3108

LA-UR-00-XXXX

97023

Approved for public release;
distribution is unlimited

Title: Classical Kinetic Mechanisms Describing Heterogeneous
Ozone Depletion

Author(s): Bryan F. Henson and Jeanne M. Robinson (CST-6)

Submitted to: DOE Office of Scientific and Technical Information (OSTI)

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Classical Kinetic Mechanisms Describing Heterogeneous Ozone Depletion

Bryan F. Henson* and Jeanne M. Robinson (CST-6)

RECEIVED

NOV 13 2000

OSTI

Abstract

This is the final report of a three year Laboratory Directed Research and Development, LDRD, project in which we investigated the kinetic mechanisms of two important classes of heterogeneous reactions in the stratosphere, hydrolysis and reaction with HCl. Utilizing a combination of experimental techniques unique to our laboratory at Los Alamos, and applying a very successful program of modeling, we have proposed a model of stratospheric hydrolysis which enables calculation of uptake coefficients in agreement with essentially all of the data in the literature, and have produced the first thermodynamically consistent model of the adsorption of HCl on two ice surfaces believed to be important in the stratosphere. Among the conclusions of this work, we have shown that the uptake of HCl on these surfaces is consistent with the classic HCl/H₂O binary phase diagram, and that such uptake is too small for HCl to serve as a surface adsorbed reagent under most conditions, as had been previously believed.

Background and Research Objectives

Since the first report of the south polar 'ozone hole', field observations and laboratory measurements have established that heterogeneous (gas/surface) reactions on polar stratospheric cloud (PSC) particles activate gas phase chemical reactions and sedimentation processes that are directly responsible for north and south polar ozone depletion. In a complex stratospheric meteorology of variable relative humidity and reagent pressure, these reactions will be coupled in a complex manner by the surface concentration of the reagents and products. Furthermore, the quantitative nature of the coupling will depend on the classical kinetic mechanism of reaction, either Eley-Rideal, involving one adsorbed and one gas phase reagent, or Langmuir-Hinshelwood, involving two adsorbed reagents.

The set of coupled reactions under consideration in the present work is

These reactions proceed on particulate ice in the stratosphere and serve to activate the Cl_2 as a gas phase product which subsequently attacks ozone, or to sequester ozone restoring NO_x and remove it from the stratosphere via sedimentation as HNO_3 . These reactions are believed to contribute significantly to the overall ozone depletion mechanism, particularly in the very cold polar winter, where conditions are prepared for the 'ozone hole' events that accompany sunrise and subsequent photochemistry in the polar spring.

The hypothesis that heterogeneous chemistry on polar stratospheric clouds activates chlorine catalyzed ozone destruction^[1] inspired considerable interest in the interaction of HCl with ice following the discovery of the Antarctic ozone hole. Fast reaction of HCl with ClONO_2 , R1, on laboratory ice surfaces^[2,3] produces photolabile Cl_2 , via interaction of surface deposited HCl and ClONO_2 vapors. The detailed physicochemical mechanism^[4-9] explaining experimentally observed HCl coverage^[10-17] on ice has proven elusive. Difficulties in adequately simulating stratospheric temperatures and pressures, as well as considerable uncertainties in characterizing ice substrates, have led to uncertainties in the measured uptake of HCl by ice of fully two orders of magnitude. Thus, despite the importance of reaction with what is believed to be adsorbed HCl, there is no experimental consensus or physical model for the uptake of this species under stratospheric conditions.

The experiments on HCl reported here remedy both of these shortcomings. We present vapor pressure measurements of HCl adsorption onto well-characterized, porous, polycrystalline H_2O ice films of measured surface area at three temperatures over the range 180 K to 200 K and HCl pressures approaching stratospheric. We simultaneously monitor surface thermodynamic phase directly by the surface-sensitive laser scattering technique

second harmonic generation. By measuring HCl uptake onto a surface of known area we directly associate HCl partial pressure with coverage, generating a classic physical adsorption isotherm. The isotherms have classic single layer adsorption character, with fast early uptake, a plateau at constant pressure during midcoverage uptake, and a dramatic pressure rise near monolayer coverage. It is a central observation of this work that the sharp pressure rise precipitates the nucleation of a crystalline hydrate phase. By subsequent heating of the ice we have identified the $\text{HCl}(\text{H}_2\text{O})_6$ hydrate as the phase created. These observations serve to characterize fully the adsorption of HCl under these conditions. It is important to stress that the single layer nature of the adsorption, and the formation of the hydrate phase as an endpoint for monolayer titration, allow the quantitative definition of fractional surface coverage. We are thus able to model the form and temperature dependence of the submonolayer isotherms generated from 180 K to 200 K using classic single layer Langmuir adsorption with a Bragg-Williams correction for lateral adsorbate-adsorbate interactions. We have thus fully characterized the experimentally determined interfacial equation of state of this important stratospheric species.

