LABORATORY MEASUREMENTS OF POLAR STRATOSPHERIC CLOUD RATE PARAMETERS

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Abstract

It is now clear that heterogeneous reactions play an important role in controlling the concentration of ozone in the stratosphere. In this work, the loss of N_2O_5 on ice substrates has been studied in a flow reactor in an attempt to gain a more fundamental understanding of these reactions. The apparent reaction probability in this system was found to decrease as the substrate was exposed to N_2O_5. A model which corrected for the loss of surface sites was developed and although it appears to fit the data for a given experiment quite well, it is concluded that the loss of reactive sites is not the full explanation. In addition, the results of an experimental and modelling study suggest that reaction on the internal surface of the ice substrates is not a major loss mechanism for N_2O_5 in the current work.

1 Introduction

It is now recognized that reactions which occur on the surfaces of aerosols in the stratosphere have a significant effect on the concentrations of ozone. Before laboratory measurements can be used with confidence in atmospheric models to explain and predict the effects of heterogeneous chemistry in the stratosphere, much more detailed information about these processes is required. In this study, the reaction of N_2O_5 with water ice substrates has been chosen as a sample system in order to address several fundamental questions about heterogeneous processes as studied in the laboratory.

This system has been studied by several groups [*Hanson and Ravishankara*, 1991; *Leu*, 1988; *Quinlan et al.*, 1990; *Tolbert, Rossi and Golden*, 1988] and it was shown that the product of the reaction is nitric acid which is retained in the solid-phase.

$$N_2O_{5(g)} + H_2O_{(s)} \longrightarrow 2HNO_{3(s)} \qquad (1)$$
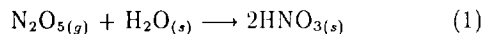
where (g) and (s) refer to species in the gas and solid phases respectively. As the reaction proceeds, the surface of the substrate is increasingly contaminated with nitric

acid which is thought to react further with water to form nitric acid trihydrate (NAT) [*Hanson and Ravishankara*, 1991; *Kenner, Ryan and Plumb*, 1992]. Using low initial concentrations of N_2O_5 and short measurement times to minimize the build-up of HNO_3 product on the surface of the ice, Hanson and Ravishankara [*Hanson and Ravishankara*, 1991] estimated a value of $\approx 2 \times 10^{-2}$ for the collisional reaction probability of N_2O_5 on ice at 200 K. They found that the apparent reaction probability decreased on continued exposure of the ice to N_2O_5 to a limiting value of 6×10^{-4}. They interpreted the latter value as being the reaction probability on NAT which they reasoned would have covered the surface completely at the doses of N_2O_5 used.

If the observed decrease in reaction probability is only due to the gradual conversion of the original ice surface into one which is covered with NAT, it should be possible to model the experiments and obtain a value of the reaction probability of N_2O_5 on pure ice, γ_{ice}. Then using the model it should be possible to predict the reaction probability of N_2O_5 on surfaces which are intermediate between pure ice and pure NAT. In this work the reaction probability of N_2O_5 on ice substrates with submonolayer coverage of the surface by HNO_3 was measured and modelled.

The second question addressed in this work is the determination of the correct surface area to use in converting the observed wall-loss rate to a reaction probability. Most authors have assumed that the surface of their substrates are smooth and non-porous and have used a surface area calculated from the dimensions of their apparatus. Recently, Leu and coworkers [*Keyser, Moore and Leu*, 1991; *Leu, Moore and Keyser*, 1991] have observed that, for nitric acid hydrate substrates, the measured wall-loss rate increases with the thickness of the film in a manner which suggests that reaction on internal surfaces of those films is important. They showed that correction factors as large as 50 may need to be applied to laboratory data to account for the increased area of the substrate due to its porous structure.

In this work, two approaches have been taken to determine the possible importance of reaction on internal

surfaces of the substrate in the current system. (1) The reaction probability of N_2O_5 on ice substrates has been measured as a function of the thickness of the substrate. (2) A model has been developed to fit the data which includes diffusion into and reaction on the surface of idealized pores.

