The HCl + ClONO\(_2\) reaction rate on various water ice surfaces

Shan-Hu Lee \(^1\), Danna C. Leard, Renyi Zhang \(^2\), Luisa T. Molina, Mario J. Molina \(^*\)

Department of Earth, Atmospheric and Planetary Sciences and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139 USA

Received 8 September 1999; in final form 22 September 1999

Abstract

The reaction ClONO\(_2\) + HCl \(\rightarrow\) Cl\(_2\) + HNO\(_3\) on ice surfaces was investigated using a fast flow reactor coupled to a chemical ionization mass spectrometer. Rough and relatively smooth ice surfaces and single-crystal ice particles were employed to investigate the effect of the different surface morphologies on the reaction mechanism. Large reaction probabilities (\(\gamma > 0.1\)), independent of HCl partial pressure in the range from \(2 \times 10^{-7}\) to \(8 \times 10^{-6}\) Torr, were measured on these three ice surfaces. These results are consistent with an ionic reaction mechanism involving HCl solvation on a liquid-like surface layer. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Heterogeneous reactions on polar stratospheric clouds (PSCs) are known to play a crucial role in polar ozone depletion. Perhaps the most important heterogeneous reaction that converts the inert chlorine reservoirs ClONO\(_2\) and HCl into photochemically active chlorine is the following:

\[
\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3
\]  

(1)

This reaction has been studied on liquid sulfuric acid solutions as well as on several different solid surfaces, such as ice, nitric acid trihydrate (NAT), sulfuric acid tetrahydrate, alumina, and Pyrex glass [1–5]. So far, the reaction mechanism on ice and on the acid hydrates remains controversial. The most commonly proposed mechanism assumes conventional physical adsorption of the reactants on the surface [6–8]. We have proposed an alternative mechanism involving the uptake and solvation of HCl vapor to form a liquid-like surface layer as a first step, followed by a rapid ionic reaction with ClONO\(_2\) [9].

In order to further elucidate the reaction mechanism, we report in this Letter measurements of HCl uptake and of the HCl partial pressure dependence of the rate of Reaction (1) on ice surfaces with various morphologies: films with relatively smooth or rough surfaces and micron-sized particles consisting of single crystals.

2. Experimental

The experiments were conducted with a fast flow reactor attached to a differentially pumped quad-
rupole mass spectrometer (Extrel EXM-280). Reactants and products were monitored with chemical ionization mass spectrometry. SF$_6^-$ ions, generated with a glow discharge, were used to ionize HCl, ClONO$_2$, and HNO$_3$. For Cl$_2$ detection, we introduced NO$_2$ gas as chemical reagent in addition to SF$_6$ to improve the detection sensitivity. The detection limit for Cl$_2$ was estimated to be $\sim 2 \times 10^{-8}$ Torr (S/N = 2).

The technique employed for measurements on ice films is similar to that used in our previous studies of heterogeneous reactions [4,5,10]. Two types of ice films were prepared. The first one is similar to that used in most of the previous heterogeneous chemistry experiments on ice [2,3,11,12]: water vapor was injected for about one hour into a cold flow tube kept at 201 K. The thickness of the ice film formed was approximately 10 $\mu$m, with a geometric area of $\sim 110$ cm$^2$ (3 cm diameter and $\sim 12$ cm long). The second type of film was generated using a method similar to that described by Abbott [13]: a Pyrex tubing (with an internal diameter slightly less than 3 cm) was cleaned with a 5% aqueous HF solution, wetted with deionized water and then inserted snugly into the cold flow tube. Thin ice films were formed immediately. Helium was employed as the buffer gas; the total pressure in the flow reactor was 1–3 Torr, the flow velocities were 900–1400 cm s$^{-1}$, and the temperature was maintained at 201 K. The isotope exchange experiments were carried out by coating the flow tube walls with a rough H$_2$O ice film, and subsequently introducing DCl vapor through the moveable injector while monitoring both HCl and DCl with the mass spectrometer operated in electron-impact mode. The isotope exchange experiments have been described in detail by Zhang [14].

The techniques employed for the measurements on ice particles are described more extensively by Leard [15]. Briefly, particles with sizes in the 1–5 $\mu$m range were generated by injecting water vapor into a chamber held at $\sim 220$ K under highly supersaturated conditions. The particles, entrained in nitrogen carrier gas, were injected into a flow tube operated at a total pressure of 760 Torr; the flow velocities were 50–100 cm s$^{-1}$ and the temperature in the flow tube was $\sim 210$ K. The size distribution and number density of the particles were monitored with a Malvern MS1000 Mastersizer light scattering device; they were characterized as single crystals by means of optical microscopy. A small portion of the gas was sampled and injected into a chemical ionization reactor operated at 100–200 Torr.

