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Young-Kwang Kim, Seong-Chan Park, Jung-Hwan Kim, Chun-Woo Lee, and Heon Kang

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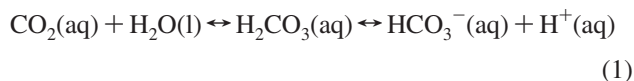
Young-Kwang Kim,[†] Seong-Chan Park,[†] Jung-Hwan Kim,[†] Chun-Woo Lee,^{*,‡} and Heon Kang^{*,†}*Department of Chemistry, Seoul National University, Gwanak-Gu, Seoul 151-747, Republic of Korea, and Department of Chemistry, Ajou University, Wonchun-Dong, Paldal-Gu, Suwon, 443-749, Republic of Korea**Received: February 25, 2008; Revised Manuscript Received: September 23, 2008*

We studied the interactions of CO₂ with ice films prepared in either a neutral or basic condition, with emphasis on the examination of feasibility for the reaction between CO₂ and hydroxide ion present at the ice surfaces. To this end, Cs⁺ reactive ion scattering (RIS) and low-energy sputtering (LES) techniques were used to scrutinize the chemical species present at the surfaces, in conjunction with temperature-programmed desorption (TPD) to monitor the desorbing species. Ice films were grown in a nonporous amorphous phase or a crystalline phase. Excess hydroxide ions were added onto the ice film surfaces by the hydrolysis of Na atoms. TPD experiments showed that CO₂ molecules desorbed from the ice film surfaces before the onset of water sublimation near 140 K, regardless of the presence or absence of excess hydroxide ions. CO₂ adsorption did not produce CO₂–water complexes nor hydrolysis products on both film surfaces in the temperature range 80–180 K. The nonreactivity of CO₂ toward hydroxide ion at the ice surface contrasts with facile occurrence of the reaction between CO₂ and hydroxide ion in the gas phase and liquid water. It is suggested that the unique structure of hydroxide ions at ice surfaces with efficient hydrogen bonding to water molecules suppresses their reactivity toward CO₂. The OH[−] reactivity may also be affected by the presence of neighboring Na⁺ ions.

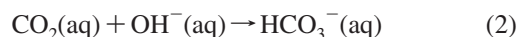
Introduction

Understanding the interactions of CO₂ with ice surfaces is of fundamental importance in atmospheric chemistry and environmental sciences. The uptake and desorption of CO₂ from snow and ground ice surfaces may influence the balance of atmospheric CO₂ level.¹ The CO₂ uptake efficiency might affect the natural sampling processes of ice surfaces and therefore the ice core records of the past atmospheric CO₂ changes.² Possible storage of CO₂ as a gas hydrate is a subject of keen environmental research.³ Also, CO₂ exists along with ice in a variety of places in low temperature environments, including the terrestrial atmosphere, Mars, the moons of Jupiter, and dense clouds in interstellar space.^{4–7}

The interactions of CO₂ with aqueous solutions have been extensively studied and well documented.⁸ CO₂ hydrolysis in neutral or acidic aqueous solutions can be described by the following reaction.



The first step of the reaction is slow and requires an activation energy of substantial magnitude.^{9,10} Indeed, the concentration of “carbonic acid” (H₂CO₃) is less than 1% of the total concentration of the whole dissolved CO₂ species, and H₂CO₃ can be considered to be an intermediate in the net reaction producing HCO₃[−]. At high pH, CO₂ hydrolysis is strongly catalyzed by OH[−]. The reaction involves the direct nucleophilic attack of OH[−] as a critical step.



The activation energy for this reaction is measured to be 55.6 kJ mol^{−1} over the temperature range of 0 to 40 °C in aqueous solution,¹¹ while it is calculated to be zero in the gas phase.¹² This suggests that the activation energy in aqueous solution may come from the solvation of OH[−], and such a conjecture is confirmed theoretically by the reference interaction site model SCF (RISM-SCF) method¹³ and ab initio molecular dynamics study.¹⁴ Yang and Castleman¹⁵ have observed that the gas-phase reactions of CO₂ with hydrated hydroxides [OH[−](H₂O)_{*n*}] proceed with zero activation energy when the hydration number *n* is small, which can be regarded as indirect evidence for the zero activation energy of the reaction between CO₂ and OH[−] in the gas phase.¹⁶ In the living organisms, reaction 2 is accelerated by the catalytic action of carbonic anhydrases, the mechanism of which is rather complicated but is considered to avoid the solvation of OH[−] in the enzymatic active site, thereby lowering the energy barrier.¹⁷

