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Molecular Activation by Surface Coordination: New Model for HCl Reactivity on Water−Ice Polar Stratospheric Clouds

R. S. MacTaylor,[†] J. J. Gilligan, D. J. Moody, and A. W. Castleman, Jr.*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

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Results of studies of the uptake of HCl by the deuterated analogue of protonated water clusters are reported. The successive uptake of nHCl $n = 1-4$ is observed, $n = 2-4$ appearing in a stepwise manner with a ratio of 6:1 D_2O/HCl for the bimolecular reaction products. This primary uptake scheme is observed over a range of pressures (0.24−0.46 Torr) and temperatures (130−170 K). However, for increased flows of HCl, enhanced uptake is observed at a lower ratio of D_2O/HCl, a trend that is effected by an increased buffer gas pressure. Two distinctly dominant mechanisms of HCl uptake are operative: the bimolecular uptake of HCl in a 6:1 ratio with water and a subsequent association mechanism of HCl binding to water in a 3:1 ratio. The atmospheric implications are discussed along with a proposed molecular activation by surface coordination (MASC) model for HCl uptake and subsequent reactivity on polar stratospheric clouds.

1. Introduction

Atmospheric Significance. The annual depletion of the ozone layer in the polar stratosphere has received considerable scrutiny, particularly in the area of conversion chemistry involving chlorine.[1−6] Numerous studies have implicated polar stratospheric clouds (PSCs) as playing a fundamental role in the conversion of “reservoir” chlorine species, such as HCl and $ClONO_2$, into “active” forms of chlorine such as Cl_2.[2,6−13] PSCs consist of two main types: nitric acid trihydrate (NAT), type I; water−ice, type II. These clouds form in the relatively dry polar stratosphere, are of limited dimension (submicrometer particle sizes), and, evidence suggests,[2,14−22] may also contain one or more ion sites. The key reactions that both activate chlorine and convert odd nitrogen species into nitric acid are

$$ClONO_2(g) + H_2O(s) \rightarrow HOCl(g) + HNO_3(s) \qquad (1)$$

$$HOCl(g) + HCl(s) \rightarrow Cl_2(g) + H_2O(s) \qquad (2)$$

$$ClONO_2(g) + HCl(s) \rightarrow Cl_2(g) + HNO_3(s) \qquad (3)$$

$$N_2O_5(g) + HCl(s) \rightarrow ClNO_2(g) + HNO_3(s) \qquad (4)$$

$$N_2O_5(g) + H_2O(s) \rightarrow 2HNO_3(s) \qquad (5)$$

Reactions involving the reservoir species HCl are considered key in understanding these processes. It has been suggested that the likely first step in reactions 2−4 is accumulation of HCl by the PSCs followed by reaction with HOCl, $ClONO_2$, or N_2O_5.[8,14] With this in mind, many studies have been geared toward developing an understanding of the uptake of HCl by PSC mimics; these include investigations with ice surfaces and thin ice films,[2,3,8,14−16,18,23−30] gas-phase water clusters,[31] as well as computational studies[19−22,32−38] involving both surfaces and clusters.

HCl Uptake by Protonated Water Clusters. Previous work involving reactions of HCl with protonated water clusters was conducted by Schindler et al.[31] in a Fourier transform ion cyclotron resonance (FT-ICR) apparatus. Protonated water clusters are often employed in studies of atmospherically relevant systems. Water clusters, with or without the presence of an ion core, will approach mimicry of a bulk system as cluster size increases. Furthermore, unique behavior of ion-site components of a larger system can be studied in this manner. The water clusters in this experiment were found to undergo fragmentation by nonreactive collisions with HCl, along with an observed bimolecular reaction process. The reported reaction channels, based on mass-selected ion exposure to HCl included

$$H^+(H_2O)_n + HCl \rightarrow H^+(HCl)(H_2O)_{n-1} + H_2O \qquad n \geq 11 \quad (6)$$

$$H^+(H_2O)_n + HCl \rightarrow H^+(HCl)(H_2O)_{n-2} + 2H_2O \qquad n \geq 17 \quad (7)$$

$$H^+(HCl)(H_2O)_n + HCl \rightarrow H^+(HCl)_2(H_2O)_{n-1} + H_2O \qquad n \geq 13 \quad (8)$$

