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LETTERS

Kinetics of Ice Particle Conversion to the Hydrates of HCl

Nevin Uras-Aytemiz, Charles Joyce, and J. P. Devlin*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74075

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Reaction rates for the conversion of ice nanocrystals within 3-D arrays to mono-, tetra- and hexahydrates of HCl have been determined for different HCl(g) exposure levels and reaction temperatures. The extent of reaction was monitored and the hydrate product identified, using transmission FT-IR spectroscopy. The direct method of observation provides evidence that HCl diffusion through the hydrate encrusting the ice particles is often the rate-limiting factor in the conversion of ice to a hydrate phase. Values for the HCl diffusion coefficient for the mono- and tetrahydrate are reported. By comparison, diffusion of HCl in ice is considered to be a nonfactor in most ice−HCl interactions.

Introduction

It is well established that certain vapors, such as of a strong acid or a Lewis base, including ethers and amines, can react with ice at levels of surface coverage in excess of a monolayer to eventually convert ice to known hydrates of these substances.[1,2] Recently we described the conversion of ice nanocrystals within 3-D arrays to the mono- and hemihydrates of ammonia for temperatures in the range 100 to 128 K.[2] When the chemical activity of NH_3(g) exceeded a minimum level, above that for surface saturation, NH_3 was observed to nucleate a hydrate phase. Subsequently, for conditions such that the supply of NH_3 reaching the 3-D array was the rate-limiting factor, nanoparticles of the monohydrate of ammonia were observed to form. By contrast, when an abundance of NH_3 was made available at the gas−solid interface, the hemihydrate of ammonia formed at a rate determined by the rate of diffusion of NH_3 through the hydrate layer that quickly encrusts the ice particles. The molecular diffusion supplies NH_3 to the reaction zone at the hydrate−ice interface.

The present study was prompted by the great interest in HCl−ice H-bond chemistry[1,3] as well as the above results from the ammonia−ice study.[2] It has been common practice to relate the uptake of HCl(g) by ice to the diffusion of HCl in ice.[1b,4] The ammonia−ice results challenge that view since, by analogy, HCl diffusion in ice is replaced by diffusion through an acid-hydrate product encrusting the ice. It has been noted that the conversion of ice to an acid hydrate slows dramatically following a limited amount of reaction.[1e] In this analogy, a dramatic slowing of reaction is anticipated since a small diffusion coefficient of HCl in the hydrate crust must result in diminishingly slow transport of HCl to the ice−hydrate interface as the crust thickens. Relative to ice film deposits, diffusion distances for extensive conversion of ice nanocrystals to hydrates are usually small. As a consequence, slow diffusion through a hydrate crust does not prohibit the complete conversion of nanocrystals of ice to an amorphous hydrate at quite low temperatures.[1d]

On the basis of TPD data, Sadtchenko et al. proposed a role for diffusion of HCl through a hydrate layer.[5] To further evaluate the importance of HCl diffusion through the crust of a hydrate product, we have determined the reaction rates for the conversion of 3-D arrays of ice nanocrystals to the hydrates of HCl at temperatures ranging from 110 to 135 K and varying levels of HCl exposure, using FT-IR spectroscopy. The spectroscopy of the hydrates of HCl has a considerable history.[1] Infrared spectra of mono-, di-, tetra-, and hexahydrates of HCl have been reported along with assignments of vibrational modes of the hydronium ion and waters of hydration.[1a] On the basis of comparative spectra, it is accepted that different ionic hydrates

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of HCl form under regimes of varying pressure, temperature, and exposure time. For example, if the amount of HCl arriving at the reaction interface (above some minimum temperature (~100 K)) is limited, the product is generally the hexahydrate. By contrast, high exposure regimes give the lower hydrates, particularly at low temperatures. Further, temperatures below ~140 K favor formation of the amorphous rather than crystalline hydrates. Unlike the amorphous hydrates of nitric acid, the amorphous as well as crystalline phases of the HCl hydrates are all dominantly ionic.

