Particle formation from homogeneous reactions of sulphur dioxide and nitrogen dioxide

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ABSTRACT

Some recent laboratory results relating to the conversion of gaseous sulphur dioxide and nitrogen dioxide into particulate material and the implication of these results on the atmospheric chemistry of these gases is discussed. Homogeneous oxidation of SO_2 by photochemically initiated reactions may occur at a rate ranging from 0.1 % hr^{-1} in clean air to a 0–10 % hr^{-1} in urban air. The oxidation rate of NO_2 is more raped (up to 25% hr^{-1}) but may be effectively less due to the reversible nature of the reactions. Theoretical and experimental results suggest that the rate of formation of H_2SO_4 in urban air (from SO_2) is sufficient for heteromolecular nucleation to form aqueous sulphuric acid aerosols but in background areas condensation on the existing aerosol is the main fate of the SO_2 oxidation products. Sufficient gaseous HNO_3 for nucleation is unlikely to be produced from NO_2 in the atmosphere and condensation on aerosol particles, particularly hygroscopic particles, is an important removal mechanism for HNO_3. A large effect of relative humidity on the rate of the nucleation and condensation processes is demonstrated experimentally.

1. Introduction

The chemical transformation of gases into particles is an important factor in the life-cycles of traces gases in the atmosphere (Robinson & Robbins, 1968) and also in its influence on the size distribution of the atmospheric aerosol (Junge, 1963). The formation of particles when air containing small amounts of sulphur dioxide is irradiated with U.V. light is a well known phenomenon, although the factors which govern this process have only recently begun to be understood. Particle formation from atmospheric nitrogen dioxide is inferred from the presence of particulate nitrate in the atmosphere but no clear picture as to the nature of this gas-to-particle conversion has yet emerged.

The physico-chemical processes involved in gas-to-particle conversion are (*a*) chemical conversion of a gas to a product which is supersaturated with respect to the condensed phase in the atmospheric environment, and (*b*) nucleation and condensation of the product either homogeneously or with the aid of existing particles or ions.

In the first part of the present paper the homogeneous oxidation of the two trace gases SO_2 and NO_2 to the low volatility products H_2SO_4 and HNO_3 respectively is discussed. In the second part some experimental results relating to nucleation in the H_2SO_4–H_2O system are presented and the role of the SO_2 and NO_2 oxidation in the formation of new particles in the atmosphere is assessed.

2. Oxidation of sulphur dioxide and nitrogen dioxide

Photo-oxidation of SO_2

U.V. irradiation of SO_2 mixed with O_2 or air leads to the formation of sulphur trioxide which reacts rapidly with water vapour to give H_2SO_4 molecules. At high concentrations of SO_2 the photo-xidation proceeds by the reaction

$$^3SO_2 + SO_2 \rightarrow SO_3 + SO \qquad (1)$$

where $^3SO_2$ represents excited triplet SO_2 molecules which are formed following excitation of SO_2 within the first allowed absorption band (260–330 nm). $^3SO_2$ is also quenched by collisions with the other atmospheric gases and therefore at the SO_2 concentrations encountered

in the atmosphere ($\lesssim 10^{-1}$ ppm) reaction (1) is negligible. However, reaction of $^3SO_2$ with atmospheric O_2 may lead to oxidation:

$$^3SO_2 + O_2 \rightarrow SO_3 + O \qquad (2)$$

In this case the maximum photo-oxidation rate of atmospheric SO_2 computed from laboratory data for $^3SO_2$ quenching is 2.1% hr^{-1} (Sidebottom et al., 1972).

From quantum yield measurements for SO_3 formation in the photolysis of SO_2-air mixtures made in this laboratory, a photo-oxidation rate of 0.03 ± 0.018% hr^{-1} has been estimated for low concentrations of SO_2 at 23 ± 2°C (Cox, 1972). This value, which is considered to be an upper limit for atmospheric SO_2, is lower than previous experimental estimates of the rate (Bufalini, 1971); evidently reaction (2) is very inefficient if it occurs at all.

