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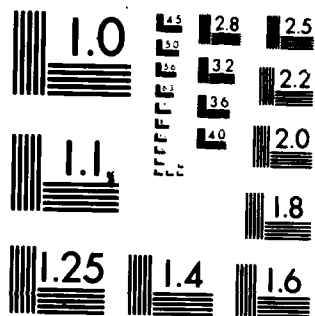
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Kinetics of the Heterogeneous Hydrolysis of Dinitrogen Pentoxide Over the Temperature Range 214-263K

Office of Environment
and Energy
Washington, D.C. 20591

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April 1981

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ABSTRACT

The kinetics of the heterogeneous hydrolysis of dinitrogen pentoxide (N_2O_5) on sulfuric acid-water surfaces was studied over the temperature range 214 to 263K for reactive surfaces containing 48 to 100 mole% sulfuric acid (H_2SO_4). The measurements were made in a flow reactor system in which the gaseous reactants and products were monitored by infrared spectroscopy. The results of the experimental study showed the surface reaction to be mechanistically first order with respect to gaseous N_2O_5 , the reactive surface area and time. The surface reaction rate was observed to increase with the water content of the reactive surface over the range 0 to 52 mole% $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ and to have a positive activation energy over the temperature range studied. A significant decrease in the reaction rate was observed with the state change of the reactive surface from liquid to solid. Over the range of conditions studied the hydrolysis reaction efficiency was observed to be between 10^{-5} and 10^{-4} reactions per collision with the temperature dependence of the collision efficiency being described by the expression $\gamma = 2.94 \times 10^{-3} \exp(883/T)$ (reactions/collision) with an estimated $\pm 50\%$ experimental uncertainty for a 52 mole% $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ frozen surface for between 221 and 263K. The magnitude of this rate coefficient indicates that the heterogeneous hydrolysis of N_2O_5 is significant in establishing the overall partitioning of NO_x in the photochemical ozone- NO_x stratospheric cycle.

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1.0 INTRODUCTION

The concern over the effects that anthropogenic emissions, both from aircraft and ground based sources, may have upon the chemistry of the stratosphere and the potential for decreasing the level of stratospheric ozone has led to the development of predictive models to describe the chemical and transport cycles in the upper atmosphere.¹ These models rely on homogeneous gas phase reactions to describe the chemistry occurring in the stratosphere, with heterogeneous gas-surface reactions involving atmospheric particles being considered insignificant with the exception of specific events such as volcanic eruptions or atmospheric nuclear tests. It has been pointed out, however, by H.S. Judeikis² and Cadle, Crutzen, and Enhalt³ that there are a number of heterogeneous gas-particle reactions which could potentially play a significant role in establishing the stratospheric concentrations of some trace gas species.

Based on gas kinetic theory, Cadle et al demonstrated that at 20 km altitude a gas molecule spends on the average about 10^4 seconds before colliding with an aerosol particle surface, while typically those gases whose residence time in the lower stratosphere are controlled by removal to the troposphere by transport processes will remain in the stratosphere for 10^7 to 10^8 seconds. Hence, if the gas molecules were to react with the particle surfaces once in every 10^4 collisions, these heterogeneous reactions might prove significant in establishing their stratospheric concentrations.

Heterogeneous reactions which have been considered as likely to have high collisional reaction efficiencies in the stratosphere include the decomposition of ozone and the recombination of oxygen atoms on sulfuric acid surfaces, the hydrolysis of dinitrogen pentoxide by surface bound water, and the oxidation of sulfur dioxide by adsorbed hydrogen peroxide.

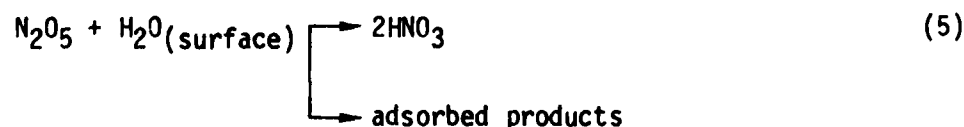
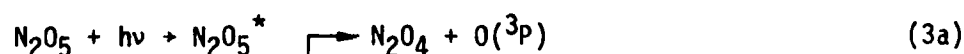
Work at this laboratory by Harker and Ho⁴ and that of Olszyna, Cadle, and de Pena⁵ has demonstrated that ozone decomposition on super cooled and frozen sulfuric acid surfaces is negligibly slow at stratospheric temperatures. Hence the heterogeneous reaction most likely to have an effect upon the

stratospheric ozone balance is that of dinitrogen pentoxide (N_2O_5) with surface bound water on aerosol particles.

N_2O_5 is an intermediate in the O_3 - NO_x stratospheric cycle, formed primarily at night via the reaction of NO_2 with O_3 as shown by



The N_2O_5 built up during the night then decays after sunrise by photodissociation, thermal decomposition, homogeneous reaction with $\text{O}(^3\text{P})$ atoms, and heterogeneous reaction with particulate surfaces as described by



N_2O_5 decay reactions (2b), (3b), (3c), (4), and (5) produce a net ozone destruction during the night-day cycle, while photodissociation reaction (3a) regenerates odd oxygen making the cycle neutral with respect to ozone. The heterogeneous decomposition of N_2O_5 (5) does act to remove ozone in the single

night-day cycle, however, the products of the reaction, either HNO_3 or adsorbed material, provide a "sink" for reactive NO_x species. By converting NO_x to HNO_3 or other less reactive adsorbed species this reaction would tend to lower the overall efficiency of the NO_x ozone decomposition cycle.

