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Soot-Catalyzed Oxidation
Of Sulfur Dioxide

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SOOT-CATALYZED OXIDATION OF SULFUR DIOXIDE*

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Abstract

Experimental results are reviewed which demonstrate that combustion-generated soot particles can oxidize SO_2 in both the absence ("dry" mechanism) and the presence ("wet" mechanism) of liquid water. The "wet" mechanism is much more efficient than the "dry" one, and is applicable to situations where the aerosol particles are covered with a liquid water layer. Calculations are presented which suggest that the soot-catalyzed oxidation of SO_2 can be the dominant mechanism under realistic atmospheric conditions.

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I. Introduction

Over the past 4 to 5 years, the principal objective of LBL's Atmospheric Aerosol Research group has been to assess the contribution of primary carbonaceous particles to the ambient particulate burden and to evaluate the role of these primary particles in the formation of suspended sulfates.

During the early days of environmental awareness, primary particulate emissions were easily visible; and smoke or soot was the first air pollutant to be recognized and controlled. In more recent times, improvements in combustion technology and use of better-grade fuels have led to a substantial reduction of visible smoke emissions. Consequently, the importance of soot as a pollutant became less obvious; and the emphasis of air pollution control moved away from primary emissions toward controlling gaseous emissions, especially those considered to be precursors for the production of secondary particles — sulfur dioxide for sulfate; hydrocarbons for organic particulates, etc.

Nevertheless, there is considerable evidence that primary soot particles are still very important contributors to atmospheric pollution in California and elsewhere. The difference between our concept of soot and visible smoke is largely confined to the size of the particles. Smoke consists of large particles that are responsible for the opacity of plumes. Soot is any carbonaceous particulate material emitted from sources, even if these do not produce visible plumes or smoke. In most cases soot particles are very small when emitted, having diameters of the order of 100 \AA , and are therefore invisible to the naked eye. Soot can also be described as a chemically complex carbonaceous material which consists of a "graphitic" component and an organic component. There are significant differences in the overall properties of the two components. For example, the "graphitic" component is nonvolatile, insoluble in organic solvents, and is a strongly light-absorbing material. In contrast, the organic component of soot is volatile, soluble in solvents, and does not appreciably absorb light. Novakov et al. previously stated they find as much as 80% of the ambient particulate carbon collected in different parts of California is in the form of soot.^{1,2}

More recently, Rosen et al.^{3,4} have employed Raman spectroscopy and an optical attenuation technique to identify the "graphitic" component of ambient carbonaceous particles and used this component as a tracer for primary emissions. The "graphitic" soot tracer technique suggests that a major and possibly dominant fraction of the ambient carbonaceous aerosol burden is due to primary emissions. The results also indicate that if there are significant concentrations of secondary species, their production does not seem to depend on the photochemical activity as manifested by the ozone concentration.

Soot particles, in addition to being a major constituent of ambient particles, are a catalytically and surface chemically active material. For example, Novakov et al.¹ have shown that SO_2 oxidation to sulfate can be catalyzed by combustion-generated soot particles. They propose that the soot-catalyzed SO_2 oxidation plays a major role in atmospheres characterized by high concentrations of primary particulate carbon. Chang et al.⁵ have recently extended research on the role of soot particles as catalysts for SO_2 oxidation by studying the effect of liquid water on the soot-catalyzed reaction. The effects of liquid water are important because, in plumes, liquid water may condense on the soot particles; and soot particles may encounter liquid water in their passage through fogs and clouds. Also, hygroscopic and deliquescent materials associated with soot particles may hold significant amounts of liquid water, even at a relatively low relative humidity. This "wet" mechanism is much more efficient for SO_2 oxidation than the corresponding "dry" mechanism that was suggested previously.

In this paper we shall review laboratory results on heterogeneous oxidation of SO_2 on soot particles in air and present results of simple numerical calculations which suggest that soot-catalyzed oxidation can be the dominant heterogeneous mechanism for sulfate formation under realistic atmospheric conditions.

II. Experimental Studies of Catalytic SO_2 Oxidation on Soot Particles

Novakov et al.¹ used photoelectron spectroscopy (ESCA) to study the oxidation of SO_2 on soot particles produced by a propane flame. The investigators found that under some conditions, a significant amount of sulfate can be produced by the catalytic action of soot particles.

Photoelectron spectra representing the sulfur(2p) and carbon(1s) regions of propane soot particles produced by a Bunsen burner are shown in Figure 1a. The S(2p) photoelectron peak at a binding energy of 169 eV corresponds to sulfate. The C(1s) peak appears essentially as a single component line and corresponds to a substantially neutral charge state consistent with the soot structure. It is of interest to note that even the combustion of very low sulfur-content fuels (0.005% by weight) results in the formation of an easily detectable sulfate emission.

The specific role of soot particles as a catalyst for the oxidation of SO_2 is demonstrated with the aid of Figure 1b. Here the S(2p) and C(1s) photoelectron peaks of soot particles are shown, generated in an analogous manner, but with SO_2 added to the laboratory-confined "plume". A marked increase in the sulfate peak intensity relative to carbon is evident. The atomic ratios of sulfur to carbon in Figures 1a and 1b are about 0.15 and 0.50 respectively.

The sulfate associated with soot particles was water soluble and contributed to the acidification of the solution. The hydrolysis product of this sulfate behaves chemically as sulfuric acid because it forms ammonium sulfate easily in reaction with gaseous ammonia.

Experiments like those just described have been found difficult to reproduce quantitatively because it is difficult to control important parameters such as soot concentration, temperature, and relative humidity. Although these early experiments were qualitative, it was nevertheless possible to conclude the following:

1. Soot-catalyzed oxidation of SO_2 is more efficient at a higher humidity.
2. The oxygen in air plays an important role in SO_2 oxidation.
3. Soot-catalyzed oxidation exhibits a saturation effect.
4. The saturation level of sulfate produced is probably related to properties of carbon particles, such as size, active surface area, and adsorbed surface oxygen.
5. SO_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 et al.⁷ and Siedlewski⁸.

The experiments just described provide a hint about the importance of water in the catalytic oxidation of SO_2 on carbonaceous particles. For example, the oxidation was apparently more efficient when prehumidified, rather than dry, air was used to dilute the SO_2 . However, the role of water, and specifically of liquid water, was not made clear in these experiments. An understanding of the effect that liquid water may have on this type of SO_2 oxidation is imperative because of the ubiquitous presence of liquid water in the atmosphere.

Chang et al.⁵ recently investigated the kinetics of SO_2 in an aqueous suspension of soot particles. The reaction was studied in systems containing various concentrations of sulfurous acid and suspended carbonaceous particles. The range of carbon concentrations used in the suspensions was from 0.005% to 0.32% by weight, and that of sulfurous acid was between 1.5×10^{-4} M and 1.00×10^{-3} M. The concentration of sulfurous acid was monitored, using iodometric titration during the course of the reaction. In some selected runs, the concentration of sulfuric acid was followed by the turbidimetric method. Soots that were produced by the combustion of acetylene and natural gas, as well as that produced by a diesel engine and collected by impinging the effluent into water, were used in this study and found to be good catalysts.