Oxidation of SO_2 in other photochemical systems

The photo-oxidation of SO_2 is known to be accelerated in the presence of oxides of nitrogen (NO_x) and olefinic hydrocarbons (Leighton, 1961). In laboratory experiments (Cox & Penkett, 1971) it has been shown that the addition of as little as 0.03 ppm NO_x and 0.10 ppm pentene-2 increased the rate of photochemical aerosol formation from SO_2 by a factor of at least 10 compared to pure air. Extrapolation of this data to the atmospheric conditions indicates an SO_2 photo-oxidation rate of 1–10% hr^{-1} in polluted atmospheres, under atmospheric conditions.

Further studies have shown that the enhanced oxidation is primarily due to a reaction involving ozone which is produced in the NO_x-hydrocarbon photo oxidation (Cox & Penkett, 1971, 1972). SO_2 does not react directly with ozone either in the dark or under irradiation. In the presence of ozone and unsaturated hydrocarbons, however, a rapid thermal oxidation of SO_2 to H_2SO_4 aerosol occurs. The olefin promotes the oxidation by its reaction with ozone, forming oxidising intermediates which react very rapidly with SO_2 to form H_2SO_4.

The nature of the oxidising intermediate is not known with certainty. It may be an ozone-olefin complex or zwitterion or, alternatively, a free radical formed by decomposition of the latter. A possible free radical intermediate is HO_2 which has recently been shown to react rapidly with SO_2 (Davis et al., 1973).

Table 1. *SO_2 oxidation rates*

	Conversion rate (% hr^{-1})		H_2SO_4 formation rate (ppb hr^{-1})	
	Urban[a]	Background[b]	Urban	Background
Direct photo-oxidation	2×10^{-2}	2×10^{-2}	0.02	0.0002
Photo-oxidation with NO_x and hydrocarbon	1 to 10	–	1–10	–
Thermal with ozone and olefins	1 to 10	~0.1	1–10	0.001

[a] $SO_2 = 10$ pphm. [b] $SO_2 = 1$ ppb.

Summary of homogeneous oxidation rates of SO_2

The oxidation rates of SO_2 estimated on the basis of the laboratory data are given in Table 1 for both urban and unpolluted air. The figure for thermal oxidation in unpolluted air was calculated for concentrations of ozone and olefin of 30 ppb and 5 ppb respectively. A similar result ($\simeq 0.1$% hr^{-1}) is obtained if the major homogeneous oxidation path in clean air is

$$SO_2 + HO_2 \rightarrow SO_3 + OH \qquad (3)$$

and the daytime HO_2 concentration of 5×10^{-8} molecules cm^{-3} calculated by (Levy, 1973) is used together with the value $k_3 = 3 \times 10^{-16}$ cm^3 $molecule^{-1}$ sec^{-1} (Davis et al., 1973).

Oxidation of atmospheric NO_2

Three processes have been considered as possible routes for the oxidation of NO_2 in the atmosphere. It will be noted that, unlike the oxidation of SO_2 to H_2SO_4, the processes leading to the formation of the oxyacids from the oxides of nitrogen are reversible and extrapolation of data to atmospheric conditions is difficult on account of this. The processes are:

(*a*) Reaction with water vapour according to the overall eq. (4)

$$^3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO \qquad (4)$$

The rate equation is complex (England, 1970) and takes the form

$$-\frac{d[NO_2]}{dt} = 2k_A[NO_2]^2[H_2O] - 2k_B[HNO_2][HNO_3]$$

The initial reaction rate (i.e. in the absence of the reverse reaction) is 0.02% hr^{-1} at 50% relative humidity (R.H.) for an NO_2 concentration of 40 ppb; the process is therefore rather slow at normal atmospheric concentrations.

