Chemistry of Ice Surfaces. Elementary Reaction Steps on Ice Studied by Reactive Ion Scattering

HEON KANG

Department of Chemistry, Seoul National University, Gwanak-Gu, Seoul 151-747, Republic of Korea

Received August 5, 2005

ABSTRACT

This Account describes a recent study of reactions on ice surfaces with the emphasis on the mechanistic features of elementary reactions steps. Cs^+ reactive ion scattering (Cs^+ RIS) and low-energy sputtering (LES) techniques monitor the reactions by detecting the molecules and ions on the ice surface. The types of reactions include molecule diffusion and migration, proton transfer, and some simple reactions on frozen water and alcohol surfaces. Ice surface reactions exhibit unique behaviors due to a kinetic constraint, resulting in the isolation of reaction intermediates, preferential stabilization of charged species, and diversity of reaction products.

Introduction

Chemistry of ice surfaces has received increasing attention in recent years. Research on this subject was partly stimulated by the discovery that ice particles in the polar stratospheric clouds play catalytic roles in the seasonal depletion of the ozone layer.[1] In addition, chemical processes on ice surfaces play important roles in many other natural phenomena at low temperatures. For example, snow and ground ice covering presently constitute more than 10% of Earth's land area, and they influence

the chemical composition and heat balance of the atmosphere.[2] Sea salt ice or aerosols in the marine boundary layer are considered to be responsible for the generation of active halogen species in the Arctic troposphere.[3] Interstellar icy grains are considered a catalyst in the formation of extraterrestrial organics.[4] Infrared astronomical observations, organic molecules found in meteorites, and laboratory experiments support the possibility that simple chemicals are transformed to more complex molecules in the ice layers accreted on the dust particles of interstellar clouds.[4]

Ice surfaces offer a unique reaction environment that is much different from that formed by liquid water, gas, or even bulk ice. At the temperature of ice, the rate of thermal reaction surmounting an Arrhenius activation barrier is much slower. In addition, the rate of reagent diffusion is reduced by several orders of magnitude upon the phase transition from liquid to solid. With such drastic changes, the occurrence of a chemical reaction with an appreciable speed might be considered doubtful, and this expectation is generally fulfilled in bulk ice. However, recent studies show that reactions occur even at substantially low temperatures at the surface of ice, sometimes with rates having sufficient speeds to affect the global environment or to guide the molecular evolution processes in outer space. Since the chemistry of ice surfaces is in its early stage of investigation, the subject is not yet well understood. Studies of elementary reactions at well-defined ice surfaces have been limited to several prototypical systems.[5-26] However, these investigations have already highlighted some important aspects of ice surface chemistry. In this Account, we describe the experimental studies of elementary reactions on ice carried out in our laboratory; these reactions include the self-diffusion of water molecules, ion migration, proton transfer, and the S_N1 and S_N2 reactions of alcohols. Further, we outline several important mechanistic features of ice surface reactions deduced from these experiments. This Account is hoped to provide insights into the basic understanding of ice surface chemistry and assist future research in this new exciting field.

Heon Kang received his undergraduate degree in chemistry at Seoul National University and Ph.D. degree in physical chemistry at the California Institute of Technology in 1985. After holding a postdoctoral position at the University of Houston, he joined the chemistry faculty at the Pohang University of Science and Technology in 1987. In 2001, he moved to Seoul National University, where he is currently a professor of chemistry. His major research has been in the field of surface chemistry, and currently his interest dwells on ice surfaces and liquid/solid interfaces.
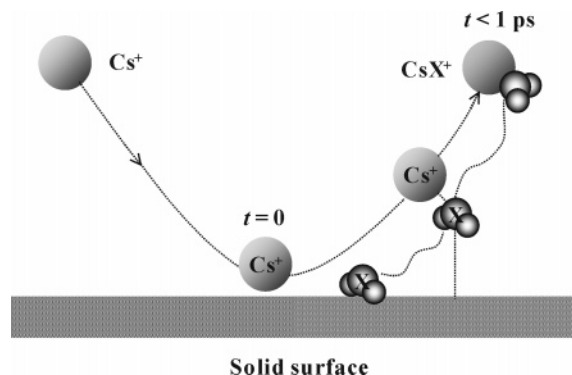
FIGURE 1. Illustration of the Cs$^+$ RIS process. Cs$^+$ collides with the surface at $t = 0$ to release most of its initial kinetic energy, and the slow outgoing Cs$^+$ drags molecule X along with it to form a CsX$^+$ complex.

Methods of Study

A systematic study of elementary reactions on ice requires the preparation of clean and well-defined ice surfaces. This can be carried out in ultrahigh vacuum (UHV), where surface contamination and water adsorption from residual gases can be minimized. The UHV sample handling necessitates that ice films be grown and maintained at a temperature below that of water sublimation (<160 K). The growth temperature controls the morphology of the film to be either amorphous (<130 K) or a crystalline phase (>145 K). Ru(0001) or Pt(111) crystals are favored as substrates for film growth because their lattice parameters match well with those of crystalline ice.

The analysis techniques need to have the capability for molecular identification and to monitor the reactions occurring right on the surfaces. The Cs$^+$ reactive ion scattering (Cs$^+$ RIS) technique is ideally suitable for this purpose, because it can monitor neutral molecules on ice surfaces with a depth resolution of 1 bilayer (BL).[27-29] In this technique, a Cs$^+$ ion beam of low energy (10−100 eV) is scattered from a surface, and the mass of the scattered ions is analyzed. Figure 1 schematically illustrates the Cs$^+$ RIS process by showing the scattering trajectory. A Cs$^+$ ion collides with the surface and subsequently drags molecule X away from the surface along its outgoing trajectory. The Cs$^+$−X association is driven by the ion−dipole attraction force. The mass of the adsorbate is determined by mass spectrometric detection of a CsX$^+$ complex. The molecule abstraction from the surface occurs instantaneously (<1 ps); thus, any slow secondary reactions at the surface caused by the ion impact do not interfere with the CsX$^+$ formation. The Cs$^+$ RIS dynamics has been described in detail.[29]

