Propane Clathrate Hydrate Formation Accelerated by Xenon

Joanne A. Abbondondola, Everly B. Fleischer, and Kenneth C. Janda*

Department of Chemistry, University of California at Irvine, Irvine, California 92697

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Experiments are reported that show propane is incorporated into clathrate hydrate cages much more rapidly using propane−xenon mixtures than for pure propane gas. Uptake rates for pure propane type II clathrate hydrate, pure xenon type I clathrate hydrate, and propane and xenon binary type II clathrate were studied for several different synthesis procedures. Upon adding a 0.92 xenon:propane ratio gas mixture to ice particles, the time required for achieving 62% of the theoretical yield of propane enclathration is 20 min, versus 3 days for pure propane. Although the acceleration of clathrate formation decreases as xenon is depleted, enhancement continues even after the composition falls below 3% Xe. It appears that xenon serves to nucleate the dodecahedral 5^{12} cages while propane nucleates the larger $5^{12}6^4$ cages. The type II xenon−propane structure is not only more thermodynamically stable than either pure hydrate; it is also formed much more quickly than propane clathrate, nearly as fast as type I xenon clathrate.

Introduction

The study of gas clathrate hydrates has recently accelerated due to renewed interest in harvesting natural deposits and using clathrate hydrates as a storage and transportation medium for hydrogen and hydrocarbon gases.[1] The latter application requires the rapid synthesis of gas clathrate hydrates on a large scale. Even on a smaller scale, synthesis can be quite slow.[2−4] Neither hydrogen nor methane nor propane is miscible in water, therefore, simply freezing a mixture is not an option. Often, exposing liquid water to the gas results in the formation of a thin crust on the liquid surface.[5−8]

Stern et al. have partially surmounted this problem by exposing finely powdered ice to the gas, but synthesis is still slow and extended cycling about the ice freezing point is required to drive the synthesis to completion.[9,10] In general, it is difficult to perform quantitative formation kinetics studies for these systems because the surfaces of ice grain particles are both rough and constantly changing. Although Staykova et al. have studied hydrate growth from well-defined ice spheres, only small numbers of such spheres were employed so that only small amounts of gas were enclathrated.[11] We are investigating techniques for producing macroscopic samples more quickly.[12] Our goal is to rapidly produce large quantities of binary clathrate product through the use of helper gases or promoters.[13−16] Gulluru and Devlin have shown that a moderately good proton-acceptor molecule, such as ethylene oxide, greatly accelerates hydrate formation at temperatures as low as 120 K.[12] Here, we report results using xenon as the promoter gas.

We have chosen propane clathrate hydrate for this study because its type II structure is stable near ambient conditions so that neither cryogenic temperatures nor high pressures are necessary. The type II structure has a unit cell made up of 136 water molecules forming 16 dodecahedral 5^{12} cages and 8 hexakaidecahedral $5^{12}6^4$ cages. Propane only fits into the $5^{12}6^4$ cages leaving the 5^{12} cages available to store another gas. (5^{12} dodecahedral cages are made of 20 water molecules forming 12 pentagonal faces; $5^{12}6^4$ cages are made from 28 water molecules forming 12 pentagonal faces and 4 hexagonal faces.) If an efficient formation mechanism can be found for a mixed methane/propane hydrate, two methane molecules would be contained for each propane molecule, resulting in efficient energy storage at near ambient temperature and pressure.

Stern et al. developed a synthesis technique that involves bathing small ice particles in liquid propane and cycling the cell temperature about the ice melting point,[9,10] To achieve 100% propane hydrate formation typically took 17−21 days. At the end of this procedure, the consistency of the sample has changed from that of a powder to a fused, porous solid cylinder. The original ice particles have grown together via clathrate growth at the interface between particles.[11,17]

In this paper, we report that the rate of propane enclathration is accelerated by over an order of magnitude if xenon is added to the reaction mixture. We have made quantitative measurements of the gas uptake for several different experimental procedures. Although the propane in propane/xenon mixtures is enclathrated much faster than pure propane, the xenon is not acting simply as a catalyst because it is also being enclathrated. The presence of xenon in the mixture results in propane enclathration in a type II structure almost as fast as pure xenon forms its preferred type I structure. Adding a 0.92:1 Xe:C_3H_8 gas mixture to ice particles yields 62% of the theoretical yield of propane enclathration in 20 min. The same ice particles exposed to pure propane gas require 3 days to achieve 67% theoretical yield. Here "theoretical yield" is defined relative to complete conversion of ice to type II clathrate with a propane molecule in every large cage, i.e., a 1:17 propane to H_2O ratio.