3. Results

3.1. HCl uptake measurements

The amount of HCl vapor taken up by the smooth ice film was measured to be $(1.1 \pm 0.6) \times 10^{14}$ molecule cm$^{-2}$ at HCl partial pressures, $P_{\text{HCl}}$, between $10^{-7}$ and $1.5 \times 10^{-6}$ Torr (average of 14 individual measurements); and $(3.9 \pm 1.6) \times 10^{14}$ molecule cm$^{-2}$ at $P_{\text{HCl}}$ between $2 \times 10^{-6}$ and $4 \times 10^{-6}$ Torr (average of 13 measurements). For the rough ice film the amount measured was $\sim 3 \times 10^{14}$ molecule cm$^{-2}$ at $P_{\text{HCl}} \sim 2 \times 10^{-6}$ Torr, that is, the uptake was comparable to that on the smooth surface. These uptake values were estimated assuming an ice area equal to the geometric area of the flow tube; considering surface roughness the actual uptake should be smaller. Assuming that a monolayer of HCl corresponds to $10^{15}$ molecule cm$^{-2}$, the surface coverage $\theta$ measured falls between 0.1 and 0.4. The scatter in the data is probably a consequence of surface roughening for the smooth ice, and annealing for the rough ice. In the case of the ice particles we are able to place a lower limit to the uptake of $\sim 2 \times 10^{13}$ molecule cm$^{-2}$ at $P_{\text{HCl}}$ between $5 \times 10^{-6}$ and $2 \times 10^{-5}$ Torr; uncertainties in surface area and flow dynamics precluded more accurate measurements.

The results of the isotope exchange experiments indicate that the ice surface promotes exchange on a time scale of at most a few seconds. The HCl signal appeared practically instantaneously following the injection of DCl into the H$_2$O-ice coated flow tube, with a magnitude corresponding to the amount of HCl introduced.

3.2. Reaction rate measurements

The rate of Reaction (1) was determined by monitoring the concentration of ClONO$_2$ as a function of injector position. To ensure pseudo first-order condi-
tions, the HCl concentrations used were significantly greater than those of ClONO₂. For the ice film experiments the rate was also determined by measuring the Cl₂ signal, as shown in Fig. 1; the slightly higher values appearing immediately after repositioning the injector occurred most likely because of surface deactivation resulting from the accumulation of HNO₃. As expected, analysis of the ClONO₂ decay and Cl₂ growth curves yielded essentially the same value for the first order rate constant, k_{obs}.

Within experimental error, the values of k_{obs} measured on the ice films showed no dependency on the ice morphology or on the HCl partial pressure, which was varied between 2 × 10⁻⁷ and 8 × 10⁻⁶ Torr (see Fig. 2). The ClONO₂ concentrations ranged from 6 × 10⁻⁸ to 8 × 10⁻⁷ Torr. For the smooth ice films k_{obs} = 365 ± 97 s⁻¹ (average ± 1σ; 25 runs); for the rough films k_{obs} = 369 ± 55 s⁻¹ (89 runs). The reaction probability γ calculated using standard flow tube analysis techniques [16,17] was in all cases larger than 0.3; under our experimental conditions the reaction was diffusion-limited, and hence we could only establish γ as a lower limit. Similarly, for the ice particle experiments the reaction rate did not show any measurable dependency on P_{HCl}, which was varied between 1 and 2 × 10⁻⁶ Torr; as expected, neither was there a dependency on particle size. In these experiments the rate of reaction was also diffusion-limited, but we were able to determine a lower limit to γ of 0.1.

4. Discussion

Our HCl uptake results are in reasonable agreement with previously reported values in terms of surface coverage θ [2,11,12,18–20]. There is, however, some disagreement in the literature with respect to the dependency of θ on P_{HCl}; Hanson and Ravishankara [2] and Foster et al. [19] did not observe any dependency, whereas Chu et al. [12] obtained a square root dependency. Our results show only a mild dependency: θ increases by at most a factor of three or four for a 40-fold increase in P_{HCl}; the data is too scattered to establish any specific functional form. It is also clear that for HCl partial pressures above those corresponding to the solid–liquid coexistence line, the uptake increases dramatically because of melting [11,18,19].

The expectation from the model that assumes simple physical adsorption of HCl on active surface sites is that θ should increase with P_{HCl} until the surface is saturated. More importantly, the expectation is that the reaction probability γ for Reaction (1) should also increase with P_{HCl}, since the overall rate should increase as more active sites are occupied by HCl [6–8]. In fact, using such an adsorption
model for Reaction (1), Carslaw and Peter [22] suggested that the value of $\gamma$ on NAT surfaces should be nearly proportional to $P_{\text{HCl}}$, and hence they concluded that our NAT results [10] (e.g., $\gamma > 0.1$ for relative humidity > 50% and $P_{\text{HCl}} = 4-10 \times 10^{-6}$ Torr) are inconsistent with those reported by Hanson and Ravishankara [3] (e.g., $\gamma > 0.1$ for relative humidity > 60% and $P_{\text{HCl}} = 6-200 \times 10^{-8}$ Torr). Carslaw and Peter's model is based on our observation that for low relative humidities, $\theta$ on NAT is indeed nearly directly proportional to $P_{\text{HCl}}$ [10]. However, this is not the case at the higher humidities relevant to the stratosphere [10].