The ions on ice surfaces can be probed by the low-energy sputtering (LES) method.[9,27] Ice surfaces can stabilize charged species such as hydronium (H$_3$O$^+$) and ammonium (NH$_4$$^+$) ions through solvation by water molecules. The impacting low-energy Cs$^+$ ions can desorb such preexisting ions from the surface. The impact energy is controlled to be only slightly above the desorption threshold of the ions to minimize molecular fragmentation and suppress secondary ion emission, which occurs
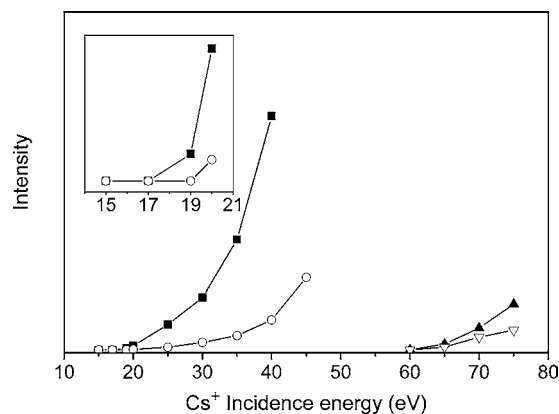

FIGURE 2. The intensity of emitted hydronium and ammonium ions as a function of collision energy from two different types of ice surfaces. For a surface prepared by the co-exposure of 0.3 L HCl and 0.15 L NH$_3$ on an ice film to form NH$_4$$^+$ and H$_3$O$^+$ ions, the emission of ammonium (■) and hydronium (○) ions exhibit threshold energies much lower than those for emission of hydronium (▲) and ammonium (▽) ions from a pure H$_2$O or NH$_3$ film. The inset shows the magnification of the threshold region. The film temperature is 100 K.
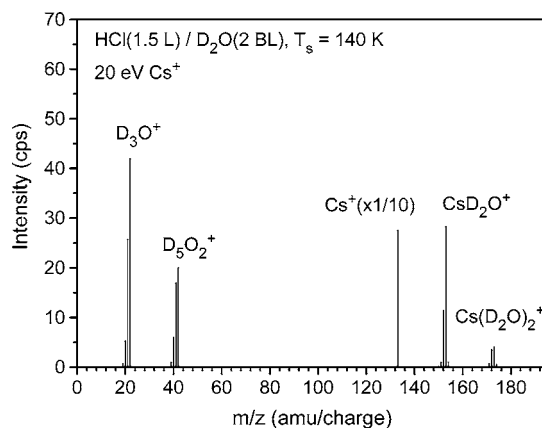

FIGURE 3. Positive ion mass spectrum obtained on a D$_2$O-ice surface exposed to 1.5 L of HCl at 140 K. The D$_2$O-ice film is 2 BL thick, prepared on a Ru(0001) surface. The Cs$^+$ peak intensity is reduced by 1/10.

during high-energy sputtering. Figure 2 shows that LES causes only the desorption of preexisting ions, and the secondary ion emission can be prevented by the proper tuning of the beam energy.[9] The preformed NH$_4$$^+$ and H$_3$O$^+$ ions on the ice surface are emitted at Cs$^+$ impact energies above 17 and 19 eV, respectively. On the other hand, on pure H$_2$O and NH$_3$ surfaces where none of these ions exists, H$_3$O$^+$ and NH$_4$$^+$ ions are emitted only above 60 eV due to collision-induced secondary ionization processes.

The Cs$^+$ RIS and LES experiments can be performed simultaneously with a single Cs$^+$ beam, such that both neutral and ion species on the surface can be recorded in a single mass spectrum. Figure 3 shows the mass spectrum of positive ions emitted from a D$_2$O-ice surface exposed to HCl gas at 140 K.[11] RIS signals appear at masses greater than the reflected Cs$^+$ primaries ($m/z = 133$ amu/charge). CsD$_2$O$^+$ and Cs(D$_2$O)$_2$$^+$ are produced due to the pickup of one and two water molecules, respectively, from
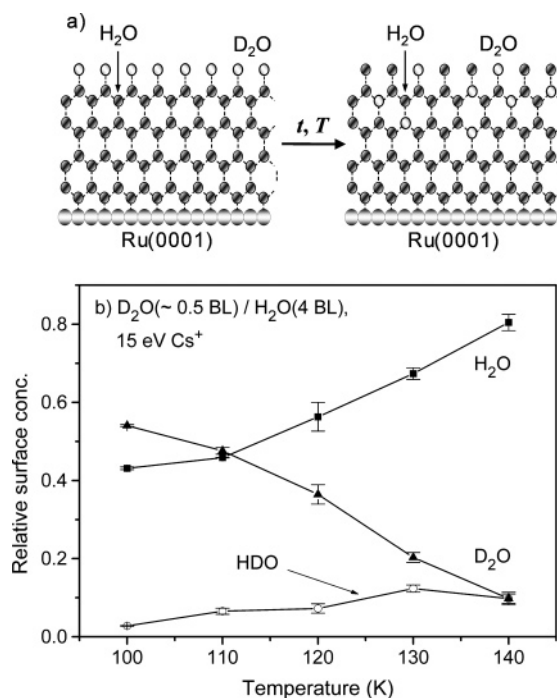
FIGURE 4. (a) Schematic illustration of the procedure for kinetic measurement of self-diffusion on ice surfaces. A H$_2$O-ice film with a thickness of 4.0 BL is prepared on a Ru(0001) substrate, and then D$_2$O molecules are deposited onto it to a coverage of 0.5 BL. The changes in the H$_2$O and D$_2$O surface concentrations resulting from self-diffusion are measured after a diffusion time t at temperature T. (b) The result of the measurement for self-diffusion rate as a function of temperature between 100 and 140 K. The vertical axis shows the relative surface abundance of H$_2$O, D$_2$O, and HDO measured after a duration of 23 s, from which the speed of self-diffusion is deduced.

