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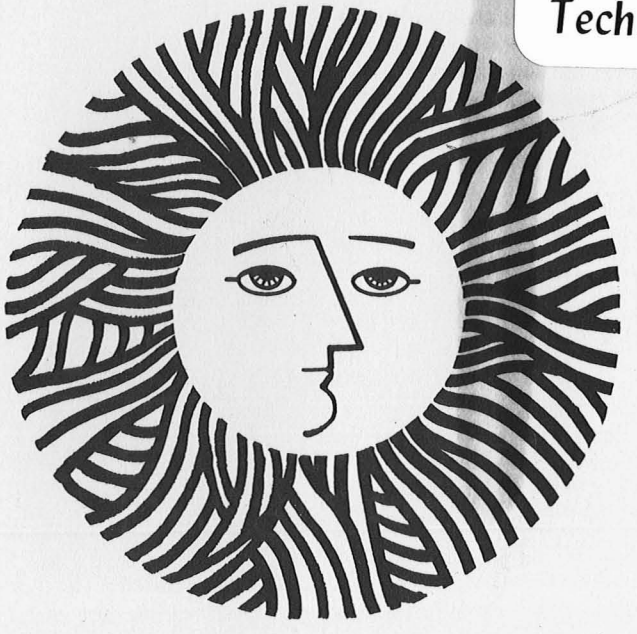

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THE ROLE OF SOOT IN AEROSOL CHEMISTRY*

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Abstract

Carbonaceous material constitutes a major component of aerosol particles. This material consists of a secondary and a primary fraction. The secondary fraction is made up of organic compounds produced by atmospheric reactions. The primary fraction, or soot, is produced in combustion processes and consists of an organic component and a component variously called elemental, graphitic, or black carbon. Soot is important in atmospheric chemistry because of its catalytic and surface chemical properties. In order to assess the role of soot in aerosol chemistry, we have developed an experimental methodology to empirically determine the soot concentrations in various regions of the United States. These results, when combined with laboratory results on the mechanism and kinetics of SO_2 oxidation, are used to establish the relative importance of soot-catalyzed SO_2 oxidation in the atmosphere. In this paper we review the methods used for determining soot concentrations and the experimental results on SO_2 oxidation.

Introduction

Atmospheric aerosol particles are classified as primary or secondary, depending on their origin. Primary particles are produced by sources such as combustion devices and are introduced into the atmosphere in particulate form. Secondary particles are formed in the atmosphere by chemical reactions among primary and secondary gaseous species, primary particles, and gaseous and liquid water.

Depending on the phases of the reactants, atmospheric reactions can be homogeneous or heterogeneous. Homogeneous reactions involve only gaseous species, while heterogeneous processes may involve gases and solid particles, gases and liquid droplets, or three-phase systems with gases, liquid droplets, and solid materials occluded in these droplets. These heterogeneous processes may be catalytic or stoichiometric; they may proceed in the bulk of a droplet, on the gas-solid interface, or on the solid-liquid interface.

In this paper we shall discuss the last two categories, specifically in conjunction with the role of combustion-generated soot particles in the oxidation of sulfur dioxide. Soot is synonymous with primary carbonaceous particulate material; it is a chemically complex material consisting of an organic component and a component variously referred to as elemental, graphitic, or black carbon; but for consistency we shall use the term "black carbon" here.

Soot in the atmosphere not only contributes to the total particulate concentration in ambient air but also may serve as an efficient catalyst for atmospheric reactions such as the oxidation of SO_2 to sulfate because soot has properties similar to those of activated carbon, which is well known to be a catalytically and surface chemically active material.

The assessment of the chemical role of soot in the atmosphere has to start with an empirical assessment of the soot concentrations. The results of these studies, as shown below, have clearly demonstrated that soot is ubiquitous not only in urban atmospheres but also in remote regions such as the Arctic. [1]

Soot in the Atmosphere

The principal approach used in our laboratory relies on the use of black carbon as a tracer for primary carbonaceous [2,3] material because black carbon can be produced only in a combustion process and is therefore definitely primary. The methodology that we adopted involved systematic measurements of the ratio of black carbon to total carbon for a large number of samples collected directly from sources, source-dominated environments, and well-aged ambient air (24-hour samples). [4] The ambient samples were collected in areas with widely different atmospheric chemical characteristics (e.g., degree of photochemical activity, source composition, geographic location). Measurements of this ratio from a number of source samples give insights into the relative black to total carbon ratio of primary emissions and the source variabilities. Secondary material will not contain the black component but will increase the total mass of carbon and therefore reduce the black to total carbon fraction. That is, under high photochemical conditions one would expect this ratio to be significantly smaller than under conditions obviously heavily influenced by sources.

