the quality of air, and the subsequent effects of polluted air on the environment, it should be remembered that the air quality in cities in the U.K. is probably better now than at any time in the previous several hundred years. Thus John Evelyn, in 1611, said:

> "It is this horrid smoake which obscures our churches, and makes our palaces look old, which fouls our clothes and corrupts the waters"

Matters really did not improve much until after the disaster of December 5th, December 8th 1952, when the combined effects of a temperature inversion, particulate matter and sulphur dioxide emissions, largely from domestic coal fires, resulted in the premature deaths of some 4000 people, mainly elderly and those suffering from respiratory problems. This led directly to the Clean Air Act of 1953, which on a fairly rapid timescale led to the control of particulate matter emissions, and is a good example of the speed with which Governments can act if suitably motivated. As a child in urban Tyneside, it never occurred to me that the colour of buildings was anything other than jet-black. Indeed, if you visit many urban buildings nowadays which had been repaired prior to 1952 and have subsequently been cleaned you will find pieces of stone which do not match the originals. There was no need, since within twelve months, the colour would in any case be black. No one could argue that the environment has been significantly improved by the control of particulate matter, the days of the London "pea-souper" are now long gone, but it could be said that the success of this legislation may have led to complacency with regard to the other, invisible emissions, most notably that of SO_2.

Again, this is not a new phenomenon. In 1846 Michael Faraday was asked by his club, the Athenaeum, to explain why new leather armchairs were disintegrating rapidly, and it did not take him long to diagnose that the cause was atmospheric SO_2 from domestic coal fires denaturing the leather.

The emission of tropospheric sulphur oxide, and that of NO_x emission, is now of great concern, known colloquially, but inaccurately as "acid rain". Acid deposition would be a better description of the phenomenon.

The immediate consequences of emission of SO_2 and NO_x are of course simply stated, the production downwind, either locally, or more often nowadays far away, of sulphuric acid and nitric acid, which may be deposited dry or in precipitation on the ground.

An attempt is made here to identify some of the remaining problems in understanding the chemistry, particularly the photochemistry, of these processes.

Photochemistry associated with acid rain

There is clear evidence that the photochemical conversion of sulphur dioxide to acid is a minor but significant process. The possible mechanisms for the photochemical oxidation have been dealt with by many authors, but the review by Cox provides a basis for discussion [1].

The possible mechanisms are:

(i) Homogeneous direct photolysis of sulphur dioxide in the presence of oxygen.

(ii) Homogeneous gas-phase oxidation by hydroxyl radicals, OH, HO_2, and peroxy radicals, of photochemical origin.

(iii) Homogeneous gas-phase reactions involving ozone-olefin interactions in urban atmospheres.

(iv) Heterogeneous reactions on the surface of particulate matter.

(v) Homogeneous aqueous phase reactions in water droplets in the atmosphere.

The mechanisms of direct photolysis, reaction (1) – (5), oxidation by OH, HO_2, RO, and RO_2, reactions (6) – (11), and ozone-olefin reactions, (12) lead to the estimated rates of SO_2 conversion shown in Table 1.

Reactions

$$SO_2\,(X\,^1A_1) + h\nu\,(340 < \lambda < 400) \rightarrow SO_2\,(^3B_1) \tag{1}$$

$$\begin{aligned} SO_2\,(X\,^1A_1) + h\nu\,(240 < \lambda < 330) &\rightarrow SO_2\,(^1B_1)\ \text{(short)} \\ &\rightarrow SO_2\,(^1A_2)\ \text{(long)} \end{aligned} \tag{2}$$

$$SO_2 + h\nu \rightarrow SO_2^* \tag{3}$$

$$\rightarrow SO\,(^3\Sigma^-) + O\,(^3P) \tag{4}$$

$$SO_2\,(^3B_1) + O_2 \rightarrow SO_3 + O\,(^3P_1) \qquad \Delta H = -159\ \text{kJ mol}^{-1} \tag{5}$$

