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Kinetics and Mechanism for the Catalytic Oxidation of Sulfur Dioxide on Carbon in Aqueous Suspensions

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Combustion-produced soot (carbonaceous) particles have been found to be efficient catalysts for SO₂ oxidation, especially in the presence of liquid water. A kinetic study of the catalytic oxidation of SO₂ on carbon particles suspended in solution has been carried out. The reaction was found to be first order with respect to the concentration of carbon particles, 0.69th order with respect to dissolved oxygen, between zero and second order with respect to S(IV) concentrations, and independent of the pH. Temperature studies were carried out, and an activation energy for this reaction was determined. A four-step mechanism is proposed for this carbon-catalyzed oxidation reaction.

Introduction

Because of its adsorptive properties, activated carbon has long been used as a scrubber for gases and organic molecules. It is also used as a catalyst in industry for the control of gaseous emissions from smoke stacks. The catalytic oxidation of SO₂ on activated carbons has been shown to occur¹ and has been used in certain industrial scrubber processes.² Novakov et al.^{3,4} have shown by photoelectron spectroscopy that SO₂ oxidation can be catalyzed by combustion-generated soot particles and have suggested that this mechanism may be important in the formation of atmospheric sulfates. These studies showed that the soot-catalyzed reaction is more efficient in humidified air than in dry air, but the specific role of water was not clear from their experiments. In the atmosphere, liquid water is important because it may form as a condensate on soot particles in stack plumes or in fogs and clouds and affect the chemical processes at the particle surface. Estimated values of the concentration of carbon in droplets can range from 10 mg/L in a fog or cloud to more than 10 g/L as the liquid evaporates.⁵

We have examined the effect of liquid water on the carbon-catalyzed SO₂ oxidation reaction. In this paper, we present a reaction rate law and propose a reaction mechanism for the catalytic oxidation of SO₂ on carbon particles in an aqueous suspension. (Note: Because in solution SO₂ can form the three species, SO₂·H₂O, HSO₃⁻ (bisulfite), and SO₃²⁻ (sulfite), the terms "sulfurous acid" and "H₂SO₃" have been used to signify all of the S(IV) species in solution.)

Experimental Section

The reaction was studied in systems containing various concentrations of sulfurous acid and suspended carbonaceous particles. The carbonaceous particle concentrations used in the suspensions ranged from 20 mg/L to 3.2 g/L, and the sulfurous acid concentration ranged from 7.0 × 10⁻⁸ to 1.00 × 10⁻³ M.

Soots produced by the combustion of acetylene and natural gas and by a diesel engine were collected by imp-

TABLE I: Elemental Composition of Nuchar-C190 (wt %)^a

C	74.7	K	0.091	Ni	0.001
O	23.6	Al	>0.055	Cl	<0.001
H	0.9	Ti	0.016	As	0.0004
N	0.1	Mn	0.013	Br	0.0004
Ca	0.221	Cr	0.002	Rb	0.0004
S	>0.166	Cu	0.002	Zr	0.0004
Si	>0.111	Zn	0.002	Pb	0.0004
Fe	0.117	Sr	0.002	Ga	0.0001

^a BET surface area = 550 m²/g. C, H, N: combustion. O: difference. Other elements: X-ray fluorescence.

ing the exhaust effluent into water and using this solution as the catalyst by adding sulfurous acid. An activated carbon (Nuchar-C190, a trademark of West Virginia Pulp and Paper Co.; elemental composition shown in Table I) was used as a model system since it is difficult to prepare reproducible soot suspensions.

The reaction mixture was prepared by combining the activated carbon and water in an Erlenmeyer flask. A known concentration of sulfurous acid was added, and the mixture was stirred constantly with a magnetic stirring bar at ~300 rpm. Aliquots of the reaction mixture were removed, filtered, and analyzed for sulfurous acid and sulfate during the course of the reaction.

Two separate techniques were used to monitor sulfurous acid concentration, depending on the concentration. A Dionex Model 14 anion chromatography system was used for sulfurous acid and sulfate concentrations of less than 10⁻⁴ M. The operating conditions used were an eluent of 0.002 M NaOH/0.0035 M Na₂CO₃ at a flow rate of 138 mL/h and a pressure of 600 psi, through a system consisting of a 3 × 50-mm concentrator, a 3 × 150-mm pre-column, a 3 × 500-mm separator, and 6 × 250-mm suppressor columns. Elution times were 10 and 15 min for sulfite and sulfate, respectively. For concentrations greater than 10⁻⁴ M, the concentration of sulfurous acid was monitored by using iodometric titrations. The concentration of sulfuric acid was followed by the turbidimetric method in selected runs.

