Entropy-Driven Spontaneous Reaction in Cryogenic Ice: Dissociation of Fluoroacetic Acids

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Supporting Information

ABSTRACT: Chemical reactions are extremely difficult to occur in ice at low temperature, where atoms and molecules are frozen in position with minimal thermal energy and entropy. Contrary to this general behavior, certain weak acids including fluoroacetic acids dissociate spontaneously and more efficiently in cryogenic ice than in aqueous solution at room temperature. The enhanced reactivity of weak acids is an unexpected consequence of proton-transfer equilibrium in ice. The configurational entropy of protons in ice shifts the acid dissociation equilibrium forward. This configurational entropy, although a solid-state property, is comparatively large in magnitude with the entropy of vaporization and can effectively drive proton-transfer reactions in ice.

Ice is far more abundant than liquid water in the universe and plays an important role as media for chemical transformation in terrestrial and extraterrestrial environments at low temperatures.1–4 According to conventional knowledge, chemical reaction is extremely difficult to occur spontaneously in ice at low temperature because of the lack of enough thermal energy to surmount the reaction energy barrier, not to mention the immobility of atoms and molecules in the cryogenic solid. For this reason, external energy sources are considered necessary to make reactions occur in cryogenic ice environments. For example, chemical transformations taking place in outer planets of the solar system or interstellar ice particles have been modeled in terms of the reactions induced by ultraviolet (UV) radiation or energetic particle bombardment.1–3 Contrary to such expectation, we observe that certain reactions do occur spontaneously in ice, even at very low temperature. Fluoroacetic acids, which hardly dissociate in aqueous solutions at room temperature, dissociate almost completely in ice at 8–140 K. Our observation shows that the enhanced dissociation of weak acids in ice is an unexpected result of proton-transfer equilibrium between the acids and ice. Protons released from the acids into ice increase the configurational entropy of the system and make the acid dissociation equilibrium shift in the forward direction, although most constituent molecules are frozen in position in this cryogenic environment. We expect that this entropic effect may operate for a variety of physical and chemical phenomena involving proton transfer in ice.

We prepared a mixture of acid and D₂O in solid form by condensing their vapors onto a Pt(111) substrate at low temperature inside an ultrahigh vacuum chamber. The acid–D₂O mixture in the form of a thin film (thickness 40–80 monolayers; MLs) was sandwiched between two D₂O spacer layers (thickness 20–30 MLs) to protect the acid molecules from being exposed at the sample surfaces. Reflection absorption infrared spectroscopy (RAIRS) was used to detect molecular and dissociated forms of the acids. The temperature of the sample was controlled between 8 and 160 K during preparation and spectroscopic characterization. The morphology of solid D₂O varied depending on the preparation temperature, from amorphous solid water (ASW) typically at <120 K to crystalline ice at >140 K.5,6 In the following discussion, we use "ice" as the generic term for all forms of solid water, without morphological distinction.

Figure 1 shows RAIR spectra of acid–D₂O samples for monofluoroacetic acid (MFA; pK_aq = 2.82; spectrum a), difluoroacetic acid (DFA; pK_aq = 1.34; spectrum b), and trifluoroacetic acid (TFA; pK_aq = 0.50; spectrum c) measured at 70–80 K. The spectrum of a pure DFA sample is also shown for comparison (spectrum d). The ν(O-H) stretch band of molecular carboxylic acid appeared around 1770 cm⁻¹ in the pure DFA spectrum. This molecular acid band was absent from the spectra of the mixture samples for all acids (spectra a−c). At the same time, the sharp ν(C = O) band at ~1650 cm⁻¹, which is characteristic of a molecular carboxylic group, changed to the CO band shape of carbonate anions in the 1600–1800 cm⁻¹ region in spectra a−c.8,9 These changes clearly indicate that molecular acids dissociated to H⁺ and carbonate anion in ice at 70–80 K.

Other changes include the appearance of the ν(O-H) stretch band of HDO at ~3300 cm⁻¹ for the mixture samples. This signal had two contributions. One was the formation of


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HDO by H/D exchange reaction of acid and D₂O in the sample. This HDO species forms when proton transfer occurs in D₂O–ice in conjunction with water reorientation, which requires thermal activation.⁰¹ Therefore, the intensity of this band varied with sample temperature. The other source was the deposition of residual HDO gas in the chamber during sample preparation.

