Reports

Heterogeneous Atmospheric Reactions: Sulfuric Acid Aerosols as Tropospheric Sinks

Abstract. *The collisional reaction probabilities of several atmospheric species on bulk sulfuric acid surfaces indicate that heterogeneous processes may be important in tropospheric chemistry.*

There is great interest in developing quantitative models of the chemistry of the atmosphere in order to predict the effect of anthropogenic pollutants (*1*). For example, an understanding of the depletion of the ozone layer in the stratosphere or the formation of photochemical oxidants in the troposphere requires a detailed knowledge of the chemical reactions that are occurring. Current models consist almost entirely of homogeneous elementary reaction steps, although it is known that there is a significant concentration of aerosol particles present (*2*). We have obtained evidence that several atmospheric species react at a significant rate on a sulfuric acid (H_2SO_4) surface. These results indicate that heterogeneous reactions can exert a profound effect on atmospheric chemistry.

We have measured the probability of reaction per collision (γ) of many atmospheric species with a bulk H_2SO_4 surface. The experiments were conducted at low pressure in a Knudsen cell flow reactor (Fig. 1). The number of collisions of the reactant with the surface could be varied by a factor of 10 depending on the size of the exit aperture of the reactor (*3*). The reaction products and unreacted starting material leaving the reactor were formed into a molecular beam and detected by a phase-sensitive mass spectrometer. The reactive surface was isolated from the main reactor by a ground glass seal, which was opened to measure the extent of reaction. Laboratory concentrated H_2SO_4 was used after pumping at $\sim 10^{-7}$ torr and therefore contained less than 5 percent water.

The results are shown in Table 1. The measured values of γ were independent of the surface area of the H_2SO_4, the bulk volume of the H_2SO_4, the pressure of the gaseous species, and the number of collisions. The species in the bottom half of Table 1 showed no detectable reactivity in our system. We also attempted to discover whether the H_2SO_4 would act as a catalyst for the following bimolecular reactions: $O_3 + NO_2$, $O_3 + SO_2$, O_3 + alkene, $O_3 + NO$, and $O_2 + NO$. No reaction was observed with $\sim 10^{-3}$ torr of reactants for the first three of these reactions in the presence or absence of the H_2SO_4 surface. The last two reactions occurred homogeneously, and there was no enhancement of the rate with exposure of the H_2SO_4 surface. All of the above experiments were conducted at 300 K; lowering the temperature by 30 K produced no significant change in the results.

We also investigated a soot surface formed by condensation from a methane diffusion flame. Initially, we found that NH_3 reacted very rapidly ($\gamma > 1.0 \times 10^{-3}$), but the reaction rate decreased quickly with exposure of the surface. The following species showed no reactivity ($\gamma < 1.0 \times 10^{-6}$) with the soot surface: NO, NO_2, SO_2, HNO_3, H_2O_2, and N_2O_5.

In order to determine the effect of the above results, it is necessary to incorporate them into a detailed atmospheric model. This would also require a detailed knowledge of the chemical composition, concentration, and size distribution of the aerosol particles. However, we can make some estimates based on "typical" data to indicate which reactions may be important. In the stratosphere, the aerosol particles are reasonably well characterized and consist primarily of H_2SO_4 (*4, 4a*). A simple kinetic theory calculation indicates that the collision frequency between a molecule and an aerosol particle is $\sim 10^{-5}$ sec^{-1}. Thus, for a typical γ of 10^{-5}, the heterogeneous loss rate constant is 10^{-10} sec^{-1}. These heterogeneous reactions are therefore not of great importance in the stratosphere, unless γ

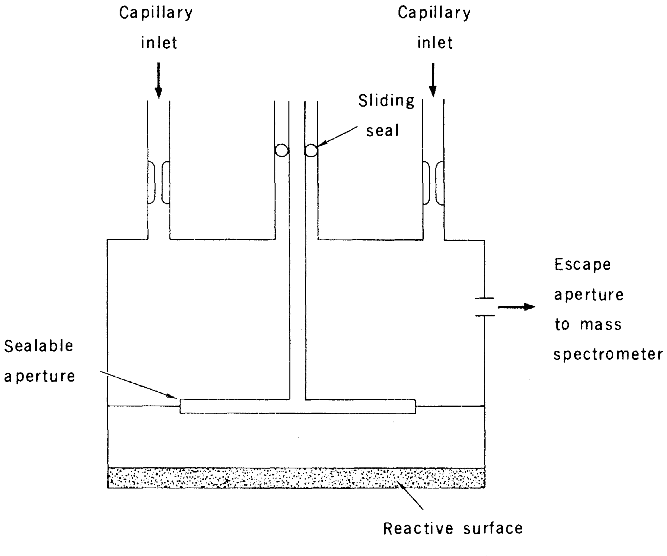

Fig. 1. The two-chamber Knudsen cell reactor.