In this study flow reaction experiments have been conducted to observe the collisional reaction efficiency, γ , for N_2O_5 decomposition on sulfuric acid-water surfaces as a function of the water content of the surface and temperature over the range 214-263K. Infrared spectroscopy was used to observe the gas phase concentrations of N_2O_5 , HNO_3 , and NO_2 in the system to provide mechanistic information on the N_2O_5 decomposition. During the course of the study it was observed that N_2O_5 is efficiently decomposed by $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ surfaces in a first order reaction with a γ of 10^{-5} to 10^{-4} reactions per collision at stratospheric temperatures. The N_2O_5 decomposition rate was also observed to be directly dependent upon the water content of the acid surface. Mechanistically, this study showed adsorption of the reaction products to dominate over release of gaseous HNO_3 , and the reaction rate was found to increase significantly when super-cooled liquid was present vs frozen surfaces. As a result of the experimental technique, it was also observed that HNO_3 was effectively adsorbed by the acid surfaces with γ values on the order of 10^{-5} (reaction/collision).

The results of these experiments demonstrate that the heterogeneous reactions of N_2O_5 , and HNO_3 are sufficiently rapid to be of significance in the chemistry of the upper troposphere and lower stratosphere.

2.0 EXPERIMENTAL

2.1 Apparatus

In this study primary attention was given to designing an experimental apparatus in which a reproducible reactive surface of uniform composition and known geometric area could be established in a flow system where gaseous reactants and products could be observed spectroscopically. To accomplish this a rotating flow reaction chamber was constructed which consists of two concentric Pyrex cylinders of diameters D_1 and D_2 with the reactant gas flowing between the cylinder walls as diagrammed in Fig. 1.

The purpose of the rotating feature of the flow system was to provide a means of uniformly coating the reactor walls with the $H_2SO_4-H_2O$ mixtures. By filling the bottom of the all Pyrex reactor to a depth of $(D_2-D_1)/2$ with the $H_2SO_4-H_2O$ mixture to act as a reservoir, a uniform wall coating on both the inner and outer cylinder walls can be obtained by rotating the entire reactor about its axis. The surface area to volume ratio of this flow reactor can be varied by changing the diameter of the inner cylinder. However for the bulk of the experiments carried out in this study a surface area to volume ratio of only $2.6 \text{ (cm}^{-1}\text{)}$ was required, which could be obtained by coating only the outer cylinder surface with the acid mixture and using the inner cylinder to establish the flow path and available reactor volume.

The overall experimental apparatus is shown schematically in Fig. 2. The apparatus was designed to provide a steady-state flow of N_2O_5 directly into the 3.5 meter optical path White Cell for infrared analysis or through the cooled flow reactor and then into the White Cell. The gas flow system was set up such that predistilled N_2O_5 collected in a flow saturator could be used or the N_2O_5 could be generated directly by reacting NO_2 with O_3 formed by an electric discharge through O_2 . Matheson Ultra-high Purity nitrogen was used as the carrier gas. All gases were passed through both a P_2O_5 column and a cold trap at or below the temperature of the flow reactor before entering the system to avoid any problems with condensation of the reactants in the chamber.

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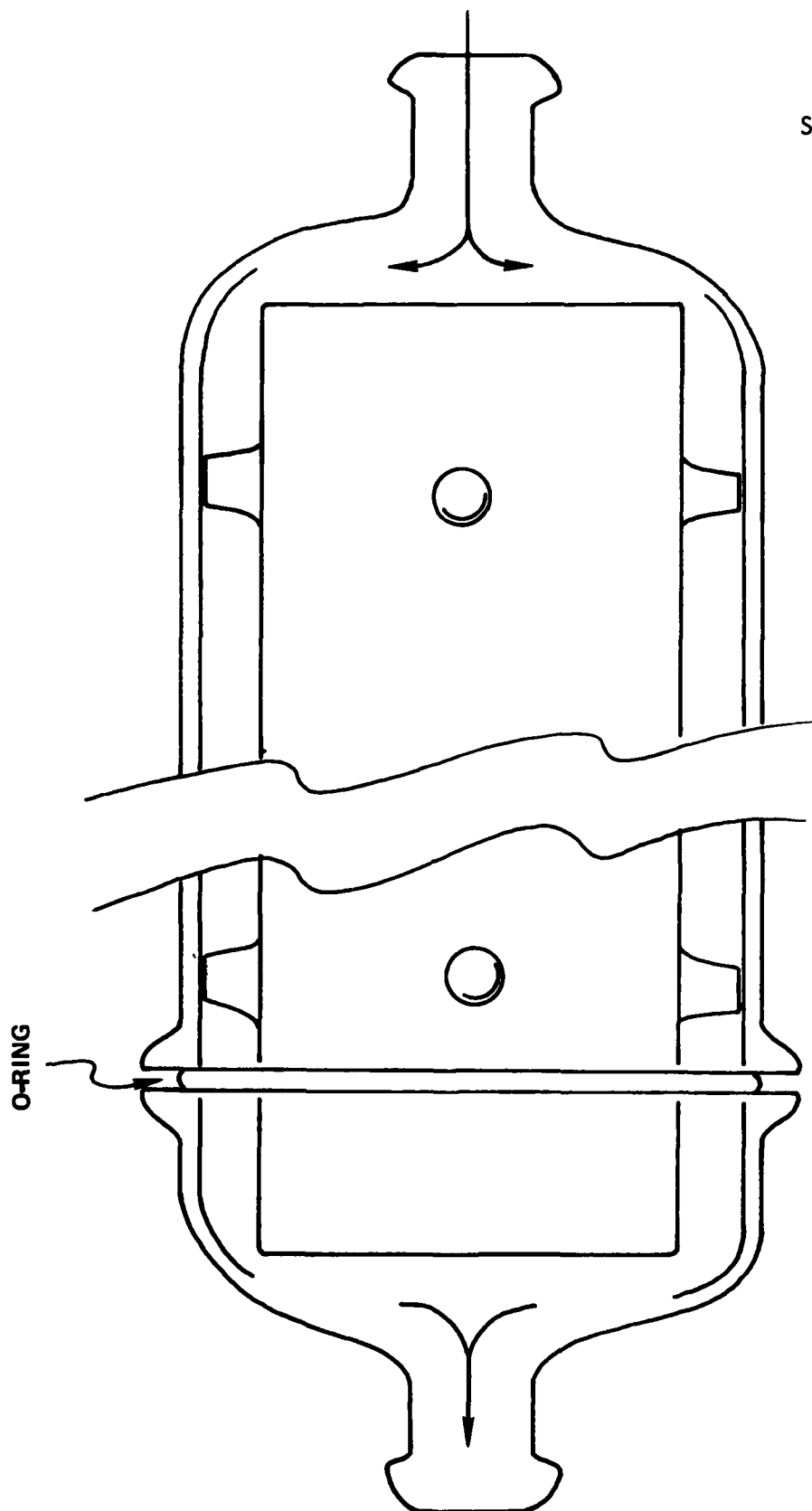