The work presented herein involves reactions of protonated water clusters with HCl, but there are several key differences in how the study is conducted and hence the results obtained and the insights derived. First of all, in the present investigation the reactions are run in a variable-temperature fast-flow reactor, where ions and neutrals are thermalized in a buffer gas at a well-defined temperature. This eliminates the fragmentation channel and allows observable reactions with a wide size range of water clusters; it also allows for investigations leading to a greater degree of uptake of HCl by the water clusters and a study of bimolecular (pressure-independent) versus (pressure-dependent) association reactions. Another noteworthy feature of the present study is the employment of heavy water D_2O in place of H_2O; this eliminates the mass degeneracy of $(H_2O)_3 = 36$ amu and the primary peak of HCl = 36 amu.

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* Present address: Department of Chemistry and Physics, Salem State College, Salem, MA.

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2. Experimental Section

The fast-flow reactor employed in the present study has been described in detail previously elsewhere.[39−41] A continuous flow of ~7000 sccm (standard cubic centimeters per minute) helium buffer gas is employed to transport the ions into the flow tube, which is maintained at a selected monitored pressure of a few tenths of a Torr. The helium also serves to thermalize the ions. Temperatures ranging from room temperature to −140 °C can be achieved and maintained through the employment of regulated-flow liquid nitrogen cooling. The flow tube and helium precooling vessel are enclosed in an evacuated chamber that serves as insulation. The pressure at a fixed buffer gas flow can be altered by throttling the gate valve leading to the high-volume roots blower. A neutral reactant gas is introduced approximately 30 cm downstream of the ion source and is allowed to react for a few milliseconds before a small fraction of the flow mixture is sampled through an orifice. The actual reaction time is determined by an electric pulsing technique that yields a direct measure of the ion residence time in the reaction zone of the flow tube under each specific reaction condition employed in a given experiment. Reactant ion intensity is monitored by mass selection with a quadrupole mass spectrometer and detection with a channeltron electron multiplier (CEM). The average pressure within the reaction region of the flow tube is monitored halfway between the reactant gas inlet and the sampling orifice. The flow rate of reactant gas is regulated by a 1−200 sccm range flow controller. The desired flows of typically less than 2 sccm of reactant are achieved by making a dilution of reactant neutral in helium, within a ballast tank. Lecture bottles of 99.9% chemically pure HCl were obtained from Matheson Gas Products, East Rutherford, NJ.

3. Results

The motivation for collecting the data presented in Figures 1−4 and summarized in Figure 5 was the observation of a change in distribution of the secondary reaction products when running the experiments at higher pressures. All of these data were collected with the flow tube temperature maintained at 153 K, which is a lower temperature than the relevant polar stratospheric temperatures of 185−225 K. To generate and maintain water clusters of a sufficient size distribution to allow observation of the complex chemistry described herein, it was necessary to conduct these experiments at 153 K. Many of the experiments reported in the literature designed to gain insight into PSC-mediated processes also report results in this temperature range,[15,16,27−29,31] so it is also convenient for comparison purposes. A series of experiments were then conducted in order to assess the pressure-independent versus pressure-dependent formation processes of the secondary reaction products. The key aspect of these experiments is taking advantage of the fact that observation of product ion formation in a fast-flow reactor over a range of pressures can yield data depicting not only the chemical reaction in terms of reactants and products but also insight into the mechanism by which the products are formed, specifically, whether the transformation process is bimolecular or termolecular. The gate valve leading to the roots blower was throttled such that pressures of 0.24, 0.30, 0.39, and 0.46 Torr were achieved for these experiments. All data were collected with the flow tube maintained at a temperature of 153 K (−120 °C) (the temperature at which the largest distribution of water clusters could be generated). HCl was prepared over a range of dilutions and the flow controller set such that directly comparable concentrations of HCl could be injected into the flow tube at each pressure. The ion residence time in the reaction region of the flow tube changes with different pressures (range 8.36−14.22 ms), and this factor is accounted for in the *y*-axis values in terms of concentration of HCl [molecules per cm^3], accounting for each measured value of ion residence time presented as [HCl]*s*, a measure of the exposure to the reactant molecule. Plotted in each of the figures is the exposure of HCl which corresponds to the initial appearance of the product ion.

