GEOPHYSICAL RESEARCH LETTERS, VOL. 20, NO. 5, PAGES 355-358, MARCH 5, 1993

EFFECT OF COMPETITIVE ADSORPTION ON POLAR STRATOSPHERIC CLOUD REACTIONS

Michael Mozurkewich

Department of Chemistry and Centre for Atmospheric Chemistry, York University

Abstract. Existing laboratory data for reaction rates on ice and nitric acid trihydrate are interpreted in terms of a simple, speculative mechanism for these reactions. The mechanism assumes that the solid phase is either pure H_2O or pure $HNO_3(H_2O)_3$ and that the state of the surface depends largely on the gas phase composition. This dependence is described by Langmuir adsorption isotherms. The adsorption of a non-reactive species can affect the rate of reaction by inhibiting the adsorption of reactive species. In particular, differences in reaction rates observed on ice and $HNO_3(H_2O)_3$ are attributed to the adsorption of gas phase HNO_3 produced by the decomposition of $HNO_3(H_2O)_3$. The interpretation of heterogeneous reaction rates requires detailed measurements of the rates as a function of gas phase composition.

Introduction

The dramatic loss of ozone observed in the springtime in the Antarctic is due to high levels of photochemically active chlorine produced from inactive reservoir species by the heterogeneous reactions

$$HOCl + HCl \rightarrow H_2O + Cl_2 \quad (1)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (2)$$

$$ClNO_3 + H_2O \rightarrow HNO_3 + HOCl \quad (3)$$

$$N_2O_5 + HCl \rightarrow HNO_3 + ClNO_2 \quad (4)$$

$$ClNO_3 + HCl \rightarrow HNO_3 + Cl_2 . \quad (5)$$

These reactions occur on the surfaces of polar stratospheric cloud (PSC) particles consisting chiefly of water ice and solid nitric acid trihydrate $HNO_3(H_2O)_3$. Various laboratory investigations of the rates of these reactions show significant discrepancies. These may be because of differences in the surface state of the PSC materials used in the experiments. If so, this raises concern for the applicability of the measurements to atmospheric particles since the degree of surface coverage may differ from the laboratory materials.

Most investigations of reaction rates on PSC materials have treated the surface as though it is the same as the underlying substrate. More recently, workers have begun to recognize that the surface will be altered by adsorbed species (Elliott et al., 1991; Abbatt and Molina, 1992; Hanson and Ravishankara, 1992). Here I propose a simple model for the effect of adsorbed species on the surface reaction rates. This model is speculative and is presented in the hope that attempts to test it will help to elucidate the true mechanism and will act as a guide in obtaining further data.

The first assumption of this model is that PSCs consist of only two types of solids: pure ice and pure nitric acid trihydrate. It is assumed that there are no significant amounts of dissolved HCl, HNO_3, or H_2O. This issue is not yet fully resolved; evidence that solubility of gases, especially HCl, in these materials is small is given by Wolff et al. (1989) and Elliott et al. (1990). These species may, however, adsorb on the solid surface. As pointed out by Elliott et al. (1991), the assumption that the HCl resides on the surface explains why all the HCl in PSCs is available for reaction.

The second assumption is that it is the degree of surface adsorption, not the substrate composition, that determines the reaction rate. The relationship between surface coverage and gas phase partial pressures is assumed to be described by Langmuir adsorption isotherms. The actual isotherms may be much more complex; however, the existing data is hardly sufficient to evaluate even this simple model. If there are a limited number of surface sites, the adsorption of multiple species is a competitive process. The fractional surface coverage, θ, of a particular species in the presence of other adsorbed species is given by (Adamson, 1967, pp 570-572)

$$\theta_i = \frac{b_i P_i}{1 + \sum_j b_j P_j} \quad (6)$$

where b are adsorption equilibrium constants and P are partial pressures. For weakly adsorbed species ($b_iP_i << 1$), θ_i will be proportional to P_i; for strongly adsorbed species ($b_iP_i >> 1$), θ_i will be nearly independent of P_i. An important feature of this equation is that the coverage of a reactant of interest is determined, in part, by the presence of other species that are not directly involved in the reaction.