Experimental Section

A typical experiment was performed as follows. First, ice pellets were formed by dripping nanopure water into liquid nitrogen. The ice pellets were then ground in a cold coffee grinder. After the powder was sieved through a 250 μm mesh screen, a 10 g sample was placed into a 260 cm^3 cell, warmed to 272 K, and exposed to the absorbate gases. The gas was delivered to the cell through 6.4 mm tubing that is coiled and submerged in the cooling bath to avoid heating of the ice particles during gas addition. The cell pressure and temperature

* To whom correspondence should be addressed. E-mail: kcjanda@uci.edu.

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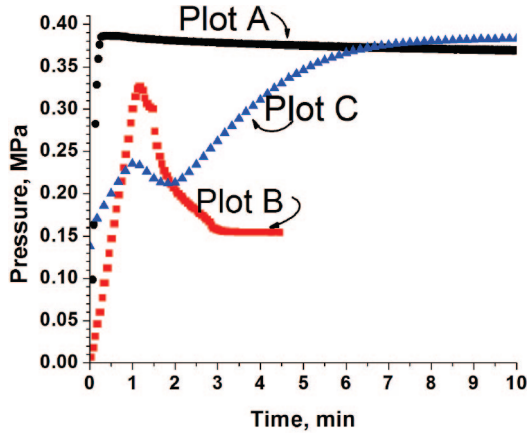

Figure 1. Pressure vs time when xenon and/or propane is added to 10 g samples of ice grains. Plot A: For pure propane the pressure was quickly raised to 0.38 MPa. Uptake was very slow: equilibrium was not reached after 3 days. Plot B: For xenon, the pressure was raised to 0.33 MPa more slowly and, upon closing the inlet valve, equilibrium was reached in 2 min. Plot C: Xenon was first added to 0.14 MPa and then propane was added slowly. Gas uptake initiated when the combined pressure reached 0.23 MPa. In this case, the inlet valve was not closed, so it is not possible to state if equilibrium was reached.

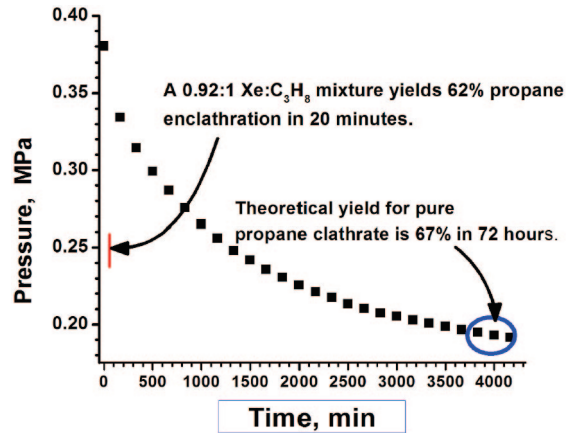

Figure 2. Pressure vs time when 0.38 MPa of propane is quickly added to the reaction cell containing 10.8 g of ice grains. Although equilibrium was not reached after 72 h, 67% of the ice was converted to clathrate. In contrast, a 0.92:1 Xe:C_3H_8 mixture achieves a 62% yield in 20 min, over 2 orders of magnitude faster.

were monitored and recorded over time throughout the experimental run, including clathrate formation and decomposition. Gas chromatography[18] analysis was performed on the gas phase in the clathrate cell before and after clathrate decomposition. The quantity of ice particles converted to clathrate hydrate and the amount of propane and xenon incorporated into the clathrate hydrate were calculated from the cell pressure and gas-phase composition. All gas analysis was performed with the total pressure below the propane vapor pressure. The pressure data below is precise to ±1%, the temperature data to ±0.5 K, and the yield values to ±3%. However, the reproducibility of that data is limited to ±10%. The main source of variability is, we believe, due to variations in the particle size distribution from the ice grinding and sieving process.

Results

Pressure versus time data were plotted and analyzed for absorbate uptake into ice grains. Figure 1 shows three runs that illustrate qualitative trends for different gases. Plot A shows the pressure changes versus time when 10 g of ice particles is exposed to pure propane gas at 272 K. In this case, the propane was added as quickly as possible up to a pressure of 0.38 MPa. When the inlet valve was closed (t = 0.3 min), the propane pressure dropped slowly, 0.024 MPa in 20 min. At this pressure and temperature, the propane compressibility is 0.915; therefore, 0.0029 moles of propane were absorbed in 20 min, yielding an overall solid stoichiometry 0.083 C_3H_8:17 H_2O, for an 8.3% theoretical yield of propane clathrate hydrate. As shown in Figure 2, the uptake rate decreases from a slow initial rate, and even after 3 days the solid has only achieved 67% of the theoretical uptake, and has not yet reached the equilibrium vapor pressure, 0.17 MPa.