An interesting medium for the study of reaction 2 will be ice films prepared in a vacuum at low temperature. Water molecules undergo restricted thermal motions at the ice surfaces, and the solvation of reactants and products may occur only to a partial extent.^{18–20} From the viewpoint of water solvation, the reactivity of CO₂ toward OH[−] in such an environment is expected to be somewhere between that of the fully solvating situation in liquid water and that of no solvation in the gas phase.²¹ Therefore, reaction 2 may be anticipated to be plausible at ice surfaces, if the solvation of OH[−] is averted for some reason so that the activation energy barrier can be greatly reduced. In addition, the sticking probability of CO₂ gas is higher for ice surfaces at low temperature than for liquid water surfaces at room temperature.²² The increased residence time of CO₂ at the ice surfaces might also increase the probability for subsequent

* Corresponding authors. E-mail: surfion@snu.ac.kr. Fax: +82 2 889 8156 (H.K.) and cleee@ajou.ac.kr (C.-W.L.).

[†] Seoul National University.

[‡] Ajou University.

reaction. On the other hand, the opposite effect may also be expected that CO_2 hydrolysis is hampered by restricted molecular movements at ice surfaces at low temperature. Theoretical aspects of CO_2 gas interacting with ice surfaces have been a subject of increasing research effort in recent years.^{23,24}

Experimental studies of the interactions of CO_2 with ice surfaces have been carried out by several researchers to date.^{3–6,25–29} Deposition, diffusion, and sublimation of CO_2 –water ices have been investigated by using the techniques of temperature-programmed desorption (TPD) and IR spectroscopy.^{3–6,25,26} The studies provide estimates of the activation energy for CO_2 desorption from ice surfaces, which ranges from 21 to 25 kJ mol^{-1} for amorphous ice^{5,26,27} and from 20 to 21 kJ mol^{-1} for crystalline ice.^{26,28} Souda has investigated the intermolecular interactions between CO_2 and water molecules by monitoring the wetting, dewetting, and intermixing processes of CO_2 –water ices by using time-of-flight secondary ion mass spectrometry (TOF-SIMS).²⁹ Andersson et al. have examined the collision and trapping of CO_2 molecules at ice surfaces with molecular beam techniques.²⁸ In the present paper, we study the interactions of CO_2 with ice film surfaces prepared in either a neutral or basic condition. Emphasis is given for exploration of the reactivity of CO_2 toward excess hydroxide ions at ice surfaces. Surface chemical species derived from CO_2 adsorption are inspected by using the techniques of RIS and LES, and the desorbing species are examined with TPD.

Experimental Section

The experiment was carried out in an ultrahigh vacuum (UHV) surface analysis chamber described in detail in ref 30. Ice films were grown on the (0001) face of a Ru single crystal by a back-filling method at a water vapor pressure of 1.0×10^{-8} Torr. This procedure produced a nonporous, amorphous ice film at the deposition temperature of 130 K, and a crystalline ice film at 140–145 K.³¹ The thickness of ice films was typically 4 bilayers (BLs) as deduced from TPD experiments. D_2O was used for growing ice films instead of H_2O , because D_2O does not dissociate in the first chemisorbed layer on Ru(0001).³² An additional advantage of a D_2O -film was the easy monitoring of unwanted residual H_2O adsorption on the film surface.

After the preparation of an ice film, the sample temperature was lowered to 80 K to adsorb CO_2 gas. CO_2 gas was introduced through a tube doser positioned 10 cm apart from the surface, and the CO_2 local pressure near the surface was estimated to be about 5×10^{-8} Torr. The amount of adsorbed CO_2 molecules was determined from TPD experiments, as described in the literature.²⁶ The deposition of Na vapor onto an ice film was done by using a commercial alkali-metal dispenser (SAES Getters Inc.). The surface coverage of Na atoms was determined by recording TPD spectra as a function of Na deposition time.³³ The Na coverage is given in units of monolayer equivalents (MLE) on the ice film surface, where 1 MLE corresponds to the full monolayer coverage of Na on a bare Ru(0001) surface, i.e., 53% of surface Ru atoms. The rate of Na deposition was about 0.1 MLE per minute. The temperature of a Ru substrate was measured by using a K-type thermocouple with an accuracy of ± 0.1 K and controlled with a PID (Proportional-Integral-Derivative) temperature controller (Eurotherm).