The pH of the solution was adjusted by the addition of H₂SO₄ to SO₂·H₂O for pH < 2.5, and various combinations

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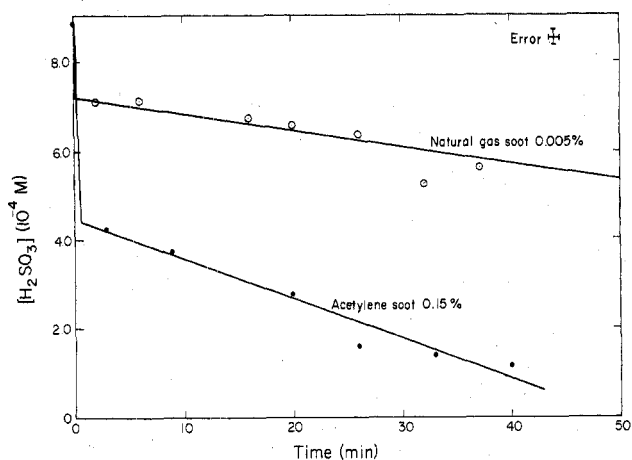


Figure 1. H_2SO_3 concentration as a function of time for acetylene and natural-gas soot suspensions.

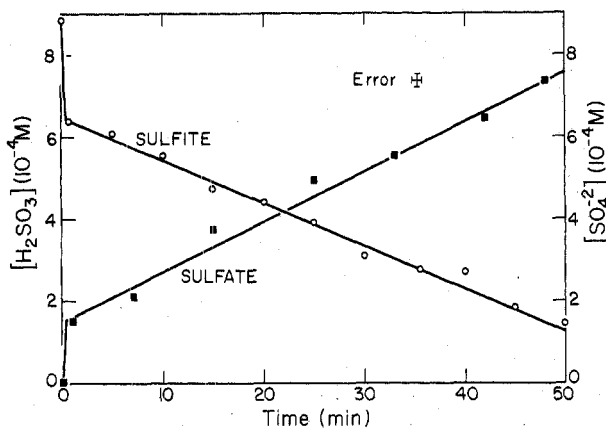


Figure 2. H_2SO_3 and SO_4^{2-} concentrations as a function of time for a 1.6 g/L activated carbon suspension.

of $\text{SO}_2\text{-H}_2\text{O}$, NaHSO_3 , Na_2SO_3 , and NH_4OH were used to control the pH above 2.5. The pH was measured by using a Beckman digital pH meter with combination probe.

All reactions, except for those in which temperature or dissolved oxygen concentration were specifically controlled, were done at room temperature (20°C) and open to the air (dissolved $\text{O}_2 = 2.64 \times 10^{-4} \text{ M}$). Oxygen-dependence studies were performed in a contained atmosphere glovebox with various mixtures of N_2 and O_2 . The dissolved O_2 was equilibrated by vigorously shaking the water to be used and then bubbling the $\text{N}_2\text{-O}_2$ mixture through the water. Known amounts of carbon and sulfurous acid were then added to form the reaction mixture. Dissolved oxygen was measured with a Yellow Springs Instrument Model 57 dissolved-oxygen meter.

A few experiments were performed with activated carbon that had been degassed. The carbon was degassed by exposure to vacuum (0.1 torr) at 75°C for 3 days. One atmosphere of N_2 was then introduced for 24 h.