$$OH + SO_2 \xrightarrow{(M)} HOSO_2 \tag{6}$$

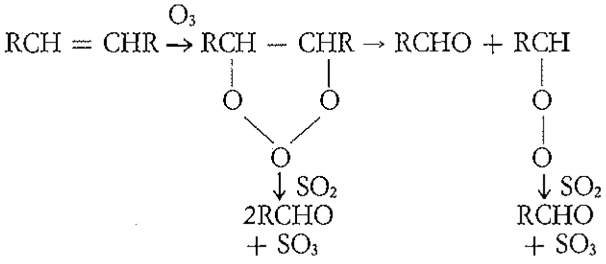
$$HO_2 + SO_2 \rightarrow OH + SO_3 \tag{7}$$

$$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3 \tag{8}$$

$$HOSO_2 + O_2 \rightarrow HOSO_2O_2 \tag{9}$$

$$HOSO_2O_2 + NO \rightarrow HOSO_2O + NO_2 \tag{10}$$

$$HOSO_2O + NO_2 \rightarrow HOSO_2ONO_2\ \text{(nitryl sulphuric acid)} \tag{11}$$



(12)

TAB. 1 [1] - *Rates of Homogeneous SO_2 Oxidation.*

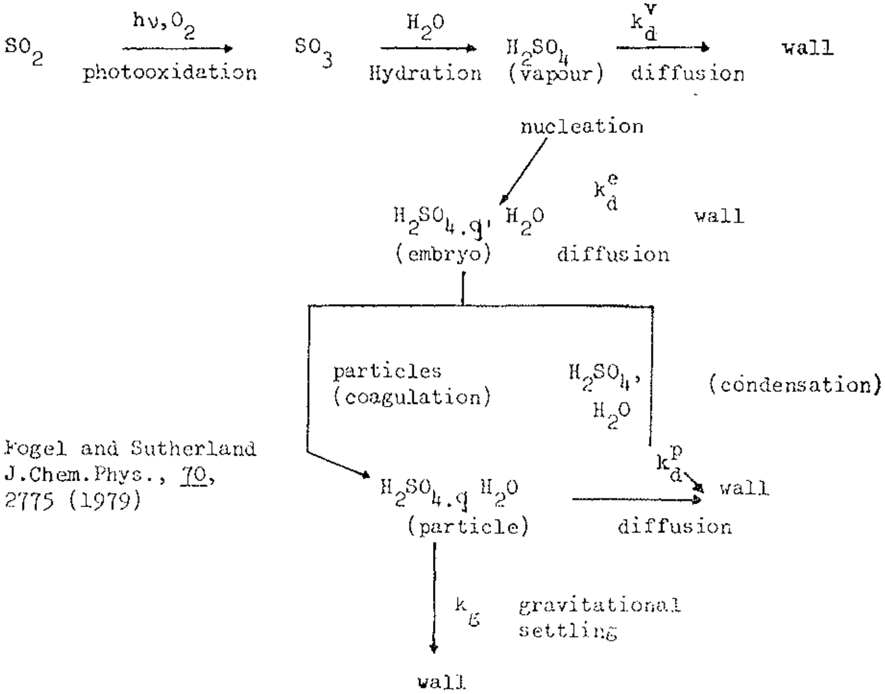
	k cm^3 $molecule^{-1}$ s^{-1}	active species molecules cm^{-3}		100 × SO_2 oxidn rate h^{-1}
DIRECT	1.6×10^{-15}	2.3	(SO_2 $^3B_1$)	0.026
OH	8×10^{-13}	7×10^6	(OH)	2.0
		(7×10^5)		0.2
HO_2	9×10^{-16}	2×10^9	(HO_2)	0.6
		(1×10^8)		(0.03)
CH_3O_2	5×10^{-15}	2×10^9	(CH_3O_2)	1.7
		(1.5×10^7)		(0.03)
O_3/alkene		2.5×10^{12}	(O_3)	0.07
		2.5×10^{11}	(CH_3H_6)	

It is clear from this work that the homogeneous free radical reactions are probably the most significant, but the role of aqueous phase oxidation by H_2O_2 and of heterogeneous oxidation are still in doubt, and require further investigation. The formation of aerosols is also of some importance. It has been suggested that in clouds, the rate of droplet formation may be proportional to the light intensity, which clearly deserves further attention. The formation of particles in the atmosphere is also very poorly understood, and requires much further work. The sole paper [2] dealing with this phenomenon in any quantitative way investigates the processes occurring, summarized in Scheme 1, upon the direct excitation of SO_2 into the second singlet state at wavelengths > 190 nm, a process clearly not of importance in the troposphere.