Neutral and ionic species present at the ice film surfaces were identified by making use of the RIS and LES methods, respectively.^{20,30} In these experiments, a low-energy Cs^+ beam collided with the sample surface to be analyzed, and the positive and negative ions emitted from the surface were detected by a quadrupole mass spectrometer (QMS; ABB Extrel) with its

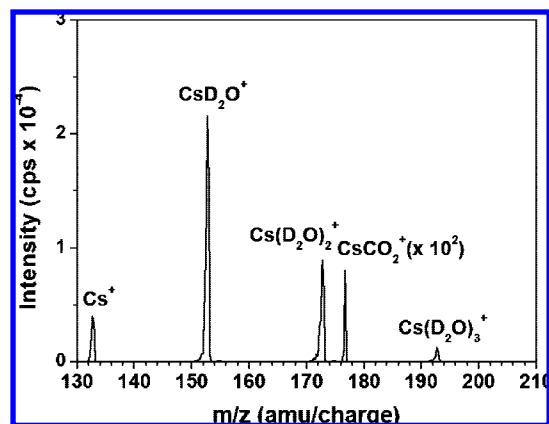


Figure 1. RIS mass spectrum taken from a D_2O -ice film covered with 0.2 ML of CO_2 . The ice film was deposited to be about 4 BL thick at a temperature of 130 K and then exposed to CO_2 gas at 80 K. The spectrum was acquired at 80 K with a Cs^+ beam of 35 eV energy. The CsCO_2^+ peak is shown on the magnified intensity scale.

ionizer filament switched off. The ions detected were composed of reflected Cs^+ primaries, RIS ions in the form of association products (CsX^+) of scattered Cs^+ with neutral molecules (X) present at the surface, and LES ions emitted as a result of sputtering of the ions preexisting at the surface. Thus, the RIS and LES signals reveal the identities of molecular neutrals and ionic species, respectively, present at the ice film surface. The mechanisms of RIS and LES processes on thin ice films have been investigated.²⁰

The incident energy of a Cs^+ beam was chosen to be 35–50 eV and the beam current density was controlled as low as 1 nA/cm^2 . The beam incidence and detector angles were both fixed at 45° with respect to the surface normal. The spectral acquisition time was typically 10 s, during which the surface damage or contamination by a Cs^+ beam was negligible. When a longer acquisition time was necessary, the accumulated dose of the Cs^+ beam was reduced by moving the beam to new positions on the sample surface or by making the measurements on fresh samples. The probing depth of LES and RIS measurements was 1 BL on ice films at the incident energy of 35 eV. The probing depth increases greater than 1 BL at the incident energy above 50 eV, with accompanying increase in the probability of causing secondary ionization of adsorbates.

Results

In this section we present the RIS and LES spectra obtained with nonporous, amorphous ice films grown at temperature of 130 K, unless specified otherwise, and these samples will be called “ice films” in the text hereafter. Crystalline ice films prepared at 140–145 K produced basically the same RIS and LES features as those from nonporous amorphous films with regard to the interaction with CO_2 . Therefore, the spectra and their interpretations to be presented below are equally valid for crystalline ice films as well. Figure 1 shows the RIS mass spectrum taken from a D_2O -ice film adsorbed with 0.2 ML of CO_2 gas at a temperature of 80 K. At mass-to-charge ratios higher than m/z 133 amu/charge of the reflected Cs^+ ions, a series of RIS peaks appear due to the pickup of n D_2O molecules by Cs^+ projectiles [$\text{Cs}(\text{D}_2\text{O})_n^+$ at m/z 153 ($n = 1$), 173 ($n = 2$), and 193 ($n = 3$)]. Another peak at m/z 177, corresponding to CsCO_2^+ , verifies the adsorption of CO_2 molecules on the film surface at 80 K. This signal is much weaker than the $\text{Cs}(\text{D}_2\text{O})_n^+$ signals, because the RIS efficiency for picking up a nonpolar CO_2 molecule is smaller than that for a polar water molecule.

