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### **Title**

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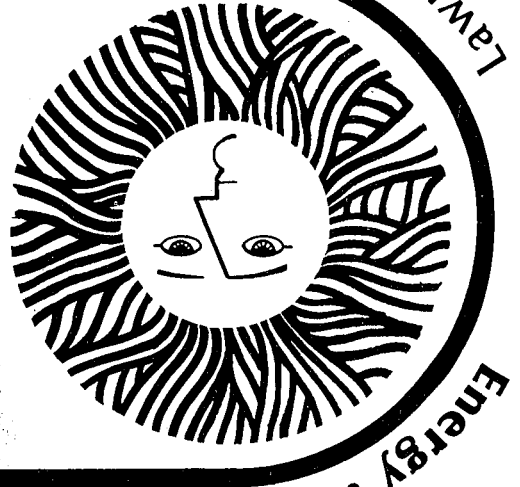
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ROLE OF CARBON SOOT IN SULFATE FORMATION \*

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This paper reviews laboratory results on heterogeneous oxidation of SO<sub>2</sub> on soot particles in air and presents results of numerical calculations suggesting that soot-catalyzed oxidation can be the dominant heterogeneous mechanism for sulfate formation under realistic atmospheric conditions. Soot is any carbonaceous particulate material emitted from sources, even if these do not produce visible plumes or smoke. In most cases soot particles are very small when emitted, having diameters of the order of 100<sup>o</sup>A, and are therefore invisible to the naked eye. Soot can also be described as a chemically complex carbonaceous material which consists of a "graphitic" component and an organic component. There are significant differences in the overall properties of the two components. For example, the "graphitic" component is nonvolatile, insoluble in organic solvents, and is a strongly light-absorbing material. In contrast, the organic component of soot is volatile, soluble in solvents, and does not appreciably absorb light.

There is considerable evidence that primary soot particles are still very important contributors to atmospheric pollution in California and elsewhere. For example, Rosen et al.<sup>1</sup> have recently employed Raman spectroscopy and an optical attenuation technique to identify the "graphitic" component of primary emissions. The "graphitic" soot tracer technique suggests that a major fraction - possibly the dominant fraction - of the ambient carbonaceous aerosol burden is due to primary emissions. Puxbaum and Malissaz<sup>2</sup> used thermal methods for characterizing the carbonaceous material from the Vienna, Austria, air and have concluded that the major part of this material is polymeric or graphitic carbon, i.e., of primary origin.

Soot particles, in addition to being a major constituent of ambient particles, are a catalytically and surface chemically active material. For example, Novakov et al.<sup>3</sup> used photoelectron spectroscopy (ESCA) to study the oxidation of SO<sub>2</sub> on soot particles produced by a propane flame. The investigators found that under some conditions, a significant amount of sulfate can be produced by the catalytic action of soot particles. Although these early experiments were qualitative, it was nevertheless possible to conclude the following:

1. Soot-catalyzed oxidation of SO<sub>2</sub> is more efficient at a higher humidity.
2. The oxygen in air plays an important role in SO<sub>2</sub> oxidation.
3. Soot-catalyzed oxidation exhibits a saturation effect.
4. The saturation level of sulfate produced is probably related to properties of carbon particles, such as size, active surface area, and adsorbed surface oxygen.

5. SO<sub>2</sub> can be oxidized on other types of graphitic carbonaceous particles, such as ground graphite particles and activated carbon.

Chung et al.,<sup>4</sup> using a special chamber, were able to observe directly in a transmission electron microscope the interaction of soot with a mixture of SO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O. They observed the growth of reaction products (sulfate) on soot. These experiments provided a hint about the importance of water in the catalytic oxidation of SO<sub>2</sub> on carbonaceous particles because the oxidation was apparently more efficient when prehumidified, rather than dry, air was used to dilute the SO<sub>2</sub>. However, the role of water, and specifically of liquid water, was not made clear in these experiments.

An understanding of the effect that liquid water may have on this type of SO<sub>2</sub> oxidation is imperative because of the ubiquitous presence of liquid water in the atmosphere (plume, fog, clouds).  
Chang et al.<sup>5</sup> recently investigated the kinetics of SO<sub>2</sub> in an aqueous suspension of soot particles. The reaction was studied in systems containing various concentrations of sulfuric acid and suspended carbonaceous particles. The concentrations of sulfuric acid and of sulfuric acid were monitored in these experiments. Soots that were produced by the combustion of acetylene and natural gas, as well as soot produced by a diesel engine and collected by impinging the effluent into water, were used in this study and found to be good catalysts.

The reaction occurs in two steps - an initial rapid oxidation followed by a much slower one. The rate of the first process is too fast to be followed. The reaction of the second process has the following characteristics:  
1. The reaction rate is first order, zeroth order, and a fractional order (0.7th) with respect to the concentration of carbon, sulfuric acid, and dissolved oxygen respectively.  
2. The reaction rate is pH independent.  
3. There is a mass balance between the consumption of sulfuric acid and the production of sulfuric acid.

Eatough et al.<sup>6</sup> have performed a calorimetric study of the conversion of sulfite to sulfate in aqueous suspensions of activated carbon. Their results indicate that groups are present in the carbon which are capable of complexing with sulfite and rapidly oxidizing sulfite to sulfate. According to these authors, the rate limiting step for oxidation of sulfite is the oxidative regeneration of active sites.  
Based on experimental observations, Chang et al. proposed a reaction mechanism and carried out a simple box-type calculation to compare the relative importance of "wet" soot-particle-catalyzed reactions with other reactions involving liquid water. The systems which were considered are: SO<sub>2</sub>-H<sub>2</sub>O(λ)-air; NH<sub>3</sub>-SO<sub>2</sub>-H<sub>2</sub>O(λ)-air; O<sub>3</sub>-SO<sub>2</sub>-H<sub>2</sub>O(λ)-air; Mn<sup>2+</sup>-SO<sub>2</sub>-H<sub>2</sub>O(λ)-air; and soot-SO<sub>2</sub>-H<sub>2</sub>O(λ)-air. These calculations and available field results indicate that the soot-catalyzed oxidation of SO<sub>2</sub> can be the dominant mechanism under realistic atmospheric conditions.

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