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Acid Dissolution by Aqueous Surfaces and Ice: Insights from a Study of Water Cluster Ions[†]

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Reaction mechanisms of protonated water clusters [$D_3O^+(D_2O)_n$, $n = 4-30$] with hydrogen bromide (HBr) and nitric acid (DNO_3) were elucidated using a fast-flow reactor operated at thermal conditions over a temperature range of 143−173 K. The dissolution of these acid species is found to occur at critical cluster sizes as reported herein. Rate coefficients of the thermal energy reactions of DNO_3 and $D_3O^+(D_2O)_n$ ($n = 6-22$) were investigated and found to display a dependence on cluster size. We also report findings on the minimum cluster size necessary for the first uptake of nitric acid and hydrogen chloride by hydrated sodium and potassium cluster ions and compare the values with those for protonated water clusters. The present work is considered along with previous literature results obtained using surface sensitive and mass spectrometric techniques, with the objective of providing complementary information about the uptake of acid molecules on ice/aqueous surfaces.

Introduction

Heterogeneous catalysis of stratospheric reservoir species such as chlorine nitrate and hydrogen chloride into the more active forms of chlorine on the surface of ice crystals plays an important role in the annual depletion of ozone over the Antarctic.[1] The following reaction mechanism has been proposed to occur on the surfaces of polar stratospheric clouds (PSCs):

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \tag{1}$$

There is growing support that the first step in reaction 1 is the ionization of hydrogen chloride (HCl) through a dissolution process at the surface of PSCs,[2,3] a process that could potentially contribute significantly to the observed reactivity of reservoir species on PSCs.[4] Since reactions on the surfaces of PSCs are likely to be localized processes, small segments of the local hydrogen bonding network can be used to mimic the catalytic properties of PSC surfaces.[5−7] We have studied numerous cluster reactions which have direct applications to atmospheric chemistry and have recently highlighted the findings in a comprehensive review article.[8] A molecular level understanding of the prevailing mechanisms on PSCs requires detailed knowledge of the reaction mechanisms of acid dissolution. An important factor to be determined is the minimum number of water molecules necessary to initiate the process of ion-pair formation in water clusters. Our approach for reaching this goal is to evaluate the uptake of acid molecules with various cluster ions. These ions are comprised of the hydronium ion and alkali metal ions (Na, K). Through a comparison of the findings of various cluster ions, this study enables us to ascertain the conditions whereby an ion is acting largely as a spectator and is not significantly influencing the observed points of acid uptake.

There has been a growing interest in the behavior and uptake of other acid molecules on liquid and ice surfaces, including nitric acid and hydrogen bromide.[9−13] Nitric acid has an important role in the atmosphere as a temporary reservoir for both OH and NO_2 species involved in reactions relevant to the ozone budget in the stratosphere.[14−16] HNO_3 is the major component of the more prevalent type I polar stratospheric clouds.[17] There have been very few reports regarding the heterogeneous reactivity of bromine species on ice surfaces because these species are less abundant and have shorter lifetimes in the atmosphere. However, current research suggests that reactions of halogen containing species on ice surfaces is rapid.[18−22]

In earlier studies by the Bondybey research group using Fourier transform cyclotron resonance apparatus, protonated water clusters with HCl were investigated and the dissolution of one and two HCl was observed.[23] A detailed description of the further uptakes of HCl was left unanswered. The reaction kinetics and mechanisms of protonated water clusters and HCl have been investigated in our laboratory using a variable temperature fast-flow reactor.[24,25] Two distinctly dominant mechanisms of HCl uptake are operative: the bimolecular uptake of HCl in a 1:6 ratio with water and a subsequent association or adsorption mechanism of HCl binding to water in a 1:3 ratio. The critical number of water molecules required for the dissolution of one, two, three, and four HCl molecules by protonated water clusters was determined by the fast-flow reactor experiments as displayed in column 4 of Table 1. In Table 1, *m* is the number water molecules required for the dissolution of an acid species, and *n* is the number of acid molecules that dissolve. The association of HCl to protonated water clusters appears in a ratio of 1:1 with dissolved HCl. Molecular HCl was found not to associate onto bare protonated water clusters under any conditions of pressure, temperature, or concentration accessible in our experiments, which prompted the conclusion that dissolved HCl plays a role in the association of subsequent HCl uptake beyond the first. Reactions of other

