Reversible Reactions of Gaseous Ions.
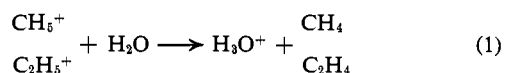## II. Propane–Water System

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Abstract: Reversible reactions in the propane–water system have been studied, namely, the hydrated proton equilibria, $H(H_2O)_n^+ + H_2O \rightleftarrows H(H_2O)_{n+1}^+$, and the hydrated propyl ion equilibria, $C_3H_7(H_2O)_{n-1}^+ + H_2O \rightleftarrows C_3H_7(H_2O)_n^+$. Mathematical models are constructed of sequential reversible ionic reactions occurring in a mass spectrometer ion source operating under chemical ionization conditions. From these models, information is obtained about the degree of attainment of equilibrium, and rationalizations are found for certain experimentally observed nonlinearities in van't Hoff plots and inconstancies in equilibrium constant vs. pressure plots. Thermodynamic values for the several reversible reactions are obtained from the experimental equilibrium constants and their temperature coefficients. For the proton hydrate reactions, the changes in free energy are more negative in the propane–water system than in the methane–water system. The free energy changes for the hydrated proton equilibria are -11.2, -9.7, and -8.6 kcal/mol for the $n = 1$, 2, and 3 cases, respectively. Our value for the change in free energy of the first hydrated proton equilibrium is approximately half that found by Kebarle,[3] while our value for the second hydrated proton equilibrium is three-quarters of Kebarle's value. The free energy change for the addition of sec-$C_3H_7^+$ to H_2O is less negative than that for addition of H_3O^+ to H_2O, but the addition of more H_2O molecules to $C_3H_7 \cdot OH_2^+$ and $H_3O \cdot H_2O^+$ occurs with identical free energy changes. The proton affinity of i-C_3H_7OH is found to be 190 kcal/mol.

We have undertaken a series of investigations of the reversible reactions of gaseous ions, and the first system studied was the methane–water system (see preceding paper[2]). The water is ionized by chemical ionization from methane

$$\begin{matrix} CH_5^+ \\ + H_2O \longrightarrow H_3O^+ + \begin{matrix} CH_4 \\ \\ C_2H_4 \end{matrix} \\ C_2H_5^+ \end{matrix} \qquad (1)$$

which is followed by the reversible formation of the higher hydrates of the proton

$$H(H_2O)_n^+ + H_2O \rightleftarrows H(H_2O)_{n+1}^+ \qquad (2)$$
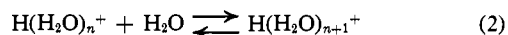
Equilibrium constants for (2) are defined by

$$K_P = (I_{H(H_2O)_{n+1}^+}/I_{H(H_2O)_n^+})(1/P_{H_2O}) \qquad (3)$$

and thermodynamic values for the reactions 2 are obtained from the values of K and the temperature variations of these quantities. An extensive previous study of the water system has been made by Kebarle and coworkers.[3] In their work the initial formation of H_3O^+ was by the reaction

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \qquad (4)$$
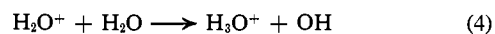
At the time that our study of the methane–water system was nearly complete, a paper on the formation and collision-induced dissociation of the hydrates of the proton by DePaz, Leventhal, and Friedman[4] appeared, and these workers presented data which they interpreted to mean that it is unlikely or perhaps impossible to attain true thermodynamic equilibrium in experiments such as Kebarle's. Our experiments and those of Kebarle are similar enough that this allegation applies with

full force to our studies also. The gist of the argument by Friedman and coworkers is that both the initial formation of H_3O^+ and the subsequent formations of the higher hydrates are exothermic reactions, and insufficient collisions can occur in the ionization chamber of the mass spectrometer to remove the heat of reaction and produce an equilibrium distribution of energy. Calculations based on the accepted values of ionic heats of formation[5a] and the value of 164 kcal/mol for the proton affinity of water[5b] give the result that in reaction 1 proton transfers from CH_5^+ and $C_2H_5^+$ are 39 and 5 kcal/mol exothermic, respectively. Since CH_5^+ and $C_2H_5^+$ each comprise about half the ions in the methane plasma, the average exothermicity for the protonation of water by methane is 22 kcal/mol. The exothermicity for reaction 4 involved in Kebarle's work is 23 kcal/mol. The exothermicities for the formation of the higher hydrates of the proton vary according to the reaction and the investigator,[2,3] but the range of heats of reaction proposed is from -36 to -8.5 kcal/mol. Thus the heats released by the reactions are appreciable, and the point made by Friedman is worthy of consideration. One must also keep in mind that in the experiments of Kebarle the gas present in the ionization chamber was water or water plus rare gas, and in the Friedman experiments only water (D_2O) was present. The number of degrees of freedom in these gases is not large, and they will not be very efficient at removing excitation energy from the proton hydrates.

