ories can only be tested with good data. Beliefs and preconceptions about the way nature should work provide no scientific basis for rejecting predictive empirical models.

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## **References and Notes**

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- 4.5°C for Lake Huron.

11 June 1980

## Synergistic Effects in Trace Gas-Aerosol Interactions

Baldwin and Golden (1) recently reported some results of a study of the reaction of various atmospheric gases with both H<sub>2</sub>SO<sub>4</sub> and soot surfaces. They reported that SO<sub>2</sub> and NO<sub>2</sub> (as well as several other gases) did not react appreciably with the soot. We have similarly observed no effect when dry SO<sub>2</sub> and NO2 are exposed to carbon surfaces individually, but significant reaction is observed when SO<sub>2</sub> and NO<sub>2</sub> are exposed to such surfaces in combination.

Our experimental procedure (2) consists of a microgravimetric determination of chemisorption with subsequent analysis of the chemisorbed species by various techniques. A substrate sample is placed on the pan of a continuously recording microbalance and is exposed for a given time to a measured flow of carrier gas (dry or humidified) which contains small quantities (10 to 100 parts per million) of one or more test gases. The sample is then exposed to a flow of dry N<sub>2</sub> to desorb any physically adsorbed species. In control measurements, the substrate is exposed to pure carrier gas and the system with an empty pan is exposed to the various gases.

When samples of commercially available carbon black (used as a soot surrogate to maintain uniformity) are exposed to either  $SO_2$  or  $NO_2$  in dry air or  $N_2$  as the carrier gas, no quantitative chemisorption (< 5  $\mu$ g on  $\approx$  1 mg of substrate) is observed. However, exposure of the same grade of carbon to a combination of SO<sub>2</sub> and NO<sub>2</sub> in dry air or N<sub>2</sub> results in significant chemisorption (180 to 280  $\mu$ g/mg), a major fraction of which is analyzed as sulfate. The NO<sub>2</sub> appears to be an oxidizing agent, since reaction occurs in either N<sub>2</sub> or air. In fact, a slightly higher yield is observed with N<sub>2</sub> than with air; some constituent of air (perhaps NO) may inhibit the reaction somewhat. The reaction is believed to be heterogeneous and to occur on the substrate because no reaction is observed in appropriate control measurements. Humidification of the carrier gas, whether air or N<sub>2</sub>, increases both the total chemisorption and the amount of sulfate by about an order of magnitude. These values are measured after desorption of the samples by dry  $N_2$  and therefore do not merely represent adsorbed water.

The effect of humidity in converting

SO<sub>2</sub> on carbon black is so pronounced that some chemisorption and sulfate yield is observed with SO<sub>2</sub> in humid air without the addition of NO<sub>2</sub>, but addition of NO2 increases the yield by an order of magnitude or more. Quantitative chemisorption on carbon black has not been observed (i) with SO<sub>2</sub> in dry air, in dry  $N_2$ , or in humidified  $N_2$  in the absence of NO<sub>2</sub> or (ii) with NO<sub>2</sub> in these carriers in the absence of  $SO_2$ .

We have also observed chemisorption and sulfate formation on an Al<sub>2</sub>O<sub>3</sub> substrate with  $SO_2 + NO_2$  in humidified air, but with lower yields than on carbon black. Barbaray et al. (3) have reported enhancement of the chemisorption and oxidation of SO<sub>2</sub> by NO<sub>2</sub> and H<sub>2</sub>O on a V<sub>2</sub>O<sub>5</sub> substrate, and Novakov and his coworkers (4) have demonstrated the importance of both gaseous and liquid H<sub>2</sub>O on heterogeneous SO<sub>2</sub> oxidation in the presence of carbon surfaces.

We agree with Baldwin and Golden on potential importance of heterothe geneous processes in the atmosphere. We strongly urge, however, that research on such processes should consider synergistic effects among atmospheric trace gases. Baldwin and Golden considered such effects in their studies with the H<sub>2</sub>SO<sub>4</sub> surface, with negative results for  $O_3 + NO$  and  $O_2 + NO$ .

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20 December 1979