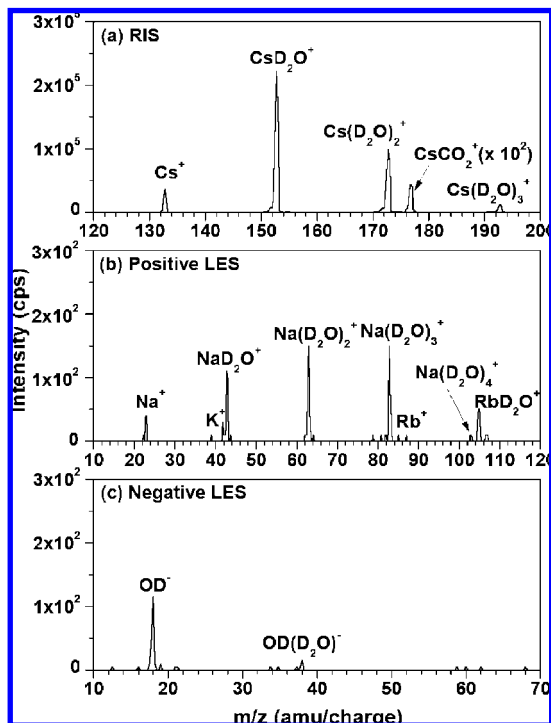


Figure 2. Mass spectra obtained from a D₂O-ice film exposed in sequence to Na and CO₂ vapors: (a) RIS, (b) positive LES, and (c) negative LES measurements. Na vapor was deposited onto a D₂O-ice film at 130 K for Na coverage of 0.2 MLE. The exposure to CO₂ gas followed for a coverage of 0.2 ML at 80 K. The measurements were made at 80 K with a Cs⁺ beam of 35 eV energy.

The LES spectra taken from the same sample surface (not shown) do not reveal any sign of preexisting ions at the surface. In the negative ion LES spectra, an OD[−] peak appears at m/z 18. However, this peak has very weak intensity, which is about equal on both neat and CO₂-adsorbed ice films. Thus, it is attributed to OD[−] produced by the collision-induced ionization of D₂O molecules, not related to the hydrolysis of CO₂ at the ice surface.

In Figure 2, Na vapor was deposited onto a D₂O-ice film at a temperature of 130 K to provide excess hydroxide ions, and then CO₂ was adsorbed on the surface at 80 K. The RIS spectrum taken from this surface, shown in Figure 2a, is nearly identical to that in Figure 1a. The only small difference is that the CsCO₂⁺ signal intensity is weaker in Figure 2a. Figure 2b shows the positive ion LES spectrum, where new peaks appear at m/z 23 + 20 n amu/charge with n = 0–4, corresponding to Na⁺ and a series of its hydrates. The small K⁺ and Rb⁺ peaks are due to the scattering of alkali ion impurities in the Cs⁺ beam.

The negative ion LES spectrum in Figure 2c shows OD[−] peak at m/z 18 and its hydrated signal at m/z 38 [OD(D₂O)[−]]. The OD[−] intensity (~120 cps) is much higher than that measured from a neat ice film in the absence of Na adsorption (~25 cps). The increased OD[−] intensity and the appearance of Na⁺ and its hydrated peaks indicate that Na atoms are hydrolyzed at the ice surface to produce Na⁺ and OD[−] ions, in agreement with literature reports.^{34–36} In addition, the strong OD[−] intensity indicates that OD[−] ions have a substantially high population at the surface.³⁷

Panels b and c of Figure 2 reveal no ionic species derived from CO₂ adsorbates, including DCO₃[−]. This indicates that CO₂ does not react with OD[−] on the surface. Here, one might suspect the detectability of DCO₃[−] by LES. To check this possibility, we bombarded the ice film with high-energy (150 eV) Cs⁺

