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THE ROLE OF CARBON PARTICLES IN ATMOSPHERIC CHEMISTRY

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Publication Date
1982
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January 1982
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Carbonaceous particles in the atmosphere consist of two major components--graphitic or black carbon (sometimes referred to as elemental or free carbon) and organic material. The latter can be either directly emitted from sources (primary organics) or...
produced by atmospheric reactions from gaseous precursors (secondary organics). For the sake of clarity, we define soot as the total primary carbonaceous material, i.e., the sum of black carbon and primary organics. Black carbon is a chemically and catalytically active material and can be an effective carrier for other toxic air pollutants through their adsorptive capability. The chemical, adsorptive, and catalytic behaviors of black carbon particles depend very much on their crystalline structure, surface composition, and electronic properties. This paper discusses these properties and examines their relevance to atmospheric chemistry.

The assessment of the chemical role of black carbon in the atmosphere in general, and in photochemical environments such as Los Angeles in particular, had to start with an empirical assessment of the black carbon concentrations. While at one time the presence of soot in the atmosphere of industrial cities was obvious, it became less obvious in more recent times. Improvements in combustion technology and the use of better-grade fuels have led to the virtual elimination of visible smoke emissions. The emphasis of air pollution control thus shifted away from primary particulate emissions toward controlling gaseous emissions, especially in view of the newer concept of Los Angeles-type photochemical smog, which was believed to contain neither smoke nor fog. According to such a view, the haze over the Los Angeles Air Basin on polluted days is due almost entirely to the
photochemical conversion of certain invisible gases to light-scattering particles consisting of sulfates, nitrates, and secondary organics but almost no soot. The results of our 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 (Rosen et al., 1981). Los Angeles, with its abundant coastal fog, contains both components of London-type fog—smoke (or soot) and fog.

2. ABUNDANCE

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) (Hansen et al., 1980). 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 (Rosen et al., 1980) was used for determining black carbon. The validity of the optical attenuation method was checked by performing Raman spectroscopic (Rosen et al., 1978) and opto-acoustic (Yasa et al., 1978) measurements on some of the ambient and source samples. Total particulate carbon was determined by a combustion method.

The 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:

\[ [C_{\text{black}}] = \frac{1}{K} \times \text{ATN}, \]  
(1)

where \( \text{ATN} = -100 \ln(I/I_0) \). \( I \) 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

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

We define specific attenuation (\( \sigma \)) as the attenuation per unit mass of total carbon:
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 (Hansen et al., 1980). 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 (Novakov, 1981):

$$\frac{[\text{Soot}]}{C} = \frac{\sigma_{\text{ambient}}}{\sigma_{\text{source}}}.$$  \hspace{1cm} (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 $\sigma$ 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 $\sigma$ and soot fractions obtained by using Eq. 4 and $\sigma_{\text{source}} = 5.85.$
Table 1. Specific attenuation ($\sigma$) and black carbon (BC) (% of total C) of source samples.

<table>
<thead>
<tr>
<th>Source</th>
<th>Number of samples</th>
<th>Average $\sigma$</th>
<th>Average % BC</th>
<th>Highest $\sigma$</th>
<th>Highest % BC</th>
<th>Lowest $\sigma$</th>
<th>Lowest % BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parking garage</td>
<td>12</td>
<td>5.4</td>
<td>27</td>
<td>7.7</td>
<td>39</td>
<td>2.25</td>
<td>11</td>
</tr>
<tr>
<td>Diesel</td>
<td>6</td>
<td>5.6</td>
<td>28</td>
<td>5.7</td>
<td>29</td>
<td>3.5</td>
<td>18</td>
</tr>
<tr>
<td>Scooter</td>
<td>9</td>
<td>5.1</td>
<td>26</td>
<td>6.1</td>
<td>31</td>
<td>4.2</td>
<td>21</td>
</tr>
<tr>
<td>Tunnel</td>
<td>63</td>
<td>6.3</td>
<td>32</td>
<td>12.5</td>
<td>63</td>
<td>3.7</td>
<td>19</td>
</tr>
<tr>
<td>Natural gas</td>
<td>6</td>
<td>2.6</td>
<td>13</td>
<td>3.3</td>
<td>17</td>
<td>1.9</td>
<td>10</td>
</tr>
<tr>
<td>Garage and tunnel</td>
<td></td>
<td>5.85</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Mean specific attenuation of ambient samples.

<table>
<thead>
<tr>
<th>Site</th>
<th>Number of samples</th>
<th>Standard deviation</th>
<th>Soot (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>New York</td>
<td>211</td>
<td>5.69</td>
<td>1.34</td>
</tr>
<tr>
<td>Gaithersburg</td>
<td>155</td>
<td>4.72</td>
<td>1.51</td>
</tr>
<tr>
<td>Argonne</td>
<td>221</td>
<td>4.35</td>
<td>1.64</td>
</tr>
<tr>
<td>Berkeley</td>
<td>513</td>
<td>4.28</td>
<td>1.47</td>
</tr>
<tr>
<td>Anaheim</td>
<td>444</td>
<td>3.99</td>
<td>1.71</td>
</tr>
<tr>
<td>Fremont</td>
<td>461</td>
<td>3.74</td>
<td>1.25</td>
</tr>
<tr>
<td>Denver</td>
<td>42</td>
<td>3.47</td>
<td>1.49</td>
</tr>
</tbody>
</table>
Based on this estimate, the New York City carbonaceous aerosol is essentially primary soot. A different value of $\sigma_{\text{source}}$ would certainly change the estimated soot percentage. However, New York City's average soot content would nevertheless remain the highest, irrespective of the actual numerical value of $\sigma_{\text{source}}$. It is logical that samples from this location have the highest soot content because the site represents a heavily traveled street canyon. Fremont and Anaheim samples have the smallest soot content on the average, as might be expected, because both sites represent receptor sites.

These results demonstrate that black carbon 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 so that the assessment of its role in heterogeneous atmospheric chemistry is warranted.