Fig. 1 Details of rotating flow reaction chamber.

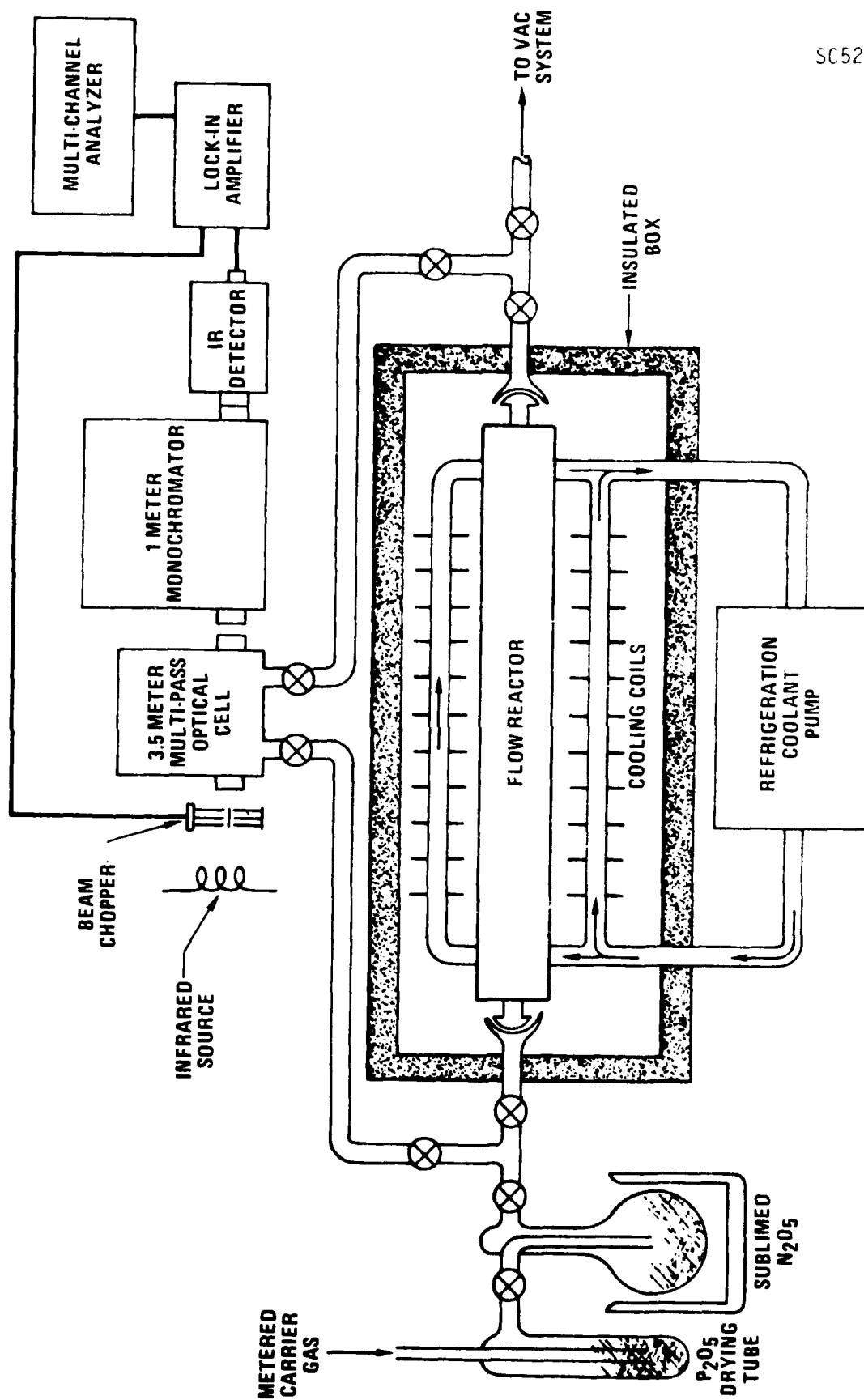


Fig. 2 Schematic of experimental apparatus.