Figure 2 shows the typical reaction curves of the oxidation of H_2SO_3 by dissolved oxygen in aqueous suspensions of soot particles collected from acetylene and natural gas flames. The reaction occurs in two steps. The rate of the initial disappearance of H_2SO_3 is so fast that it could not be followed by the analytical technique used. The second process is characterized by a much slower linear reduction of H_2SO_3 . The results obtained with these combustion-produced soots are essentially reproduced (Fig. 3) by suspensions of similar concentrations of activated carbon (Nuchar). Figure 3 shows that there is a mass balance between the sulfurous acid consumed and the sulfuric acid produced. Since it is difficult to reproducibly prepare soot suspensions, suspensions of Nuchar were used as a model system.

In order to investigate the reaction rate and mechanism, a series of experiments were done with Nuchar as a model catalyst. The effects of the concentrations of carbon, sulfurous acid, and dissolved oxygen on the rate of oxidation of sulfurous acid were studied (Figs. 4, 5, and 6).

The amount of sulfurous acid oxidized, at a constant temperature, by the rapid first step process is linearly proportional to the concentration of the carbon particles (Fig. 7). It was found that there was a linear relationship between the half-life of the second process and the reciprocal of the carbon concentration and the initial sulfurous acid concentration respectively. This behavior suggests a first order reaction with respect to the carbon catalyst concentration and zeroth order with respect to the sulfurous acid concentration under the conditions of this experiment (Nuchar, between 0.005% and 0.32% by weight; sulfurous acid, between 1.5×10^{-4} and 10^{-3} M; pH, between 1.5 and 7.5). The rate of reaction with respect to the concentration of dissolved oxygen was found to be a fractional order (0.7th) in Figure 8, which was plotted by using data given in Figure 6.

In order to assess the dependence of the SO₂ oxidation reaction on pH, a known volume of H₂SO₄ or NH₄OH was mixed into the sulfurous acid solution before adding Nuchar. In a separate run at a high pH, an Na₂SO₃ solution was used for the experiment. The pH of the solution decreases during the course of the reaction. The change in pH varies from 0.05 to 1.0 pH unit, depending on the pH of the solution. The larger the pH, the larger the change. The results, represented in Figure 9, demonstrate that the reaction rate essentially does not depend on the pH of the aqueous suspension under the conditions of this investigation. The pH of these experiments ranged from 1.45 to 7.5, which should cover the entire range of interest at atmospheric conditions. This latter observation is very striking, as it differs from other heterogeneous reactions involving liquid water in not being dependent on the pH of the liquid water.

In summary, the reaction occurs in two steps — an initial rapid oxidation followed by a much slower one. The rate of the first process is too fast to follow. The reaction of the second process has the following characteristics:

1. The reaction rate is first order, zeroth order, and a fractional order (0.7th) with respect to the concentration of carbon, sulfurous acid, and dissolved oxygen respectively.
2. The reaction rate is pH independent.
3. There is a mass balance between the consumption of sulfurous acid and the production of sulfuric acid.

III. Discussion

It is obvious from the foregoing review of experimental results that soot particles can oxidize SO_2 in both the absence and the presence of liquid water. In this discussion we shall refer to these two situations as the "dry" and the "wet" mechanisms respectively. The "wet" mechanism is much more efficient than the "dry" one, and is applicable to the situations in plumes and in 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.

We are unaware of a reaction rate study involving dry combustion-produced soot particles. However, Yamamoto et al.^{9,10} did study the reaction kinetics on dry activated carbon in the presence of O_2 and H_2O vapor. The rate of reaction was found to be first order with respect to SO_2 , provided the concentration of SO_2 was less than 0.01%, and depended on the square root of the concentration of O_2 and H_2O vapor. The activation energy was found to vary from -4 to -7 kcal/mole between 70 and 150°C, depending on the origin of the activated carbon. The effect of the physical properties of activated carbon, such as surface area and micro- and macropore volumes, on the rate of oxidation of SO_2 was also investigated by Yamamoto et al.^{9,10} 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 H_2SO_4 reaches about 10 wt % of the carbon. Beyond that amount, the rate gradually decreases with the reaction time until the micropore volume is filled up by H_2SO_4 . The reaction continues only on the macropores with a constant, but much slower, rate than initially.

According to the results given by Yamamoto et al.,^{9,10} a rate expression until the amount of H_2SO_4 formed reaches 10 wt % of the carbon can be written as follows:

$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = -\frac{98}{64} \frac{d[\text{SO}_2]}{dt} = C_x [\text{SO}_2] [\text{O}_2]^{0.5} [\text{H}_2\text{O}]^{0.5} (k_1 + k_2) e^{-E_a/RT}$$

where C_x is the concentration of carbon; k_1 and k_2 are the rate constants on the surface of the micro- macropores respectively; and E_a is the activation energy. The rate of oxidation of SO_2 depends on the origin of carbon.

Based on their experimental observations, Chang et al.⁵ proposed the following reaction mechanism:



Equation (1) indicates that dissolved oxygen is adsorbed on the soot particle surface to form an activated complex. This adsorbed oxygen complex then oxidizes the sulfurous acid to form sulfuric acid according to Equations (2)-(4). If one assumes that the reaction follows the condition of Langmuir adsorption equilibrium, the rate of acid formation is:

$$\begin{aligned} \frac{d[SO]}{dt} &= 2k_4 [C_x \cdot O_2 \cdot S^2] \\ &= 2k_4 [C_x] \left\{ \frac{K_1 [O_2]}{1 + K_1 [O_2] + K_W [H_2O] + K_S [S]} \right\} \left\{ \frac{K_2 [S]}{1 + K_2 [S]} \right\} \cdot \left\{ \frac{K_3 [S]}{1 + K_3 [S]} \right\} \end{aligned}$$

If $k_2[S] \gg k_{-2}$ and $k_3[S] \gg k_{-3}$, the rate law simplifies to

$$\frac{d[SO]}{dt} = 2k_4 [C_x] \left\{ \frac{K_1 [O_2]}{1 + K_1 [O_2] + K_W [H_2O] + K_S [S]} \right\}$$

If the power rate form (Freundlich isotherm) instead of the Langmuir form is used, the rate law becomes

$$\frac{d[SO]}{dt} = k [C_x] [O_2]^n,$$

which corresponds to the experimental results where C_x = soot, S = sulfite species, SO = sulfate species, and $n = 0.7$. The value of k at 20°C was

taken to be 1.8×10^{-4} $\ell/\text{sec-g}$ which represents the average of the rate constant determined from natural gas and acetylene soot (Fig. 2).

