References and Notes

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2. "Final report: Emission inventory for the State of New Jersey" (IBM Corporation, Gaithersburg, Maryland, 1971); "Profile of air pollution control" (Air Pollution Control District, County of Los Angeles, Los Angeles, California, 1971); "New York City metropolitan area air quality implementation plan" (New York State Department of Environmental Conservation, Albany, 1972).
3. This seasonal pattern of O_3 production is evident in the data we have analyzed and has also been noted by J. S. Jacobson and G. D. Salottolo ["Photochemical oxidants in the New York–New Jersey metropolitan area" (Boyce Thompson Institute, Yonkers, New York, 1973)].
4. With one exception, the O_3 concentrations discussed herein were determined by the chemiluminescent technique. The Yonkers measurements are of "photochemical oxidants," a collection of oxidizing gases of which O_3 is the principal constituent [B. D. Tebbens, in *Air Pollution*, A. C. Stern, Ed. (Academic Press, New York, ed. 2, 1968), vol. 1, p. 43], as determined by KI oxidation. Any SO_2 interference was prevented by dichromate scrubbing of the incoming air sample. No correction for NO_2 was made, but tests show its effect on the oxidant concentration to be < 30 ppb at this site.
5. High O_3 concentrations in rural areas have also been reported; see, for example: W. Attmannspacher and R. Hartmannsgruber, *Pure Appl. Geophys.* **106**, 1091 (1973); L. A. Ripperton and J. J. B. Worth, paper presented at 2nd Joint Conference on Sensing of Environmental Pollutants, Washington, D.C., 11 December 1973; W. N. Stasiuk, Jr., and P. E. Coffey, *J. Air Pollut. Control Assoc.* **24**, 564 (1974); "High oxidant levels in Wisconsin" (Report of the Department of Natural Resources, State of Wisconsin, Madison, 15 February 1974).
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17 May 1974; revised 2 July 1974 ■

Sulfates as Pollution Particulates: Catalytic Formation on Carbon (Soot) Particles

Abstract. *Experimental evidence (obtained by electron spectroscopy for chemical analysis) is presented which shows that finely divided carbon (soot) particles may play a major role in the catalytic oxidation of sulfur dioxide to sulfate in polluted atmospheres. The results obtained with sulfates produced in the laboratory by the oxidation of sulfur dioxide on graphite particles and combustion-produced soot particles are compared with the properties and behavior of ambient sulfates. The proposed sulfur dioxide oxidation mechanism is qualitatively consistent with field observations.*

Because of the adverse effects of sulfate particles as atmospheric pollutants, the study of the oxidation of SO_2 to sulfate is of prime importance in air pollution research. In the past most attention has been devoted to the study of the photochemical and solution chemical mechanisms for the oxidation of SO_2. There is, however, increasing evidence that these two kinds of processes alone cannot adequately account for the observations, and it is now thought that perhaps some catalytic reaction on suspended particulates is involved. The possible role of suspended metal oxides, for example, has been examined by some workers (*1*). However the concentrations of such oxides in the atmosphere are small. This report concerns the role that finely divided carbon (soot) particles, a common pollutant and a catalyst abundantly present in the atmosphere, play in the oxidation of SO_2. Even though the surface chemical and catalytic properties of carbon are known (*2, 3*), the relevance of soot-catalyzed reactions to air pollution chemistry has not been appreciated. We show here that the soot-catalyzed oxidation of SO_2 to sulfate is an important process and that the proposed oxidation mechanism is in qualitative agreement with the field observations. The experiments reported here were obtained by the technique of electron spectroscopy for chemical analysis (ESCA).

Carbon is the most abundant element associated with pollution particulates; actually, carbon constitutes about 50 percent of the total particulate emissions in urban atmospheres such as those in California (*4*). From our ESCA studies of ambient particulates, we find that perhaps as much as 80 percent of the particulate carbon is in the form of soot. Soot is basically carbon with a graphite-like structure, with some small soot particles consisting of only a few unit cells (*5*) and thus possessing extremely high surface area.

We studied the interaction of SO_2 with graphite particles with the experimental setup shown in Fig. 1a, which produces small graphite particles with a fresh (reactive) surface (diameter $\simeq$ 20 μm). The ESCA spectrum of graphite particles exposed to SO_2 reveals two sulfur (2*p*) peaks corresponding to sulfate and to sulfide (*6*). Blank filters without graphite particles, under identical SO_2 exposure conditions, do not collect measurable amounts of sulfate (or sulfide). These experiments show that even fresh graphite particles in air may bring about the oxidation of SO_2 to sulfate.