3. COMPOSITION

3.1. Bulk Structure

The diameter of black carbon particles varies from 50 Å or even smaller to several thousand Angstroms. The results of x-ray diffraction (Hofmann and Wilm, 1936) have shown that each particle is made up of a large number of crystallites 20 to 30 Å in diameter. Each crystallite consists of several carbon layers with a graphitic hexagonal structure, having defects, dislocations, and discontinuities.
in the layer planes, and thus containing high concentrations of unpaired electrons which constitute the active sites. Carbon atoms located at these sites show strong tendencies to react with other molecules because of residual valencies. During particle formation, interactions of air, water, flue gas, etc., with carbon particles occur, resulting in the incorporation of 5-15% oxygen, 1-3% hydrogen, and traces of nitrogen into the structure.

3.2. Surface Functional Groups

Nearly every type of oxygen-containing functional group known in organic chemistry has been postulated to exist on the carbon surface (Figure 1). The functional groups most often suggested are carboxyl groups, phenolic hydroxyl groups, and quinone carbonyl groups (Garten and Weiss, 1957; Boehm, 1966; Coughlin and Ezra, 1968; Puri, 1970, 1966; Smith, 1959; Zary'yanz et al., 1967). Less often suggested are ether, peroxide, and ester groups in the forms of normal and fluorescein-like lactones (Garten et al., 1957), carboxylic acid anhydrides (Boehm et al., 1964), and cyclic peroxide (Puri, 1962). The relative amounts of these complexes and their structure depends on the thermal history of carbon particles (Hart et al., 1967; Laine et al., 1963; Palmer and Cullis, 1965; Weller and Young, 1948). Little is known about the structure of surface nitrogen species, although the capability of fixation of nitrogen (Emmett, 1948) in carbon particles and the promoting effect of the catalytic activity
of nitrogenous carbon (Larsen and Walton, 1940) have been observed. Therefore, black carbon particles may be regarded as a complex three-dimensional organic polymer with the capability of transferring electrons, rather than merely as an amorphous form of elemental carbon.

4. ACIDITY

Depending on the thermal history, black carbon particles may possess either acidic or basic character. Because of this property, soot may influence the pH of atmospheric water droplets (Chang and Novakov, 1975). It has been shown that activation of elemental carbon by exposure to \( \text{O}_2 \) at temperatures between 200 and 400\(^\circ\)C produces an acidic type. By contrast, activation of carbon at high temperatures either in pure \( \text{CO}_2 \) or under vacuum, followed by exposure to oxygen at room temperature, results in a basic type.

The acidic character can be explained by the dissociation of acidic oxygen functional groups such as carboxyl and hydroxyl in solution. The nature of the basic character has been a topic of considerable discussion and controversy (Schilow, Schatunowskja, and Tshmutow, 1930; Rivin, 1963; Frumkin et al., 1931; Steenberg, 1944; Mattson and Mark, 1971). The idea of the presence of basic sites in the form of surface oxides has been proposed by Schilow, Schatunowskja, and Tschmutow (1930), among others, to account for the chemisorption of acids. The latter suggested that the oxides were in the form of a chromene-like structure after neutralization with acid, which would result in the formation of
carbonium ion. The presence of carbonium cationic sites on the surface of acid-treated carbon was confirmed by Rivin (1963), but it could not be established whether the basic sites are due to the presence of the chromene-like surface oxides or the inherent property of the polynuclear aromatic structures of the carbon particles. Frumkin et al. (1931) proposed an electrochemical theory in which the adsorption of the acids by carbon is determined by the electrical potential at the carbon solution interface and by the capacity of the double layer. According to Steenberg (1944), adsorption of acids involved primary adsorption of protons by physical force and secondary adsorption of anions in the diffuse double layer. On the contrary, Mattson and Mark (1971) attributed the neutralization of acids at high acid concentrations to the primary adsorption of the anions and secondary adsorption of the protons.

5. CHEMICAL ACTIVITY

We have investigated the reaction between black carbon particles and \( \text{NH}_3 \) in both an oxidizing and a reducing atmosphere. The first set of experiments involves the exposure of combustion-produced soot with \( \text{NH}_3 \) in air. The nature of nitrogen species thus formed was studied with the aid of ESCA. Soot particles for these experiments were generated by a premixed propane-oxygen flame. The exposure of soot particles to \( \text{NH}_3 \) was done under two different experimental conditions: in a static regime, with propane soot precollected on a silver membrane filter subsequently exposed to the reactant gas
at ambient temperature; and in a flow system, by introducing the reactant gas downstream from the propane-oxygen flame, i.e., while the soot particles are still at high temperature.

ESCA spectra of the nitrogen (1s) region of soot samples prepared in these ways are shown in Figures 2 and 3. Interaction of NH$_3$ with "cold" soot particles can result in ammonium-like species (Figure 2). However, as seen from Figure 3, NH$_3$ interacting with "hot" soot particles produces species with ESCA peaks of binding energies designated as N$_x$ species. Ammonium in these samples is probably produced on soot particles after they have been collected on the filter and cooled down.

Using ESCA to analyze ambient particulates, Novakov et al. (1972) have observed, in addition to commonly occurring nitrate and ammonium, two reduced nitrogen species with N(1s) binding energy corresponding to N$_x$ surface species produced under laboratory conditions. Chemical equivalency of ambient and synthetic N$_x$ species is demonstrated by their thermal behavior. The experimental procedure is to measure ESCA spectra at gradually increasing sample temperatures. The results of such measurements for one ambient particulate sample, collected in Pomona, California, during a moderate smog episode (24 October 1972) and for a sample prepared by NH$_3$-hot soot interaction are shown in Figures 4 and 5.

The spectrum of the ambient sample (Figure 4) at 25°C shows the presence of NO$_3^-$, NH$_4^+$, and N$_x^-$. At 80°C the entire nitrate
peak is lost, accompanied with a similar loss in ammonium peak intensity. The shaded portion of the ammonium peak in the 25°C spectrum represents the ammonium fraction volatilized between 25 and 80°C. It appears therefore that the nitrate in this sample is mainly in the form of ammonium nitrate. At 150°C the only nitrogen species remaining is $N_x$. The ammonium fraction still present at 80°C but absent at 150°C is associated with some ammonium compound more stable than $\text{NH}_4\text{NO}_3$, possibly ammonium sulfate. At 250°C the appearance of another peak, labeled $N'_x$, is seen. This peak continues to increase at 350°C. The total peak areas of spectra recorded at 150, 250, and 350°C remain constant, indicating that the $N_x$ component is transformed into $N'_x$ by heating in vacuum.

