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Photochemical Oxidation of Atmospheric Sulphur Dioxide [and Discussion]

R. A. Cox and M. F. R. Mulcahy

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Photochemical oxidation of atmospheric sulphur dioxide

By R. A. Cox
Environmental and Medical Sciences Division, A.E.R.E., Harwell,
*Oxfordshire OX*11 0*RA, U.K.*

Oxidation of atmospheric sulphur dioxide can occur by homogeneous photochemically initiated gas-phase reactions as well as by heterogeneous reactions in cloud and fog droplets. Gas phase oxidation can result from reactions of excited SO_2 molecules formed by absorption of solar u.v. radiation by ground state SO_2, from reactions of SO_2 with photochemically generated OH and RO_2 free radicals, and from its reaction with transient species produced in thermal ozone–alkene reactions. Evaluation of the available mechanistic and rate data reveals that, of these three processes, oxidation by free radicals, particularly OH, is likely to be the most important in the atmosphere. Oxidation rates of up to 4 % h^{-1} are predicted for a hydrocarbon–NO_x polluted atmosphere under western European summertime conditions. This can lead to the formation of elevated concentrations of sulphuric acid and sulphate aerosol in polluted air. In the natural background troposphere oxidation rates are much less, *ca.* 0.3 % h^{-1} averaged over 24 h, but probably still significant as a source of atmospheric sulphates.

Introduction

Sulphur dioxide is one of the most widely recognized atmospheric pollutants, world-wide emissions amounting to approximately 150×10^6 t, 90 % of which originates in the Northern Hemisphere (Robinson & Robbins 1970). These man-made sulphur emissions are superimposed on emissions of natural gaseous sulphur compounds, mainly H_2S and organic sulphur compounds, but it is generally acknowledged that in populated and industrial regions, e.g. NW Europe, the man-made sources dominate. A significant fraction of all gaseous sulphur compounds are oxidized within the atmosphere to form sulphate, which can be detected in rain and as a component of the atmospheric aerosol in the form of sulphuric acid, acid and neutral ammonium sulphates, and other sulphates. The sulphates in atmospheric precipitation elements have environmental significance in their health effects (Higgins & Ferris 1973), their effects on visibility (Eggleton 1969) and in the ecological consequences of acid rainfall (U.N. 1971).

Over the years a number of mechanisms have been proposed to explain the oxidation of atmospheric SO_2 to H_2SO_4 and sulphates, and these may be broadly classified into two types, namely:

(*a*) homogeneous gas-phase oxidation, usually photochemically initiated;
(*b*) heterogeneous oxidation either in aqueous cloud or fog droplets or on aerosol particles.

The evidence seems to point to the occurrence in the atmosphere of both types of process, the contribution of each to the overall conversion of SO_2 to SO_4^{2-} depending on the prevailing ambient conditions. In the present discussion a brief survey of the various homogeneous, photochemically initiated mechanisms which have been proposed for SO_2 oxidation will be given. The quantitative conversion rates resulting from the more important processes will be discussed in terms of sulphuric acid formation in polluted air and the overall life-cycle of atmospheric SO_2.

HOMOGENEOUS GAS-PHASE OXIDATION OF SO_2

Three distinct mechanisms have been discussed for the homogeneous gas-phase oxidation of SO_2. They are:

(*a*) direct photooxidation involving the reactions of excited SO_2 molecules produced by the absorption of solar u.v. radiation in the first and second absorption bands of SO_2;

(*b*) oxidation of SO_2 by atoms and free radicals which are generated photochemically;

(*c*) oxidation of SO_2 by reactive intermediates in ozone–olefin reactions.

A summary of the available information on the mechanism and rates for each of these three processes is given below.