Because of the large number of samples that had to be analyzed, a fast-throughput optical attenuation method [2] was used for determining black carbon. This optical attenuation method compares the transmission of a 633-nm He-Ne laser beam through a loaded filter relative to that of a blank filter. The relationship between the optical attenuation and the black carbon content can be written as:

$$[C_{black}] = (1/K) \times ATN , \quad (1)$$

where $ATN = -100 \ln(I/I_0)$. I and I_0 are the transmitted light intensities for the loaded filter and for the filter blank.

Besides the black carbon, particulate material also contains organic material which is not optically absorbing. The total amount of particulate carbon is then

$$[C_{tot}] = [C_{black}] + [C_{org}] . \quad (2)$$

We define specific attenuation (σ) as the attenuation per unit mass of total carbon:

$$\sigma \equiv \frac{ATN}{[C_{tot}]} = K \times [C_{black}]/[C_{tot}] . \quad (3)$$

The determination of specific attenuation therefore gives an estimate of black carbon as a fraction of total carbon.

The proportionality constant K, which is equal

to the specific attenuation of black carbon alone, was recently shown to have an average value of 20. [4] In principle the percentage of soot (i.e., primary carbonaceous material) in ambient particles can be determined from the ratio of ambient specific attenuation and an average specific attenuation of major primary sources [3]:

$$[\text{Soot}]/C = \sigma_{\text{ambient}}/\sigma_{\text{source}} \quad . \qquad (4)$$

Table 1 lists the average and extreme values of specific attenuation and the black carbon fraction of a number of source samples.

The percentage of soot in ambient carbonaceous particulates can be estimated by comparing the σ of sources with that of ambient samples. The fraction of soot is given in Eq. 4. Table 2 lists the mean specific attenuation of ambient samples (weekends excluded) in order of decreasing σ and soot fractions obtained by using Eq. 4 and $\sigma_{\text{source}} = 5.85$.

These results demonstrate that soot is certainly a major fraction of ambient particulate carbon at all locations studied. These findings also suggest that in the atmosphere there is a catalytically active material which is present in high concentrations.

Soot-Catalyzed SO_2 Oxidation

In this section we review some of our laboratory results on heterogeneous oxidation on soot particles in air and present results of numerical calculations which suggest that soot-catalyzed oxidation can be an important mechanism for sulfate formation in the atmosphere.

Novakov et al. [5,6] used photoelectron spectroscopy (ESCA) to study the oxidation of SO_2 on soot particles produced by a propane flame. They 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. The reaction product is in a 6^+ oxidation state (i.e., sulfate).
2. Soot-catalyzed oxidation of SO_2 is more efficient at a higher humidity.
3. The oxygen in air plays an important role in SO_2 oxidation.
4. Soot-catalyzed oxidation exhibits a saturation effect.
5. SO_2 can be oxidized on other types of graphitic carbonaceous particles, such as ground graphite particles and activated carbon.

Soot-catalyzed SO_2 oxidation can proceed by two mechanisms: a "dry" mechanism, in the presence of water, and a "wet" mechanism, when the soot particles are covered by a liquid water layer. The experiments mentioned above involved the dry mechanism. The wet mechanism is much more efficient than the dry and is applicable to situations in plumes, clouds, fogs, and the ambient atmosphere when the aerosol particles are covered with a liquid water layer. The dry mechanism is expected to operate in stacks or under conditions of low relative humidity.