Before passing on to other aspects of atmospheric *photochemistry*, we might just anticipate later discussion of the effects of acid deposition, and indeed the location of this. From the parochial UK viewpoint the region most affected is southern Scandinavia, Tables 2 and 3 giving the total contributions by country to deposition in this region [3].

Other later papers in this volume will comment upon the effects on soil and water in lakes and rivers, of this acid deposition, but it may be noted in passing that the Royal Society of London, the Norwegian Academy of Science and Letters, and the Royal Swedish Academy of Sciences have recently agreed to initiate a further long term collaborative programme of research into the effects of acidification of surface waters in Norway

Scheme 1



Fogel and Sutherland
J.Chem.Phys., 70,
2775 (1979)

Tab. 2 [3] - *Average Contributions of Deposition in S. Norway (1972-1974).*

region	distribution of wet deposition (%)	distribution of dry deposition (%)	distribution of total deposition (%)	total deposition mg SO_2 m^{-2} a^{-1} annual average	per 100 kt emission
British Isles	34.3	22.2	30.7	895	15.0
Norway	10.9	32.2	17.4	507	323
G.D.R.	11.0	9.9	10.7	312	6.3
F.R.G.	11.4	7.2	10.1	295	7.3
Sweden	4.4	6.9	5.2	152	14.8
Holland	4.3	2.9	3.9	114	9.5
Poland	3.4	3.9	3.5	102	2.7
Denmark	3.3	3.7	3.4	99	26.2
France	4.1	1.9	3.4	99	4.1
Belg./Lux.	3.9	2.3	3.4	99	8.1
Czech.	3.5	2.7	3.2	93	2.9
U.S.S.R.	2.3	2.4	2.4	70	0.7
Italy	1.1	0.5	0.9	26	0.9
Finland	0.5	0.5	0.5	14	3.0
Others	1.5	0.8	1.3	38	1.0
TOTAL	100.0	100.0	100.0	2915	

Annual average wet deposition 2022 mg SO_2 m^{-2} a^{-1}
Annual average dry deposition 893 mg SO_2 m^{-2} a^{-1}

TAB. 3 [3] - *Deposition by Regions for Each Year 1972-1974* (percentages of grand total for each year).

	1972 total: 3698 mg m^{-2}		1973 total: 2231 mg m^{-2}		1974 total: 2883 mg m^{-2}	
region	dry deposition	deposition in rain	dry deposition	deposition in rain	dry deposition	deposition in rain
British Isles	5.3	20.9	7.2	22.6	8.5	28.7
Norway	7.8	5.5	12.7	11.3	10.3	7.5
G.D.R.	3.9	11.3	2.5	5.1	2.3	4.9
F.R.G.	2.2	8.5	1.8	6.9	2.5	7.9
Sweden	1.9	3.1	2.1	3.5	2.4	2.7
Holland	0.9	3.4	1.0	3.2	0.9	2.4
Poland	1.1	2.9	0.8	2.0	1.6	1.8
Denmark	1.4	3.1	1.0	2.1	0.9	1.4
France	0.7	3.2	0.5	2.3	0.5	2.9
Belg./Lux.	0.7	2.9	0.8	2.6	0.6	2.4
Czech.	1.1	3.9	0.8	1.7	0.5	1.1
U.S.S.R.	0.5	1.0	0.5	3.3	1.2	1.1
Italy	0.2	1.0	0.1	0.0	0.1	1.0
Finland	0.1	0.1	0.1	0.3	0.3	0.6
others	0.2	1.2	0.2	1.0	0.3	0.7
TOTAL	28.0	72.0	32.1	67.9	32.9	67.1

Europe presently emits ~ 33 M Tonnes/yr.

and Sweden and the implication for fisheries. Specifically excluded, however, from this programme will be the questions of how industrial discharges create acid deposition, and to what degree reductions in UK sulphur dioxide emissions would change the acidity of rainfall over affected areas of Scandinavia. The questions to be addressed are:

1. In the affected areas of Norway and Sweden, what are the factors, in addition to pH, that in practice determine the fishery status of lakes?