We have also developed a model of the hydrolysis reactions of chlorine nitrate, R2, and nitrogen pentoxide, R3, on surrogate polar stratospheric cloud surfaces composed of solid sulfuric acid and nitric acid hydrates. Chlorine nitrate hydrolysis alone is not believed to impact ozone concentrations to the same degree as reaction with HCl, R1. However, it is clear from R2a and R2b that hydrolysis may couple with the HCl mechanism through intermediate formation. Additionally, R2 may prove significant under conditions where HCl ambient pressures are low. By contrast, R3 contributes significantly to the south polar ozone hole through sedimentation of the product HNO_3 out of the stratosphere.

The model is based on the reaction of gas phase ClONO_2 and N_2O_5 with surface adsorbed water via an Eley-Rideal mechanism. The fraction of the hydrate surface covered by water as a function of the water activity is determined from Brunnauer-Emmett-Teller (BET) multilayer adsorption theory. The model parameters are ΔQ , the difference between the energy of adsorption of a water molecule on the acid hydrate surface or on another adsorbed water layer, and γ_0 , the reaction probability over pure ice, which has been measured in several laboratories for these reactions. For water adsorption on nitric acid trihydrate (NAT), we measured ΔQ directly using second harmonic generation. In this work, we have modeled the full suite of reaction probability measurements for ClONO_2 and N_2O_5 hydrolysis from many

laboratories on several different hydrates as a function of temperature and water activity. We find that the normalized reaction probabilities for both N_2O_5 and ClONO_2 on NAT, NAM (nitric acid monohydrate) and SAT (sulfuric acid tetrahydrate) are directly proportional to the calculated surface coverage of water. The model is a global parameterization of these two reactions which reproduces the observed reactivity over four decades in both reaction probability and water activity.

Importance to LANL's Science and Technology Base and National R&D Needs

Prior to the discovery of the so-called "ozone hole", heterogeneous processes were ignored in atmospheric chemistry models. Field measurements, supported by laboratory experiments and modeling, have confirmed the pivotal role of reactions of photoinactive (reservoir) chlorine and nitrogen gases on ice and nitric and sulfuric acid ice aerosols in the Antarctic polar vortex. It was subsequently recognized that the determination of chemical mechanism would be required in order to adequately model the heterogeneous rates as a function of the complex ice surfaces. Attention is now turning to mechanistic studies which incorporate the full thermodynamic and substrate complexity in these systems.

This work builds on a program unique to LANL with the capability to address these questions by probing the complex surface directly. The development of quantitative models of reactivity, which accurately model a wide range of reaction rate data, demonstrates the ability to deconvolute and characterize very complex and important heterogeneous chemical systems.

Scientific Approach and Accomplishments

The experiments on the HCl equation of state involved classic volumetric adsorption in a closed system, coupled with pressure measurement by mass spectrometry and nonlinear light scattering from the ice surface. A temperature-controlled ice sample of known surface area and porosity characterized *in situ* was prepared in a closed vacuum system. During controlled addition of HCl vapor, mass spectrometric measurements of the vapor pressures of HCl (p_{HCl}) and H_2O ($p_{\text{H}_2\text{O}}$) were used to monitor the HCl/ice equilibrium in the submonolayer regime as well as the state of solid and liquid phases that nucleated at coverage exceeding one monolayer (ML). Concurrent second harmonic generation (SHG) measurements were used to monitor HCl hexahydrate formation^[18]. Surface coverage was determined directly from the

added HCl vapor and calibrated ice area.

Observed pHCl and SHG intensity are plotted versus moles of HCl introduced over the ice in Figure 1a for three ice samples with varying total surface areas. PH₂O (not shown in Figure 1) was virtually constant at the ice vapor pressure during submonolayer adsorption. In all three cases, pHCl initially rises, then plateaus and finally rises sharply, the latter being nearly coincident with a sharp rise in the SHG signals. In Figure 1b, the x-axis has been recast as surface coverage by dividing HCl moles by the measured surface area of each sample. The HCl pressure isotherms approximately overlay one another, exhibiting similar sharp rises in pHCl at 2.1×10^{14} molecules/cm² characteristic of saturated monolayer adsorption.^[19] Further, the near coincident rise in SHG intensity indicates the formation of a bulk hydrate phase^[18] after surface saturation. The monolayer density of HCl on H₂O ice is thus 2.1×10^{14} molecules/cm².