the surface. The LES peaks include D$_3$O$^+$ and its hydrated clusters (D$_5$O$_2^+$). The hydronium ions are produced by ionization of HCl on ice at this temperature. The isotopomeric distributions of the LES and RIS signals indicate the occurrence of characteristic H/D exchange reactions between hydronium ions and water molecules at the surface. These isotopomer signals quantitatively reflect the isotopomeric distributions at the surface because isotopic scrambling does not occur in a mass spectrometer with the ionizer switched off.[30]

Molecule Diffusion and Migration near the Ice Surface

The diffusion of water molecules, or self-diffusion, enables the adsorbates on an ice surface to be solvated and ready for chemical transformation. Self-diffusion also facilitates the migratory motion of reagent molecules at the surface. Thus, self-diffusion not only affects the reaction behavior on ice but also controls the reaction speed. Jung et al.[5] examined the self-diffusion on ice surfaces in a direction normal to the surface for the temperature range of 100–140 K. They prepared thin films of H$_2$O ice on a Ru(0001) substrate and then deposited a fractional coverage of D$_2$O molecules on them (see Figure 4a). The temporal changes in the H$_2$O and D$_2$O surface concentrations were monitored with a depth resolution of 1 BL, which revealed self-

diffusion kinetics in the vertical direction. Figure 4b shows the result of the measurements, in which the ice surfaces initially possess equal amounts of H$_2$O and D$_2$O at different temperatures, and the variations in the H$_2$O and D$_2$O surface concentrations are measured after a fixed duration of the diffusion time. The rate of depletion of the surface D$_2$O molecules due to their inward diffusion increases at higher temperatures, accompanied by an increase in H$_2$O population at the surface. The result yields the first-order rate coefficient for the vertical diffusion of water molecules, which ranges from $k = (5.7 \pm 0.6) \times 10^{-4}$ s^{-1} at 100 K to $k = (6.7 \pm 2.0) \times 10^{-2}$ s^{-1} at 140 K with Arrhenius activation energy of 13.7 ± 1.7 kJ mol^{-1}.

The measured activation energy for the surface diffusion is several times smaller than the activation energy for bulk water diffusion (52–70 kJ mol^{-1}).[2] The extrapolation of the diffusion rates to a higher temperature indicates that the surface and bulk diffusion rates become similar at 150–160 K, the temperature at which liquidlike translational diffusion begins.[31] At a lower temperature (<150 K), the self-diffusion at the surface is faster than that in bulk due to the lower activation energy for the former. Interestingly, the activation energy for the surface diffusion is quite close to the migration energy of interstitial molecules in bulk ice (15 kJ mol^{-1}).[2] The proximity to the interstitial migration energy suggests that surface water molecules diffuse in a manner similar to that of interstitials in bulk. The outermost region of the ice surface appears to have a highly disordered molecular arrangement, which offers a high density of "interstitial-like" molecules.

In addition to self-diffusion, other factors can influence the motions of reactant species at an ice surface. For instance, chemical species may have different thermodynamic propensities for residing at the surface of ice or in the interior, depending on its interaction with the ice surface and the degree of solvation by water molecules. Kim et al.[6] examined the migratory motions of Na$^+$ and Cl$^-$ ions on ice surfaces, driven by thermodynamic forces. They prepared Na$^+$ and Cl$^-$ ions on the ice surface by the ionic dissociation of NaCl vapor.[7] The variation of the ion populations at the surface was monitored by LES, which revealed the migratory behaviors of the ions.[6] Figure 5 shows the Na$^+$ and Cl$^-$ populations at the surface as a function of ice temperature for 100–140 K. The Na$^+$ intensity gradually decreases with an increase in the temperature over 110–130 K, whereas the Cl$^-$ intensity remains almost constant. The result indicates the inward migration of Na$^+$ at elevated temperatures, in contrast to the surface residence of Cl$^-$. The interior residence of Na$^+$ agrees with the result of metastable impact electron spectroscopy (MIES) experiments on NaCl at ice surfaces.[22] Interestingly, the Cl$^-$ signals in the MIES experiments indicate the solvated Cl$^-$ structure for $T > 120$ K. Considering that MIES monitors the tail of a surface electronic wave function, whereas LES detects the species in the first bilayer of ice, we may conclude that Cl$^-$ is located in the first bilayer of the ice surfaces in partially solvated forms.
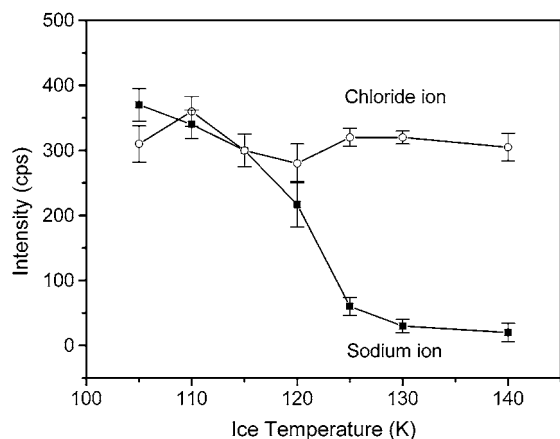
FIGURE 5. Variation of LES intensities for Na$^+$ (■) and Cl$^-$ (○) ions as a function of ice film temperature. NaCl exposure was 0.8 ML on D$_2$O-ice films with a thickness of 4.0 BL. The LES measurements were carried out after 2 min from the time of NaCl deposition at the indicated temperatures. The D$_2$O films are nonporous, amorphous ice deposited at 130 K.
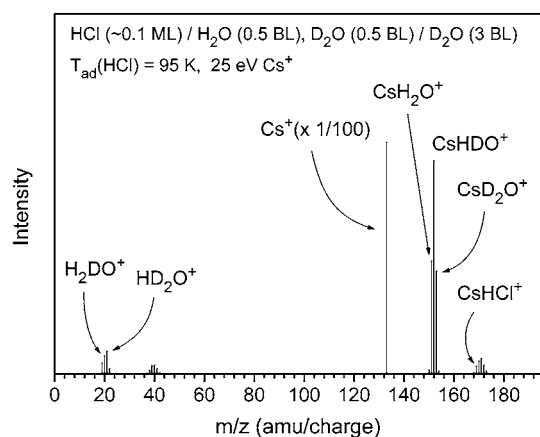

FIGURE 6. RIS mass spectra from a D$_2$O-ice film with a mixture of H$_2$O and D$_2$O on the surface in the ratio 1:1 and exposed to 0.1 ML HCl. The underlying D$_2$O films were deposited at 135 K. The D$_2$O film was exposed to HCl at 95 K, and then the film temperature was maintained at 95 K for 10 min before the RIS measurement.

