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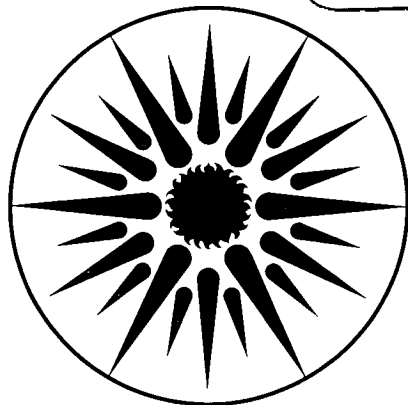
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A CLOUD CHAMBER DEMONSTRATION
OF HETEROGENEOUS SULFUR DIOXIDE OXIDATION
BY COMBUSTION PRODUCTS*

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Abstract

A mixing-type cloud chamber coupled to a propane combustor was used to study sulfate formation in water droplets nucleated on carbon soot particles. Rapid SO_2 oxidation to sulfate ($>100\%$ hr^{-1}) was observed when the chamber atmosphere contains ammonia, carbon particles, and water droplets. The sulfate formation was found to be either negligible or minimal when ammonia and carbon particles were absent from the system. The results are in qualitative agreement with wintertime field observations in polluted source-dominated atmospheres.

Introduction

This study experimentally tests a hypothesis for heterogeneous aerosol sulfate formation in polluted urban atmospheres. This hypothesis, based on our results from several field studies in urban regions (Bizjak et al., 1984; 1986; 1987; Dod et al., 1986), can be stated as follows: Substantial sulfate formation (with the sulfate present mostly in the form of ammonium salts) occurs under nonphotochemical conditions when pollutant concentrations are high and physical properties of the atmosphere favor formation of fog droplets or wet aerosol particles. Sulfur dioxide is oxidized by a heterogeneous, aqueous process (or processes). The oxidants and/or catalysts involved in sulfate formation are combustion products. The oxidation process is fast, occurring essentially immediately after the combustion effluent interacts with liquid water.

If this hypothesis is correct, enhanced sulfate formation should be observed in the laboratory when water droplets are nucleated on combustion-generated particles in the presence of SO_2 and other combustion products. The experiments were performed with a mixing-type cloud (fog) chamber coupled to a propane combustor (Benner et al., 1987). Rapid, efficient SO_2 oxidation is observed when the chamber atmosphere contains liquid water droplets, soot particles (and other combustion products), and ammonia. If any one of those ingredients is absent, either no or very low sulfate formation occurs. These results substantiate the hypothesis and are consistent with ambient observations and demonstrate the role of combustion products in SO_2 oxidation.

Experimental Apparatus

A schematic representation of the experimental apparatus is shown in Fig. 1. It consists of a combustor (not shown), a dilution manifold, and the cloud chamber. The combustor is a propane torch enclosed in a glass cylinder maintained at a slight positive

pressure. Propane was burned in a diffusion flame at a rate of 110 ml min^{-1}. H$_2$S could be added to propane to increase its sulfur content. H$_2$S was added to propane at a flow rate of 0-4 ml min^{-1}, corresponding to a fuel sulfur content of 0-2.7% (wt. S/wt. fuel). Because nominally sulfur-free propane was used, the H$_2$S addition to the fuel increases the fuel sulfur content and therefore the amount of primary sulfate generated by the flame. This primary sulfate when incorporated into soot particles also increases their cloud nucleation potential (Benner et al., 1987) and therefore the likelihood for the occurrence of heterogeneous aqueous reactions.

Additional SO$_2$ and NH$_3$ can be introduced into the system through a dilution mani-fold as indicated in Fig. 1. Particulate and gaseous effluent from the combustor is diluted with filtered room air before entering the chamber. The fraction of combustion effluent reaching the dilution manifold can be varied by adjusting the flow between the combustor and the main dilution tube. In this way the concentrations of SO$_2$, NH$_3$, and carbon parti-cles delivered to the chamber could be varied to encompass the concentration ranges found in polluted ambient air. Under adverse meteorological conditions, 2-hr SO$_2$ and particulate carbon concentrations of $\sim$ 300 ppb and 250 μg/m^3, respectively, are com-monly observed in some source-dominated atmospheres The concentration ranges in the chamber were 0.1-9 ppm SO$_2$ and 100-1000 μg C/m^3. When NH$_3$ was used in the experi-ments, its concentration was kept constant at 2.5 ppm.