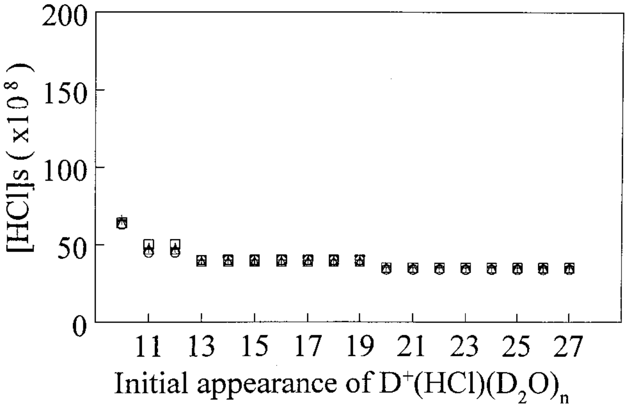

Figure 1. Reactive uptake of the first HCl into the cluster, from product ion appearance plotted versus exposure to HCl for a variety of pressures at −120 °C: (+) 0.24 Torr; (△) 0.30 Torr; (○) 0.39 Torr; (□) 0.46 Torr. Units of ordinate are molecules cm^{-3} s^{-1}.

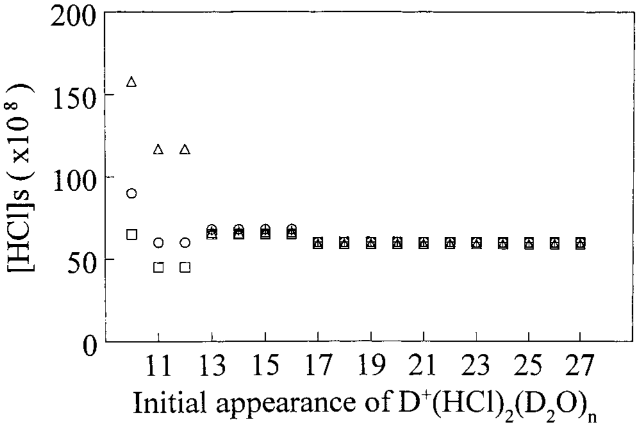

Figure 2. Reactive vs associative uptake of a second HCl into the cluster, from product ion appearance plotted versus exposure to HCl for a variety of pressures at −120 °C: (+) 0.24 Torr; (△) 0.30 Torr; (○) 0.39 Torr; (□) 0.46 Torr. Units of ordinate are molecules cm^{-3} s^{-1}.

By way of example, the product ion peak $D^+(HCl)(D_2O)_{10}$ (mass 238 amu) in Figure 1 appears at an injected flow of HCl corresponding to [HCl]*s* ≥ (65 ± 2) × 10^8 molecules cm^{-3} s^{-1} at all pressures. For the primary reaction products (depicted in Figure 1) the *y*-axis value correlates to the bimolecular rate coefficient of the corresponding reactant ion. All subsequent (nonprimary) reaction products, presented in Figures 2−4, do not correlate to rate constants, since the “reactant” in each case is produced in the course of the experiment. In Figure 2, the association of a second HCl onto the cluster $D^+(HCl)(D_2O)_{10}$ (for example) is described; at 0.24 Torr no product ion corresponding to $D^+(HCl)_2(D_2O)_{10}$ (mass 274 amu) is observed over the range of HCl concentrations injected ((5−200) × 10^8 molecules cm^{-3} s^{-1}). At 0.30 Torr the product ion appears at [HCl]*s* ≥ 158 × 10^8, at 0.39 Torr the product ion appears at [HCl]*s* ≥ 90 × 10^8, and finally, at 0.46 Torr at [HCl]*s* ≥ 65 × 10^8. These results are interpreted simply as indicating that a