One of the advantages of the chemical ionization technique is its versatility, and we have found that it is possible to protonate water and study the formation of the higher hydrates of the proton using propane as the reactant. This paper gives the results of our investigation of the propane–water system. The major ion

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(2) D. P. Beggs and F. H. Field, *J. Amer. Chem. Soc.*, **93**, 1567 (1971).

(3) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *ibid.*, **89**, 6393 (1967).

(4) M. DePaz, J. J. Leventhal, and L. Friedman, *J. Chem. Phys.*, **51**, 3748 (1969).

(5) (a) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 26 (1969); (b) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

in the spectrum of propane at a pressure of 0.8–1.0 Torr is that with m/e 43, which may reasonably be assumed to be sec-$C_3H_7^+$. When water is added to the propane, H_3O^+ and the higher proton hydrates are formed, although the total amount of water ions formed is appreciably smaller for a given amount of water than is the case in the chemical ionization of water using methane as reactant. One's first thought is that in the chemical ionization of water by propane the major protonating ion is sec-$C_3H_7^+$, thus

$$sec\text{-}C_3H_7^+ + H_2O \longrightarrow H_3O^+ + C_3H_6 \qquad (5)$$

However, if one takes $\Delta H_f(sec\text{-}C_3H_7^+) = 190$ kcal/mol,[5a] one calculates that reaction 5 is 16 kcal/mol endothermic. The proscriptions on endothermic reactions which apply to ion–molecule reactions at relatively low pressures do not necessarily apply at chemical ionization conditions wherein enough collisions occur to permit thermal activation of reactions. Thus (5) may be the source of the H_3O^+ ions initially formed. Even if we grant that we are somewhat uncertain about their source, from these energetic considerations and from the fact that water ions are not formed with high intensity it seems clear that the exothermicity involved in water ion formation from propane will be significantly less than the exothermicities of their formation from methane and from water itself (reaction 4). In addition, propane has 27 vibrational degrees of freedom, compared with 9 for methane, 3 for water, and none for the rare gases. Propane thus should be significantly more efficient in the absorption of the exothermic heats of reaction than the substances involved in the previous studies.

In our methane–water study,[2] and in some previous experiments on neat water,[6] our results for the 1,2 and 2,3 hydrated proton equilibria 2 were in serious disagreement with those of Kebarle.[3] Any effect of the exothermicity of the initial protonation would appear most strongly in these lower equilibria, and thus the study of the propane–water system was undertaken in the hope that it would provide information concerning our discrepancy with Kebarle as well as about the Friedman exothermicity thesis.

In addition, we give a mathematical analysis of reversible ionic reactions occurring under chemical ionization conditions to help in forming judgments about the extent to which equilibrium is attained by these reactions.

Experimental Section

The experiments were done with the Esso chemical physics mass spectrometer using the new source (source III) described in the methane–water paper.[2] The general technique and the types of experiments performed were identical with those of the methane–water work. Laboratory distilled water and Matheson CP propane were used. Gas chromatographic analysis of the propane showed that it contained 0.48% isobutane, 0.17% ethane, and 0.17% unidentified impurity. The mass spectrometer showed that it contained enough water to cause problems, but this was removed to a sufficient extent by passing the propane through a refrigerant bath at −40°.

Results

A. Mathematical Analysis. We are concerned in this work with the reversible reactions of gaseous ions occurring in the ionization chamber of a mass spec-

(6) F. H. Field, *J. Amer. Chem. Soc.*, **91**, 2827 (1969).

trometer operated in the chemical ionization mode. The total pressure, and, to a greater extent, the partial pressures of the reactants are low by conventional standards, and the residence times of the ions in the ionization chamber are also low. Specifically, the total pressure is usually on the order of 1.0 Torr, the partial pressures of reactants may be only 10^{-2}–10^{-3} as large, and the ion residence times lie in the range 10^{-5}–10^{-4} sec. Under these circumstances questions arise about the extent to which equilibrium can be achieved by the reversible reactions occurring, and in this section we undertake a mathematical analysis to provide some answers to these questions.