Averaged data for HCl uptake on ice at 180, 190 and 200 K are shown in Figure 2a as solid lines together with other laboratory measurements (mostly flow tube studies) plotted as individual points. For stratospheric HCl levels ($\sim 10^{-7}$ torr) the HCl coverage (< 0.01 ML) observed here is much lower than the other measurements (~ 1 -2 ML). In contrast to present work, those other HCl coverages are reported assuming geometric surface areas, with some exceptions^[10,13,15]. For example, Chu et al.^[13] reported BET measurements that would reduce their HCl coverages by a factor of 25. While characterization of ice surface area and porosity has been debated,^[20,21] variability in surface areas of vapor condensed ices (up to factors of 10^6)^[22] can readily account for the variability in reported HCl coverage on uncharacterized samples. We have also measured the adsorption isotherm on a dry NAT surface at 190 K (Figure 2b). In contrast to the results for ice, our isotherm is in good agreement with the data of Abbatt and Molina^[23] and one point from Chu et al.^[13]

The dependence of pHCl on HCl surface density, particularly the sharp pressure increase as coverage approaches a monolayer, indicates that HCl forms a 2D phase on ice that is restricted to single layer coverage of the surface. In the low coverage regime, the isotherms exhibit a variable slope between 1 and 2, intermediate between what has been previously assumed to indicate molecular and dissociative uptake, respectively. The plateau in pHCl in the intermediate coverage regime is indicative of strong lateral interactions. We also note the differences in the pressure dependence of the other reported experimental results in Figure 2a.

The dependence of pHCl on HCl coverage (and its dependence on temperature) can be

explained by a Langmuir's isotherm modified to include lateral interactions through the Bragg-Williams approximation^[24]. We assume full dissociation on the surface, $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$, with an equilibrium between unassociated ions adsorbed on distinct sites and associated ions occupying the same site. The resulting pressure isotherm is given by

$$P = (2\pi mkT)^{3/2} \frac{kT}{h^3} \left(\frac{f\theta}{1-f\theta} \right)^f q_U^{-3\alpha} q_A^{-3\beta} \exp(-(\alpha\Delta H_U + \beta\Delta H_A + f^2\theta\varepsilon)/RT) \quad (1)$$

where P = HCl pressure, m = HCl mass, k = Boltzman's constant, T = temperature, and h = Planck's constant. The coverage of the associated and unassociated ionic species is θ_A and $2\theta_U$ respectively, with $\alpha=2\theta_U/(\theta_U + \theta_A)$, $\beta=\theta_A/(\theta_U + \theta_A)$, and $f=\alpha+\beta$. The low coverage limit of the isotherm is thus $P = (2\pi mkT)^{3/2} (kT/h^3) 4\theta^2 q_U^{-6} \exp(-2\Delta H_U/RT)$; however, this limit is only accurate for stratospheric HCl pressures below 200K. The vibrational component of the molecular partition function of species j is $q_j = \frac{e^{-\phi_j/2T}}{1-e^{-\phi_j/T}}$, where ϕ_j is the vibrational

temperature characterizing harmonic oscillation in the adsorption well^[24]. The three energies of the system are that for adsorption of the associated species, ΔH_A , the unassociated species, ΔH_U , and the energy derived from adjacent adsorbed species, ε . The coverage of the unassociated species is calculated via the equilibrium constant

$$K = \frac{q_U^2}{q_A} \exp(4\Delta H_U - \Delta H_A) \quad (2)$$

as

$$\theta_U = \frac{\sqrt{K^2 + 4K\theta} - K}{2} \quad (3)$$

where $\theta = \theta_U + \theta_A$.

The experimental observable is the loss of HCl to the surface, θ , which is calculated as the ratio of the measured uptake, in HCl molecules/cm² (Fig. 2) and an adsorption site density, ρ_o , in sites/cm². The adsorption energy varies between $2\Delta H_U$ and $\Delta H_A + \varepsilon$, in the limit of low and high coverage, respectively. The dashed curves in Fig. 2a and 2b show the least squares fit of Eq. 1 to the data via simultaneous optimization of ΔH_U , ΔH_A , ε , ϕ_U , ϕ_A and ρ_o (Table 1). The solid curve at 202 K (Fig. 2b) was then calculated for direct comparison with Ref. 23.

The model is rigorously grounded in the statistical mechanics of the canonical ensemble, with four of the six parameter severely constrained by comparison with the thermodynamics of

bulk HCl/H₂O. Most importantly, model adsorption energies can be related directly to the thermodynamics of solid and liquid HCl/H₂O phases (Figure 3). This comparison is made by estimating an interfacial concentration from the ratio of the density of sites, $\sim 2.44 \times 10^{14}$ sites/cm², and the surface density of H₂O in ice, $\sim 1.15 \times 10^{15}$ molecules/cm², or 4.7 H₂O molecules/site. Thus, in the associated phase each H⁺-Cl⁻ pair interacts with 4.7 H₂O molecules, and in the unassociated phase H⁺ and Cl⁻ each interact with one site for a total of 9.4 H₂O molecules. A correspondence can be made from Figure 3 both between the surface unassociated phase and the bulk liquid, and between the surface associated phase and the bulk trihydrate.