Results

Figure 1 shows the typical reaction curves of the oxidation of H_2SO_3 in aqueous suspensions of soot particles collected from acetylene and natural gas flames. The reaction occurs in two steps. The initial disappearance of H_2SO_3 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 H_2SO_3 . The results obtained with these combustion-produced soots were reproduced (Figure 2) by suspensions of similar concentrations of Nuchar-C190. Figure 2 also shows that there is a mass balance between the sulfurous acid consumed and

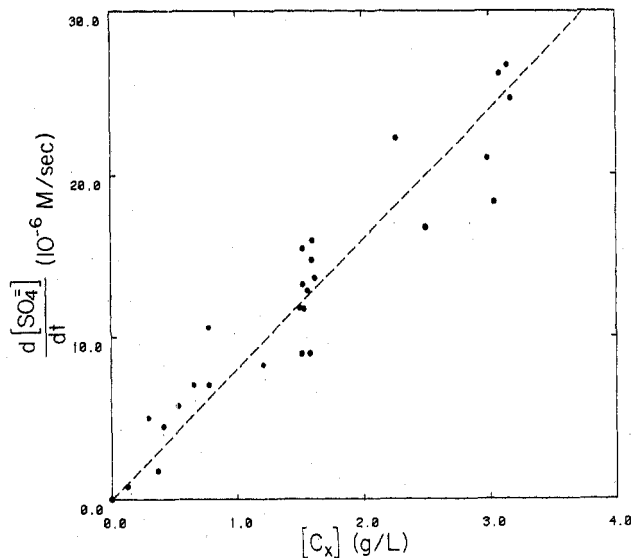


Figure 3. Rate of reaction vs. concentration of activated carbon suspensions. Initial H_2SO_3 concentration range: 5×10^{-4} – $1.2 \times 10^{-3} \text{ M}$.

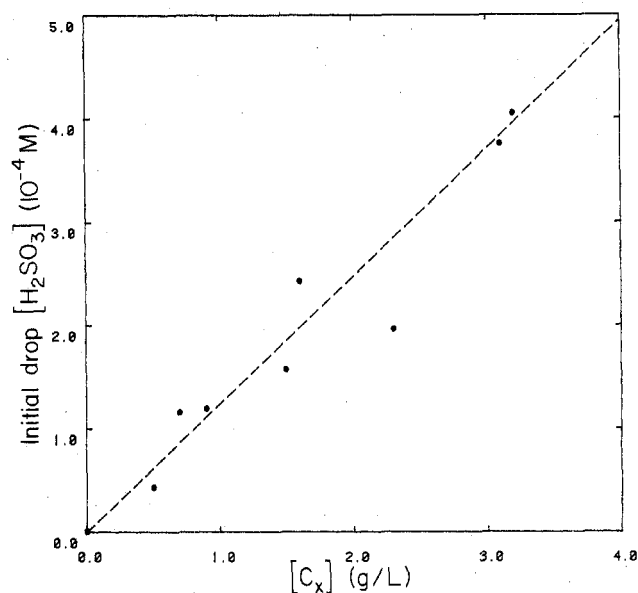


Figure 4. Initial drop in H_2SO_3 concentration vs. concentration of activated carbon suspension. Initial H_2SO_3 concentration was $8.85 \times 10^{-4} \text{ M}$.

the sulfuric acid produced. Figure 3 shows the effect of varying activated carbon concentration on the reaction rate. At a constant temperature, the amount of H_2SO_3 oxidized by the rapid first step process was found to be proportional to the carbon-particle concentration, as shown in Figure 4.

Figure 5 illustrates the effect of dissolved-oxygen concentration on the rate of reaction. The temperature dependence of the rate of reaction is shown in Figure 6. The rate of diffusion of oxygen into solution does not affect the reaction rate, since the concentration of dissolved oxygen was determined to be constant during the course of the reaction. The temperature-dependence data of Figure 6 were obtained at pH 2.9. Identical results were obtained at pH 1.2 and 7.0. The oxygen dependence of the reaction is of 0.69th order; the temperature dependence yields an activation energy of 49.0 kJ/mol for the reaction.

The effects of pH are shown for the higher H_2SO_3 concentration experiments in Figure 7. The pH of the solution decreased during the course of the reaction. The change in pH varied from 0.05 to 1.5 pH units, depending

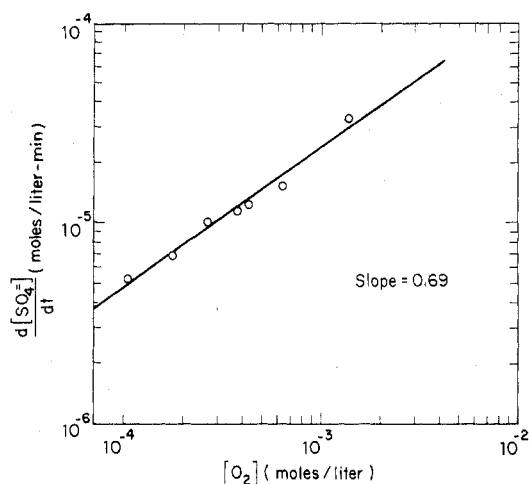


Figure 5. The rate of formation of sulfate vs. dissolved oxygen concentration for 1.6 g/L activated carbon suspensions.