2. What are the biological, chemical and hydrogeological characteristics of catchments which determine whether the composition of surface waters falls within a range acceptable to fish?

3. In Norway and Sweden, to what extent are these characteristics being adversely affected by the acid deposition itself?

4. What changes would be brought about in water chemistry and fishery status in Norway and Sweden by given levels of reduction of man-made sulphur deposition?

Photochemistry of course plays a crucial role in the whole of tropospheric atmospheric chemistry, not just in locally confined events such as those involving acid deposition discussed above, and in the well-documented "photochemical smog" of Californian cities, which is now a local problem of very widespread incidence throughout the world.

The key intermediate chemical species in the troposphere is undoubtedly the hydroxyl radical OH, the major source being the photolysis of tropospheric ozone, and subsequent reaction of the product $O(^1D)$ with water (13), (14), in competition with collisional quenching to give $O(^3P)$ (15), which subsequently reforms ozone (16).

$$O_3 + h\nu \ (\lambda < 310 \text{ nm}) \rightarrow O_2 + O(^1D) \qquad (13)$$

$$O(^1D) + H_2O \rightarrow OH + OH \qquad (14)$$

$$O(^1D) + M \rightarrow O(^3P) + M \qquad (15)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (16)$$

The hydroxyl radical so produced is the major oxidising species in the troposphere, and a complete picture of its chemistry holds the key to furthering progress in understanding tropospheric chemistry. The chemistry discussed in detail elsewhere, is of course very complex. To take, for example, the cycle of reactions with carbon monoxide, which may be net producers or destroyers of tropospheric ozone depending upon the concentration of oxides of nitrogen present. In the presence of NO, the cycle (16)-(20) occurs, without loss of OH or NO, whereas at low NO concentrations, the cycle (17), (18) and (21), again without loss of OH.

$$CO + OH \rightarrow H + CO_2 \qquad (17)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (18)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (19)$$

$$NO_2 + h\nu \rightarrow NO + O \ (< 400 \text{ nm}) \qquad (20)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (16)$$

$$\text{Net} \quad CO + 2O_2 \rightarrow CO_2 + O_3$$

$$CO + OH \rightarrow H + CO_2 \tag{17}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{18}$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{21}$$

$$\text{Net} \quad CO + O_3 \rightarrow CO_2 + O_2$$

Thus ozone may be correlated positively with carbon monoxide or negatively with carbon monoxide, depending upon local oxide of nitrogen concentrations, as indicated in Figure 1 [4].

Since methane reacts with hydroxyl, the level of methane in the troposphere is of great interest. There are some indications that the methane level is increasing, which could be due to an increased methane release rate, or a decrease in hydroxyl concentration. Clearly it will be of great importance to establish which of these possibilities is occurring.

Despite progress in understanding tropospheric chemistry, there is still a pressing need for improvements, with the following problems requiring attention

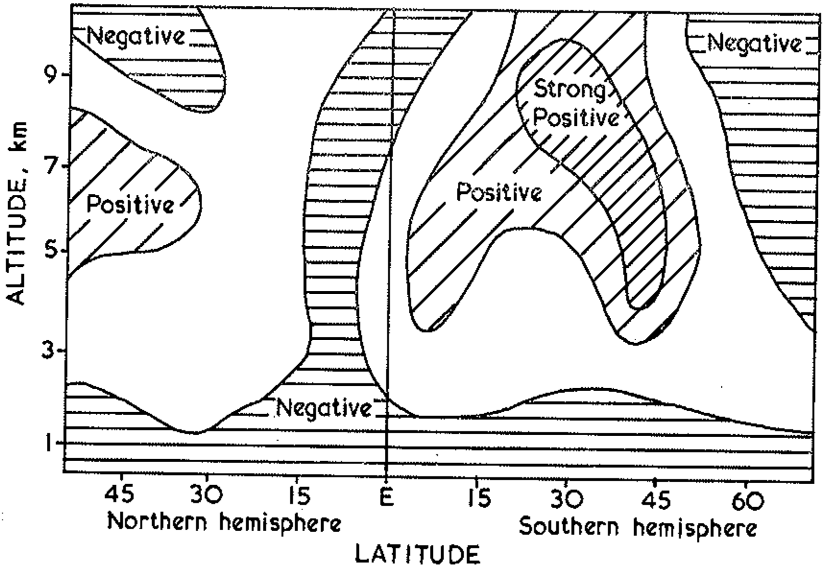


FIG. 1. Latitude-altitude depiction of regions where O_3 and CO variability are positively and negatively correlated (after Figure 3, ref. 4).