This can also be seen in Figure 4 where a plot of p_{HCl} versus p_{H₂O} for a 180 K adsorption experiment is superimposed on the bulk phase diagram. The initial rise in p_{HCl} (ca. p_{HCl} rise for low HCl coverage in Fig. 1b) is followed by a dense region of points representing the plateau in p_{HCl} for coverage >0.2, all at near constant p_{H₂O}. Pressure fluctuations in this region are largely accounted for by temperature fluctuations of ± 1 K during the ~ 6 hour experiment. As HCl coverage approaches monolayer saturation, the rise in p_{HCl} is accompanied by a slight decrease in p_{H₂O}, such that the pressures move along the calculated phase line for a liquid solution at 180 K. The decrease in p_{H₂O} indicates that condensing liquid has covered the geometric surface of the sample, isolating the vapor from the ice substrate¹⁹. After reaching a maximum, the p_{HCl} dropped promptly below our detection limit, simultaneous with the rise in SHG intensity (as in Figure 1a) indicated by the asterisk on the figure. Both of these effects indicate a crystalline hydrate (with low p_{HCl}) formed. The solid phase was identified as HCl hexahydrate during heating of the sample to 225 K. Observed pressures (after rising above detection limits at 189 K, plotted as squares) followed the hexahydrate/ice coexistence line until melting at 202 K, whereupon the SHG signal disappeared, and the liquid/ice coexistence line thereafter.

As modeled in Eq. 1, adsorbed HCl shifts from the solution-like to the hydrate-like state in the plateau region of the 180 K isotherm, where HCl surface density increases from ~ 0.2 to saturated monolayer coverage (see Figure 1b). The free energy of the system is minimized by the equilibrium between these two surface states. The success of this simple two-phase thermodynamic model argues that the HCl-H₂O surface structure is labile enough to reorient into configurations similar to those found in bulk systems. We observe no evidence for quasiliquid formation at submonolayer coverage.

The hydrate-like adsorption state described here for low coverage HCl adsorption on ice (Figure 3) is consistent with recent calculations^[25], where HCl interacted with both prism and basal faces of hexagonal ice through dissociation and formation of a contact ion pair (CIP). Indeed the average free energy of CIP formation for the 14 interaction configurations studied was 32.3 kJ/mole, in good agreement with the ensemble average value of $\Delta H_A = 30.8$ kJ/mole measured here. Those authors also concluded that the formation of a quasi-liquid⁴ is not necessary for dissociative uptake. Our measurements thus appear to close much of the gap between experiment and calculation. Calculations need to be extended to include HCl-HCl interactions at high coverage, ideally at a level of theory sufficient to model bulk phase thermodynamics. Surface spectroscopic experiments designed to identify the adsorbed states would fill out the picture.

Our experimental approach is unique in two important respects. First, by systematically varying (and characterizing) the ice sample area, we have shown that HCl pressure depends on HCl surface density, not sample area (Figure 2). This is shown most clearly by the constant monolayer saturation density of HCl on three ices of varying total surface area (Figure 1). Second, vapor/solid equilibrium was continuously monitored. At slow HCl introduction rates p_{H_2O} closely tracked equilibrium Ih ice pressures, p_{HCl} was reproducible within ~30%, and, subsequent to monolayer HCl uptake both pressures obey the equilibrium HCl/H₂O phase diagram (Figure 4). To our knowledge, this is the only study in which HCl vapor/solid equilibrium has been so precisely maintained and monitored. Thus we believe the differences between the isotherms observed here and those previously reported can be largely explained by differences in experimental approach.

The other important point of this work is the correlation of the interfacial and bulk thermodynamic states derived from the adsorption model (Figures 3 and 4). This contrasts with higher HCl uptake at lower pressures reported in other studies (Figure 2), which implies higher adsorption energies at higher interfacial concentrations. This would appear to contradict bulk HCl/H₂O thermodynamics where heats of solution and sublimation increase with dilution in bulk HCl/H₂O mixtures. Our observation of low HCl coverage on ice and NAT under stratospheric conditions is in agreement with several previous studies^[8,26,27], but not with heterogeneous reaction mechanisms that invoke high HCl surface concentration¹¹. Given the high reaction probability of ClONO₂ and HCl vapor in the presence of an ice or NAT surface observed in many laboratories, an alternative mechanism of adsorption and

chemical reactivity is called for in these systems.

Our model provides a clear relationship between bulk and interfacial thermodynamics in condensed systems. Using statistical mechanical formulations for the interfacial free energy and associating the state variables and surface concentrations in these theories with those of condensed phase thermodynamics, we have constructed a general method of solution. Many other systems, including the uptake of HCl on NAT and SAT at high relative humidity, water uptake on tropospheric salt systems, and the nucleation and formation of Type I solid PSCs, are amenable to this experimental and modeling strategy.