Table 1. Collisional reaction probabilities on a H_2SO_4 surface at 300 K.

Species	Collisional reaction probability (γ)	Reference
H_2O_2	7.8×10^{-4}	
HNO_3	$\geq 2.4 \times 10^{-4}$	(*7*)
HO_2NO_2	2.7×10^{-5}	
$ClONO_2$	1.0×10^{-5}	
N_2O_5	$\geq 3.8 \times 10^{-5}$	(*7*)
H_2O	$\sim 2.0 \times 10^{-3}$	(*8*)
NH_3	$> 1.0 \times 10^{-3}$	(*9*)
O_3	$< 1.0 \times 10^{-6}$	
NO	$< 1.0 \times 10^{-6}$	
NO_2	$< 1.0 \times 10^{-6}$	
SO_2	$< 1.0 \times 10^{-6}$	
Alkenes	$< 1.0 \times 10^{-6}$	
Alkanes	$< 1.0 \times 10^{-6}$	
CF_4	$< 1.0 \times 10^{-6}$	
CCl_2F_2	$< 1.0 \times 10^{-6}$	

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has a significant temperature dependence.

Because the nature of tropospheric aerosols varies greatly with time, location, and other atmospheric constituents, characterization is extremely complex. If we take typical data from a polluted atmosphere, such as the Los Angeles basin, we calculate a gas kinetic collision frequency between a molecule and an aerosol particle of $\sim 1\ \mathrm{sec}^{-1}$ (5). These aerosols are known to contain significant concentrations of H_2SO_4. We would therefore predict a heterogeneous loss rate constant of $\sim 10^{-5}\ \mathrm{sec}^{-1}$ for most of the species in the upper half of Table 1 (6). Comparison with typical photolysis rate constants (per second) (N_2O_5, 10^{-5}; H_2O_2, 10^{-5}; and HNO_3, 10^{-6}) indicates that heterogeneous reactions may be the dominant loss process for several atmospheric species, particularly late in the day and at night.

Several common atmospheric species thus react at a significant rate on bulk H_2SO_4 surfaces. At typical tropospheric aerosol concentrations, heterogeneous reactions may provide very important sinks or loss mechanisms for these species.

ALAN C. BALDWIN
DAVID M. GOLDEN
Chemical Kinetics Department,
SRI International,
Menlo Park, California 94025

References and Notes

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5. In this calculation, we followed the method of N. Davidson [*Statistical Mechanics* (McGraw-Hill, New York, 1962), p. 101], using aerosol data taken from (2).
6. The basis of this calculation is that the chemical characteristics of the aerosol particle are essentially the same as those of our bulk H_2SO_4 surface.
7. We monitored HNO_3 and N_2O_5 in terms of their mass peak at a mass-to-charge ratio (m/e) of 46; a product, presumably NO_2, also having a mass peak at m/e 46, formed in the reaction; thus the measured γ values were upper limits.
8. Water reacted almost completely within the minimum number of collisions obtainable with our present apparatus.
9. In our system, NH_3 reacted completely; γ may be much larger than 10^{-3}.
10. Supported was provided by the Division of Biomedical and Environmental Research, Department of Energy, under contract EP-78-C-03-2109; additional support was obtained from the National Aeronautics and Space Administration under contract 954815.