Chang et al.⁵ have also carried out a simple box-type calculation to compare the relative importance of "wet" soot-particle-catalyzed reactions with other reactions involving liquid water. The systems which were considered are: $\text{SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; $\text{NH}_3\text{-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; $\text{O}_3\text{-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; $\text{NH}_3\text{-O}_3\text{-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; $\text{Fe}^{+3}\text{-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; $\text{NH}_3\text{-Fe}^{+3}\text{-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; $\text{Mn}^{+2}\text{-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; and $\text{soot-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$. The kinetics of each of these processes, other than the soot-catalyzed reactions, have been studied by many investigators. The results of Beilke et al.¹¹, Erickson et al.¹², Freiberg¹³, and Matteson et al.¹⁴ for oxygen, ozone, iron, and manganese systems respectively were used in this calculation. 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 . 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. 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.¹⁵ A soot particle concentration of $10 \text{ }\mu\text{g/m}^3$ was assumed.

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 and NH_3) is governed by chemical reactions.
2. There is no mass transfer of any species across the box during the reaction. Therefore, the SO_2 (and NH_3) in each box is depleted with time. The mass balance of the sulfur and ammonia (i.e., $\Delta[\text{SO}_2]_g = \Delta[\text{SO}_2 \cdot \text{H}_2\text{O}] + \Delta[\text{HSO}_3^-] + \Delta[\text{SO}_3^{=}] + \Delta[\text{HSO}_4^-] + \Delta[\text{SO}_4^{=}]$, and $\Delta[\text{NH}_3]_g = \Delta[\text{NH}_3 \cdot \text{H}_2\text{O}] + \Delta[\text{NH}_4^+]$) are always maintained.
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 amount of sulfate formed as a function of time was calculated according to the following procedure:

1. Initially, the droplets achieve chemical equilibrium with CO_2 , SO_2 , and NH_3 at the partial pressures adopted. The $[\text{H}^+]$, $[\text{SO}_2 \cdot \text{H}_2\text{O}]$,

$[\text{HSO}_3^-]$, $[\text{SO}_3^{=}]$, $[\text{NH}_3 \cdot \text{H}_2\text{O}]$, and $[\text{NH}_4^+]$ are calculated when $[\text{HSO}_4^-]$ and $[\text{SO}_4^{=}]$ are equal to zero.

2. Assuming a time step Δt , the $[\text{HSO}_4^-]$ and $[\text{SO}_4^{=}]$ are calculated with the aid of the corresponding reaction rate law for each process.

3. The gaseous SO_2 and NH_3 are depleted. The remaining $[\text{SO}_2]$ and $[\text{NH}_3]$ are calculated using the mass balance equation.

4. Then the $[\text{H}^+]$, $[\text{SO}_2 \cdot \text{H}_2\text{O}]$, $[\text{HSO}_3^-]$, $[\text{SO}_3^{=}]$, $[\text{NH}_3 \cdot \text{H}_2\text{O}]$, and $[\text{NH}_4^+]$ are again calculated and the process is repeated until a 24-hour period is completed.

The result of this calculation is given in Table I and in Figure 10.

From this calculation, we can conclude that the soot-catalyzed oxidation of SO_2 can be the dominant mechanism under realistic atmospheric conditions.

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

| Mechanisms | 1 hr | | 6 hr | | 12 hr | | 24 hr | |
|------------------------------|--|----------------------|--|----------------------|--|----------------------|--|-----------------------|
| | $\text{SO}_4^{=}$ $\mu\text{g}/\text{m}^3$ | % conv. | $\text{SO}_4^{=}$ $\mu\text{g}/\text{m}^3$ | % conv. | $\text{SO}_4^{=}$ $\mu\text{g}/\text{m}^3$ | % conv. | $\text{SO}_4^{=}$ $\mu\text{g}/\text{m}^3$ | % conv. |
| Mn^{+2} | 2.55×10^{-5} | 6.2×10^{-5} | 1.6×10^{-4} | 3.9×10^{-4} | 3.1×10^{-4} | 7.5×10^{-4} | 6×10^{-4} | 1.45×10^{-3} |
| O_2 | 1.8×10^{-3} | 4.3×10^{-3} | 9.6×10^{-3} | 2.3×10^{-3} | 1.8×10^{-2} | 4.4×10^{-2} | 3.4×10^{-2} | 8.2×10^{-2} |
| Fe^{+3} | 4.7×10^{-3} | 1.1×10^{-2} | 2.1×10^{-2} | 5×10^{-2} | 3.3×10^{-2} | 8.0×10^{-2} | 4.8×10^{-2} | 0.12 |
| O_3 | 0.13 | 0.33 | 0.27 | 0.66 | 0.35 | 0.85 | 0.47 | 1.13 |
| $\text{O}_2\text{-NH}_3$ | 0.52 | 1.26 | 1.54 | 3.7 | 2.02 | 4.89 | 2.50 | 6.1 |
| $\text{Fe}^{+3}\text{-NH}_3$ | 2.3 | 5.6 | 3.2 | 7.76 | 3.6 | 8.73 | 3.9 | 9.45 |
| $\text{O}_3\text{-NH}_3$ | 4.51 | 10.94 | 5.14 | 12.5 | 5.28 | 12.8 | 5.28 | 12.8 |
| C_x | 1.8 | 4.4 | 10.8 | 26.4 | 21.6 | 52.4 | 41.25 | 100 |

Concentration: $\text{H}_2\text{O}(\ell)$: $0.05 \text{ g}/\text{m}^3$; SO_2 : 0.01 ppm (10^{-8} atm); NH_3 : 5 ppb ($5 \times 10^{-9} \text{ atm}$);
 O_3 : 0.05 ppm ($5 \times 10^{-8} \text{ atm}$); Mn^{+2} : $20 \text{ ng} \times 0.25\%/\text{m}^3$; Fe^{+3} : $250 \text{ ng} \times 0.13\%/\text{m}^3$;
 C_x : $10 \mu\text{g}/\text{m}^3$; temp.: 10°C .