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TABLE 1: Size Dependence for Acid−Molecule Dissolution in Protonated Water Clusters

$$A_3O + (A_2O)_{m+k} + X \rightarrow A_3O + (A_2O)_m(\mathbf{X})_n + kA_2O$$
$$(A = H \text{ or } D)$$

	uptake values (m)		
n	X = DNO_3[a]	X = HBr[b]	X = HCl[c]
1	4	7	9
2	8	11	12
3	11	15	18
4	15	19	24

[a] (1) This work. (2) Reference 6. [b] This work. [c] (1) Reference 25. (2) Reference 23.

acid species (HNO_3 and HBr) are investigated in this paper to elucidate the nature of the uptake of HCl by protonated water clusters at these distinct cluster sizes.

To determine the effect of the hydronium ion on the degree of hydration required for ion-pair formation in water cluster ions, reactions of hydrated alkali metal ions (sodium and potassium) with nitric acid and hydrogen chloride were studied. The hydronium ion−water interaction is stronger than the corresponding alkali metal ion−water interactions,[26] which enables an examination of the ion core effect on the acid uptake process and a quantitative description of the influence of the water network on the acid dissociation process.

Experimental Section

Experiments are conducted in a fast-flow reactor affixed with a high-pressure ion source. The details of this apparatus and experimental procedure have been described in previous publications,[27−30] and only a brief outline is presented here. In the ion source, protonated water clusters are generated by a discharge ionization of a H_2O/helium mixture. Alkali metal ions are generated by resistively heating a platinum filament (32 gauge) coated with a 1:2:1 MNO_3:SiO_2:Al_2O_3 mixture, M = Na, K[31]. Water vapor was introduced into the source to generate $M^+(H_2O)_n$ clusters. In generating $M^+(H_2O)_n$ clusters, enough water vapor was added to the source to effectively deplete the excited alkali metal species.[32] Employing D_2O (20 amu) as a source gas is critical in the determination of reaction mechanisms of different acid species with the water cluster ions. DNO_3 was also used to avoid mass degeneracies (the mass of two HNO_3 is equal to that of seven H_2O). Water cluster ions are carried into the flow tube by a continuous flow of 7000 standard cubic centimeters per minute of helium buffer gas. The pressure of the flow-tube and reaction region is maintained in the range of 0.25−0.5 Torr by throttling a gate value that is located between the flow tube and a roots vacuum pump. The pressure was controlled with an accuracy of ±0.01 Torr. A predetermined concentration of reactant gas (acid species) is introduced approximately 30 cm downstream of the source by a heated stainless steel reactant gas inlet.[33] Mass spectra are recorded for each addition of neutral reactant gas for a precise amount of time to ensure an effective sampling of reactant and product ions. The water cluster ions and neutral reactant gas are allowed to react for several milliseconds before a small fraction of reactant and product ions are sampled through an orifice, scanned by a quadrupole mass spectrometer, and detected by a channeltron electron multiplier. The distance between the reactant gas inlet and sampling orifice is ~71 cm. The flow-tube and helium buffer gas temperatures ranged from 143 to 173 K. The flow-tube and helium buffer gas temperature was controlled with an accuracy of ±1 K.