$N_x$ species produced by surface reactions of hot soot with $\text{NH}_3$ have the same kind of temperature dependence as the ambient samples. This is illustrated in Figure 5. The spectrum taken at room temperature shows that most nitrogen species in this sample are of the $N_x$ type. Heating the sample in vacuum to 150°C does not influence the line shape or intensity. At 250°C, however, the formation of $N'_x$ is evident. Further transformation of $N_x$ to $N'_x$ occurred at 350°C.

Both ambient and synthetic $N'_x$ species will remain unaltered even if the temperature is lowered back to room temperature if the sample remains in vacuum. However, if the sample is taken out of vacuum and exposed to moisture, $N'_x$ will be transformed back to the original $N_x$ compound. It can be concluded that $N_x$ species are
produced by dehydration of $N_\times$.

The outlined results indicate that the thermal behavior of nitrogen species of the $N_\times$ and $N_\times'$ type observed in ambient pollution particulates is identical to the reduced nitrogen species produced by reactions at elevated temperature of ammonia with finely divided carbon or soot.

Based on these experimental results, $N_\times$ was assigned to a mixture of amines and amides, and $N_\times'$ to nitrile. Since prior to the interaction with NH$_3$, the soot particle surface was in contact with air and flue gas, it therefore should be covered with surface oxygen complexes. By using the most often-mentioned surface oxygen-carbon functional groups (i.e., carboxyl groups and phenolic hydroxyl groups) and in analogy with organic chemistry, we can describe some possible reactions of NH$_3$ and soot leading to the formation of amides, amines, nitriles, and ammonium-salt-like compounds associated with the black carbon component of soot particles.

At low temperatures black carbon covered with surface carboxyl or phenolic groups may act as a Bronsted acid when interacting with NH$_3$. Carboxyl ammonium or phenolic ammonium salts will be formed as the result of proton exchange. Ammonia may also be physically adsorbed by hydrogen bonding to surface OH or COOH groups. At elevated temperatures the carboxyl group carbon is electrophilic and has the tendency to accept an electron pair from the basic species in the process of coordination. The nucleophilic substitution reaction of NH$_3$ with carboxylic acid yields an amide which may
dehydrate and become a nitrile upon further heating. Carboxyl and phenolic hydroxyl ammonium salts may dehydrate at elevated temperature to produce amides and/or nitriles and amines respectively.
The photoelectron spectroscopic results indicate that the amides and amines correspond to the \( N_x \) species. These appear as broad peaks indicating the presence of more than one chemical species. Nitriles formed from amides by dehydration on heating correspond to the \( N'_x \) species. We have established the reversibility of the

\[
N_x + H_2O \rightleftharpoons N'_x - H_2O
\]

process. The carboxyl ammonium and phenolic hydroxyl ammonium salts produced by \( NH_3 \) chemisorption correspond to the volatile ambient ammonium species.

We have studied the stability of ambient particulate nitrogen in water by combining ESCA measurements with determination of total nitrogen by proton activation (Gundel et al., 1979). Our results with samples from several locations (Berkeley, Los Angeles, and St. Louis) indicate that 1) a large fraction of \( N_x \) (85%) originally present in ambient particulate matter can be removed by water extraction; and 2) more \( NH_4^+ \) appears in the extract than was present on the untreated sample and less \( N_x \) appears in the extract than was present on the untreated sample. The \( N_x \) deficiency in the extract matches the surplus in \( NH_4^+ \). The former behavior could be attributed to water-soluble stoichiometric compounds such as amines and surface species such as amides and nitrile which can undergo hydrolysis.
The latter could be attributed to the hydrolysis of amide and nitrile groups. These behaviors may be responsible for the disagreement of chemical composition in black episodes with those predicted from the equilibrium phase diagram as constructed by Brosset (1980).

The other set of experiments (Novakov and Chang, 1977) involves the grinding of a purified grade POCO graphite in NH$_3$ in the absence of air at room temperature. The concentration of nitrogen with respect to carbon was determined by ESCA. The information on the structure of surface nitrogen species was obtained with the aid of Fourier transform infrared spectroscopy. To help in the assignment of vibrational frequencies, infrared spectra of graphite particles after reaction with deuterated ammonia were also obtained.

The grinding reduced particle sizes and creates fresh surfaces. Surface carbon atoms of graphite particles show a strong chemical reactivity because of unsaturation in valency. Figures 6a and 6c show infrared spectra of the graphite particles after extensive grinding in an atmosphere of NH$_3$ and ND$_3$, with expansions of these spectra in Figures 6b and 6d. These infrared spectra suggest the occurrence of dissociative chemisorption of NH$_3$ on the carbon particle surface. Vibrational frequencies associated with the surface groups C-NH$_2$, C=N-H, C≡N, and C-H are observed in Figures 6a and 6b. The isotope shifts shown in Figures 6c and 6d support these assignments. Surface CNH$_2$ groups give rise to two bands near 3400 cm$^{-1}$ that are attributed to symmetric and antisymmetric N-H stretching modes. These two bands should shift to 2500 cm$^{-1}$ for CND$_2$. This shift is
shown in Figures 6c and 6d. A NH$_2$ bending mode near 1580 cm$^{-1}$ should shift to about 1200 cm$^{-1}$ for the ND$_2$ groups. However, a strong band due to the k=0, E$_{2g}$ phonon mode of the graphite lattice (Tuinstra and Koenig, 1970) and/or a vibrational mode of the aromatic structure of graphite (Friedel and Hofer, 1970) also occurs at about 1580 cm$^{-1}$. Likewise, the C-N stretching mode vibrates at approximately 1200 cm$^{-1}$ and appears in both the C-NH$_2$ and the C-ND$_2$ surface groups.