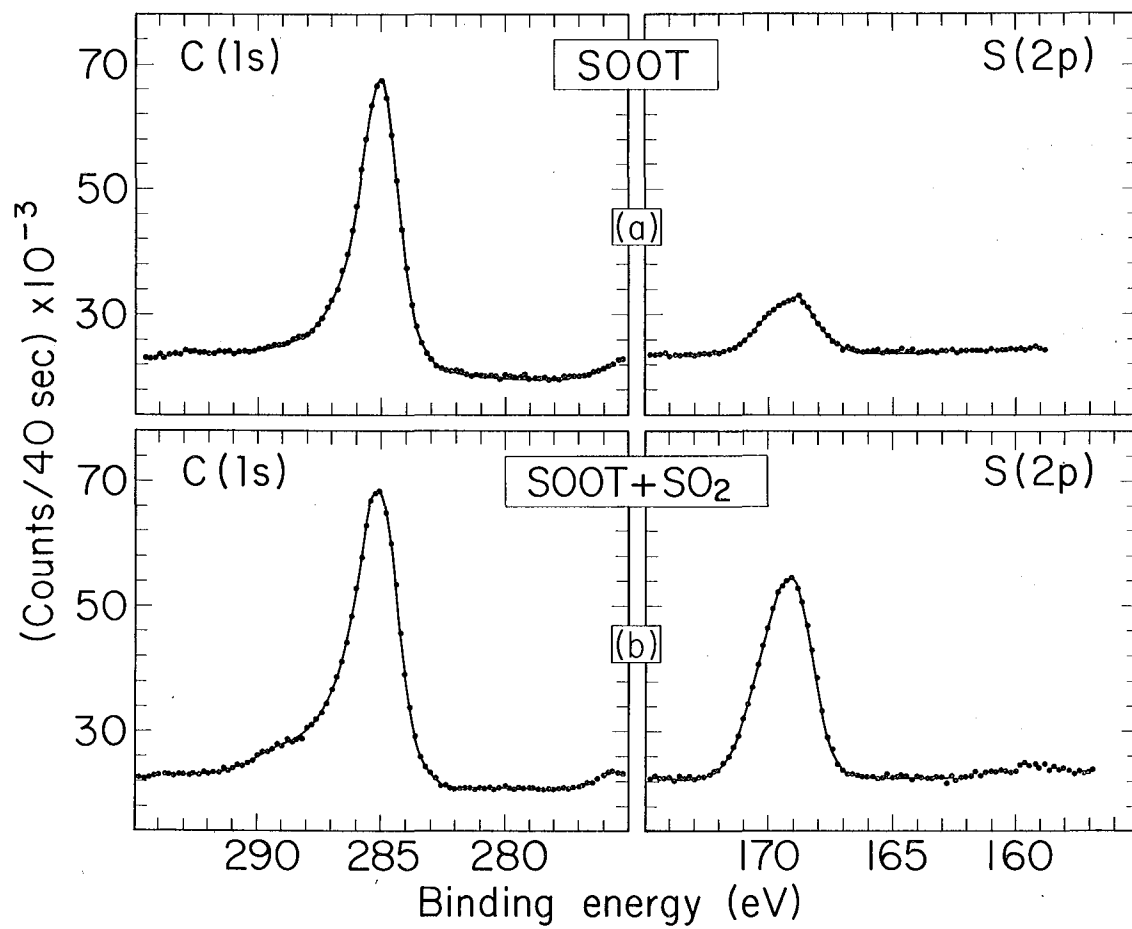
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Figure Captions

- Figure 1. Carbon(1s) and sulfur(2p) photoelectron spectra of (a) soot particles produced by combustion of propane saturated with benzene vapor (sulfur content of this fuel, 0.005% by weight); and (b) soot particles generated in a manner analogous to (a), but exposed to additional SO_2 in humid air.
- Figure 2. H_2SO_3 concentration vs. time for acetylene and natural gas soot suspensions.
- Figure 3. H_2SO_3 and H_2SO_4 concentrations vs. time for Nuchar suspensions.
- Figure 4. H_2SO_3 concentration vs. time for various Nuchar concentrations. The initial H_2SO_3 concentration was 8.85×10^{-4} M.
- Figure 5. H_2SO_3 concentration vs. time for various initial concentrations of H_2SO_3 at a fixed Nuchar concentration of 0.16% by weight.