In contrast, when a similar experiment was performed with xenon gas, Figure 1, plot B, it is impossible to get the starting pressure up to 0.38 MPa before the onset of rapid xenon clathrate formation. The xenon was added more slowly to the cell to emphasize changes in the uptake kinetics with time. When the pressure reached about 0.33 MPa, clathrate hydrate formation rapidly accelerated resulting in a pressure drop, and the inlet valve was quickly closed. The xenon pressure then dropped to the hydrate vapor pressure of 0.15 MPa at 272 K within 1.5 min. During this short period of time, 0.021 moles of xenon were absorbed yielding a solid stoichiometry of 1.7 Xe:46 H_2O, or a 21% theoretical yield relative to a perfect type I hydrate.[14,19] In contrast to the case of propane for which 8.3% of the ice was converted to clathrate in 20 min, 21% of the ice is converted to xenon clathrate in only 1.5 min, and the reaction only stops because the xenon clathrate equilibrium vapor pressure is reached. If more xenon is added after the system reaches equilibrium, further uptake is slower, showing that the remaining ice surface is less exposed to the ambient gas because of clathrate crust formation, as expected.

Plot C in Figure 1 was obtained by sequentially exposing 10 g of ice particles first to xenon and then to propane. First, xenon was added to achieve a pressure of 0.14 MPa, low enough to avoid the formation of type I xenon hydrate. Next, propane was added slowly to the cell through a needle valve to yield a final pressure of 0.38 MPa in 10 min. After another 10 min of annealing, the needle valve was closed and the remaining gas was analyzed for composition. Finally, after quickly reducing the gas pressure in the cell to 0.14 MPa, the solid was decomposed and the gas phase was analyzed again. The reason for venting some of the head gas before decomposition is to avoid the production of liquid propane, which would compromise the stoichiometric analysis. Samples were never vented to pressures lower than the expected clathrate vapor pressure to avoid hydrate decomposition before the analysis period.

The most interesting aspect of Figure 1, plot C, is the downturn in pressure just past t = 1 min: rapid clathrate formation ensued and lasted for 1.5 min. The cell pressure dropped while the propane gas still flowed into the cell. We estimate that 12 mmol of gas are absorbed into the ice during this time. After 20 min the remaining gas-phase composition was 97% ± 2% propane and only 3% xenon. The cell pressure was then decreased to 0.14 MPa at 272 K and the solid phase was decomposed. After decomposition the pressure was 0.37 MPa at 293 K and the gas phase was composed of 65% ± 2% propane and 35% xenon. Analyzing these results shows that the stoichiometry of the solid was 0.40 Xe:0.28 C_3H_8:17 H_2O. After the initial fast uptake of 12 mM of gas, another 11.6 mM was absorbed during the next 18.5 min. For the ideal type II clathrate, with the small cages filled by Xe and the large cages filled with C_3H_8, the stoichiometric ratio would be 2 Xe:1 C_3H_8: 17 H_2O. Propane uptake was at the expense of consuming

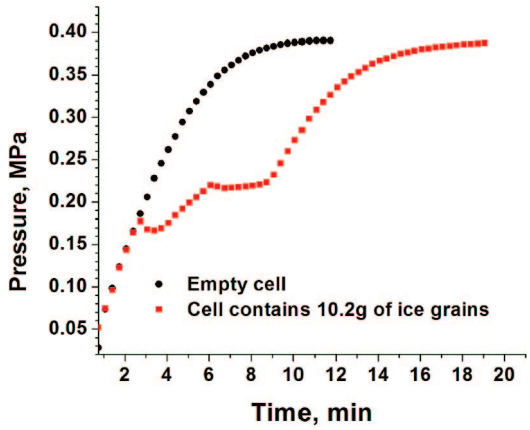

Figure 3. Pressure vs time when a 1.7/1 Xe:C_3H_8 mixture is allowed to flow through a needle valve into an empty cell (solid circles), and a cell that contained 10.3 g of ice grains (open circles). The gas flow rate is a function of the pressure drop across the needle valve, so any difference between the slopes of the two curves at a given pressure is due to gas uptake by the ice. It is apparent that the period of maximum gas uptake occurs between 3 and 9 min.

xenon; 1.4 times as much xenon as propane was enclathrated, compared to the "ideal" 2:1 ratio.