We have detected surface nitrogen groups indicating the dissociation of more than one bond in a molecule of ammonia. A band between 1600 and 1700 cm$^{-1}$ could be assigned to immines (C=NH and C=N-C), a weak band at 2300 cm$^{-1}$ to nitrile (C≡N), and one at 2180 cm$^{-1}$ to isocyanide (-N$^+$=C$^-$).

The evidence of the dissociative chemisorption of ammonia on carbon particle surfaces is also supported by the appearance of the C-D stretching band at 2050 cm$^{-1}$. The assignment of the C-H stretching is ambiguous because the C-H stretching is near 2900 cm$^{-1}$ where a vibrational band appears on both NH$_3$ and ND$_3$ samples. This band could be the overtone and/or combination bands resulting from the strong absorption band between 1300 and 1600 cm$^{-1}$. There is also a band, possibly of the same nature, at 2700 cm$^{-1}$ in both samples.

6. CATALYTIC ACTIVITY

6.1. Atmospheric Reactions Catalyzed by Carbon Particles

Black carbon particles are effective catalysts (Coughlin, 1969) for many different types of reactions including oxidation-reduction,
halogenation, hydrogenation-dehydrogenation, dehydration, polymerization, and isomerization. Table 3 lists a few reactions catalyzed by carbon that could have direct bearing on atmospheric chemistry. It is difficult to assess the importance of all these reactions in the atmosphere at this time because useful rate equations have not been determined. We have recently performed a study (Chang et al., 1979; Brodzinsky et al., 1980) on the kinetics and mechanism for the catalytic oxidation of SO$_2$ on carbon in aqueous suspensions and have obtained a rate equation applicable to atmospheric conditions.

6.2. SO$_2$ Oxidation Catalyzed by Carbon Particles

Novakov et al. (1974) used photoelectron spectroscopy (ESCA) to study the oxidation of SO$_2$ on carbon 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 carbon 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.
Table 3. Some reactions catalyzed by carbon.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3 )</td>
<td>Novakov et al. (1974), Chang et al. (1979), Brodzinsky et al. (1980), Chang et al. (1981)</td>
</tr>
<tr>
<td>2. ( \text{SO}_2 + \text{NO}_2 \rightarrow \text{SO}_3 + \text{NO} )</td>
<td>Cofer et al. (1980), Britton and Clarke (1980)</td>
</tr>
<tr>
<td>3. ( \text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_3 + \text{O}_2 )</td>
<td>Cofer et al. (1981)</td>
</tr>
<tr>
<td>4. ( \text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2 )</td>
<td>Rao and Hougen (1952)</td>
</tr>
<tr>
<td>5. ( 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 )</td>
<td>Bente and Walton (1943)</td>
</tr>
<tr>
<td>6. ( \text{CO} + \text{Cl}_2 \rightarrow \text{COCI}_2 )</td>
<td>Dulou (1945)</td>
</tr>
<tr>
<td>7. ( \text{SO}_2 + \text{Cl}_2 \rightarrow \text{SO}_2\text{Cl}_2 )</td>
<td>Dulou (1945)</td>
</tr>
<tr>
<td>8. ( \text{HCOOH} \xleftarrow{\text{H}_2\text{O} + \text{CO}} \text{H}_2 + \text{CO}_2 )</td>
<td>Stumpp (1965)</td>
</tr>
<tr>
<td>9. ( \text{CHO} \rightarrow \text{COOH} )</td>
<td>Gundel (1979)</td>
</tr>
<tr>
<td>10. Hydroquinone → quinhydrone → quinone</td>
<td>Bente and Walton (1943)</td>
</tr>
</tbody>
</table>
5. \( \text{SO}_2 \) can be oxidized on other types of graphitic carbonaceous particles, such as ground graphite particles and activated carbon.

Results from the experiments with combustion-produced soot particles are essentially similar to those obtained for activated carbon by Davtyan and Tkach (1961) and Siedlewski (1965).

Soot-catalyzed \( \text{SO}_2 \) 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 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.

6.2.1. Dry mechanism

A description of the dry mechanism was given by Yamamoto et al. (1972), who studied the reaction kinetics on dry activated carbon in the presence of \( \text{O}_2 \) and \( \text{H}_2\text{O} \) vapor. The rate of reaction was found to be first order with respect to \( \text{SO}_2 \), provided that the concentration of \( \text{SO}_2 \) was less than 0.01%, and depended on the square root of the concentration of \( \text{O}_2 \) and \( \text{H}_2\text{O} \) vapor. The activation energy was found to vary from -4 to -7 kcal/mole between 70\( ^\circ \text{C} \) and 150\( ^\circ \text{C} \), depending on the origin of the activated carbon. Initially the reaction occurs on the surface of both micropores and macropores, and the rate is
constant for a given activated carbon until the amount of accumulated H₂SO₄ 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 H₂SO₄. The reaction continues only on the macropores at a constant, but much slower, rate.

According to Yamamoto et al. (1972), a rate expression (until the amount of H₂SO₄ formed reaches 10% by weight of the carbon) for activated carbon used can be written as follows:

\[
\frac{d[H₂SO₄]}{dt} = [C_x][SO₂][O₂]^{0.5}[H₂O]^{0.5}(k_{micro} + k_{macro})e^{-\frac{E_a}{RT}},
\]

where \( t \) is time, \([C_x]\) is the concentration of carbon, \( k_{micro} \) and \( k_{macro} \) are the rate constants on the surface of the micropores and macropores, \( E_a \) is the activation energy, \( R \) is the universal gas constant, and \( T \) is absolute temperature.

The dry mechanism is relatively inefficient because the reaction product remains on the carbon surface and acts as the catalyst poison.

6.2.2. Wet mechanism

The situation is entirely different when soot (or black 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. (1979, 1981) and Brodzinsky et al. (1980),
who used both combustion soots and activated carbons.

6.2.2.1. Kinetic studies

The reaction was studied by batch (flask) experiments, from which a rate law was derived. This rate law has been confirmed by fog chamber studies (Benner, 1980). The flask experiments were performed using suspensions of commercially available activated carbons as well as suspensions of combustion-produced soots.