Different possible scenarios for particle reaction with the vapors of an adsorbate have been described.[2] For the reaction of HCl with ice nanocrystals in 3-D arrays, likely possibilities can be selected based on the sampling conditions and the results reported for ice particle conversion to ammonia hydrates. Generally, the HCl molecules must diffuse to the array and through passageways between the particles of the array to reach the particle surfaces. During the earliest stages of the conversion of ice particles to hydrate particles, and/or for low HCl pressures, this vapor-phase process may be slower than the diffusion of HCl through the hydrate crust to the ice−hydrate reaction zone within the particles. If this is the case, all HCl molecules that cross the array-vacuum boundary react and, for a constant HCl vapor pressure, the rate law is effectively zero order. However, as reaction proceeds and the crust of product thickens, the transport of HCl through the crust must slow and may become rate determining. Such diffusion control is progressively more pervasive with an increasing size of the ice particles.

However, diffusion within the hydrate crust to the reaction zone can also be rate determining throughout all but the very initial phase of reaction, provided an abundance of HCl is available at the particle surface and reaction at the ice−hydrate interface is rapid. Since HCl is both very reactive and quite volatile, even in the 110−125 K range, this condition can be established by exposing the ice to the saturation vapor pressure of HCl(s). Then the diffusion of HCl through the crust of hydrate product enveloping the particle can be rate determining throughout most of the reaction. Analysis of this case can be based on established equations for conversion of a spherical particle to a new substance through a vapor−particle reaction under diffusion control (i.e., the shrinking core model).[6] The experimental data for NH_3 hemihydrate formation correlated well with these equations,[2] and the new data for HCl will be subjected to a similar test.

Experimental Section

The methodology employed to prepare 3-D arrays of ice nanocrystals has been described.[7] Following the formation of a 3-D array of ice nanocrystals, reaction rate measurements were made after loading an excess amount of HCl(s) into the cluster cell at temperatures in the range 110−125 K, or while providing a flow of HCl(g), at a fixed dynamic pressure of ~0.3 μm, to the cell at temperatures ranging from 130 to 140 K. The former methodology exposed the particles of an array to an abundance of HCl(g) and resulted in the formation of the monohydrate of HCl. The restricted availability of HCl of the latter approach resulted in the formation of either hexahydrate or tetrahydrate, depending on the reaction temperature and extent of particle conversion to the hydrate.

The identity of the reaction products and the extent of the reaction taking place within the arrays on the cluster cell windows were both determined using transmission FTIR spectroscopy. Example spectra of the amorphous monohydrate, tetrahydrate, and hexahydrate of HCl are given in Figure 1. A quantitative measurement of the amount of reacted ice at any stage of reaction was obtained as one minus the particular subtract factor required to null the residual-ice band intensities using the initial bare-ice 3-D array spectrum.[2]

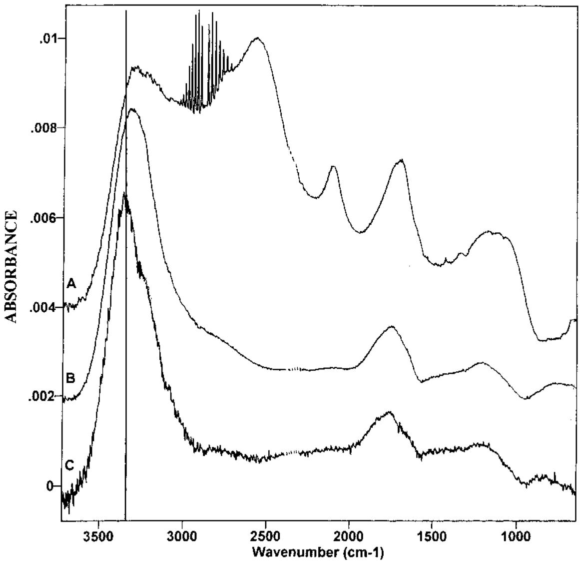

Figure 1. Infrared spectra of (A) monohydrate, (B) tetrahydrate, and (C) hexahydrate of HCl. The sharp bands near 2900 cm^{-1} in (A) are of HCl(g).