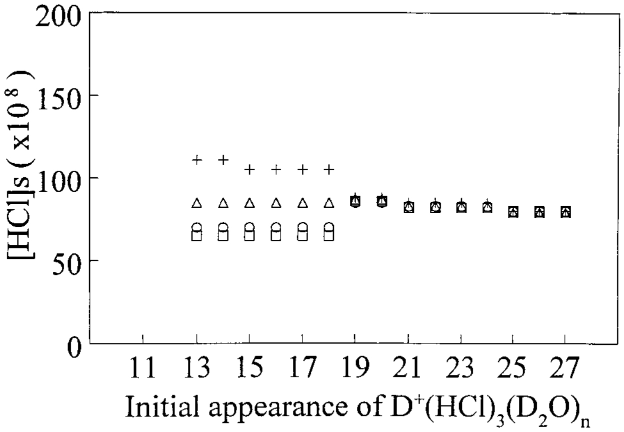

Figure 3. Reactive vs associative uptake of a third HCl into the cluster, from product ion appearance plotted versus exposure to HCl for a variety of pressures at −120 °C: (+) 0.24 Torr; (△) 0.30 Torr; (○) 0.39 Torr; (□) 0.46 Torr. Units of ordinate are molecules cm^{-3} s^{-1}.

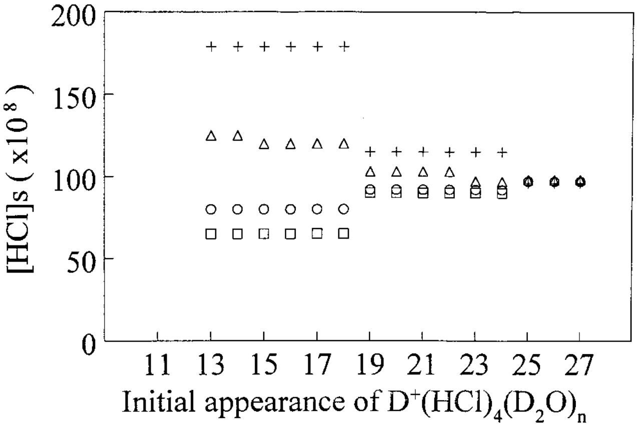

Figure 4. Reactive vs associative uptake of a fourth HCl into the cluster, from product ion appearance plotted versus exposure to HCl for a variety of pressures at −120 °C: (+) 0.24 Torr; (△) 0.30 Torr; (○) 0.39 Torr; (□) 0.46 Torr. Units of ordinate are molecules cm^{-3} s^{-1}.

pressure-dependent formation processis operative for the reaction

$$D^+(HCl)(D_2O)_{10} + HCl \rightarrow D^+(HCl)_2(D_2O)_{10} \qquad (9)$$

The termolecular uptake of HCl, as opposed to the bimolecular processes depicted in reactions 6−8, is distinguishable by the pressure dependence of the product appearance.

$$D^+(HCl)_y(D_2O)_n + HCl \rightarrow [D^+(HCl)_y(D_2O)_n{\cdot}HCl]^* + He \rightarrow D^+(HCl)_y(D_2O)_n{\cdot}HCl \qquad (10)$$