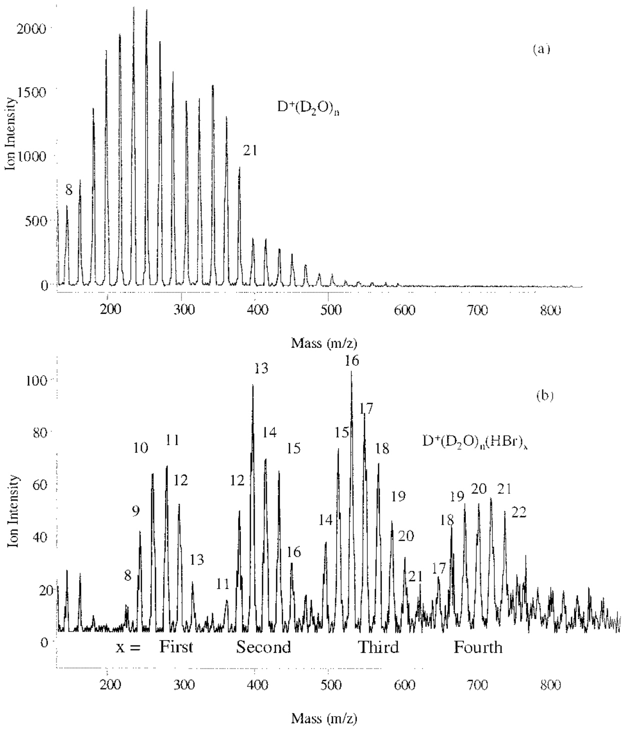

Figure 1. Mass spectra of $D^+(D_2O)_n$ obtained before (a) and after (b) the addition of 5.74 × 10^{12} cm^{-3} HBr: pressure, 0.3 Torr; temperature, 146 K.

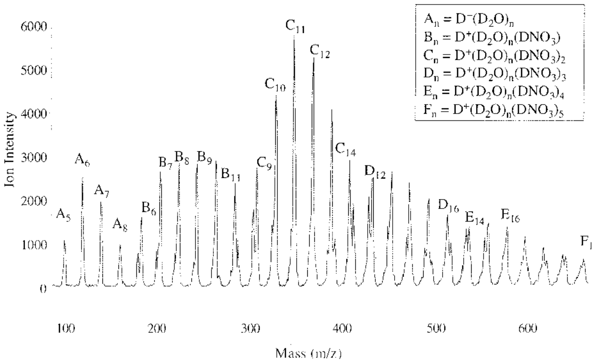

Figure 2. Reactions of $D^+(D_2O)_n$ with 1.39 × 10^{12} cm^{-3} DNO_3 at T = 158 K and P = 0.36 Torr.

Results

Figures 1 and 2 present mass spectra representative of the uptakes of HBr and DNO_3 by protonated water clusters, respectively. Figure 1 displays mass spectra taken before and after the addition of 5.74 × 10^{12} cm^{-3} HBr. The addition of HBr at this concentration and conditions was required to obtain the distribution of reaction product ions $[D^+(D_2O)_n(HBr)_{1-4}]$ displayed in Figure 1b. In typical experiments, HBr was added to the flow tube in small increments from lower concentrations (~1 × 10^{11} cm^{-3}) to larger concentrations(~1 × 10^{13} cm^{-3}) in a sequence of mass spectra. As the concentration of HBr increased, the first uptake would occur followed by the second uptake and onward. Figure 2 shows a mass spectrum taken after the addition of 1.39 × 10^{12} cm^{-3} DNO_3 to a similar distribution of protonated water cluster shown in Figure 1a. The uptake of one to five nitric acid species by the protonated water clusters is evident.

Monitoring the formation of the product cluster ions as a function of pressure, concentration of reactant gas, and ion