The rates of heterogeneous reactions are generally expressed as reaction probabilities, γ; this is the fraction of collisions with the surface that result in reaction. I will assume that γ depends on the probability that the second reactant is already adsorbed at the collision site. Thus, γ for the gas phase reactant is proportional to θ for the adsorbed reactant. Since the effects of surface coverage have not been systematically investigated, the analysis given here is speculative and is intended largely to outline the type of data that is needed to interpret these reactions.

Equilibria of PSC materials

At equilibrium the surface must be in equilibrium with both the gas phase and the substrate. For ice the consequences are simple; at equilibrium the partial pressure of H_2O is equal to the vapor pressure of ice. For $HNO_3(H_2O)_3$ the situation is not so simple. It has generally been assumed that the partial pressures of both H_2O and HNO_3 may be fixed independently and that the solid phase adjusts its composition much as a liquid solution would. In fact there is no experimental or theoretical basis for this assumption. From conventional ideas in physical chemistry, we expect a solid phase such as $HNO_3(H_2O)_3$ to exclude both H_2O and HNO_3. Smith et al. (1991) present evidence, based on infrared spectra, that this is so. We also expect that the equilibrium constant, K_p, for the decomposition of the solid should be given by

Paper number 93GL00475
0094-8534/93/93GL-00475$03.00

$$K_P = P_{HNO3}\, P_{H2O}^3 \quad (7)$$

Smith (1990) has analyzed the data of Hanson and Mauersberger (1988) to obtain K_p in the form of equation (7) and has shown that this is consistent with an estimate based on thermodynamic data. However, these thermodynamic data may be used to obtain a more accurate value of K_p. The entropy of decomposition as a function of temperature may be obtained by combining the heat capacity and absolute entropy for $HNO_3(H_2O)_3$ with entropy data for $H_2O(g)$ and $HNO_3(g)$. For the enthalpy of decomposition, we can construct a cycle consisting of heating the gases to 298.15 K, condensing the vapors, mixing the liquids to form a solution, cooling the liquid to the melting point, freezing it, and cooling the solid to the original temperature. The gas phase data and heat of vaporization of H_2O are given by Chase et al. (1985); the condensed phase data and heat of vaporization of HNO_3 are given by Forsythe and Giauque (1942). Neglecting ΔC_P results in errors of less than 1% over the temperature range 180 to 220 K. Using the enthalpy and entropy of reaction at 200 K yields

$$\ln(K_P) = 75.32 - \frac{27881}{T} \quad (8)$$

with K_P in bar^4. The uncertainty in K_P should be no more than 15%, due mostly to the uncertainty in the standard heat of vaporization of HNO_3. When K_P is computed from measured vapor pressures of H_2O and HNO_3 (Hanson and Mauersberger; 1988) the uncertainty is 20 to 30%.

Equation (8) is compared to other estimates of K_P in Figure 1; the agreement is good. However, the temperature dependencies are different so that extrapolations of the vapor pressure measurements will lead to substantial differences. The thermodynamic data does not depend on an extrapolation; therefore equation (8) should be preferred for calculating K_P at temperatures below 200 K. The near agreement of K_P values along the two coexistence curves is consistent with there being no significant solubility of HNO_3 or H_2O in $HNO_3(H_2O)_3$. Smith (1990) has given additional arguments in support of this view.