The model of stratospheric hydrolysis is based on the Eley-Rideal mechanism. The Eley-Rideal mechanism is characterized by reaction of a gas phase molecule, either ClONO_2 or N_2O_5 in this application, with a surface adsorbed H_2O molecule upon collision. The reaction rate is proportional to the surface collision rate of the gaseous species,

$$\frac{fn}{fA ft} = \gamma_0 \theta_1 \frac{fz}{fA ft}, \quad (4)$$

where n is the number of reactive collisions through surface area A , z is the total number of collisions, θ_1 is the fraction of A occupied by reagent and γ_0 is the probability of reaction upon collision. The measured reaction probability is the ratio of reactive to total collisions, or

$$\frac{fn}{fA ft} / \frac{fz}{fA ft} = \gamma = \gamma_0 \theta_1. \quad (5)$$

To first order, there is no explicit dependence of the reaction probability on area or gaseous reagent pressure. The reaction probability, γ_0 , is simply that measured over pure ice and θ_1 is the coverage of the ice hydrate surface by H_2O .

We model the coverage of the surface by H_2O using the classic BET isotherm. In the BET isotherm the adsorbing species is treated as two systems: the ensemble of adsorbing molecules on the surface, interacting via the surface adsorption energy Q_s , and the subsequent layers formed by adsorption onto this layer. These successive layers are modeled as the analogous bulk phase and inter-layer interaction occurs via the bulk adsorption energy, Q_a . The total uptake of a gaseous species by a surface is then calculated as a function of the

activity, x (the ratio of the partial pressure of the species to the condensation pressure of the bulk phase, P/P_o , equivalent to the relative humidity in this application). The only other parameter describing the system is a proportionality constant, usually denoted c . This parameter is constructed from the difference in adsorption energies for the two surface ensembles, $c \sim \exp((Q_s - Q_a)/RT)$

The total uptake, θ , is then

$$\theta(c, x) = \frac{1}{(1-x)} \frac{cx}{(1-x+cx)}, \quad (6)$$

where θ is in units of monolayers and x is the activity. The fractional coverage of the surface is given by

$$\theta_1(c, x) = \frac{cx}{(1-x+cx)}. \quad (7)$$

From combination of Eqs. 5 and 7 the reaction probability may be expressed as a function of the activity as

$$\gamma = \gamma_o \frac{cx}{(1-x+cx)}. \quad (8)$$

The reaction probability, γ , as a function of the fractional relative humidity (activity, x), measured in several laboratories is shown in Figure 5. Data for R2a on NAT are plotted as open squares.^[23] Data for R2a on sulfuric acid tetrahydrate (SAT) are plotted as open triangles.^[30] Data for R3 on sulfuric acid monohydrate (SAM) are plotted as open circles.^[31] Data for R2a and R3 on SAT and R2a on NAT are shown as solid triangles, inverted solid triangles and solid squares, respectively.^[32] A single data point for R2a on SAM is plotted as an open diamond.^[31] Another single data point for R2a on a dry NAT is plotted as a solid diamond.^[33] In Figure 6 data obtained as a function of temperature are plotted as γ versus temperature. The data for R2a on SAT and R3 on SAM are again plotted as open triangles,^[30] and open circles,^[31] respectively. This data set (Figures 5 and 6) represents all the reported data that we are aware of for which we could reliably determine the H_2O activity dependence.

The reaction probability dependence on activity and temperature shown in Figures 5 and 6 may be calculated from Eq 8. The parameters necessary for the calculation of the three curves are the reaction probability on pure ice, γ_o , for $ClONO_2$ and N_2O_5 , and the adsorption

energy difference, ΔQ , for H_2O adsorption on NAT, SAT and SAM.

The five parameters of the model were optimized as follows. The reaction probability of N_2O_5 on pure ice was held at the average from the literature, $\gamma_0(\text{N}_2\text{O}_5) = 0.019$. The other four parameters, $\Delta Q(\text{NAT})$, $\Delta Q(\text{SAT})$, $\Delta Q(\text{SAM})$ and $\gamma_0(\text{ClONO}_2)$, were allowed to vary in a calculation of γ from Eq. 8 for each point in the entire data set of Figures 5 and 6. The parameters were optimized by least squares minimization of the reaction probability as,

$$\chi^2 = \frac{1}{N} \sum_{\gamma_i} \frac{(\gamma_i - \gamma_i(x))^2}{\gamma_i} \quad (9)$$

with a resulting $\chi^2 = 0.0010$. The optimized parameters for the model are shown in Table II. This broader optimization procedure results in values of $\gamma_0(\text{ClONO}_2)$ and $\Delta Q(\text{SAT})$ which are only slightly different than reported previously.²⁶ The resulting value of ClONO_2 reactivity on ice is $\gamma_0(\text{ClONO}_2) = 0.008$.

The solid lines in Figures 5 and 6 are the result of calculations of γ as a function of activity and temperature from Eq. 8 using the parameters of Table II. The agreement between the calculations and laboratory data is excellent, given the difficulties in these experiments, encompassing both the quantitative values of γ and the trends of dependence on activity and temperature. It is important to note that for the calculation of γ for R2a on NAT, Figure 5 (open squares), the model is entirely constrained by data.

