Rate Study of Ice Particle Conversion to Ammonia Hemihydrate: Hydrate Crust Nucleation and NH_3 Diffusion

Nevin Uras and J. Paul Devlin*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

Received: February 21, 2000; In Final Form: April 21, 2000

Reaction rates for the conversion of ice nanocrystals within 3-D arrays, to the hemi- and monohydrates (and deuterates) of ammonia, have been determined for temperatures in the range 100 to 128 K. The loss of ice and the growth of the hydrate product, as a function of time, temperature, and the activity of ammonia at the surface of the particles, has been monitored using transmission FT-IR spectroscopy. Though this study has focused on the ammonia−ice system, the results may provide general insights to the low-temperature formation of hydrates from ice particles. The ammonia hydrate formation follows a nucleation stage that occurs only after saturation of the ice surface with ammonia molecules; the propagation of the reaction depends on ammonia diffusion, not within the ice but through a hydrate crust that quickly envelops the particles. Apparently, adsorbed ammonia molecules do not achieve a free energy consistent with the nucleation of a new (hydrate) phase until saturation of the low free energy ice surface sites is complete. After nucleation occurs, diffusion of ammonia through the hydrate crust may be rate controlling, the determining parameters being the chemical activity of the ammonia adsorbed on the particle (hydrate) surface and the thickness of the hydrate crust. A diffusion coefficient for ammonia in the amorphous "hemihydrate" has been determined as 2.8×10^{-19} cm^2/s at 102 K with $E_a = 15$ kcal/mol, while the coefficient found for the crystalline hemihydrate was 1.1×10^{-17} at 107 K with E_a estimated as 12 kcal/mol.

Introduction

In a recent transmission FT-IR study, it was shown that the conversion of ice nanocrystals within a 3-D array to an amorphous ionic hydrate of HCl occurs in stages for temperatures below 125 K.[1] For very low levels of HCl exposure, ice nanocrystals become slowly saturated with a "monolayer" of the adsorbed acid that forms a stable equilibrated coating on the ice.[2] However, the acid molecules have the potential to break the H bonds of the ice surface region and penetrate the ice structure. So, when the HCl chemical activity (concentration) was raised to some minimum level above "surface saturation", the acid molecules nucleated a new water phase with the amorphous acid hydrate having a composition near that of the hexahydrate.[1] If the HCl activity was maintained at this high level, the entire ice array converted to the hexahydrate, but reduction of the HCl activity to the equilibrium surface-saturation level at 120 K reverses the hydrate formation and the system reverts to an ice array with the surface saturated with adsorbed HCl.[3]

It has been established that ice coated with a monolayer of ammonia and equilibrated with NH_3 (g) is also stable indefinitely at 120 K,[4a] while ice nanocrystals convert rapidly to the ammonia monohydrate at higher exposure levels. The conversion is considered to be molecular in nature, since the $NH_3 \cdot D_2O$ forms without significant isotopic scrambling,[4a] but otherwise, the process by which ice converts to the ammonia monohydrate appears analogous to the sequence by which the acid hydrate of HCl is formed.

The early stages of the sequence by which nanocrystals of ice are converted to the hydrate of an adsorbate resembles the process by which (water) droplets accommodate a gaseous substance to form a liquid solution. That is, before entering the liquid solution phase, a gas adsorbate participates in the nucleation of a critical cluster.[5] A molecular level view of the formation of the nucleating complex has been developed for the ammonia−liquid water case using ab initio methods.[5c] An ongoing simulation of the sequence of events at the ice surface invokes analogous H-bonded structures for the adsorbed state of ammonia.[6] However, in the ice−HCl and ice−NH_3 systems, the new aqueous solution phase is a *glassy* hydrate,[7] so, following nucleation, ammonia diffusion to a receding ice−hydrate interface may become the important rate factor. It is likely that a similar sequence occurs in the general case of the conversion of crystalline ice to a hydrate, whether the product is an acid, base, or clathrate hydrate, and independent of the amorphous or crystalline nature of the hydrate product.

The previous studies of the conversion of ice nanocrystal 3-D arrays to arrays of hydrate particles have been qualitative in nature.[1,4] Here, we report the results of the first quantitative rate study of the conversion of 3-D arrays of ice nanocrystals to amorphous and crystalline hydrates; namely, the mono- and hemihydrates of ammonia. Of these studies, the formation of the hemihydrate has proven more interesting as the monohydrate forms only under conditions such that the supply of ammonia reaching the 3-D array is the rate-limiting factor. By contrast when an abundance of ammonia is made available at the gas−solid interface, the rate of the *hemihydrate* formation is determined by the rate of diffusion of the ammonia through the hydrate layer that quickly encrusts the ice particles. This condition for gas-particle reaction has a long history of study[8−10] but has not previously been invoked in an effort to quantitate reaction rates of ice particles.

Various scenarios can be imagined when a particle is bathed in the vapors of an adsorbate reactant. If the vapor is sufficiently

10.1021/jp000676g CCC: $19.00

dilute, the particle may become partially or fully coated with the adsorbate, at which point equilibrium is achieved without a new substance being nucleated. If the vapor density (free energy) is sufficient to nucleate a new phase but the reactivity of the vapor with the particle is low, the conversion of the particle to a new substance may proceed with the rate controlled by that reactivity. However, if the reactivity is great, there are three likely situations. The rate may be controlled by (1) the rate at which adsorbate molecules reach the outer surface of the reacting particle, (2) by the rate at which the adsorbate molecules diffuse through the product that encrusts the particle, or (3) some combination of these two possibilities.

In the reaction of ammonia with ice nanocrystals in 3-D arrays, two of these possibilities are prominent. When an array is exposed to the equilibrium vapor pressure of solid ammonia over the temperature range 115−128 K, the ammonia must diffuse through the passageways between the particles of the array to reach a particular particle. With the equilibrium pressure in the submicron range, this migration is slow so the rate at which ammonia molecules reach the outer surface of a reacting particle is slow compared to either the diffusion of ammonia through the crust of product to the reaction interface or reaction at that interface. As a result, ammonia molecules that cross an imaginary plane at the front surface of the 3-D array react; the rate law is effectively zero order in the presence of the equilibrium vapor of NH_3(s).