The similarity of soot particles to graphite with respect to the oxidation of SO_2 is demonstrated by the following experiments. Soot specimens from a premixed C_3H_8-O_2 flame collected on (silver membrane) filters were used for experiments with different SO_2 exposure conditions, in the apparatus shown in Fig. 1b. Dry air or prehumidified particle-free air or N_2 was used with an SO_2 concentration of about 300 parts per million (ppm) and an exposure time of 5 minutes. The ESCA spectra of soot exposed to SO_2 are shown in Fig. 1b. The sulfate peaks were always more intense in the case of prehumidified air than in the case of dry air. However, both dry and prehumidified N_2, when used instead of air, produced only very low, background level sulfate peaks. This result indicates that, in addition to soot particles, the O_2 in air is important for SO_2 oxidation. Although water molecules enhance the observed sulfate concentration in the air-SO_2-soot system, the contribution of sulfate produced by SO_2 oxidation via dissolved molecular oxygen in water droplets is not significant; that is, blank filters exposed to SO_2 and prehumidified air showed at most only low, background level sulfate peaks.

It is of interest to assess the role of soot-catalyzed oxidation in or near combustion devices where both SO_2 and soot concentrations are highest. Here, however, the SO_2 oxidation may be, at least in principle, caused by reactions with reactive combustion-produced radical species (*7*). The experimental arrangement is shown in Fig. 1c. Soot samples were collected while a constant SO_2 flow (300 ppm, 4 minutes) was introduced at ports 1 through 4, with the C_3H_8-O_2 flame on. The amounts of sulfate detected on filters are shown in the graph in Fig. 1c. The similarity of the sulfate concentrations produced when SO_2 was passed over the flame (port 1) and when SO_2 was introduced outside (downstream) of the flame envelope (port 2) indicates the relatively minor significance of the homogeneous gas phase oxidation (no particles present) in this system.