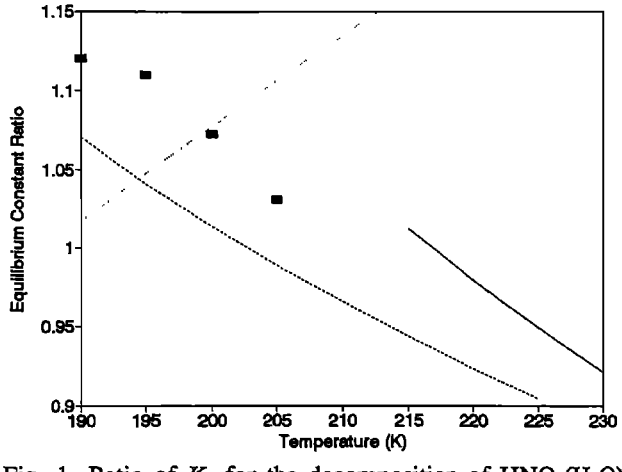

Fig. 1. Ratio of K_P for the decomposition of $HNO_3(H_2O)_3$ calculated from the data of Hanson and Mauersberger to K_P calculated from thermodynamic data. (—) is for coexistence with ice and (---) is for coexistence with $HNO_3{\cdot}H_2O$; these extend over the temperatures for which partial pressures of both HNO_3 and H_2O were measured. The points are from Table 1 of Smith (1990) and (·····) is from his equation (7).

Reaction of HOCl with HCl on PSC materials

Ice. Measurements of the adsorption of HOCl on ice at 202 K yield $b_{HOCl} = 5 \times 10^6$ bar^{-1} (Abbatt and Molina; 1992) or $b_{HOCl} = 2.5 \times 10^6$ bar^{-1} (Hanson and Ravishankara; 1992). Abbatt and Molina found that reaction (1) on ice is first order in P_{HOCl} and that γ_{HOCl} increased from 0.14 to 0.24 as P_{HCl} increased from 2.7 to 9.3 nbar. We can interpret this by assuming that the reaction is controlled by collisions of gas phase HOCl with adsorbed HCl so that γ for HOCl is proportional to the surface coverage of HCl. If the rate of reaction depends on surface coverage of both species, then high concentrations of HCl should reduce the reaction rate by driving HOCl off the surface; there is no evidence that this occurs. With $b_{HOCl}P_{HOCl} << 1$, equation (6) yields

$$\gamma = \gamma_o\theta_{HCl} = \frac{\gamma_o b_{HCl} P_{HCl}}{1 + b_{HCl} P_{HCl}} \quad (9)$$

where γ_0 is the reaction probability on a surface with a monolayer coverage of HCl. With equation (9), the data of Abbatt and Molina yield $b_{HCl} > 3 \times 10^8$ bar^{-1} and $\gamma_o < 0.33$. These are bounds since the difference between the two values of γ may be much smaller because of experimental uncertainties. This lower bound on b_{HCl} is about a factor of ten larger than a value suggested by Elliott et al. (1991).

Hanson and Ravishankara (1992) measured the uptake of HCl onto ice at 191 K and found that the surface is nearly saturated for P_{HCl} as low as 0.05 nbar. This implies that b_{HCl} is at least 5×10^{10} bar^{-1} at this temperature. We can adjust this value to 202 K by using an estimated entropy of adsorption of -100 J mol^{-1} K^{-1}. Elliott et al. (1991) give values of ΔS_{ads} between -80 and -120 J mol^{-1} K^{-1} for a variety of species; this is consistent with ΔS_{ads} being dominated by the loss of translation degrees of freedom (Adamson, 1967, pp 575-578). The data of Hanson and Ravishankara then imply a minimum heat of adsorption for HCl of 58 kJ mol^{-1} and $b_{HCl} > 6 \times 10^9$ bar^{-1} at 202 K. Such a large value would imply no dependence of γ on P_{HCl} in the experiments of Abbatt and Molina.