(*b*) NO_2 undergoes a rapid reaction with OH radicals:

$$OH + NO_2 \rightarrow HNO_3 \qquad (5)$$

Using (Levy's, 1973) calculated value for the average daytime OH concentration (3×10^6 molecule cm^{-3}) and a recent estimate of k_5 at atmospheric pressure (Morley & Smith, 1972), ($k_5 = 1.2 \times 10^{-11}$ cm^3 $molecule^{-1}$ sec^{-1}), an oxidation rate of NO_2 (to HNO_3) of 13% hr^{-1} is obtained.

(*c*) NO_2 *is oxidised to* N_2O_5 *by ozone in a two* step process.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (6)$$

$$NO_3 + NO_2 \rightleftharpoons N_2O_5 \qquad (7)$$

Reaction (6) is rate determining and consistent values of the rate constant (at 25°C) have been determined independently at both high (Johnson & Yost, 1949) and low concentrations (Ford et al., 1957; Cox, unpublished results, $k_6 \simeq 3 \times 10^{-17}$ cm^3 $molecule^{-1}$ sec^{-1}) at normal atmospheric ozone concentrations the conversion rate of NO_2 is 18% hr^{-1} at 25°C and about half this value at 10°C.

It appears therefore that both processes (*b*) and (*c*) may be important oxidation paths for NO_2 in the lower troposphere. Process (*b*) is restricted to daylight hours whilst (*c*) may also occur at night. The latter reaction has generally been assumed to go to completion because, although the reaction forming N_2O_5 is reversible (N_2O_5 dissociates to NO_2 and NO_3 with a half life of 3 sec at 25°C), N_2O_5 was believed to react rapidly in the gas phase with water to produce HNO_3

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (8)$$

Results obtained in this laboratory (Cox, unpublished results) and also by Johnson (1973) show, however, that N_2O_5 vapour at low concentration is apparently stable towards water vapour. It is, however, rapidly absorbed by surfaces. Thus when NO_2 (1.6 ppm) was allowed to react with ozone (0.7 ppm) most of the NO_2 oxidised disappeared from the gas phase under conditions where HNO_3 vapour, if formed, would have remained in the gas phase. Similar observations have been made by (Gay & Bufalini, 1971). When the reaction was carried out in the presence of an artificial aerosol (ammonium sulphate or ferric oxide), nitrate was collected on the aerosol particles. At high r.h. (70%), when the ammonium sulphate aerosol consisted of droplets, the incorporation of the NO_2 oxidation products in the aerosol was particularly efficient; most of the oxidised NO_2 appeared in the aerosol whilst the extent of absorption of NO_2 (in the absence of ozone) both on the dry and the wet aerosols was very small. Fig. 1 shows a summary of these results. The kinetics of ozone removal were not significantly affected by the presence of the aerosols indicating that the homogeneous reaction (6) was still operative and that a heterogeneous oxidation process was not being observed. No spontaneous aerosol formation was observed from low concentrations of NO_2 either alone or in the presence of ozone.

The consequences of these observations on the behaviour of NO_2 in a real atmosphere, i.e.

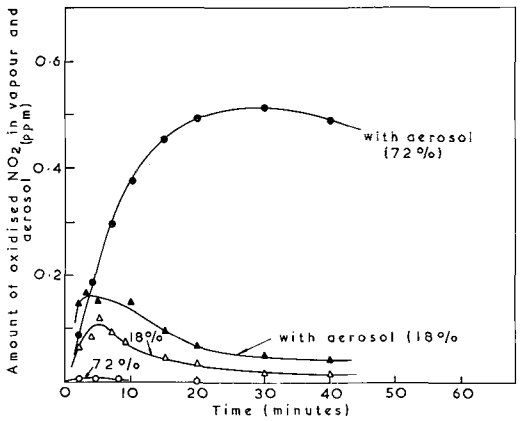

Fig. 1. Formation of nitrogen containing oxidation products (expressed as ppm NO_x) in the gas phase reaction between NO_2 (1.5 ppm) and ozone (0.7 ppm) at 24 ± 2°C. ○, no aerosol present; the NO_x concentrations refer to the total gas phase water soluble oxides and oxyacids of nitrogen *except* NO_2. ●, ammonium sulphate aerosol present: NO_x concentrations refer to the total oxides and oxyacids of nitrogen (except NO_2) in the gas phase and absorbed on the aerosol. Measurements made with a chemiluminescence NO_x analyser and by analysis of chemical samples for NO_3^- ion.