A description of the dry mechanism was given by Yamamoto et al. [7], who studied the reaction kinetics on dry activated carbon in the presence of O_2 and H_2O vapor. The rate of reaction was found to be first order with respect to SO_2, provided that the concentration of SO_2 was less than 0.01%, and depended on the square root of the concentration of O_2 and H_2O vapor. The activation energy was found to vary from -4 to -7 kcal/mole between 70°C and 150°C, depending on the origin of the activated carbon. The rate is constant for a given activated carbon until the amount of accumulated H_2SO_4 reaches about 10% by weight of the carbon. Beyond that amount, the rate gradually decreases with the reaction time until the micropore volume is filled up by H_2SO_4. The reaction continues only on the macropores at a constant, but much slower, rate.

The dry mechanism is relatively inefficient because the reaction product remains on the carbon surface and acts as the catalyst poison. The situation is entirely different when soot (or another carbon) is covered with a layer of liquid water and the catalytic oxidation occurs at the solid-liquid interface: there is constant regeneration of active sites because the reaction product is soluble in water and therefore leaves the soot surface.

Such reactions were studied in detail by Chang et al. [8] and Brodzinsky et al., [9] who used both combustion soots and activated carbons. These studies used suspensions of activated carbon in water to which different concentrations of sulfurous acid were added. The results of these studies can be summarized as follows:

1. The reaction rate is first order and 0.69th order with respect to the concentration of carbon and dissolved oxygen respectively.
2. The reaction rate is effectively pH independent (pH < 7.6).
3. The activation energy of the reaction is 11.7 kcal/mole.
4. There is a mass balance between the consumption of sulfurous acid and the production of sulfuric acid.
5. The reaction rate has a complex dependence on the concentration of H_2SO_3, ranging between a second and zeroth order reaction.

The oxidation of S(IV) to S(VI) can be expressed simply by the symbolic net reaction,

$$2S(IV) + O_2 \rightarrow 2S(VI) \quad .$$

(For this and the following reactions, let C_x = carbon surface; $S(IV) \equiv H_2O{\cdot}SO_2$, HSO_3^-, and $SO_3^=$; $S(VI) = HSO_4^-$, and $SO_4^=$.) The experimental results yield the following empirical rate law for this reaction: (5)

$$\frac{d[S(VI)]}{dt} = k[C_x][O_2]^{0.69} \frac{\alpha[S(IV)]^2}{1 + \beta[S(IV)] + \alpha[S(IV)]^2} \quad ,$$

where $k = 1.69 \times 10^{-5}$ moles$^{-.31}{\cdot}\ell^{.69}$/g·sec,

$\alpha = 1.50 \times 10^{12}\ \ell^2/\text{mole}^2$,

$\beta = 3.06 \times 10^6\ \ell/\text{mole}$,

$[C_x]$ = grams of carbon/ℓ,

$[O_2]$ = moles of dissolved oxygen/ℓ, and

$[S(IV)]$ = total moles of S(IV)/ℓ.

Using the Arrhenius equation, the rate constant may be expressed as

$$k = Ae^{-E_a/RT} \quad ,$$

where E_a = 11.7 kcal/mole, and

$$A = 9.04 \times 10^3 \text{ moles}^{\cdot.31}\cdot\ell^{\cdot.69}/\text{g}\cdot\text{sec}.$$

The reaction rate's being first order with respect to the activated carbon catalyst is representative of a surface catalysis. The reaction will then proceed via the adsorption of the reaction species onto a catalytically active site. A series of adsorption steps can explain the fractional and varying order of reaction with respect to O_2 and S(IV) and were proposed [8,9] in the following four-step reaction:

$$C_x + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_x\cdot O_2 \quad (6)$$

$$C_x\cdot O_2 + S(IV) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C_x\cdot O_2\cdot S(IV) \quad (7)$$

$$C_x\cdot O_2\cdot S(IV) + S(IV) \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} C_x\cdot O_2\cdot S^2(IV) \quad (8)$$

$$C_x\cdot O_2\cdot S^2(IV) \xrightarrow{k_4} C_x + 2S(VI) \quad (9)$$

Chang et al. [10] have carried out box-type calculations to compare the relative importance of sulfate production mechanisms by soot particles and other mechanisms involving liquid water. The following initial conditions were used in the calculation: liquid water, 0.05 g/m^3; SO_2, 0.01 ppm; O_3, 0.05 ppm; NH_3, 5 ppb; and CO_2, 0.000311 atm. Concentrations of particulate Fe and Mn of 250 ng/m^3 and 20 ng/m^3 respectively were assumed. However, only 0.13% of the total iron and 0.25% of the Mn are water soluble, according to Gordon et al. [11] The concentration of soot was taken as 10 μg/m^3.