The reaction chamber itself was insulated in a styrofoam box with a NesLab Lt-9 refrigeration unit pumping isopropyl alcohol through cooling coils around the chamber. The White Cell, a Perkin-Elmer commercial unit with gold mirrors, had a maximum path length of 10 meters and the monochromator was an Interactive Technology 1 meter unit with a 15 cm gating blazed at 10 microns. A HgCdTe detector cooled to liquid nitrogen temperature was used to detect the IR radiation from a Nernst glower whose output was chopped at 260 Hz for signal processing with a lock-in amplifier. The output from the lock-in was fed into a Nicolet 535 multichannel analyzer coupled to a DEC 11/05 computer for spectrum recording and data handling.

2.2 Reagents

The basic reactants in this study were N_2O_5 , water, and sulfuric acid. Baker reagent concentrated H_2SO_4 and fuming H_2SO_4 were used with distilled water to form the reactive surface. The H_2O to H_2SO_4 ratio in the mixtures was determined by density measurements.

The N_2O_5 preparation consisted of reacting NO_2 in the gas phase with an excess of ozone in oxygen. The ozone was formed by passing Matheson Ultra-high purity oxygen through an electric discharge. The products of this reaction are primarily N_2O_5 and HNO_3 . These were passed through a P_2O_5 trap and condensed at 210K in a saturator which could be purged with nitrogen and attached to the inlet of the flow reactor system. An infrared spectrum of the vapor over the condensed N_2O_5 and HNO_3 is shown in Fig. 3. Using Harker's⁶ cross-sections for these species gave the concentration ranges for this study to be about 10^{14} to 10^{15} molecules/ cm^3 for N_2O_5 with HNO_3 initially being about 50 to 70% of the N_2O_5 level. These same levels of reactants could also be generated directly into the flow reactor without condensing out the N_2O_5 when ozone removal from the flow stream was not required.