Results and Discussions

Conversion of Ice Nanocrystals to HCl Monohydrate Particles. Exposure to the saturation vapor pressure of HCl at 110−125 K converted the ice nanocrystals to the amorphous monohydrate of a known spectrum[1a] (Figure 1). Spectra showing the hydrate product as a function of time at 110 K are presented in the inset of Figure 2. These are difference spectra obtained by nulling the ice spectrum within the sample spectrum for each reaction time as noted in the Experimental Section. The variation of the fraction of reacted ice vs time for four different reaction temperatures is also shown in Figure 2. It should be noted that, when the same sampling method was used to observe the reaction rates of NH_3 with ice particles, constant reaction rates were observed[2] (since the rate-determining step was the availability of NH_3 at the vacuum-array interface). However, with the equilibrium vapor pressure of HCl(s) much greater than for NH_3(s), the reaction rates decrease smoothly with time, consistent with a rate dependent on diffusion through the hydrate crust.[2,6]

Conversion of Ice Nanocrystals to Tetra- and Hexahydrates of HCl Particles. For relatively higher temperatures (130−135 K) and lower levels of HCl exposure, the ice particles were converted to higher hydrates of HCl. Representative rate data are presented in Figure 3 along with spectra obtained by nulling the ice band intensities within the spectra of the partially reacted array. Attention is called to a sudden change in the form of the rate plot. After a smooth decrease in rate for the first ~1.7 h, a sudden increase in the reaction rate was observed. A similar jump in rate was also noted for a second run at the same temperature. The cause of this sudden jump in rate is clear from the spectra of the inset compared to those of Figure 1. Initially the product was the amorphous hexahydrate but, with ~50% of the ice converted, the tetrahydrate became the dominant product.

If the diffusion of HCl through the hydrate crust enveloping the ice particles is the rate-controlling factor, then a switch to

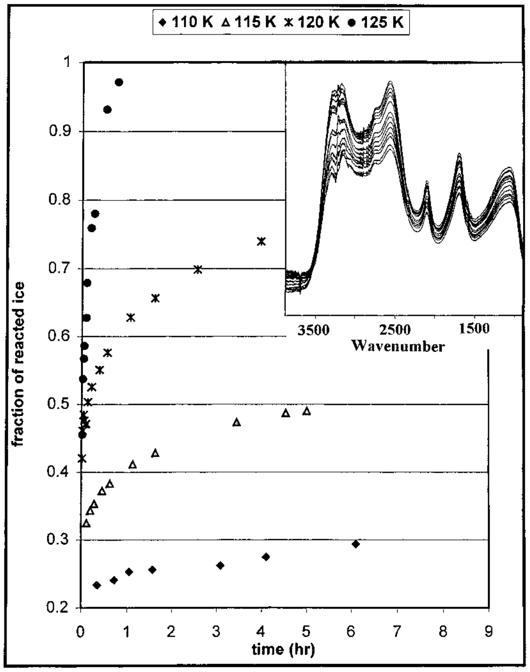

Figure 2. Plots showing the fraction of ice within 3-D arrays converted to the HCl monohydrate as a function of time for the indicated temperatures. The inset shows infrared spectra of the monohydrate of HCl as a function of time during the 110 K conversion of an ice particle array. The data points, with increasing time, correlate with the spectra, with increasing intensity.

