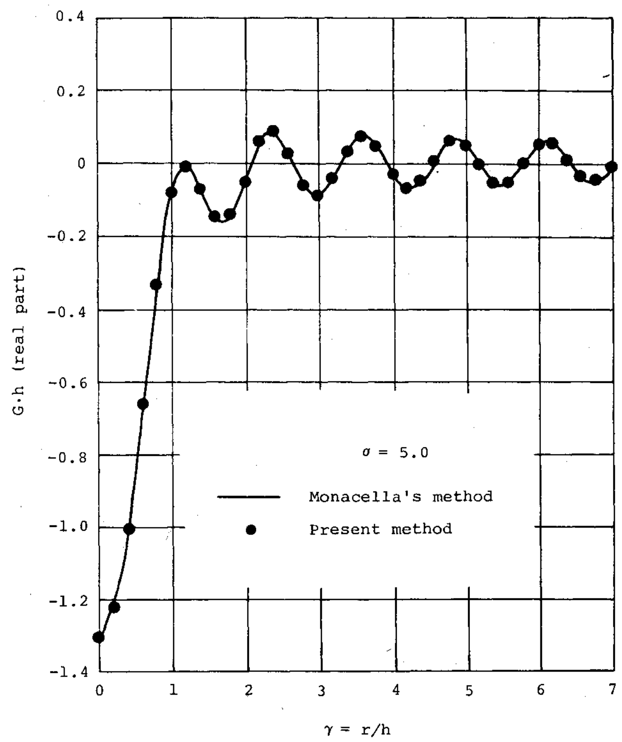

Fig. 1 Comparison between Monacella's method and present method.

Verification and Comparison

To verify this method, the Green's function in Eq. (7) is evaluated for the condition $\mu_0 = 5.000454$ and $\sigma = 5.0$. A comparison is made in Fig. 1 of the real part of the value of *Gh* obtained by the present technique with that obtained by a technique of Monacella.[1] Gauss-Laguerre quadrature $n = 64$ is used and CPU time is 2.81 s for 36 values in Fig. 1. On the other hand, it takes 32.33 s by Monacella's method. The digital computer used was HITAC M-180. As can be judged, the results are virtually identical and the present method is computationally much faster than Monacella's method.

Acknowledgments

This Note is taken from the author's Ph.D. Thesis submitted to Department of Ocean Engineering at the University of Hawaii at Manoa on April 20, 1981. The author is greatly indebted to Dr. Charles L. Bretschneider for his financial support throughout the author's Ph.D. program. Dr. G. Venezian, currently associate professor of ocean engineering, Texas A&M University, and formerly of University of Hawaii at Manoa, is also acknowledged for the suggestion which led to the development of this technique.

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Carbon Catalyzed SO_2 Oxidation by NO_2

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Introduction

VARIOUS mechanisms have been suggested to account for the atmospheric transformation of SO_2 to sulfate. These mechanisms have ranged from purely gas phase reactions[1] to reactions in aqueous cloud droplets.[2,3] The catalytic oxidation of SO_2 on particulates has received increased attention since Novakov[4] demonstrated that carbon particles could effectively catalyze SO_2 oxidation to sulfate in air at room temperature. Chang and Novakov[5] subsequently suggested that carbon particles covered with a liquid water phase could dominate the atmospheric conversion of SO_2 to sulfate under certain realistic conditions. Cofer et al.[6,7] then demonstrated that SO_2 oxidation on carbon particles could be enhanced significantly by trace amounts of gaseous NO_2 and O_3. In those experiments, initially dry graphitic carbon particles on the pan of a microbalance were exposed to continuously flowing gaseous mixtures of SO_2/air and SO_2/air/NO_2 (or O_3) at 65% relative humidity and then analyzed for sulfate. A significant enhancement in sulfate production resulted with the incorporation of either NO_2 or O_3 into the SO_2/air mixtures. The initially dry carbon particles, however, were observed to progressively "wet" and agglomerate with increasing exposure time. Thus, it was next to impossible to assess from these experiments the extent that aqueous solution chemistry influenced the SO_2 transformation process on the carbon particles. The assessment was achieved partially by conducting a second set of experiments that contrasted the transformation of SO_2 to sulfate in carbon/water suspensions with pure water blanks. This Note represents a review of the bubbler experiments[8] and a comparison of these results with the results from the microbalance studies.