Figure 7 shows the typical reaction curves of the oxidation of S(IV) in aqueous suspensions of soot particles collected from acetylene and natural gas flames. The reaction occurs in two steps. The initial disappearance of S(IV) is so fast that its rate could not be followed by the analytical techniques used. The second step is characterized by a much slower reduction of S(IV). The results obtained with these combustion-produced soots were reproduced (Figure 8) by suspensions of similar concentrations of one of the commercially available activated carbons (Nuchar C-190, a trademark of West Virginia Pulp and Paper Co.). Figure 8 also shows a mass balance between the S(IV) consumed and the sulfate produced. At a constant temperature, the amount of S(IV) oxidized by the rapid first step process was found to be proportional to the carbon particle concentration.

The reaction of the second step has the following characteristics:

1. The reaction rate is independent of pH (pH < 7.6), and
therefore \( \text{SO}_2 \cdot \text{H}_2\text{O}, \text{HSO}_3^- \), and \( \text{SO}_3^{2-} \) are indistinguishable in terms of oxidation on the carbon surfaces.

2. The reaction is first order with respect to the concentration of carbon particles.

3. The activation energy of the reaction is \( \sim 8.5\) kcal/mole, being slightly different for different carbons.

4. The reaction rate has a complex dependence on the concentration of S(IV), ranging between a second and zeroth order reaction as the S(IV) concentration increases.

5. The reaction rate has a complex dependence on the concentration of dissolved \( \text{O}_2 \), with the order of reaction between zeroth and first.

Figure 9 shows the effective rate of reaction (normalized carbon concentration, room temperature--20°C, and air) as a function of the sulfurous acid concentration for the activated carbons studied (see also Table 4). From the Nuchar C-190 curve, the rate of reaction is second order with respect to S(IV) below \( 10^{-7} \) M, moves through a first order reaction around \( 5 \times 10^{-6} \) M, and becomes independent of S(IV) concentrations above \( 10^{-4} \) M. The other curves are seen to be similar in their behavior.

Based on the experimental results, we propose the following reaction mechanism

\[
C_x + O_2(\ell) \xrightarrow{k_1} C_x \cdot O_2(\ell) \quad \xleftarrow{k_{-1}}
\]  

(1)
Table 4. Summary of kinetic data for the catalytic oxidation of SO$_2$ by various elemental carbon particles in aqueous suspension.

Reaction rate equation:

$$\frac{d[SO_4^{2-}]}{dt} = Ae^{\frac{-E_a}{RT}} [C_x] \left\{ \frac{K_1 [O_2]}{1 + K_1 [O_2]} \right\} \left\{ \frac{\alpha [S(IV)]^2}{1 + \beta [S(IV)] + \alpha [S(IV)]^2} \right\}$$

<table>
<thead>
<tr>
<th>Elemental carbon</th>
<th>Nuchar C-190 (WESVACO)</th>
<th>Nuchar SN (WESVACO)</th>
<th>Aktivkohle (MERCK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic data</td>
<td></td>
<td></td>
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<tr>
<td>A (moles/g-sec)</td>
<td>0.874</td>
<td>0.158</td>
<td>2.473</td>
</tr>
<tr>
<td>$E_a$ (kcal/mole)</td>
<td>8.8</td>
<td>8.1</td>
<td>8.8</td>
</tr>
<tr>
<td>$K_1$ (l/mole)</td>
<td>$2.103 \times 10^3$</td>
<td>$7.427 \times 10^3$</td>
<td>$4.372 \times 10^3$</td>
</tr>
<tr>
<td>$\alpha$ (l$^2$/mole$^2$)</td>
<td>$2.404 \times 10^{12}$</td>
<td>$4.915 \times 10^8$</td>
<td>$9.519 \times 10^{11}$</td>
</tr>
<tr>
<td>$\beta$ (l/mole)</td>
<td>$1.219 \times 10^7$</td>
<td>$2.956 \times 10^5$</td>
<td>$3.738 \times 10^7$</td>
</tr>
</tbody>
</table>
\[ C_x \cdot O_2(\ell) + S(IV) \xrightarrow{k_2} C_x \cdot O_2(\ell) \cdot S(IV) \quad \text{(II)} \]

\[ C_x \cdot O_2(\ell) \cdot S(IV) + S(IV) \xrightarrow{k_3} C_x \cdot O_2(\ell) \cdot 2S(IV) \quad \text{(III)} \]

\[ C_x \cdot O_2(\ell) \cdot 2S(IV) \xrightarrow{k_4} C_x + 2S(VI), \quad \text{(IV)} \]

where \( C_x = \) soot, \( O_2(\ell) = \) dissolved oxygen molecule, \( S(IV) = \) sulfite species, and \( S(VI) = \) sulfate species.

Equation (I) indicates that dissolved oxygen is adsorbed on the soot particle surface to form an activated complex. This adsorbed oxygen complex then oxidizes the \( S(IV) \) to form sulfate according to Equations (II)-(IV). If one assumes that the reaction follows the condition of Langmuir adsorption equilibrium (Clark, 1970), the rate of acid formation is

\[
\frac{d[S(VI)]}{dt} = 2k_4[C_x] \left( \frac{K_1[O_2]}{1 + K_1[O_2]} \right) \left( \frac{K_2[S(IV)]}{1 + K_2[S(IV)]} \right) \left( \frac{K_3[S(IV)]}{1 + K_3[S(IV)]} \right) \quad \text{(5)}
\]

where \( K_1 = k_1/k_{-1}, \ K_2 = k_2/k_{-2}, \ K_3 = k_3/k_{-3}. \)

The experimental results yield the following rate law for this reaction:

\[
\frac{d[S(VI)]}{dt} = k[C_x] \left( \frac{K[O_2]}{1 + K_1[O_2]} \right) f[S(IV)] \quad \text{(6)}
\]
where $f[S(IV)] = \left( \frac{\alpha[S(IV)]^2}{1 + \beta[S(IV)] + \alpha[S(IV)]^2} \right)$.