(i) understanding the sources and sinks of minor constituents, such as CH_4, CO, O_3, NO, NO_2, NH_3, N_2O, H_2, OH, HO_2 etc., and their detailed geographical location and intensities on a global scale. On a very parochial level this will improve understading of local conditions such as photochemical smog, which can be considered merely to be an exaggerated or perturbed normal troposphere.

(ii) in situ measurements of radical intermediates, particularly OH on a global scale, a problem which has to date been barely tackled.

(iii) laboratory measurements of rate-constants, particularly those of organic reactions involving peroxy and exy-radicals.

(iv) modelling of the chemistry, transport, dynamics, radiative transfer, etc., of the troposphere. Here 3D models are desirable, but as yet too expensive in computer time.

On the whole it is probably true to say that tropospheric chemistry is rather less well understood than that of the stratosphere, although of course, since the input of material from the troposphere to the stratosphere must affect the chemistry of the latter, the uncertainties in tropospheric chemistry are reflected in that of the stratosphere.

STRATOSPHERIC CHEMISTRY

In this introductory paper there is no attempt to preempt the discussions by later authors concerning these problems. However, an attempt is made here to pin-point some remaining problems.

On the simplest possible level, the ozone in the stratosphere is maintained by the Chapman mechanism, (13), (16), (22-24) plus the catalytic cycles which in cryptic form are shown as (25)-(30)

$$O_2 + h\nu \rightarrow O + O \qquad (22)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (16)$$

Chapman mechanism

$$O_3 + h\nu \rightarrow O_2 + O \qquad (13)$$

$$O_3 + O \rightarrow O_2 + O_2 \qquad (23)$$

$$O + O + M \rightarrow O_2 + M \qquad (24)$$

Catalytic cycles

NO_x

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (25)$$

$$NO_2 + O \rightarrow NO + O_2 \quad (26)$$

$$\text{Net} \quad O + O_3 \rightarrow 2O_2$$

HO_x

$$OH + O_3 \rightarrow HO_2 + O_2 \quad (27)$$

$$O + HO_2 \rightarrow OH + O_2 \quad (28)$$

$$\text{Net} \quad O + O_3 \rightarrow 2O_2$$

ClO_x

$$Cl + O_3 \rightarrow ClO + O_2 \quad (29)$$

$$ClO + O \rightarrow Cl + O_2 \quad (30)$$

$$\text{Net} \quad O + O_3 \rightarrow 2O_2$$

These cycles are of importance in the unpolluted atmosphere and the concern for the past decade has been

1) To understand the chemistry of the unpolluted stratosphere.

2) To predict the effects of release of man-made chemical species in the stratosphere.

The latter question will of course become clearer in time as accurate measurements of the ozone concentration are made, and can be compared both with release rates of pollutants, and models. Until relatively recently only local columnar concentrations of ozone had been measured, typified by the Arosa data, shown in Figure 2.

However, since April 1970, *global* measurements have been available from the Nimbus 4 backscatter UV measurements, and Nimbus 7 (SBUV) has been gathering data since 1978. This set of data may be extensive enough soon to allow statistical analysis of long-term trends. Ground-based measurements of the critical 34-36 km layer suggest virtually no change in ozone in north temperature latitudes over the decade 1970-1980. A comparison of the satellite SBUV data for March 1979 with BUV results for the same month in 1971 or 1972 show a negative trend of 0.4 → 0.7% per year at 38 km. If the comparisons are valid, this is not inconsistent with recent model predictions.