Experimental

Selected gas mixtures of SO_2 in air or SO_2/air + NO_2/N_2 were bubbled through distilled water and carbon black suspensions in distilled water. Typically, 100 mg of commercial carbon black (BET-N_2 surface area = 240 m^2/g) was suspended in 10 ml of water and placed in one of two matched

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Presented as Paper 82-0089 at the AIAA 20th Aerospace Sciences Meeting, Orlando, Fla., Jan. 11-14, 1982; submitted Jan. 25, 1982; revision received May 11, 1982. This paper is declared a work of the U.S. Government and therefore is in the public domain.

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bubblers. The other bubbler was loaded with 10 ml of pure water and served as a blank. Both bubblers were immersed in a water bath and held at 23°C. Gases were then flow blended to form the desired mixture which was split equally between bubblers. This arrangement insured that both the blank and the carbon suspension would be exposed under identical conditions and that any observed differences in sulfate production would be a direct measure of the effect of the carbon.

Gaseous reactants were supplied directly from pressurized gas cylinders which were analyzed individually and certified by the vendor. The concentrations used were 100±5 ppmv SO_2 in air, 100±ppmv SO_2 in N_2, and 100±5 ppmv NO_2 in N_2. All flows were monitored with mass flowmeters. After exposing both the blank and the carbon/water sample for a prescribed time, chemical analysis was performed on the liquid phase. Another set of experiments had been conducted[6] in which ~1-mg samples of carbon particles (uniformly spread over a 12-mm-diam Teflon weighing pan) were exposed to a continuous flow of adsorbate (80 ppmv SO_2 + 10 ppmv NO_2) at 65% relative humidity. These samples were quenched in 20 ml of distilled water after various exposure time and analyzed for sulfate. Samples were either filtered and analyzed for sulfate by a barium turbidity method[10] or centrifuged to separate the carbon and analyzed by ion chromatography. The barium turbidity method generally was used when sulfate concentrations were anticipated to exceed 20 ppmM in solution. The background level of sulfate on the carbon samples (before exposure) was determined by immersing 100 mg of carbon black in 10 ml of distilled water for an hour and then analyzing the liquid for sulfate. The samples were found to yield an average sulfate background contamination equivalent to 6.4 μg of $SO_4^=$ per mg of carbon.

Results

The enhanced oxidation of SO_2 on carbon black by NO_2 which was observed in the previous study[6] was confirmed in the bubbler experiments, and is demonstrated in Fig. 1. Data points plotted in this figure (and in Fig. 2) represent the average of two or more runs (individual data points are presented in Ref. 8). The highest yields of sulfate were obtained from the carbon suspensions exposed to 100 cm³/min of 100 ppmv SO_2 in air + 100 cm³/min of 100 ppmv NO_2 in N_2. When equivalent carbon suspensions were exposed to 100 cm³/min of 100 ppmv SO_2 in N_2 + 100 cm³/min of 100 ppmv NO_2 in N_2, a smaller yield of sulfate was observed. This yield, however, can be seen (Fig. 1) to be substantially larger than that for SO_2 in air without NO_2. Hence, NO_2 can be deduced (based on concentrations) to be a much more efficient oxidizer in SO_2-carbon suspensions than is molecular oxygen. Since the SO_2/N_2 mixtures in air yielded more sulfate than those in N_2, oxidation by NO_2 and oxygen appear to be additive. When these gaseous mixtures simultaneously were bubbled through the distilled water blanks, sulfate production was negligible relative to the carbon suspensions. The carbon, therefore, must have provided sites for SO_2 oxidation.