We first consider a system involving chemical ionization of a substance by a reactant, and the ionized substance can then enter into a reversible reaction with neutral substrate to produce a new ion. We write

$$RH^+ + A \xrightarrow{k_i} AH^+ + R \qquad (6)$$

followed by

$$AH^+ + A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A_2H^+ \qquad (7)$$
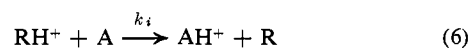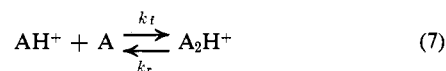
Using the point of view previously advanced for the chemical ionization process,[7] we consider that the reactant ions RH^+ are formed in or very near to the electron beam, and reactions 6 and 7 occur as the ions are drifting out of the ionization chamber under the influence of the repeller field. We may treat the system as a set of coupled reactions occurring in elements of volume drifting between the electron beam and the ion exit slit.

The differential equation for the kinetics of (6) and (7) is

$$d(AH^+)/dt = k_i(RH^+)(A) +$$
$$k_r(A_2H^+) - k_f(AH^+)(A) \qquad (8)$$

In our experiments, (A) is not a function of t; *i.e.*, the forward reactions are pseudo first order. The relationship between the several concentrations is

$$(A_2H^+) = (RH^+)_0 - (RH^+) - (AH^+) \qquad (9)$$

Substitution of eq 9 into eq 8 and solving leads to the expression

$$\frac{(AH^+)}{(AH^+)_0} = \frac{1}{(1 - e^{-k_i(A)t})R(k_i(A) - R)} \times$$
$$\{k_r(k_i(A) - R)(1 - e^{-Rt}) +$$
$$R(k_i(A) - k_r)(e^{-Rt} - e^{-k_i(A)t})\} \qquad (10)$$

where

$$R = k_r + k_f(A) \qquad (11)$$

$$(AH^+)_0 = (AH^+) + (A_2H^+) \qquad (12)$$

Thus

$$(AH^+)_0/(AH^+) = 1 + (A_2H^+)/(AH^+) =$$
$$1 + K^a(A) \qquad (13)$$

With the use of appropriate values for the various quantities in (10) and (11) and with the use of (12) we can calculate the relative concentrations of the species involved in the reversible reaction 7. Using these con-

(7) F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).

Table I. Mathematical Model Calculations. Chemical Ionization and Equilibrium[a]

	K^a and K^t values					
	Variation of k_r[b]					
k_r	10^2	10^3	10^4	10^5	10^6	10^7
K^a	7.2×10^{-15}	7.0×10^{-15}	7.7×10^{-15}	4.6×10^{-15}	9.3×10^{-16}	1.0×10^{-16}
K^a/K^t	0.00072	0.0070	0.077	0.46	0.93	1.0
$(A_2H^+)/(AH^+)$	0.72	0.70	0.77	0.46	0.093	0.01
	Variation of (A)[c]					
(A), molecules/cm^3	10^{13}	10^{14}	10^{15}			
(A), Torr	0.0005	0.005	0.050			
K^a	2.9×10^{-15}	4.6×10^{-15}	1.0×10^{-14}			
K^a/K^t	0.29	0.46	1.0			
$(A_2H^+)/(AH^+)$	0.029	0.46	10			
	Variation of t[d]					
t, sec	10^{-5}	10^{-4}				
K^a	7.7×10^{-15}	1.0×10^{-13}				
K^a/K^t	0.077	1.0				
$(A_2H^+)/(AH^+)$	0.77	10				

[a] $RH^+ + A \xrightarrow{k_i} AH^+ + R$; $AH^+ + A \rightleftharpoons A_2H^+$ (k_f, forward; k_r, reverse). [b] $(A) = 10^{14}$ molecules/cm^3 (0.005 Torr), $t = 10^{-5}$ sec. [c] $k_r = 10^5$ sec^{-1}, $t = 10^{-5}$ sec. [d] $(A) = 10^{14}$ molecules/cm^3 (0.005 Torr), $k_r = 10^4$.

centrations an apparent equilibrium constant, K^a, can be calculated by means of (13), and this can be compared with the true equilibrium constant $K^t = k_f/k_r$. By making calculations over ranges of values appropriate to our experiments, we are able to obtain information about the extent to which (7) approaches equilibrium.

Appropriate values for the ionic residence time, t, the rate constants k_i, k_f, k_r, and the concentration (A) were arrived at in the following ways. We have previously calculated[6] that under chemical ionization conditions in our mass spectrometer the ionic residence time is about 10 sec at a repeller potential of 5 V. In the present series of studies of reversible reactions we have employed lower repeller potentials, which increases the residence times. In addition, we have previously mentioned[2] the possibility that the ions are to a degree subject to a restraining force in the ionization chamber, and this would further increase the residence time. Thus, for these calculations we take the ion residence time to be in the range 10^{-4}–10^{-5} sec.