In the recent centennial edition of this journal Nobel Laureate Mario Molina, commenting on the role of heterogeneous reactions in atmospheric chemistry, concluded that “...*much remains to be learned ... before heterogeneous chemistry can be placed on a firm theoretical foundation analogous to that which exists for gas phase kinetics.*”^[34] Again last year, in a special issue of Science on tropospheric chemistry A. R. Ravishankara reiterated “*Frameworks are available for including multiphase reactions in numerical modeling, but they do not yet exist for heterogeneous reactions.*”^[35] The mature state of gas phase kinetics alluded to involves a powerful and predictive transition state theory (TST) to describe the reaction process. However, the theory of chemical transformation embodied in the TST rests upon the older kinetic theory of gases, which provides a quantitative mechanism of binary collision upon which most gas phase applications of TST are based. A chemical theory of transformation rests upon a physical theory of interaction. Our understanding of heterogeneous reactivity in semi-volatile molecular systems is in this sense been even more primitive than implied above, as few physical mechanisms of interaction with the surface

have been identified which could provide the physical theory of interaction analogous to the kinetic theory of gases. The work presented in this report represents the first attempt to formulate a general, physical model of interaction of gas phase reagent species with the semi-volatile ice surfaces which characterize the lower stratosphere, combined with classic kinetic models of reaction which will provide a sound mechanistic understanding of upper atmospheric heterogeneous chemistry.

Publications

1. B.F. Henson, K. R. Wilson, and J.M. Robinson, *Quantitative Measurements of Multilayer Physical Adsorption on Heterogeneous Surfaces From Nonlinear Light Scattering*, Phys. Rev. Lett. **79**, 1531 (1997).
2. B. F. Henson, and J. M. Robinson, *A Physical Model of Heterogeneous Hydrolysis in the Stratosphere*, submitted to J. Phys. Chem.
3. B. F. Henson, K. R. Wilson, J. Casson, C. A. Noble, D. R. Worsnop and J. M. Robinson, *Experimental isotherms of HCl on ice under stratospheric conditions*, submitted to Nature.
4. B. F. Henson, K. R. Wilson, and J. M. Robinson, *Models of HCl adsorption and ClONO₂ Reactivity on Simulated PSC Surfaces*, Contributed talk presented at the Fall meeting of the American Geophysical Union, San Francisco, CA, December 15 - 19, 1996.
5. B. F. Henson, K. R. Wilson, and J. M. Robinson, *Measurements of HCl adsorption isotherms on H₂O ice from 180 K to 200 K at near stratospheric pressures*, Contributed talk presented at the Fall meeting of the American Chemical Society, Los Vegas, NE, September 7 - 11, 1997.
6. J. M. Robinson, B. F. Henson, K. R. Wilson, J. Casson, M. K. Dubey, M. Johal, L. Foster and D. Worsnop, *Investigations of Simulated Polar Stratospheric Clouds by Surface Second Harmonic Generation, Physical Adsorption, and Mass Spectrometry*, Invited talk presented at the 23rd Informal Conference on Photochemistry, May 10-15, 1998, Pasadena, CA.

References

- [1] Solomon, S. *Nature* **347**, 347 (1990).
- [2] Molina, M. J., Tso, T.-L., Molina, L. T., Wang & F. C.-Y. *Science* **238**, 1253 (1987).
- [3] Tolbert, M. A., Rossi, M. J., Malhotra, R. & D. M. Golden, *Science* **238**, 1258 (1987).
- [4] Molina, M. J., *Chemravn VII*, ed. J. G. Calvert (Blackwell, Oxford 1992).
- [5] Robertson, S. H. & Clary, D. C. *Faraday Discuss.* **100**, 309 (1995).
- [6] Gertner, B. J. & Hynes, J. T. *Science* **271**, 1563 (1996).
- [7] G. -J. Kroes and D. C. Clary, *J. Phys. Chem.* **96**, 7079 (1992).
- [8] R. R. Friedl, J. H. Goble, S. P. Sander, *Geophys. Res. Lett.* **13**, 1351 (1986).
- [9] A. Tabazadeh and R. P. Turco, *J. Geophys. Res.* **98**, 12727 (1993).
- [10] Marti, J. & Mauersberger, K. *Geophys. Res. Lett.* **18**, 1861 (1991).
- [11] Hanson, D. R. & Ravishankara, A. R. *J. Phys. Chem.* **96**, 2682 (1992).
- [12] Abbatt, J. P. D. *et al.*, *J. Geophys. Res.* **97**, 15,819 (1992).
- [13] Chu, L. T., Leu, M.-T. & Keyser, L. F. *J. Phys. Chem.* **97**, 12798 (1993).
- [14] Abbatt, J. P. D. *Geophys. Res. Lett.* **24**, 1479 (1997).
- [15] Leu, M.-T., Keyser, L. F., & Timonen, S. *J. Phys. Chem. B* **101**, 6259 (1997).
- [16] Foster, K. L., Tolbert, M. A., & George, S. M. *J. Phys. Chem. A* **101**, 4979 (1997).
- [17] N. Uras, M. Rahman, & Devlin, J. P. *J. Phys. Chem. B* **102**, 9375 (1998).
- [18] Henson, B. F., Wilson, K. R., & Robinson, J. M. *Phys. Rev. Lett.* **79**, 1531 (1997).