with natural ozone and a low specific surface area, are interesting. In this situation the concentrations of NO_2, NO_3 and N_2O_5 may approach a pseudoequilibrium. The loss mechanism for NO_x will be by attachement to particulate where conversion to nitrate occurs. Similarly the major loss mechanism for HNO_3 produced in reaction (5) is likely to be by attachment to particulate aerosols. Typical NO_2 concentrations in non-urban air are 5 ppb and in urban air a factor of 10 or more higher. Thus typical HNO_3 formation rates in the lower troposphere are 1 and 10 ppb hr^{-1} respectively for these localities.

3. Nucleation of the oxidation products of NO_2 and SO_2

Having established approximately the rates of chemical conversion of NO_2 and SO_2 to HNO_3 and H_2SO_4 respectively under atmospheric conditions, it is necessary to examine whether these rates are sufficient to supply enough of the oxidation products to nucleate homogeneously in the presence of water vapour to produce a droplet aerosol under the prevailing temperature and humidity.

Theoretical calculations have been made by Doyle (1961) for the nucleation of the two component system H_2SO_4–H_2O at 50% R.H. and, more recently by Kiang & Stauffer (1973) for the H_2SO_4–H_2O and HNO_3–H_2O systems. The latter authors adopted the title "heteromolecular nucleation" for the process and the following general conclusions result from these theoretical investigations:

(*a*) H_2SO_4 partial pressures of the order of 10^{-8}–10^{-10} torr (10^{-9} torr = 1.3×10^{-3} ppb) are predicted to give rise to heteromolecular nucleation at 50% R.H.

(*b*) The heteromolecular nucleation rate and also the subsequent heteromolecular condensation process governing the growth of the nucleation embryos depends greatly on the water vapour activity (i.e. relative humidity).

(*c*) Whereas H_2SO_4 seems a prime candidate for nucleation in atmospheric air, rather high vapour pressures are required for HNO_3 aerosol formation even at > 90% R.H.

Laboratory experiments

In the present experimental work, no aerosol was formed when 15 ppm HNO_3 was present in air at 75% R.H. Since this concentration is unlikely to be achieved by the reactions discussed it is unlikely that fresh aerosol particles can be produced directly from heteromolecular nucleation of HNO_3 under ordinary atmospheric conditions. Aerosols do, however, play an important role in the oxidation of atmospheric NO_2. Thus ammonium sulphate droplets at 70% R.H. absorbed up to twice their mass of nitrogen pentoxide (which presumably forms nitric acid in the aqueous phase). On the other hand, absorption on dry particles at lower humidities was rather inefficient. This large effect of relative humidity suggests that heteromolecular condensation is the controlling factor in determining the incorporation of the NO_2 oxidation products into aerosols.

In all experiments in which the homogeneous oxidation of SO_2 was examined in the laboratory, rapid self-nucleation of the sulphur containing products was observed. Experimental work has been carried out to investigate the effect of relative humidity on the production of aerosol particles in the photo oxidation of SO_2 and to estimate the concentration of H_2SO_4 necessary to achieve nucleation (Cox, 1973).

