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THE ROLE OF SOOT AND PRIMARY OXIDANTS IN ATMOSPHERIC CHEMISTRY*

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ABSTRACT

This paper discusses the role of soot in atmospheric sulfur chemistry. A methodology for estimating the primary and secondary particulate carbon concentrations is outlined. The relationship between ambient SO_2 , sulfate, and primary carbon is examined; and certain regularities in their behavior are defined. An explanation of these regularities is proposed, based on a mechanism involving oxygen chemisorbed on combustion-generated carbon particles and its subsequent reaction with aqueous sulfite.

INTRODUCTION

Carbon is the largest elemental fraction of atmospheric aerosol particles and is found in many different chemical and physical forms. These carbonaceous particles play important roles in atmospheric chemistry and physics and are crucially involved in a number of ecological and environmental effects, including human health. These may be broadly classified according to their origin or structure, using the following definitions:

Total carbon, C - Total particulate carbonaceous material.

Black carbon, C_b - Combustion-produced black particulate carbon having a graphitic microstructure.

Primary carbon, C' - Particulate carbon derived directly from sources, being the sum of primary organic species, C'_o , and black carbon. The term "soot," C_s , is synonymous with primary carbon derived from combustion.

Secondary carbon, C'' - Organic particulate carbon formed by atmospheric reactions from gaseous precursors, defined as $C'' = C - C'$.

The units of all these quantities are micrograms of carbon, either per cubic meter of air or per square centimeter of filter.

This paper discusses 1) methods for determining the concentrations of primary and secondary carbonaceous material, 2) an examination of evidence that suggests a chemical link between the carbonaceous fraction and other aerosol species such as sulfates, and 3) the role of primary carbonaceous species in the atmospheric

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oxidation of sulfur dioxide to particulate sulfate. The discussions are limited mostly to polluted atmospheres where combustion is the principal direct or indirect source of carbonaceous aerosol particles.

DETERMINATION OF PRIMARY AND SECONDARY CARBON

Two methods for determining the relative abundances of primary and secondary carbon in ambient particles will be discussed. The first uses a fast and simple technique to measure the black carbon component, C_b , and compares the ambient C_b/C (black carbon/total carbon) to the ratio C_b/C for sources and source-dominated sites (ref.1). The second approach relies on the more elaborate methodology of evolved gas analysis (EGA) to obtain characteristic "signatures" of primary and secondary carbon components (ref.2).

The first approach uses the laser transmission method (LTM) (ref.3) to measure the black carbon concentration on a filter by its optical absorption. The method has been shown to be linear, sensitive, and free of interferences for ambient samples (ref.4). It gives a measurement of the optical attenuation $ATN = \sigma C_b$, proportional to the surface concentration of black carbon on a filter. The total carbon concentration C is determined by a conventional combustion technique.

Specific attenuation $\Sigma = ATN/C = \sigma \cdot C_b/C$ gives the ratio of black to total carbon. Primary particulates contain black carbon and primary organics (C'_o) and have a specific attenuation of $\Sigma' = \sigma \cdot C_b/(C_b + C'_o)$. Gas-to-particle conversion mechanisms contribute secondary carbon, C'' , to the particles but cannot produce black carbon. The specific attenuation of such a mixed carbon aerosol sample is then $\Sigma = \sigma \cdot C_b/(C_b + C'_o + C'')$. The inclusion of C'' in the denominator reduces Σ , so that the fraction of primary carbon may be determined by the relation $[C'/(C' + C'')] = \Sigma/\Sigma'$. The validity of this approach depends on the constancy of Σ' for primary ambient carbonaceous particles. In Fig. 1 we show the

Fig. 1. Monthly average specific attenuation values, Σ , for Manhattan. Σ' is the adopted value for primary carbon. The range of Σ values for automotive sources is also shown.

range of Σ values for samples from automotive sources and the monthly average values for ambient samples collected in Manhattan, New York. This location is heavily impacted by vehicular and local stationary sources, and we therefore expect its carbonaceous aerosol to be dominantly primary in character. The data show this constancy, without seasonal effects and with a mean similar to the mean value for sources. The mean Σ value for Manhattan, 5.7 ± 0.5 , will be adopted as the Σ' value for this discussion. Fig. 2 shows monthly average Σ/Σ' ratios, total carbon, and calculated primary carbon data for samples from Anaheim (southern California). It is clear that the Σ values for Anaheim are significantly lower than for New York and that they show a seasonal variability with lowest values (i.e., highest C''/C) during the summer. Time-resolved California samples also tend to show lower values in the daytime than at night (ref.5). These results are consistent with the photochemical production of secondary carbonaceous particulate matter.