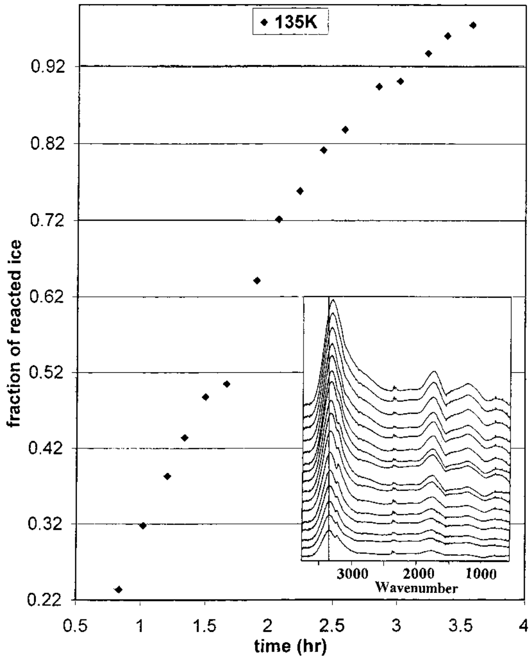

Figure 3. Plot of the fraction of reacted ice within a 3-D array of ice nanoparticles vs time at 135 K. The inset shows infrared spectra of the hydrates as a function of reaction time. The data points, with increasing time, correlate with the spectra, with increasing intensity.

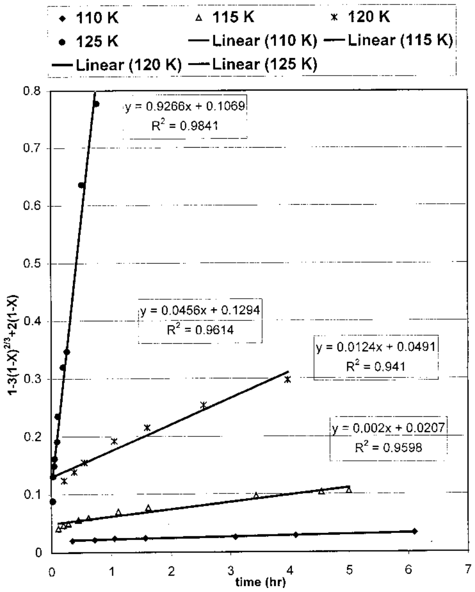

Figure 4. Straight-line characteristics of plots obtained according to eq 1 for the conversion of nanoparticles of ice to the amorphous monohydrate of HCl at 110, 115, 120, and 125 K.

formation of a lower hydrate can be expected. When the diffusion length exceeds some value, the HCl, arriving at the surface of the reacting particles at a steady rate, will begin to accumulate. Eventually a lower hydrate must be nucleated. Since the structure of the tetrahydrate is different than that of the hexahydrate, this will alter the reaction rate to reflect the different diffusion coefficients for the two amorphous hydrates. Thus, the jump in reaction rate is independent evidence that HCl diffusion through the growing product crust is the rate-determining step, with the diffusion rate much greater for the lower hydrate (vide infra).

Rate Analysis. An equation, based on a shrinking-core model,[6] was applied successfully to reaction of ice particle arrays with NH_3.[2] Briefly, the equation for gas A reacting with a particle of initial composition B is given by

$$t = \tau[1-3(1 - X_B)^{2/3} + 2(1 - X_B)] \qquad (1)$$

Here, t is time, X_B is the fraction of reacted ice, $\tau = R^2\rho/6bD_eC_A$, for which R is the particle radius, D_e is the diffusion coefficient of A (HCl) in the product (hydrate) crust, C_A is the concentration of A at the particle surface, ρ is the molar density of the particle (ice; 0.052 mol/cm^3), and b is the stoichiometric ratio of moles of B reacted per mole of A. If the reaction rate is controlled by diffusion through the product crust, the plot $[1-3(1 - X_B)^{2/3} + 2(1 - X_B)]$ versus t gives a straight line with the slope of the line equal to $1/\tau$.

Among the parameters required to calculate D_e, the concentration of HCl (C_A) on the particle surface is least well known. For NH_3, hydrate formation was not initiated until the vapor pressure of ammonia exceeded the equilibrium value required for surface saturation.[2] This stage was recognized by the complete occupation of the dangling-oxygen and 4-coordinated surface sites.[1d] Similarly, the HCl surface concentration required for hydrate nucleation/growth likely approaches that of a condensed phase. The liquid value of C_A (0.024 mol/cm^3) has been used.