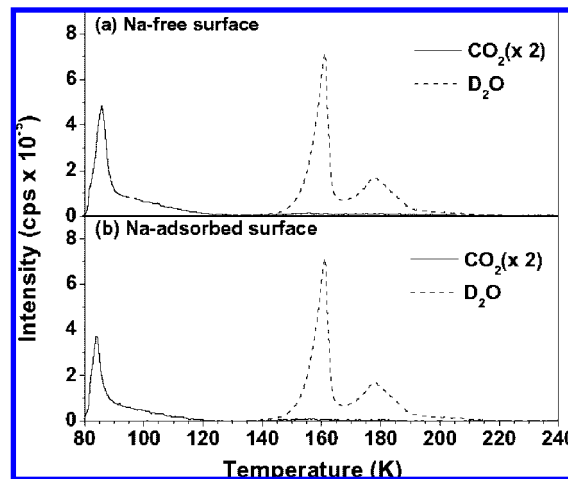


Figure 3. TPD spectra of D₂O (dashed lines) and CO₂ (solid lines) measured from D₂O-ice films exposed to CO₂. Panel a shows the result from a CO₂/D₂O-ice film, prepared with the same procedure as that in Figure 1. Panel b corresponds to the result from a CO₂/Na/D₂O-ice film, prepared with the procedure described in Figure 2. The temperature ramping rate is 1 deg s^{−1}.

beams for 5 min, a procedure that can generate various impact-induced secondary products including DCO₃[−] at the film surface. Subsequent LES analysis of the surface at 30 eV showed a clear signal of DCO₃[−], indicating that this species can be well detected by LES. In addition, we raised the Cs⁺ incident energy to 50 eV in the analysis of the ice film in Figure 2, which increased the LES probing depth beyond the first monolayer of the surface. No additional LES peaks appeared in this analysis with the higher energy Cs⁺ beam.

Figure 3 compares the TPD spectra of D₂O and CO₂ measured from ice films prepared in different surface compositions: (a) CO₂ (0.2 ML)/D₂O (4 BL) and (b) CO₂ (0.2 ML)/Na (0.2 MLE)/D₂O (4 BL). The desorption is monitored with the mass spectrometric signals of D₂O⁺ (m/z 20) and CO₂⁺ (m/z 44) created by electron impact ionization (70 eV) of the desorbing flux. The TPD spectra of D₂O are essentially identical for both samples, showing a multilayer desorption peak near 160 K and the first-monolayer desorption peak near 180 K, in agreement with reports in the literature.³² The CO₂ desorption peak appears below 90 K from both samples, with a tail extending to about 120 K. This shows that desorption of CO₂ adsorbates is complete before the onset of water desorption near 140 K. Some CO₂ molecules may be trapped within the ice films and desorb concurrently with water molecules at the higher temperature. However, the portion of the trapped CO₂ molecules is only minute (<5%) in these samples, as estimated from the area under the CO₂ desorption curves. This indicates that diffusion of CO₂ into a nonporous amorphous ice film is inefficient, similar to a crystalline ice film, regardless of the presence or absence of excess hydroxide ions. Such a nontrapping behavior contrasts with efficient CO₂ trapping observed for porous amorphous solid water.²⁶

The TPD peak of CO₂ is shifted only slightly by the adsorption of Na atoms from 86 K in spectrum (a) to 84 K in spectrum (b). The corresponding activation energy for CO₂ desorption is estimated to be 23 kJ mol^{−1} in spectrum (a) and 22 kJ mol^{−1} in spectrum (b) by using the Redhead analysis³⁸ and assuming the first-order desorption kinetics with a pre-exponential factor of 10^{13.32} s^{−1}.²⁸ These desorption energies are within the range of the literature values for CO₂ desorption from bare ices.^{5,26–28} The area of the CO₂ desorption peak is

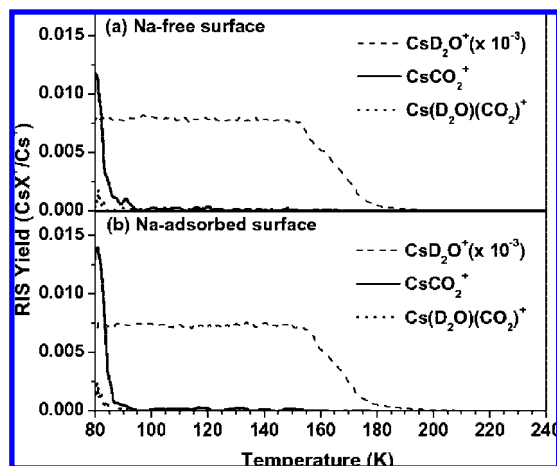


Figure 4. TP-RIS spectra measured for the chemical species of interest that exist at the surface of D_2O -ice films exposed to CO_2 . Panels a and b are for the Na-free and Na-adsorbed films, respectively. The films for panels a and b were prepared in the same procedure as described in Figures 1 and 2, respectively. The RIS yield is defined as the intensity ratio of the RIS products to reflected Cs^+ primaries. The temperature ramping rate is 1 deg s^{-1} .