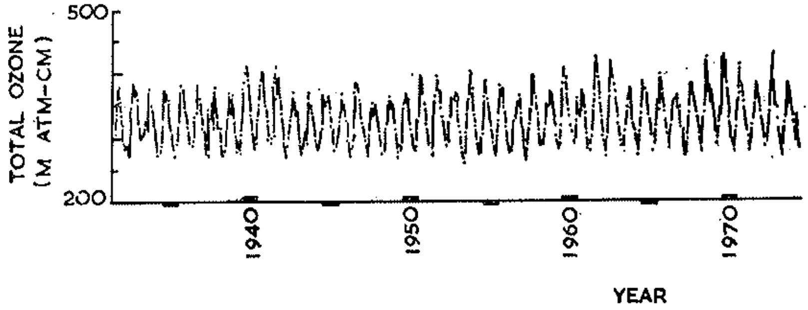


Fig. 2. Columnar ozone concentration variation, Arosa data.

The recent solar mesosphere explorer (SME) satellite (Oct. 1981) measures simultaneously [O_3], T, and solar uv intensity in the upper stratosphere [5, 6, 7]. This is a good altitude to test photochemical theories since photochemical lifetimes of species here are appreciably shorter than the time-scale for horizontal North to South redistribution. In the mesosphere, the results show quite clearly that the temperature (rather than solar flux) determines the O_3 concentration, although the results of other physical phenomena such as the solar flare of July 13, 1982 were clearly observeable.

The anthropogenic perturbations to the stratosphere include inputs of NO_x from nuclear weapons testing, high flying aircraft, and of Cl from the photolysis of chlorofluorocarbons, discussed in detail in a later article, but represented by

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl \tag{31}$$

followed by the complex sequence of reactions involving the catalytic cycles represented by (25) – (30), but in fact involving a very large number of interconnected chemical reactions.

Since predicted effects upon ozone concentration due to chlorofluorocarbons, for example, cannot yet be identified unambiguously from measurements of O_3, modelling is still vital. This requires

a) Accurate rate data for critical reactions.

b) Stringent testing of models against *measured* concentrations of atmospheric species.

What of rate data? It is surely true to say that thermal rate data are on a more secure footing than the photochemical, where the rate of a photochemical reaction is given by a pseudo rate-constant j multiplied by concentration of reactants. Accurate assessments of j require knowledge of absorption coefficients, solar flux, quantum yields of photodecomposition and of course since j varies diurnally, seasonally and geographically, values thus represent averages. As an example of the insecurity of photochemical rate-data, it can be said that even as basic a mechanism as the Chapman mechanism given earlier is the subject of recent conflict. Thus it has been suggested that the O_2 absorption cross-sections for absorption in the Herzberg continuum between 200-220 nm widely used in models until recently are significantly in excess of correct values [8]. The use of the wrong O_2 cross-section would greatly affect the rate of photodissociation of a number of species which must be used in modelling. The adjustment of the downward adjustment of the absorption coefficient of O_2, hence j_2, has a profound effect upon calculated concentrations of other species absorbing competitively; thus at 30 km, the concentration of N_2O, CF_2Cl_2, $CFCl_3$ are reduced by factors of 0.70, 0.62, and 0.19 respectively, whereas CH_4, H_2 and CO profiles are essentially unchanged. The predicted concentration of HNO_3 above 30 km is 50% less, yielding better agreement with observation. The result of these adjustments is to cause a 10-20% decrease in computed ozone concentration above about 35 km, but a fairly large increase ($\sim$ 30%) around 20-25 km. This uncertainty in absorption cross-sections also extends to NO_3, where recent measurements by Wayne and Cox, independently, give results much less than those of Johnston or Wine.

The effect that adjustment of other rate parameters has upon modelling is further illustrated by the paper of Ko and Sze [9]. The revised rate constants are shown in Table 4.

Adaptation of the new rate for reaction 31, a factor of 2 greater than the previous recommendation, results in a factor of 1.3 increase in the concentrations of OH above 40 km. This higher OH reduces the concentration of CH_4 above 40 km by $\sim$ 20%.