Rate Analysis for Particle Conversion to the Monohydrate. Application of eq 1 to the data of Figure 2 gave the nearly linear plots of Figure 4 (nonlinearity is anticipated near time zero, since diffusion cannot be the rate factor until the crust achieves some minimum thickness). From the slope values, the stoichiometric ratio of unity, and particle size of 30−35 nm, [8] D_e (cm^2/s) for HCl diffusion in the amorphous monohydrate was calculated as 4.5×10^{-19} at 110 K; 2.8×10^{-18} at 115 K; 1.0×10^{-17} at 120 K; 2.8×10^{-16} at 125 K. These values correspond to an activation energy of 11 kcal/mol for HCl diffusion in the amorphous monohydrate.

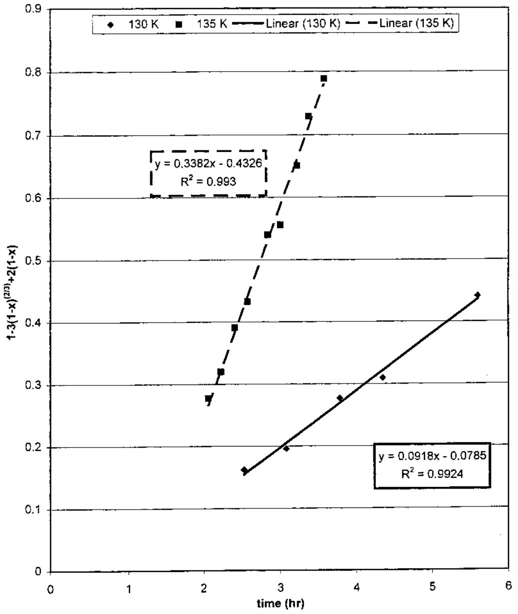

Figure 5. Same as Figure 4, except for conversion of nanoparticles of ice to the amorphous tetrahydrate of HCl at 130 and 135 K.

Rate Analysis for Conversion to Acid Tetrahydrate. When eq 1 was applied to the data for tetrahydrate formation (Figure 3; after a reaction time of 2 h) as well as similar 130 K data, the plots shown in Figure 5 were obtained. The stoichiometric ratio (b) for tetrahydrate formation is 4, and the average particle size was ~40 and 45 nm at 130 and 135 K, respectively. From these values, the diffusion coefficients were calculated as 9.2×10^{-18} cm^2/s at 130 K and 4.3×10^{-17} cm^2/s at 135 K.

Conclusions

The straight-line character of the plots of Figures 4 and 5 is consistent with particle reactions for which the conversion rate is determined by diffusion rates through hydrate crusts. Many researchers over the years have identified HCl diffusion in ice as an important factor in the conversion of ice to an acid hydrate. However, from the reaction of HCl(g) with an ice particle viewed from the shrinking-core model, no basis is found for assuming that HCl diffusion in ice has a roll in the conversion of ice to an acid hydrate. After nucleation of the hydrate and the formation of a monolayer or more of hydrate, the interface of the hydrate with the remaining ice becomes the reaction zone. The reaction can continue only if a supply of HCl can reach that zone. Transport to the zone requires motion of HCl through the crust of hydrate that has formed, but, regardless of the shape of the ice sample, there appears to be no need for HCl diffusion through the ice itself.

An unanswered question is the mechanism of the transport of HCl through the crust of hydrate. We have shown, for the case of conversion to the hemihydrate of ammonia, that the mechanism must be molecular in nature since there is no isotopic exchange between reacting NH_3(g) and D_2O ice particles.[2] Certainly further study is needed, but it is proposed that the diffusion through the acid hydrate crust may also have a molecular character.[5] On the basis of the new values of D_e, HCl moves much more readily through the lower hydrates than the higher hydrates, while excess HCl should ionize more readily in the water-rich hydrates. This hints at a molecular diffusion mechanism, particularly for the monohydrate. However, it is not proposed that individual HCl molecules diffuse through any HCl hydrate in a strictly molecular form.

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References and Notes

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