Oxidation of sulphur dioxide in artificial fogs by ozone

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ABSTRACT

The rate of oxidation of sulphur dioxide by ozone at atmospheric concentrations has been measured in fogs which were formed in a specially constructed steel chamber. At 10°C the rate was proportional to the first power of the ozone concentration, and its absolute value was in agreement with that calculated from data obtained on the reaction between ozone and bisulphite ions in water using the stopped-flow method (Penkett, S. A., *Nature Phys. Sci. 240*, 105, 1972). The reaction at an ozone concentration of 0.05 p.p.m. was substantially faster than the reaction of SO_2 with air alone in the fogs and it is shown that the ozone reaction is sufficiently rapid to account for most observations of sulphate levels found in cloud and rain water.

Introduction

Oxidation of sulphur dioxide in cloud and fog droplets is an important route for the production of sulphate aerosols in the atmosphere (Junge, 1963). It also contributes to the washout of sulphur dioxide by rain (Beilke & Georgii, 1968). Sulphur dioxide in water can be oxidised directly by oxygen (Fuller & Crist, 1941). This reaction is promoted by the presence of ammonia (Van den Heuvel & Mason, 1963) since it depends on the presence of sulphite ions which are suppressed in solutions of low pH. At lower pH values oxidation by oxygen also occurs but only in the presence of soluble catalysts such as iron and manganese salts (Junge & Ryan, 1958) and it is reasonable to assume that this represents oxidation of bisulphite ions, which predominate in sulphurous acid solutions between pH 2 and 7. This latter mechanism is only likely to occur in a highly polluted environment however where concentrations of catalytic ions are high.

A mechanism which has not been considered so far is the reaction of ozone with dissolved sulphur dioxide. This reaction, with SO_2 in the form of bisulphite ions, has recently been investigated using the stopped-flow technique (Penkett, 1972). It was found that the rate was first order with respect to both reactants and the rate constant was measured at 10°C. Using the data it was predicted that the rate would be substantially larger than oxidation of sulphite ions by oxygen in the conditions prevailing in the atmosphere. This paper reports results obtained in a fog chamber experiment designed to simulate atmospheric conditions as closely as possible and shows that the ozone droplet mechanism is of considerable importance.

Experimental

A diagram of the apparatus is shown in Fig. 1. The experiments were performed inside a double walled chamber made of stainless steel; its volume was about 8 m^3. The temperature of the walls of the chamber was maintained at 10°C ± 0.1°C by air circulating between the inner and outer walls. One half of the floor of the chamber was covered by a shallow water tank, thermostatically maintained at 23°C. At the beginning of the experiment the chamber was flushed through with ambient air and then sealed. The air soon became saturated and a film of water condensed on the walls. A slow circulation of air in the chamber set in, due to the presence of the warm water tank, and mixing of warm and cool saturated air above the tank caused a supersaturation of up to 5%, so that fog began to form. The circulation spread the fog throughout the volume of the chamber and an equi-

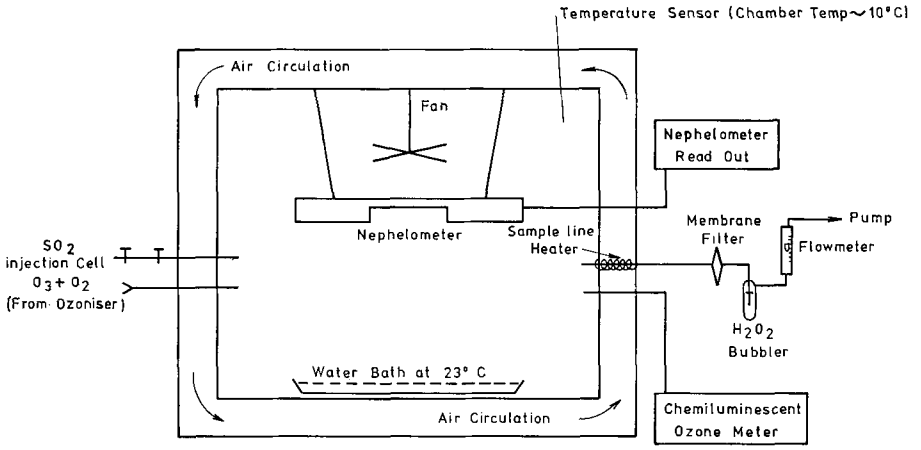

Fig. 1. Diagram of Fog chamber and associated apparatus.

librium situation was reached within 30 minutes. The visibility was measured using a nephelometer (Garland & Rae, 1970) which was suspended from the top of the chamber and gave a reading every 20 seconds. This was used to estimate the liquid water content of the fog.