We examine the effect of temperature on acid dissociation by varying the sample preparation and characterization temperatures between 8 and 140 K for the mixture samples of MFA, DFA, and TFA (spectra shown in Supporting Information Figures S1–S3). Spontaneous dissociation was observed for all acids at different temperatures examined (8, 60–80, and 140 K). The spectra were basically identical to those shown in Figure 1 in major features, including the disappearance of the ν(O–H) stretch band of molecular acids and the appearance of the carboxylate anion bands. At 140 K, the spectrum showed other minor changes (Supporting Information Figure S1), including the change of the bulk ν(O–D) band shape due to the crystallization of ice⁰³ and the increase in the ν(O–H) band of HDO due to H/D exchange reactions.⁰⁰,⁰¹ These observations showed that the spontaneity of acid dissociation was unaffected by temperature changes between 8 and 140 K.

The dissociation yield (α) of acids can be estimated from the change of the acid ν(O–H) intensity at ~3050 cm⁻¹ in a straightforward manner because this band does not exist for carboxylate anion. The absence of the ν(O–H) intensity in spectra a–c indicated almost complete dissociation (α > 0.9) of the acids, where the lower limit of α was determined solely by the background noise level of the spectrum. The spectra at 8 and 140 K showed a similar acid dissociation yield. In an aqueous solution at a similar acid concentration (4%), the dissociation yield ranged from α = 0.03 (MFA; pKₐₐ = 2.82) to 0.3 (TFA; pKₐₐ = 0.50). These observations suggest that dissociation yield in ice is much greater than that in aqueous solution.

Weaker acids than those discussed above were also examined. Figure 2a shows the spectrum of a mixture film of formic acid (FA; pKₐₐ = 3.75) and H₂O, which was prepared at 80 K and heated to 140 K. The spectrum of a pure FA film is shown overlapped. The FA–H₂O mixture sample showed the ν(O–H) stretch (2584, 2752, and 2924 cm⁻¹) and ν(C=O) (~1710 cm⁻¹) bands of molecular FA, with their shape and intensity remaining little changed from that of a pure FA sample. The spectrum of a sample as prepared at 80 K (not shown) was almost identical to that shown in Figure 2a. Therefore, FA did not dissociate in the ices. The dissociation yield of FA in ice was estimated to be <0.1 based on the spectral intensities. Acetic acid (AA; pKₐₐ = 4.76) did not dissociate in ice either.⁰¹ These observations located the boundary of spontaneous dissociation of carboxylic acids in ice to be between pKₐₐ = 2.82 and 3.75 in terms of the acidity scale in aqueous phase.

Figure 2b shows the spectrum of a FA–D₂O mixture sample as prepared at 80 K (blue line) and after heating at 140 K (magenta line). The ν(O–H) stretch bands (2752 and 2924 cm⁻¹) of molecular FA were visible at 80 K on the slope of the intense bulk ν(O–D) band but were absent after heating to 140 K. The ν(C–H) band of FA became visible in this region after disappearance of the ν(O–H) bands. Interestingly, the ν(O–D) bands (2050 and 2188 cm⁻¹) of HCOOD, and the ν(O–H) band (~3300 cm⁻¹) of HDO appeared at 140 K. Despite these changes, the acid ν(C=O) band at ~1710 cm⁻¹ remained invariant from 80 to 140 K. These spectral features indicate that FA underwent efficient H/D exchange with D₂O to form HCOOD and HDO at 140 K, although apparently FA did not dissociate. This behavior resembles the dynamic equilibrium of weak acids in aqueous solutions, suggesting that FA is in proton-transfer equilibrium with ice. The proton transfer between FA and water may readily occur at 80 K also, although HCOOD and HDO are not formed at this temperature because of the nonoccurrence of thermal reorientation of water.⁰⁰,⁰¹ This can be inferred from the spontaneous dissociation of fluoroacetic acids at this temper-
The thermodynamic driving force underlying the enhanced dissociation of acid in ice is discussed. In aqueous solution at room temperature, dissociation of carboxylic acid is governed mostly by solvation effects. However, cryogenic solid water does not effectively solvate dissociated ions or screen their charges because of the low dielectric constant ($\varepsilon_r \approx 2$). Therefore, the acid dissociation is not expected to be more favored in ice than in aqueous solution in terms of the energy of reaction. The dissociation equilibrium of carboxylic acids exhibits a very small temperature dependence in aqueous solution at $273-333$ K. Extrapolation of this temperature dependency known for some of these acids to a hypothetical aqueous phase at $70$ K does not predict the dissociating behavior of the acids observed in ice.