2 Results and Discussion

2.1 Experiments and Models Concerning the Conversion of Reactive Sites

The flow reactor and detection system used in these studies have been described previously [Plumb and Ryan, 1981; Ryan and Plumb, 1982] and its modification and application to the study of heterogeneous reactions at low temperatures is described elsewhere [Kenner, Ryan and Plumb, 1992]. N_2O_5 was prepared by a method similar to that described by Davidson et al. [Davidson et al., 1978] and Cantrell et al.[Cantrell et al., 1987]and was detected at its NO_2^+ (m/e 46) fragment.

Results for two experiments measuring the loss of N_2O_5 on ice-coated walls of the flow reactor are shown in Figure 1 as points in semilogarithmic plots of $[N_2O_5]$ as a function of inlet distance. The error bars are the statistical uncertainties in each point. The points in Figure 1 were obtained by measuring $[N_2O_5]$ at fixed positions 100 mm apart as the movable inlet is moved from an inlet distance of ≈ 50 mm to an inlet distance of 450 mm and back i.e. the points were measured in order going round the loop in a counter-clockwise direction. The curves shown in Figure 1 are the results of fits using a model to be discussed below.

In all experiments in the current investigation, loops such as those shown in Figure 1 were obtained and show that the reaction probability of N_2O_5 on the surface changes during the course of an experiment. The shapes of the loops depend on a number of experimental variables. For example, with all other parameters held constant, the loops are broader with a more horizontal major axis for: i) higher $[N_2O_5]_0$ (compare curves a and b in Figure 1) or ii) longer count times.

For the purposes of modelling, it is possible to represent the overall process by a single reaction

$$N_2O_{5(g)} + sfH_2O_{(s)} \longrightarrow 2(HNO_3 \cdot nH_2O)_{(s)} \qquad (2)$$
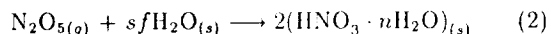
For $HNO_3 \cdot nH_2O_{(s)} = NAT$, $n = 3$ and sf, the stoichiometric factor, would be 7 if all water molecules of hydration are derived from the surface monolayer. A model has been constructed to fit the current experiments based on Reaction (2) in which sf and γ are adjustable parameters whose values were obtained by fitting the experimental points using non-linear least-squares fitting techniques based on the Levenberg-Marquardt method [Press et al., 1988]. This method includes uncertainty estimates for the fitted parameters.

As the experiment proceeds, the ice sites are lost due to the formation of nitric acid hydrates and the model must
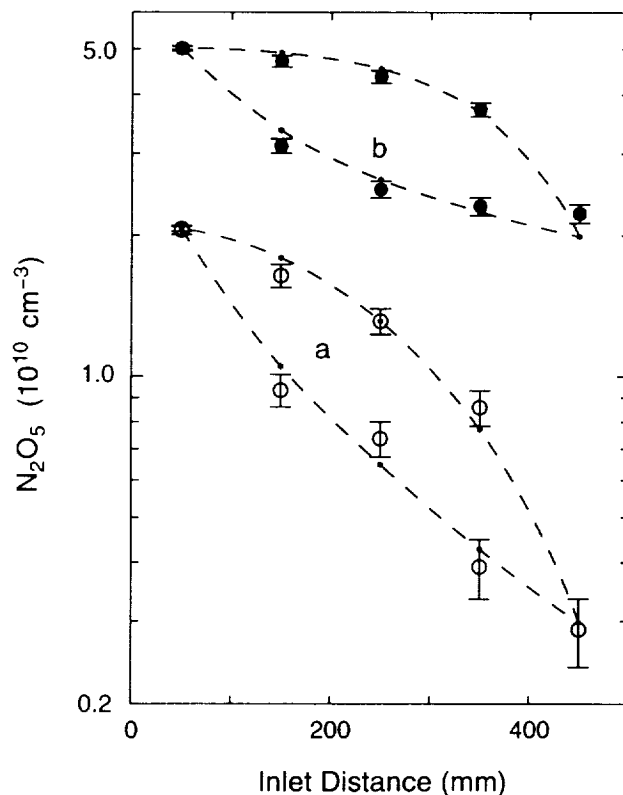