The chamber is a double-wall glass cylinder 1.5 m tall and 0.2 m wide. The diluted stream of gaseous and particulate species was humidified and introduced into the chamber through a slightly heated tube in the center of the perforated bottom plate at a flow rate of 1.2 l min^{-1}. Cold mixing air (t = -13 °C, flow rate 10.5 l min^{-1}) was introduced into the chamber through this plate. When the temperature of the chamber air is lower than the dew point (typically 48 °C) of the humidified input air stream, dense cloud nucleated on

combustion particles forms in the chamber. The cloud density was visually monitored by observing the light scattering of a He-Ne laser beam. The cloud temperature at the center of the chamber was approximately 20 °C. An upward net flow of 14.5 l min^{-1} was maintained in the chamber due to the aspiration through two aerosol samplers. Under such flow conditions, the calculated transit time in the chamber is about 3 min.

Aerosol samples for chemical analyses were collected on heated quartz filters from the top part of the chamber. Sampling times were usually between 10 and 30 min. Two 47-mm in-line filter holders with flow rates of 7.3 l min^{-1} were used. Chamber aerosol was extracted through heated stainless steel tubings (1 cm diameter). Heating the airstream evaporates the water droplets and minimizes sulfate artifact formation due to water condensation on the filters. One of the two sampling tubes was equipped with a mesh impaction droplet separator consisting of three layers of polypropylene mesh (100 μm fibers, 96% void volume) held in a 1.4-cm diameter tube. This separator is similar to that developed by Brewer et al. (1983) for ambient fog sampling. Based on the mesh manufacturer's data (Kimre, Inc., Perrine, Florida), we have estimated the 50% droplet cut point to be about 2.5 μm for our sampling flow rate. Particles that penetrate through this separator are somewhat arbitrarily defined as the interstitial aerosol. We shall refer to particles collected without size segregation as the total aerosol, consisting of evaporated cloud droplets and the interstitial aerosol.

The chemical composition of primary particles (i.e., before they have entered the chamber) was determined by analyzing filter samples collected from the dilution train. The filter holder was preceded by a diffusion drier/denuder to keep the artifact sulfate formation at a minimum. The concentration of primary particles in the chamber was calculated from the measured dilution factors. These are referred to as input concentrations. For primary species such as black carbon, a good correspondence has been found

between the calculated and measured input concentrations in the chamber in the absence of the cloud. Sulfur dioxide concentrations were determined by passing the air from the dilution train through bubblers containing 0.01 M solution of H_2O_2. The SO_2 concentrations in the chamber were calculated from the sulfate concentration in the bubblers and the known dilution factor. NH_3 concentrations were not directly determined but estimated from the measured flow rates. Liquid water content was determined in a few experiments by weighing the cloud water collected by the mesh impactor. The average liquid water content in these experiments was about 1.5 g m^{-3}.

Water-soluble filter extracts and bubbler solution were analyzed for anions by ion chromatography (Dionex, Model 12). Black carbon content of filter samples was determined optically by the laser transmission method (Rosen and Novakov, 1983; Gundel et al., 1984). The ratio of total to black carbon concentration for some of the filter samples was determined by thermal temperature-programmed evolved gas analysis. The data presented in Tables I and II were corrected by this ratio (Black C/Total C = 0.51) and expressed as total carbon.

Results and Discussion

The experiments consisted of measuring the sulfate and carbon concentrations of the aerosols before (input) and after (output) they were processed by the cloud in the chamber. Two sets of experiments were performed. In the first series of measurements, the chamber atmosphere consisted of liquid water droplets, SO_2, and diluted combustion effluent only. The second series was performed in an analogous manner but with addition of gaseous ammonia.