The more interesting case, wherein an abundance of ammonia is available at the particle surfaces and the diffusion through the product crust is slow compared to the reaction at the crust-ice interface, is the focus of the present paper as it applies to the formation of the ammonia *hemihydrate* in the 100−112 K range. The general case of particle reaction has been well modeled in the past[8−10a] so the pertinent rate equations need not be developed here.

Experimental Section

Basic to the present study was the development of a method by which an abundance of ammonia molecules was made uniformly available to nanoparticles within a three-dimensional array at ∼100 K. The method of forming the 3-D array of ice nanocrystals, which has been described several times,[1,4] consists of letting ice nanocrystals within an inert gas aerosol collect on the window surfaces of an infrared cold-cluster cell; a cluster cell isolated within a larger vacuum container, as modeled after a larger cell originally described by Ewing.[11] A small percentage of the particles of a given aerosol collect on the vertical cell windows so that, by repeating many aerosol formation pump cycles, a particle array of a desired thickness can be achieved. It is certain, from the infrared spectra, that the particles are crystalline. From known structures of related systems, for which diffraction data are available,[12,13] it can be assumed that the nanocrystals are cubic ice. Since strong adsorbates such as ammonia cannot diffuse through a 3-D ice array without being preferentially adsorbed/reacted near the array−vacuum interface, a simple diffusional process cannot be used to supply an abundance of ammonia simultaneously to each particle; particularly at the low temperatures ($<$140 K) required to fully stabilize an ammonia hydrate product in a vacuum.[14]

The method used to supply an abundance of ammonia vapor uniformly to the particle surfaces was based on the alternate loading of ice aerosol and NH_3(s) aerosol nanocrystals into the cluster cell. The loading was controlled so that the 3-D array was built layer-by-layer with the alternating ammonia layers designed to provide an excess of ammonia throughout the array. By forming this alternating ice−ammonia particle array at 90 K, the amount of reaction during loading was insignificant and the average ice particle size of ∼20 nm was known from previous study of the infrared band intensity of monolayer coatings of adsorbed CF_4.[15] The reaction rates were then monitored after stepping the sample temperature rapidly into the 100−112 K range; a range chosen so that hydrate formation during the temperature equilibration period was not excessive. The ammonia particles vaporized at a rate determined by the chosen reaction temperature, and in a manner that provided an abundance of adsorbed ammonia to the ice particles throughout the array.

The presence of this abundance was apparent, since a large fraction of the ammonia within an array was observed to cryopump from the array rather than react. The windows that support the sample are the warmest part of the cluster cell, so over the many hours of a reaction the excess ammonia within a 3-D array is slowly cryopumped to the coldest region of the cell, estimated to be 3−5 K cooler than the windows. This temperature differential has been estimated from the temperature corresponding to the observed vapor pressure of CF_4(s) within the cell compared with the measured temperature at the cell windows. The extensive cryopumping of the ammonia from the windows was clear evidence that ammonia molecules, moving within an array, undergo numerous particle collisions for each reaction (provided the original amount of ammonia within the array was sufficiently large).

With an abundance of ammonia present at the particle surfaces, the nucleated hydrate phase was $2NH_3{\cdot}H_2O$. By eliminating the availability of ammonia molecules as a possible rate factor, the conditions were thus established for observation of the ice-to-hemihydrate conversion with the rate determined by either (1) the diffusion of the ammonia to the reaction interface through the hydrate product crust or (2) the inherent reactivity at the crust−ice reaction interface. The available models for particle−vapor reactions allow identification of the controlling rate factor from these choices.[8−10a]

A series of reaction rate measurements were also made by loading a large amount of solid ammonia into the cluster cell following the formation of a 3-D array of ice nanocrystals. The NH_3(s) then supplied ammonia to the array at a fixed rate determined by the vapor pressure for the chosen cell reaction temperature. For useful reaction rates of the array, the cell temperature was set in the 115−127 K range, so it was necessary to prepare larger ice particles (∼50 nm) at an elevated temperature (135 K) to prevent Ostwald ripening[16] that would otherwise occur in this reaction temperature range. These conditions resulted in the formation of the monohydrate of ammonia.

The identity of the reaction products, and the measurement of the extent of reaction, was determined by transmission FT-IR spectroscopy of the samples on the windows of the cluster cell. The spectra of the mono- and hemihydrates of ammonia are well known.[17,18] Quantitative measurement of the amount of ice converted to hydrate at any time of reaction was from the peak absorbance intensities of the hydrates or by difference spectroscopic methods that gave the quantitative difference in the original amount of ice and the ice remaining at the reaction time. Measurements focused particularly on the reaction of NH_3 with D_2O, so reference will be primarily to the deuterates rather than hydrates. Since there was no detectable isotopic exchange during the reactions, this choice of isotopomers had the advantage that the NH_3 and D_2O bands, used to monitor extent of reaction, did not interfere with one another.

Results and Discussion

It has been reported that exposure of a 3-D array of D_2O ice nanocrystals to ammonia vapor at low-pressure results in the uptake of the ammonia to monolayer levels throughout the array.[4] Two spectroscopically detected levels of saturation have been reported. The first corresponds to the uptake level at which the most reactive sites toward ammonia, the dangling-D sites, become fully coated so are no longer observed as a spectral feature near 2726 cm^{-1}. At the second saturation level, the other surface sites, dangling oxygen and 4-coordinated sites, apparently become fully coated, as the corresponding bands (2640 and ~2570 cm^{-1}) are observed to red shift into the stronger D-bonded part of the ice spectrum. At this saturation level, the d−D band that originated at 2726 cm^{-1} appears, as anticipated, near 2230 cm^{-1}.[19]

Despite the tendency of ammonia vapor to adsorb preferentially near the array−vacuum interface, H-bond chemistry, resulting in the formation of a hydrate of ammonia, is not observed, provided the ammonia vapor pressure is no greater than required to reach this second level of surface saturation (approximately one micron pressure at 120 K). This earlier report, summarized in Figure 1 of ref 4 has been reaffirmed in the present study. Here it will be understood that the availability of ammonia exceeds that required for this second level of surface saturation, and attention will be focused on the nucleation and growth of new hydrate phases promoted by the higher free energy of the adsorbed ammonia.