The levels of trace impurities in the air were not established but in view of the rapid decay of soluble gaseous species in the chamber it is unlikely that much would be present at the time of the experiment. Ozone was introduced into the chamber from an ozoniser and was allowed to remain for a period prior to the injection of sulphur dioxide. This would ensure that gases such as olefins which would react with ozone to oxidise SO_2 (Cox & Penkett, 1972*a*) are consumed before the experiment commenced. The ozone concentration was monitored continuously using a chemiluminescent detector based on the ozone-ethylene reaction (Atkins et al., 1972). Air was withdrawn from the chamber at the rate of 1 litre/min and passed through the detector. The minimum detectable ozone concentration was about 0.001 p.p.m. and most experiments were performed in the range 0.05 to 0.5 p.p.m. which is well within the range of the instrument.

When the visibility had stabilised at about 150 metres, radioactive sulphur dioxide ($^{35}SO_2$) was injected into the chamber by blowing a small quantity of clean air through the containing glass cell. The fan was switched on for 15 seconds to mix the SO_2 thoroughly; this produced no detectable disturbance in the fog as measured by the nephelometer. The SO_2 concentration and the level of oxidation product were determined at various intervals by taking samples of the chamber air. This was passed through the glass sampling system shown in the figure at 1 litre/min for 2 minutes. The product, which was assumed to be sulphuric acid, was separated from the gaseous SO_2 on a membrane filter (type A.A. Millepore); this had previously been exposed to high concentrations of inactive SO_2 to prevent further gaseous uptake. The $^{35}SO_2$ was collected in a bubbler containing 1 volume hydrogen peroxide solution. It was essential to warm the sampling lines to prevent uptake of SO_2 on the inner surfaces (Cox & Penkett, 1972*b*). A small 20 watt heater was used for this purpose and this probably evaporated the fog droplets before the air sample reached the filter. The ^{35}S activity in both bubblers and filters was assayed by liquid scintillation counting techniques (Cox & Penkett, 1970) and this was related to the amount of sulphur collected.

Results and discussion

Fig. 2 shows the formation of sulphuric acid at 10°C in a typical fog with a visibility of 170 metres. The initial concentrations of ozone and sulphur dioxide were 0.13 and 0.1 p.pm. respectively. About 1.4% of the original SO_2 (calculated by extrapolation of the SO_2 decay line to zero time) is oxidised within 5 minutes,

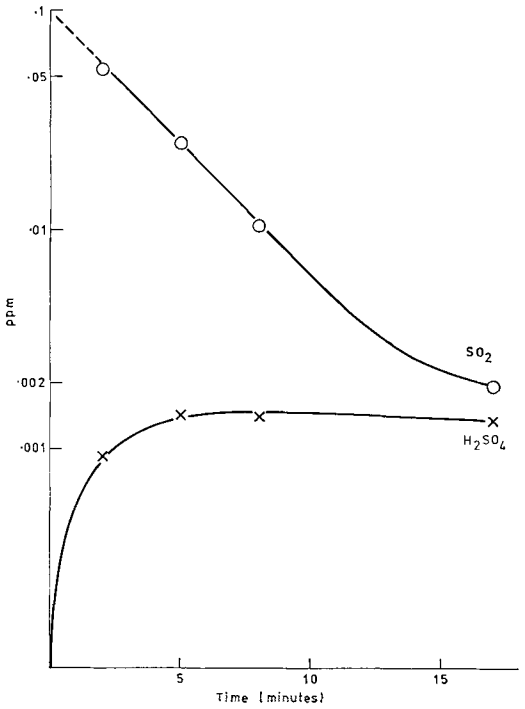

Fig. 2. Formation of sulphuric acid in the fog, and decay of SO_2 on the chamber walls in a typical experiment at 10°C with an initial ozone concentration of 0.13 p.p.m.

and thereafter no further oxidation was observed. The sulphur dioxide concentration decays rapidly due to irreversible uptake on the walls of the chamber. The decay is first order with a half-life of 2 minutes, although it is possible to observe deviation from linearity over the last 5%. (The half-life for SO_2 is similar in experiments performed in the absence of ozone.) Fig. 3 shows the effect of SO_2 injection on the decay of ozone in the chamber during the same experiment. A marked discontinuity is observed at this time corresponding to the reaction of ozone with SO_2 in the water film on the surrounding walls. This same phenomenon probably occurs with SO_2 but it is not observable using the present apparatus and accordingly no correction to the initial SO_2 concentration is applied. The decay of ozone is also first order with a half-life of 12 minutes in the absence of much SO_2.