[$C_x$] = grams of carbon particles per liter,

[$O_2$] = moles of dissolved oxygen per liter, and

[$S(IV)$] = total moles of S(IV) per liter.

For Nuchar C-190 the following constants were determined: $k = 0.874 e^{-4428/T}$ moles/g·sec ($T = ^\circ K$); $K_1 = 2.103 \times 10^3$ L/mole, $\alpha = 2.404 x 10^{12}$ L$^2$/mole$^2$, and $\beta = 1.219 \times 10^7$ L/mole.

The dependence of the rate of formation of sulfate on the partial pressure of $SO_2$ ($P_{SO_2}$) in the atmosphere can be obtained from Eq. 6. Because the effect of $P_{SO_2}$ on the rate is contained in $f[S(IV)]$, we illustrate the relationship of $f[S(IV)]$ with $P_{SO_2}$ and pH of the aqueous droplets as shown in Figures 10 and 11. $f[S(IV)]$, or the rate of production of sulfate (because the rate is linearly proportional to $f[S(IV)]$, decreases as the pH decreases at a given $P_{SO_2}$. The magnitude of $f[S(IV)]$'s changing per unit pH change is much larger at a lower $P_{SO_2}$. Also $f[S(IV)]$ (or the rate) depends only slightly on $P_{SO_2}$ under most atmospheric conditions when $P_{SO_2}$ is between 1 and 10 ppb and the pH ranges between 5 and 6. $f[S(IV)]$ increases only 1/10 and twofold respectively at pH of 6 and 5 when $P_{SO_2}$ increases from 1 to 10 ppb. However, $f[S(IV)]$ depends strongly on $P_{SO_2}$ when the pH is low.

The catalytic oxidation of sulfurous acid on carbon particles of different origins shows the same kinetic behavior. However, the rate constants of several different types of carbon particles were
studied and found to differ from type to type. In principle, the reaction rate should be proportional to the concentration of active sites on the carbon particles, rather than to the concentration of carbon particles. The number of active sites per unit mass of carbon particles is different from type to type and is not necessarily proportional to the surface area. Sidelewski (1965) has shown, by means of the electron paramagnetic resonance method, that free electrons on carbon particles can serve as active centers for the adsorption of oxygen molecules and for the oxidation of \( \text{SO}_2 \). The concentration of free electrons is related to the origin and thermal history of the carbon particles.

It is therefore impractical to formulate a generally applicable rate constant for atmospheric soot particles because these particles may arise from the combustion of different types of fossil fuel under different combustion conditions and thus possess a different catalytic activity.

6.2.2.2. Relative importance of some wet \( \text{SO}_2 \) oxidation mechanisms

We have carried out a box-type calculation (Chang et al., 1979, 1981) to compare the relative importance of sulfate production mechanisms by black carbon particles with other mechanisms involving liquid water. The systems considered in the batch reactor include the \( \text{SO}_2-\text{CO}_2-\text{H}_2\text{O(\&)}-\text{air} \) and any of the oxidizing agents such as \( \text{O}_2 \), \( \text{O}_3 \), \( \text{HNO}_2 \), or catalysts such as \( \text{Fe}^{+++} \), \( \text{Mn}^{++} \), and black carbon. The role of \( \text{NH}_3 \) is investigated in these reactions. The kinetic results
of Chang et al. (1981) and Oblath et al. (1980), Beilke et al. (1975), Erickson et al. (1977), Freiberg (1975), and Matteson et al. (1969) for nitrous acid, oxygen, ozone, iron, and manganese systems respectively were used in this calculation.

All the oxidation mechanisms considered except Mn$^{++}$ are pH dependent. Most of these mechanisms have lower oxidation rates at a lower pH, but some are more sensitive to the change in pH than others. The HNO$_2$ mechanism shows a larger oxidation rate when the solution is more acidic, however. 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; 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 manganese are water soluble, according to Gordon et al. (1975). The concentrations of black carbon and HNO$_2$ were taken as 10 $\mu$g/m$^3$ and 8 ppb respectively. The latter corresponds to 25 ppb of NO and 50 ppb of NO$_2$ at equilibrium conditions. For NH$_3$ a concentration of 5 ppb was used, which is higher than the highest equilibrium partial pressure of NH$_3$ over the United States as calculated by Lau and Charlson (1977). Tables 5 and 6 list the equilibrium equations and oxidation rate equations used for this comparative study.

The following assumptions were made in the calculations:

1. The size of liquid water drops suspended inside the box is so small that the absorption rate of gaseous species (SO$_2$, NH$_3$,
Table 5. Chemical equilibrium constants at 25°C.\(^a\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(K)</th>
<th>(K_2)</th>
<th>(K_1)</th>
<th>(K_{1c})</th>
<th>(K_{2c})</th>
<th>(K_a)</th>
<th>(K_s)</th>
<th>(K_{1s})</th>
<th>(K_{2s})</th>
<th>(K_{3s})</th>
<th>(K_N)</th>
<th>(K_N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_2O) (\not\equiv) (H^+ + OH^-)</td>
<td>(K_w)</td>
<td>1.008 (\times) 10(^{-14})</td>
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<tr>
<td>(CO_2(g) + H_2O(\ell) \not\equiv CO_2\cdot H_2O)</td>
<td>(K_c)</td>
<td>3.4 (\times) 10(^{-2})</td>
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<tr>
<td>(CO_2\cdot H_2O \not\equiv CO_3^{2-} + H^+)</td>
<td>(K_{1c})</td>
<td>4.45 (\times) 10(^{-7})</td>
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<tr>
<td>(HCO_3^- \not\equiv HCO_3^- + H^+)</td>
<td>(K_{2c})</td>
<td>4.68 (\times) 10(^{-11})</td>
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<tr>
<td>(NH_3(g) + H_2O(\ell) \not\equiv NH_3\cdot H_2O)</td>
<td>(H^a)</td>
<td>57</td>
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<tr>
<td>(NH_3\cdot H_2O \not\equiv NH_4^+ + OH^-)</td>
<td>(K_a)</td>
<td>1.774 (\times) 10(^{-5})</td>
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<tr>
<td>(SO_2(g) + H_2O(\ell) \not\equiv SO_2\cdot H_2O)</td>
<td>(H^s)</td>
<td>1.24</td>
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<tr>
<td>(SO_2\cdot H_2O \not\equiv HSO_3^- + H^+)</td>
<td>(K_{1s})</td>
<td>1.7 (\times) 10(^{-2})</td>
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<tr>
<td>(HSO_3^- \not\equiv SO_3^{2-} + H^+)</td>
<td>(K_{2s})</td>
<td>6.24 (\times) 10(^{-8})</td>
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<tr>
<td>(HSO_4^- \not\equiv H^+ + SO_4^{2-})</td>
<td>(K_{3s})</td>
<td>1.2 (\times) 10(^{-2})</td>
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<tr>
<td>(HNO_2(g) + H_2O \not\equiv HNO_2\cdot H_2O)</td>
<td>(H_N)</td>
<td>49</td>
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<tr>
<td>(HNO_2\cdot H_2O \not\equiv H^+ + NO_2^-)</td>
<td>(K_N)</td>
<td>5.1 (\times) 10(^{-4})</td>
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<tr>
<td>Reaction</td>
<td>Concentration</td>
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</tr>
<tr>
<td>$\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{O}_2\cdot\text{H}_2\text{O}$</td>
<td>$\text{H}_2\text{O} = 1.08 \times 10^{-3}$</td>
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<tr>
<td>$\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{O}_3\cdot\text{H}_2\text{O}$</td>
<td>$\text{H}_3\text{O} = 1.23 \times 10^{-2}$</td>
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</tbody>
</table>