Conversion of Ice Nanocrystals to Ammonia Monodeuterate Particles. When ammonia is added by vapor transport to a cold cluster cell containing a D_2O 3-D ice array (formed on all surfaces within the cell), $NH_3(s)$ condenses near the entry port and is not observed immediately at the infrared windows that support the ice sample. If the cell temperature is held below 110 K, many hours pass before significant ammonia vapor reaches the ice sample on the cell windows. To observe conversion of the array to the monodeuterate of ammonia on a time scale of hours, it was necessary to raise the cell temperature to >115 K. Temperatures in the range of 115 to 123 K have proven useful in monitoring the conversion to the monodeuterate.

Detailed infrared spectra of the different isotopomeric mixes of ammonia and water have been reported along with assignments of the numerous vibrational modes.[17,18] Example spectra of the monodeuterate, $NH_3{\cdot}D_2O$, and hemideuterate, $2NH_3{\cdot}D_2O$, are given in Figure 1. Since the progress of reaction has been monitored using the infrared band intensities, $NH_3{\cdot}D_2O$ and $2NH_3{\cdot}D_2O$ offer the advantage of having regions of the spectra with strong bands produced exclusively by either NH_3 or D_2O and are therefore the examples we will emphasize here and in the next section.

Data typical of the spectroscopic monitoring of the conversion of a D_2O ice array to $NH_3{\cdot}D_2O$ are presented in Figure 2. These spectra are difference spectra obtained by subtracting the proper fraction of the original bare ice spectrum from that measured at each reaction time. A series of spectra measured as a function of time at a given temperature gives an abundance of data useful in the construction of plots showing the time dependence of the fraction of the ice converted to hydrate. Since the hydrate formation goes to completion, there is no difficulty in normalizing the hydrate spectra to the fraction of total hydrate or to the fraction of reacted ice.

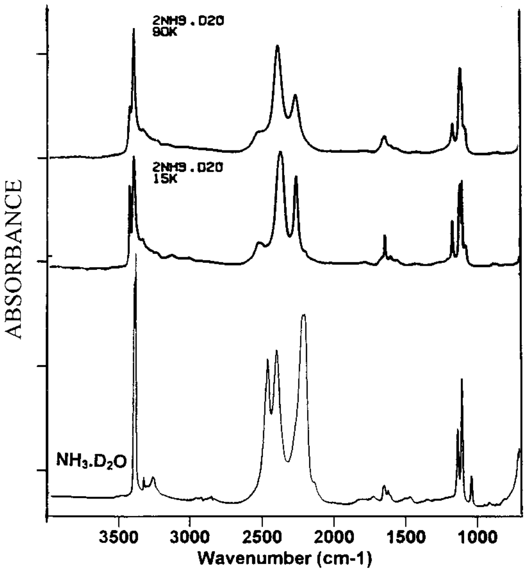

Figure 1. Infrared spectra of thin films of the hemideuterate of ammonia (90 and 15 K; top) and an array of ~60 nm particles of the monodeuterate of ammonia at 120 K.

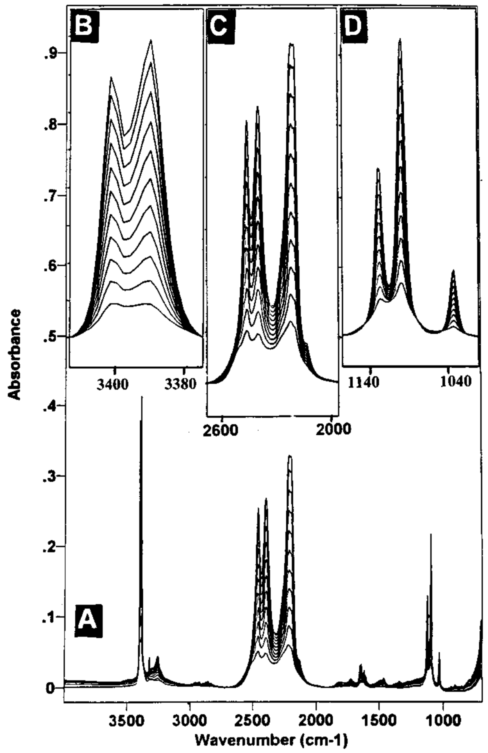

Figure 2. Infrared spectra of the monodeuterate of ammonia ($NH_3{\cdot}D_2O$) as a function of time during the 120 K conversion of an ice particle array to the monodeuterate. Insets are expanded portions of the broad range spectrum at the bottom.

Plots showing the variation of the fraction of reacted ice with time for five different temperatures are given in Figure 3. An induction period, which followed the rapid admission of ammonia to the sample cell during which the vapor pressure of the ammonia rose to the equilibrium value of $NH_3(s)$, is apparent for the initial phase at each temperature. This induction phase was followed by a long period for which the reaction rate was constant, as shown by the straight-line segments. In each case the rate began to decrease only as the conversion to the deuterate neared completion. Then, the ammonia diffusion through the thickening deuterate crust became a rate-limiting factor (along with a nonuniform extent of reaction with depth in the ice array (vide infra)).

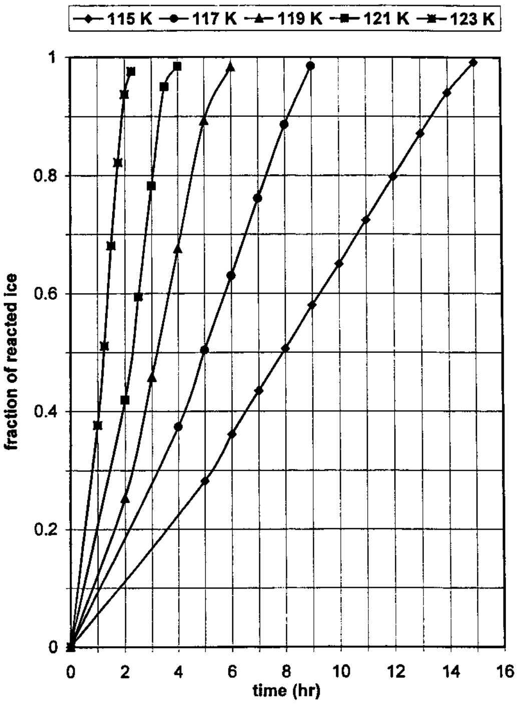

Figure 3. Plots showing the fraction of ice within 3-D arrays converted to the NH_3 monodeuterate as a function of time for the indicated temperatures.