Nitric acid trihydrate. Abbatt and Molina (1992) have measured the rate of reaction (1) on $HNO_3(H_2O)_3$ as a function of the partial pressure of H_2O. Their data are reploted in Figure 2. These data could be fit by a straight line; however, γ must lie between zero and some value less than unity. Thus, the outstanding feature of these data is the rather abrupt transition between the limits. This transition can be reproduced by assuming that γ for HOCl is proportional to θ_{HCl} and that HNO_3 poisons the surface by occupying surface sites. In this case, with $b_{HCl}P_{HCl}+b_{HNO3}P_{HNO3} >> 1+b_{H2O}P_{H2O}+b_{HOCl}P_{HOCl}$, equation (9) is replaced by

$$\gamma = \gamma_o\theta_{HCl} = \frac{\gamma_o b_{HCl} P_{HCl}}{b_{HCl} P_{HCl} + b_{HNO3} P_{HNO3}} \quad . \quad (10)$$

If HNO_3 is in equilibrium with the substrate, P_{HNO3} may be calculated from P_{H2O} using equation (7). The best fit gives $\gamma_o = 0.19$ and $b_{HNO3}/b_{HCl} = 51$; this gives the line in Figure 2. The rapid change in γ is because of the rapid change in P_{HNO3}. H_2O has little effect if $b_{H2O}/b_{HCl} < 0.002$.

Hanson and Ravishankara (1992) report that the uptake of HCl on $HNO_3(H_2O)_3$ at 191 K is about half as great as on ice. If this reduction is because of competitive adsorption then we can estimate the relative adsorption coefficients from equation (6). In these experiments, the gas phase was nearly saturated with respect to water ice so equations (7) and (8) yield $P_{HNO3} = 3.7$ pbar. If we assume $P_{HCl} \approx 0.3$ nbar (in the middle of the range used for experiments on ice), $\theta_{HCl} \approx 0.5$,

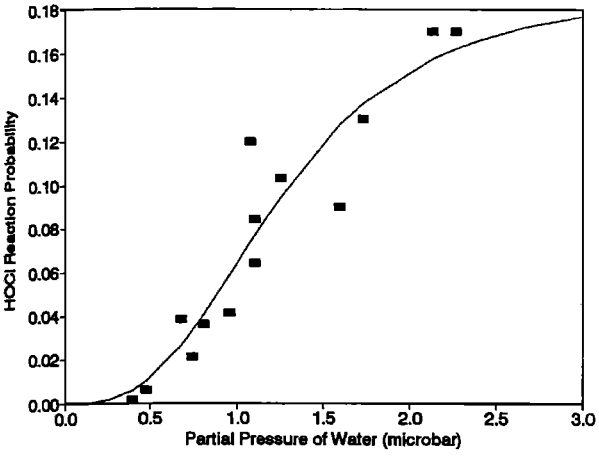

Fig. 2. Reaction probability of reaction (1) on $HNO_3(H_2O)_3$ at 202 K. The points are data of Abbatt and Molina (1992) with P_{HOCl} = 8 to 11 nbar, P_{HCl} = 13 nbar, vapor pressure of ice = 2.20 μbar; the line is calculated from equation (10).

and both $b_{HCl}P_{HCl}$ and $b_{HNO3}P_{HNO3}$ much greater than one, then we get $b_{HNO3}/b_{HCl} \approx 81$ at 191 K. Adjusting this to 202 K (by assuming the same ΔS_{ads} for both species) reduces the ratio to 64. Since $b_{HCl}P_{HCl} \approx b_{HNO3}P_{HNO3}$, the uptake of HCl should depend strongly on both P_{HCl} and P_{HNO3} under these conditions. However, if the lower uptake is due to there being fewer surface sites on $HNO_3(H_2O)_3$ than on ice, the HCl uptake should not depend on P_{HCl}. Further experimental data are needed to determine which is the case.

The uptake of HOCl on $HNO_3(H_2O)_3$ was observed to be reduced by a factor of 10 or more from the uptake on ice (Hanson and Ravishankara, 1992). With $b_{HOCl}P_{HOCl} << 1$ and $b_{HNO3}P_{HNO3} >> 1$, equation (6) implies that θ_{HOCl} will be inversely proportional to $b_{HNO3}P_{HNO3}$. From the preceding estimates we find $b_{HNO3}P_{HNO3} > 15$ at 191 K, consistent with the observed reduction in HOCl adsorption.