The results of this calculation, shown in Fig. 1, indicate that O_3 and soot can be important mechanisms for sulfate aerosol formation. In general the O_3 mechanism is more important under high pH and/or photoactivity conditions when the concentration of O_3 is high, whereas the soot process is more important when the lifetime of fog or clouds is long and the pH of the droplets is low.

Acknowledgment

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References

1. H. Rosen, T. Novakov, and B.A. Bodhaine, "Soot in the Arctic," Atmos. Environ. 15, 1371 (1981).
2. H. Rosen, A.D.A. Hansen, R.L. Dod, and T. Novakov, "Soot in urban atmospheres: Determination by an optical absorption technique," Science 208, 741 (1980).
3. T. Novakov, "Microchemical characterization of aerosols," in Nature, Aim, and Methods of Microchemistry, H. Malissa, M. Grasserbauer, and R. Belchers, eds. (Vienna, Springer-Verlag, 1981), p. 141.
4. A.D.A. Hansen et al., "The use of an optical attenuation technique to estimate the carbonaceous component of urban aerosols," in Atmospheric Aerosol Research Annual Report FY-1979, Lawrence Berkeley Laboratory Report LBL-10735 (1980), p. 8.
5. T. Novakov, "Chemical characterization of atmospheric pollution particulates by photoelectron spectroscopy," in Proceedings, 2nd Joint Conference on Sensing of Environmental Pollutants (Pittsburgh, Instrument Society of America, 1973), p. 197.
6. T. Novakov, S.G. Chang, and A.B. Harker, "Sulfates as pollution particulates: Catalytic formation on carbon (soot) particles," Science 186, 259 (1974).
7. K. Yamamoto, M. Seki, and K. Kawazoe, "Absorption of sulfur dioxide on activated carbon in the flue gas desulfurization process. III. Rate of oxidation of sulfur dioxide on activated carbon surfaces," Nippon Kagaku Kaishi 6, 1046 (1972).
8. S.G. Chang, R. Brodzinsky, R. Toossi, S.S. Markowitz, and T. Novakov, "Catalytic oxidation of SO_2 on carbon in aqueous suspensions," in Proceedings, Conference on Carbonaceous Particles in the Atmosphere, Lawrence Berkeley Laboratory Report LBL-9037 (1979), p. 122.
9. R. Brodzinsky, S.G. Chang, S.S. Markowitz, and T. Novakov, "Kinetics and mechanism for the catalytic oxidation of sulfur dioxide on carbon in aqueous suspensions," J. Phys. Chem. 84, 3354 (1980).
10. S.G. Chang, R. Toossi, and T. Novakov, "The importance of soot particles and nitrous acid in oxidizing SO_2 in atmospheric aqueous droplets," Atmos. Environ. 15, 1287 (1981).
11. G.E Gordon, D.D. Davis, G.W. Israel, H.E. Landsberg, and T.C. O'Haver, Atmospheric Impact of Major Sources and Consumers of Energy, Report NSF/RA/E-75/189 (1975).

Table 1. Specific attenuation (σ) and black carbon (BC)(% of total C) of source samples.

Source	No. of samples	Average σ	Average % BC	Highest σ	Highest % BC	Lowest σ	Lowest % BC
Parking garage	12	5.4	27	7.7	39%	2.25	11
Diesel	6	5.6	28	5.7	29%	3.5	18
Scooter	9	5.1	26	6.1	31%	4.2	21
Tunnel	63	6.3	32	12.5	63%	3.7	19
Natural gas	6	2.6	13	3.3	17%	1.9	10
Garage and tunnel		5.86	29				

Table 2. Mean specific attenuation of ambient samples.