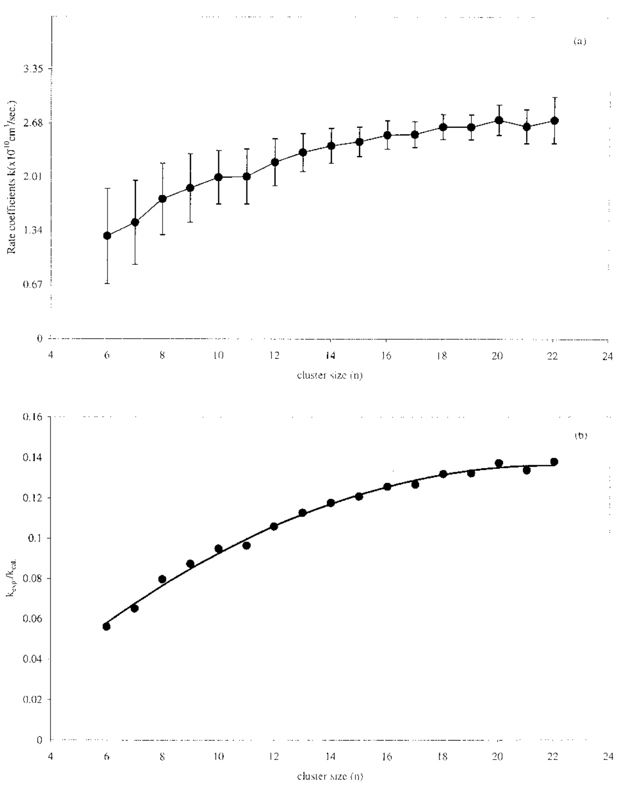

Figure 3. (a) Cluster size dependence of the rate coefficients for the reactions of DNO_3 and $D^+(D_2O)_n$ ($n = 6-22$) at $T = 156$ K and $P = 0.3$ Torr. (b) The ratio of experimental rate coefficient to the calculated collisional rate coefficient[45,46] for the reactions of DNO_3 and $D^+(D_2O)_n$ ($n = 6-22$) at $T = 156$ K and $P = 0.3$ Torr.

residence time enabled the determination of the points of dissolution of the various acid molecules.[25] The points of dissolution of these acid species do not display any dependence on temperature over the range studied. However, the rate of initial uptake of these acid species does have a temperature dependence[24] as expected. The points of dissolution are presented in Table 1. In the hydrogen bromide system, a minimum of 7 water molecules bound to a hydronium ion is required for the dissolution of one HBr, 11 for two, 15 for three, and 19 for four HBr. In another similar study, reactions of nitric acid and protonated water clusters were investigated to determine the rate coefficients and to evaluate the points of dissolution of nitric acid within the water clusters. In the nitric acid system, a minimum of 4 water molecules bound to a hydronium ion was required for the dissolution of one DNO_3, 8 for two, 11 for three, and 15 for four DNO_3. The initial points of dissolution (the minimum water cluster size) were found to be pressure independent, but dependent on the solvation size of the water cluster ions. The partial pressure of the acid species in the flow tube was found to influence the distribution and amount of acid uptake by the water clusters. Rate coefficients are determined in the usual manner by measuring the decrease in reactant ion intensity as a function of the concentration of the reactant gas and by measuring the ion residence time.[34] Reactant ions are not in equilibrium with product ions in this study. Reaction conditions normally required for equilibrium studies were not accessible. The bimolecular rate coefficients, at $T = 156$ K, between protonated water cluster and nitric acid were found to increase as cluster size increased. See Figure 3.

The critical size necessary for the first uptake of HCl and HNO_3 by hydrated alkali metal ions was also investigated. For hydrated potassium and sodium ions, uptake with these acid species was found to occur at the same cluster sizes for protonated water cluster (9 waters for HCl, and 4 waters for HNO_3). See Table 2. Figure 4 displays mass spectra of $Na^+(H_2O)_n$ before and after the addition of HNO_3. The addition of HNO_3 to the flow tube was observed to deplete sodium ion water clusters starting at $n = 5$, which led to the formation of $Na^+(H_2O)_{n\geq 4}(HNO_3)$ as is evident in Figure 4.

TABLE 2: Reactions of Cationic Water Clusters

$$A^+(H_2O)_{k+m} + X \rightarrow A^+(H_2O)_m(\mathbf{X}) + kH_2O$$

	uptake values (m)	
A	X = HNO_3[a]	X = HCl[a]
H_3O	4	9
K	4	9
Na	4	9

[a] This work.

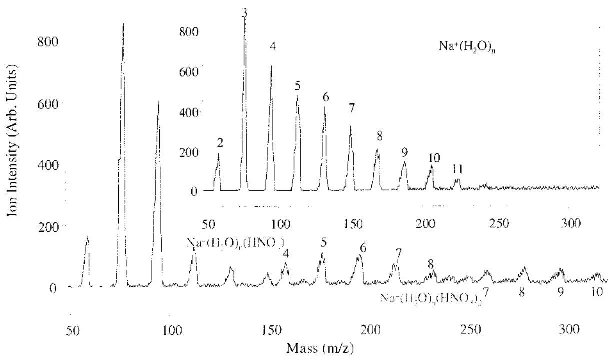

Figure 4. Mass spectra of $Na^+(H_2O)_n$ before (a) and after (b) the addition of 1.23×10^{12} cm^{-3} HNO_3 at $T = 172$ K and $P = 0.3$ Torr.