Reactions of N_2O_5 and $ClNO_3$ on PSC materials

Ice. For both N_2O_5 and $ClNO_3$, γ is unaffected by the addition of sufficient HCl to produce virtually complete coverage of HCl (Hanson and Ravishankara, 1991). However, the addition of HCl causes reaction (4) to replace reaction (2) (Tolbert et al., 1988; Leu, 1988) and reaction (5) to replace reaction (3) (Hanson and Ravishankara, 1991). This implies that H_2O and HCl are equally reactive towards N_2O_5 and $ClNO_3$ so that the relative coverage of H_2O and HCl does not affect the overall reaction rate.

Reactions with H_2O on nitric acid trihydrate. Hanson and Ravishankara (1991) found that exposing ice surfaces to HNO_3 lowered γ by a factor of 40 to 50 for both reactions (2) and (3) at 201 K. They attribute this to conversion of ice to $HNO_3(H_2O)_3$. Another possibility is that γ is proportional to θ_{H2O} and that this coverage is reduced to about 0.02 because of adsorption of HNO_3. Applying equation (6) for the case where H_2O is weakly adsorbed and HNO_3 is strongly adsorbed we have

$$\theta_{H2O} = \frac{b_{H2O}P_{H2O}}{b_{HNO3}P_{HNO3}} \quad . \tag{11}$$

Setting $\theta_{H2O} \approx 0.02$ and assuming coexistence of ice and $HNO_3(H_2O)_3$ this yields $b_{H2O}/b_{HNO3} \approx 5 \times 10^{-7}$.

Reaction of N_2O_5 with HCl. Hanson and Ravishankara (1991) found that for the reaction of N_2O_5 on $HNO_3(H_2O)_3$ the addition of about 0.1 nbar of HCl increased γ from 0.0006 to 0.0032. If HCl and H_2O are equally reactive, as they appear to be on ice, this implies that $\theta_{HCl} \approx 4\theta_{H2O}$ on this surface. This in turn implies that $b_{HNO3}/b_{HCl} \approx 26$.

Reaction of $ClNO_3$ with HCl on nitric acid trihydrate. Leu et al. (1991) report that both γ for reaction (3) and the sticking coefficient, α, for the adsorption of HCl varied strongly with the ratio of HNO_3 to H_2O used in coating the walls of their reactor. They attribute this to lower values of γ and α on $HNO_3(H_2O)_3$ than on ice. However, the resulting value of γ is much smaller than reported by Hanson and Ravishankara (1991). In the experiments of Leu at al., the heated injector tube caused evaporation of the coating from the walls. As a result, the gas phase concentrations of HNO_3 were probably much larger than in the experiments of Hanson and Ravishankara. These high HNO_3 concentrations may have resulted in almost complete saturation of the cold downstream surface and left few sites for either reaction of $ClNO_3$ or adsorption of HCl. Since gas phase HNO_3 concentrations were not reported, a quantitative analysis of this effect does not appear to be possible.

For reaction (5), Leu et al. (1991) and Hanson and Ravishankara (1991, 1992) report $\gamma \approx 0.3$, independent of the amount of HNO_3 present. This is surprising since HCl uptake and γ for reactions (1) and (3) depend strongly on P_{HNO3}. The model proposed here implies that HNO_3 should poison all reactions on this surface. One way to explain this is to make the ad hoc assumption that $ClNO_3$ is strongly co-adsorbed with HNO_3 and that this co-adsorbed $ClNO_3$ reacts with HCl molecules impinging on the surface. For these experiments, the frequency of HCl collisions with the surface was large compared with $ClNO_3$ collisions. Thus the overall rate of reaction may be controlled by the rate of $ClNO_3$ adsorption. γ will then be equal to the mass accommodation coefficient for $ClNO_3$; a value near unity is reasonable for this. Since there is no a priori reason to expect a specific interaction between $ClNO_3$ and HNO_3 it will be interesting to see if competitive adsorption experiments support this.