The visibility observed by the nephelometer remains approximately constant during the course of the experiment (Fig. 4) and this is taken to indicate that the water content also remains constant. Unfortunately no measurements of the droplet size distribution could be made during these experiments but examination of the fog by observing a beam of light projected through the chamber showed numerous droplets large enough to be individually visible, as are seen in a natural fog. These droplets must have been several microns in diameter and it is concluded that at the observed visibility the liquid water content would have been approximately 0.1 gm/m^3 (Garland, 1971).

In Fig. 5 sulphuric acid formation in two experiments with initial ozone concentrations 0.13 p.p.m. and 0.056 p.p.m. is compared with an experiment in which no ozone was added (O_3 less than 0.001 p.p.m.). In the cases where ozone is present the build up of acid on the filters is seen to follow a smooth curve. The initial rate and the total acid product increases with increasing ozone concentration. The gas phase reaction between ozone and SO_2 will not account for these observations since no oxidation was observed in previous experiments at higher concentrations of reactants (Cox & Penkett, 1972*a*). The rapid decline in rate could be due to the disappearance of SO_2 but more

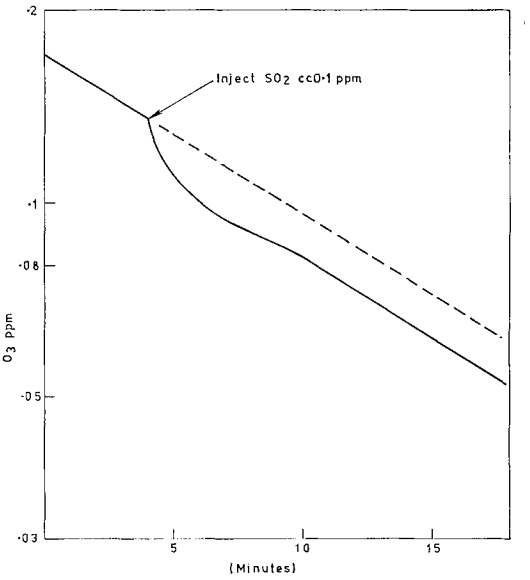

Fig. 3. Effect of SO_2 injection on ozone decay on the chamber walls in the same experiment.

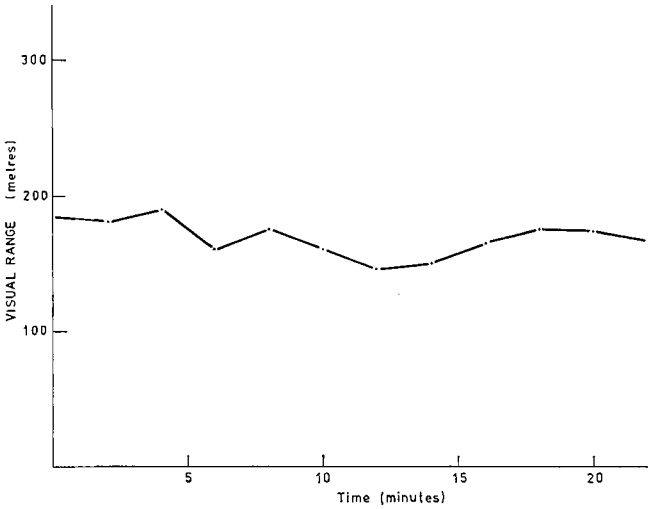

Fig. 4. Visual range in the fog during the course of the same experiment.

likely is due to acid formation which reduces the total solubility of sulphur dioxide in the fog droplets due to suppression of hydrolysis. No samples of the fog water were taken so the nature of the product remains uncertain, however, if it were sulphuric acid then the pH of the water would be about 3. The fog system is not stable enough to allow a determination of the slower rates, which should occur at this pH value. When no ozone is present the filters also intercept some ^{35}S activity which is taken to be due to oxidation of SO_2 by oxygen in the fog droplets. The extent of oxidation was very similar in several experiments performed in the absence of ozone and this information was used as an indication of the experimental error involved.