Two additional aspects of the ion migration experiments[6] are mentioned. First, the Na$^+$ migration starts to occur above 110−120 K, which is the onset temperature for activating the self-diffusion. This suggests that Na$^+$ migration requires the diffusion of surface water molecules. Second, ice surfaces provide an opportunity to study the kinetics of ion segregation in slow motion. The mobility of ions on ice at these temperatures is extremely low in comparison to that in liquid water. Nevertheless, the thermodynamic state of amorphous ice may be considered at the extrapolation from liquid water. In this respect, the kinetic measurements on an amorphous ice surface may supplement those on a liquid water surface, which is barely accessible for sophisticated surface analytical techniques.

Proton Transfer

Proton transfer is ubiquitous in aqueous media and is related to diverse phenomena ranging from acid−base neutralization to enzymatic reactions. Due to its special nature, proton transfer will be discussed separately from other reactions in this Account. Protons have a significantly greater mobility than other ions in liquid water due to the Grotthuss mechanism, in which the effective motion of a proton involves the rearrangement of hydrogen bonds in the molecular chain of water. For ice, such motions are expected to be hampered by the rigid tetrahedral structure of the hydrogen bond network. The mechanism of proton transfer in such structurally constrained environments is an interesting subject.[2,8,9,12−15]

Park et al.[8] studied the resonant proton transfer between the water molecules on ice surfaces by monitoring the H/D exchange between H$_2$O and D$_2$O, given by the following reaction:

$$H_2O + D_2O \leftrightarrow 2HDO \quad \text{(reaction 1)}$$

On pure ice surfaces at low temperatures, the H/D exchange is very slow due to the lack of sufficient protons to mediate the proton transfer. The reaction occurs in a time scale of several minutes at 140 K, even when the surface is prepared as a homogeneous mixture of H$_2$O and D$_2$O molecules.
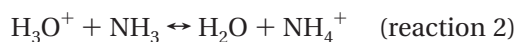
The addition of HCl onto the ice surface generates excess protons and significantly accelerates the isotopic exchange.[8] In Figure 6, a small amount of HCl is added at 95 K onto an ice film, whose first bilayer is a homogeneous mixture of D$_2$O and H$_2$O in a population ratio of 1:1. The underlying sublayer is a D$_2$O-ice film. The RIS products at $m/z = 151−153$ amu/charge show that the isotopomeric ratio of surface water molecules is H$_2$O/HDO/D$_2$O = 1:2:1, indicating that the isotopic exchange is complete between equal amounts of surface H$_2$O and D$_2$O molecules. The result also indicates that the isotopic exchange is confined to the first bilayer of the surface and does not propagate to the underlying D$_2$O layer. Thus, proton transfer efficiently occurs only on the surface at this temperature.

When the temperature is increased to 140 K, the surface abundance of D$_2$O increases relative to H$_2$O and HDO, indicating that the D$_2$O molecules in the sublayer participate in the isotopic exchange.[8] However, this vertical H/D exchange involving the sublayer molecules occurs very slowly in comparison to the rapid exchange in the first bilayer of the surface. In addition, the vertical exchange reaction occurs only to a depth of about 3 BL for the investigated temperature (140 K) and duration (15 min). Thus, proton transfer is highly anisotropic near the surface of ice. It is estimated[8] that protons propagate across 40 water molecules along the surface but only across a thickness of 3 BL in the normal direction. This suggests two possibilities: (i) a higher proton mobility at the surface of ice than in the bulk or (ii) a thermodynamic propensity of a proton to reside at the surface of ice rather than in the interior. The surface residence of protons is consistent with the strong H$_3$O$^+$ desorption observed from the surfaces of H$_3$O$^+$-containing ice films in LES experi-

ments (Figure 3).[11] Theoretical works also indicate that H_3O^+ prefers to stay near the surface of aqueous solutions.[32]

When we compare the speed and distance of propagation, the vertical H/D exchange process exhibits a similarity to the self-diffusion of water. Thus, it can be argued[8] that the vertical H/D exchange may be dependent on the vertical diffusion of water, that is, self-diffusion carries the isotopomers that are produced at the surface by the lateral H/D exchange to the sublayer, and vice versa. This implies that a separate proton transfer route, if it exists, must be slower than the vertical self-diffusion of water at 140 K. Recently, we observed that the proton transfer occurs faster than self-diffusion at lower temperature (120−130 K).

Next, an example of the proton transfer between different donor and acceptor species is discussed, which is depicted by reaction 2.

$$H_3O^+ + NH_3 \leftrightarrow H_2O + NH_4^+ \quad \text{(reaction 2)}$$

This is a prototypical example of heterogeneous proton transfer. The reaction is substantially exoergic, proceeding instantaneously in an aqueous phase with an equilibrium constant $K_{eq} = 1.7 \times 10^9$ at 298 K. It is even more facile in a gas phase with $K_{eq} = 1 \times 10^{30}$. Reaction 2 has been studied on ice surfaces by IR spectroscopy[17] and by Cs^+ RIS and LES.[9] In the latter work, the reaction was examined by carrying out H_3O^+−NH_3 titration experiments; the hydronium-ion-containing ice surfaces were prepared by exposure to HCl, and then NH_3 was added in varying amounts to change the ratio of the proton donor and acceptor. Figure 7 shows the result of the titration experiments performed on D_2O-ice films at 100 K, in which the progress of the H_3O^+−NH_3 reaction is monitored by quantitatively measuring all four components of the reaction (LES measures H_3O^+ and NH_4^+, and RIS measures NH_3 and H_2O).