- Figure 6. H_2SO_3 concentration vs. time for various concentrations of dissolved oxygen at a fixed Nuchar concentration of 0.16% by weight.
- Figure 7. The amount of H_2SO_3 oxidized by the first rapid process for various concentrations of Nuchar.
- Figure 8. The rate of formation of sulfuric acid for various concentrations of dissolved oxygen at a fixed Nuchar concentration of 0.16% by weight.
- Figure 9. H_2SO_3 concentration vs. time at a Nuchar concentration of 0.16% by weight at various pH's of the solution. The initial H_2SO_3 concentration was 8.85×10^{-4} M.
- Figure 10. Comparison of the relative significance of various SO_2 conversion processes in aqueous droplets.



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Figure 1

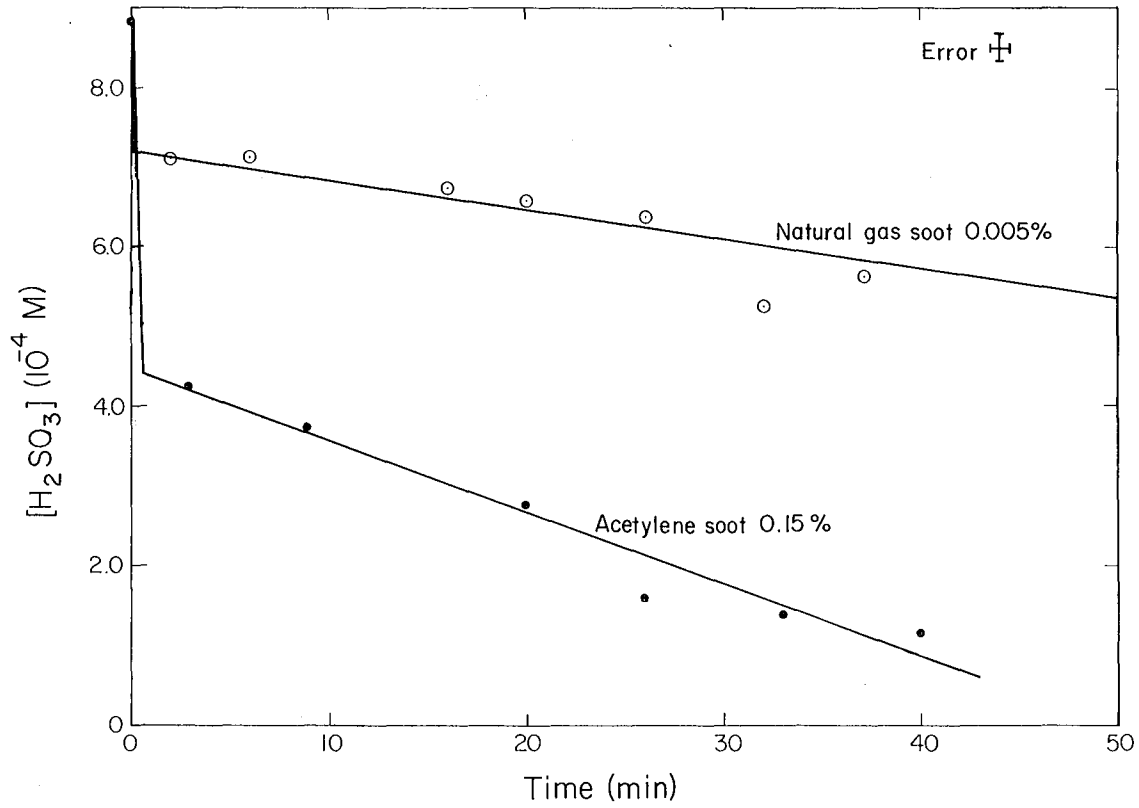
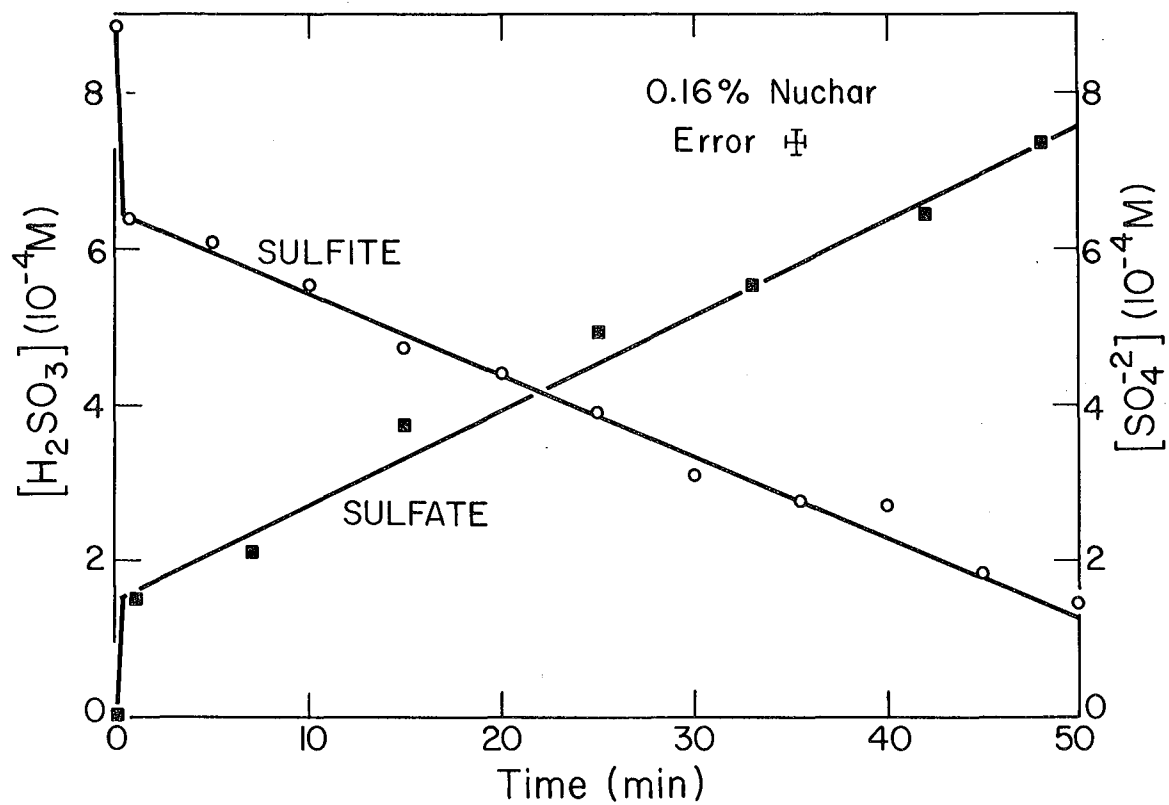