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Morphologies and Origin of Elemental Carbon in the Environment

Abstract. *Carbon particles extracted from sediments collected by box coring from southeastern Lake Michigan were compared with carbon particles extracted from oil, coal, and wood fly ash. Sediments deposited after 1900 contained coal, oil, and wood carbons; older sediments contained only wood carbon.*

A measure of the relative intensities of fossil-fuel burning (coal, oil, and natural gas) and of wood burning, both natural and man-instigated, is found in the amounts of the combustion products. Both the organic compounds and the elemental carbon particles may be characteristic of the burned materials, based either on their compositions or on the parameters of the combustion. Under

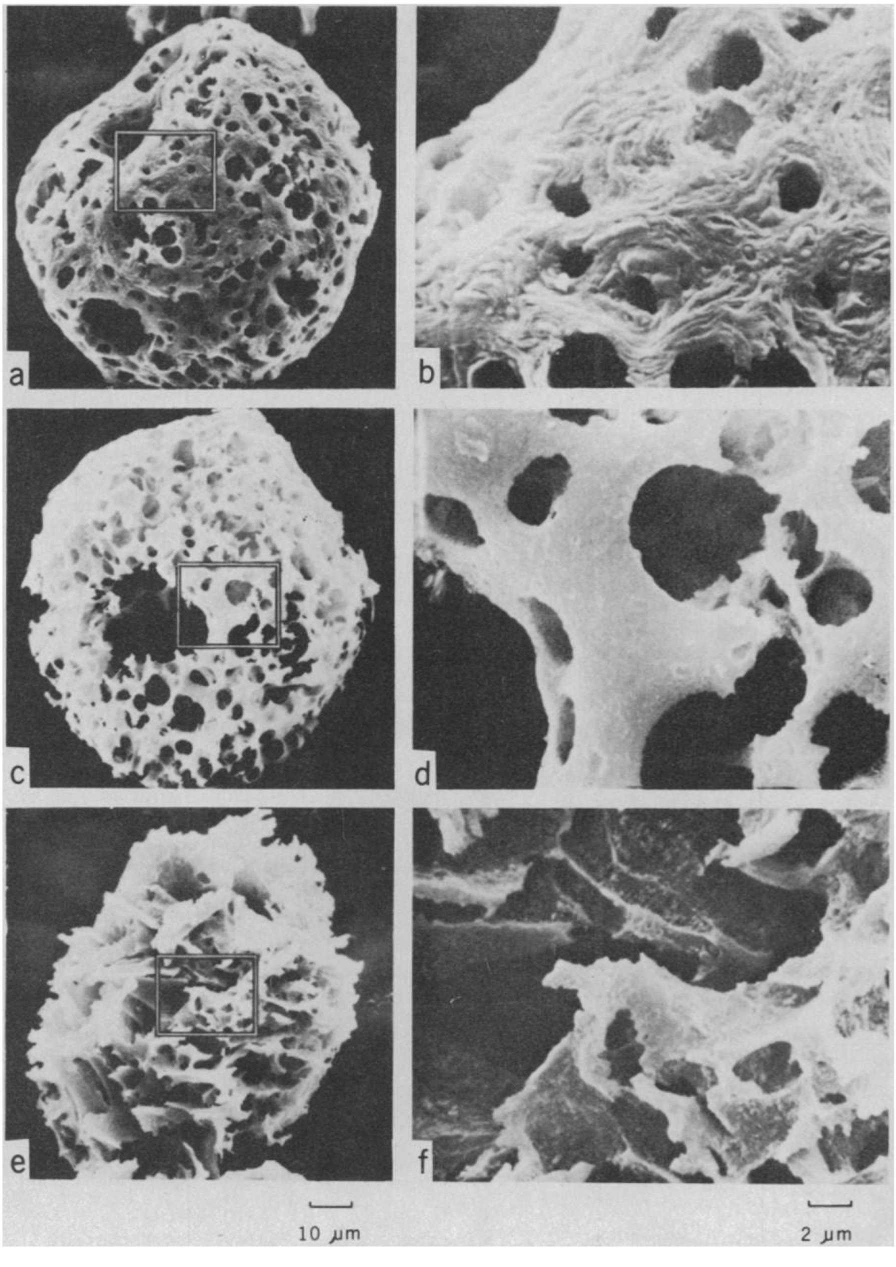

Fig. 1. Scanning electron micrographs of the carbon particles used as standards in this study: (left) single cenosphere; (right) higher magnification close-up of the surface area inside the square outlined at left. The oil carbon particles (a and b) were extracted from fly ash provided by the Florida Power and Light Company and collected from the dust collector of a oil-fired power plant. The coal carbon particles (c and d) were extracted from fly ash provided by the city of St. Louis, Missouri, and collected from the electrostatic precipitator of a pulverized coal-fired power plant. The wood carbon particles (e and f) were extracted from material taken from the flue of a residential wood-burning fireplace.