The constant reaction rate observed for the monodeuterate formation reflects a rate-limiting factor that is constant throughout most of the reaction. The most likely factor is the vapor pressure of the ammonia within the cluster cell, which was fixed by equilibration with the solid ammonia. It is difficult to identify any other possible controlling factor that remains constant during a large portion of the conversion of ice to hydrate. The area of the reaction interface, between the crust of hydrate product and the ice, decreases rapidly during this period. The diffusion length of the ammonia through the hydrate crust to the interface increases accordingly. Thus, control, either from condensed-phase diffusion or from the inherent reaction rate at the shrinking interface, would be reflected in a decreasing rate of reaction (as observed for hemihydrate formation; see the next section).

It was also found that the rate of reaction, in moles of deuterate formed per unit time, was independent of the array thickness as long as the rate was monitored during the constant rate part of the reactions. This establishes that the ice particles near the vacuum-array interface react to completion prior to reaction of particles deeper within the array. It also provides further evidence of the rapid inherent reaction rate at the reaction interface and the relatively rapid diffusion of the ammonia through the deuterate product crust (compared to the time scale for diffusion through the 3-D array of particles). The observation of a constant reaction rate with increasing particle size at a specified temperature, but with an earlier onset of the decreasing reaction rate from thickening hydrate crust, also gave support to this general view of the factors that control the reaction rate for monodeuterate formation.

Finally, control of the ice-to-hydrate conversion by the vapor pressure of the solid ammonia in the cluster cell (for this particular sampling approach) should be reflected in an apparent activation energy equal to the heat of vaporization of ammonia for this temperature range. Determination of the activation energy from an Arrhenius plot using rates from the straight-line segments, such as in Figure 3, gave values of 5.8, 6.5, and 7.8 kcal/mol, for formation of $NH_3 \cdot H_2O$, $NH_3 \cdot D_2O$, and $ND_3 \cdot D_2O$. This suggests a match, within experimental error, with a value of 7.5 kcal/mol for the heat of sublimation of solid NH_3 at 120 K deduced from a modified Clausius−Clapeyron equation.[20]

Conversion of Ice Nanocrystals to Ammonia Hemideuterate Nanoparticles. Though the results of the rate study of the conversion of ice 3-D arrays to nanocrystals of the *monodeuterate* of ammonia are of minor interest, showing only that the conditions were such that the rate was determined primarily by the arrival rate of ammonia at the vacuum−array boundary, the results of the study did suggest an ability to make credible quantitative rate measurements for reactions of the 3-D ice arrays. In the case of ammonia, the study would gain interest should the availability of ammonia at the particle surfaces be increased to the point where that availability was no longer the rate-controlling factor. Raising the temperature to increase this abundance was not an option, since that would also accelerate the inherent reaction rate as well as the condensed phase diffusional processes that might otherwise become rate controlling. The limits of stability of the hydrates in a vacuum environment also impose an upper limit on practical reaction temperatures of ∼140 K.[14,18]

The use of larger ice particles was identified in the previous section as a ploy to gain information about diffusional rates since diffusion through the associated thicker hydrate crusts becomes a rate factor, particularly near the end of the particle conversion. However, particle sizes used in the study were near a practical upper limit set by the ripening temperature (∼150 K) at which the nature of the sample changes irreversibly toward bulk ice. It is clear from Figure 3 that, to deduce diffusional rates, information about diffusion must be deconvolved from the dominating influence of ammonia availability (as well as the variation in exposure to ammonia with depth in the ice array). To avoid this complexity, in this initial rate study of the H-bond chemistry of ice nanoparticle arrays we have altered the rate factor by changing the sampling method to one in which an abundance of ammonia is available at the reaction interface throughout the conversion of the ice array to an ammonia hydrate. As described in the Experimental Section, this abundance of ammonia was made available by forming the array with alternating layers of ice and ammonia particles.

Data for the conversion of the D_2O ice nanocrystals to the hemideuterate of ammonia in the presence of an abundance of ammonia vapor, for temperatures in the 102−110 K range, are presented in Figures 4−8. Spectra, shown as insets, reflect the growth of the deuterate product starting at time zero, defined as the time at which the sample reached the chosen reaction temperature following warming from the sample formation temperature of 90 K. The reaction rates, indicated by the slope of the plots vs time of the fraction of the original ice converted to hydrate, are of similar magnitude to those observed at much higher temperature (+15 K) when the rates were controlled by the equilibrium vapor pressure of solid ammonia in the cell (i.e., during the formation of the monodeuterate as represented in Figure 3).

The rate plots (Figure 4−8) show a sharply decreasing rate of reaction with time, particularly near time zero at the reaction temperature, and a sharply increasing reaction rate as the temperature was raised through the 102−112 K range. In contrast to the approach of the previous section, with an abundance of ammonia available at the ice-particle surfaces, control of the reaction rate was clearly transferred to a parameter of the system that varies strongly with extent of reaction. Before