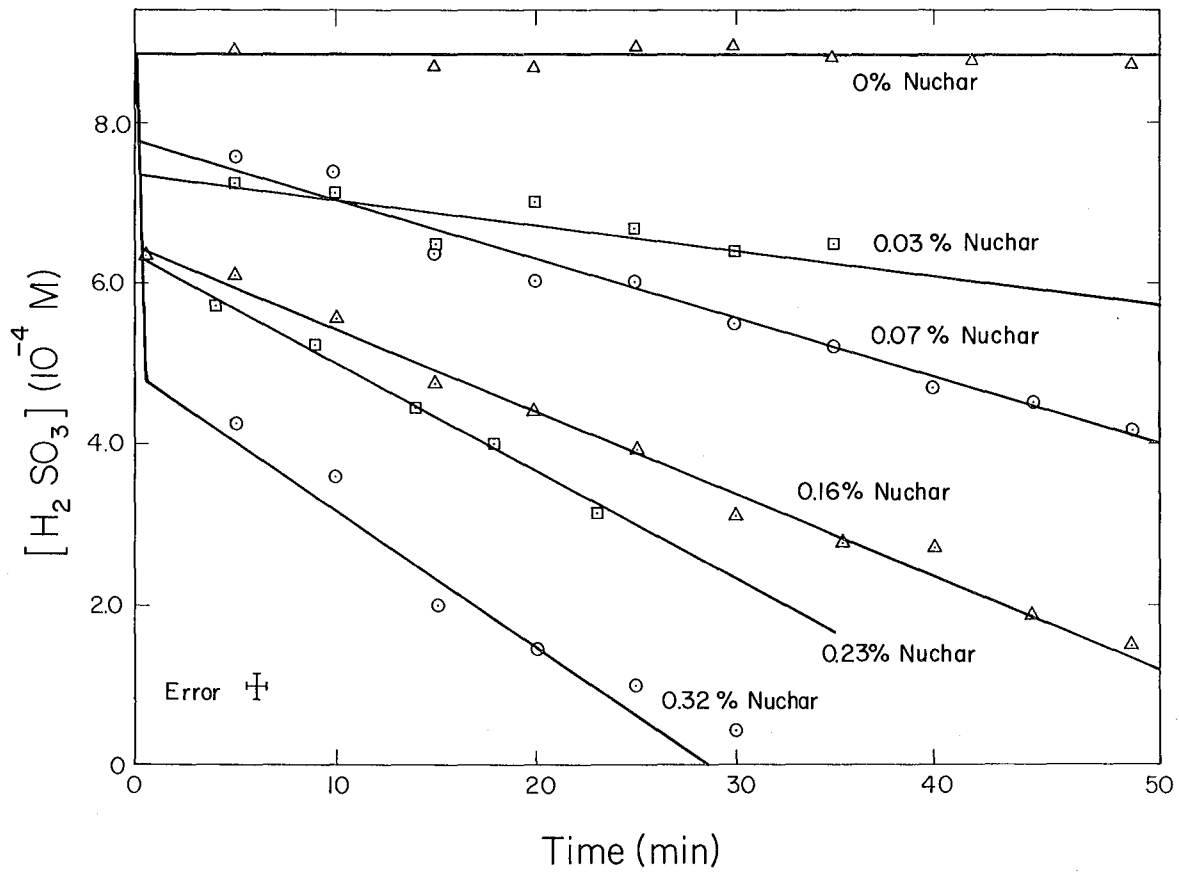
Figure 2

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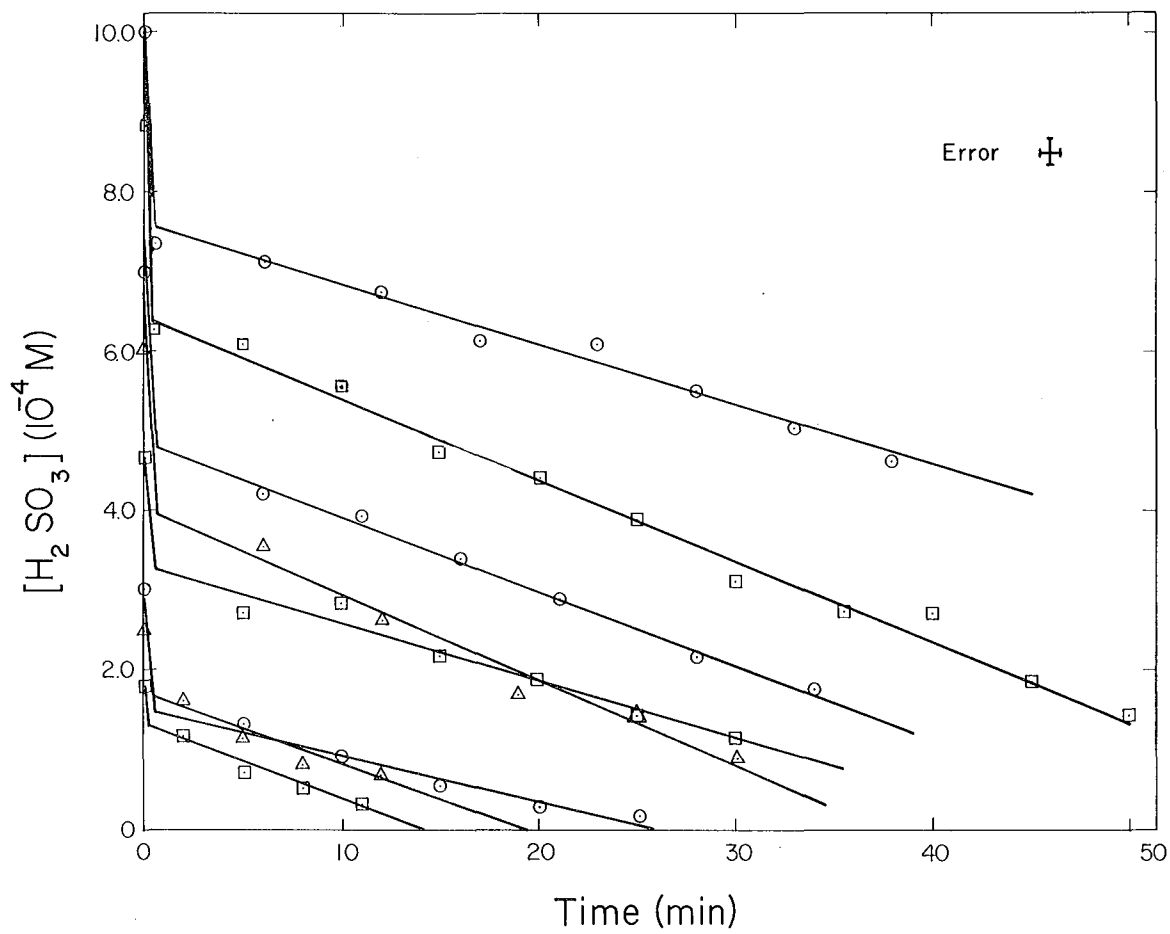
Figure 3



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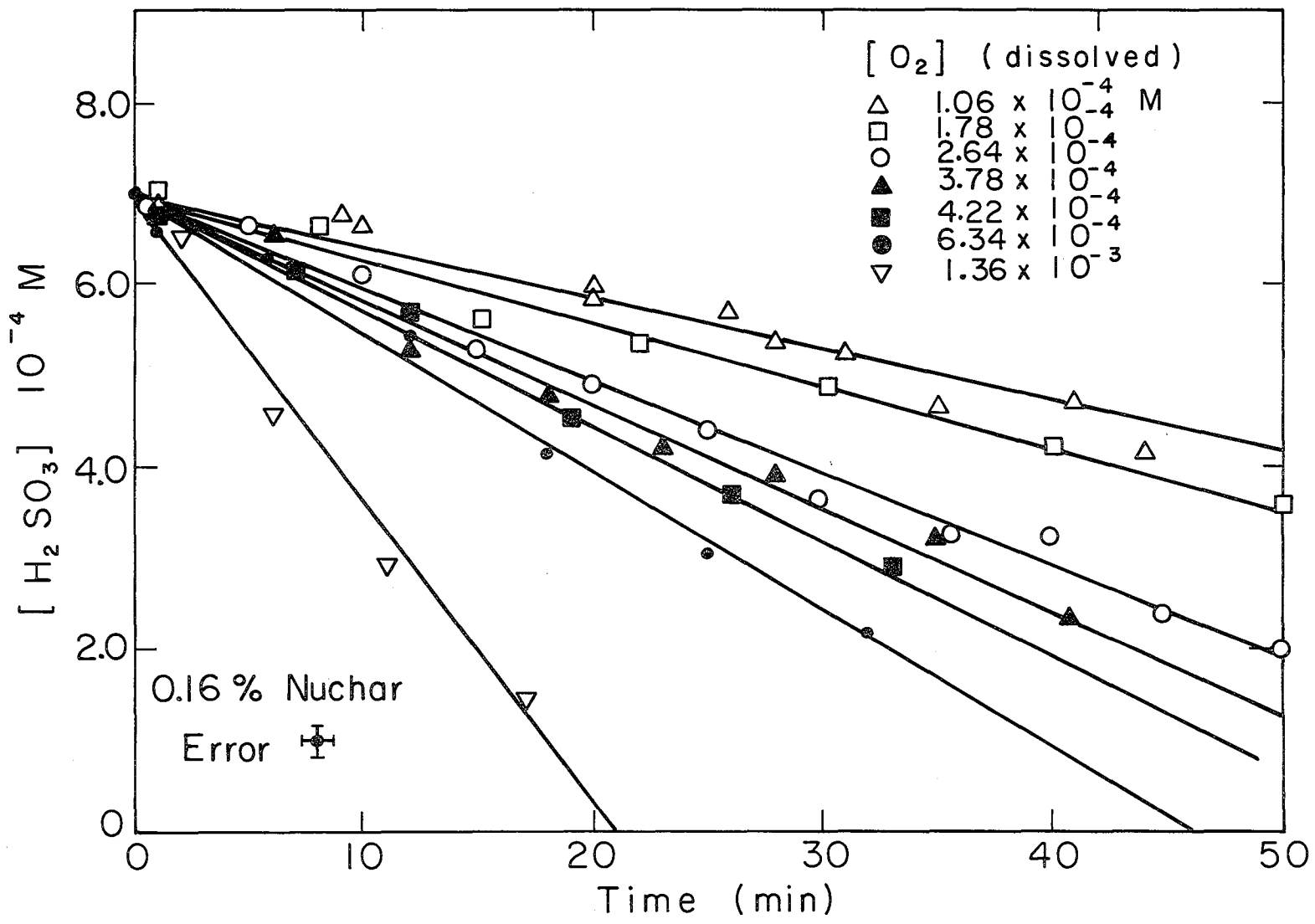
Figure 4