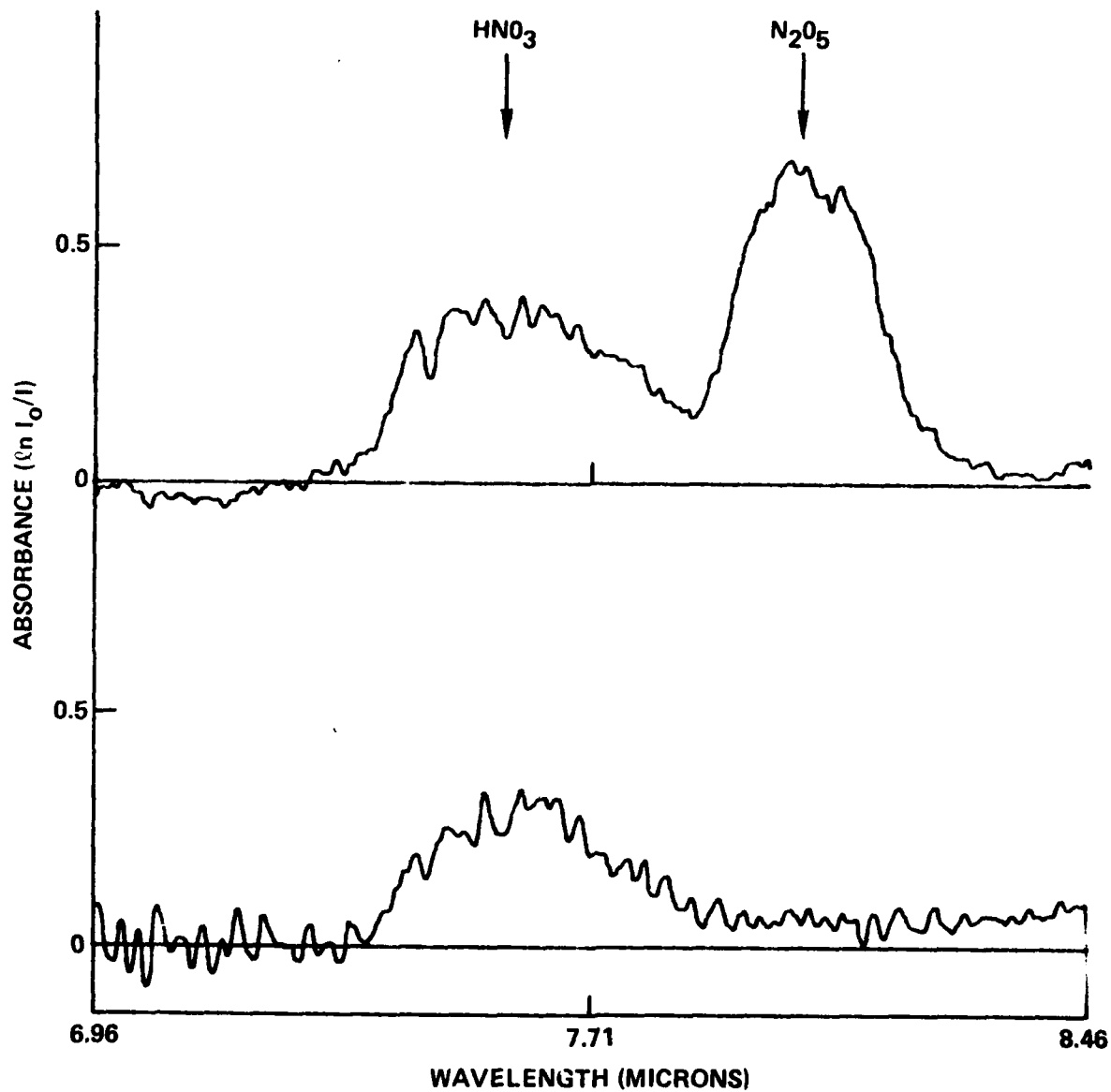


Fig. 3 Infrared spectra of the reactant gas stream before and after exposure to a 16.5 mole% $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ reactive surface at 262K. Both N_2O_5 and HNO_3 decrease can be seen indicating that the hydrolysis products of the N_2O_5 reaction are being adsorbed on the reacting surface.

2.3 Experimental Procedures

The basic experimental approach consisted of establishing a known surface area of the reactive $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ mixture by rotating the flow chamber while it cooled to produce a uniformly coated geometric area while purging with N_2 . Once the desired cell temperature was established as monitored by a thermocouple in the cell outlet gas stream the $\text{N}_2\text{O}_5/\text{HNO}_3$ background steady-state levels were established spectroscopically by flowing the reaction mixture directly into the IR cell. When stable conditions were established the reaction mixture was passed through the flow reactor then into the IR cell to determine the extent of the reaction. The background levels were then checked by running the flow again directly into the IR cell. This process was repeated as a function of temperature, flowrate, $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ ratio, and reactive surface area to volume ratio to establish the effects of the independent variables.

The data collected by this procedure provided a change in the N_2O_5 concentration that could be related to the heterogeneous hydrolysis rate by integrating the expression,

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = -\gamma \bar{C}[\text{N}_2\text{O}_5] \quad , \quad (I)$$

where γ is the efficiency of the heterogeneous reaction (reactions/collision) and $\bar{C}$ is the average number of wall collisions per second at the chamber temperature. As long as the residence time in the flow cell is long compared to the diffusion time to the walls, the average wall collision rate can be described by gas kinetic theory to be

$$\bar{C} = \frac{A}{4V} \left(\frac{8RT}{\pi M} \right)^{1/2} \quad , \quad (II)$$

where A is the reactive surface area, V the chamber volume, R the gas constant, T the absolute temperature and M the molecular weight of the gas. This relationship can be integrated as a function of time to give the expression,

$$[N_2O_5]_t = [N_2O_5]_{t=0} \exp (-\gamma Ct) \quad . \quad (III)$$

Assuming uniform flow for the gas in the chamber, the average residence time for a molecule is given by the ratio of the cell length, ℓ , to the flow velocity, v , $t = \ell/v$. Using this relationship (III) can be rewritten to express the reaction efficiency as

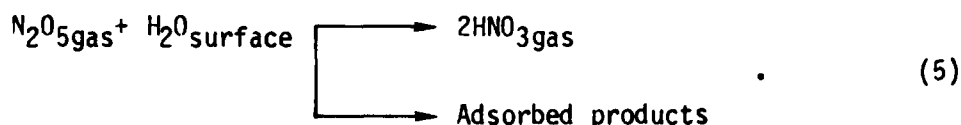
$$\gamma = \frac{v}{\ell C} \ln \left(\frac{[N_2O_5]_{\ell=0}}{[N_2O_5]_{\ell}} \right) \quad . \quad (IV)$$

Using this expression the change in the optical density of the N_2O_5 infrared adsorption due to its passing through the flow reactor yields a value for γ .

It is difficult to assess the experimental uncertainties in a heterogenous reaction system, however, one can be sure that the absolute uncertainty is greater than the precision of the measurements. Based upon the errors associated with maintaining uniform wall temperatures and flow patterns in the cell an experimental uncertainty on the order of $\pm 50\%$ has been estimated for the γ values obtained in this work.

3.0 EXPERIMENTAL RESULTS

The initial experiments were conducted to confirm the heterogeneous reaction to be first order in both time and reactant concentration as well as to determine the reaction products. The expected reaction was the hydrolysis of N_2O_5 to form HNO_3 either as a gas or a surface species, as shown by reaction (5),



The N_2O_5 decay reaction in the flow chamber was shown to be first order with respect to residence time in the cell, initial N_2O_5 concentration, and reactive surface area. The degree of the first order dependence upon cell residence time is demonstrated in Fig. 4, where the logarithm of the optical density of the N_2O_5 exiting the cell is plotted vs its residence time in the flow chamber. (l/v).

Analysis of the IR spectrum of the reactant gases showed that the reaction products normally were adsorbed onto the reaction surface. As can be seen in the before and after spectra in Fig. 3 the HNO_3 as well as the N_2O_5 peak decreased in intensity after exposure to the 16.5 mole% H_2O/H_2SO_4 surface at 262K. This absorption of HNO_3 was pronounced when the reactive surface was in the liquid state, and only at the lower temperature ($< 230K$) was an increase in gaseous HNO_3 observed. The lower temperature runs confirm that HNO_3 is the primary product of the hydrolysis reaction. However the actual form of the absorbed products could not be ascertained by the techniques of this study.