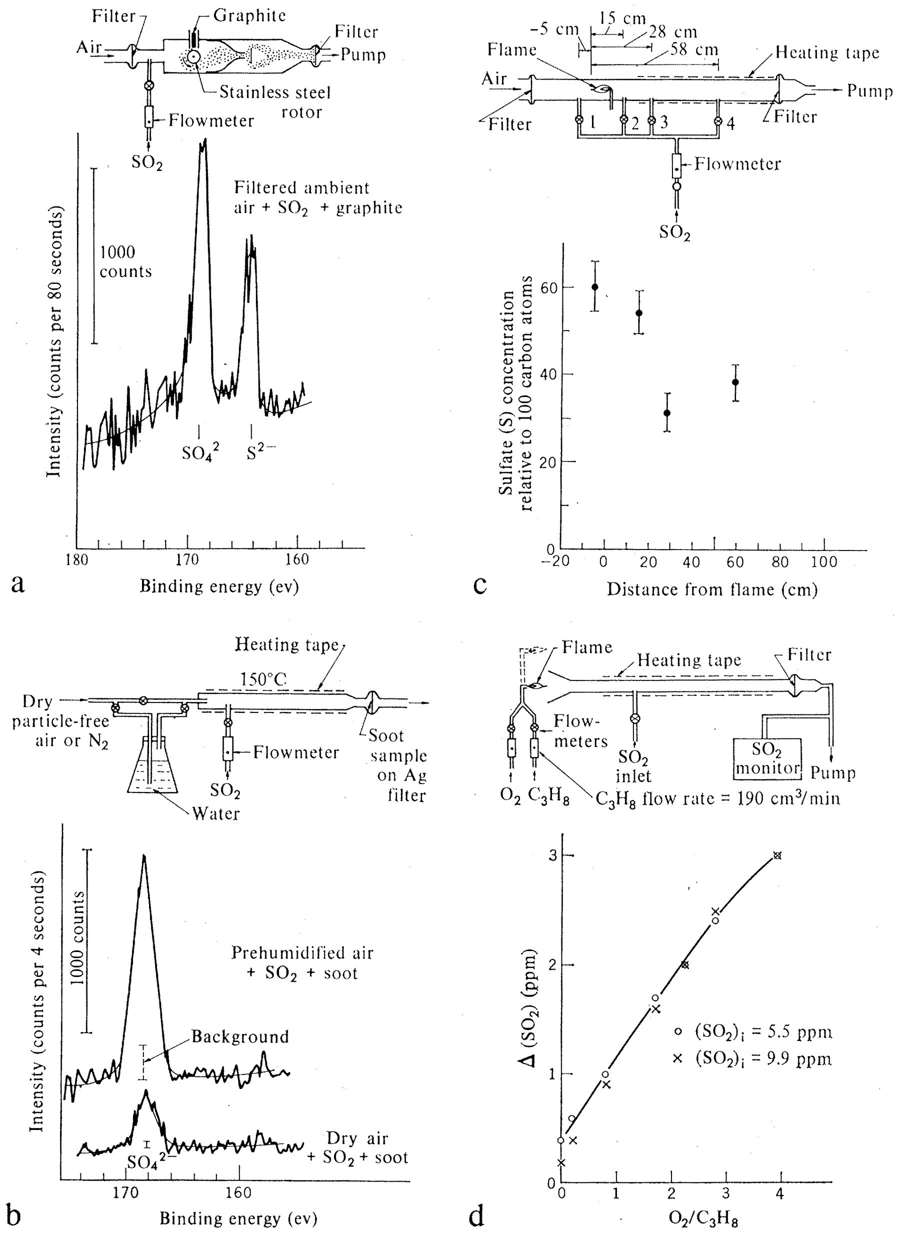

Fig. 1. (a) The ESCA spectrum of graphite particles exposed to SO_2 and filtered ambient air reveals both sulfate and sulfide on those particles. Sulfate is produced by the catalytic oxidation of SO_2 on graphite particles. The sulfide peak is the result of SO_2 chemisorption on those parts of the particle surfaces that are "atomically" clean. (b) Soot exposed to prehumidified air and SO_2 produces sulfate concentrations higher than in the case of dry air. Blank filters (without soot particles), exposed to SO_2 and prehumidified air, show only background level sulfate. (c) Four soot samples were prepared with the apparatus shown. A constant flow of SO_2 was introduced while the premixed C_3H_8-O_2 flame was on, at ports 1 through 4 located at the indicated distance from the flame. The resulting sulfate concentrations are plotted as a function of the distance of the port from the flame. (d) The SO_2 concentration is adjusted to the desired initial value, $(SO_2)_i$, with the flame removed from its position in front of the intake funnel. A decrease in the SO_2 concentration, $\Delta(SO_2)$, is observed when the flame is placed in the intake position. For a given combustion regime $\Delta(SO_2)$ is independent of $(SO_2)_i$ and increases with the O_2/C_3H_8 ratio. The former effect is related to the saturation of active sites on the soot particles, whereas the latter reflects the increase in the number of ultrafine, high-surface-area particles.

We have also studied the SO_2 oxidation on soot particles produced in the premixed C_3H_8-O_2 flame by observing the decrease in the gaseous SO_2 concentration, $\Delta(SO_2)$, occurring as a result of sulfate formation (Fig. 1d). The SO_2 concentration is adjusted to the desired initial value, $(SO_2)_i$, with the flame removed from its position in front of the intake funnel. A decrease in the SO_2 concentration is observed within the response time of the SO_2 monitor, when the flame is placed in the intake position so that combustion-generated aerosol comes in contact with SO_2. Removal of the flame causes the SO_2 concentration to rise to its initial value. Because gaseous species will suffer about 10^8 collisions on the path between the flame and the SO_2 input, it can be expected that reactive radical species will be largely neutralized by the time they reach the SO_2 port. This and the evidence described earlier suggests that the observed decrease in the SO_2 concentration is caused by the action of soot particles. The possibility that the reduction in the SO_2 concentration is related to the formation of H_2SO_3 was ruled out in a separate experiment, in which the combustion-generated aerosol was replaced by steam. No detectable change in the SO_2 concentration was observed in this case.

The plot in Fig. 1d shows the amount of SO_2 converted to sulfate as a function of the O_2/C_3H_8 ratio, for initial concentrations of 5.5 and 9.9 ppm. For a given combustion regime $\Delta(SO_2)$ is independent of $(SO_2)_i$. This feature is probably related to the saturation of active sites (*8*) on soot particles. The $\Delta(SO_2)$ value increases, however, with the O_2/C_3H_8 ratio, reflecting the increase in the number of very small, high-surface-area particles produced in oxygen-rich flames.

In summary, laboratory experiments show that: (i) both graphite and soot particles oxidize SO_2 in air; (ii) soot-catalyzed SO_2 oxidation plays a major role even in the presence of flames and combustion-produced gases; and (iii) soot-catalyzed oxidation shows a prominent saturation effect.