reduced by 24% from spectrum (a) to (b). This suggests that the presence of Na adsorbates decreases the sticking probability of CO_2 gas on the surface. Na does not desorb from the surface in the temperature scan range of Figure 3. The TPD signal of Na^+ appears at 900–1000 K from sample (b), which matches with the TPD result of Na adsorbed on a bare Ru(0001) surface.³³

Figure 4 shows the result of temperature-programmed RIS (TP-RIS) experiments, which measure the temperature-dependent variation in the surface populations of chemical species of interest. TP-RIS and TPD experiments are complementary,^{30b} giving information on the species present at the surface and desorbing from the surface, respectively. In the figure, TP-RIS results are shown for the Na-free ice film (Figure 4a) and the Na-adsorbed film (Figure 4b). The temperature scan is made between 80 and 240 K, and the surface population of chemical species is indicated by its RIS yield, defined as the intensity ratio of the RIS products to reflected Cs^+ ions. For both samples, the RIS yield for $CsCO_2^+$ decreases sharply between 80 and 90 K to become basically zero above 95 K. The drop in the surface population of CO_2 in this temperature range matches nicely with the CO_2 desorption feature shown by TPD curves in Figure 3. The surface population of CO_2 stays zero at the higher temperatures. This confirms the TPD observation in Figure 3 that CO_2 desorbs completely from the surface above 95 K, with an insignificant amount of CO_2 diffusion into the film. Importantly, the TP-RIS spectra of $CsCO_2^+$ are identical in panels a and b of Figure 4 over the entire temperature range. This implies that Na exposure and the OD^- species thereupon created at the surface do not significantly affect the nature and binding strength of CO_2 at the ice surface.

The TP-RIS measurements also trace the signal at m/z 197, which can be assigned as either $CsD_2CO_3^+$ or $Cs(D_2O)(CO_2)^+$. This signal is too weak to be recognized as a peak in a RIS spectrum recorded in the normal mass-scanning mode, like those shown in Figures 1 and 2. The signal-to-noise ratio is enhanced in the TP-RIS mode, because RIS signals can be accumulated for a longer collection time at only a few preselected masses. We preferably assign the m/z 197 signal to be $Cs(D_2O)(CO_2)^+$ rather than $CsD_2CO_3^+$, because molecular carbonic acid (D_2CO_3) is known to be extremely unstable upon contact with

even a single water molecule in the gas phase.³⁹ This interpretation is supported by the observation that the TP-RIS curves of this signal and $CsCO_2^+$ vary similarly during the scan for 80–90 K, in which CsD_2O^+ intensity stays invariant. This behavior is best explained by assuming a double RIS process, in which $Cs(D_2O)(CO_2)^+$ is formed as a result of the pickup of both D_2O and CO_2 adsorbates by a Cs^+ projectile. In this case the RIS product intensity will be proportional to the surface populations of both CO_2 and D_2O , and in turn to CO_2 only because D_2O population is fixed. Were this signal indicative of carbonic acid, the TP-RIS curve would appear differently.

We searched for the presence of other plausible species that can be formed by the reaction of CO_2 with hydroxide ion or water molecule, including DCO_3^- and CO_3^{2-} . None of these ions was observed in the temperature-programmed LES measurements with Na-free and Na-adsorbed ice films in the entire temperature range of investigation (80–240 K). Specifically, only OD^- and Na^+ signals and their hydrates resulting from Na hydrolysis were detected by LES. The ionic products of interest mentioned above, if they were formed, would remain most likely at the surface of an ice film without desorption or inward migration at temperature below 100 K, because the diffusion of ionic species is extremely difficult at the low temperature.⁴⁰ We also examined if these species of interest were trapped within the ice film rather than being formed at the surface. When we scan the film temperature across the ice sublimation region (140–180 K), water molecules in the physisorbed upper layers desorb first, followed by desorption of chemisorbed water molecules. Therefore, at a certain stage of the temperature scan where only the chemisorbed D_2O layer remained on the Ru surface, nonvolatile species trapped within the ice film would become exposed to the film surface to be detectable by LES and RIS. This experiment did not detect any hydrolysis product either. These results, altogether, indicate that CO_2 is not hydrolyzed at the surface or interior of the ice films. Control experiments performed with H_2O -ice films showed TP-RIS results similar to Figure 4, indicating that the present results were not distorted by isotope effects.