The results of experiments without NH_3 are summarized in Table I. In this table the input (C,S) and output (C_i, C_t, S_i, S_t) concentrations (expressed as carbon and sulfur) and

the ratios S/C and S_t/C_t are given. (Subscripts i and t refer to interstitial and total aerosol respectively.) The results for different runs are arranged approximately by the increasing input carbon concentrations. Numerous replicate control samples gave reproducible S/C ratios. The first run was with commercial-grade propane. The next was with H_2S added to the propane, and the last two runs were with additional SO_2. The purpose of the SO_2 addition was to see if secondary sulfate (in excess of primary sulfate) is formed in cloud chemical reactions.

It is obvious from the approximate constancy of the S/C ratios for the input particles that the input S is primary sulfate produced by the H_2S oxidation in the flame. These data also demonstrate that the cloud processing of the input aerosol, under these experimental conditions (i.e., in the absence of NH_3), did not result in the formation of secondary sulfate, as evidenced by the similar values of S/C and S_t/C_t ratios. Actually, the output sulfate concentrations were somewhat lower than the input, indicating that some sulfate was lost either in the chamber or in other parts of the system. In contrast input and output carbon concentrations were practically the same. That the output sulfate in these experiments is essentially primary and unaffected by cloud processing is also suggested by the fact that interstitial sulfur is a major fraction of the total particulate sulfur.

In contrast to the experiments without ammonia, increased in-cloud SO_2 oxidation was observed when NH_3 was supplied to the system. The results of these experiments are presented in Table II, arranged in the actual sequence in which they were obtained. The first run was with H_2S supplied to the fuel and without SO_2 added into the dilution manifold. Runs 2-5 were with various SO_2 concentrations as indicated in Table II. The input carbon concentrations in these runs varied from about 800 to 100 μg m^{-3}. The last two runs were performed at the end of this series of experiments after the carbon particle

input was discontinued by extinguishing the flame. NH_3 and SO_2 continued to be supplied to the chamber during these two runs. We note, however, that the cloud in the chamber persisted during the last two runs.

The most obvious conclusion from the experiments with NH_3 is that the output sulfate greatly exceeds the input aerosol sulfate concentrations. This is evident from both absolute concentrations and the S/C ratios (Table II). The effect of cloud processing on the sulfate concentrations is demonstrated by the results shown in Fig. 2. In this figure the sulfate concentrations of the input, interstitial, and total aerosol, and the cloud water (difference between total and interstitial) are plotted against the input carbon particle concentration.

The data in Fig. 2 and Table II show that input sulfate concentrations are generally low and independent of carbon concentration. The output sulfate is markedly higher even for the run when the only source of sulfur is H_2S in the fuel. Substantially higher sulfate concentrations were measured for all runs when additional SO_2 was introduced to the system. It is obvious from these data that the sulfate concentrations show a definite dependence on input soot concentrations. No such dependence on SO_2 concentrations was observed (Table II). The lowest sulfate concentration was detected in the absence of carbon particles (runs 6 and 7).

The results of these experiments demonstrate that efficient heterogeneous, aqueous SO_2 oxidation occurs in the cloud droplets when ammonia is present in the system. That the oxidation under these conditions involves an aqueous process or processes is also evident from the fact that most sulfate is found in the cloud droplets and not in the interstitial aerosol. This is in contrast with the results of experiments without ammonia when the sulfate was found to be essentially primary and confined to the interstitial particle size range. Another finding of our experiments is that the SO_2 oxidation is fast because

the residence time of the species in the chamber is several minutes. Nevertheless, a very high fraction of SO_2 was oxidized during this short time (see S_t/S_t+S_g ratios in Table II). These correspond to oxidation rates well in excess of 100% hr^{-1}.

The importance of ammonia in aqueous SO_2 oxidation has been well documented (Scott and Hobbs, 1967). Its principal role is in controlling the pH value of the droplets and thus the equilibrium between the dissolved S(IV) species and the gaseous SO_2. Most SO_2 oxidation mechanisms are pH dependent, with oxidation rates increasing with the pH of the solution. Such dependence is also evident from our data. Furthermore, our experiments demonstrate that higher sulfate formation occurs in the chamber when carbon particles are also present. (On the average about 13% of carbon by mass is incorporated in droplets.) This is indicative of the catalytic action of carbon particles and is at least qualitatively in agreement with the known pH dependence of this catalytic oxidation process (Brodzinsky et al., 1980). Because $[SO_2] > [NH_3]$, it is assumed that the droplets were acidic and thus the carbon reaction could proceed.