A prominent feature of the above-mentioned experiment is that the reaction quotient (Q) can be obtained.

$$Q = [H_2O][NH_4^+]/([H_3O^+][NH_3]) \quad (1)$$

The Q value is observed to be large only at the initial stage of the NH_3 titration, and it decreases as the titration proceeds to reach a limiting value of ca. 20. This value is much smaller than the K_{eq} of reaction 2 in liquid water or in the gas phase. K_{eq} on ice should have an intermediate value between the two equilibrium constants because these species are partially solvated at the surface. The much lower value of Q than K_{eq} indicates that reaction 2 does not reach thermodynamic equilibrium on ice, and the proton transfer is incomplete.

The incomplete proton transfer from H_3O^+ to NH_3 contrasts the very efficient proton transfer observed between water molecules on ice (Figure 6). In the latter part, the resonant proton transfer appears to be able to propagate along the hydrogen bonds in the molecular chain of water. On the other hand, in the heterogeneous proton transfer between water and ammonia, the am-
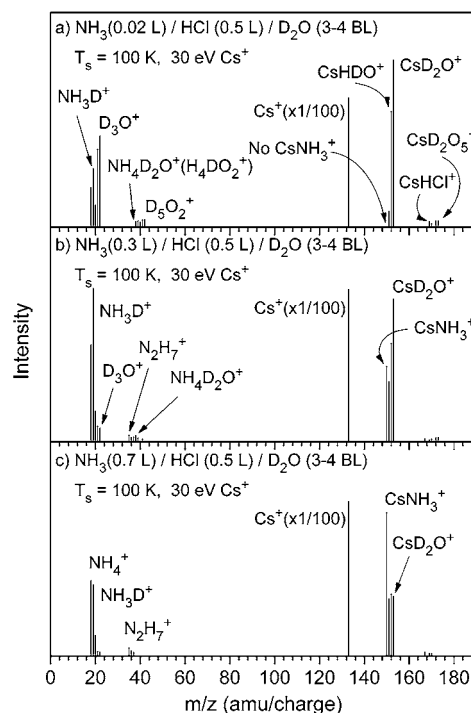

FIGURE 7. LES and RIS spectra measured with the progress of the H_3O^+−NH_3 reaction on ice. An amorphous D_2O film (3−4 BL) was first exposed to 0.5 L of HCl to generate hydronium ions, and then to NH_3 at varying exposures: (a) 0.02 L, (b) 0.3 L, and (c) 0.7 L. The reaction temperature was 100 K.

monium ion can act as a proton trap that terminates the proton-transfer chain. Moreover, the ammonium ions are rather immobile on ice surfaces due to solvation. The solvated ions generate kinetic barriers, and the reaction stops at an intermediate stage trapped between the barriers. The coexistence of H_3O^+, NH_3, H_2O, and NH_4^+ at the surface represents a kinetically trapped, metastable state of the reaction.
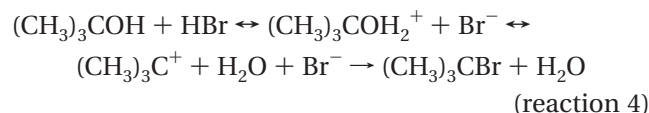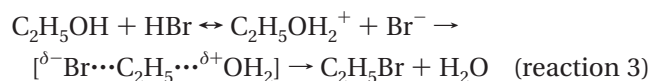
Chemical Reactions

Chemical reactions on ice surfaces reveal more interesting features of kinetic trapping. The most extensively investigated reaction so far is the ionization of HCl molecules on ice, which has received prolonged attention owing to its implication for stratospheric ozone depletion.[1] A detailed mechanism of this reaction is still under active investigation,[11,15,16] and a review of the burgeoning reports on this subject is beyond the scope of this Account. Infrared spectroscopic studies and the theoretical aspects of this reaction have been reviewed.[15] Other reaction studies include the radiolysis of frozen molecules,[18,19] solvation of weak acids and bases,[20,21] and reactions of alkali metal atoms,[23,24] propene,[25] and alcohols.[10,24,26] Among these, two specific examples will be discussed here as follows: (i) the reactions of Na atoms with ice surfaces investigated by Kempter and co-workers[23,24] and (ii) the reactions of HBr with frozen alcohol surfaces.[10]

The reaction of Na atoms with water is a well-known exoergic reaction in the liquid phase, yielding NaOH and H_2 as the final products. The reaction is believed to occur

with the ionization of Na atoms and the subsequent solvation of detached electrons. However, it has been difficult to directly observe the intermediate stages. Kempter and co-workers[23,24] examined this reaction on ice films using MIES, ultraviolet photoelectron spectroscopy (UPS), and density functional theory (DFT) calculations. Upon reaction of Na atoms with an ice surface at 90 K, the MIES features show a Na 3s electron solvated by water molecules at the surface. The spectra suggest that the 3s electron is delocalized from its Na core, such that it is trapped between Na and the protons of the hydrating water molecules pointing toward Na. Obviously, the ice surface stabilizes the solvated 3s electron, which is only a transient intermediate in the liquid phase. The Na 3s signal disappears when the film is heated to 115 K; this is consistent with the discussion in the previous section that Na^+ migrates inward above this temperature due to the increased self-diffusional activity.[6] The reaction of Na on frozen methanol films also indicates the stabilization of the solvated 3s electron and the eventual production of methoxy species.[24]

Park et al.[10] examined the reactions of hydrogen bromide with frozen films of ethanol (C_2H_5OH) and *tert*-butyl alcohol [$(CH_3)_3COH$]. In the liquid phase, these are exemplary S_N2 and S_N1 reactions, proceeding through reaction paths 3 and 4.

$$C_2H_5OH + HBr \leftrightarrow C_2H_5OH_2^+ + Br^- \rightarrow$$
$$[^{\delta-}Br\cdots C_2H_5\cdots^{\delta+}OH_2] \rightarrow C_2H_5Br + H_2O \quad \text{(reaction 3)}$$

$$(CH_3)_3COH + HBr \leftrightarrow (CH_3)_3COH_2^+ + Br^- \leftrightarrow$$
$$(CH_3)_3C^+ + H_2O + Br^- \rightarrow (CH_3)_3CBr + H_2O$$
$$\text{(reaction 4)}$$

The reactions proceed all the way up to alkyl bromides in the liquid phase, where the reactions are governed by thermodynamics. Intermediate species such as protonated alcohol and carbocation exist only for transient lifetimes along the pathway.