Figure 2. Monthly average Σ/Σ' ratios, total carbon C , and primary carbon C' concentrations for Anaheim, California.

The method described above is suitable for the rapid study of large numbers of samples, with the objective of determining average compositional properties. For more detailed studies of the composition of individual samples, evolved gas analysis (EGA) can be used (refs.2,6,7). In this method, a small punch taken from a quartz fiber filter sample is heated at a constant rate in an oxidizing (O_2) or neutral (N_2) atmosphere. The evolved gases are passed over an oxidizing catalyst to convert all carbonaceous gases to CO_2 , which is then detected by a CO_2 analyzer. The carbon evolution rate plotted as a function of sample temperature gives the carbon "thermogram." By simultaneous measurement of the optical

attenuation, a high-temperature peak corresponding to the decomposition of the black carbon component can be identified. The EGA-based approach to the differentiation of primary and secondary fractions depends on the construction of an average thermogram for primary carbonaceous material. After normalization of the black carbon peak (because this is unchanged by secondary mechanisms), the difference between the thermogram of an ambient sample and the primary thermogram is due to the secondary carbon. This method was used to estimate the primary and secondary carbon in a number of samples from the Los Angeles area, collected during intense smog episodes when the highest concentrations of secondary carbon are expected (ref.8). The samples were collected simultaneously at a receptor site (Duarte) and a source-dominated site (Lennox).

The potential of the EGA method is illustrated in Fig. 3, with thermograms of a daytime and a nighttime sample from the receptor site. The common features of both are the black carbon peak, δ , and the group of volatile organic species, α . However, only the daytime sample shows the presence of β and γ peaks. Because thermograms of the nighttime samples from this location were found to be similar to those at the source-dominated site, the β and γ peaks have been identified as belonging to secondary carbon. Detailed descriptions of the procedure and discussions of the chemical nature of secondary carbon are presented in ref. 8. The results of these analyses agree well with theoretical source apportionment calculations (ref.9).

Fig. 3. Carbon thermograms for a daytime and a nighttime sample collected at a receptor site (Duarte) in southern California. α represents volatile species, β and γ have been assigned to secondary carbon, and δ is the black carbon peak.

THE ROLE OF SOOT AND PRIMARY OXIDANTS IN SO₂ OXIDATION

Correlations between sulfate concentration and soot or total carbon concentration have been observed first in Sweden (ref.10) and subsequently in California (ref.11), even during intense photochemical smog conditions (ref.12). It is striking to find such similar behavior at locations so different. To better understand the causes of these correlations, we have initiated several collaborative field sampling programs. This discussion will present the most pertinent results from studies in New York City (ref.13); Anaheim, California (ref.13); and Ljubljana, Yugoslavia (ref.14). Twenty-four-hour ambient samples were collected on open-face 47-mm quartz fiber and Millipore filters. These samples were analyzed for total carbon, black carbon, and particulate sulfur. A number of samples were also analyzed by EGA. In Ljubljana, average 24-hour SO₂ concentrations were also determined.

The samples from Ljubljana are particularly interesting because there are high concentrations of pollutants during winter, when almost all the particulate carbon is primary and photochemical processes are negligible. Daily concentrations of particulate sulfur (mostly present as sulfate), carbon, and SO₂ are shown in Figs. 4a, b, and c, which show clearly that SO₂ and carbon concentrations exhibit a similar pattern, suggesting common sources. It is also evident

Fig. 4. Twenty-four-hour average concentrations of a) particulate sulfur S, b) primary carbon C', and SO₂. S/C' ratios are also shown.

that the variations of particulate sulfur and carbon are similar. We may examine these similarities more quantitatively by means of the S/C' ratios (here, $C = C'$, ref.14), which are shown in Fig. 4d.

Figure 4d shows that the S/C' ratio is relatively constant after the C' concentration reaches $\sim 30 \mu\text{g}/\text{m}^3$. At lower C' concentrations, this ratio is higher by approximately a factor of 2. This behavior is shown in Table 1, which gives the average Ljubljana S/C' ratio for several C' concentrations. Average S/C'

TABLE 1

Average sulfur to primary carbon ratios.

