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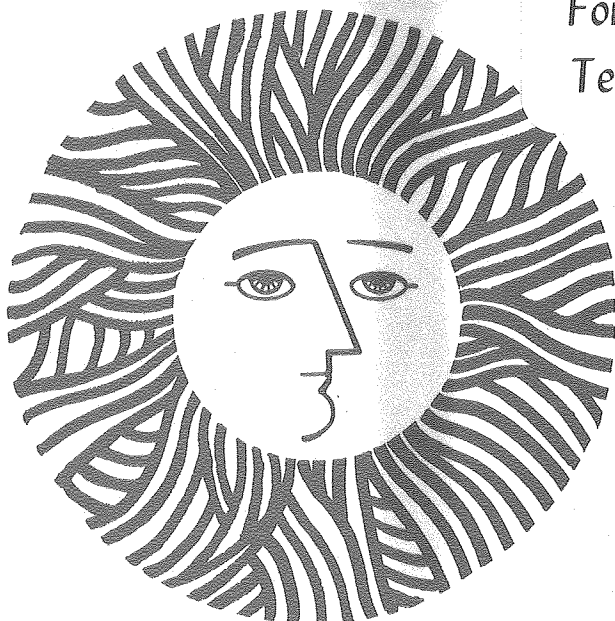
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W.H. Benner, R. Brodzinsky, and T. Novakov

November 1980

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FOG CHAMBER STUDIES OF SOOT-CATALYZED SO₂ OXIDATION*

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The oxidation of SO₂ by wet soot particles has been suggested as an important reaction pathway for the production of particulate sulfate in the ambient atmosphere. We studied this reaction in two systems. The first consisted of a flask-type reaction study. H₂SO₃ (diluted final concentration between 7x10⁻⁸ M and 1x10⁻³ M) was added to a flask containing several hundred milliliters of a constantly stirred aqueous suspension of Nuchar-SN in which the soot particle concentration was between 0.002 and 0.32% w/v carbon. For H₂SO₃ concentrations less than 10⁻⁴ M, sulfite and sulfate were determined by ion chromatography. Above 10⁻⁴ M H₂SO₃, sulfite concentration was determined by iodometric titrations while sulfate was measured turbidometrically only in selected runs. The pH of a soot suspension was controlled by the buffering capacity of the SO₂·H₂O, HSO₃⁻, SO₃⁼ system. The following oxidation mechanism was developed from the flask-type reaction study.

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

where $[C_x]$ = soot concentration in droplet, (g/L)

$$[S(IV)] = [SO_2 \cdot H_2O] + [HSO_3^-] + [SO_3^{=}]$$

$$\alpha = 4.915 \times 10^8 \text{ L}^2/\text{mole}^2$$

$$\beta = 2.956 \times 10^5 \text{ L/mole}$$

$$k = 1.336 \times 10^{-7} \text{ mole/g} \cdot \text{sec}$$

The rate expression describes an oxidation mechanism which is not sensitive to solution pH for $\text{pH} < 7.6$. (See Brodzinsky¹ for experimental evidence for the lack of effect of H^+ on S(IV) oxidation by wet soot particles.)

In Fig. 1, a family of curves is presented which shows the rate of sulfate formation, normalized to $[\text{C}]$, as a function of $[\text{SO}_2]$ for various initial $[\text{H}^+]$'s from Eq. 1 calculations. The family of curves in Fig. 1 indicates a pH effect on sulfate formation, but pH only becomes a factor when soot suspensions are exposed to SO_2 . The pH effect is related to the absorption of SO_2 by the droplet. For example, two droplets, one of which has an initial pH of 3 and the other a pH of 5, are equilibrated with 1 ppm SO_2 . The droplet with the lower initial pH will have a lower equilibrium $[\text{S(IV)}]$ and the oxidation rate will be similarly slower. The family of curves was calculated assuming that the droplet had a specified initial pH and was then equilibrated with SO_2 and 320 ppm CO_2 to produce a certain equilibrium $[\text{S(IV)}]$ before the oxidation started. The resultant $[\text{S(IV)}]$ was then used to calculate the reaction rate using Eq. 1.