Fig. 2 shows the formation of aerosol both in terms of mass of H_2SO_4 and number of con-

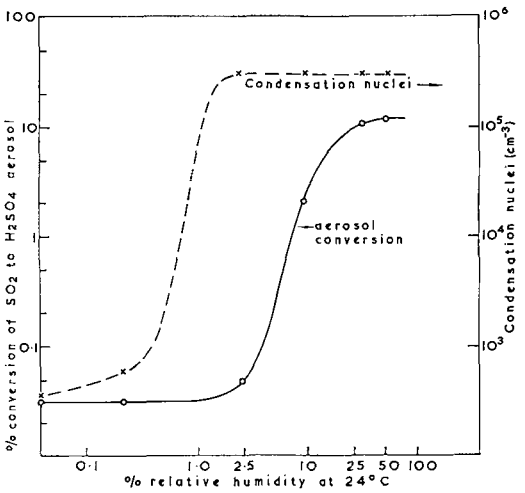

Fig. 2. Formation of sulphuric acid aerosol in the photolysis of SO_2 at 185 nm as a function of water vapour concentration. ○, percentage of SO_2 oxidised which appeared in the aerosol collected in the effluent from the flow reactor. ×, number of condensation nuclei (cm^{-3}) in the effluent stream.

densation nuclei as a function of water vapour concentration when SO_2 (11.5 ppm in N_2) was photolysed in a flow system. Short wavelength radiation (185 nm) was used and this gave approximately 10 % conversion of the SO_2 to SO_3 with reactor residence time of 12 sec (i.e. approximately 1 ppm of SO_3 was produced by photolysis). $^{35}SO_2$ was used to measure the mass of H_2SO_4 aerosol formed.

At low R.H. ($\lesssim 0.25$ %) very little aerosol formation occurred in terms of mass or number of particles. Above this R.H. the nuclei count increased very rapidly (at 2.5 % R.H. the condensation nucleus counter was saturated) but there was still very little aerosol in terms of mass of SO_2 converted. The mass of aerosol formed then increased with water vapour concentration up to approximately 50 % r.h. This experiment demonstrates clearly the critical effect of relative humidity both on the nucleation process and on the condensation process in the formation and growth of a stable H_2SO_4 aerosol.

An upper limit estimate of the concentration of H_2SO_4 required for nucleation was obtained in similar experiments using longer wavelength U.V. radiation (290–400 nm) when the photo oxidation rate of SO_2 is much slower. SO_2 (5–1 000 ppm) in high purity N_2 and O_2 (4:1) was passed through a 5 l spherical pyrex flow reactor irradiated with a medium pressure mercury arc. The residence time in the irradiated volume was 2.5 min and the average H_2SO_4 concentration in the reactor (assuming complete mixing and no losses) was estimated from the light intensity and the quantum yield (0.3×10^{-4} as discussed above) to be $10^{-5} \times SO_2$ ppm.

Fig. 3 shows the effect of SO_2 concentration on the number of condensation nuclei in the effluent stream at four different humidities. At the lower humidities the particle formation rate (as measured from the condensation nucleus count) increased with SO_2 concentration in the range 5–100 ppm. At the lowest humidity ($\lesssim 1$ %) the particle formation rate was slow (2×10^{-2} particles cm^{-3} in the outlet stream) at $SO_2 \simeq 5$ ppm whereas at 80 % R.H. the counter was saturated at the same SO_2 concentration. At 24 % R.H. particle formation was already rapid (10^4 cm^{-3}) at 5 ppm SO_2 (i.e. 5×10^{-5} ppm or 4×10^{-8} torr H_2SO_4). Thus the threshold H_2SO_4 concentration for nucleation at this humidity appears to be of the order of 10^{-8} torr