C' ($\mu\text{g}/\text{m}^3$)	LJBA ^a	NYC ^b	S/C' ANAC ^c	BRW ^d	SWE ^e
<5				0.5 $\pm$ 0.1	0.40
10	} 0.26 $\pm$ 0.08 } 0.23 $\pm$ 0.03 } 0.14 $\pm$ 0.05 } 0.14 $\pm$ 0.03	} 0.19 $\pm$ 0.07	} 0.28 $\pm$ 0.10		} 0.22 ^f
20					
30					
60					
>60					

^aLJB - Ljubljana; 70 samples taken Sept., Oct., Nov., Dec. 1981.

^bNYC - New York City; 56 samples taken Feb., March, April, May, June 1979.

^cANA - Anaheim; 48 samples taken Sept., Oct., Dec. 1977.

^dBRW - Barrow; 12 samples taken Jan., Feb., March 1983.

^eSWE - Sweden; samples taken Oct., Nov., Dec. 1974, Jan. Feb., March 1975.

^fFrom ref. 16.

ratios corresponding to different C' concentration ranges from several other locations are also presented. Included are our data for Manhattan (ref.13), Anaheim (ref.13), and Barrow, Alaska (ref.15). Swedish data for S/soot ratios are taken from ref. 16. For Manhattan, it was assumed that $C = C'$, while Anaheim and Barrow data use values of C' calculated by methods described earlier. The ratios from these entirely different locations show remarkably consistent behavior with respect to C' concentrations (see Fig. 5).

Detailed analysis of these data shows the following general regularities:

- For the same range of C' concentration, the S/C' ratio is approximately the same at all locations studied.
- The S/C' ratio increases at low concentrations.
- Only a fraction of the available sulfur is converted to sulfate.
- Once particulate sulfur has formed, there is no evidence for significant further oxidation of SO₂ to sulfate.

Most atmospheric oxidation processes dependent on SO₂ concentrations would lead to concentrations of S uncorrelated with those of C', depending instead on conditions of meteorology, stagnation, solar radiation, etc. Primary sulfate emission, if strictly defined as the high-temperature oxidation product of fuel sulfur, is inadequate in magnitude and insufficiently correlated with soot emission to explain the data. The remainder of this paper outlines a theory that

Fig. 5. Average S/C' ratios for different C' concentrations. The data are for Manhattan (NYC); Ljubljana, Yugoslavia (LJB); Anaheim, California (ANA); Sweden (SWE) (from ref. 16); and Barrow, Alaska (BRW) (from ref. 15).

can semiquantitatively explain the observed behavior of ambient particulate sulfate. This theory involves two mechanisms: 1) the reaction of sulfite with oxygen chemisorbed on water-covered soot particles and 2) the reaction of sulfite with primary combustion-generated peroxides.

The role of soot in the oxidation of SO_2 to sulfate has been extensively studied in our laboratory using both combustion-produced soots and activated carbon (ref. 17). The principal features of this oxidation process are illustrated in Fig. 6, which shows sulfite and sulfate concentrations as a function of time after a known amount of dry activated carbon is added to a dilute sulfite solution. It is clear that the oxidation proceeds in two stages. The first (I in Fig. 6) causes the initial disappearance of sulfite and the formation of sulfate. This is a very fast process that could not be followed by the analytical techniques used. The second stage (II in Fig. 6) is a slower process, resulting in a gradual linear conversion of sulfite to sulfate. The mechanism and kinetics of the stage II process have been studied in detail (ref. 17), and its significance in atmospheric sulfate formation has been assessed (refs. 18, 19). This second stage process cannot fully explain by itself the observed regularities for ambient sulfate.

The first stage process, however, has features qualitatively similar to those inferred from the analysis of ambient samples. Fig. 6b shows that the amount of sulfite oxidized is linearly proportional to the concentration of carbon; Fig. 6c shows that for a fixed carbon concentration, the amount of sulfate produced saturates despite a considerable excess of available sulfite. Such a process in the atmosphere would produce sulfate in proportion to carbon, i.e., a constant S/C' ratio, and would consume only part of the total available SO_2 .

Figure 6. a) Soot-catalyzed SO_2 oxidation, showing the fast (stage I) and slower (stage II) processes. b) Initial drop in sulfite concentration vs. carbon for constant sulfite concentration. c) Initial drop in sulfite concentration vs. sulfite concentration for constant carbon concentration.