The dashed line in Fig. 1 shows the S(IV) oxidation rate expected for wet soot particles in equilibrium with SO_2 . This curve was calculated assuming that the soot droplet initially had a pH of 7 and was then equilibrated with SO_2 and 320 ppm CO_2 to produce a certain equilibrium $[\text{S(IV)}]$ and equilibrium pH before oxidation started. The resulting $[\text{S(IV)}]$ was used to calculate the reaction rate using Eq. 1. It was also assumed in the calculation that the soot possessed no pH-altering species.

The flask-type reaction study indicated that $\text{SO}_3^=$ was easily oxidized to $\text{SO}_4^=$ and the question remained whether or not droplets which contained soot particles could oxidize SO_2 . A second experimental system was designed (Fig. 2) to answer this question. Particles of Nuchar-SN, pre-extracted to remove

sulfate, were resuspended by nebulization and the resultant mist was passed over heated water and subsequently cooled to cause the nebulized particles to grow into larger droplets. These droplets were exposed to SO_2 and introduced into the bottom of the fog chamber. The fog droplets were forced upwards through the chamber at a velocity which permitted approximately 30-min reaction time between droplets and SO_2 . A pre-fired quartz fiber filter and a Fluoropore (0.5- μm pore) filter were used simultaneously to collect samples from the top of the chamber. The filter holders and tubing leading to the filters were heated to decrease the relative humidity of the air stream to at least 30%, and reactions involving liquid water were thereby prevented. After collection of the sample, the Fluoropore filter was extracted in water and analyzed for sulfate using ion chromatography. A portion of the quartz filter was analyzed for total carbon by combustion analysis.

When pure water droplets were exposed to SO_2 in the fog chamber, the rate of sulfate formation ($\mu\text{g SO}_4/\text{m}^3 \cdot \text{hr}$) equals $4.06 [\text{ppm SO}_2]^{.0007}$. If the droplets contained Nuchar-SN particles, the rate of sulfate formation was found to be significantly faster than for pure water droplets. For example, wet soot particles exposed to 0.007 ppm SO_2 produced sulfate faster than pure water droplets exposed to 222 ppm SO_2 . The data for sulfate formation by wet soot particles is plotted with open circles in Fig. 1. The experimental equation which best fits these points is $\text{SO}_4^-/\text{c} \cdot \text{hr} = 0.222 [\text{ppm SO}_2]^{.147}$.

The difference between the fog chamber data and the dashed line in Fig. 1 is due to the alkaline nature of Nuchar-SN. The release of alkaline species into the droplet from the Nuchar-SN neutralized some of the absorbed $\text{SO}_2 \cdot \text{H}_2\text{O}$ and/or HSO_3^- and thus the equilibrium $[\text{S(IV)}]$ was larger than that predicted by Henry's Law for pure water and SO_2 . This neutralization increased the oxidation rate because it brought more $\text{SO}_2 \cdot \text{H}_2\text{O}$ and HSO_3^- into the droplet. The

magnitude of the difference between the fog chamber data line and the dashed line depends on the $[\text{SO}_2]$. At low $[\text{SO}_2]$, the alkaline species on the soot particles attract into solution more $\text{SO}_2 \cdot \text{H}_2\text{O}$ or HSO_3^- than would be expected for pure water, and thus these alkaline species strongly influence the resultant $[\text{S(IV)}]$. At high $[\text{SO}_2]$, the dissolved SO_2 overwhelms the buffering capacity of the alkaline species and the $[\text{SO}_2]$ becomes the dominant factor for controlling the resultant $[\text{S(IV)}]$. Therefore, at high $[\text{SO}_2]$ the fog chamber data line and the dashed line in Fig. 1 coincide.

Calculations by Chang² indicated that oxidation of SO_2 by wet soot particles is an important source of atmospheric sulfate. These calculations were based on the assumption that SO_2 in the atmosphere would enter the droplet and form SO_3^- , which would be converted finally to $\text{SO}_4^{=}$. Data presented here show that wet soot particles, Nuchar-SN being a type of soot, can oxidize SO_2 to $\text{SO}_4^{=}$. For the particular type of soot studied, the SO_2 oxidation rate is faster than anticipated because of the alkaline nature of Nuchar-SN.