This mechanism clearly does not occur for reaction (3). In the gas phase, reaction (3) is endothermic by 7 kJ mol^{-1}. Also, the temperature dependence reported for reaction (3) (Hanson and Ravishankara, 1992) implies a small activation energy. If $ClNO_3$ is strongly co-adsorbed, the surface reaction will be thermodynamically even less favorable and so may not proceed at all on the sites occupied by HNO_3. The gas phase reaction (5) is exothermic by 69 kJ mol^{-1}, so the corresponding surface reaction may still be exothermic.

Possible effect of porosity on adsorption

In contrast to the results of Hanson and Ravishankara (1991), Quinlan et al. (1990) report $\gamma = 0.015$ for reaction (2) on $HNO_3(H_2O)_3$. This much larger value may be due to porosity. Keyser et al. (1991) show that if $\gamma = 6 \times 10^{-4}$, as reported by Hanson and Ravishankara, the apparent value of γ on a porous solid could be a factor of 20 larger, consistent with the value reported by Quinlan et al. Although Hanson and Ravishankara have shown that their ice surfaces are not porous, this may not apply to the surfaces used by other researchers. Quinlan et al. noted that the amount of HNO_3 taken up by their surface was suggestive of an effective surface area much larger than the geometric surface area and that γ depended on the way the ice layer was produced; these observations are consistent with a porous surface.

A more puzzling aspect of the results of Quinlan et al. is the observation that on ice γ_{N2O5} initially rose to about 0.03 then dropped to a value near that for $HNO_3(H_2O)_3$. Quinlan et al. suggest that at low coverages of HNO_3 the reaction is acid catalyzed. If the ice is porous, there is an alternative explanation, I will adopt a simplified picture of the effect of the pores; the part of the ice surface that is exposed directly to N_2O_5 will be the "external" surface and the part that is accessible only through pore diffusion will be the "internal" surface. A detailed analysis, using the approach of Keyser et al. (1991), is not justified by the present data.

In the experiments of Quinlan et al., once the ice film was formed the chamber containing it was temporarily closed off. During this time, we might expect that HNO_3 will outgas from the glass surface of the reaction cell and collect on the colder ice surface. This will occur chiefly on the external surface since HNO_3 should have a large mass accommodation coefficient, α. When the reaction chamber is opened, the external surface is already poisoned by HNO_3. Pumping on the chamber removes gas phase HNO_3 and causes HNO_3 to evaporate from the external surface; thus, the reactivity of this surface increases. Meanwhile, the reaction of N_2O_5 on the internal surface gradually coats it with HNO_3 and its reactivity decreases. Since $\alpha >> \gamma$, it is plausible that the time scale for HNO_3 evaporation from the external surface is much shorter than the time scale for poisoning the internal surface. In this case, the observed γ will first increase and then decrease before both the internal and external surfaces reach the same steady state coverage of HNO_3.

Conclusions

The existing data for reaction rates on $HNO_3(H_2O)_3$ and ice may be interpreted in terms of a simple, speculative model, based on Langmuir adsorption isotherms. The critical factor in this model is the surface coverage of the reactants, not the nature of the substrate. The coverage of a particular adsorbent will be determined in part by its partial pressure and in part by competition with other adsorbed species. At high partial pressures, the surface tends to saturate so that a lack of dependence of the rate of reaction on the partial pressure of one reactant may not be indicative of a lack of dependence at lower partial pressures.

Preliminary analysis of existing data indicates that the adsorption coefficients increase in the order H_2O, HOCl, HCl, HNO_3. The strong adsorption of HNO_3 appears to make it especially effective at reducing the adsorption of other species. The effect of HNO_3 on surface reaction rates implies that $b_{HNO3}/b_{H2O} \approx 2 \times 10^6$ at 201 K. Three different data sets imply $b_{HNO3}/b_{HCl} = 50 \pm 25$ at 202 K. However, the data are too sparse to provide either a true test of this model or reliable values of the adsorption coefficients.