- [19] The pressures in Fig. 1b do not exactly overlap due to the difficulty in achieving equilibrium between the gas phase and surface area within the film. A lack of equilibration with the surface is manifest as a pressure higher than that at equilibrium, as a time lag is introduced for HCl diffusion into the sample. This is most apparent in iii, which is the largest area ice and the highest dosing rate. Intermediate behavior is seen in ii. The smallest sample with slow dosing rate, i, demonstrates an *equilibrium* pressure dependence. This was confirmed by stopping the HCl flow at points along the isotherm and confirming that the HCl pressure remained constant over the ice. Additionally, for HCl coverages greater than a monolayer, H₂O pressure tended to drop below ice equilibrium even at low HCl introduction rates, as liquid or solid HCl phases began to nucleate and cover the top layer of the ice film.
- [20] Keyser, L. F. , Leu, M.-T., Moore, S. B. *J. Phys. Chem.* **97**, 2800 (1993).
- [21] Hanson, D. R., & Ravishankara, A. R. *J. Phys. Chem.* **97**, 2802 (1993).
- [22] Mayer, E. & Pletzer, R. *J. Chem. Phys.* **80**, 2939 (1984).
- [23] Abbatt, J. P. & Molina, M. J. *J. Phys. Chem.* **96**, 7674 (1992).
- [24] Hill, T. L. *An Introduction to Statistical Thermodynamics* (Dover, 1986).
- [25] Gertner, B. J. & Hynes, J. T. *Faraday Discuss.* **110**, 301 (1998).
- [26] Henson, B. F. , Wilson, K. R. , & Robinson, B. F. *Geophys. Res. Lett.* **23**, 1021 (1996).
- [27] Carslaw, K. S. & Peter, T. *Geophys. Res. Lett.* **24**, 1743 (1997).
- [28] Carslaw, K. S. , Clegg, S. L. , & Brimblecombe, P. *J. Chem. Phys.* **99**, 11557 (1995).
- [29] Woolridge, P. J., Zhang, R., & Molina, M. J. *J. Geophys. Res.* **100**, 1389 (1995).
- [30] Zhang, R., Jayne, J. T., Molina, M. J. *J. Phys. Chem.* **98**, 867 (1994).
- [31] Zhang, R., Leu, M.- T., Keyser, L. F. *J. Geophys. Res.* **100**, 18845 (1995).
- [32] Hanson, D. R, Ravishankara, A. R. *J. Geophys. Res.* **98**, 22,931 (1993).
- [33] Leu, M.-T., Moore, S. B., Keyser, L. F. *J. Phys. Chem.* **95**, 7763 (1991).
- [34] Molina, M. J., Molina, L. T., Golden, D. M. *J. Phys. Chem.* **100**, 12888 (1996).
- [35] Ravishankara, A. R., *Science* **276**, 1058 (1997).

Figure Captions

Figure 1.: (a) Three HCl adsorption experiments at 180 K. Simultaneous pressure and SHG measurements are plotted as a function of the moles of HCl introduced. Experiments *i*, *ii* and *iii* were conducted on samples of surface area 8, 36, and 80 m² and with introduction rates of 1.4x10⁻⁸, 8.2x10⁻⁹ and 7.6x10⁻⁸ moles/sec, respectively. The abrupt rise in the SHG intensity marks the nucleation of the hydrate phase, which is driven by the preceding pressure rise. The water vapor pressure (not plotted) remained constant in each experiment at the ice pressure until decreasing slightly just prior to crystal nucleation. The pressure and SHG transient are correlated in each of *i*, *ii*, and *iii*. (b) The three HCl adsorption experiments of (a) plotted as a function of surface density by dividing the measured uptake of HCl by the surface, in molecules, by the measured total surface area of each sample, in cm².

Figure 2.: (a) Adsorption isotherms for HCl on H₂O ice at 180, 190 and 200 K. The data are plotted in red as the HCl surface density as a function of HCl pressure. Black curves are isotherms calculated from Eq. (1), using the parameters of Table 1. Data from other laboratories are plotted in green as follows: dashed box¹¹, solid box¹², solid triangular and square points¹³, open square¹⁴, open inverted triangle¹⁰, open circle¹⁵. The isotherm shown at 180 K is the average of six measurements, the 190 K data a set of two, and the data at 200 K are from one measurement. (b) Adsorption isotherm for HCl on NAT at 190 K, plotted as in (a). Black curves as in (a) at 190 and 202 K. Data from other laboratories are shown as follows: solid inverted triangular points²³, open triangle¹¹, solid circles¹³.