Discussion

According to the results in the previous section, the adsorption of CO_2 on a neat ice film does not form CO_2 –water complexes nor hydrolysis products. The result suggests that CO_2 hydrolysis cannot be facilitated solely due to an increase in the sticking coefficient and surface residence time of CO_2 at ice surfaces, and thermal activation is additionally needed to initiate the reaction. The observation goes in harmony with results of the investigations of CO_2 interacting with solid water surfaces,^{23–29} and the extrapolation from known properties of liquid water surfaces.^{8,22,41} Gas uptake measurements²² and vibrational sum frequency spectroscopic study⁴¹ suggest that CO_2 –water complexes do not form at gas–liquid water interfaces.

On the other hand, it is rather surprising that CO_2 does not react with excess hydroxide ions at the ice surfaces, because in a basic aqueous solution the dissolved CO_2 molecule reacts promptly with excess OH^- to form HCO_3^- . (In the following discussion, hydroxide ion is represented by the formula OH^- instead of OD^- for consistency; the isotope effect is negligible in the present result as mentioned above.) Reaction 2 is even more facile in the gas phase because of zero activation energy due to the absence of water solvation.^{12–14} Thus, a similar trend may be anticipated for the ice surfaces where water solvation occurs only partially.²⁰ Reaction 2 has an equilibrium constant of $K_{eq} = 2.66 \times 10^7 \text{ M}^{-1}$ in liquid water at 298 K, its value

slightly increasing with decreasing temperature ($1.75 \times 10^8 \text{ M}^{-1}$ at 273 K).⁸ From the absence of hydrolysis products in the present experiment, we estimate the upper limit of the quotient Q for reaction 2 at the ice surface: $Q < 1 \times 10^{-3} \text{ M}^{-1}$.⁴² Apparently, there is a large discrepancy between the K_{eq} and Q values, and this gap is difficult to reconcile just by the temperature difference between liquid water and the ice films. Possible reasons for the observed nonreactivity of CO_2 toward hydroxide ion at the ice surfaces will be discussed in the remaining part of this section.

Previous studies of reaction 2 in aqueous solution^{12–14} suggest that the activation energy for the reaction comes mostly from the solvation of OH^- . OH^- is hydrogen bonded to four water molecules in a quasisquare pyramidal geometry in aqueous solution.¹⁴ During the approach of OH^- to CO_2 , the four hydrogen-bonding water molecules are layered between OH^- and CO_2 . This makes it difficult for the carbon atom of CO_2 to receive an electron pair of the hydroxyl oxygen atom, and therefore creates the activation barrier.

In the ice lattice, OH^- is believed to be incorporated into the extended hydrogen bond network.⁴³ In such an environment, the reaction between OH^- and CO_2 needs to break the extended hydrogen bond network surrounding OH^- , which is presumably more difficult than breaking the first hydration shell of OH^- in aqueous solution. The low solubility of CO_2 in a nonporous ice film, indicated by the TPD result in Figure 4, will make it even more improbable for CO_2 to react with OH^- located inside the ice films.

The strong signal intensity of hydroxide ion in the LES spectrum (Figure 2c) indicates a substantial population of hydroxide ion at the present film surfaces, though its absolute surface coverage is difficult to deduce from the LES intensity alone due to the lack of a proper intensity-calibration standard. These surface hydroxide ions do not easily migrate to the interior of an ice film upon increasing the film temperature.³⁷ Since hydroxide ion is relatively less well surrounded by water molecules at the ice surface, such an environment would reduce the activation energy for reaction 2, as mentioned above. The present result, however, indicates that even surface hydroxide ions are unreactive toward CO_2 .