(*a*) *Direct photooxidation of* SO_2

The photodissociation of SO_2 by the reaction

$$SO_2 + h\nu = SO + O(^3P); \quad \Delta H^\circ_{298} = 547.6 \text{ kJ mol}^{-1}$$

requires light of wavelength $\lambda \leqslant 210$ nm. Therefore radiation in the solar u.v. at ground level ($\lambda \geqslant 290$ nm) is not sufficiently energetic to dissociate SO_2 and absorption in this region leads to the formation of electronically excited states of the SO_2 molecule:

$$SO_2 + h\nu \ (400\text{–}340 \text{ nm}) \longrightarrow SO_2(^3B_1), \text{ excited triplet } SO_2;$$

$$SO_2 + h\nu \ (340\text{–}260 \text{ nm}) \longrightarrow SO_2(^1B_1), \text{ and probably other singlet states.}$$

The photochemistry of SO_2 is therefore determined by the chemical behaviour of these excited states, the elucidation of which has proved to be a problem of some magnitude. Much of the available information on the excited states is due to the work of J. G. Calvert and coworkers, who have used fluorescence and phosphorescence emission to study the behaviour of the $^1B_1$ and $^3B_1$ states respectively (see, for example, Sidebottom *et al.* 1973) as well as chemical studies (Chung, Calvert & Bottenheim, 1975).

Absorption in the 400–340 nm 'forbidden' band is very weak and most excitation is initially into the singlet states. The singlet state is relatively unreactive chemically but is rapidly quenched by other gases including the major atmospheric components (N_2, O_2, H_2O, CO_2), e.g.

$$SO_2(^1B_1) + M \longrightarrow \underset{\text{ground state}}{SO_2(\tilde{X}\,^1A_1)} + M$$

$$\longrightarrow SO_2(^3B_1) + M.$$

A fraction of these quenching collisions lead to intersystem crossing to form the triplet state, which appears to be the dominant chemically active species in SO_2 photolysis systems. It can, for example, undergo chemical reactions with NO, SO_2 (to form SO_3), CO and hydrocarbons (to form sulphinic acids). The major atmospheric gases also quench SO_2 ($^3B_1$) to the ground state with moderate efficiency, however, and consequently the reactions of triplet SO_2 molecules with other trace constituents in the atmosphere are of negligible importance except under very special conditions. The only reactions of the $^3B_1$ state which can be significant in the normal atmosphere are possible chemical quenching reactions with O_2, e.g.

$$SO_3(^3B_1) + O_2 = SO_3 + O(^3P_1); \quad \Delta H = -159 \text{ kJ mol}^{-1}.$$

Although it is energetically favourable, this process is 'forbidden' by spin conservation rules, and might therefore be expected to be slow. Studies of the quantum yield for the photooxidation of SO_2 in the presence of excess O_2 (Cox 1972, 1973; Friend, Leifer & Trichon 1973) show this to be the case. Cox (1972) found for photolysis of SO_2 at high dilution in air,

$\Phi_{SO_3} \leqslant 3\times10^{-4}$, which is consistent with about 1% of the triplet SO_2+O_2 quenching encounters leading to chemical reaction to form SO_3.

The total rate of production of $SO_2(^3B_1)$ molecules in the atmosphere can be computed from the rate of absorption of sunlight by SO_2 in both the 'forbidden' and 'allowed' bands and the fraction of singlet SO_2 molecules which undergo intersystem crossing, approximately 10% for atmospheric conditions (Sidebottom *et al.* 1972). The relative quenching pathways for $SO_2(^3B_1)$ can also be computed from the available data and this allows an estimate of the total rate of reaction plus quenching for the $SO_2(^3B_1)+O_2$ interaction. For a solar zenith angle of 40° and 50% relative humidity the result is $2.6\pm0.8\times10^{-2}$ h^{-1}. If only 1% of this reaction flux leads to SO_3 formation, the effective SO_2 photooxidation rate is 0.026% h^{-1}. As will be shown below, this is much slower than the oxidation rate resulting from the other homogeneous processes considered.