Reaction 10 involves the formation of a collisional complex that is subsequently stabilized by collisions with the buffer gas; reactions of this type will display a varying degree of completion based on the concentration of buffer gas in the flow tube (pressure). Uptake of a third or fourth HCl onto the $D^+(HCl)_2(D_2O)_{10}$ cluster would be depicted in Figures 3 and 4; however, products corresponding to $D^+(HCl)_3(D_2O)_{10}$ and $D^+(HCl)_4(D_2O)_{10}$ are not observed. Similarly, in Figure 2, terminal HCl uptake by pressure-dependent processes are indicated for formation of $D^+(HCl)_2(D_2O)_{11}$ and $D^+(HCl)_2(D_2O)_{12}$. However, beginning with the formation of $D^+(HCl)_2(D_2O)_{13}$, a predominantly bimolecular process is found, indicated by the appearance of this product ion at $[HCl]s \geq (61 \pm 2) \times 10^8$ molecules cm^{-3} s^{-1} over the full range of pressures studied. All data were collected in this manner, leading to an identification of either a dominant bimolecular or termolecular formation processes for each product ion observed. The findings are summarized in Figure 5.

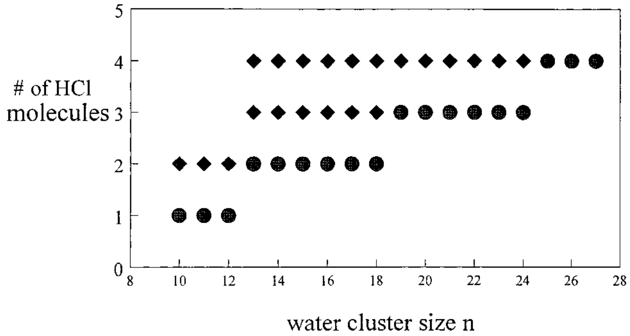

Figure 5. Uptake of HCl−cluster size dependence of $D^+(HCl)_y(D_2O)_n$: (●) bimolecular reaction; (◆) termolecular association. Successive uptake of $(HCl)_n$, $n = 1-4$, is observed, $n = 2-4$ appearing in a stepwise manner with a ratio 6:1 D_2O/HCl for the bimolecular reaction products. The association product HCl appears exclusively in a maximum ratio of 1:1 with dissolved HCl.

Beyond simply classifying the reactions as pressure-independent or pressure-dependent, there are a few other features of the data presented in Figures 1−4 that should be noted. First of all, simply stated, uptake of one HCl through a bimolecular reaction must precede uptake of a second by either a bimolecular or termolecular reaction; uptake of two HCls must precede uptake of a third, etc. This simple statement is crucial to the interpretations that follow. Note that under the present experimental conditions there is no association channel for uptake of a primary HCl by any size water cluster; only a pressure-independent bimolecular reaction is operative. All pressure-independent, bimolecular reactions are viewed as indicative of a “dissolving” of HCl into the water cluster. Subsequent uptake evidence presented herein indicates that an HCl must first be dissolved into the cluster before another HCl can “stick” to the cluster. Thus, for “bare” protonated water clusters the only accessible uptake mechanism is a bimolecular reaction involving ionic dissolution of HCl accommodated by “boiling off” one or more water molecules, as described here and previously by the FT-ICR study.

The next feature to be considered is the association channel. The prerequisite for a pressure-dependent process (“sticking”) to occur is that there must first be a dissolved HCl incorporated into the cluster. The interaction between this associated molecular HCl then must be connected to the presence of a dissolved chloride ion. In fact, the data indicate that the relationship is in a one-to-one ratio with dissolved chloride ions. Thus, the maximum uptake for clusters $D^+(HCl)(D_2O)_{10-12}$ is a second HCl but not a third or fourth. On the other hand, the maximum uptake beginning with $D^+(HCl)_2(D_2O)_{13}$ includes incorporation by a termolecular reaction of a third and fourth HCl, achieving (with the fourth) a one-to-one ratio corresponding to two dissolved and two “adsorbed” HCl molecules in the molecular state. Also noteworthy in this regard is the association product appearance for uptake of a third (“adsorbed”) HCl, resulting in $D^+(HCl)_3(D_2O)_{13-18}$ in Figure 3 versus the appearance of products $D^+(HCl)_4(D_2O)_{13-18}$ depicted in Figure 4. There is apparently a “faster” association process for the third HCl; this is interpreted as there being two available dissolved chloride ion “sites” at which the third HCl can associate. The appearance of three “steps” for the uptake of a fourth HCl, shown in Figure 4, is attributed to the following: (1) for product cluster sizes $D^+(HCl)_4(D_2O)_{13-18}$, the adsorption of a second