It has been reported that NH_3, SO_2, and water vapor in the presence of oxygen produce solid ammonium sulfate (McLaren et al., 1974). That such a reaction possibly takes place in the inlet manifold of our apparatus is suggested by the increased input sulfate concentrations when ammonia was present but carbon particles were not (Tables I and II). Such a reaction could also be the source of condensation nuclei and therefore provide an explanation for the presence of the cloud during the runs with NH_3 but without carbon particles (Table II, runs 6 and 7). The contribution of this reaction to the total sulfate formation in the chamber is minimal, however, under our experimental conditions. If runs 5 and 6 (Table II) are compared, an upper estimate of the importance of the $NH_3 + SO_2$ reaction indicates that 35% of the sulfate could come from this reaction; but realistically its importance is probably less than this because this estimate is based on the highest SO_2

but lowest carbon concentration.

Conclusions

Rapid SO_2 oxidation to sulfate ($> 100\%$ hr^{-1}) was observed in a cloud chamber when water droplets are nucleated on combustion-generated carbon particles in the presence of other combustion products and gaseous ammonia. The sulfate formation was either negligible or minimal in the absence of ammonia and carbon particles. The amount of sulfate formed depends strongly on carbon but not on SO_2 concentration. These laboratory simulation experiments are qualitatively in agreement with the ambient results obtained in source-dominated atmospheres during heavy wintertime pollution episodes.

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Table I.

Input				Output					Remarks
SO_2 ppm	C $\mu g/m^3$	S	S/C	C_i	C_t $\mu g/m^3$	S_i	S_t	S_t/C_t	
1		130	0	0	160	180	0	0	0	Propane only
2	~0.08	235	33	0.14	135	180	13	19	0.11	H_2S in fuel
3	~10.0	150	20	0.13	130	150	18	18	0.12	H_2S in fuel + SO_2
4	~10.0	430	73	0.17	400	430	52	51	0.12	H_2S in fuel + SO_2

Table II.

