

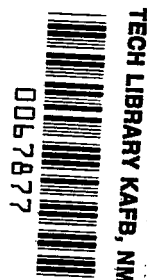
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Carbon-Catalyzed Oxidation of SO₂ by NO₂ and Air

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Carbon-Catalyzed Oxidation of SO_2 by NO_2 and Air

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National Aeronautics
and Space Administration

Scientific and Technical
Information Branch



SUMMARY

A series of experiments has been performed using carbon particles (commercial furnace black) as a surrogate for soot particles. Carbon particles were suspended in water and gas mixtures were bubbled into the suspensions to observe the effect of carbon particles on the oxidation of SO_2 by air and NO_2 . Identical gas mixtures were bubbled into a blank containing only pure water. After exposure each solution was analyzed for pH and sulfate content. It was found that NO_2 greatly enhances the oxidation of SO_2 to sulfate in the presence of carbon particles. The amount of sulfate found in the blanks was significantly less. Under the conditions of these experiments no saturation of the reaction was observed and SO_2 was converted to sulfate even in a highly acid medium ($\text{pH} > 1.5$).

INTRODUCTION

Many mechanisms have been proposed for the oxidation of SO_2 in the atmosphere. These include homogeneous reactions in the gas phase (ref. 1) and heterogeneous reactions in cloud droplets or liquid-phase aerosols (refs. 2 to 4) and on carbon particles (refs. 5 and 6). In order to assess the relative contribution of the various mechanisms and to propose enlightened control strategies, the competing processes must be evaluated in detail.

The work described here addresses one aspect of this problem, namely heterogeneous oxidation of SO_2 by air and NO_2 on carbon (soot) particles suspended in water. Similar reactions are possible in the atmosphere in liquid droplets or aerosols containing insoluble carbon particles. Novakov et al. (ref. 5) have established that soot is effective in oxidizing SO_2 to sulfate in the presence of O_2 . Carbon particles are found even in remote areas such as the Arctic (ref. 7) and are virtually ubiquitous. Therefore they are widely available to provide reactive sites.

The experiments involving carbon suspended in liquid water were prompted by our original experiments performed with dry carbon particles (ref. 8). When such particles were exposed to mixtures of humidified air, SO_2 , and NO_2 they became wetted after a certain time, and it was not clear at that point whether solution chemistry was dominant or if the soot still played an important role.

EXPERIMENTAL PROCEDURE

Carbon particles (commercial furnace black) were suspended in distilled water at a concentration of 100 mg/10 ml, and commercially prepared mixtures of gases (supplier-certified mixtures in ultrahigh-purity carrier) were bubbled into the aqueous suspension. The apparatus is shown schematically in figure 1. The same gas mixtures were also bubbled through 10 ml of pure water to serve as a blank. The gases (100 ppm SO_2 in air or N_2 and 100 ppm NO_2 in N_2) were mixed prior to splitting the flow between the two reaction vessels. The reactors were held at a constant temperature of 23°C in a water bath. This configuration allowed the blank and the aqueous carbon suspension to be exposed to identical conditions, so that the difference in amount of sulfate produced in the two reactors was a direct measure of the

effect of the carbon. After each experiment the resulting solutions were analyzed for pH and sulfate content using a barium turbidity test (ref. 8).

RESULTS AND DISCUSSION

The results of several experiments are presented graphically in figure 2. The yield of sulfate under identical exposure conditons is much larger in the presence of the carbon. The carbon acts as a catalyst for the oxidation of SO_2 by both air and air with 100 ppm NO_2 added. Apparently the carbon provides sites for the SO_2 oxidation to occur because, as the blank curves indicate, neither air nor NO_2 has any significant oxidation effect in water alone. The conversion rate of SO_2 in air at 100 ppm with 1 percent carbon is 9.3 percent per hour and increases to 58 percent per hour when 100 ppm NO_2 is added. These results are in agreement with those obtained in previous experiments in this laboratory (ref. 8) in which NO_2 significantly enhanced the oxidation of SO_2 on carbon particles. Some enhancement of the oxidation of SO_2 by NO_2 has also been observed on dry soot by Britton and Clarke (ref. 9) and on dry V_2O_5 by Barbaray et al. (ref. 10).