Figure 3.: Energy diagram illustrating the correspondence between interfacial and bulk thermodynamics in the HCl/H₂O system. Energy is plotted on the ordinate, with the heat of solution at infinite dilution and at 9.4 molar dilution shown on the left and the sublimation energies of the tri- and hexahydrate on the right. In the center of the illustration, the energies of the adsorbed phase in the limits of low and high coverage are shown. The relative zero of energy in the system and the energy of HCl gas phase dissociation are also shown.

Figure 4.: Projection of an experimental adsorption isotherm at 180 K onto the bulk HCl/H₂O phase diagram. The hexahydrate stability region is denoted by dashed lines; bold solid lines show stable (and supercooled) HCl/H₂O liquid solution/ice coexistence. The vertical dashed line matches p_{H₂O} over ice and the solid line the p_{HCl}, p_{H₂O} curve for liquid solution at 180 K. Data from curve *ii* in Fig 1b are plotted as small squares during adsorption at 180 K. Vapor pressure data during heating from 189 to 225 K are plotted as large squares. This diagram shows that the submonolayer HCl phase at 180 K (identified by the group of points for p_{HCl} between 1 and 2x10⁻⁶ torr) is metastable with respect to the liquid/ice coexistence point at p_{HCl} ~ 6x10⁻⁷ torr. All p_{HCl} values at 180 K are metastable with respect to the hexahydrate/ice coexistence point (p_{HCl} ~ 1x10⁻⁷ torr). The nucleation of crystalline hexahydrate after supercooled liquid covered the ice sample is shown by the measured vapor pressures following the hexahydrate/ice coexistence line (after heating above 189K) and by melting at 200K. The hexahydrate stability region was calculated from the hexahydrate and trihydrate pressure relations derived from Ref. 28 together with HCl/H₂O solution vapor

pressure calculated from Ref. 29. Moving along diagonal coexistence lines (from bottom left to top right) corresponds to increasing temperature, with labeled temperatures matching pH_2O over ice for experimental data.

Figure 5: Measurements of the reaction probability, γ , as a function of the relative humidity (activity, x), from the literature. Data for R2a on NAT are plotted as the open squares²³ and for SAT as open triangles.³⁰ Data for R3 on SAM are plotted as open circles.³¹ Data for R2a and R3 on SAT and R1 on NAT are shown as solid triangles, inverted solid triangles and solid squares, respectively.³² Single measurements of R2a on SAT³¹ and NAT³³ are plotted as an open and solid diamond, respectively. The solid curves are calculations of γ as a function of x from Eq. 8, where $c = \text{EXP}(\Delta Q/RT)$, with the parameter values listed in Table II.

Figure 6: Measurements of the reaction probability, γ , as a function of temperature, from the literature. The data for R2a on SAT and R3 on SAM are again plotted as open triangles,³⁰ and open circles,³¹ respectively. The solid curves are calculations of γ as a function of temperature from eq 5, where $c = \text{EXP}(\Delta Q/RT)$, $x = P/\text{Po}(T)$, and the parameter values are listed in Table II.

Table I. Parameterization of Eq. (1). All energies in kJ/mole.

	ICE	NAT	adsorption enthalpy for ice	
ΔH_U	0.2	0.4	<i>low θ,</i>	$2 \Delta H_U$ 0.4
ΔH_A	30.8	29.3	<i>high θ,</i>	$\Delta H_A + \epsilon$ 36.2
ϵ	5.4	5.4		
			bulk enthalpies	
ϕ_A (K)	3.05	2.80	<i>liquid,</i>	$\Delta H_{\text{sol}} (.11\text{M})$ 9.6
ϕ_U (K)	2.11	1.90	<i>trihydrate,</i>	ΔH_{sub} 45.6

Table II. Parameters utilized in the calculations of γ .^a

$\Delta Q_{\text{H}_2\text{O}}$ on NAT	-7.00	kJ/mole	LSO ^b
$\Delta Q_{\text{H}_2\text{O}}$ on SAT	-0.73	kJ/mole	LSO
$\Delta Q_{\text{H}_2\text{O}}$ on SAM	1.77	kJ/mole	LSO
γ_0 ClONO ₂	0.008		LSO
γ_0 N ₂ O ₅	0.019	Average of literature values	

^a The ΔH and ΔS of sublimation for ice I_h are taken from ref 9.^b Least Squares Optimization.

Figure 1. B. F. Henson, 97023, Classic kinetic mechanisms ...

Figure 2 B. F. Henson, 97023, Classic Kinetic Mechanisms ...

Figure 3: B. F. Henson, 97023, Classic Kinetic Mechanisms ...

Figure 4: B. F. Henson, 97023, Classic Kinetic Mechanisms ...

Fig. 5 B. F. Henson, 97023, Classic Kinetic Mechanisms ...

Figure 6: B. F. Henson, 97023, Classic Kinetic Mechanisms ...