Another experiment similar to that of Figure 1, plot C, except that the contents of the cell were allowed to anneal for 210 min, yielded a solid stoichiometry of 0.45 xenon:0.47 propane: 17 H_2O. Thus, propane uptake continues even after most of the xenon is depleted. Another 19 mM of propane were enclathrated during the final 190 min, and the final stoichiometry was 47% of the ideal propane uptake. This shows that even a low xenon partial pressure, <0.03 MPa Xe, still promotes further propane uptake. It is not obvious whether this is due to new clathrate growth, or due to further annealing of the existing solid. Probably both processes occur.

Experiments were also performed in which the ice grains were exposed to mixtures of xenon and propane gases rather than adding the gases sequentially. Three mixtures were prepared with xenon-to-propane ratios of 1.7, 0.92, and 0.49. The mixtures were added to the cell, again containing 10 g of ice grains, through a needle valve over a period of 20 min. Figure 3 illustrates the results for the 1.7 xenon/propane ratio. The black circles show the pressure increase when the mixture is added to an empty cell; the red squares show the pressure increase when the cell contains ice grains. The difference between these two curves is due to gas uptake by clathrate formation. In this case, rapid clathrate formation ensues when the pressure reaches 0.18 MPa, then slows for about 3 min, and again accelerates when the pressure reaches 0.22 MPa. Clearly, the clathrate formation kinetics is complicated. Analysis of the curves reveals that 43.6 mM of gas is absorbed during the 6.5 min period of rapid gas uptake. After 20 min the remaining gas was analyzed and found to have a xenon/propane ratio of 1.7, the same as the initial mixture. After the pressure was reduced to 0.10 MPa, the hydrate was decomposed and yielded a pressure of 0.66 MPa with a xenon/propane ratio of 1.7. Xenon and propane were enclathrated proportional to the initial composition ratio, and the total uptake over 20 min was 60.0 mM. The final stoichiometry 1.1 xenon:0.66 propane:17 H_2O shows that the uptake of propane was 66% of the theoretical yield in 20 min, and most of the uptake occurred in the 6 min period during which the slope is reduced from that of the empty cell.

For the other two mixtures, the uptake rates were slower and the difference between gas flow into the empty cell and that with ice grains is not as dramatic as for the data in Figure 3. The overall uptake results are reported in Table 1 for all three mixtures. For the 0.92 Xe:propane mixture, more xenon than propane was absorbed by the ice. However, the propane absorption was 62% of the theoretical yield in only 20 min.

TABLE 1: Uptake of Xenon and Propane into 10 g of Ice Grains at 272 K and 0.38 MPa

initial Xe/propane ratio	1.7	0.92	0.49
uptake period, min	20	20	20
pressure before decomposition, MPa	0.10	0.10	0.11
Xe/propane gas ratio before decomposition	1.9	0.75	0.37
pressure after decomposition, MPa	0.66	0.55	0.24
Xe/propane gas ratio after decomposition	1.7	1.2	0.61
Xe/propane ratio in solid phase	1.7	1.3	1.0
solid stoichiometry			
xenon	1.1	0.81	0.18
propane	0.66	0.62	0.18
water	17	17	17

Table 2 summarizes the molar uptake, overall uptake rates, theoretical percent yields, and stoichiometry for the experiments described above, as well as propane type II and xenon type I clathrate hydrate formation experiments. Except for the case of pure Xe, uptake amounts are reported for a 20 min exposure. Clearly the 1.7 Xe:propane ratio mixture is the most efficient by this measure, but the 0.92 Xe:propane ratio mixture is nearly as efficient. Sequential addition of first xenon and then propane appears to use up the xenon rather inefficiently, even though the initial uptake rate is quite high. Although the leanest mixture gives the slowest propane uptake, it is still twice as fast as for pure propane.