To distinguish the oxidizing effect of NO_2 from that of the O_2 in air, the same experiment was performed with the SO_2 and NO_2 mixed in N_2 . The results are shown in figure 3. Here only the oxidizing capacity of the NO_2 is measured. The experiments in N_2 indicate that NO_2 acts as an oxidizing agent independent of the O_2 in air, and comparison of results from figures 2 and 3 shows that the effects of O_2 and NO_2 are additive. The intercept of 0.64 mg sulfate in figures 2 and 3 was found to be due to sulfate present on the carbon surface as received from the manufacturer.

Several 20-hour runs were made at SO_2 and NO_2 concentrations of 100 ppm and flow rates of $100 \text{ cm}^3/\text{min}$ for each gas. The sulfate yields were the same (30 mg) as would be predicted by linear extrapolation of the data in figure 2. This indicates that SO_2 was converted to sulfate with no observable saturation effect for these long exposures. The pH of the solutions for these runs was as low as 1.5, indicating that the conversion takes place under highly acidic conditions. Saturation effects have consistently been observed for SO_2 on dry particles by others (refs. 9, 11, and 12), but we have observed no saturation in either the gravimetric or bubbler experiments as long as sufficient H_2O vapor or liquid H_2O is present.

If the 20-hour runs were extrapolated to typical atmospheric SO_2 concentrations of 0.01 ppm, this would indicate that "wet" soot particles could be exposed for 2×10^6 hours without saturation effects. This is certainly much longer than typical particle lifetimes in the atmosphere.

CONCLUSIONS

The experimental results reported herein lead to the following conclusions:

1. Carbon particles significantly catalyze the oxidation of SO_2 to sulfate by air and/or NO_2 .
2. NO_2 is an effective oxidizer for SO_2 in aqueous suspensions of carbon and its effect is independent of the presence or absence of air; the reaction is controlled by the NO_2 , provided sufficient SO_2 is present.

3. The yield of sulfate in the reactions studied appears to be independent of pH at values as low as 1.5, and no saturation occurs for long exposure times so long as sufficient H₂O is present.

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March 16, 1982

REFERENCES

1. Calvert, Jack G.; Su, Fu; Bottenheim, Jan W.; and Strausz, Otto P.: Mechanism of the Homogeneous Oxidation of Sulfur Dioxide in the Troposphere. *Atmos. Environ.*, vol. 12, no. 1-3, 1978, pp. 197-226.
2. Hegg, Dean A.; and Hobbs, Peter V.: Cloud Water Chemistry and the Production of Sulfates in Clouds. *Atmos. Environ.*, vol. 15, no. 9, 1981, pp. 1597-1604.
3. Beilke, S.; and Gravenhorst, G.: Heterogeneous SO₂-Oxidation in the Droplet Phase. *Atmos. Environ.*, vol. 12, no. 1-3, 1978, pp. 231-239.
4. Penkett, S. A.; Jones, B. M. R.; Brice, K. A.; and Eggleton, A. E. J.: The Importance of Atmospheric Ozone and Hydrogen Peroxide in Oxidising Sulphur Dioxide in Cloud and Rainwater. *Atmos. Environ.*, vol. 13, no. 1, 1979, pp. 123-137.
5. Novakov, T.; Chang, S. G.; and Harker, A. B.: Sulfates as Pollution Particulates: Catalytic Formation on Carbon (Soot) Particles. *Science*, vol. 186, no. 4160, Oct. 18, 1974, pp. 259-261.
6. Chang, S. G.; and Novakov, T.: Soot-Catalyzed Oxidation of Sulfur Dioxide. *Man's Impact on the Troposphere - Lectures in Tropospheric Chemistry*, Joel S. Levine and David R. Schryer, eds., NASA RP-1022, 1978, pp. 349-369.
7. Rosen, H.; Novakov, T.; and Bodhaine, B. A.: Soot in the Arctic. *Atmos. Environ.*, vol. 15, no. 8, 1981, pp. 1371-1374.
8. Cofer, Wesley R., III; Schryer, David R.; and Rogowski, Robert S.: The Enhanced Oxidation of SO₂ by NO₂ on Carbon Particulates. *Atmos. Environ.*, vol. 14, no. 5, 1980, pp. 571-575.
9. Britton, L. G.; and Clarke, A. G.: Heterogeneous Reactions of Sulphur Dioxide and SO₂/NO₂ Mixtures With a Carbon Soot Aerosol. *Atmos. Environ.*, vol. 14, no. 7, 1980, pp. 829-839.
10. Barbaray, Brigitte; Contour, Jean-Pierre; and Mouvier, Gérard: Effects of Nitrogen Dioxide and Water Vapor on Oxidation of Sulfur Dioxide Over V₂O₅ Particles. *Environ. Sci. & Technol.*, vol. 12, no. 12, Nov. 1978, pp. 1294-1297.
11. Baldwin, Alan C.; and Golden, David M.: Heterogeneous Atmospheric Reactions: Sulfuric Acid Aerosols as Tropospheric Sinks. *Science*, vol. 206, no. 4418, Nov. 2, 1979, pp. 562-563.
12. Judeikis, Henry S.; Stewart, Thomas B.; and Ren, Anthony G.: Laboratory Studies of Heterogeneous Reactions of SO₂. *Atmos. Environ.*, vol. 12, no. 8, 1978, pp. 1633-1641.