(*b*) *Oxidation of* SO_2 *by photochemically generated free radicals*

It can now be considered well established that the atmospheric oxidation of hydrocarbons and related substances proceeds by a photochemically initiated free radical chain process. The process occurs throughout the natural troposphere during daytime and, in polluted air, when the concentrations of trace components are large, it gives rise to the phenomenon of photochemical smog. The chain process is exemplified by the reactions involved in the oxidation of atmospheric methane to formaldehyde:

$$CH_4+OH \longrightarrow H_2O+CH_3,$$

$$CH_3+O_2 \xrightarrow{(M)} CH_3O_2,$$

$$CH_3O_2+NO \longrightarrow CH_3O+NO_2,$$

$$CH_3O+O_2 \longrightarrow HCHO+HO_2,$$

$$HO_2+NO \longrightarrow NO_2+OH.$$

The chain-carrying radicals are OH, HO_2 and their organic analogues RO and RO_2. In general, R can be alkyl, acyl or any other carbon containing fragment. The nitrogen oxides are involved through their ability to convert RO_2 (or HO_2) to RO (or OH) in the chain sequence and also through their rôle as a source of ozone, via NO_2 photolysis:

$$NO_2+h\nu(\lambda \leqslant 398\text{ nm}) \longrightarrow NO+O(^3P_1),$$

$$O(^3P_1)+O_2 \xrightarrow{(M)} O_3.$$

Ozone in turn is important as a source of OH radicals through its photodissociation to yield electronically excited oxygen atoms which react with water vapour:

$$O_3+h\nu\ (\lambda \leqslant 310\text{ nm}) = O(^1D_2)+O_2,$$

$$O(^1D_2)+H_2O = 2OH.$$

Since the free radical reactions are relatively rapid a 'steady-state' concentration of atoms and radicals is achieved in the sunlight irradiated atmosphere. Any trace gas, e.g. SO_2, which can react with the free radicals, will be removed at a rate given by

$$-d[SO_2]/dt = k_r[SO_2]\ [X],$$

where k_r is the effective bimolecular rate constant for reaction between radical X and SO_2, at the appropriate temperature and pressure. Provided the fraction of radicals reacting with SO_2 is small, the radical 'steady state' will not be affected by this process. If [X] can be evaluated by computer modelling of the major atmospheric reactions or, preferably, by direct measurements, the removal rate of SO_2 can be determined from a knowledge of k_r. Recent critical appraisals of the available literature (Eggleton & Cox 1978; Calvert & McQuigg 1975; Calvert *et al.* 1978) show that, of the possible reactions of SO_2 with radical type species, reaction with OH is probably dominant, with significant contributions due to reactions with HO_2 and CH_3O_2. Acyl peroxy and higher alkylperoxy radicals do not appear to react rapidly with SO_2 at all. We will consider here, therefore, only the relevant reactions with the reactive species:

$$OH + SO_2 \xrightarrow{(M)} HOSO_2; \tag{1}$$

$$HO_2 + SO_2 \longrightarrow OH + SO_3; \tag{2}$$

$$CH_3O_2 + SO_2 \longrightarrow CH_3O + SO_3. \tag{3}$$

The peroxy radical reactions (2) and (3) are relatively straightforward O-atom transfer reactions yielding SO_3. In the atmosphere this product will hydrolyse extremely rapidly to form sulphuric acid aerosol (Goodeve, Eastman & Dooley 1934; Castleman *et al.* 1975). The rate constant k_2 has been measured (Payne, Stief & Davis 1973) by using a competitive kinetic technique and is reasonably well defined; $k_2 = 9 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ at 298 K, relative to the current consensus value for the reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, $k = 3.5 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. Reaction (3) has been investigated by observation of the decay of CH_3O_2 in the presence of SO_2 by the technique of flash photolysis with kinetic spectroscopy. Unfortunately, aerosol formation from the reaction products made accurate optical measurements difficult but a preliminary value of $k_3 \approx 5 \times 10^{-15}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ has been reported (Whitbeck, Bottenheim, Levine & Calvert 1976).