Discussion

The present study comprises a comprehensive investigation of the critical sizes of water cluster ions required for the dissolution of several acid molecules. It is well-recognized that acid species "dissolve" at particular sizes of water clusters. Kay et al. formed $D_3O^+(DNO_3)(D_2O)_n$ ($n = 1-12$) by ionizing *neutral* clusters of nitric acid and water in molecular beam.[35] A minimum in the cluster size distribution at $n = 4$ was reported. This abrupt minimum at $n = 4$ was explained as the formation of solvated ion pairs. In studies conducted in this work and discussed in a previous publication,[6] the first point of dissolution of nitric acid by protonated water clusters occurs at $n = 4$. In a recent study, the presence of a solvated chloride ion within the water cluster was found to enhance the reactivity of protonated water clusters to $ClONO_2$.[36] In a related study, large protonated water clusters, $H^+(H_2O)_n$, $n = 1-60$, were generated and their reaction kinetics with CH_3CN, CH_3COCH_3, CH_3COOCH_3, and CH_3OH were investigated under thermal conditions in a fast-flow reactor.[37,38] Reactions between protonated water clusters and these organic reactant gases were found to occur at all cluster sizes of protonated water clusters. This is in stark contrast to reactions between protonated water cluster and acid species. Reactions of protonated water clusters with the organic ligands at thermal conditions underwent several types of reaction mechanisms such as a proton transfer, switching, and an association reaction. For reactions to occur between acid species and water cluster ions, the enthalpy of reaction must be favorable for water ligands of the cluster ion to switch with the acid species. Due to the comparatively strong bonds of the water network and the fact that the acid species do not associate to

TABLE 3: Association Energies[26] of Reactions of $M^+(H_2O)_{n-1} + H_2O \rightarrow M^+(H_2O)_n$

				$-\Delta H^\circ_{n-1,n}$ (kcal/mol)			
ion	1	2	3	4	5	6	7
H_3O^+	36.0	22.3	17.0	15.3	13.0	11.7	10.3
Na^+	24.0	19.8	15.8	13.8	12.3	10.7	
K^+	17.9	16.1	13.2	11.8	10.7	10.0	

the water cluster under conditions accessible in our experiments, sufficient energy must be available from the water cluster for the water ligands to stabilize the ion core and lead to ion-pair formation from the dissolution of the acid species. A number of water molecules will evaporate from the water cluster ion as a consequence of acid dissolution, but the observed minimum cluster size represents the point of dissolution, as a weakly bound intact (undissolved) acid molecule would be lost in the evaporation process. The evaporation of water molecules from reactions of protonated water cluster and HCl has previously been observed and reported by Bondybey and co-workers.[23]

The rate coefficients between protonated water clusters and the organic reactant gases were found to decrease as a function of cluster sizes. This trend differs from the rate coefficients determined between protonated water clusters and nitric acid, which display an increasing trend as a function of cluster size as seen in Figure 3. The observed increase in the rate coefficient between protonated water clusters and nitric acid is due to the ease of dissolution at larger cluster sizes. As water clusters grow larger, additional degrees of solvation are available to accommodate for the energy required for the dissolution of the acid species. Bondybey and co-workers investigated precipitation reactions between HCl with various hydrated metal ions (Ag^+, Al^+) using a Fourier transform cyclotron resonance apparatus.[39,40] To explain the earlier uptake of HCl by metal ion water clusters compared to reactions of protonated water clusters and HCl, a reaction mechanism was proposed in which HCl initially dissolves within the water cluster ion. The hydrated Cl^- encounters the ion core which results in the formation of MCl (M = Ag, Al) within the cluster, and the ion core changes to the hydronium ion.