*Concentrations in moles/l and gas pressure in atm.*
Table 6. Rate of SO$_2$ oxidation by various mechanisms in aqueous droplets.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Reaction rate law$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>Rate = $\frac{H_S { k_2 + k_{10} \frac{k_w}{[H^+]} } k_{2S} k_3}{k_{-2}[H^+]^2 + k_{10}[H^+] + k_{2S} k_3} \frac{P_{SO_2}}{g/\text{sec} \cdot \text{mole}}$</td>
</tr>
<tr>
<td>O$_3$</td>
<td>Rate = ${ k_4 [\text{HSO}_3^-] + k_5 [\text{SO}_3^-] } [O_3 \cdot H_2O]$</td>
</tr>
<tr>
<td>Fe$^{+++}$</td>
<td>Rate = $\frac{k_O S_H \text{PSO}_2^2 [\text{Fe}^{+++}]}{[H^+]^3}$</td>
</tr>
<tr>
<td>Mn$^{++}$</td>
<td>Rate = $3.67 \times 10^{-3} [X] - 1.17 { [\text{HSO}_4^-] + [\text{SO}_4^{2-}] }^2 { [\text{Mn}^{++}] - [X] } \times [\text{H}_2\text{O}(\ell)]^{-2}$ where $X = \frac{k_1 H_S \text{PSO}_2 [\text{Mn}^{++}]}{k_1 { H_S \text{PSO}_2 + [\text{H}_2\text{O}(\ell)] [\text{Mn}^{++}] } + 0.17}$</td>
</tr>
<tr>
<td>Black carbon</td>
<td>Rate = $k_6 [C_x] [O_2]^{0.69} \frac{a[S^{+4}]}{1 + \beta [S^{+4}] + a[S^{+4}]^2}$</td>
</tr>
<tr>
<td>HNO$_2$</td>
<td>Rate = $k_7 [H^+]^2 [\text{NO}_2^-] + k_8 [H^+] [\text{NO}_2^-] [\text{HSO}_3^-] + k_9 [\text{NO}_2^-] [\text{HSO}_3^-]^2$</td>
</tr>
</tbody>
</table>

$^a$[H$_2$O(\ell)] in cc/m$^3$, concentration in moles/\ell, gas pressure in atm, and time in sec, $k_0 = 151.69$ \ell/mole-sec, $k_S = 1.84 \times 10^{-2}$ mole/\ell, $k_1 = 8.12 \times 10^4$ \ell/mole-sec, $k_2 = 3.4 \times 10^6$ sec$^{-1}$, $k_{-2} = 2 \times 10^8$ \ell/mole-sec, $k_{10} = 2.9 \times 10^5$ \ell/mole-sec, $k_{-10} = 2.3 \times 10^{-7}$ sec$^{-1}$, $k_3 = 1.7 \times 10^{-3}$ sec$^{-1}$, $k_4 = 1.1 \times 10^5$ \ell/mole-sec, $k_5 = 7.4 \times 10^8$ \ell/mole-sec, $k_6 = 1.2 \times 10^{-4}$ mole$^{-3}$ \ell$^{-7}$/g·sec, $a = 1.5 \times 10^{12}$ \ell$^2$/mole$^2$, $\beta = 3.06 \times 10^6$ \ell/mole, $k_7 = 8 \times 10^5$ \ell$^2$/mole$^2$-sec, $k_8 = 3.8 \times 10^3$ \ell$^2$/mole$^2$-sec, $k_9 = 9 \times 10^{-4}$ \ell$^2$/mole$^2$-sec.
and HNO₂) is governed by chemical reactions.

2. There is no mass transfer of any species across the box during the reaction; therefore, the SO₂ (and NH₃ or HNO₂) in each box is depleted with time. The mass balance of the SO₂, CO₂, NH₃, and HNO₂ is always maintained (i.e., \( \Delta [\text{SO}_2]_g = \Delta [\text{SO}_2\cdot\text{H}_2\text{O}] + \Delta [\text{HSO}_3^-] + \Delta [\text{SO}_3^{2-}] + \Delta [\text{H}_2\text{SO}_4] + \Delta [\text{SO}_4^{2-}] \); \( \Delta [\text{CO}_2]_g = \Delta [\text{CO}_2\cdot\text{H}_2\text{O}] + \Delta [\text{HCO}_3^-] + \Delta [\text{CO}_3^{2-}] \); \( \Delta [\text{NH}_3]_g = \Delta [\text{NH}_3\cdot\text{H}_2\text{O}] + \Delta [\text{NH}_4^+] \); and \( \Delta [\text{HNO}_2]_g = \Delta [\text{HNO}_2] + \Delta [\text{NO}_2^-] + 2\Delta [\text{N}_2\text{O}]_g \); all units are in mole).