In the absence of complicating factors the rate constants for exothermic ion–molecule reactions are on the order of 10^{-9} cm^3/(molecule sec), and without further consideration we take this value for k_i. Reaction 7 is an association–dissociation reaction, which might in fact follow third-order kinetics in the forward direction and second-order kinetics for the reverse reaction. Of course, in the presence of a constant excess of reactant gas the reactions will be pseudo second order and pseudo first order, respectively, and the mathematical analysis given above will apply. Good, Durden, and Kebarle[5] have found that in the presence of N_2 at pressures up to 4 Torr, the lower hydrated proton association reactions (2) are third order, with rate constants of about 3×10^{-27} cm^3/(molecule^2 sec). Propane will be a more efficient third body than N_2, and it is not unreasonable to assume that in propane the rate constants are larger by a factor of 10, i. e., 3×10^{-26} cm^3/(molecule^2 sec). If the total pressure is about 1 Torr, the molecule concentration is about 3×10^{16} molecules/sec, and the pseudo-second-order rate constant for the as-

sociation will be $(3 \times 10^{-26})(3 \times 10^{16}) = 9 \times 10^{-10}$ cm^3/(molecule sec). For simplicity we thus take k_f of (7) to be 10^{-9} cm^3/(molecule sec).

To estimate a reasonable value for k_r, the reverse reaction rate constant, we note from our previous chemical ionization studies of acetate esters[6,9,10] that the unimolecular ionic decompositions occurred with rate constants in the range 10^2–10^6 sec^{-1}, depending upon the identity of the reaction and the temperature. Furthermore, for ion residence times in the range 10^{-4}–10^{-5} sec, the magnitude of k_r will need be of the order 10^4–10^5 sec^{-1} if k_r is to affect the extent to which the reversible reaction proceeds, which is the experimentally observed fact. For these calculations we will take the range of values for k_r to be 10^2–10^7 sec^{-1}.

The value of (A) was taken to be 10^{13}–10^{15} molecules/ cm^3, which corresponds to a pressure range of 0.005–0.050 Torr. Much of our work on the reversible reactions in the water system has been done in this range. The products of these concentrations and the chosen value of 10^{-9} cm^3/(molecule sec) yield forward rates in (6) and (7) in the range of 10^4–10^6 sec^{-1}.

The results of these calculations are given in Table I. Perhaps the most interesting result is the trend of K^a/K^t with the value of k_r. For k_r values between 10^2 and 10^4 the ratio $(A_2H^+)/(AH^+)$ remains constant, and then the value of the ratio decreases as k_r increases further. The ratio K^a/K^t is far from unity at the lower values of k_r, but it approaches and attains unity at the larger values of k_r. Since k_r is directly related to the temperature, these calculations predict that for a range of low temperatures, variation of temperature should have no effect on the ionic concentrations, but as the temperature becomes higher, the concentrations should approach those for equilibrium. This result is easy to understand; namely, small values of k_r mean that the equilibrium lies far to the side of products, and 10^{-5} sec is insufficient time for equilibrium conversion of reactant to occur. Variation in the temperature will have no effect upon the amount of conversion observed, since this is kinetically limited by the rate of the tem-

(8) A. Good, D. A. Durden, and P. Kebarle, *J. Chem. Phys.*, **52**, 212 (1970).

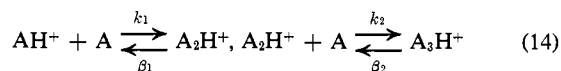(9) F. H. Field, *J. Amer. Chem. Soc.*, **91**, 6334 (1969).
(10) D. P. Weeks and F. H. Field, *ibid.*, **92**, 1600 (1970).

perature-independent forward reaction. The behavior predicted by the calculations has been observed,[2] and will be observed again in the experimental work reported later in this paper. Briefly described, van't Hoff plots of the equilibria observed in our mass spectrometer exhibit small or zero slope at low temperatures, but as the temperature increases the slope increases and eventually becomes constant. Figure 3 is a suitable example. The results given in the k_r variation portion of Table I suggest that equilibrium is approached when the ratio of product concentration to reactant concentration is 0.1 or less, and our experience has been that it is in this range that the van't Hoff plots become linear.