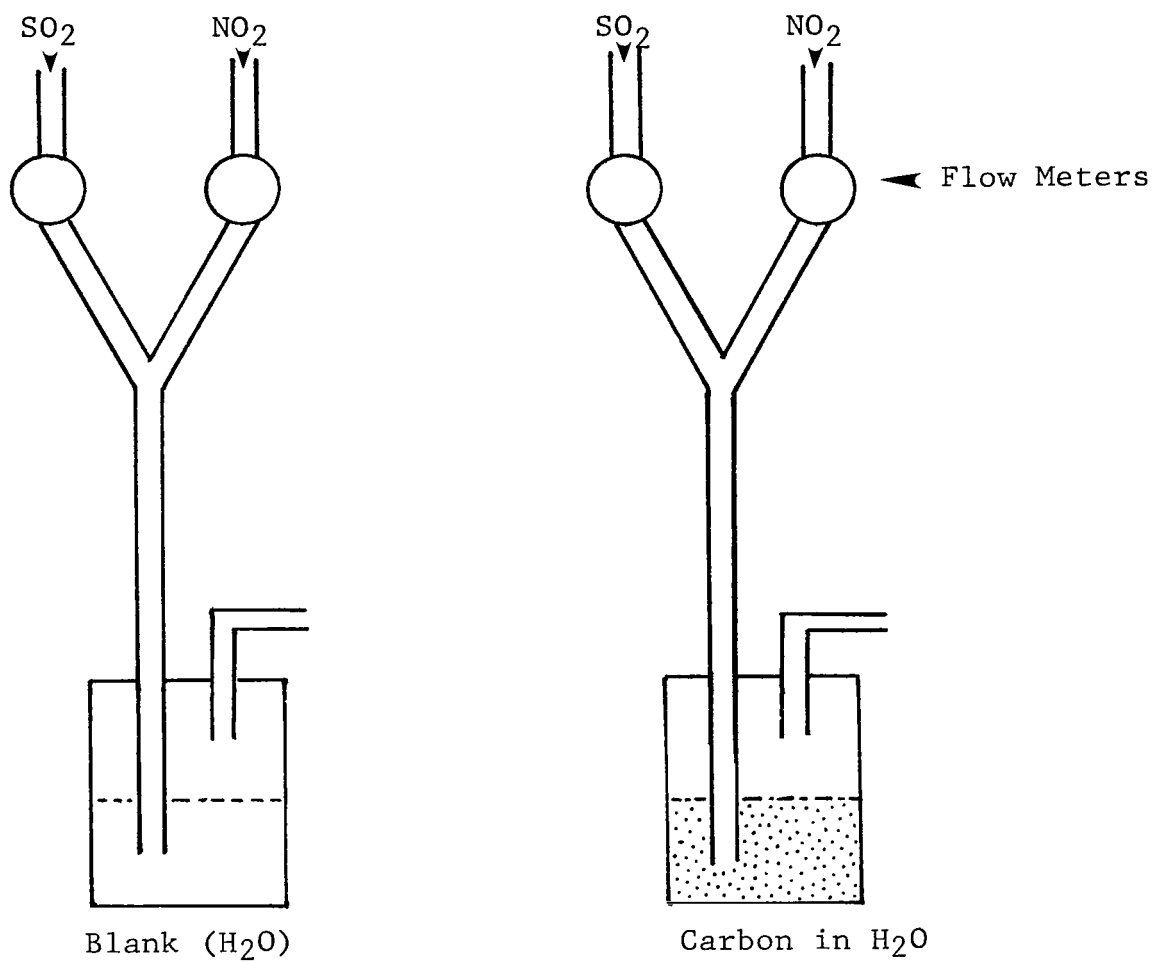


Figure 1.- Apparatus used to investigate SO_2 oxidation in presence of aqueous carbon suspension.