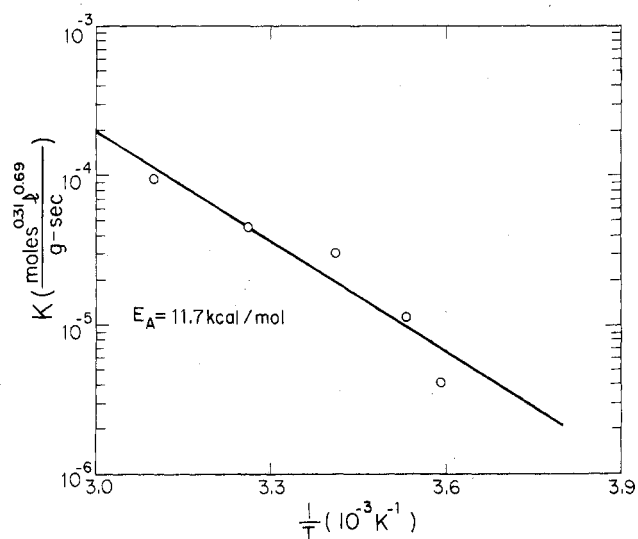


Figure 6. Rate constant vs. $1/T$ at pH 2.9. $E_a = 49.0$ kJ/mol (11.7 kcal/mol).

on the initial pH of the solution: the larger the initial pH, the larger the change. Our results demonstrate that the reaction rate does not depend on the pH of the aqueous suspension when the pH is less than 7.6. The pH range of our experiments (1.20–7.5) covers the range of atmospheric liquid water (rain, fog, etc.). For the activated carbon that was studied, no reaction occurs when the pH is greater than 7.6.

Figure 8 shows the effective rate of reaction (normalized carbon concentration, room temperature (20 °C), and air) as a function of the sulfurous acid concentration. The data points are the instantaneous rates based on three-point averages from the various experiments. The rate of reaction is second order with respect to H_2SO_3 below 10^{-7} M, moves through a first-order reaction around 5×10^{-6} M, and becomes independent of H_2SO_3 concentrations above 10^{-4} M.

In summary, the reaction occurs in two steps—an initial rapid oxidation followed by a much slower one. The rate of the first step is too fast to follow. The reaction of the second step has the following characteristics: (1) The reaction rate is first order and 0.69th in 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 49.0 kJ/mol. (4) There is a balance between the consumption of sulfurous acid and the production of sulfuric acid. (5) The reaction

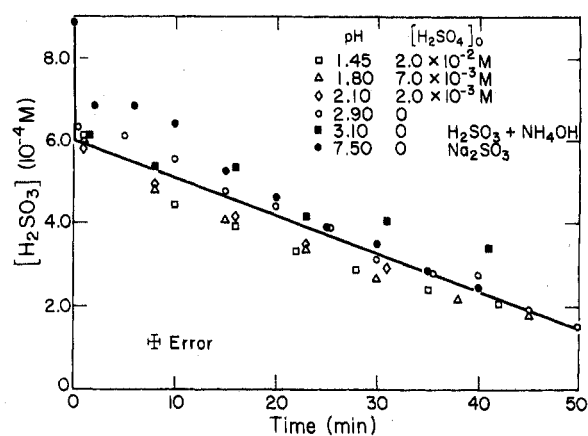


Figure 7. H_2SO_3 concentrations as a function of time at an activated carbon concentration of 1.6 g/L at various pH values. Initial H_2SO_3 concentration was 8.85×10^{-4} M.