HCl onto $D^+(HCl)_2(D_2O)_{13-18}$; (2) for product cluster sizes $D^+(HCl)_4(D_2O)_{19-24}$, the first adsorption of HCl onto cluster sizes $D^+(HCl)_3(D_2O)_{19-24}$; (3) for product cluster sizes $D^+(HCl)_4(D_2O)_{25-27}$ the bimolecular uptake process of dissolution of a fourth HCl into the water cluster. The enhanced association for the fourth HCl for step 2 clusters over step 1 clusters is considered indicative of the availability of three sites for HCl association rather than one.

Finally, one should note that in Figures 2–4, where there is a transition from an association uptake mechanism to a bimolecular reaction mechanism, the bimolecular reaction products, when compared to the association products at higher pressures, appear at higher exposures of HCl. This is likely due to the "complicated" nature of the bimolecular reaction (accommodation and dissolution of HCl followed by "boiling-off" water molecules) versus a simple association mechanism.

Bimolecular Uptake. There are clearly two types of HCl uptake by protonated water clusters; one a pressure-independent bimolecular process and the other a pressure-dependent termolecular (adsorption) process. The bimolecular process has been described previously for smaller clusters as in reactions 6–8. The present study extends these results to include the bimolecular uptake of a third and fourth HCl into the cluster. This type of HCl incorporation has been described as ionic "dissolution" of HCl into the cluster and is in good agreement with previous experimental work[15,16,18,28] and a variety of theoretical predictions.[19–22,34] The primary uptake of a single HCl into a bare water cluster requires a hydronium ion with nine water molecules (product ion); this has been observed previously by Schindler et al.,[31] and it is apparent that the minimum cluster size necessary for bimolecular incorporation of HCl is $D^+(D_2O)_{11}$.

The striking feature of this uptake process is the pattern found in our study that reveals itself as the second, third, and fourth HCl dissolve into the cluster. One should note that the species "HCl hexahydrate" has been reported previously on ice films designed to mimic polar stratospheric cloud surfaces.[16,24,26,27,29] Our study reveals an important finding: a hydronium ion with 12 water molecules is required for 2 HCl dissolution, 18 waters are required for 3 dissolved HCl molecules, and 24 waters are required for 4 dissolved HCl molecules. This pattern can be interpreted as 2, 3, and 4 "HCl hexahydrates" coordinated to a hydronium ion core.

Termolecular Uptake. The association process of HCl uptake also follows a very distinct pattern. First of all, it should be clearly noted that no association reaction of HCl onto any bare water cluster is observed under any of the experimental conditions employed in the present study. This is revealed by the fact that no pressure-dependent HCl uptake mechanism is observed below $n = 10$, which is actually a bimolecular uptake step. A pressure-dependent (association) uptake of a second HCl is only observed on those clusters that already contain one dissolved HCl but are below the minimum size needed to "dissolve" a second HCl molecule, as evidenced by a bimolecular reaction channel. This remarkable component of the association process is further revealed in the association of a third HCl; here, association does not commence simply with any cluster containing two HCls but begins with the first cluster that has dissolved two HCls. The association of a fourth HCl also first begins with the cluster that has dissolved two HCl molecules.