The reaction of OH radicals with SO_2 is an addition reaction and knowledge of the fate of the $HOSO_2$ free radical formed initially is important, as well as the overall rate constant and its pressure dependence. Some of the first investigations of this reaction at room temperature and atmospheric pressure were made by using the photolysis of nitrous acid as a source of OH radicals (Cox 1975). This study provided an estimate of k_1 relative to the rate constant for the reaction of OH with CO, and also showed that in moist air the $HOSO_2$ radical reacts to form ultimately a sulphur-bearing aerosol, similar in character to model sulphuric acid aerosols. In the presence of relatively high NO_2 concentrations, the aerosol also contained an NO_x component which hydrolysed in solution to yield NO_3^- in equimolar proportion to H_2SO_4 (Cox & Derwent 1976). Another observation of significance in this system was that oxidation of NO to NO_2 occurred in the reactions after the addition of OH to SO_2. These results provide good evidence for the occurrence of the following exothermic reactions which have been postulated by others (e.g. Calvert & McQuigg 1975) on thermochemical grounds:

$$HOSO_2 + O_2 = HOSO_2O_2;$$

$$HOSO_2O_2 + NO = HOSO_2O + NO_2;$$

$$HOSO_2O + NO_2 = HOSO_2ONO_2 \text{ (nitrylsulphuric acid).}$$

There is at present, however, no satisfactory mechanism for the conversion of the $HOSO_2O$ radical to SO_3 or H_2SO_4 under all the experimental conditions.

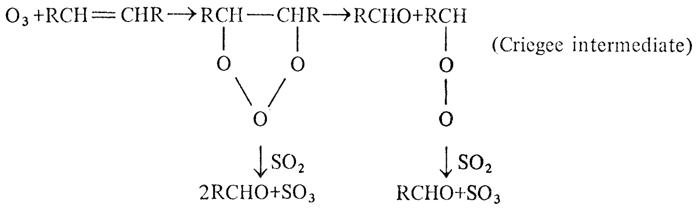
Because of the mechanistic uncertainties in the above system, k_1 could only be evaluated with limited accuracy; based on the 'high pressure' value of 3×10^{-13} cm^3 molecule^{-1} s^{-1} for the rate constant for the reaction of OH with CO, (Cox, Derwent & Holt 1976), $k_1 \approx 5 \times 10^{-13}$ with an uncertainty of $\pm 50\,\%$ (Cox & Derwent 1976). Castleman & Tang (1977), who also used a competitive technique involving the OH + CO reaction, have demonstrated the expected pressure dependence of the association reaction (1) over the range 20–1000 Torr.† At 760 Torr N_2, k_1 was 1.4×10^{-12} (again relative to the 'high pressure' OH + CO rate constant). Direct measurements of k_1 by the molecular resonance fluoresence techniques to follow OH radical decay in the presence of SO_2 (Davis & Klauber 1975; Atkinson, Perry & Pitts 1976), give values of k_1 near to 8×10^{-13} cm^3 molecule^{-1} s^{-1} for pressure of N_2 near 760 Torr. Despite the experimental difficulties in this type of measurement in the presence of SO_2, these must be considered the most reliable values at present. It should be emphasized, however, that k_1 cannot be considered as well defined as the rate constants for the reactions of OH with other simple molecules of atmospheric interest.

(*c*) *Oxidation of* SO_2 *by reactive intermediates in ozone–olefin reactions*

At the low concentrations of SO_2 and ozone present in the atmosphere, the exothermic reaction

$$SO_2 + O_3 = SO_3 + O_2; \quad \Delta H = -241.6 \text{ kJ mol}^{-1}$$

is, surprisingly, negligibly slow. However, in the presence of alkenes, which react relatively rapidly with ozone, appreciable oxidation of SO_2 occurs in the dark (Cox & Penkett 1971). The kinetics of SO_2 oxidation were well described by a mechanism involving reaction of SO_2 with a reactive intermediate, which was competitively removed by an undefined, pseudo first order process (Cox & Penkett 1972). It was suggested that the oxidizing species might be the biradical or 'zwitterionic' Criegee intermediate, $RC^{+}HOO^{-}$, or possibly the original 'molozonide' product of the addition of an ozone molecule to the olefinic double bond:



The observed increase in aldehyde products from the reaction in the presence of SO_2 provides support for the O atom transfer reactions suggested, which could occur in competition with fragmentation processes giving other products.