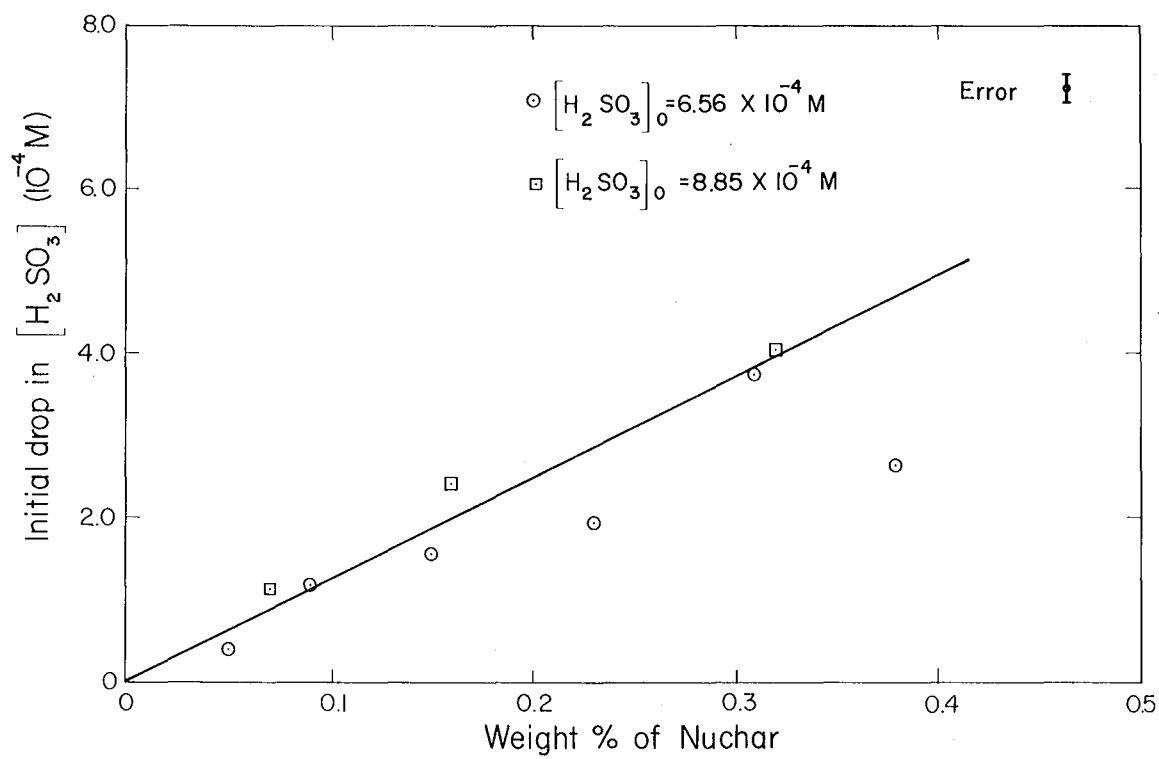
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Figure 5



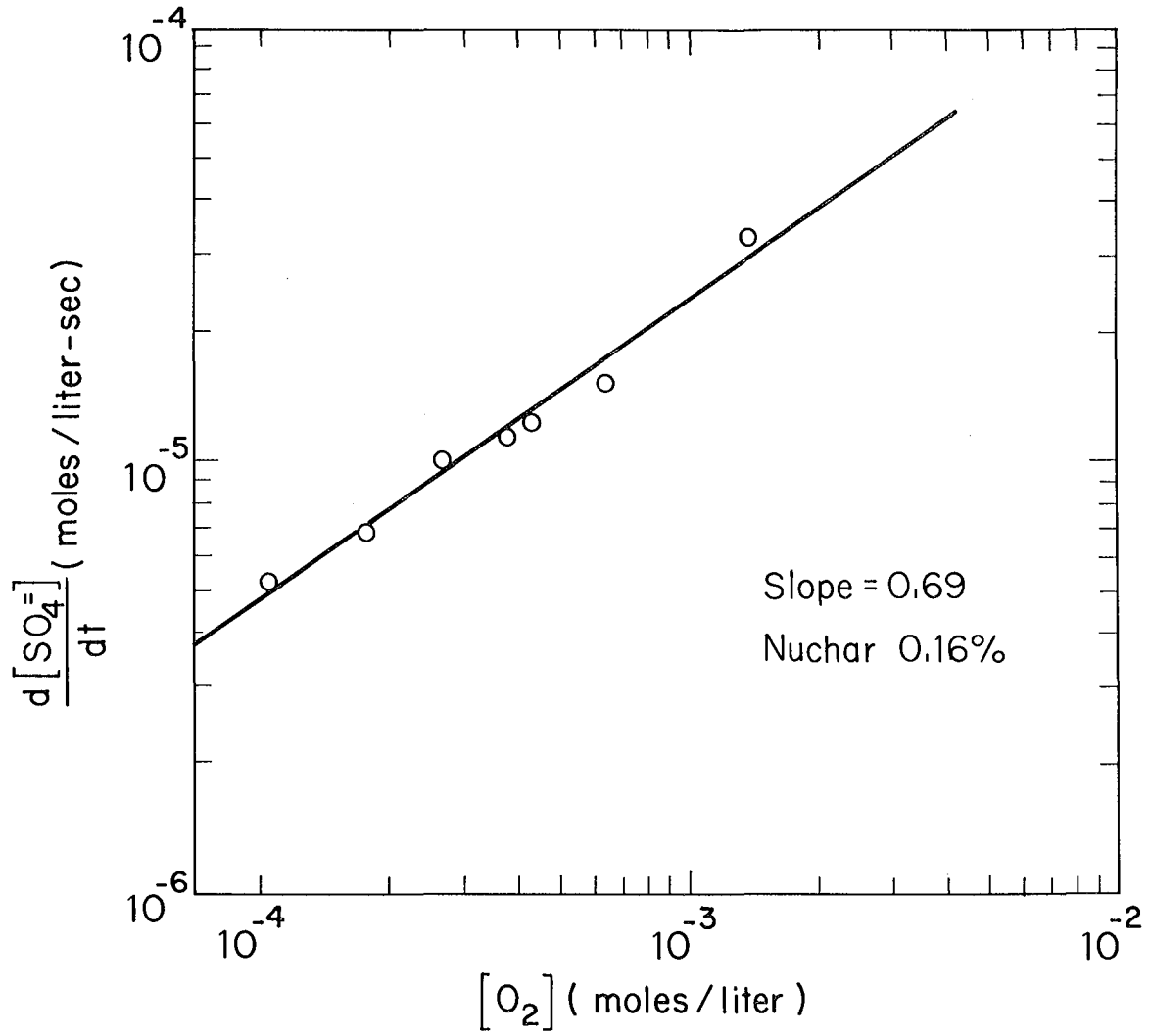
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Figure 6