That the sulfate formation process described here is consistent with field observations is evident from the following. Pollution particulate sulfates are believed to exist primarily in the form of H_2SO_4 or $(NH_4)_2SO_4$, or both (*9*). Because the sulfate produced by the laboratory soot-SO_2 interaction is

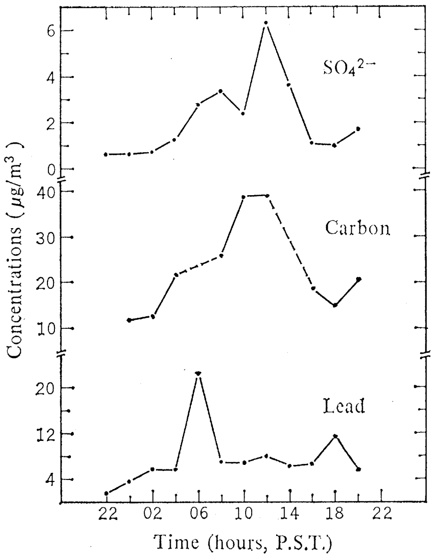

Fig. 2. Diurnal variation of particulate sulfate, carbon (*12*), and lead (*13*) concentrations. The sampling was done in downtown Los Angeles on 20 September 1972 (*14*). The similarity between the carbon and sulfate patterns is obvious.

water-soluble and could conceivably be neutralized by ambient NH_3, its chemical properties are consistent with those of ambient sulfate in the analytical sense. Moreover, ambient and laboratory-produced sulfate exhibit the same characteristic desorption in a vacuum as a function of sample temperature. The saturation effect reported for ambient sulfates (*10*) is also consistent with the proposed process. Finally, a marked correlation between the diurnal variation in the concentrations of ambient carbon and sulfate should be expected. An example of such a correlation is shown in Fig. 2. Other similar correlations have been observed more recently for other sites and pollution episodes (*11*).

The catalytic formation of sulfate on soot particles is expected to occur in the open atmosphere and especially in or near combustion sources, where both SO_2 and soot concentrations are highest. Although the sulfate formation mechanism described here may not be the only atmospheric sulfate-producing process, we believe that it plays a major role in urban atmospheres characterized by high concentrations of particulate carbon.

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Alkanes at the Air-Sea Interface from Offshore Louisiana and Florida

Abstract. *Alkanes at the air-sea interface were analyzed in 118 surface samples collected at five different intervals over a 12-month period from Timbalier Bay (Louisiana), offshore Louisiana, and offshore Florida. The alkanes were characterized by gas chromatography and mass spectrometry. Unexpectedly, methyl branched alkanes ranging in chain length from C_{15} to C_{35} and cycloalkanes were frequently the predominant components. This suggests that the alkanes are produced by natural biological sources as well as human activities.*

In recent years there has developed considerable interest in the distribution and impact of hydrocarbon residues introduced into the marine environment by petroleum production and maritime activities. Studies of the C_1 to C_5 hydrocarbons dissolved in the surface waters of the Gulf of Mexico show that the highest concentrations are apparently associated with shipping and petroleum activities (*1*). The presence of dissolved paraffins of higher molecular weights has also been reported in the Gulf of Mexico (*2*). Koons and Monaghan (*3*) concluded that the hydrocarbon content of the water in the northern Gulf of Mexico is probably less than 7 μg/liter. Concentrations of total dissolved hydrocarbons in the area of the east central Atlantic vary from 10 to 140 μg/liter (*4*), and 2 to 13 μg/liter is reported for the Nova Scotia vicinity (*5*). In the last case alkanes from C_{14} to C_{37} were present, and there was no preference for odd or even carbon numbers.

Garrett (*6*), using both a screen technique to sample the air-sea interface and a bucket sample, found that a variety of organics were present at a number of locations. More recently, samples collected at the air-sea interface in the area of the Sargasso Sea by use of a stainless steel screen were found to contain a variety of chlorinated hydrocarbons, and the highest concentrations were associated with the surface microlayer (150 μm) (*7*). Duce *et al.* (*8*), using similar techniques, showed that hydrocarbons and fatty acids, as well as pesticides, are more concentrated in the surface microlayer of Narragansett Bay than in water as deep as 20 cm below the surface.

It has been established that organics affect the physical properties of the ocean surface and many important exchange processes between the ocean and the atmosphere (*9*). For example, they reduce the capillary wave spectrum and thereby contribute to the production of sea slicks. Also, during any type of petroleum-related accident or oil spill it is the surface layer that is initially disrupted. Because of the importance of this microlayer and the general lack of qualitative and quantitative data it is important to characterize the indigenous chemical components found at the air-sea interface. This report deals with the nature and distribution of alkanes at the air-sea interface