We expect a similar mechanism to operate on NAT surfaces at these higher humidities as on ice surfaces, and the results reported here indicate that $\theta$ is only mildly dependent on $P_{\text{HCl}}$, and that $\gamma$ on ice is practically independent of $P_{\text{HCl}}$, that is, Reaction (1) is zero order with respect to HCl, again in disagreement with expectations based on the simple adsorption model. On the other hand, we do expect $\gamma$ to decrease as the HCl concentration becomes comparable to that of ClONO$_2$; in fact, with equivalent flows of HCl and ClONO$_2$, Oplinger et al. [21] report $\gamma$ for Reaction (1) on ice to be 0.14 and 0.26 at 200 and 180 K respectively. The value of $\gamma$ increases and levels off at higher HCl flow rates: with a 3-fold excess of HCl, $\gamma$ becomes 0.24 and 0.34 at 200 and 180 K respectively.

Another difficulty with the physical adsorption model is that for the $P_{\text{HCl}}$ values of interest $\theta$ should be much smaller than observed. If the HCl molecule were merely hydrogen-bonded to an active site on the ice surface, $\theta$ would be expected to have a value around $10^{-7}$ [23]. In fact, on that basis the experimental observation of a large affinity of HCl for the ice surface was initially interpreted as an artifact resulting from uptake on grain boundaries [23,24]. The results of our HCl uptake measurements on single ice crystals suspended in a gas flow clearly show that grain boundaries do not play a significant role in the process.

Besides indicating much larger $\theta$ values, the experimental evidence also points towards an ionic mechanism for the uptake, i.e., a process involving solvated HCl [9,18,19,25]; it is difficult to explain solvation unless the HCl molecule is surrounded by water molecules. In fact, there is evidence of surface disorder on ice caused by HCl uptake and solvation even at temperatures as low as 60 K [26]. The fast isotope exchange experiments further support the view involving the formation of aqueous-type ions, although in principle full ionization is not required to explain such a rapid exchange. Also, recent theoretical calculations are in better agreement with this ionic mechanism [27,28]. Note also that the large HCl uptake has been explained by considering the large flux of H$_2$O molecules in and out of the ice surface at the relevant temperatures [29], which might help to 'bury' the HCl molecules inside the ice matrix. We believe, however, that the time scale for incorporation of the HCl molecules into the ice is short enough not to be directly affected by the H$_2$O flux.

The results presented here support our view of a mechanism involving the formation of a liquid-like layer on the ice surface in the presence of HCl [9]. The observed zero-order behavior with respect to HCl for Reaction (1) can be explained by assuming that the ClONO$_2$ molecules, once taken up by the ice surface, readily find Cl$^-$ ions. The rate-determining step is the incorporation of ClONO$_2$ molecules into the condensed phase, and these molecules do not desorb or react with water [as in Reaction (2)] before reacting with the aqueous Cl$^-$ ions. This mechanism assumes significant mobility of the reactants close to the surface of the condensed phase, as is characteristic of liquid solutions. Phenomenologically, the simple physical adsorption model could be modified to accommodate the observed zero-order behavior with respect to HCl by assuming fast surface diffusion of the reactants; however, it is difficult to justify such fast diffusion at temperatures around 200 K if the reactants are bonded to specific active sites. Hence, a liquid-like surface layer appears more plausible.

5. Summary

The reaction ClONO$_2$ + HCl $\rightarrow$ Cl$_2$ + HNO$_3$ on ice surfaces has been studied to further elucidate the reaction mechanism. Relatively smooth and rough ice surfaces and single-crystal ice particles were employed to investigate the effect of the different surface morphologies on the reaction mechanism. Large HCl uptakes ($10^{13}$–$10^{14}$ molecule cm$^{-2}$) were
measured on all surfaces, indicating that surface morphology and grain boundary effects are not responsible for the incorporation of HCl on the ice surface. For HCl partial pressures in the range from $10^{-7}$ to $10^{-5}$ Torr, no significant correlation was observed between the rate constants and $P_{\text{HCl}}$. Such behavior is not consistent with the view that postulates physical adsorption of HCl on active sites on the ice surface. Instead, the results lend further support for a mechanism involving a liquid-like layer on the ice surface [9].

Acknowledgements

This research was funded by a grant from the National Science Foundation. D.C.L. acknowledges partial support from the NSF Training Grant in Chemistry of the Environment.

References