Discussion

Xenon clathrates form quickly but propane clathrates grow slowly. Under the conditions used here, pure xenon yields the type I unit cell with efficient filling of both types of cages for a typical stoichiometry of 1 Xe for 6.3 water molecules near 273 K, 1 atm.[20,21] This implies that the $5^{12}6^2$ cages are 97% occupied and the smaller 5^{12} cages are 65% filled.[21] Propane, on the other hand, resides only in the larger cages of the type II structure with an ideal stoichiometry of $C_3H_8 \cdot (H_2O)_{17}$. In the case of propane clathrate, 2/3 of the cells must form without the aid of a guest molecule to form a template. We suspect that the accelerated uptake kinetics for the Xe:propane mixture is due to xenon-induced nucleation of the small cages concomitant with propane nucleation of the large cages. Tse and Klug have performed[22] molecular dynamics simulations of xenon interacting with an ice surface and find that the xenon becomes intercalated in less than a nanosecond and that protocages are already being formed during the simulation. This is consistent with the general idea that ice surfaces near the melting point are quite labile, almost liquidlike. The interaction of propane with the ice surface is also expected to be reasonably strong, so, when both molecules are present, each of the three cage types can be formed efficiently. Thermodynamics clearly favors the formation of the xenon/propane type II double hydrate, and the data presented above shows that this indeed is the predominant outcome because the final pressure is close to the double hydrate vapor pressure.[23] The pressure at which rapid clathrate formation ensues is lower for the mixed gases, 0.17 MPa in Figure 3, than for pure xenon, 0.32 MPa in Figure 1, plot B. The xenon and propane work synergistically, filling both small and large cages, increasing the stability of the hydrate lattice and lowering the vapor pressure of the clathrate.

Although xenon clathrate formation goes to equilibrium in 3 min (Figure 1, plot B), while propane clathrate formation has

TABLE 2: Average Uptake Rates for the Pure and Binary Synthesis Experiments

experiment	C_3H_8 type II	Xe type I	Xe, followed by C_3H_8	1.7 Xe/C_3H_8 mixture	0.92 Xe/C_3H_8 mixture	0.49 Xe/C_3H_8 mixture
duration, min	20	1.5	20	20	20	20
uptake, mmol						
Xe	na	21	14	37	27	6.0
C_3H_8	2.9	na	9.7	22	20	6.0
uptake rate,[a] mmol/min/g-ice	0.013	1.4	0.11	0.29	0.23	0.057
theoretical % yield						
Xe	na	21	20	55	41	9.0
C_3H_8	8.3	na	28	66	62	18

[a] Includes xenon and propane uptake.

not obtained equilibrium in 3 days (Figure 2), the temperatures at which the two hydrates have 1 atm vapor pressure are quite similar: 262.8 K for Xe; 261.6 K for propane.[24] By this criterion the stabilities of the two hydrates are similar and, on average, each propane molecule yields more lattice stabilization than a xenon atom. The difference in the rates of formation of the two pure clathrates is due more to local dynamics than to thermodynamics. Also, because Xe clathrate formation quickly goes to equilibrium under the conditions employed here shows that any crust layer formed over the ice surface does not significantly retard Xe incorporation into the hydrate. This may be due to the relatively high temperature of these experiments.

Uptake for the premixed 1.7:1 Xe:C_3H_8 mixture exhibited the highest yield of propane enclathration, 66% in 20 min, with about three-quarters of the propane enclathrated in the first 10 min as the cell was being filled (Figure 3). Although more xenon than propane was enclathrated, xenon enclathration was a lower fraction of the theoretical yield than was that of propane. The uptake of xenon and propane was nearly proportional to the composition of the gas. These experiments do not determine whether type I xenon hydrate was formed before the onset of type II double hydrate. For the mixtures with lower partial pressure of xenon, onset of gas uptake occurred at about the same pressure as for the richer mixture, but the uptake rates were slower. For the 0.92 xenon/propane mixture, observable growth started at 0.19 MPa, but was never fast enough so that dP/dt was close to zero, and the growth period extended to nearly the end of the 20 min data acquisition period. The amount of propane trapped into the hydrate after 20 min is nearly as large for this mixture as for the 1.7 xenon/propane mixture. For the 0.49 xenon/propane mixture the onset was again about 0.18 MPa, but the uptake rate was considerably slower.

The data presented here clearly show that, under the conditions used, xenon greatly accelerates the enclathration of propane. Other additives may be equally effective while being less expensive. Devlin et al. have used ethylene oxide to stimulate clathrate crystal growth at low temperatures.[12] If the initial stabilization of the 5^{12} cage is the key step, as seems likely, then any small polar molecule may be a likely candidate to increase the clathrate formation rate. Perhaps the H_2S content of certain natural deposits could act as a clathrate growth initiator. Also, since the ultimate goal is to enclathrate both methane and propane, the methane in the small cages may also accelerate the uptake rate once the growth initiation is achieved.

It may also be possible to lower the required amount of the helper gas by employing a more sophisticated growth process, e.g., producing smaller ice particles, a more complicated sequential gas exposure, or mechanical methods to continually expose the remaining ice surface to the gas. The important practical applications for rapidly growing large quantities of clathrate justify further study of this problem.

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