It is important to establish whether the nature and rate of reaction observed in these experiments agree with observations made using

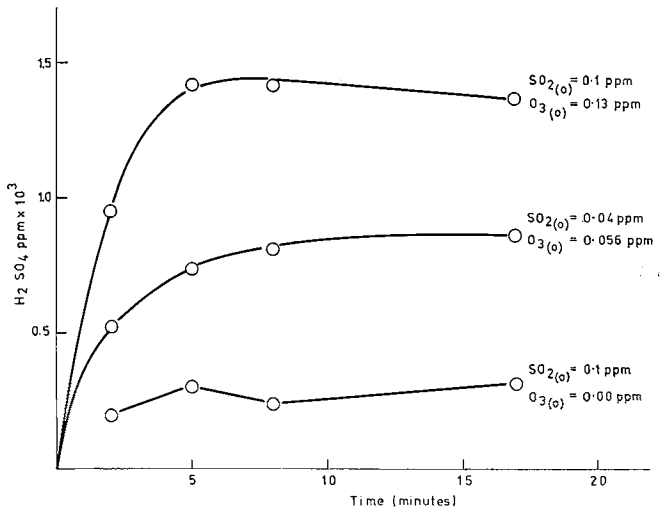

Fig. 5. Formation of sulphuric acid in different experiments with the initial ozone concentration varying from 0.0 to 0.13 p.p.m.

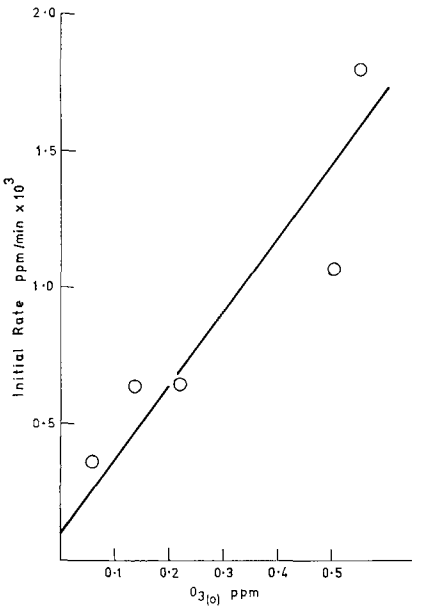

Fig. 6. Variation of initial rate of acid formation with initial ozone concentration at 10°C for experiments with similar initial SO_2 concentrations and for fogs with similar visual ranges.

the stopped-flow apparatus on the reaction between ozone and bisulphite ions in solution (Penkett, 1972). In particular the reaction should be first order with respect to both reactants. In Fig. 6 the initial rates of acid formation are plotted against the initial ozone concentration for experiments in which the fog water level (indicated by the visual range) was approximately constant and the initial SO_2 concentration varied between 0.04 to 0.1 p.p.m. Within the limits of error imposed by the nature of the experiment a linear relationship is observed. Since gas phase diffusion of ozone to the droplets is much too rapid to be the controlling process (Chamberlain, 1960) this demonstrates that the process is controlled chemically by a reaction which is first order with respect to ozone. The intercept on the rate axis at zero ozone concentration is taken to indicate the rate of the reaction with oxygen in the same conditions. The situation with regard to SO_2 is more complex since the bisulphite ion concentration in the droplets will not be a simple linear function of the SO_2 gas concentration. The existing data suggest the variation of initial rate with initial SO_2 concentration is small but this will need further investigation.

The observed rate in the fog droplets can be compared with that predicted from the earlier kinetic work (Penkett, 1972) assuming a chemical rate process. A calculated value of $R(O_3)$, the rate of oxidation by ozone, was produced at pH's from 4 to 7 using the expression shown in eq. (1). This incorporates the rate constant for the ozone oxidation of bisulphite ions at 10°C found in the kinetic work and the concentration of ozone in water in equilibrium with 0.05 p.p.m. of the gas at the same temperature

$$R(O_3) = 3.76 \times 10^{-4} [HSO_3^-] \quad (1)$$

The units are moles/litre/sec and they are applicable to oxidation in bulk liquid water. In Table 1 values of $R(O_3)$ are shown in units of more relevance to the experiment. The calculated rate at pH 6 ($R(O_3)$) and the observed rate from the present experiments ($R(O_3)_0$ obs.) are almost identical with a liquid water content of 0.1 gm/m³ in the fog.