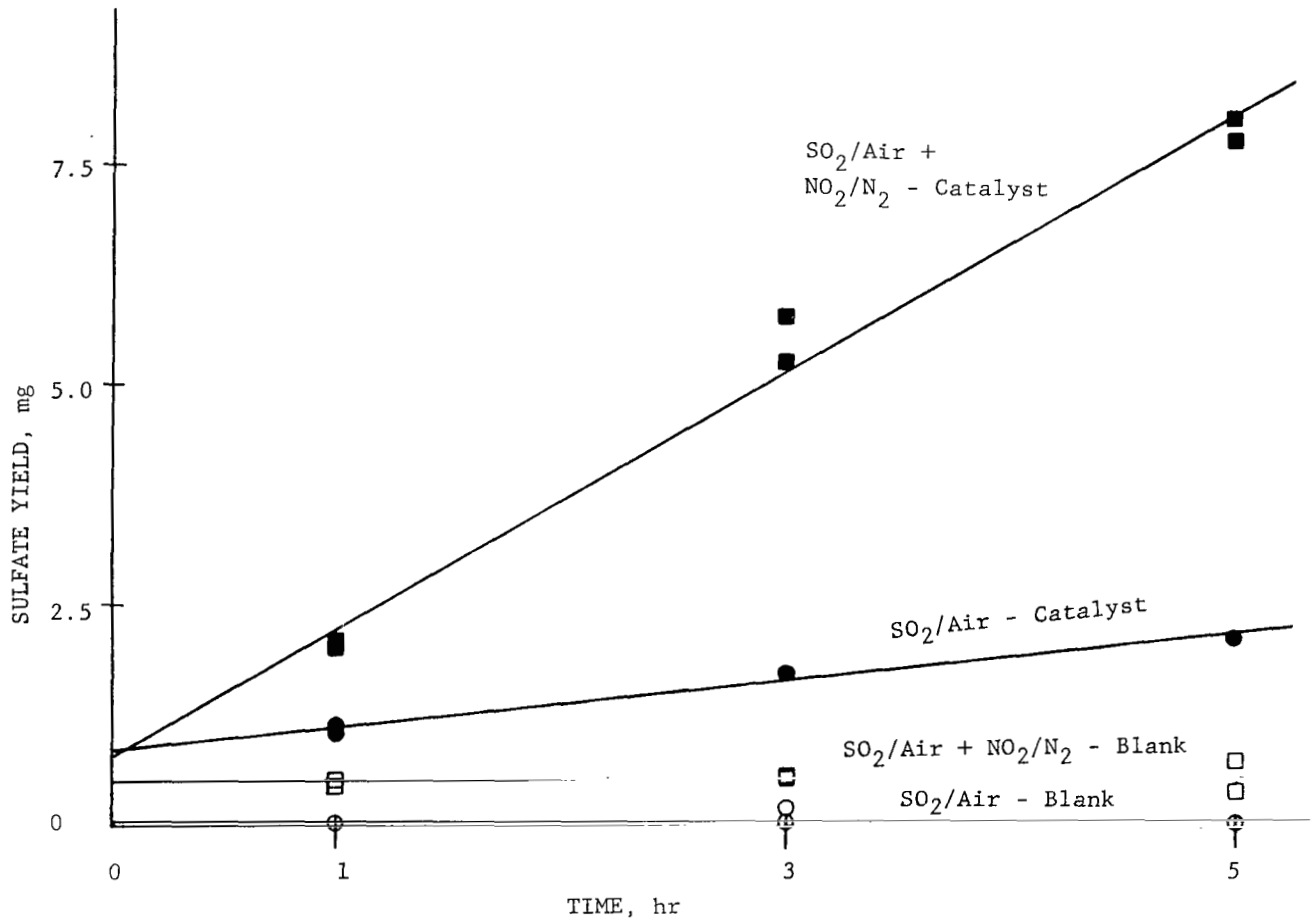


Figure 2.- Effect of NO₂ and catalyst on sulfate yield in air. Blank: 10 ml H₂O; catalyst: 100 mg carbon black in 10 ml H₂O; flow rates: 100 cm³/min, each gas; concentrations: 100 ppm, each gas.