Figure 1: N_2O_5 concentration as a function of inlet distance for ice-coated flow tube walls at a temperature of 175 K for two different starting concentrations of N_2O_5. The points are experimental data (converted to absolute concentrations using the experimentally determined sensitivity for N_2O_5) and the curves are the best fit results of the basic model described in the text.

keep track of the surface concentration of ice and NAT sites at each position along the flow tube as a function of time. The reaction probability at each point is assumed to be proportional to the number of ice sites, $[H_2O_{(s)}(z,t)]$,

$$\gamma(z,t) = \gamma_{ice}\frac{[H_2O_{(s)}(z,t)]}{[H_2O_{(s)}]_0} \qquad (3)$$

where $[H_2O_{(s)}]_0$ is the surface concentration of ice sites on pure ice. The rate equations are integrated to determine the concentrations of N_2O_5 and $H_2O_{(s)}$ as functions of position and time. The average concentration of N_2O_5 surviving to reach the detector is calculated for each position of the movable inlet. By setting the movable inlet positions, dwell time, flow velocity, inlet scan speed and $[N_2O_5]_0$ in the model to match those of a particular experiment, it is possible to simulate that experiment.

The surface concentration of ice sites at the beginning of the experiment was assumed to be 1×10^{15} cm^{-2}. Because of the way the model is constructed, the actual value chosen for the surface concentration has no effect on the value of γ obtained. However, the value of sf is directly
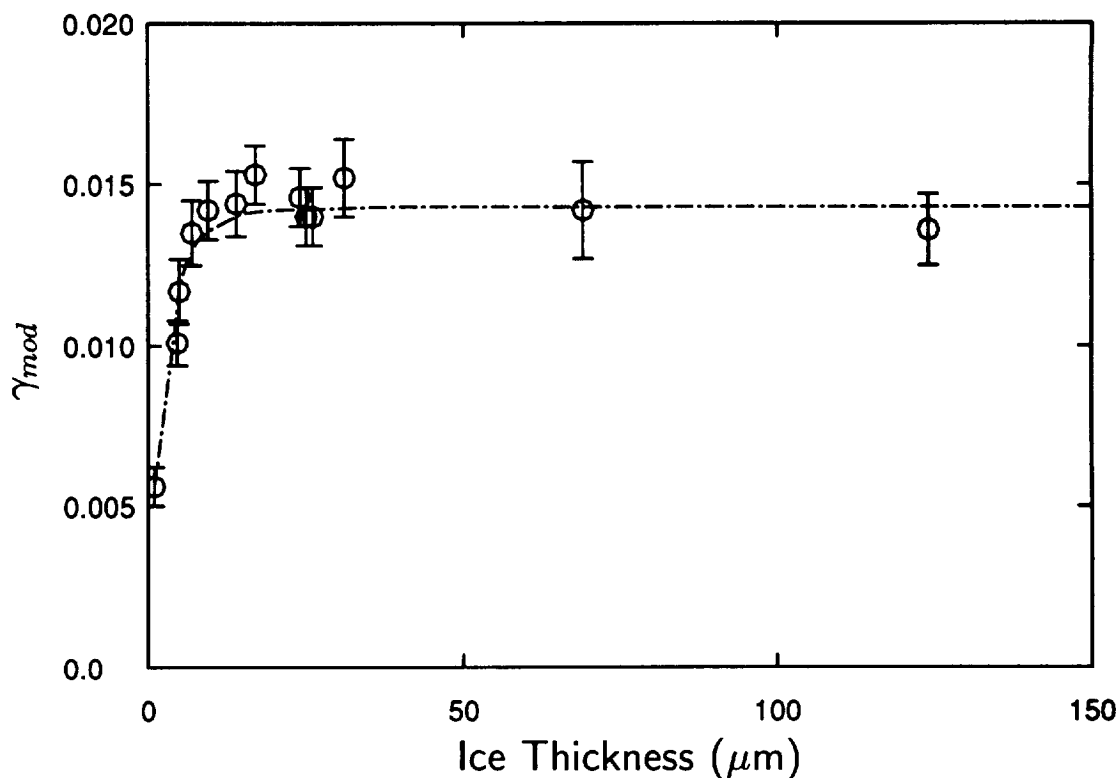
Figure 2: The values of γ_{mod} from the basic model as a function of the thickness of the ice film.