For the dissociation of acids to maintain quasi-equilibrium in ice, mobile species must play a role. Protons that are released from the acids into ice are uniquely mobile species in low-temperature ice. These excess protons migrate along the H-bonded network of the ice lattice with negligible energy barrier by means of a concerted proton hopping process (Grotthuss mechanism). The extremely high mobility of excess protons in ice was reported by Eigen and supported by more evidence from later studies. The proton hopping increases the configurational entropy of protons by $\Delta S_{\text{conf}} = k \ln W_{\text{ice}}$ where $W_{\text{ice}}$ is the number of accessible positions in the ice lattice by mobile protons. This entropy gain may shift the acid dissociation equilibrium forward and increase the dissociation yield. Two aspects of the proton migration in ice may be emphasized. First, excess protons can move only along the direction of water chain with proper H-bond polarization. Consequently, protons roam in random direction in the ice lattice through available transport paths. Protons may also oscillate in the water chain. This is because proton passage reverses the H-bond polarization of the chain, which facilitates backward proton transfer along the same path. In any case, the proton hopping process alone does not induce macroscopic polarization in the sample. This is a different situation from charge conduction through ice that is driven by external bias voltage at high temperature and causes macroscopic polarization. Second, because the sample remains macroscopically unpolarized, proton migration does not change the configurational entropy (residual entropy) of the proton-disorder structure of the ice lattice.

The effect of $\Delta S_{\text{conf}}$ of excess protons on the dissociation equilibrium can be estimated based on the thermodynamic expression of equilibrium constant ($K$)

$$K = \exp(\Delta S/R) \exp(-\Delta H/RT)$$

where $\Delta S$ is the entropy for acid dissociation, which includes the $\Delta S_{\text{conf}}$ of excess protons as well as other entropic terms, and $\Delta H$ is the enthalpy of the reaction. For the sake of simplicity, we consider only the effect of $\Delta S_{\text{conf}}$ of protons on the equilibrium constant in comparing the reactions in ice and aqueous solution. This assumes that $\Delta H$ and other entropy changes than $\Delta S_{\text{conf}}$ of protons do not differ significantly for the reactions in ice and liquid water. Then, the ratio of the acid dissociation constants in two environments can be expressed as

$$K_{\text{ice}}/K_{\text{aq}} = W_{\text{ice}}/W_{\text{aq}}$$

where $W$ is the number of accessible positions for excess protons in each corresponding environment. For an aqueous solution, we may consider that $W_{\text{aq}}$ has the order of unity because excess protons can form stable protonated water clusters such as the Eigen structure, at least momentarily on a time scale (<1 ps) shorter than dynamic rearrangement of proton solvation structure. On the contrary, proton hopping in ice occurs faster and does not require significant changes in the ice lattice structure. In this case, $W_{\text{ice}}$ may be estimated from the distance of proton migration in ice. For amorphous ice films prepared at $70-80$ K (similar to those shown in Figure 1), excess protons migrate across a distance of $5-20$ water layers in one direction. For the present samples we simply assume that the proton migration distance is $\sim 10$ water molecules in one direction, which means that a 3D1 volume of $\sim 10^3$ water molecules is accessible by a mobile proton. Each water molecule in the ice lattice has two possible positions to accept a proton, and protons are indistinguishable. This gives an estimate of $W_{\text{ice}} \approx 2 \times 10^3$ for a proton in the ice lattice and, in turn, the enhancement factor of $K_{\text{ice}}/K_{\text{aq}} \approx 2 \times 10^3$. This ratio for amorphous ice could be increased for crystalline ice because proton migration distance increases with increasing crystallinity of a sample.

The estimated enhancement factor of $\sim 10^3$ for acid dissociation in ice qualitatively agrees with observations that acids with $pK_{\text{aq}} < 2.9$ (MFA, DFA, and TFA) dissociate in ice, whereas acids with $pK_{\text{aq}} > 3.7$ (FA and AA) do not. Although this estimation for $K_{\text{ice}}/K_{\text{aq}}$ involves substantial uncertainty due to assumptions used, this agreement well supports that the configurational entropy of protons is an important thermodynamic force responsible for the enhanced dissociation of acids in cryogenic ice.