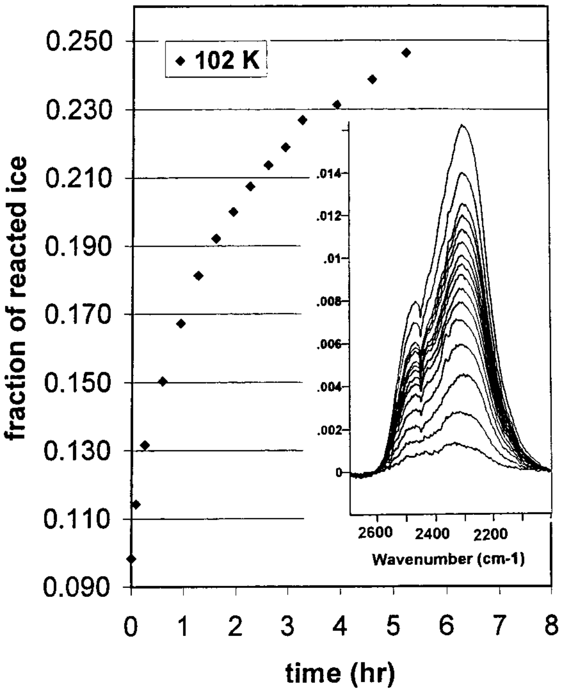

Figure 4. Plot of the fraction of reacted ice within a 3-D array of 20 nm particles converted to the "hemideuterate" of NH_3 vs time at 102 K. The broad featureless bands of the inset identify the product phase as amorphous.

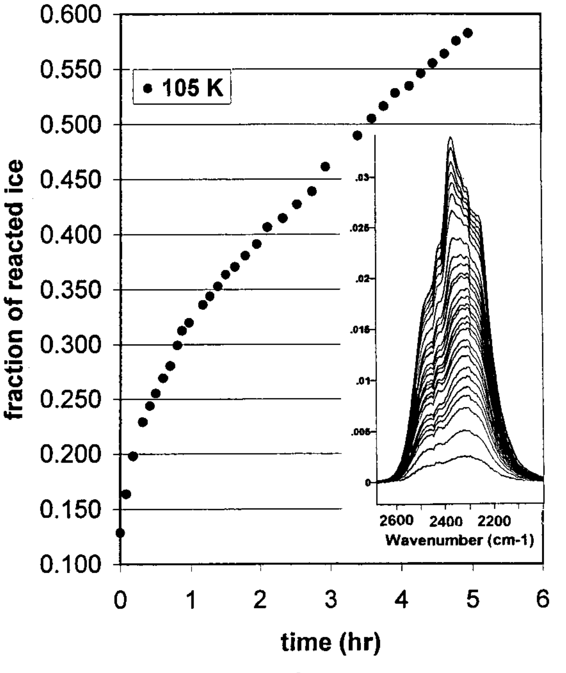

Figure 5. Same as Figure 4, except the reaction temperature was 105 K and, as shown by the inset, the product hemideuterate developed a crystalline component after ~3 h.

analyzing the data to determine the identity of that parameter, it is helpful to note a qualitative aspect of the behavior of the reaction rates. Attention is called to the change in form of the rate plot as the temperature was increased. At 100 (not shown) and 102 K, the rates are smoothly decreasing functions of reaction time. At 105, 107, and 110 K, this smooth decrease is interrupted by a sudden increase in the reaction rate after approximately half of the ice has converted to deuterate. At 112 K the rate once again decreases smoothly with reaction time.

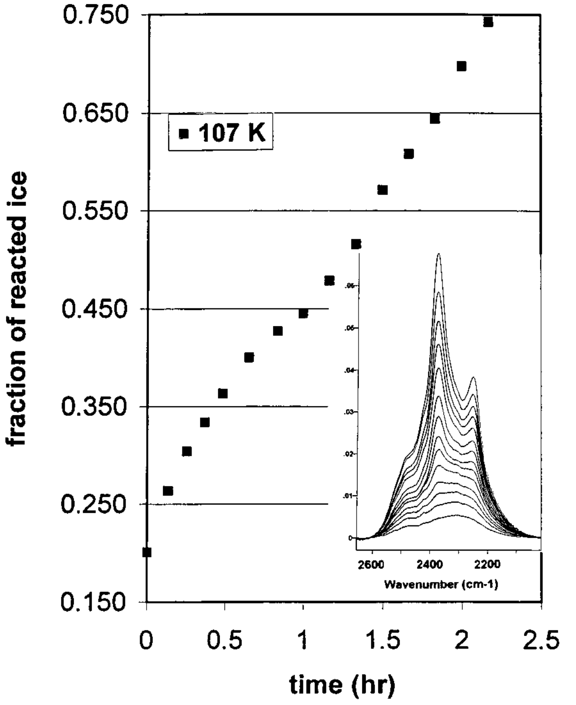

Figure 6. Same as Figure 5, except the reaction temperature was 107 K and the inset indicates that, after the first hour, the product was dominantly crystalline hemideuterate.

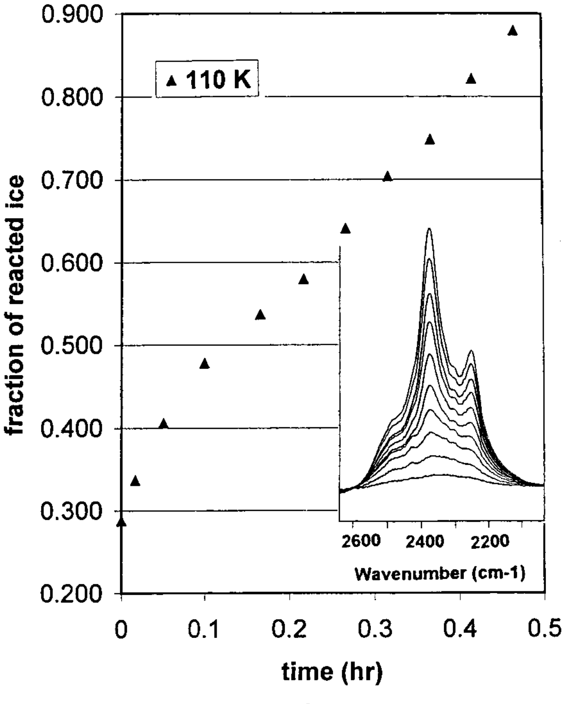

Figure 7. Same as Figure 6, except the reaction temperature was 110 K and the inset indicates that the crystalline hemideuterate was the dominant product after ~20 min.