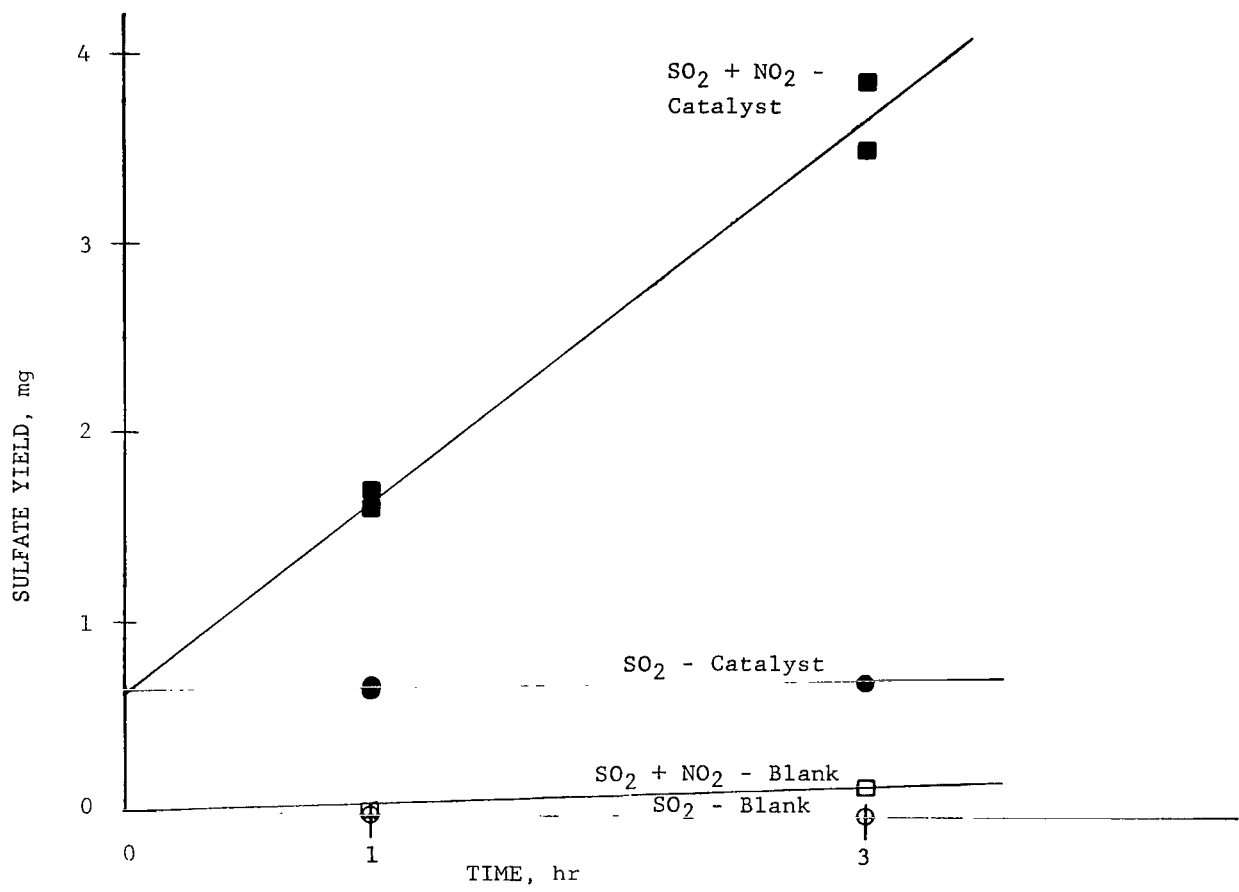


Figure 3.- Effect of NO₂ and catalyst on sulfate yield in N₂. Blank: 10 ml H₂O; catalyst: 100 mg carbon black in 10 ml H₂O; flow rates: 100 cm³/min, each gas; concentrations: 100 ppm in N₂, each gas.

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