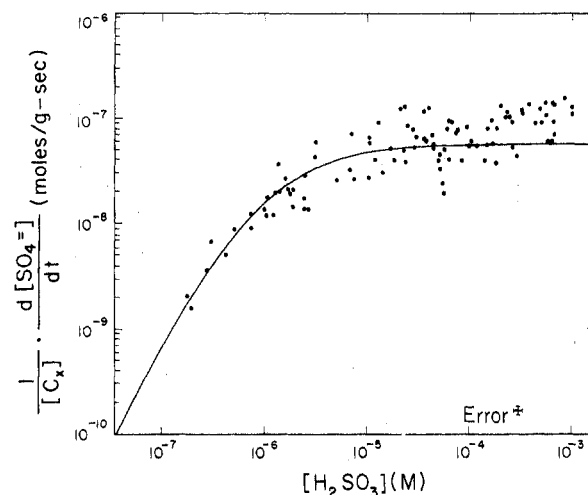
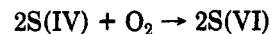


Figure 8. Effective rate of reaction vs. H_2SO_3 concentration. Curve is least-squares fit to proposed rate expression.

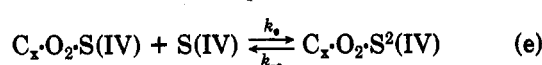
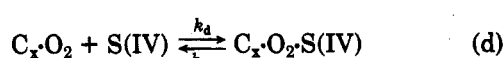
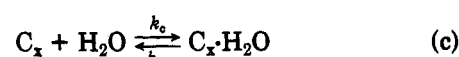
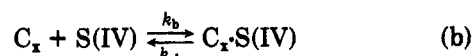
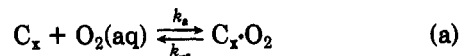
rate has a complex dependence on the concentration of H_2SO_3 , ranging between a second- and zero-order reaction as the H_2SO_3 concentration increases.

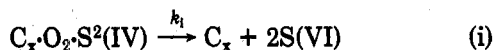
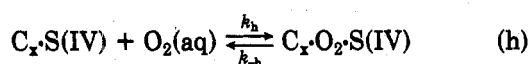
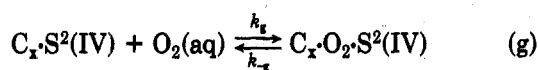
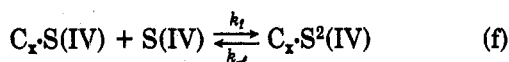
Discussion

The oxidation of S(IV) to S(VI) can be expressed simply by the following symbolic net reaction (let C_x = carbon surface; S(IV) = $H_2O \cdot SO_2$, HSO_3^- , and SO_3^{2-} ; S(VI) = H_2SO_4 , HSO_4^- , and SO_4^{2-}):



The first-order reaction rate with respect to the activated carbon catalyst is representative of a surface catalysis. The reaction will proceed via the adsorption of the reacting species onto the catalytically active site. A series of adsorption steps can explain the fractional and varying order of reaction with respect to S(IV) and O_2 :





Steps a–h are adsorptions on the surface, with the oxidation step occurring in reaction i. Under normal conditions this oxidation is irreversible (as written); and since the reaction does occur in water, the desorption of the bisulfate or sulfate ions can be considered in one step and irreversible.

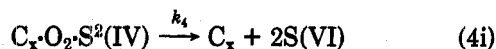
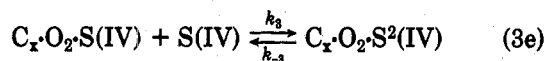
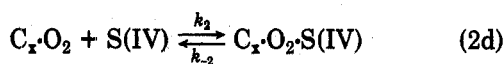
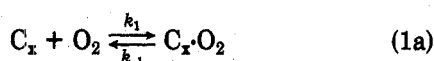
The rate of production of the sulfate species is therefore

$$\text{rate} = d[S(VI)]/dt = 2k_4[C_x \cdot O_2 \cdot S^2(IV)]$$

Steps a and b would both be initiation steps while step c would be an interference as water molecules adsorb onto the active site. A rate expression could be derived with the possibility of two distinct reaction initiators.

The experimentally observed activation energy is similar to the activation energies for the chemisorption of oxygen onto activated carbons as seen by Puri et al.⁶ Many reactions have activation energies of this magnitude (50 kJ/mol); however, this agreement, together with the rapid initial oxidation (when the carbon is added to a solution containing H_2SO_3), indicates that the first step in the reaction is the adsorption of oxygen onto the active sites. Since the oxygen from the air has already adsorbed onto the carbon prior to going into solution, the rapid initial oxidation would be the reaction of S(IV) species with the already formed $C_x \cdot O_2$ complex. Changing the amount of adsorbed oxygen present changes the magnitude of the initial oxidation. Degassing under vacuum and saturation with nitrogen yields no rapid oxidation; further, as the oxygen concentration increases in oxygen/nitrogen mixtures, so does the magnitude of the rapid oxidation.