proportional to the choice of the initial surface concentration of reactive sites. Based on the results of consecutive experiments performed using the same substrate, regeneration of the ice sites through solid state diffusion and/or evaporation of the HNO_3 is considered to be sufficiently slow that it can be ignored for $T \leq 200$ K.

The basic model fits the data quite well as can be seen in Figure 1, where the curves are the best fits to the data. From the good fits to the data obtained using the basic model, one can conclude that the main reason for the decrease in the reactivity during the experiments is the gradual conversion of the more reactive ice sites into less reactive NAT sites. However, one also finds that experiments that differ only in the amount of exposure of the substrate to N_2O_5 yield different values for the reaction probability on pure ice. This is a clear indication that the conversion of sites is not the full explanation.

Several additional mechanisms have been considered, for example, higher than first-order dependence on $[H_2O_{(s)}]$, sites of different reactivities and involvement of more than just the top monolayer of the substrate. Models to fit the data have been developed based on each of these and although they each improve the fits to the data and reduce the dependence of γ on the experimental conditions, they introduce too many parameters about which no information is available and no conclusion can be reached as to the correctness of any given model.

2.2 Dependence of the Reaction Probability on the Thickness of Ice and the Porous Substrate Model

The dependence of the reaction probability of N_2O_5 on ice has been investigated in this work for $T = 190$ K, bath gas pressure $= 0.23$ Torr and $[N_2O_5]_0 = 3.5 \times 10^{10}$ cm^{-3} for ice thicknesses, h_{ice}, in the range $0 \leq h_{ice} \leq 124$ μm. The results are shown in Figure 2 where γ_{mod} given by the basic model are plotted as a function of h_{ice}. It will be seen that γ_{mod} increases with h_{ice} for $0 \leq h_{ice} \leq 7$ μm and is independent of h_{ice} for $h_{ice} > 7$ μm. The authors believe that the lower values of γ observed for ice thicknesses less than 7 μm are caused by the walls of the flow tube being incompletely covered with ice in those experiments. This view is supported by the large values of sf obtained for the experiments on thin ice substrates [Kenner, Ryan and Plumb, 1992].

The possible porosity of the ice in the current experiments has been tested further by developing a model which includes idealized pores to investigate what ranges of pore diameters and porosities (the ratio of the volume of internal space to the volume of solid) are capable of explaining the current data. By comparing the calculated loops with the experimental data for a range of values of the mean pore diameter and of the porosity of the substrate, it has been found that mean pore diameters of 0.1 μm and porosities

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of 0.03 are required to reproduce the data. These values of mean pore diameter and porosity were tested by fitting the same data sets used in evaluating the other models. The deduced values of γ differed by $<20\%$ from those obtained using the basic model. The average value of χ^2 and the dependence of the calculated reaction probability on experimental conditions were similar to those obtained using the other 'improved' models. Based on these results, it is concluded that in the current system reaction on the internal surface of the substrate is not a large effect but may explain some details of the current experiments. Any further evaluation of this model must await experimental measurements of the pore diameters and porosities of the substrates.

Acknowledgement

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