The dependence of the N_2O_5 heterogeneous decay upon the water content of the reactive surface supports the N_2O_5 decay mechanism as being the

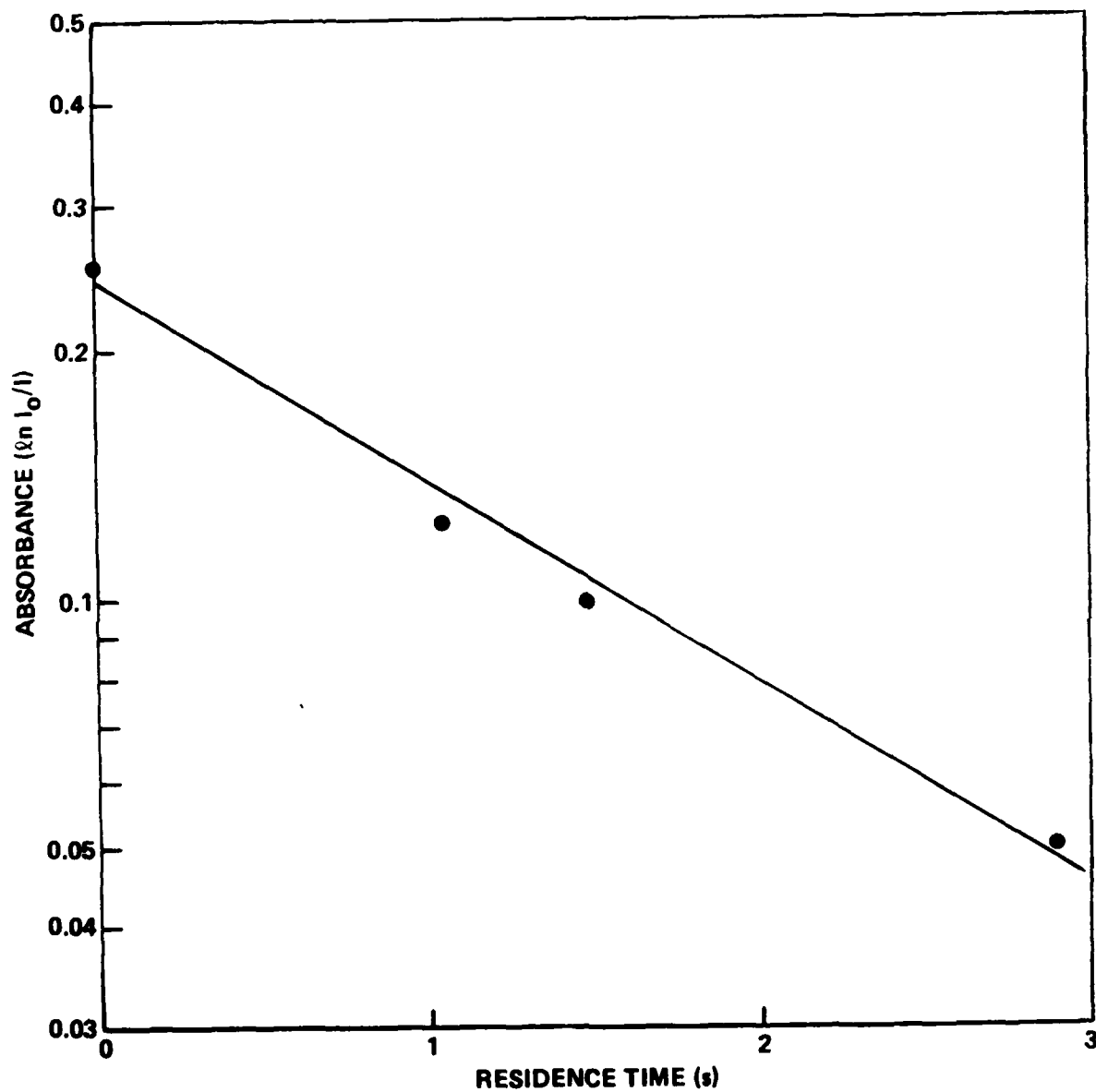


Fig. 4 Plot of logarithm of optical density versus flow chamber residence time demonstrating first order time dependence of the reaction.

hydrolysis reaction (5). As shown in Fig. 5 the reaction rate increased with the mole% water in the frozen surface over the range of the measurements. The large increase in the reaction rate observed at 32 mole% corresponds to a region where the acid-water mixture goes through an abrupt freezing point depression. The 32 mole% mixtures existed as cooled liquid at temperatures down to 220K and demonstrated the significant dependence of the heterogeneous reaction rate upon the phase state of the reaction surface.