Several 20-h runs were made with the 100 cm³/min flow blended mixture of 100 ppmv SO_2 in air + 100 ppmv NO_2 in N_2. The sulfate yields were the same as would be predicted by linear extrapolation of the curve in Fig. 1 (30 mg). No saturation effects were observed with these 20-h exposures. The pH of the solutions for these runs was as low as 1.5 indicating that SO_2 transformations on carbon can occur efficiently under very acidic conditions.

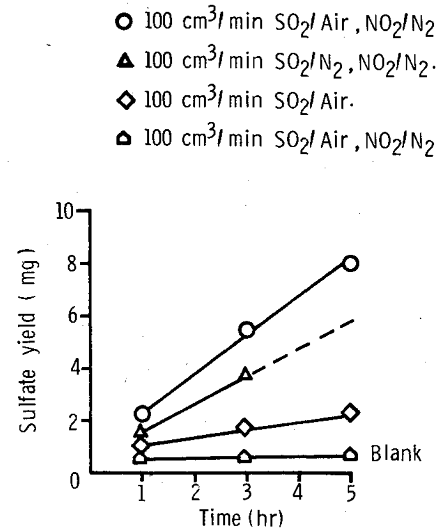

Fig. 1 Effect of NO_2 on sulfate yield.

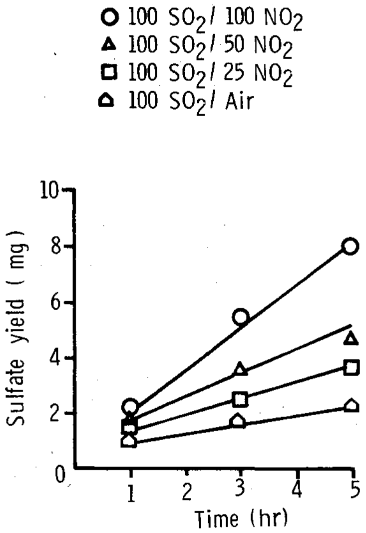

Fig. 2 Effect of NO_2 concentration on sulfate yield.

Another set of runs were conducted in which a constant 100 cm³/min of 100 ppmv SO_2 in air was flow blended with either 100, 50, or 25 cm³/min of 100 ppmv NO_2 in N_2 and then directed through the bubblers. Again, one bubbler served as a blank containing 10 ml of water, the other bubbler contained 100 mg of carbon black suspended in 10 ml of water. The results of these runs are shown in Fig. 2. With constant concentrations of carbon, the yields of sulfate can be seen to be proportional to the amount of NO_2 available.

When carbon suspension runs exposed to SO_2/NO_2 mixtures were analyzed by ion chromatography, the accompanying nitrate concentrations were obtained. Nitrate concentrations were typically less than sulfate concentrations by a factor of 5-10 (mole/mole). Since HNO_3 is volatile, aqueous suspensions of 10 ml of 2×10^{-3} molar HNO_3 + 100 mg of carbon were exposed to 200 cm³/min of air to estimate NO_3^- loss. HNO_3 loss from these suspensions was found to be about 10% (mole/mole) for 4-h exposures.

The disproportionation of NO_2 in solution[9] to produce NO_2^- and NO_3^-, therefore, with NO_2^- serving as the oxidizer for dissolved SO_2, would not appear to have been the dominant mechanism for sulfate production. The sulfate/nitrate ratios were much too high.

The production of sulfate (mg $SO_4^=$ produced per m² of carbon surface per h) was compared between 1) bubbler runs with 100-mg carbon in 10 ml water exposed to 80 ppmv SO_2 + 20 ppmv NO_2 (100 cm³/min of 100 ppmv SO_2 + 25 cm³/min of 100 ppmv NO_2) and 2) samples of 1-mg carbon on the pan of microbalance exposed to continuously flowing gaseous mixtures of 80 ppmv SO_2 + 10 ppmv NO_2 at 65%