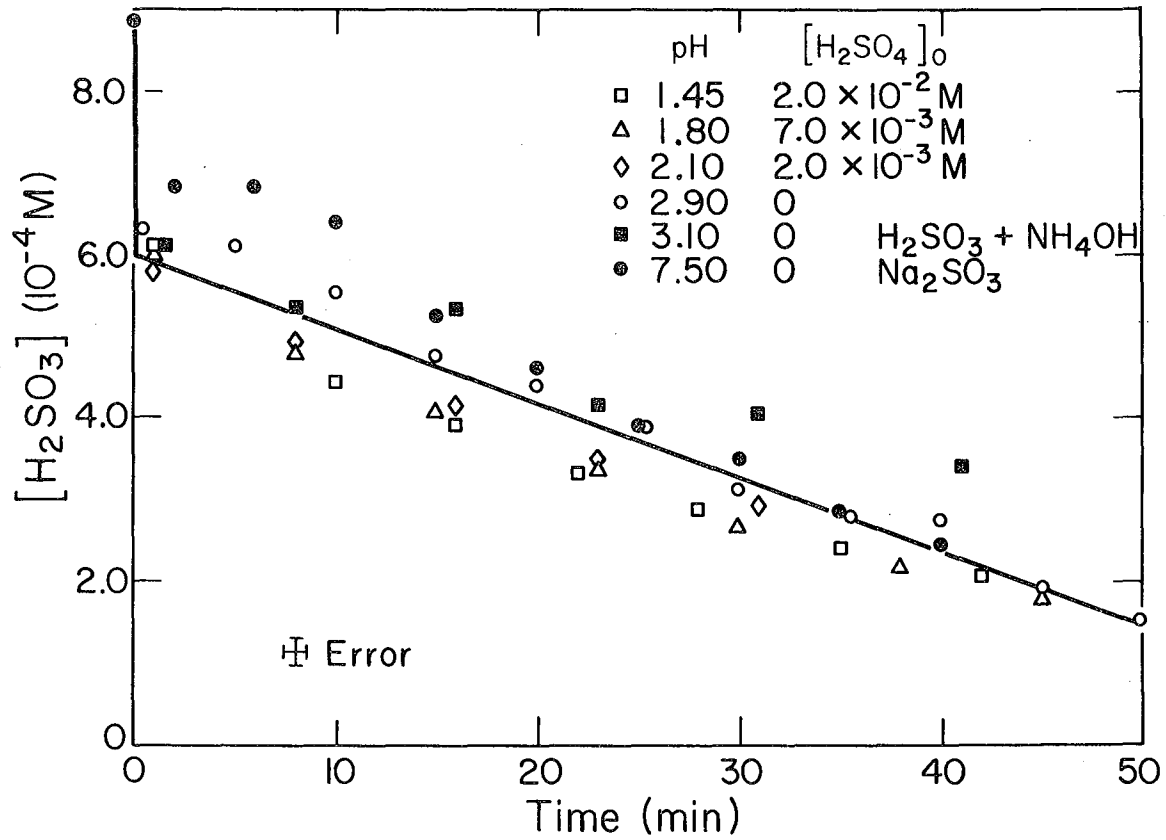
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Figure 7



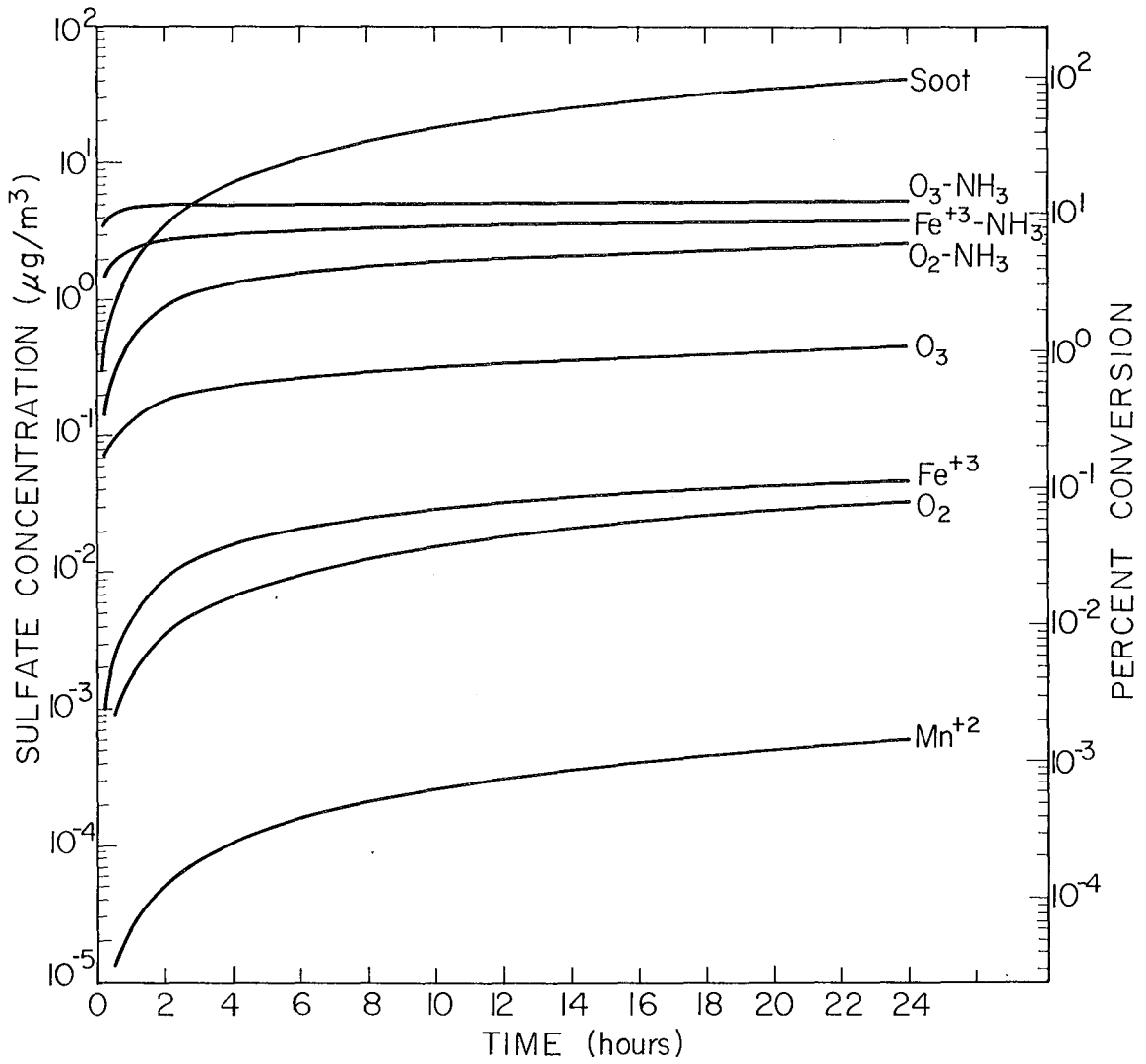
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Figure 8



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Figure 9



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Figure 10

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