We interpret that the unreactivity of surface hydroxide ions may be due to their efficient hydrogen bonding at the ice surface. Surface OH^- ions are typically found hydrogen bonded to neighboring water molecules through its oxygen atom, with its hydrogen atom pointing into the gas phase.⁴⁴ In this case, the oxygen atom of OH^- is supposed to be fully hydrogen bonded by neighboring water molecules, i.e., by three water molecules in the tetrahedral ice structure. This is because if the oxygen atom is not fully coordinated, an L-defect is expected to exist next to OH^- . Since the L-defect inherently has a negative charge, it would be energetically unfavorable for OH^- to have an L-defect attached to it.⁴⁵ At present, the only reasonable source of estimation of the activation barrier for reaction (2) with a hydration number n smaller than three may be Figure 5, parts b and c, of ref 14, which display the free energy of the reaction as a function of the hydration number in aqueous solution, not in ice though. The barrier for the reaction associated with losing one hydration number is read to be about half of the barrier for the aqueous reaction, which corresponds to losing two hydration numbers. With the activation energy of $\sim 28 \text{ kJ mol}^{-1}$ (half of the barrier for the aqueous reaction), and a prefactor of $10^{13.32} \text{ M}^{-1} \text{ s}^{-1}$ estimated from the CO_2 desorption rate,²⁸ and $[\text{OH}^-] \approx 8.90 \text{ M}$ corresponding to 1 MLE, the fraction of CO_2 reacted in 1 min is calculated to be 0.01 at 80 K and 1 (completed) at

90 K. (With full activation barrier in aqueous solution expected in the case of full hydration, the calculation shows that no reaction can occur in the temperature range 80 to 140 K.) This calculation predicts that if OH^- at the ice surface has an L-defect attached to it, or in other words, the oxygen atom of OH^- is not fully hydrogen bonded, the reaction can take place easily at temperatures around 90 K and above. Therefore, the unreactivity of surface OH^- toward CO_2 found in this work suggests that the oxygen atom of OH^- at the topmost surface is fully hydrogen bonded by three water molecules.

There may be the possibility that OH^- reactivity is affected by neighboring Na^+ ions in the present experiments. According to the mechanism of Na hydrolysis in ice,^{46,47} Na^+ and OH^- ions can be produced either close to each other or separated, depending on the delocalization of the solvated 3s electron released from the Na atom. If Na^+ and OH^- ions are produced as a contact ion pair, the ability of OH^- for nucleophilic attack on CO_2 will be significantly reduced and this may block the reaction. On the other hand, this effect will be much weakened for isolated OH^- ions produced from Na hydrolysis at low Na exposure. Further study will be necessary to understand the effects of counterion on OH^- reactivity more precisely.

Summary

In this paper, we have studied the interactions of CO_2 molecules with neat D_2O -ice films and those containing excess hydroxide ions at the surface in the temperature range of 80–240 K, with emphasis on the search for plausible hydrolysis products of CO_2 . Chemical species present at the ice film surfaces are identified by LES and RIS, and the desorbing gaseous species are detected by TPD. The possible presence of nonvolatile species trapped in the ice films is inspected by TP-RIS, which performs the real-time analysis of surface species while the film temperature is scanned across the ice sublimation region.

CO_2 adsorption on a neat ice film does not lead to the formation of CO_2 –water complexes nor hydrolysis products. The interaction of CO_2 with hydroxide ion is also examined, for which excess hydroxide ions are produced on the ice film by the hydrolysis of Na atoms and then CO_2 is adsorbed on the surface. Inspection of this surface for possible products of CO_2 hydrolysis and comparison with the observation made from the inert, neat ice film reveal that CO_2 does not react with hydroxide ion at the ice film surface or in the interior. The CO_2 molecule desorbs cleanly from these ice films, with only a very small portion of CO_2 molecules diffusing into the films to become trapped.

The nonreactivity of CO_2 toward hydroxide ion at the ice surface provides a vivid contrast with facile occurrence of this reaction in the gas phase or aqueous solution. The ice surface effectively blocks CO_2 hydrolysis probably because hydroxide ion is efficiently hydrogen bonded at ice surfaces, perhaps to a full extent by bonding with three nearest-neighbor molecules, which reduces the intrinsic ability of hydroxide ion for nucleophilic attack on CO_2 . The effect of Na^+ ion on the reactivity of hydroxide ion will need further study.

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