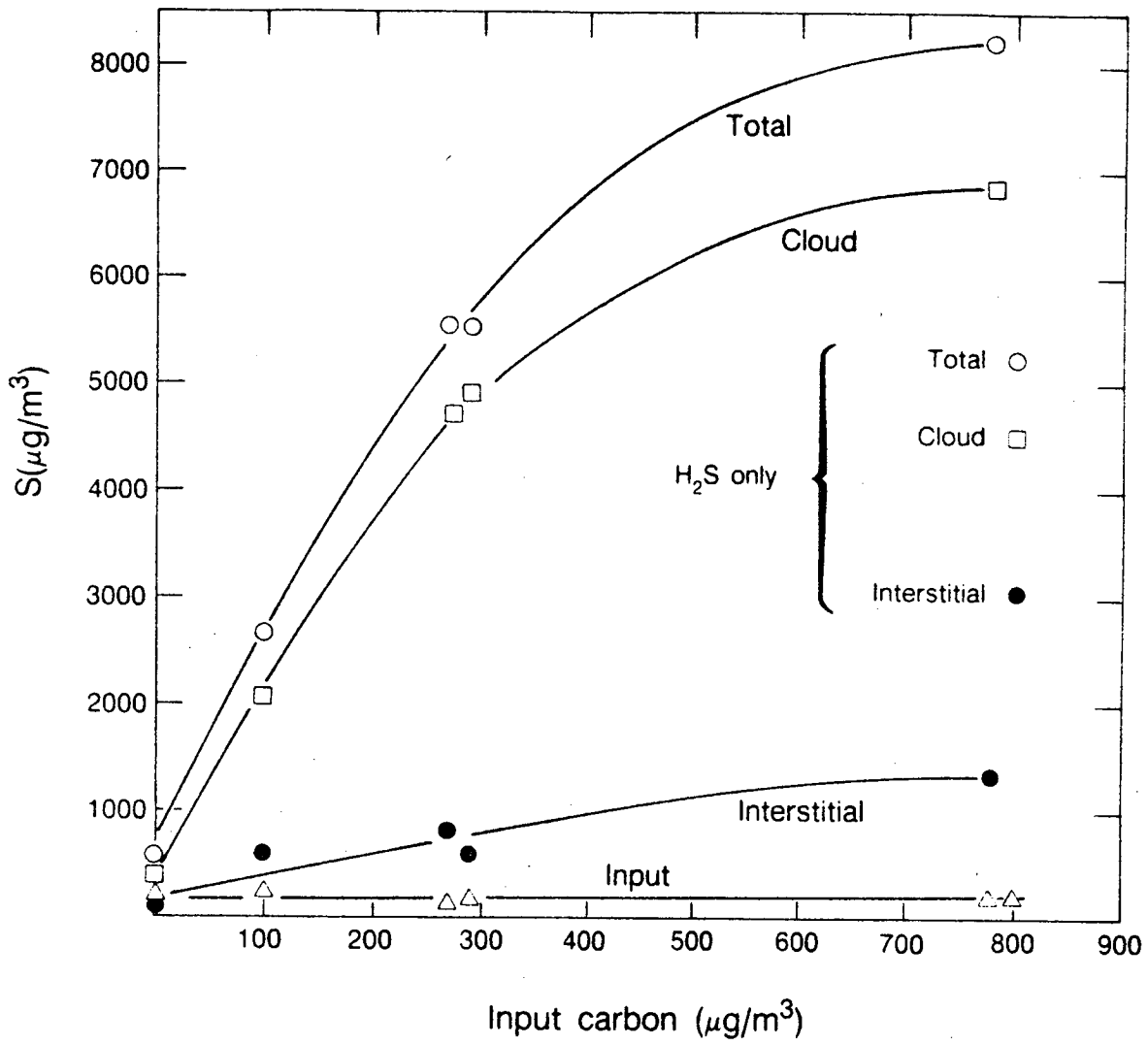|	Input				Output						Remarks
	SO_2 ppm	C $\mu g\ m^{-3}$	S	S/C	C_i	C_t $\mu g\ m^{-3}$	S_i	S_t	S_t/C_t	$S_t/S_i + S_g$	
1	0.08	800	200	0.25	1160	1140	1140	3330	2.9	0.97	H_2S in fuel
2	5.9	780	180	0.23	1180	1290	1360	8190	6.3	0.52	H_2S in fuel + SO_2
3	9.1	270	150	0.55	290	380	830	5550	14.6	0.32	H_2S in fuel + SO_2
4	4.5	290	180	0.62	250	260	610	5540	21.3	0.48	H_2S in fuel + SO_2
5	4.5	100	260	<2.6	210	250	610	2660	10.6	0.31	H_2S in fuel + SO_2
6	4.5	0	110	0	0	0	110	940	0	0.14	SO_2 only, no flame
7	6.4	0	110	0	0	0	70	200	0	0.02	SO_2 only, no flame

Figure Captions

Figure 1. Schematic representation of the cloud chamber. The cloud is produced by lowering the air temperature in the chamber below the dew point of the combustion effluent entering the chamber. The chemical composition of the combustion effluent can be modified by adding NH_3 and SO_2 to the dilution manifold. Interstitial and total aerosol are sampled from the top of the chamber.

Figure 2. Concentrations of sulfate (expressed as S) in the total and interstitial aerosol and in cloud water (calculated as the difference between total and interstitial) plotted as a function of input carbon concentration. The input sulfate concentration is considerably less than the sulfate concentrations after cloud processing. The points at the right of the drawing were obtained by adding H_2S to the propane fuel. All other points were obtained by introducing additional SO_2 to the dilution manifold. Numerical data corresponding to this figure are given in Table II.

Figure 1

XBL 878-9759 A

Figure 2

XBL 878-9756