The reaction of HBr with a frozen *tert*-butyl alcohol surface is illustrated by the RIS spectra in Figure 8. For a pure *tert*-butyl film before the reaction (Figure 8a), the spectrum shows the RIS signals of a *tert*-butyl alcohol molecule and a small amount of water physisorbed from residual gas. When the surface is reacted with HBr gas at 100 K, as shown in Figure 8b, the $C_4H_9^+$ and $C_4H_{11}O^+$ peaks are newly observed, representing the formation of *tert*-butyl cation [$(CH_3)_3C^+$] and protonated *tert*-butyl alcohol [$(CH_3)_3COH_2^+$], respectively. The increased water population (the increased CsH_2O^+ intensity) indicates the liberation of water by the conversion of $(CH_3)_3COH_2^+$ to $(CH_3)_3C^+$ (reaction 4). Importantly, *tert*-butyl bromide is not formed in the reaction, which is validated by the absence of $CsC_4H_9Br^+$ peaks ($m/z = 269$ and 271 amu/charge). On a frozen ethanol surface, similar studies show that HBr reacts with the surface to yield protonated ethanol as the exclusive product.[10] Ethyl bromide is not formed from the reaction.

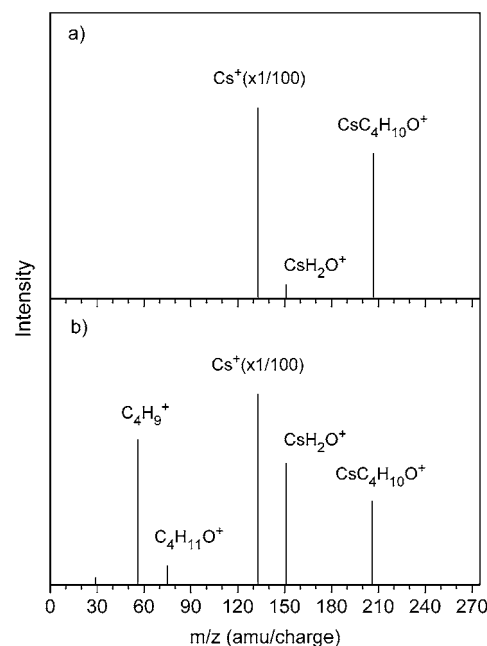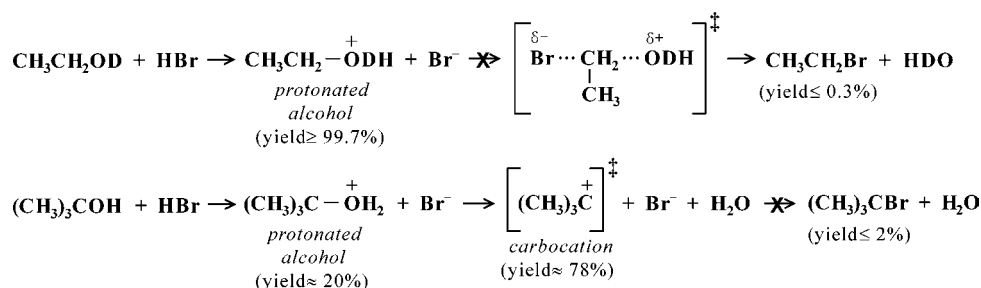The reactions on frozen ethanol and *tert*-butyl alcohol surfaces are summarized in Scheme 1. On the ethanol

FIGURE 8. LES and RIS spectra obtained on a pure $(CH_3)_3COH$ film (a) and on a $(CH_3)_3COH$ film after HBr exposure of 0.3 L (b). Alcohol films were deposited at 120 K, and HBr exposure and RIS analysis were carried out at 100 K.

surface, protonated ethanol is the only product, and the formation of the S_N2 transition state and ethyl bromide is prohibited. The reaction with *tert*-butyl alcohol produces protonated *tert*-butyl alcohol (20% yield) and *tert*-butyl cations (78%). The yield of *tert*-butyl bromide is negligible ($\leq 2\%$). Notably, the species formed on the frozen molecular surfaces correspond to the intermediates in the liquid-phase reactions. This result not only confirms the S_N1 and S_N2 mechanisms of the liquid-phase reactions but also reveals the nature of kinetic trapping on ice. The kinetic barrier prohibits the S_N2 transition state of reaction 3 and the recombination of $(CH_3)_3C^+$ and Br^- in the S_N1 path of reaction 4. As such, the reactions do not reach alkyl bromides, although they are thermodynamically the most stable. The kinetic trapping observed in this case is distinguished from the retardation of the reaction speed at low temperature. The trapped intermediates are metastable and do not deplete appreciably with time. Thus, they can be regarded as characteristic reaction products, rather than transitory species, under the given environment.

It is worthwhile to discuss the kinetic trapping on a frozen molecular surface in greater detail. A close examination of Scheme 1 reveals that charged species are preferentially isolated, and their subsequent reactions are prohibited. For example, protonated alcohols and the *tert*-butyl cation are isolated along the reaction paths. Further, the nucleophilic attack of protonated ethanol by Br^- is blocked in the S_N2 path, while the association of a *tert*-butyl cation and Br^- leading to *tert*-butyl bromide is blocked in the S_N1 path. On the other hand, reactions involving the movement of neutral molecules are facile, such as the initial reactive encounter of HBr with alcohol molecules producing protonated alcohols, and the libera-