The mechanism of the gas phase reaction of ozone with alkenes is exceedingly complex and although recent work has provided more information on the kinetics of the reaction and on the products which are formed, a satisfactory mechanistic description of all of the experimental observations has not been achieved to date (see, for example, O'Niel & Blumstein 1973). The ozone–alkene–SO_2 system has also been investigated by other workers (McNelis 1974; Schulten & Shurath 1975). The results substantially confirm the original findings of Cox & Penkett but do not allow any firm conclusion regarding the nature of the oxidizing species. Irrespective of the nature of this species, the laboratory results giving the SO_2 oxidation rate as a function

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† 1 Torr ≈ 133.3 Pa.

of reactant concentrations can be used as a basis for extrapolation to the atmosphere. These rates together with those estimated for the other homogeneous oxidation processes are summarized in the following section.

TABLE 1. RATES OF HOMOGENEOUS OXIDATION OF SO_2 IN THE ATMOSPHERE

reaction	rate constant cm^3 $molecule^{-1}$ s^{-1}	concentration of (active species) molecules cm^{-3}	100 × oxidation rate of SO_2 h^{-1}
(*a*) direct photooxidation			
$SO_2(^3B_1) + O_2 \rightarrow SO_3 + O(^3P)$	*ca.* 1.6×10^{-15}†	2.3 ($SO_2[^3B_1]$)‡	0.026
(*b*) free radical oxidation			
$OH + SO_2 \rightarrow HOSO_2$	8×10^{-13}	7×10^6§ (OH)	2.0
		(7×10^5)¶	(0.2)
$HO_2 + SO_2 \rightarrow OH + SO_3$	9×10^{-16}	2×10^9§ (HO_2)	0.6
		(1×10^8)¶	(0.03)
$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$	5×10^{-15}	2×10^9§ (CH_3O_2)	1.7
		(1.5×10^7)¶	(0.03)
(*c*) ozone–alkene reaction			
$RCHOO + SO_2 \rightarrow RCHO + SO_3$	—	2.5×10^{12} [O_3]	0.07‖
		2.5×10^{11} [C_3H_6]	

† 0.4% of total quenching of $SO_2[^3B_1]$ at 50% relative humidity.
‡ Solar zenith angle = 40°; [SO_2] = 10 parts/10^9.
§ Typical maximum daytime OH and RO_2 concentrations computed for 50° N latitude, 1 July; see text.
‖ Extrapolated from laboratory measurements of O_3–propene–SO_2 system.
¶ Mean summertime concentrations in the background troposphere at 50° N latitude.

RATE OF HOMOGENEOUS OXIDATION OF SO_2 IN THE ATMOSPHERE

Table 1 shows a summary of the estimated rates of oxidation of SO_2 in the atmosphere based on the experimental studies discussed above for the three types of homogeneous oxidation mechanism. It will be seen that the direct photooxidation is very much slower than the free radical processes and can therefore be neglected in determining overall sulphate formation rates. The concentrations of free radical species OH, HO_2 and CH_3O_2 used to calculate the respective SO_2 oxidation rates are derived from a photochemical model of an urban air-shed, 1 km in height, irradiated by sunlight of intensity corresponding to 12 noon on July 1 at 50° N latitude (R. G. Derwent & R. A. Cox, unpublished work). The concentration of CO, NO_x, SO_2 and C_1–C_5 hydrocarbons in this model were typical average values taken from pollutant measurements in London and should be fairly representative for most European cities. The SO_2 oxidation rates calculated on this basis indicate almost equal contributions from reaction with OH and peroxymethyl radicals, with a lesser contribution from HO_2. By taking propene as a representative alkene in urban air, the contribution of the ozone–alkene–SO_2 oxidation process is also small compared to the free radical processes. However, in the presence of more reactive alkenes, which would of course only have a short atmospheric lifetime, faster SO_2 oxidation would occur, e.g. 1.4 % h^{-1} with 10 parts/10^9† as Butene 2 + 100 parts $O_3/10^9$. Thus this process is almost certainly significant in some circumstances, in particular since it can operate during night-time and wintertime when photochemical processes are either absent or occur at much reduced intensity.

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† 1 part/10^9 = 2.45×10^{10} molecules cm^{-3} at 298 K, 760 Torr.