Site	No. of samples	$\bar{\sigma}$	SDEV	Soot (%)
New York	211	5.69	1.34	97
Gaithersburg	155	4.72	1.51	81
Argonne	221	4.35	1.64	74
Berkeley	513	4.28	1.47	73
Anaheim	444	3.99	1.71	68
Fremont	461	3.74	1.25	64
Denver	42	3.47	1.49	59

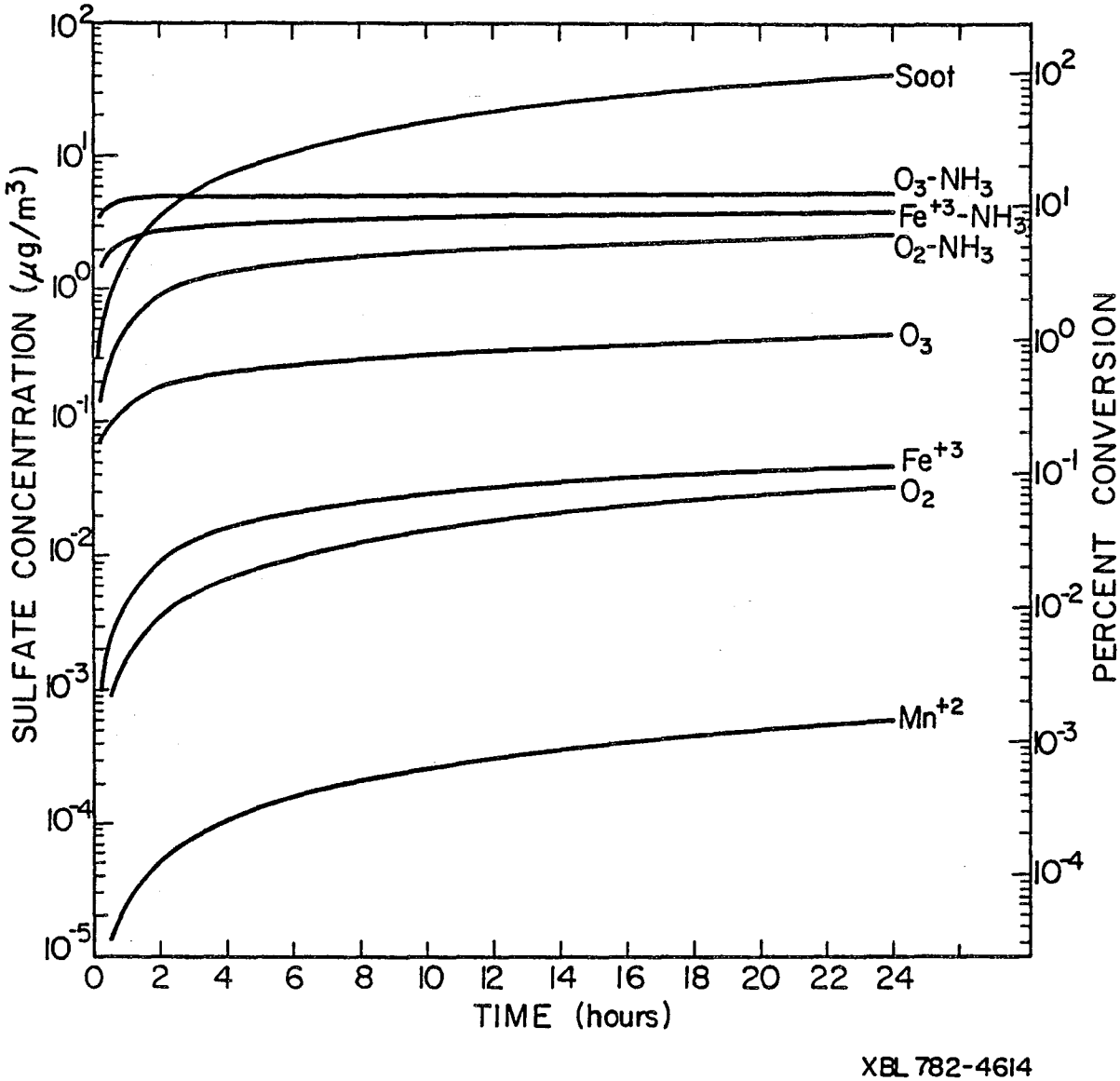

Figure 1. Comparison of the relative significance of various SO_2 conversion processes in aqueous droplets.

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