4. Discussion

These results should be considered in the larger context of the numerous studies that have been directed toward gaining a more complete picture of the uptake and subsequent reactivity of HCl on PSC surfaces. The aforementioned PSC-mimic work provides information on the observed uptake of HCl by ice (water–ice and NAT) surfaces. Studies have indicated that initial coverage of a water–ice surface takes place by formation of the hexahydrate of HCl and that increased exposure to HCl results in enhanced uptake in such a ratio as to be considered HCl trihydrate coverage.[16,27,29] Our results are consistent with these observations. There is compelling experimental evidence that adsorbed HCl (DCl) dissociates ionically on ice films.[15,16,18,28] The bimolecular reactions reported here and by Schindler et al.[31] are consistent with ionic dissociation, whereby the enthalpy of dissolution is accommodated by "boiling off" one or more water molecules in the ion cluster. This is also supported by computational studies that provide thermodynamic and/or mechanistic evidence suggesting the likelihood of ionic dissociation.[19,20,22,34] The reactivity of $HCl-ClONO_2$ is reported on water–ice surfaces[7–10] and is observed to be quite efficient, which could be interpreted as indicative of an ion–molecule reaction process. Studies of the uptake of HCl molecules onto quiescent liquid surfaces provide one type of middle ground between the bulk ice and water cluster regimes and have yielded remarkable results.[10,11] We believe the results of the work presented herein serve to further bridge the gap between the bulk/surface studies and gas-phase ion–molecule results. First, however, some details of selected previous studies should be considered.

Temperature-Programmed Desorption Results. Graham and Roberts report on temperature-programmed desorption (TPD) of HCl from ultrathin water films.[16] Their assignment of two distinct states of HCl, designated α- and *β*-HCl was supported by H–D exchange studies and desorption at 140 and 180 K, respectively. Initial surface coverage by *β*-HCl, believed to be HCl hexahydrate, was found to freely isotope-exchange with ice-d_2, suggesting ionic dissociation. A low isotopic exchange rate by α-HCl was evidence that this HCl remained molecular, and the activation energy for desorption of 33 ± 5 kJ/mol was considered by the authors as suggestive of hydrogen bonding to the surface.

The α-HCl is depicted as hydrogen-bonded to the surface of the ice either by an (ice surface–O)···H–Cl bonding scheme or by an (ice surface–H)···Cl–H scheme. They do note the disparity between their measured desorption energy and Kroes and Clary's[32] computed value for HCl hydrogen-bonded to water molecules at an ice surface of 19 kJ/mol. They conclude that molecular HCl hydrogen-bonded to the ice surface should not be very reactive and would therefore be of limited atmospheric significance.

Laser-Induced Thermal Desorption Results. Foster et al.[29] present results of a laser-induced thermal desorption (LITD) study of HCl deposited onto ice films. At temperatures comparable to the TPD study and the ion-cluster study reported herein (below 148 K), the LITD signals indicate HCl trihydrate coverage. The trihydrate is characterized by optical interference measurements of the real refractive index and by comparing this experimental value with a calculated refractive index for HCl trihydrate (values derived from those for 40 wt % HCl solution).

Proposed Molecular Activation by Surface Coordination (MASC) Model. We propose a molecular activation by surface coordination (MASC) model for HCl surface reactions on PSCs depicted in Figure 6. This model accounts for the trend in HCl uptake observed here and elsewhere as an initial dissolving of HCl into a PSC followed by subsequent coordination of HCl

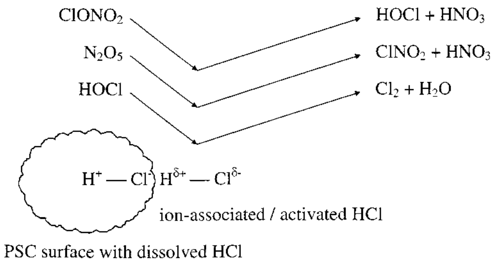

Figure 6. Simplified representation of the proposed mechanism for HCl reaction on PSC surfaces.

onto the PSC surface. We suggest that the fast reaction rates necessary to explain the high levels of ozone depletion observed can be accounted for by having numerous ion-associated/activated HCls on the surface of PSCs. HCl on the surface of the PSC would be coordinated on the surface by the dissolved acid and also chemically activated by an ion-induced dipole.