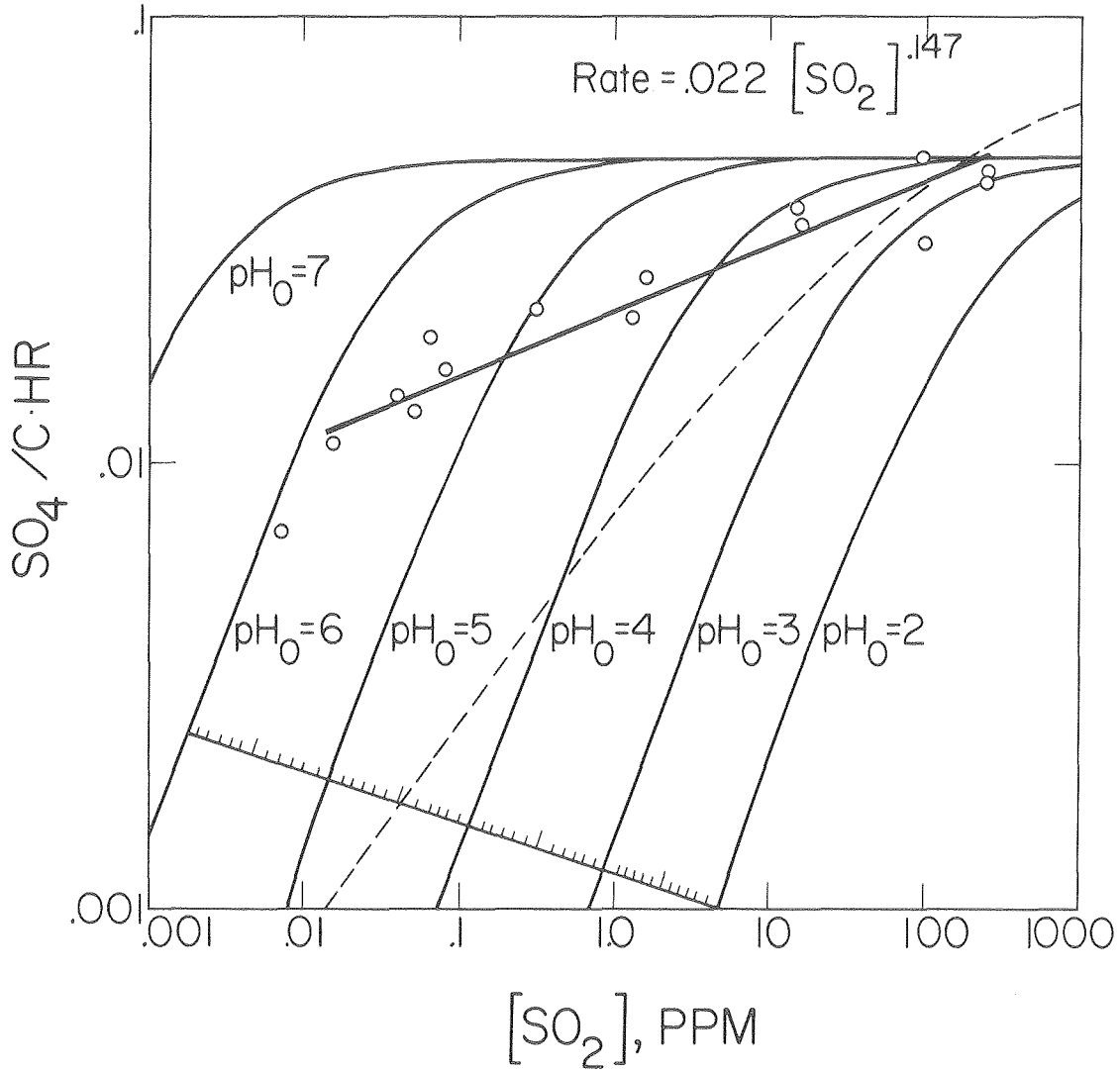
1. Brodzinsky, R., S.G. Chang, S.S. Markowitz, and T. Novakov, "Kinetics and Mechanism for the Catalytic Oxidation of Sulfur Dioxide on Carbon in Aqueous Suspensions," J. Phys. Chem, to be published 27 November 1980.
2. Atmospheric Aerosol Research Annual Report 1977-78, Lawrence Berkeley Laboratory Report LBL-8696 (1978).