For comparison $R(O_2)$, the rate of oxidation of SO_2 in the fog by oxygen in the absence of catalytic materials, has been calculated assuming the same water content. McKay's (McKay, 1971) modification of Fuller & Crist's (1941) rate equation was used (eq. (2)),

$$R(O_2) = (4.18 \times 10^{-4} + 1.77(H^+)^{\frac{1}{2}})[SO_3^{--}] \quad (2)$$

The units are again moles/litre/sec. McKay's values for the constants in the expression have been modified to take account of Schroeter's

Table 1. *Oxidation rates of 0.1 p.p.m. SO_2 in fogwater[a] by 0.05 p.p.m. ozone at 10°C*

pH	$R(O_2)$	$R(O_3)$ (ppm/min)[c]	$R(O_3)_0$ obs.[b]
4	7.3×10^{-8}	2.1×10^{-6}	
5	2.5×10^{-7}	2.1×10^{-5}	
6	9.1×10^{-5}	2.1×10^{-4}	$2.4 \times 10^{-4} \pm 1.0 \times 10^{-4}$
7	4.2×10^{-3}	2.1×10^{-3}	

[a] In a fog containing 0.1 ml of liquid water per m³.
[b] The observed value of the initial rate was taken from the data shown in Fig. 5, and the error is estimated from data from a series of experiments performed in the absence of ozone. The rate of oxidation by oxygen, indicated by these experiments, has been subtracted.
[c] Under these conditions a rate of 1×10^{-4} ppm/min is equivalent to the formation of 4.2 μg of sulphate per minute per ml of water.

finding (Schroeter, 1963) that the rate constant for the reaction in air was 5 times smaller than in oxygen and they have been corrected to 10°C using a value for the activation energy of 22 k.cals/mole. This value was chosen to fit the data assuming that the intercept on the initial rate axis of figure 6 at zero ozone concentration reflects oxidation of SO_2 by oxygen. It is only slightly higher than the value quoted by Barron and O'Hearn (Barron & O'Hearn, 1966) (18.3 k.cals/mole) for the copper catalysed oxidation of sulphite ions.

$R(O_2)$ at pH 6 is seen to be less than half the value of $R(O_3)$ and as the pH decreases $R(O_2)$ becomes insignificant by comparison with $R(O_3)$. At pH 5, which is a typical value for unpolluted cloud water samples (Petrenchuk & Selezneva, 1970), the calculated ratio $R(O_3)/R(O_2)$ exceeds 80 and it is therefore considered that oxidation by ozone is the more important process in the atmosphere. The calculated rates in Table 1 when expressed in terms of a growth of sulphate concentration in the water drops are of a sufficient magnitude to account for most observations on the sulphate concentration of cloud and rainwater that have been taken.

In general the gaseous concentration of ozone will be greatly in excess of SO_2 so it is not expected that consumption of ozone by other reactions will impede the oxidation of SO_2. Also the concentration of SO_2 in cloud water will be several orders of magnitude higher than most other trace contaminants which are known to react with ozone. The exception here may be NO_2 dissolved in solution. The rate of oxidation of nitrite ions by ozone in water has also been studied by the stopped flow method (Penkett, 1972) and it was shown that the reaction was second order overall with a rate constant slightly less than the value found for the bisulphite reaction. The formation of nitrate by this process may thus occur in parallel with sulphate formation.

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ОКИСЛЕНИЕ ДВУОКИСИ СЕРЫ ОЗОНОМ В ИСКУССТВЕННЫХ ТУМАНАХ

Измерялась скорость окисления двуокиси серы озоном при атмосферных концентрациях в искусственных туманах, образуемых в специально сконструированной стальной камере. При 10°C скорость была пропорциональна первой степени концентрации озона и ее абсолютная величина была в согласии с вычисленной из данных, полученных из реакции между озоном и ионами бисульфита в воде при использовании метода остановленного течения (Penkett S. A., 1972). Реакция при концентрациях озона $5 \cdot 10^{-8}$ была существенно быстрее реакции SO_2 только с воздухом в туманах и показано, что реакция с озоном достаточно быстра, чтобы объяснить большинство наблюдений уровня сульфатов, найденных в облаках и дождевой воде.