Assuming then that the first step in the reaction is the adsorption of oxygen, we have the following four-step reaction:



With the Langmuir adsorption equation, $[C_x \cdot O_2 \cdot S(IV)]^2$ can be solved for as

$$[C_x \cdot O_2 \cdot S^2(IV)] = \left(\frac{K_3[S(IV)]}{1 + K_3[S(IV)]} \right) [C_x \cdot O_2 \cdot S(IV)]$$

For steps 1a and 2d, the following is derived in a similar manner for the rate expression:

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

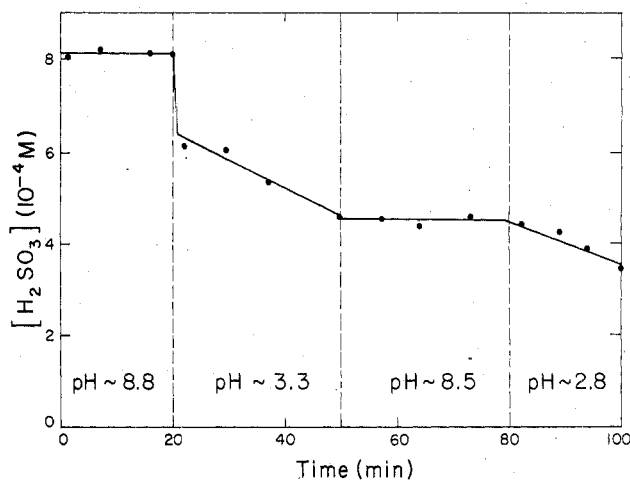


Figure 9. Behavior of H_2SO_3 concentration as function of time as pH is quickly changed from base to acid.

where $K_1 = k_1/k_{-1}$, $K_2 = k_2/k_{-2}$, and $K_3 = k_3/k_{-3}$.

The experimental results yield the following rate law for this reaction

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

where $k = 1.69 \times 10^{-5} \text{ mol}^{0.31} \text{ L}^{0.69} / (\text{g s})$, $\alpha = 1.50 \times 10^{12} \text{ L}^2 / \text{mol}^2$, $\beta = 3.06 \times 10^6 \text{ L/mol}$, $[C_x]$ = grams of Nuchar-C190 per liter, $[O_2]$ = moles of dissolved oxygen per liter, and $[S(IV)]$ = total moles of S(IV) per liter. From the Arrhenius equation, the rate constant may be expressed as

$$k = A e^{-E_a/RT}$$

where $E_a = 49.0 \text{ kJ/mol}$, and $A = 9.04 \times 10^3 \text{ mol}^{0.31} \text{ L}^{0.69} / (\text{g s})$.

Equation I can be changed simply to eq II. A fractional order adsorption reaction is achieved by substituting the Freundlich isotherm $\theta = k[X]^n$, where θ is the fraction of the surface covered by adsorbed species X, for the Langmuir⁷ $\theta = K[X]/(1 + K[X])$. Multiplication of the S(IV) terms yields the experimentally seen expression, where $K_2 K_3 = \alpha$ and $K_2 + K_3 = \beta$.

Preliminary experiments with other activated carbons, as well as laboratory-generated combustion soots, have shown the same rate-law behavior, although the actual numerical constants are different. For a specific activated carbon, the concentration of active sites present will be proportional to the effective (or interfacial) surface area. However, this proportionality is different for other activated carbons.