Scheme 1

$$CH_3CH_2OD + HBr \rightarrow CH_3CH_2\overset{+}{-}\underset{|}{ODH} + Br^- \xrightarrow{\times} \left[\overset{\delta-}{Br}\cdots\underset{\underset{CH_3}{|}}{CH_2}\cdots\overset{\delta+}{ODH} \right]^{\ddagger} \rightarrow CH_3CH_2Br + HDO$$

protonated
alcohol
(yield ≥ 99.7%) (yield ≤ 0.3%)

$$(CH_3)_3COH + HBr \rightarrow (CH_3)_3C\overset{+}{-}OH_2 + Br^- \rightarrow \left[(CH_3)_3\overset{+}{C}\right]^{\ddagger} + Br^- + H_2O \xrightarrow{\times} (CH_3)_3CBr + H_2O$$

protonated   carbocation
alcohol   (yield ≈ 78%)   (yield ≤ 2%)
(yield ≈ 20%)

tion of a water molecule from $(CH_3)_3COH_2^+$. In the reactions of a Na atom with frozen water and methanol surfaces also,[23,24] the solvated electron is preferentially trapped due to its charge. Such selective trapping of charged species again suggests that reactant mobility is a critical factor in controlling the cold surface reactions. While neutral molecules such as water and alcohol have some mobility on the surfaces at the examined temperatures,[5] charged species such as $C_2H_5OH_2^+$, $(CH_3)_3C^+$, $(CH_3)_3COH_2^+$, Br^-, e^-, and Na^+ are strongly solvated and their mobility is greatly reduced.

Finally, it may be pointed out that although both the primary and tertiary alcohols produce alkyl bromides as final products in the liquid phase, the two alcohols result in different product distributions on frozen molecular surfaces. Ethanol exclusively produces protonated alcohol, whereas *tert*-butyl alcohol produces protonated alcohol and carbonium ions. A subtle chemical difference in the reactant molecules appears to be well distinguished on cold molecular surfaces, leading to diversified reaction products.

Conclusion and Perspective

We have shown that the reactions on ice surfaces exhibit unique behaviors that are significantly different from liquid phase reactions. The primary factor that controls the ice surface reactions is the mobility of molecules. Water molecules are distinctively more mobile at the surface of ice than in bulk ice for temperatures <150 K, causing chemical processes occur on ice with appreciable speed and enhanced selectivity, though much more slowly than in the liquid phase. Under such circumstances, the reaction behavior is guided by kinetic constraints rather than thermodynamics. The kinetic trapping on ice results in the following: (i) incomplete proton transfer between different donor and acceptor species, (ii) isolation of reaction intermediates, (iii) preferential stabilization of charged species, and (iv) diversity of reaction products. Another merit of studying reactions on ice is that reaction kinetics can be studied in greater detail. Reaction intermediates isolated on the frozen surfaces can be directly probed by surface spectroscopic techniques. Also, the motions of reagent species can be sufficiently slowed to perform the kinetic measurements in real time for some simple processes such as migration of ions.

Investigations of the chemistry of ice surfaces are still very limited, and the discovery of additional interesting features is certainly anticipated as more types of reactions are examined. The reaction mechanisms and dynamics at a molecular level are interesting and pose fundamental questions in this field. To answer these questions, the combined efforts made in both experiments and theory will be effective, as has been demonstrated in a few recent studies.[15,16,23,24,33] Some immediate questions that need to be examined include the following: (i) Why is the resonant proton transfer efficient only for surface water molecules? Is the Grotthuss mechanism also responsible for the efficient proton transfer? (ii) How do the ice temperature and the resulting change of surface morphology from an amorphous state to a crystalline or liquidlike phase influence reactions? (iii) What are the effects of surface microscopic structures, such as defects, pores, and clathrate hydrates? (iv) How will reactions be affected by external energy sources such as photons and electron beams? This question may be relevant for radiation-induced chemistry in outer space, such as in comet tails and interstellar space.

The constraint by kinetic barriers is an essential feature for guiding reactions to produce complex systems not in thermodynamic equilibrium, such as chemical processes in life and self-organization. Ice surfaces provide a similar effect, which might have important implications for low-temperature chemistry in nature. For example, interstellar ice grains are considered to catalyze the transformation of simple molecules to more complex prebiological molecules.[4] In this process, a necessary step is the trapping of various reactive species produced from the radiolysis of simple molecules in ice mantles so that they are available for subsequent reactions to increase molecular complexity. The present finding supports this possibility and further suggests that charged intermediates might be important in interstellar molecular evolution.

References

(1) Molina, M. J.; Tso, T.-L.; Molina, L. T.; Wang, F. C.-Y. Antarctic stratospheric chemistry of chlorine nitrate, hydrogen chloride, and ice: release of active chlorine. *Science* **1987**, *238*, 1253–1257.

(2) Petrenko, V. F.; Whitworth, R. W. *Physics of Ice*; Oxford University: Oxford, U.K., 1999; Chapters 6 and 10.

(3) Barrie, L. A.; Plat, U. Arctic tropospheric chemistry: an overview. *Tellus* **1997**, *49B*, 450–454.

(4) Greenberg, J. M. Cosmic dust and our origins. *Surf. Sci.* **2002**, *500*, 793−822.

(5) Jung, K.-H.; Park, S.-C.; Kim, J.−H.; Kang, H. Vertical diffusion of water molecules near the surface of ice. *J. Chem. Phys.* **2004**, *121*, 2758−2764.

(6) Kim, J.-H.; Shin, T.; Jung, K.-H.; Kang, H. Direct Observation of Segregation of Sodium and Chloride Ions at Ice Surfaces. *ChemPhysChem* **2005**, *6*, 440−444.

(7) Park, S.-C.; Pradeep, T.; Kang, H. Ionic dissociation of NaCl on frozen water. *J. Chem. Phys.* **2000**, *113*, 9373−9376.

(8) Park, S.-C.; Jung, K.-H.; Kang, H. H/D isotopic exchange between water molecules on ice surface. *J. Chem. Phys.* **2004**, *121*, 2765−2774.

(9) Park, S.-C.; Maeng, K.-W.; Pradeep, T.; Kang, H. Unique Chemistry at Ice Surfaces: Incomplete Proton Transfer in the $H_3O^+-NH_3$ System. *Angew. Chem., Int. Ed.* **2001**, *40*, 1497−1500.