TABLE 4

REACTIONS		NASA-JPL (1982)	WMO/NASA (1982)
$O+HO_2 \rightarrow OH+O_2$	(32)	$3.0\,(-11)\exp(200/T)$	$3.5\,(-11)$
$OH+HO_2 \rightarrow H_2O+O_2$	(33)	$(7+4P_{at}) \times 10^{-11}$	$8.0\,(-11)$
$HO_2+HO_2 \rightarrow H_2O_2+O_2$	(34)	$(3.4+2.5P_{atm}) \times 10^{-14}\exp(1150/T)$	$3.0\,(-12)$
$OH+HNO_4 \rightarrow H_2O+NO_2+O_2$	(35)	$1.3\,(-12)\exp(380/T)$	$4.0\,(-12)$
$ClO+NO_2 \overset{M}{\rightarrow} ClNO_3$	(36)	$4.5\,(-32)\,(T/300)^{-3.8*}$ $1.8\,(-31)\,(T/300)^{-3.4*}$	$4.5(-32)(T/300)^{-3.8*}$

* Low-pressure limit rate-constant.

Consequently reaction (37)

$$OH + HCl \rightarrow H_2O + Cl \qquad (37)$$

is more efficient, while the recycling of Cl to HCl via (38)

$$CH_4 + Cl \rightarrow HCl + CH_3 \qquad (38)$$

is less efficient, resulting in a factor of 1.4 inverse in concentrations of $Cl^{\cdot}$ and $ClO^{\cdot}$ around 40 km.

The effect of change in (36) is restricted to the region below 30 km where the concentration of $ClNO_3$ is appreciable. The agreement of the model with some in-situ measurements of ClO seems reasonable (but see below).

For a given concentration of ClY, ($Cl + ClO + HCl + ClNO_3 + HOCl$) partition between Cl, ClO and HCl is determined mainly be reactions (37) and (38). The choice of rate for (36) clearly has an impact on the concentration of $ClNO_3$ calculated. Using the fast rate, a chlorine nitrate concentration of 0.6 ppbv at 30 km is calculated, in agreement with measurements by Murray.

While on this subject, further comment concerning chlorine nitrate, $ClONO_2$ is required. Postulated isomers such as ClOONO, OClONO are now discounted [10], although the rate-constant for formation is still in doubt, as we have seen.

To return to the models of Ko and Sze [9], calculated ozone profiles can now be compared. (Table 5)

TAB. 5 - [O_3] *at altitudes 20-50 km.* (10 [11] molecule cm^{-3}).

ALTITUDE	CALCULATED			OBSERVED			
	WMA/NASA	A	B	US std. 1976	STRAT	SABE-2	IOR 1
50	0.58	0.49	0.45	0.66	—	—	0.57
45	1.8	1.5	1.3	2.2	—	1.8	2.0
40	5.4	4.9	4.3	6.1	6.3	5.5	6.3
35	16	15	14	14	14	17	16
30	34	35	34	25	28	31	31
25	51	51	54	43	45	38	54
20	50	50	57	48	31	36	—

Ko and Sze, Geophys. Res. Letters, 1983, *10*, 341.

In Model *A* (high $\sigma(O_2)$) there is 10-20% lower [O_3] above 40 km than in the previous model (WMO/NASA).

In Model *B* (lower $\sigma(O_2)$). Above 40, [O_3] is further reduced by 10%.

In the lower stratosphere, there is more ozone in model B than in model A due to an increase in the photolysis rate of O_2 resulting from the greater solar flux. The net effect is an approximate 7% increase in column density of O_3 when the smaller cross-section for oxygen absorption $\sigma(O_2)$) is used (Model B).

Above 40 km altitude the observed concentration of O_3 is greater than that calculated with a faster rate for reaction 32, and a low $\sigma(O_2)$, the agreement is significantly *worsened* in this 1-D model.

Other papers will no doubt comment on this, but here we merely wish to point out the need for very accurate rate data.

At steady-state, as we noted before the downward revision of $\sigma(O_2)$ causes the ozone depletion $-\Delta O_3$ to diminish, (Table 6) no doubt due to the smaller peak value of ClY as a result of the shorter lifetime of the chlorofluorocarbons.

Correlation of models with measurements

The crucial test of a model must be the ability to assess correctly the concentrations of trace species as well as that of ozone. Unfortunately,

TAB. 6 - *Calculated steady-state O_3 depletion.*

MODEL	Peak ClY (ppbv)	$-\Delta O_3$ (%) slow $ClNO_3$	$-\Delta O_3$ (%) fast $ClNO_3$
A	9.3	5.9	4.5
B	8.0	4.4	3.2
WMO/NASA	9.4	6.1	—

as yet there are few global measurements of trace gases or radical intermediates. Some progress has been made in the simultaneous measurement of, for example OH, ClO, HO_2 together with O_3, NO_x, but these generally refer to one geographical location, and to one launch day. It is to be hoped that Professor Anderson's experiments and the MAP-GLOBUS campaign might do much to help in this area.