The cause of these qualitative differences is clear from the spectra of the insets. At the higher temperatures, after significant reaction, the deuterate product spectrum is clearly that of the *crystalline* hemideuterate of ammonia (see ref 18 and Figure 1). However, at lower temperatures and shorter reaction times, the product spectrum is *not* like that of the crystalline deuterate, being much broader-banded and less structured in form. This indicates that, for an ultrathin crust of deuterate or for a deuterate crust formed below ~105 K, the crystalline form is not

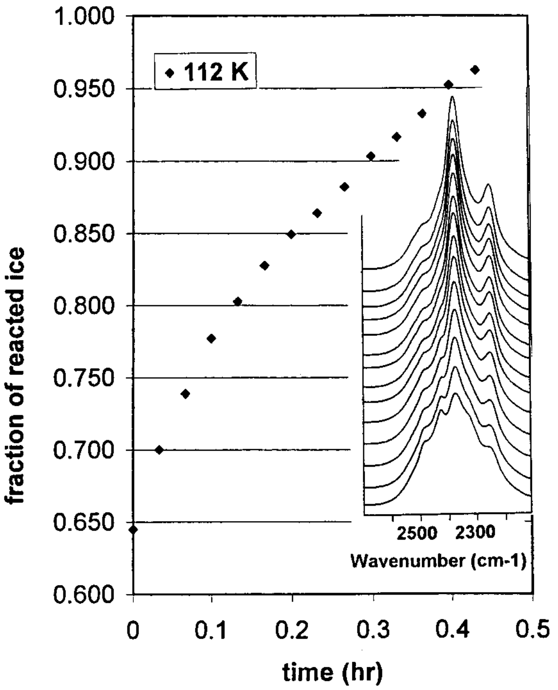

Figure 8. Same as Figure 7, except the reaction temperature was 112 K and the inset indicates that the crystalline hemideuterate was the dominant product after the first few minutes.

nucleated; rather the nucleated product is the *amorphous* ~2:1 deuterate. Often, diffusion of a molecule in an amorphous structure is slower than within the corresponding crystal. Here, as the crystalline structure became dominant the reaction rate increased. If the diffusion of the molecule, in this case ammonia, is rate controlling, then the increased reaction rate, observed in Figures 5−7, would reflect a more rapid diffusion through the crystalline crust. This is tentative evidence that diffusion of ammonia through the deuterate crust is a rate-limiting factor.

(i) Rate Analysis for Conversion to the Amorphous Deuterate. Since the rate data divide into two parts, identified with the formation of an amorphous or crystalline deuterate crust, a separate rate analysis can be made for the two regions. The lower temperature data, for formation of the amorphous "hemideuterate",[21] will be considered first. A straightforward analysis, based on established equations, is possible if the reaction system is describable as *a spherical particle of known radius undergoing conversion to a new substance by diffusion of adsorbed molecules through a crust of product to the reaction interface, with that diffusion being the rate controlling factor.* A derivation based on such a model was presented[8] and later modified slightly.[9] That development, for the case of gas A reacting with a particle of initial composition B, led to the equation[9]

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

Here, t is time and X_B is the fraction of reacted ice while $\tau = R^2\rho/6bD_eC_A$, for which R is the particle radius (10 nm), D_e is the diffusion coefficient of A (ammonia) in the product (deuterate) 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) in cm^3, and b is the stoichiometric ratio of moles of B reacted per mole of A (1/2 in our case).

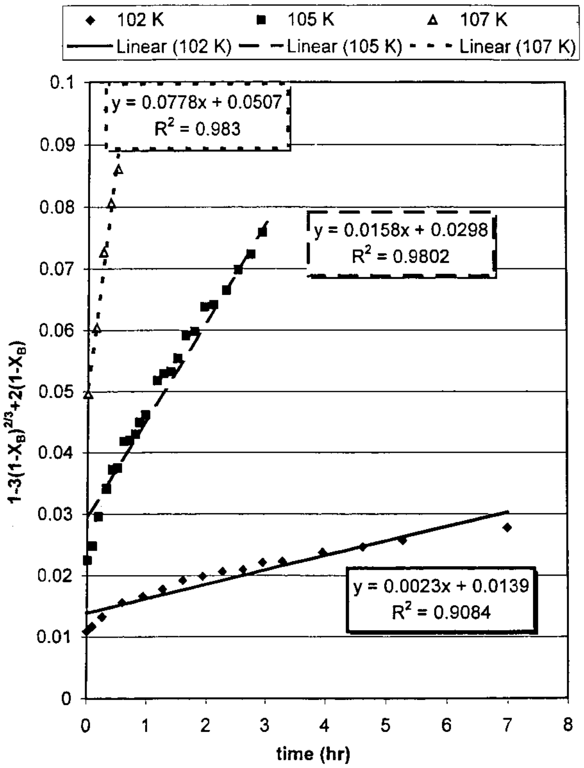

Figure 9. Straight line characteristics of plots of eq 1 for the rate of conversion of 20 nm particles of ice to amorphous NH_3 "hemideuterate" at 102, 105, and 107 K. The slopes of the plots give $1/\tau$ values used to determine D_e.

If the model assumptions are valid for the present case and the rate is diffusion controlled, a plot of $[1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)]$ vs t should be a straight line of slope $1/\tau$. Such plots are presented in Figure 9 using data from Figures 4−6 for the conversion of ice to the amorphous deuterate at reaction temperatures 102, 105, and the early stages of 107 K. The indicated R^2 values, particularly for 105 and 107 K, suggest the plots are meaningful. Of the system parameters required to determine the values of D_e (using the definition and experimental values of τ), C_A is perhaps least well determined. However, it has been argued above that ammonia activity at the particle surface must exceed that of the first monolayer of adsorbed ammonia. Thus, C_A is presumed to be similar to the value for physically adsorbed ammonia in layers beyond the first; which should resemble that of liquid ammonia (0.040 mol/cm^3). Using this value of C_A and the values of τ from Figure 9 (after conversion to units of seconds rather than hours), D_e for diffusion of NH_3 within the amorphous deuterate crust has been determined, in units of cm^2/s, as 2.8×10^{-19} at 102 K, 2.0×10^{-18} at 105 K, and 9.4×10^{-18} at 107 K. These values correspond to an activation energy of 15.1 kcal/mol for diffusion of NH_3 within the amorphous "hemideuterate".