Based on the known mechanism of carbon-catalyzed reaction (ref.17), the following scenario is proposed to explain the formation of particulate sulfate. When freshly formed soot particles are exposed to air, oxygen is chemisorbed onto the surface and becomes "activated" by the adsorption process. As the combustion effluent cools, a film of liquid water will condense on the particles, in which SO_2 can dissolve. When this aqueous sulfite gets in contact with the active oxygen at the solid-liquid interface, it will immediately react to form sulfate. The product sulfate dissolves in the water, leaving the surface temporarily free of oxygen. This constitutes the rapid stage I process. Dissolved oxygen from the water will slowly diffuse to the carbon surface to form a similar surface oxygen complex, which will also react with aqueous sulfite. This process is diffusion controlled and is responsible for the slower (stage II) catalytic oxidation process. Because these processes occur on the liquid-solid interface, a few monolayers of condensed water are sufficient. The rapid (stage I) process will lead to sulfate formation in the plume as soon as conditions for the condensation of liquid water and solution of SO_2 have been reached. Particulate sulfate will be formed by this mechanism relatively close to the source and could therefore be termed quasi-primary sulfate.

Soots produced by combustion of propane, natural gas, and automotive (tunnel) soot have been found to behave qualitatively like activated carbon. From graphs like the one in Fig. 6b, S/C' ratios for the fast oxidation stage are derived for different carbons: 0.004, 0.05, and 0.1 for activated carbon, tunnel soot, and natural gas, respectively. The latter two agree well with the lower ranges of S/C' ratios determined from ambient measurements (c.f. Fig. 4).

The following arguments show the consistency of these results with the proposed surface chemical mechanism. Assuming that each sulfite ion occupies an area of $3 \times 10^{-15} \text{ cm}^2$ on the surface at the time of reaction, one gram of activated carbon must have a solid-liquid interfacial area of approximately 22 m^2 in order to accommodate 0.004 grams of sulfur. This area is about 5% of the surface area obtained by nitrogen adsorption. This result seems correct because most of the gas-solid surface area is the internal pore area that may not be available to reactions of the liquid-solid interface. The liquid-solid interface areas calculated for tunnel soot and natural gas soot are $280 \text{ m}^2/\text{g C}$ and $560 \text{ m}^2/\text{g C}$, which are reasonable because soot particles immediately after formation have diameters from about 50 to a few thousand Ångströms. Such particles have surface areas of hundreds of meters square per gram.

During the short time when sulfate formation occurs, most of the particle surface area is available for reaction. After residing in the atmosphere, the surfaces become covered with sulfate as well as other species, resulting in a surface that is chemically and physically different and generally less active. Recent research in our laboratory has shown that aged ambient aerosol particles, in contrast to source particles, are practically inactive as catalysts for SO_2 oxidation (ref.20).

From the foregoing discussion, it is plausible that surface reactions on soot particles can produce enough particulate sulfur to account for at least the lower limit of the S/C' ratios observed in ambient air. There are at least two possible explanations for the higher S/C' ratios. The apparently systematic increase of the S/C' ratio at low carbon concentrations could be related to the lack of size segregation of the samples used in our studies. Large particles, more likely to be present at high carbon concentrations, have lower S/C' ratios because they have low specific surface areas. Additional particulate sulfur can be produced after longer reaction times by the slower (stage II) oxidation process, which could also be enhanced by nitrogen oxides (ref.21), or by the SO_2 oxidation mechanisms involving peroxide-type primary oxidants.

The concept of primary oxidants in the context of atmospheric chemistry is new because it is generally assumed that all oxidants, including peroxides, are secondary in origin. However, it is known (ref.22) that hydrogen peroxide and organic peroxides are formed in precombustion reactions, and under conditions of incomplete combustion, could appear in the effluent. We have recently demonstrated that propane flames and internal combustion engines emit substantial amounts of hydrogen peroxide and organic hydroperoxides, which rapidly oxidize sulfite to sulfate when dissolved in water (ref.23). Their emission rates per unit of fuel consumed depend greatly on the combustion conditions. For example, a very turbulent propane flame produces more peroxide than a steady diffusion flame. This in turn produces more than a premixed propane-air flame, and a

premixed propane-oxygen flame produces the least. These results imply that more primary peroxides will be produced by sooty flames than by nonsooty ones. The sulfate produced by the reaction of primary peroxides would therefore generally follow the soot concentrations, thereby retaining the S-C' correlation. The reactions involving primary oxidants, in addition to forming particulate sulfates, may play a role in cloud and fog chemistry, and thus contribute to the overall atmospheric sulfate burden.

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