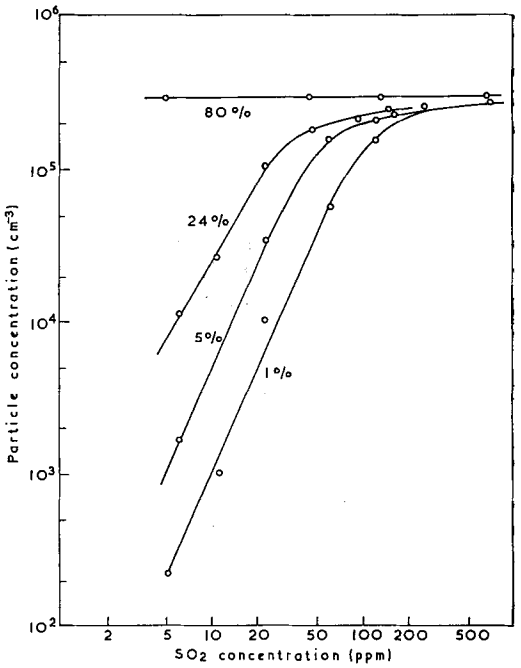

Fig. 3. Nucleation of H_2SO_4 from the photo-oxidation of SO_2 at 290–400 nm. Plot shows the number of condensation nuclei (cm^{-3}) in the effluent from the flow reactor as a function of SO_2 concentration at four different humidities.

and at higher humidities it is probably considerably lower.

These results confirm the theoretical predictions of Doyle and Kiang and Stauffer that heteromolecular nucleation in H_2SO_4–H_2O systems occurs at an appreciable rate at partial pressures of the order of 10^{-9} torr H_2SO_4 provided the water vapour content is high enough. The predicted large effect of relative humidity on the nucleation rate is also confirmed qualitatively.

Particle formation in the atmosphere

From the SO_2 oxidation rates given in Table 1 it is seen that the rate of H_2SO_4 production from SO_2 in sunlight in urban atmospheres is 1–10 ppb hr^{-1}. This rate is sufficient to produce H_2SO_4 concentrations of the order of 10^{-3} to 10^{-2} ppb in the time scale of a few minutes. Thus it seems very likely that fresh aerosol particles will be produced from SO_2 in the atmosphere in this situation. In clean air with 1 ppb SO_2, a time scale of hours would be re-

quired to produce 10^{-3} to 10^{-2} ppb H_2SO_4. Since it is doubtful whether free H_2SO_4 molecules would have a lifetime of the order of hours with respect to collisions with existing aerosol particles, a rapid production of new H_2SO_4 particles by SO_2 oxidation in unpolluted air does not seem likely.

In the above discussion nucleation has been considered only for systems containing pure acid gases (H_2SO_4 and HNO_3). If these gases undergo further chemical reaction to yield products of lower volatility the conditions for heteromolecular nucleation will change. For example, the addition of ammonia (0.5 ppm) to HNO_3 vapour (0.1 ppm) gave rise to a rapid formation of particles at 20 % R.H. presumably due to the formation of ammonium nitrate which has a much lower vapour pressure than nitric acid. The role of other components in atmospheric particle formation requires further experimental and theoretical evaluation.

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ОБРАЗОВАНИЕ ЧАСТИЦ ПРИ ГОМОГЕННЫХ РЕАКЦИЯХ ДВУОКИСИ СЕРЫ И ДВУОКИСИ АЗОТА

Обсуждаются некоторые недавние лабораторные результаты, имеющие отношение к превращению газообразных двуокисей серы и азота в твердые частицы, и следствия из этих результатов для атмосферной химии этих газов. Гомогенное окисление SO_2 путем фотохимически инициируемых реакций может идти со скоростью, меняющейся от 0,1 % в час в чистом воздухе, до 1–10 % в воздухе города. Скорость окисления NO_2 быстрее (до 25 % в час), но она может быть менее эффективна, благодаря обратимой природе реакций. Теоретические и экспериментальные результаты показывают, что скорость образования H_2SO_4 в городском воздухе (из SO_2) достаточна для того, чтобы многомолекулярная нуклеация образовала водные аэрозоли серной кислоты, однако, в остальных областях конденсация на уже существующих аэрозолях представляет собой основную судьбу продуктов окисления SO_2. Вряд ли количество газовой кислоты HNO_3, производимое из NO_2 в атмосфере, достаточно для нуклеации, поэтому конденсация на аэрозольных частицах, особенно, на гигроскопических частицах, является важным механизмом вывода HNO_3 из атмосферы. Экспериментально показан большой эффект относительной влажности на скорости процессов нуклеации и конденсации.