The temperature dependence of the heterogeneous reaction was observed over the temperature range 221 to 263K for a 52 mole% $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ solution. The reaction efficiency had an increase with temperature which was quite linear when plotted as $\ln$ vs $1/T$ as shown in Fig. 6. The solid line through the data is the least squares fitted behavior predicted by the equation $\gamma = A \exp(-\Delta E/RT)$. A correlation coefficient of $r^2 = 0.914$ was found for this equation with the fitting parameters

$$\gamma = 2.94 \times 10^{-3} \exp (-883/T) \text{ (reaction/collision).}$$

This type of temperature behavior can be compared with the description of heterogeneous reactions derived by Judeikis and Seigel,⁷ based upon a simplified kinetic model and transition state theory. Their model describes a critical factor in determining the efficiency of heterogeneous reactions to be the difference between the activation energies for reaction and desorption ($E_r - E_d$) of the adsorbed gas molecule. The smaller this difference the greater the probability of a given reaction occurring versus simple desorption. This derivation describes the temperature dependence of a heterogeneous reaction by the expression

$$\gamma = \alpha(1 + \beta \exp [(E_r - E_d)/RT])^{-1} \quad (V)$$

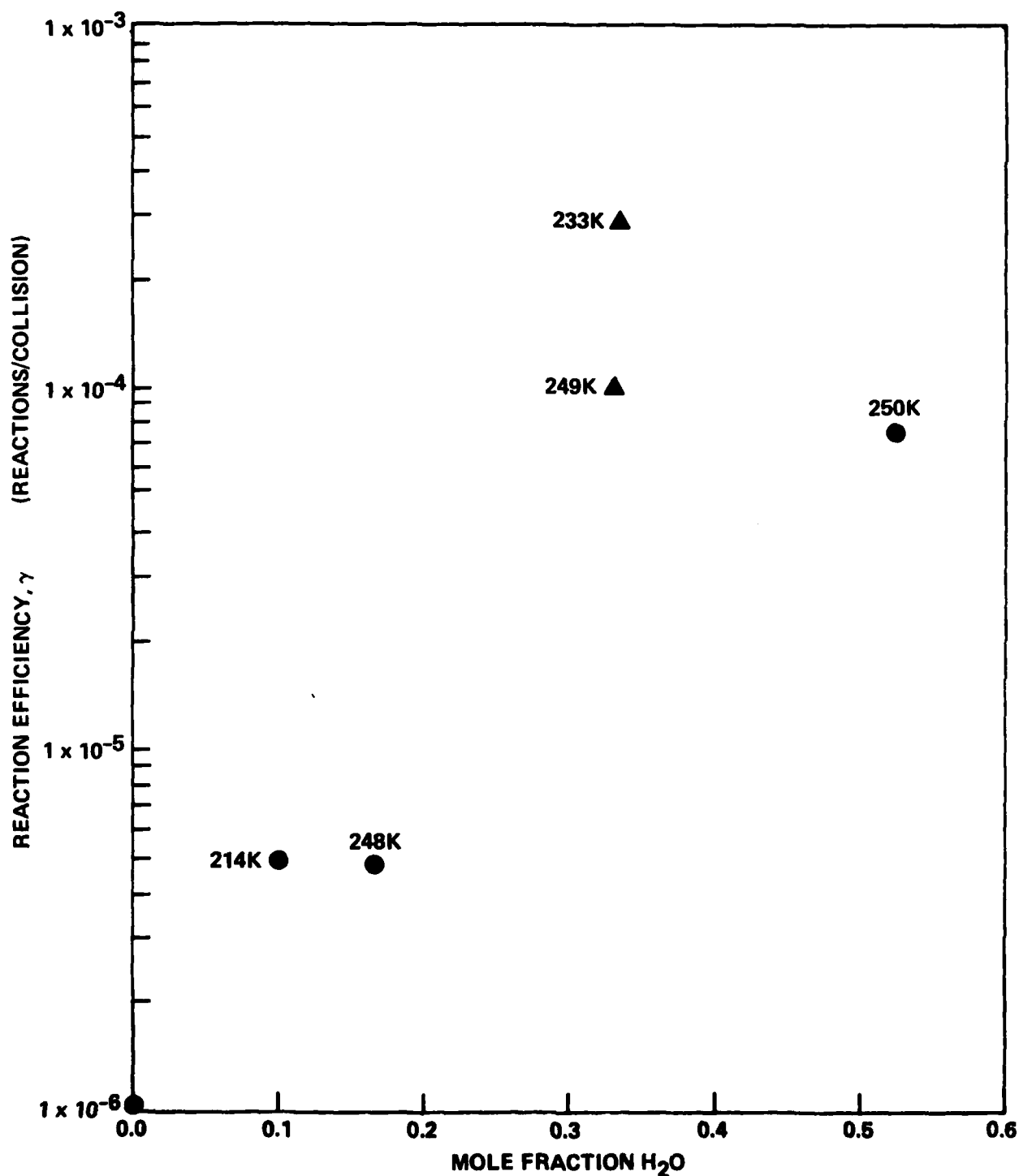


Fig. 5 A plot of the observed reaction efficiency, γ , as a function of the mole% H_2O in the H_2SO_4 of the reactive surface. The large increase in the γ values at 30 mole% H_2O occurs due to the mixture existing as a cooled liquid at the temperatures of this study.

