Carbon-Catalyzed Oxidation of SO₂ by NO₂ and Air

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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 SO₂ by air and NO₂. 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 NO₂ greatly enhances the oxidation of SO₂ 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 SO₂ was converted to sulfate even in a highly acid medium (pH > 1.5).

Many mechanisms have been proposed for the oxidation of SO₂ 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 SO₂ by air and NO₂ 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 SO₂ to sulfate in the presence of O₂. 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, SO₂, and NO₂ 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.

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 SO₂ in air or N₂ and 100 ppm NO₂ in N₂) 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 conditions is much larger in the presence of the carbon. The carbon acts as a catalyst for the oxidation of SO₂ by both air and air with 100 ppm NO₂ added. Apparently the carbon provides sites for the SO₂ oxidation to occur because, as the blank curves indicate, neither air nor NO₂ has any significant oxidation effect in water alone. The conversion rate of SO₂ 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 NO₂ is added. These results are in agreement with those obtained in previous experiments in this laboratory (ref. 8) in which NO₂ significantly enhanced the oxidation of SO₂ on carbon particles. Some enhancement of the oxidation of SO₂ by NO₂ has also been observed on dry soot by Britton and Clarke (ref. 9) and on dry V₂O₅ by Barbaray et al. (ref. 10).

To distinguish the oxidizing effect of NO₂ from that of the O₂ in air, the same experiment was performed with the SO₂ and NO₂ mixed in N₂. The results are shown in figure 3. Here only the oxidizing capacity of the NO₂ is measured. The experiments in N₂ indicate that NO₂ acts as an oxidizing agent independent of the O₂ in air, and comparison of results from figures 2 and 3 shows that the effects of O₂ and NO₂ 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 SO₂ and NO₂ concentrations of 100 ppm and flow rates of 100 cm³/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 SO₂ 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 SO₂ 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 H₂O vapor or liquid H₂O is present.

If the 20-hour runs were extrapolated to typical atmospheric SO₂ concentrations of 0.01 ppm, this would indicate that "wet" soot particles could be exposed for 2 x 10⁶ 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 SO₂ to sulfate by air and/or NO₂.

2. NO₂ is an effective oxidizer for SO₂ in aqueous suspensions of carbon and its effect is independent of the presence or absence of air; the reaction is controlled by the NO₂, provided sufficient SO₂ 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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REFERENCES


Figure 1.— Apparatus used to investigate SO$_2$ oxidation in presence of aqueous carbon suspension.
Figure 2.- Effect of NO\textsubscript{2} and catalyst on sulfate yield in air. Blank: 10 ml H\textsubscript{2}O; catalyst: 100 mg carbon black in 10 ml H\textsubscript{2}O; flow rates: 100 cm\textsuperscript{3}/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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