relative humidity for equivalent exposure times. Average sulfate production for the carbon suspensions in the bubbler was 0.042 mg/m^2 h, while that for the initially dry particulates exposed to the flowing gas mixture was 0.051 mg/m^2 h. We feel that these values are in good agreement and demonstrated the significance of the role of carbon surface area on the conversion process. The production of sulfate (based on surface area) in the bubbler was lower than that on the particles, even though the NO_2 concentration in the bubbler was higher. Two simple observations are offered that may help to explain this result. The total mass (not concentration) of SO_2 available for oxidation per unit of carbon surface was lower in the bubbler experiment, and the ratio of liquid water to carbon surface was higher. Either, or both, of these conditions may have influenced sulfate production somewhat. Nevertheless, as noted, the agreement between the specific sulfate yields is quite good considering the significant differences in experimental techniques and conditions, and suggested that as long as sufficient H_2O is present to alleviate saturation, the transformation process will not be highly sensitive to bulk water concentrations. These results also suggest that the SO_2 transformation chemistry observed on the initially dry carbon particles, once "wetted" by contact with the 65% relative humidity air, behaved chemically as a carbon/water suspension.

Conclusions

The results of these experiments indicate that graphitic carbon particles effectively catalyze the oxidation of SO_2 to sulfate by NO_2 in the presence of gaseous or liquid H_2O. Water (vapor or liquid) enhances the capacity of carbon to catalyze SO_2 oxidation, but once a surface water film has formed, the transformation process is not highly dependent upon additional water. The transformation of SO_2 to sulfate by NO_2 on carbon does not appear to be inhibited at low pH.

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A Simple Model for Elastic Two-Dimensional Sails

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Introduction

THE flow around flexible lifting membranes (sails) is of interest because the equilibrium shape of the membrane emerges as part of the solution. The exact shape depends upon the pressure distribution on the surface, and this is turn depends upon the sail shape. The equations of fluid motion and sail equilibrium can be linearized if it is assumed that the sail camber and angle of attack are small, although Nielsen[1] and Thwaites[2] found that a numerical procedure was still required to solve the resulting "sail equation." It is shown here that quite good solutions can be obtained by assuming that the sail has a cubic shape. The standard results of thin-airfoil theory can then be combined with the conditions for force equilibrium on the sail to produce a relatively small set of equations. The equations are nonlinear and do not appear to have explicit solutions, except in some limiting cases, but they have the advantage that important variables like lift and sail tension appear directly. Numerical solutions are easily obtained, and are shown to be close to those obtained by Nielsen.[1]

The analysis is also extended to include the effects of sail stretch. This leads to a particular nondimensional combination of variables whose magnitude quantifies the relative significance of stretch, but it is found that the qualitative effects are quite predictable.

Simple Sail Model

A two-dimensional flexible membrane of length l is constrained by fixing its leading and trailing edges at the points $(0,b)$ and $(0,-b)$, as shown in Fig. 1. It then takes up an equilibrium shape under the action of an inviscid fluid whose freestream has dynamic pressure $\frac{1}{2}\rho V^2$, and makes an angle a with the horizontal axis. The forces acting on the membrane can thus be normalized by $\rho V^2 b$, giving coefficients C_L for the lift force and C_T for the tension in the sail.

The sail shape will usually be convex, but its details will depend upon the distribution of pressure along the surface. The pressure distribution depends in turn upon the details of the shape, but some of its overall effects are easily obtained from thin-airfoil theory. If the sail shape is assumed to be a cubic,

$$\frac{y}{b} = \frac{1}{4}\left(1 - \frac{x^2}{b^2}\right)\left(A + \frac{Bx}{b}\right) \tag{1}$$

then the theory gives for the coefficients of lift and leading-edge moment (from Ref. 4, p. 50)

$$C_L = 2\pi\left(a + \frac{A}{4} + \frac{B}{8}\right) \tag{2}$$

and

$$C_M = \pi\left(\frac{a}{2} + \frac{A}{4} + \frac{5B}{32}\right) \tag{3}$$

Received April 9, 1982.

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