The model used here is taken as appropriate for the present data sets, although it does not account for the change in particle volume[10a] during the conversion to the deuterate. We are not aware of other information about the ammonia diffusion coefficient in the hemihydrate, whether amorphous or crystalline, but an order of magnitude check of the values reported here is encouraging. D_e values estimated from the equation[22] $d = (D_et)^{1/2}$, using reasonable values for d (diffusion distance) and t (diffusion time), resemble the above values. For example, if the 25% particle conversion to amorphous deuterate is taken as indicative of a diffusion distance of 1.0 nm (through a 1.0 nm deuterate crust of an ice particle of 10 nm radius), the estimated coefficient values are 5×10^{-19} and 5×10^{-18} cm^2/s for 102 and 105 K, respectively, from the reaction times of Figures 4 and 5.

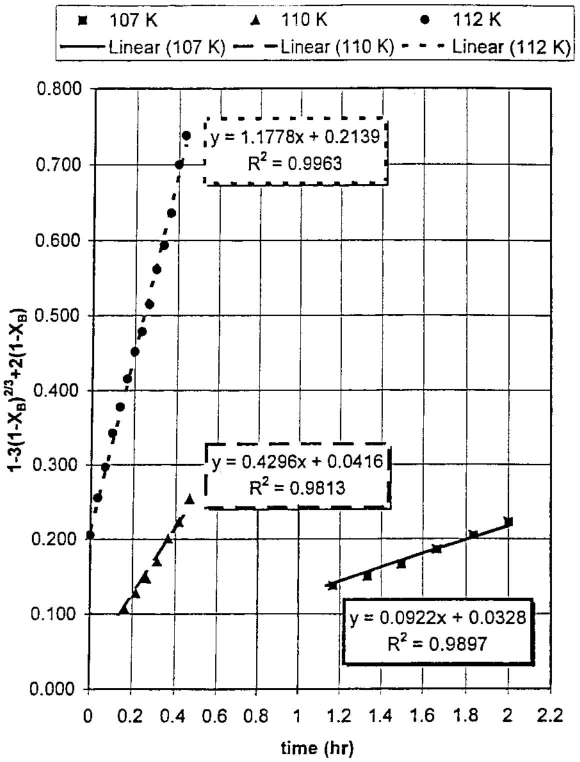

Figure 10. Same as Figure 9, except the data are for formation of the crystalline NH_3 hemideuterate at 107, 110, and 112 K.

(ii) Rate Analysis for Conversion to the Crystalline Hemihydrate. The data for the time/temperature regions for which the product is the crystalline hemihydrate are presented in Figures 6−8 and the corresponding plots, based on eq 1, appear in Figure 10. Again, the high R^2 values suggest that the model and the equation are applicable to the present data. Using the same parameter values as in the preceding section and the values of τ determined from the slopes of the plots of Figure 10, D_e values (cm^2/s) have been calculated for NH_3 diffusion in the crystalline $2NH_3{\cdot}D_2O$ crust as 1.1×10^{-17} at 107 K, 5.9×10^{-17} at 110 K, and 1.4×10^{-16} at 112 K. These values correspond to an Arrhenius activation energy for diffusion in the crystalline deuterate of 12.1 kcal/mol.

A comparison of the diffusional activation energies for the amorphous and crystalline hemideuterates is informative. The value for the crystalline deuterate (12.1 kcal/mol) is significantly less than for the amorphous form (15.1 kcal/mol). The lower crystalline hemideuterate value is consistent with an exceptionally open structure with sizable channels running through the crystal.[18,23] In fact, the unusual situation that ammonia isotopomers within the hemihydrate become isotopically scrambled at $T > 130$ K, while water isotopomers do not, has been tentatively related to the relative ease of ammonia migration through such channels.[14] On the other hand, the (extrapolated) values of the diffusion coefficients vs temperature for the two deuterate phases cross, with the amorphous phase value exceeding that of the crystal phase above ~109 K. This is a result of a much larger Arrhenius preexponential factor for the amorphous phase that is consistent with more numerous but less open diffusional pathways.

(iii) Isotopomer Influence on Ammonia Diffusion in the Hemihydrate. Though the focus of this study has been on $2NH_3{\cdot}D_2O$, less extensive results have also been obtained for $2NH_3{\cdot}H_2O$ and $2ND_3{\cdot}D_2O$. The data for the all protiated systems were nearly indistinguishable from those of the NH_3-D_2O system described above. For example, a value for D_e(cm^2/s) of 2.1×10^{-18} for ammonia in the amorphous protiated "hemihydrate" at 105 K can be compared with the corresponding value of 2.0×10^{-18} given above for $2NH_3{\cdot}D_2O$. This suggests that any isotopic effect from deuteration of the water is smaller than our experimental error.

By contrast, a sizable isotope effect was observed when NH_3 was replaced by ND_3. For example, the average value of the ammonia diffusion coefficient for the amorphous deuterate at 102 and 105 K was reduced by a factor of ~4, with the value at 105 K being 5.0×10^{-19}. Similarly, the estimated diffusion coefficient for NH_3 in crystalline $2NH_3{\cdot}D_2O$ was ~4 times the value for ND_3 in *crystalline* $2ND_3{\cdot}D_2O$. The ammonia effect is not surprising since it corresponds to a temperature shift of ~3 K that is similar to the influence of deuteration of ammonia on properties such as the melting and boiling points of the pure substance. Ongoing computational studies of the behavior of ammonia at the ice surface and within the ammonia hydrates[6] are expected to increase the molecular-level insight to the uptake and reaction of ammonia with ice, including the reasons for these large ammonia and negligible water isotope effects.