It should be noted that a recent paper by Mumma *et al.* [11] using a ground-based ir heterodyne method to measure the concentration of the important species ClO failed totally to observe any ClO, putting a limit of a factor of 1/7 of the "accepted" value, based upon "in situ" measurements. Professor Anderson will comment on this.

In conclusion then, it seems evident that hetter laboratory rate constants are required for some reactions, and particularly photochemical data on quantum yields, channels, and cross-sections, and wavelength dependencies of such species as NO_3, HNO_4, HOCl, $ClNO_2$, while global measurements of trace species are equally vital for the understanding of this complex chemistry.

It is hoped that this introductory article will have identified some of the problems remaining in atmospheric chemistry, with particular emphasis on the photochemistry.

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DISCUSSION

ANDERSON

The subject of ClO will be one that comes up fairly frequently this week and perhaps this is not the time to summarize the situation completely, but I should add that there are a number of elements in this case which were not brought up here. A significant amount of work has been done in other areas, in particular the microwave millimeter emission experiments which detected the purely rotational emission of ClO from the ground at both 204 and 278 nm, and the millimeter emission work of Waters, who has detected that emission from a balloon. The background subtraction which is involved in the 1/10 to 1 percent of the level expected in the laser heterodyne work, coupled with the absorption measurement and the calculation of line strengths together with one other measurement in a laboratory of the kind that could be accepted in this level of discussion is not simply an academic issue since no ClO implies no fluorocarbon problem. The laser heterodyne method is a very, very good one. There is very little that competes with the absence or presence of an observed feature, particularly in this case the absence of that absorption at the proper frequency; and the wave length here is not the issue, rather the difficulty of the observation, the very small signal to noise ratios and the issue of the line strength. The conclusion, or the next step, I should say, in this process will be one of mixing the laser heterodyne method with the laboratory observation of the free radical, a step that most people would require before accepting and presenting the information publicly, and a step that has not been taken. So I think in the next six months the resolution of this issue will probably take place. I respect greatly the basic method applied here and I do not think there have been serious errors in its application. The interpretation of it is the issue, and the homework that precedes the release of the information publicly is the issue at point.

LIBERTI

You pointed out the importance of photochemical reactions in the atmosphere related to pollution, and you described the SO_2 oxidation, giving great emphasis to the homogeneous oxidation through free radicals. I definitely agree these are important processes; however, I strongly believe and there is experimental evidence that heterogeneous processes are also of great importance. Particulate matter is a natural component of the troposphere and it is well established that particulate matter is always absorbing most of the species in the air and also SO_2. The presence of soot in the particles responsible for the so-called "blackness index", which is usually taken as a measure of pollution, being related to particulate concentration, indicates a catalytic reaction can occur for the oxidation of SO_2. I wish to emphasize this point because most effects related to the formation of acid rain are due to the formation of strong acids, and these species are found in the aerosol fraction of the atmosphere.

PHILLIPS

I would simply echo what you said. Although I have said that the homogeneous reaction has hitherto been held to be most responsible, there is some evidence that the heterogeneous reaction is of great importance, and I think it is an area which is worthy of further research.

CHAMEIDES

There is another class of reactions. I do not know whether you want to call them homogeneous or heterogeneous as the aqueous phase: homogeneous reactions which involve heterogeneous processes in solution, and these I think can be quite important, involving peroxide as well as radicals. I'll have something to say about that during my talk.

LIBERTI

We are having in the atmosphere gases, liquids and solids. It is a common practice for scientists to tackle the problem separately by considering homogeneous and heterogeneous processes. This approach can be correct as it permits us to obtain measurements of rate of conversion, equilibrium constants and other thermodynamic data. In the environment all reactions occur simultaneously and the relative rates of reactions might be affected. So it is difficult to attribute a greater importance to one process than to another one unless some reactions are completely prevented.