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Figure Captions

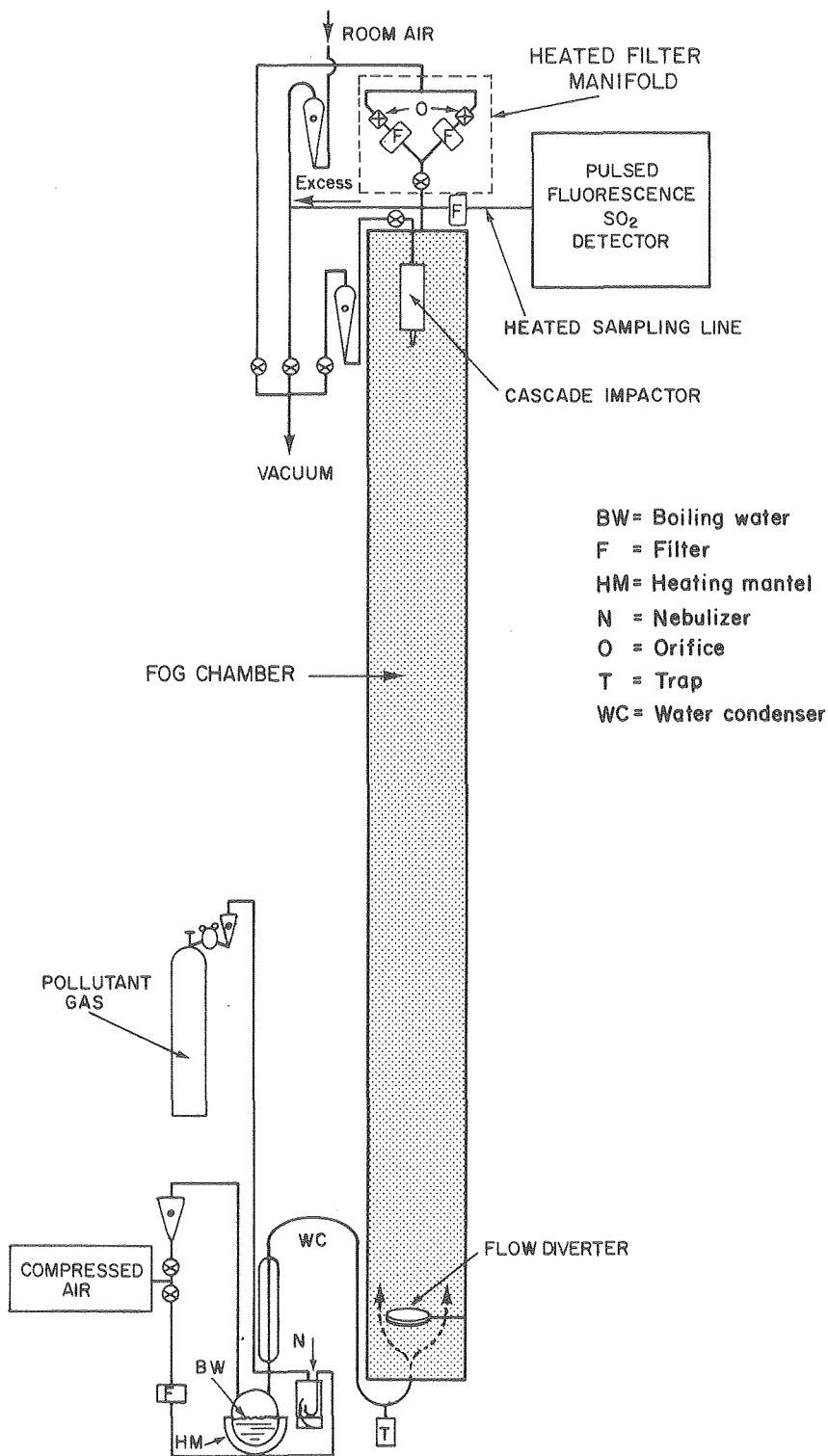
Figure 1. The normalized rate of sulfate formation in wet soot droplets vs. SO_2 . The open circles and the solid line drawn through the circles were obtained from fog chamber data. The family of curves labelled $\text{pH}_0 = 2$ through $\text{pH}_0 = 7$ was calculated from Eq. 1. The pH_0 is the droplet pH before exposure to SO_2 and CO_2 . The dashed line shows the rate of sulfate formation (Eq. 1) for wet soot droplets whose pH before exposure to SO_2 and 320 ppm CO_2 is determined by SO_2 - CO_2 - H_2O equilibria. The dashed line is juxtaposed on pH coordinates created by the family of curves labelled $\text{pH}_0 = 2$ through $\text{pH}_0 = 7$.

Figure 2. Laboratory fog chamber and associated equipment.



XBL 809-1860

Figure 1



XBL 804-4124

Figure 2