(10) Park, S.-C.; Maeng, K.-W.; Kang, H. Organic Chemistry on Cold Molecular Films: Kinetic Stabilization of S_N1 and S_N2 Intermediates in the Reactions of Ethanol and 2-Methyl-2-Propanol with Hydrogen Bromide. *Chem.—Eur. J.* **2003**, *9*, 1706−1713.

(11) (a) Kang, H.; Shin, T.-H.; Park, S.-C.; Kim, I. K.; Han, S.-J. Acidity of Hydrogen Chloride on ice. *J. Am. Chem.* Soc. **2000**, *122*, 9842−9843. (b) Park, S.-C.; Kang, H. Adsorption, Ionization, and Migration of Hydrogen Chloride on Ice Films at Temperatures between 100 and 140 K. *J. Phys. Chem. B* **2005**, *109*, 5124−5132.

(12) Cowin, J. P.; Tsekouras, A. A.; Ledema, M. J.; Wu, K.; Ellison, G. B. Immobility of protons in ice from 30 to 190 K. *Nature* **1999**, *398*, 405−xxx.

(13) Wooldridge, P. J.; Devlin, J. P. Proton Trapping and Defect Energetics in Ice from FT-IR Monitoring of Photoinduced Isotopic Exchange of Isolated D_2O. *J. Chem. Phys.* **1988**, *88*, 3086−3091.

(14) Uras-Aytemiz, N.; Joyce, C.; Devlin, J. P. Protonic and Bjerrum defect activity near the surface of ice at T < 145 K. *J. Chem. Phys.* **2001**, *21*, 9835−9842.

(15) Buch, V.; Sadlej, J.; Uras, N.; Devlin, J. P. Solvation and Ionization Stages of HCl on Ice Nanocrystals. *J. Phys. Chem. A* **2002**, *106*, 9374−9389.

(16) Devlin, J. P.; Uras, N.; Sadlej, J.; Buch, V. Discrete stages in the solvation and ionization of hydrogen chloride adsorbed on ice particles. *Nature* **2002**, *487*, 269−271.

(17) Pursell, C.; Zaidi, M.; Thompson, A.; Fraser-Gaston, C.; Vela, E. Acid−Base Chemistry on Crystalline Ice: HCl + NH_3. *J. Phys. Chem. A* **2000**, *104*, 552−556.

(18) Madey, T. E.; Johnson, R. E.; Orlando, T. M. Far-out surface science: radiation-induced surface processes in the solar system. *Surf. Sci.* **2002**, *500*, 838−858.

(19) Lilach, Y.; Asscher, M. Photochemistry of caged molecules: CD_3-Cl@ice. *J. Chem. Phys.* **2003**, *119*, 407−412.

(20) Souda, R. Temperature-programmed time-of-flight secondary ion mass spectrometry study of hydration of ammonia and formic acid adsorbed on the water-ice surface. *J. Chem. Phys.* **2003**, *119*, 2774−2779.

(21) Souda, R. Solvation of CH_3NH_2, CD_3OD, and D_2O molecules studied by temperature-programmed TOF−SIMS. *Surf. Sci.* **2003**, *547*, 403−409.

(22) Borodin, A.; Höfft, O.; Kahnert, U.; Kempter, V.; Poddey, A.; Blöchl, P. E. Interaction of NaCl with solid water. *J. Chem. Phys.* **2004**, *121*, 9671−9678.

(23) Borodin, A.; Höfft, O.; Kahnert, U.; Kempter, V.; Allouche, A. Electron spectroscopy (UPS (HeI and II) and metastable impact electron spectroscopy (MIES)) applied to molecular surfaces: the interaction of atoms and molecules with solid water. *Vacuum* **2004**, *73*, 15−24.

(24) Borodin, A.; Höfft, O.; Kahnert, U.; Kempter, V.; Ferro, Y.; Allouche, A. Electron solvation by polar molecules: The interaction of Na atoms with solid methanol films studied with MIES and density functional theory calculations. *J. Chem. Phys.* **2004**, *120*, 8692−8697.

(25) Graham, J. D.; Roberts, J. T. Chemical Reactions of Organic Molecules Adsorbed at Ice: 1. Chlorine Addition to Propene. *J. Phys. Chem. B* **2000**, *104*, 978−982.

(26) Graham, J. D.; Roberts, J. T. Chemical Reactions of Organic Molecules Adsorbed at Ice: 2. Chloride Substitution in 2-Methyl-2-propanol. *Langmuir* **2000**, *16*, 3244−3248.

(27) Rabalais, J. W. *Principles and Applications of Ion Scattering Spectrometry*; Wiley-Interscience: New Jersey, 2003; Chapter 9.

(28) Hahn, J. R.; Lee, C. W.; Han, S.-J.; Lahaye, R. J. W. E.; Kang, H. Low Energy Cs^+ Scattering from Water on Pt(111): A Kinetic Energy Analysis of the Cs^+-Water Clusters. *J. Phys. Chem. A* **2002**, *106*, 9827−9831.

(29) Lahaye, R. J. W. E.; Kang, H. Reactive ion-surface scattering as an Eley-Rideal process: a molecular dynamics study into the abstraction reaction mechanism by low energy Cs^+ from Pt(111). *ChemPhysChem* **2004**, *5*, 697−705.

(30) Kim, C. M.; Hwang, C.-H.; Lee, C.-W.; Kang, H. Real-time observation of the H/D exchange reaction between ethylene and hydrogen on Pt(111). *Angew. Chem., Int. Ed.* **2002**, *41*, 146−148.

(31) Smith, R. S.; Huang, C.; Kay, B. D. Evidence for molecular translational diffusion during the crystallization of amorphous solid water. *J. Phys. Chem. B* **1997**, *101*, 6123−6126.

(32) Mucha, M.; Frigato, T.; Levering, L. M.; Allen, H. C.; Tobias, D. J.; Dang, L. X.; Jungwirth, P. Unified Molecular Picture of the Surfaces of Aqueous Acid, Base, and Salt Solutions. *J. Phys. Chem. B* **2005**, *109*, 7617−7623.

(33) Girardet, C.; Toubin, C. Molecular atmospheric pollutant adsorption on ice: a theoretical survey. *Surf. Sci. Rep.* **2001**, *44*, 159−238.