The total SO_2 oxidation rate during the midday hours in summer is estimated to be 4 % h^{-1}, on the basis of the results in table 1. From typical urban SO_2 concentrations at this season, 50 parts/10^9 (Department of Trade and Industry 1972), the corresponding rate of sulphuric acid formation is 8.4 $\mu g\ m^{-3}\ h^{-1}$. Thus photochemical oxidation is expected to generate significant amounts of sulphuric acid in urban air, with important consequences for health and visibility.

In order to determine a realistic lifetime of SO_2 in the atmosphere with respect to homogeneous oxidation, oxidation rates in unpolluted air are also required, since the local removal processes are not rapid enough to prevent transport of SO_2 into the main tropospheric air movements. Background tropospheric concentrations of free radicals can also be computed using photochemical models.

Derwent & Curtis (1977) have recently reported a two-dimensional tropospheric model from which diurnally and seasonally averaged OH, HO_2 and CH_3O_2 concentrations can be derived. The 24 h mean concentrations of these radicals obtained from the model and the corresponding oxidation rates of SO_2, for summertime conditions at 50° N, are shown in parentheses in table 1. The total oxidation rate of $0.26 \times 10^{-2}\ h^{-1}$ corresponds to an SO_2 lifetime with respect to homogeneous oxidation of 16 days. This is rather long compared with the estimated life-time of SO_2 in the mid-latitude troposphere (3–6 days), owing to the other removal processes, dry deposition and oxidation and removal by precipitation elements. The latter would be even more important in the winter months when photochemical reactions become very slow because of the much reduced insolation at midlatitudes. It is therefore concluded that photochemical oxidation plays a minor but significant rôle in the overall oxidation of SO_2 in the natural unpolluted troposphere at mid-latitudes. In polluted urban plumes, and particularly during the summer months, quite rapid homogeneous photochemically initiated oxidation of SO_2 is predicted to occur.

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Discussion

M. F. R. MULCAHY (*Atmospheric Chemistry Section, C.S.I.R.O. Division of Process Technology, P.O. Box* 136, *North Ryde, N.S.W., Australia* 2113). Dr Cox quoted measurements of the rate of atmospheric oxidation of sulphur dioxide made under various conditions and has given his opinion as to what basically is likely to be the reaction mechanism in air containing other urban pollutants. I should like to mention some results of a study of the kinetics of oxidation in a 'remote' atmosphere which is being carried out by my colleagues Mr D. J. Williams and Mr D. B. Roberts. The investigation is conducted over Northern Australia where, near the town of Mt Isa (lat. 21° S, population 25000), the two adjacent chimneys of a metallurgical smelter constitute a strong point source of SO_2. Apart from a small coal-burning power station, there is no other industrial activity at Mt Isa. When the meteorology is favourable, a well-defined plume from the smelter flows NW over several hundred kilometres of almost uninhabited country. Thus the sulphur dioxide is in contact with air as little contaminated by other sources of pollution as perhaps is likely to be found for such an investigation anywhere.

So far, Mr Williams has studied the rate of disappearance of SO_2 from the plume by two methods. The first method makes use of a Cospec correlation spectrometer to determine the total flux of SO_2, and the second uses a photometric instrument to determine the concentration ratio $[SO_2]$:[total S] in the plume. Both instruments are carried (separately) in an aircraft, and measurements have been made successfully at various distances up to about 250 km from the source.

The total flux method has yielded an upper limit of $1\,\%\,h^{-1}$ for the total rate of loss of SO_2 from the plume; that is, by oxidation and ground absorption combined.

More precise results have been obtained by the ratio method. They can be summarized as follows. There is a strong diurnal variation in the rate of loss of SO_2: 8–10 % of the SO_2 disappears from the plume during one period of daylight (that is, 10 h) but no loss can be detected at night. The rate of deposition of SO_2 to the ground has been measured by special experiments made on location. After subtracting this from the total loss from the plume, Mr Williams estimates the rate of atmospheric oxidation of SO_2 under the prevailing conditions to be $0.6\,\%\,h^{-1}$ averaged over the hours of daylight or $0.25\,\%\,h^{-1}$ averaged over 24 h.

I believe this to be the first unequivocal experimental demonstration that the oxidation of SO_2 in the free atmosphere is indeed principally photochemical.