Summary Conclusions

In the reaction of ammonia with ice nanocrystals, the nucleation of a hydrate and the initial phase of heterogeneous reaction are both rapid at temperatures as low as 105 K, provided the ammonia activity at the reaction interface exceeds a critical level above normal surface saturation. When the activity of ammonia within the particle array was restricted, but nevertheless above this minimum level, the ammonia *monohydrate* was nucleated and encrusted the ice particles. For each reaction temperature in the range 115−128 K, a constant conversion rate of the ice to the monohydrate was observed for vapor pressures of NH_3 fixed by the presence of NH_3(s) within the cold particle cell. For these conditions, the arrival rate of ammonia at the surface of the particles within the 3-D array was rate controlling throughout most of the reaction, with the diffusion of ammonia through the thickening hydrate crust a rate factor only as the particle reaction neared completion. Since the ammonia availability was determined by the vapor pressure of solid ammonia within the cell, the observed activation energy for monohydrate formation approximated the heat of sublimation of ammonia.

However, in the presence of an abundance of ammonia, the conversion of ice particles to the ammonia *hemihydrate* ($2\,NH_3{\cdot}H_2O$) occurred with a rate that decreased rapidly with time/thickness of the hydrate crust. A kinetic analysis, using classical equations for particle conversions,[8−10a] has indicated that the rate is limited by the diffusion coefficient of ammonia in the hemihydrate layer that encrusts each ice particle. This layer may be amorphous or crystalline or a mix thereof, depending on the sample temperature and extent of reaction; so diffusion coefficients have been determined for both the crystalline and amorphous forms of the hemihydrate.

In addition to the evaluation of (at least) semiquantitative rates for ammonia diffusion within the crystalline and amorphous hemihydrate, this study is informative of the reaction rates of ammonia once it reaches the reaction interface and of the nucleation rates of the hydrate phases. The initial rates, in the limit, give the ice-to-hemihydrate conversion rate for zero product thickness, and thus for the combined processes of hydrate nucleation and reaction at the surface. These rates can be seen to be large even at these low temperatures (with the fractional conversion greater than 0.1/min at 110 K). These large nucleation and inherent reaction rates allow the (slower) diffusion rate to become the rate-controlling factor once a few molecular layers of product crust are formed.

Acknowledgment. Support of this research under NSF Grant CHE-9617120 and substantive suggestions from Prof. V. Buch of the Hebrew University are gratefully acknowledged.

References and Notes

(1) Devlin, J. P.; Uras, N.; Rahman, M.; Buch, V. *Israel J. Chem.* **1999**, *39*, 261.

(2) Uras, N.; Rahman, M.; Devlin, J. P. *J. Phys. Chem. B* **1998**, *102*, 9375.

(3) Uras, N.; Devlin, J. P., unpublished work.

(4) (a) Delzeit, L.; Powell, K.; Uras, N.; Devlin, J. P. *J. Phys. Chem. B* **1997**, *101*, 2327. (b) Devlin, J. P.; Buch, V.; *J. Phys. Chem.* **1995**, *99*, 16534.

(5) (a) Davidovits, P.; Hu, J. H.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E.; *Faraday Discuss.* **1995**, *100*, 65. (b) Davidovits, P.; Jayne, J. T.; Duan, S. X.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1991**, *95*, 6337. (c) Donaldson, D. J. *J. Phys. Chem.* **1999**, *103*, 62.

(6) Private communication from V. Buch of the Hebrew University.

(7) The first molecular layers of a new hydrate phase lack the complete lattice of a crystalline phase and are, therefore, noncrystalline (or amorphous) in form, regardless of the formation temperature.

(8) (a) Jander, W. *Z. Anorg. U. Allgem. Chem.* **1927**, *163*, 1. (b) Ginstling, A. M.; Brounshtein, B. I. *J. Appl. Chem. USSR* **1950**, *23*, 1327.

(9) Levenspiel, O. *Chemical Reaction Engineering*; Wiley & Sons: New York, 1962; p 364.

(10) (a) Carter, R. E. *J. Chem. Phys.* **1960**, *34*, 2010. (b) Salamatin, A. N.; Hondoh, T.; Uchida, T.; Lipenkov, V. Y. *J. Cryst. Growth* **1998**, *193*, 197.

(11) Ewing, G. E.; Sheng, D.-T. *J. Phys. Chem.* **1988**, *92*, 4062.

(12) Huang, J.; Bartell, L. S. *J. Phys. Chem.* **1995**, *99*, 3924.

(13) Torchet, G.; Schwartz, P.; Farges, J.; de Feraudy, M. F.; Raoult, B. *J. Chem. Phys.* **1983**, *79*, 6196.

(14) Bertie, J. E.; Devlin, J. P. *J. Chem. Phys.* **1983**, *78*, 6203.

(15) Rowland, B.; Kadagathur, N. S.; Devlin, J. P. *J. Chem. Phys.* **1995**, *102*, 13.

(16) Ostwald ripening refers to the growth of large particles and the vanishing of smaller ones caused by the greater vapor pressure of the small particles.

(17) Bertie, J. E.; Shehata, M. R. *J. Chem. Phys.* **1985**, *83*, 1449.

(18) Bertie, J. E.; Devlin, J. P. *J. Chem. Phys.* **1984**, *81*, 1559.

(19) The ammonia attached to the dangling hydrogen of the ice surface is not unlike that of one type of ammonia (ammonia II) that dangles in the open channels of the hemihydrate structure. The band position for the O−D bound to ammonia II is near 2300 cm^{-1} (see ref 18).

(20) (a) Kirshenbaun, I.; Urey, H. C. *J. Chem. Phys.* **1942**, *10*, 706. (b) Braker, W.; Mossman, A. L. *Matheson Unabridged Gas Data Book*; Matheson: East Rutherford, New Jersey, 1974.

(21) The composition of an amorphous phase may be regarded as arbitrary, dependent on the activity of the component substances during the formation. This may be generally true, although certain compositions do seem to be favored in H-bonded systems (see ref 1). Here, reference to the amorphous hemihydrate of ammonia is not limited to a precisely 2:1 composition.

(22) Budnikov, P. P.; Ginstling, A. M. *Principles of Solid State Chemistry; Reaction in Solids*; Maclaren & Sons, Ltd: London, 1968.

(23) Siemons, W. J.; Templeton, D. H. *Acta Crystallogr.* **1954**, *7*, 194.