3. The growth of liquid water droplets due to the vapor pressure lowering effect of the sulfuric acid formed in the droplets is neglected.

The rate of sulfate production is determined by a calculation scheme involving a combination of equilibrium and kinetic steps. Equilibrium between SO₂ in the gas phase and sulfur (IV) in the droplet is several orders of magnitude faster than oxidation of sulfur (IV) to sulfate (Beilke and Gravenhorst, 1978). Similar assumptions were made regarding NH₃ and CO₂ gases. Therefore, initially gases are taken to be in equilibrium with the aerosols. Then the formation of sulfate proceeds by the given time-dependent production rate. The increase in the sulfate level in the small time step \( \Delta t \) causes the reduction in pH of the solution, which in turn disturbs the equilibrium between the aerosol and its surrounding gaseous environment. More gases are dissolved in the aerosol to maintain the equilibrium. At the same time, these gases are depleted in the surrounding
atmosphere. After each calculation, the time step is adjusted and the process is repeated until a 24-hour period is completed. The results are shown in Figure 12.

Figure 12 indicates that \( O_3 \), black carbon, and \( HNO_2 \) 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 both carbon and \( HNO_2 \) processes are more important when the lifetime of fog or clouds is long and the pH of the droplets is low. Both carbon and \( HNO_2 \) processes can be dominant processes close to sources and in heavily polluted urban areas, where the concentrations of soot and \( NO/NO_2 \) are high and the pH of aqueous droplets is low.

The rate constants for atmospheric black carbon particles varies, depending on the nature and history of particle production as discussed previously. In a fog chamber study, Benner (1980) recently found that the reaction rate of soot particles from a natural gas diffusion flame can be considerably faster than the reaction rate reported here. More determination of rate constants of soot from different types of fuel is therefore warranted.

ACKNOWLEDGMENT

This work was supported by the Assistant Secretary for the Environment, Office of Health and Environmental Research, Pollutant Characterization and Safety Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48 and by the National Science
REFERENCES


spectroscopy. J. Colloid Interface Sci. 39, 225-234.


FIGURE CAPTIONS

Figure 1. Oxygen-containing functional groups on elemental carbon particle surfaces.

Figure 2. Nitrogen (1s) ESCA spectrum of cold soot particles exposed to NH₃. The setup used for exposure is also shown.

Figure 3. Nitrogen (1s) ESCA spectrum of hot soot particles exposed to NH₃. The experimental arrangement used for sample preparation is also shown.

Figure 4. Nitrogen (1s) ESCA spectrum of an ambient sample as measured at 25, 80, 150, 250, and 350°C.

Figure 5. Nitrogen (1s) spectrum of (hot) soot sample exposed to NH₃, as measured at 25, 150, 250, and 350°C.

Figure 6. Infrared spectra of the graphite particles after extensive grinding in an atmosphere of NH₃ (a) and ND₃ (c). (b) and (d) are 2X expansions along the ordinate of (a) and (c) respectively.
Figure 7. S(IV) concentration as a function of time for acetylene and natural gas soot suspensions.

Figure 8. S(IV) and $\text{SO}_4^{-2}$ concentrations as a function of time for a 0.16%-by-weight activated carbon suspension.

Figure 9. Effective rate of oxidation of S(IV) catalyzed on various activated carbon particles vs. S(IV) concentration.

Figure 10. The effect of the pH of aqueous droplets on $f[S(IV)]$ at $P_{SO_2} = 100, 10,$ and 1 ppb. $f[S(IV)]$ is a function of S(IV) that the aqueous oxidation rate of sulfites on soot particles depends on.

Figure 11. The effect of partial pressure of $SO_2$ on $f[S(IV)]$ at pH of 7, 6, 5, 4, and 3. $f[S(IV)]$ is a function of S(IV) that the aqueous oxidation rate of sulfites on soot particles depends on.

Figure 12. Comparison of the relative importance of various sulfate production mechanisms involving liquid water based on a box-type calculation. The following initial conditions were used
in the calculation: \( P_{SO_2} = 0.01 \text{ ppm} \); \( P_{CO_2} = 0.000311 \text{ atm} \); \( P_{NH_3} = 5 \text{ ppb} \); \( P_{O_3} = 0.05 \text{ ppm} \); \( P_{HNO_2} = 8 \text{ ppb} \); \([Fe^{+++}] = 1.2 \times 10^{-7} \text{ mole/l} \); \([Mn^{+}] = 1.8 \times 10^{-8} \text{ mole/l} \); soot = 10 \( \mu g/m^3 \); and liquid water = 0.05 \( g/m^3 \).
carboxyl groups  phenolic hydroxyl groups  ethers (chromene)

carboxyl groups  quinones  lactones  fluorescein-like lactones

carboxylic acid anhydrides  cyclic peroxide

Figure 1
Figure 2
Figure 4

binding energy (eV)

Intensity

Hot soot + NH₃

Nₓ

NH₄⁺
Figure 5
Figure 6
Figure 7
Figure 8
Figure 9

Graph showing the concentration of \([H_2SO_3]\) and \([SO_4^{2-}]\) over time (min). The graph includes error bars and lines for Sulfite and Sulfate. The concentrations are in \(10^{-4}\) M.
Figure 10

Rate (molecules/sec) vs. [H2S03] (M)
Figure 12
Figure 13

This figure illustrates the sulfate concentration ($\mu g/m^3$) over time (hours) for various substances, including Soot, Fe$^{+3}$, HNO$_2$, O$_3$, O$_2$, HNO$_2$-NH$_3$, and Mn$^{+2}$. The y-axis represents the concentration on a logarithmic scale, ranging from $10^{-5}$ to $10^2$, while the x-axis shows time in hours, ranging from 0 to 24. The percent conversion is also indicated on the right side of the graph.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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