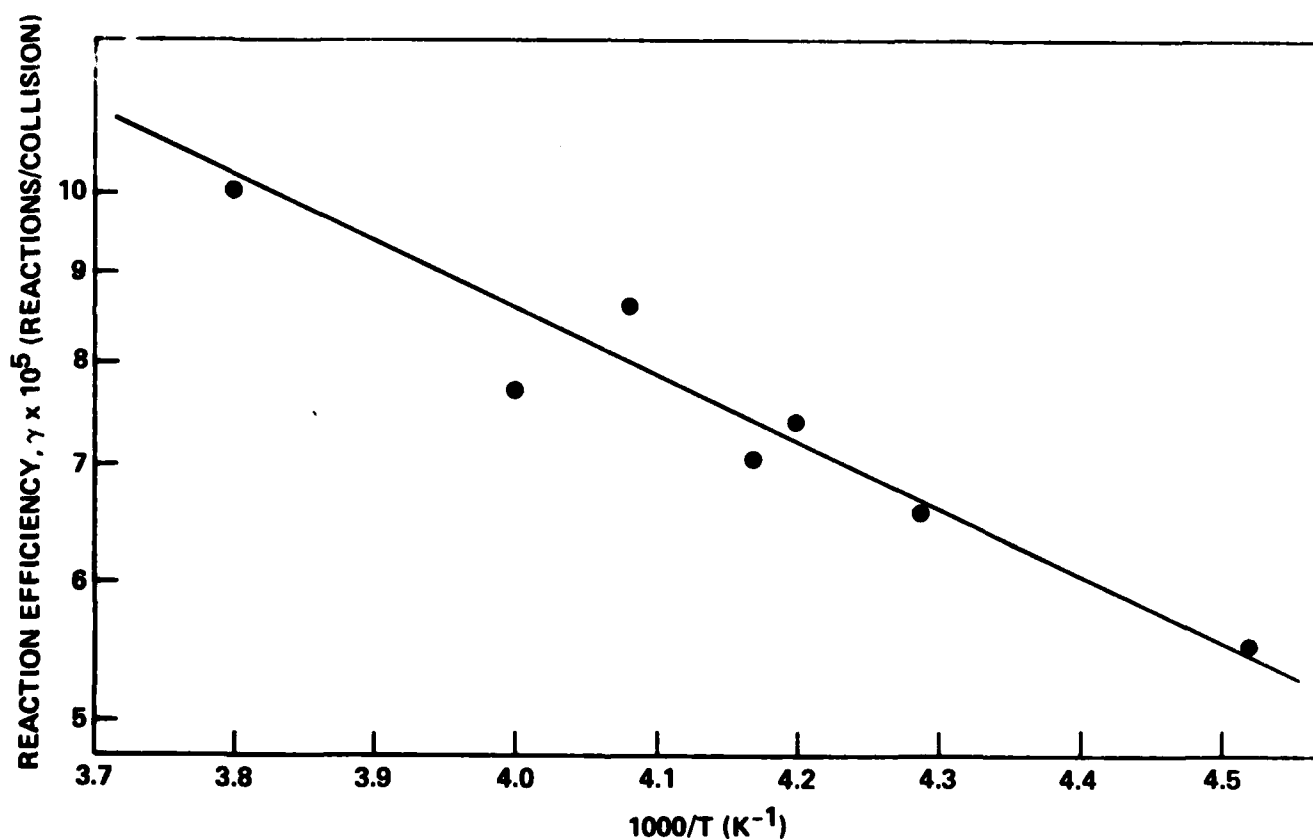


Fig. 6 A plot of the logarithm of the reaction efficiency versus reciprocal absolute temperature over the range 221 to 263K for a 52 mole% $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ reactive surface. The solid line represents the best fit to the equation $\gamma = A \exp(-\Delta E/RT)$, with the fitting coefficients $\gamma = 2.94 \times 10^{-3} \exp(-1,766/RT)$.

In this expression α is a constant determined by the sticking coefficient for adsorption onto the reactive surface and by the number of available reaction sites on the surface. The constant β is determined by of the partition functions of the activated surface complex. The magnitude of β is a measure of the mobility of the activated complex on the surface, with its value approaching unity for an immobile adsorbed species.

For the case of a mobile surface activated complex $\beta \gg 1$ hence Eq. (V) can be reduced to the form

$$\gamma \approx (\alpha\beta \exp [(E_r - E_d)/RT])^{-1} , \quad (VI)$$

which predicts the temperature behavior for γ observed in this study for N_2O_5 hydrolysis.

Using this description the ΔE controlling the temperature dependence of γ for the N_2O_5 hydrolysis was found to be for the case of a 52 mole% frozen water H_2SO_4 surface 1,766 cal/mole which is high for a mobile species with a reaction efficiency above 10^{-5} reactions/collision. This could indicate that at the higher γ values of this study the ΔE should become smaller and the reaction efficiency should become more constant with temperature, controlled by the sticking coefficient and the number of available reactive sites. The data collected in this study is not, however, complete enough to demonstrate this behavior.

4.0 DISCUSSION

The experimental results of this study demonstrate that water containing surfaces can effectively hydrolyze dinitrogen pentoxide at temperatures between 214 and 263K, with liquid phase surfaces having a significantly higher reaction efficiency. The observed efficiencies of 10^{-5} to 10^{-4} reactions per collision indicate that this reaction is probably significant in establishing the concentration of NO_x species in the upper atmosphere especially at those altitudes (16-25 km) at which there are significant levels of particulate matter. The observation that HNO_3 also adsorbs onto the acid-water surfaces with γ values on the order of 10^{-5} (reactions/collision) at temperatures above 230K provides another sink mechanism for this species in the stratosphere.

The reaction efficiencies observed in this study enter the range shown by Cadle³ to be significant when compared to the other process effecting gas phase concentrations in the stratosphere and point to the need to carry out more detailed studies of these reactions as a function of temperature and surface compositions. The role of liquid or supercooled liquid surfaces in heterogeneous reactions especially offers an area where significant results could be expected.

ACKNOWLEDGEMENT

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