The behavior of the reaction with respect to the pH of the solution indicates that all three S(IV) species, $H_2O \cdot SO_2$, HSO_3^- , and SO_3^{2-} , react in a similar manner; hence our treatment of all species as one in the derivation of the rate law and the mechanism. Below a pH of 7.6, the reaction rate is independent of the pH; but when the pH becomes greater than 7.6, the rate abruptly drops to zero. This abrupt drop in the reaction rate above a pH of 7.6 would seem to indicate a poisoning of the catalytically active surface. It has been proposed⁸ that the reacting species was bisulfite, but our results differ and indicate that it is the active site that is affected by the pH. Figure 9 shows the behavior of the reaction as the pH is changed rapidly from acid to base by addition of a few drops of concentrated NaOH or H_2SO_4 . (Concentrations have been normalized to account for dilution factors.) When the acti-

vated carbon is placed into a mildly basic sulfite solution, no reaction occurs. When the solution is made mildly acidic, the reaction begins with the expected rate. Similar behavior is seen as the solution is changed back to basic and again to acidic. Studies are planned to examine the behavior of other activated carbons. The catalytic activity may be dependent on the method of activation for the different carbons.

We have done comparisons of this reaction with the rates of the other atmospherically important SO₂ oxidation reactions.⁹ As it has been recently shown¹⁰ that carbonaceous particles are a significant portion of the ambient particulate burden, the carbon-catalyzed reaction can be a major contributor to the formation of aerosol sulfates.

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Photooxidation of Sulfur Dioxide in Low-Temperature Matrices

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The mechanism of photooxidation of sulfur dioxide has been investigated at low temperatures. Monomeric sulfur dioxide was found to be photochemically inactive, and no evidence was found for the existence of [SO₄]* in an oxygen matrix. In contrast, the dimeric species, (SO₂)₂, was found to be readily photooxidized to sulfur trioxide in an oxygen matrix at 12 K.

Introduction

A number of mechanisms have been proposed to explain the oxidation of atmospheric sulfur dioxide to sulfuric acid and sulfates. These may be classified into two types of process: (a) homogeneous gas-phase oxidation; (b) heterogeneous oxidation on droplets or particles.

Although the type-a mechanism is generally photochemically initiated, the *direct* oxidation of excited sulfur dioxide molecules is thought to be of relatively minor importance compared with reactions involving radical intermediates (e.g., OH, RO₂, etc.) produced by other photolytic processes.¹

However as part of a continuing study on photochemical reactions of monomer and dimer species at low temperatures,² we have investigated the direct photolysis of sulfur dioxide (S¹⁶O¹⁶O; S¹⁶O¹⁸O; S¹⁸O¹⁸O) in oxygen, argon, and nitrogen matrices at 12 K. Distinctive and distinguishing photooxidation behavior for sulfur dioxide was found during concentration studies in an oxygen matrix. This may indicate the importance of molecular donor-acceptor complexes in the observed photochemistry as has been previously suggested from gas-phase experiments.³

Experimental Section

Sulfur dioxide (S¹⁶O¹⁶O) was purchased from Liquid Carbonic with 99.98% stated purity. Isotopically labeled sulfur dioxide (70% atom purity S¹⁸O¹⁸O) was purchased from Prochem. Isotopically labeled oxygen ¹⁸O¹⁸O (99% atom purity) was purchased from Prochem. The matrix gases were obtained from Liquid Carbonic: argon (99.9999% stated purity); nitrogen (99.9995% stated purity); oxygen (99.999% stated purity). All of the gases were

used without further purification. Gaseous mixtures of known sulfur dioxide-matrix gas ratio (MR) were made up in 2-L bulb by standard manometric techniques at room temperature.

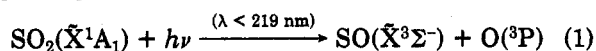
Low-temperature matrices of the above mixtures were prepared by the pulsed deposition method^{4,5} and held at 12 K by a closed-cycle helium refrigerator (Air Products, Displex CSA 202B).

The effect of photolysis by a 1000-W super-high-pressure mercury arc (Ushio 1005D) and a 20-W zinc vapor lamp (Osram) was monitored with an infrared spectrometer (Perkin-Elmer Model 281). Calibration of the spectrometer was carried out by using ammonia, carbon dioxide, and water vapor.

Results and Discussion

The present report may be divided into two photochemical regions of interest:

(a) $\lambda < 219$ nm. Photodissociation into sulfur monoxide and an oxygen atom is energetically possible in this region, ($D_0[\text{OS-O}] = 545 \pm 1$ kJ mol⁻¹)⁶ via reaction 1.



(b) $\lambda > 219$ nm. Electronically excited states of SO₂ are produced in two main spectral ranges at wavelengths greater than 219 nm (eq 2-4).