The most important conclusions to be drawn are not the details of the model but the nature of the information that is needed to properly understand these reactions. The surface coverage of the reactants must be determined as a function of partial pressure and temperature and the reaction rates must be determined as a function of coverage and temperature.

References

Abbatt, J. P. D. and M. J. Molina, The heterogeneous reaction of HOCl + HCl → Cl_2 + H_2O on ice and nitric acid trihydrate: reaction probabilities and stratospheric implications, Geophys. Res. Lett., 19, 461-64, 1992.

Adamson, A. W., The physical chemistry of surfaces, 2nd ed., Interscience, New York, 1967.

M. W. et al., JANAF Thermochemical Tables, 3rd ed., NBS, Washington, D.C., 1985.

S., et al., Incorporation of stratospheric acids into water ice, Geophys. Res. Lett., 17, 425-28, 1990.

Elliott, S., et al., Application of physical adsorption thermodynamics to heterogeneous chemistry on polar stratospheric clouds, J. Atmos. Chem., 13, 211-24, 1991.

Forsythe, W. R. and W. F. Giauque, The entropies of nitric acid and its mono- and tri-hydrates. Their heat capacities from 15 to 300°K. The heats of dilution at 298.1°K. The internal rotation and free energy of nitric acid gas. The partial pressures over its aqueous solutions, J. Amer. Chem. Soc., 64, 48-61, 1942.

Hanson, D. R. and K. Mauersberger, Laboratory studies of the nitric acid trihydrate: Implications for the south polar stratosphere, Geophys. Res. Lett., 15, 855-58, 1988.

Hanson, D. R. and A. R. Ravishankara, The reaction probabilities of $ClONO_2$ and N_2O_5 on polar stratospheric cloud materials, J. Geophys. Res., 96, 5081-90, 1991.

Hanson, D. R. and A. R. Ravishankara, Investigation of the reactive and nonreactive processes involving $ClONO_2$ and HCl on water and nitric acid doped ice, J. Phys. Chem., 96, 2682-91, 1992.

Keyser, L. F., et al., Surface reaction and pore diffusion in flow-tube reactors, J. Phys. Chem., 95, 5496-02, 1991.

Leu, M.-T., Heterogeneous reactions of N_2O_5 with H_2O and HCl on ice surfaces: implications for antarctic ozone depletion, Geophys. Res. Lett., 15, 851-54, 1988.

Leu, M.-T., et al., Heterogeneous Reactions of chlorine nitrate and hydrogen chloride on type I polar stratospheric clouds, J. Phys. Chem., 95, 7763-71, 1991.

Quinlan, M. A., et al., Heterogeneous reactions on model stratospheric cloud surfaces: reactions of N_2O_5 on ice and nitric acid trihydrate, J. Phys. Chem., 94, 3255-60, 1990.

Smith R. H., Formation of nitric acid hydrates - a chemical equilibrium approach, Geophys. Res. Lett., 17, 1291-94, 1990.

Smith, R. H., et al., Infrared spectra of solid films formed from vapors containing water and nitric acid, J. Phys. Chem., 95, 5924-30, 1991.

Tolbert, M. A., et al., Antarctic ozone depletion chemistry: Reactions of N_2O_5 with H_2O and HCl on ice surfaces, Science, 240, 1018-21, 1988.

Wolff, E. F., et al., Diffusion and location of hydrochloric acid in ice: implications for polar stratospheric clouds and ozone depletion, Geophys. Res. Lett., 16, 487-90, 1989.

M. Mozurkewich, Department of Chemistry and Centre for Atmospheric Chemistry, York University, 4700 Keele Street, North York, Ontario, M3J 1P3.

(Received: July 3, 1992;
Revised: November 4, 1992;
Accepted: January 25, 1993.)