Through a study of water clusters bound to ions of differing nature, we are able to ascertain the general influence that the ion−water bonding may have on the trends observed. Since alkali metal ions are analogous to a rare gas atom with a central charge, covalent bonding with the waters of hydration is not present. On the other hand, H_3O^+ is relatively strongly bonded to one water molecule, but further interactions with water are comparable to that of K^+/Na^+ with water. See Table 3. Our results given in Table 2 show that the dissolution of acid molecules is dependent on the number of water molecules present in the water cluster, but not on the nature of the ion core. Hence, the results from the present study are believed to accurately reflect the critical first uptake of HCl by $Na^+(H_2O)_n$ clusters. Our data conclusively show that hydronium ion and sodium ion do not change the acid dissolution phenomena displayed in these cluster systems. The ion core is interpreted to act as a spectator ion, having a small effect on reactions but not playing a major role in the dissolution of acid species.

The lower degree of solvation required for the uptake of HBr compared to HCl by water clusters is similar to the findings obtained for the uptake of the acid species on ice films.[18] Tolbert and co-workers, using a Knudsen cell reactor coupled to a Fourier transform infrared−reflection absorption spectroscopy, found HBr exposure to ice films at 110 K yielded surface coverage greater than observed by HCl by approximately a factor of 2. They suggested that fewer water molecules are required to solvate impinging HBr species than the HCl species. HCl and HBr were observed to react efficiently with crystalline and amorphous microporous ice at 110 K to form hydronium ion reaction products. Tolbert and co-workers' results strongly suggest solvation and ionization in interactions of HCl and HBr with ice films representative of atmospheric aerosols.

Using a flow-tube kinetic technique, Chu and Chu investigated the uptake rate of HI on ice surfaces and compared their results with several other uptake studies.[19] The observed rate of uptake of HX (X = Br, I, Cl, F) on ice was observed to follow the trend: HI ≅ HBr > HCl > HF. The authors suggested the uptake trend of acid halides was a result of the acidity and solvation of HX. The dissolution of acid species by water cluster ions is a convolution of the acid species' properties, and the points of dissolution observed in the present study follows a trend in the strength of the ion−molecule interaction. See Table 4. The order of increasing polarizability of the acid species (HNO_3 > HBr > HCl) is consistent with an earlier uptake of the acid species. The dissolution of an acid species in the water cluster is dependent, to an extent, on the ability of the cluster ion to distort the electron distribution of the acid species, which results ultimately in the formation of an ion pair. Lisy and co-workers have suggested that the size and polarizabilty of an anion may play an important role in the structure of water molecules about the anion.[41] The bond dissociation energies, enthalpy of ionization, and the $-pK_a$'s of the acid species did not follow the trend of acid uptake.

Rate coefficients of protonated water clusters and nitric acid were observed to increase as a function of cluster size. See Figure 3a,b. Figure 3b displays the ratio of the experimental rate coefficient to the calculated collisional rate coefficient[45,46] as a function of cluster size. The ratio can be viewed as the reaction efficiency of these cluster ions to nitric acid where the calculated collisional rate coefficient is the rate if every collision led to a reaction. As cluster ions grow, their properties gradually approach mimicry of a bulk system. At this stage, the reaction efficiency can be viewed as the accommodation coefficient for the process; see ref 24. On the basis of the rate coefficients, the initial dissolution of nitric acid by type II PSCs should be a rapid reaction. Laboratory studies of nitric acid uptake on ice films was found to be very efficient.[42]

The results of the present study offer new insights into the uptake of acid molecules by water clusters and contribute to a more complete understanding of heterogeneous processes of atmospheric significance. We believe that ionic reactions on the surfaces of atmospheric particles could contribute significantly to the observed reactivity of reservoir species as suggested by other theoretical and experimental considerations. We discuss further evidence for this conjecture in a forthcoming paper.[36]

TABLE 4: Intensive Properties[43,44] of Reactant Gases

reactant gas	polarizability (10^{-24} cm^3)	$HX + H_2O \rightarrow H_3O^+ + X$ (kcal/mol)	pK_a	bond dissociation energy (kcal/mol)	dipole moment (D)
HNO_3	∼4.5	155.4	1.37	101.2	2.17
HBr	3.61	154.4	8.72	87.6	0.83
HCl	2.63	169.3	6.2	103.2	1.11

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