The MASC model depicts chloride-ion-associated molecular HCl; the existence of this type of complex is not unprecedented. In a recent ab initio study of aqueous hydrochloric acid, with the stated objective "to gain some insight into the possible microscopic mechanisms that might limit acid solubility in water" Laasonen and Klein[43] report, for a typical laboratory strength solution of 3.6:1 H_2O/HCl ratios, the presence of a significant abundance of a hydrogen-bonded species $Cl-H\cdots Cl^-$. Perhaps there is substantial atmospheric significance to these findings. The uptake evidence presented herein is clearly indicative of the formation of ion-associated molecular HCl species. The high interaction energy reported in the TPD experiment might be accounted for by this ion−dipole complex as well.

The MASC model suggests a chemically activated ion-associated HCl; this type of chemical reactivity is not unprecedented. Rowe et al. reported a new class of chemical reactions in which a neutral molecule clustered to an ion reacts with a gas-phase neutral molecule.[44] Rate enhancement of several orders of magnitude was observed for several ion-associated neutral reactions over their neutral−neutral counterparts. Viggiano et al. experimentally expanded upon these findings and also conducted calculations providing mechanistic insight into the phenomenon.[45] Van Doren et al. specifically observed the reaction of ion-associated HCl with chlorine nitrate.[46]

$$NO_3^-\cdot HCl + ClONO_2 \rightarrow NO_3^-\cdot HNO_3 + Cl_2 \qquad (11)$$

$$k = 1.8 \times 10^{-9}\ \mathrm{cm^3\ s^{-1}}\ \text{at } 233\ \mathrm{K}$$

Also noteworthy is the reactivity of HCl dimer, over HCl monomer, reported for reaction with atomic oxygen.[47] A charge distribution effect is cited for 3 orders of magnitude rate enhancement.

The main obstacle, then, to this model cleanly explaining the experimental evidence reported in the studies discussed (though not necessarily the conclusions reached in those studies) is accounting for the surface coverage in the LITD experiment. The results presented in the LITD study were interpreted as contradicting the assignment of the surface coverage in the TPD study; the refractive index measured was exclusively attributed to HCl trihydrate. For the LITD results to be viewed as supportive evidence for the MASC model, it would be necessary that the refractive index of the dissolved ion-associated $H^+(H_2O)_6Cl^-\cdots HCl$ species coincide with that calculated for the HCl trihydrate. However, perhaps this is not much of an obstacle at all. The calculated refractive index for HCl trihydrate is based exclusively on values (tabulated or extrapolated) for 40 wt % HCl solution.[29] The reason for using 40 wt % HCl solution for molar refractivity and density values is that it represents a 3:1 ratio of H_2O to HCl. Implied therein is the assumption that 40 wt % HCl is composed of uniformly dispersed HCl trihydrates. The evidence presented by Laasonen and Klein,[43] however, strongly indicates that concentrated HCl solutions contain the very ion-associated species ($Cl^-\cdots HCl$) we describe. Therefore, the physical properties used to calculate the refractive index for HCl trihydrate may, in reality, be those of a $Cl^-\cdots HCl$ containing solution.

5. Conclusions

It is apparent that two distinct mechanisms of HCl uptake are operative: the bimolecular dissolution of HCl and subsequent association of HCl in a one-to-one ratio with dissolved HCl. The fact that HCl does not associate onto bare water clusters prompts the conclusion that dissolved HCl plays a role in the coordination (adsorption) of associated HCl. One could easily take this conclusion one step further to declare that it is the dissolved Cl^- that is involved, since no association product is observed on protonated water clusters in the absence of dissolved HCl. There has been a multipronged research effort aimed at gaining a greater understanding of the nature and reactivity of PSCs. The results presented herein are in accord with the ice-film work previously conducted, and it would appear that the uptake trends extend congruously from the ion cluster regime to the bulk surface realm. In fact, when consideration of the molecular dynamics simulation results is included, the data would indicate gas-phase (ion cluster), liquid-phase (concentrated acid solution), and solid-phase (ice film) consistency in regard to the nature of the HCl−water system. A model, molecular activation by surface coordination (MASC), which serves to account for the trends in HCl uptake observed and also to provide some mechanistic explanation for high reaction efficiencies, is proposed and discussed.

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