High proton mobility and associated configurational entropy are intrinsic properties of ice. Therefore, the configurational entropy of protons may operate for a range of ice-related phenomena involving proton transfer. For example, hydrolyses of HF ($pK_{\text{aq}} = 3.2$) and SO$_2$ ($pK_{\text{aq}}$ of H$_2$SO$_3 = 1.9$) in ice at low temperature have been observed. Ayotte and coworkers explained this reactivity of HF in ice by suggesting that HF is intrinsically a strong acid; its weak acidity in aqueous solution results from the large negative entropy of F$^-$ hydration. The present argument of configurational entropy of protons may also explain the reactivity of HF in ice; the configurational entropy generated by proton transfer in ice reduces the amount of negative entropy change for the hydrolysis of HF. It may be expected that the configurational entropic effect facilitates proton-transfer reactions in diverse ice environments in nature, such as the Earth’s upper atmosphere, outer planets of the solar system, and interstellar clouds. It has been assumed that chemical transformations in these environments proceed via external excitation mechanisms such as UV absorption, energetic particle bombardment, or thermal processing. These reaction models might need to be changed to include the possibility of spontaneous reactions in low-temperature ice. Also, it is of note that the proton entropy is unusually large ($\Delta S_{\text{conf}} = R \ln W_{\text{ice}} \approx 63$ J mol$^{-1}$ K$^{-1}$) despite its solid-phase origin. For example, it is much greater than the residual entropy of ice crystal (3.4 J mol$^{-1}$ K$^{-1}$) and comparable in magnitude to the entropy...
change of the acid dissociation reactions in aqueous solution (which ranges from $-4$ J mol$^{-1}$ K$^{-1}$ for TFA to $-92$ J mol$^{-1}$ K$^{-1}$ for AA)\textsuperscript{18} or the entropy of vaporization of water (109 J mol$^{-1}$ K$^{-1}$). Therefore, the proton entropy can be an effective thermodynamic force for driving reactions in cold ice.

### EXPERIMENTAL METHODS

The experiments were conducted in two ultrahigh vacuum chambers, both equipped with instrumentation for RAIRS and temperature-programmed desorption (TPD) mass spectrometry. In one chamber (A), the sample temperature was variable in the range of 70–1200 K using a closed-cycle helium cryostat and resistive heating.\textsuperscript{27} In the other chamber (B), the temperature was varied between 8 and 1200 K using a closed-cycle helium cryostat with better cooling efficiency and electron bombardment (2 keV) heating.\textsuperscript{27} Frozen molecular films of interest were grown on Pt(111) substrate surfaces cooled at a desired temperature. The experimental procedure was exactly the same in both chambers except the temperature of the sample. The temperature was measured using N-type thermocouple wires connected to the Pt substrate. The surface of Pt was cleaned by annealing at 1200 K and Ar$^+$ ion sputtering. The surface cleanness was checked from the well-known feature of the TPD spectra of a water monolayer adsorbed on the surface.\textsuperscript{5}

Difluoroacetic acid (Aldrich, 98%), trifluoroacetic acid (Aldrich, 99%), formic acid (Aldrich, 98%), acetic acid (Aldrich, ≥ 99.99%), H$_2$O (Milli-Q), and D$_2$O (Aldrich, 99 atom % D) were purified by freeze-and-pump-thaw cycles. Monofluoroacetic acid was prepared by the hydrolysis of ethyl fluoroacetate (Alfa Aesar, 98%).\textsuperscript{28} The molecular films were prepared on the Pt(111) surface by sequential deposition of the corresponding gases, which were introduced into the UHV chambers through variable leak valves. All acid gases were guided close to the Pt substrate by tube dosers, whereas H$_2$O and D$_2$O gases were backfilled. All acid-in-ice films were prepared in a sandwich structure, in which the acid—water (either H$_2$O or D$_2$O) mixture layer (40–80 monolayers; MLs) was located between two pure water layers (20–30 MLs each; the same isotopologue of water used as for the mixture layer) at the bottom and top, to prevent the exposure of the acid on the metal or vacuum interface. The concentration of acids in the films was determined from TPD intensity measurements.

RAIRS measurements were performed using a Fourier transform infrared (FTIR) spectrometer with a liquid-nitrogen-cooled mercury–cadmium telluride detector in grazing angle reflection geometry (84°). The IR beam path outside the UHV chamber was purged with dry nitrogen gas. All RAIR spectra were averaged over 256 times and acquired in 4 cm$^{-1}$ spectral resolution. For better visualization, all spectra were baseline-corrected by subtracting the spectra of pure Xe films with similar optical thicknesses, mainly compensating the sloping baselines caused by the greater negative absorbance with increasing wavenumbers.\textsuperscript{27,30}

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.8b01825.

RAIR spectra of of acid–water mixture samples at different temperatures (8–140 K) (PDF)

### REFERENCES


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Notes

The authors declare no competing financial interest.