The results given in Table I for variations in (A) and residence time, t, are as one would expect; that is, as residence time and/or reactant concentration are increased, equilibrium is approached more closely. The approach to equilibrium is a sharper function of time than of concentration, and in addition a complication can result from increasing concentration. This will be examined below. Taken as a whole the results given in Table I indicate that with an ion residence time of about 10 μsec and a pressure of 5–50 μ, equilibrium can be largely achieved if the temperature is maintained high enough to keep the point of equilibrium well on the side of the reactant.

A peculiar but general phenomenon observed in our investigations of reversible reactions in the mass spectrometer is the fact that under certain circumstances the apparent equilibrium constant for a reaction decreases as neutral reactant is added. An example of the behavior referred to is shown in Figure 7 of ref 2. We have observed that this behavior is found in the lower reactions in a set of sequential equilibrium reactions, and the decrease in the K^a values seems to be associated with the appearance of significant amounts of the products of higher equilibria. We have wondered if the observed behavior be a manifestation of kinetic limitations operating in the sequential equilibrium system, and we therefore make the following calculation.

We represent the sequential equilibria by the reactions

$$\text{AH}^+ + \text{A} \underset{\beta_1}{\overset{k_1}{\rightleftarrows}} \text{A}_2\text{H}^+, \quad \text{A}_2\text{H}^+ + \text{A} \underset{\beta_2}{\overset{k_2}{\rightleftarrows}} \text{A}_3\text{H}^+ \quad (14)$$

The differential equations for the kinetics of reactions 14 are

$$d(\text{AH}^+)/dt = \beta_1(\text{A}_2\text{H}^+) - k_1(\text{AH}^+)(\text{A}) \quad (15)$$

$$d(\text{A}_2\text{H}^+)/dt = k_1(\text{AH}^+)(\text{A}) + \beta_2(\text{A}_3\text{H}^+) -$$
$$\beta_1(\text{A}_2\text{H}^+) - k_2(\text{A}_2\text{H}^+)(\text{A}) \quad (16)$$

$$d(\text{A}_3\text{H}^+)/dt = k_2(\text{A}_2\text{H}^+)(\text{A}) - \beta_2(\text{A}_3\text{H}^+) \quad (17)$$

The solutions of these equations are given by Rodiguin and Rodiguina[11] for the case of significance for us where the initial concentrations are

$$(\text{AH}^+)_0, \ (\text{A}_2\text{H}^+)_0 = (\text{A}_3\text{H}^+)_0 = 0 \quad (18)$$

(11) N. M. Rodiguin and E. N. Rodiguina, "Consecutive Chemical Reactions," Van Nostrand, Princeton, N. J., 1964, pp 42–43.

namely

$$(\text{AH}^+) = (\text{AH}^+)_0 \left\{ \frac{\beta_1\beta_2}{\gamma_1\gamma_2} + \right.$$
$$\frac{\gamma_1{}^2 - \gamma_1(\beta_1 + \beta_2 + \alpha_2) + \beta_1\beta_2}{\gamma_1(\gamma_1 - \gamma_2)} e^{-\gamma_1 t} +$$
$$\left. \frac{\gamma_2{}^2 - \gamma_2(\beta_1 + \beta_2 + \alpha_2)}{\gamma_2(\gamma_2 - \gamma_2)} e^{-\gamma_2 t} \right\} \quad (19)$$
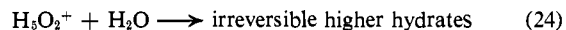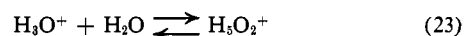
$$(\text{A}_2\text{H}^+) = k_1(\text{A})(\text{AH}^+)_0 \left\{ \frac{\beta_2}{\gamma_1\gamma_2} + \right.$$
$$\left. \frac{\beta_2 - \gamma_1}{\gamma_1(\gamma_1 - \gamma_2)} e^{-\gamma_1 t} + \frac{\beta_2 - \gamma_2}{\gamma_2(\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right\} \quad (20)$$

$$(\text{A}_3\text{H}^+) = k_1 k_2(\text{A})^2(\text{AH}^+)_0 \left\{ \frac{1}{\gamma_1\gamma_2} + \right.$$
$$\left. \frac{1}{\gamma_1(\gamma_1 - \gamma_2)} e^{-\gamma_1 t} + \frac{1}{\gamma_2(\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right\} \quad (21)$$

where t is the residence time and $(-\gamma_1)$ and $(-\gamma_2)$ are the solutions to the equation

$$\gamma^2 + \gamma(\beta_2 + \beta_1 + k_1(\text{A}) + k_2(\text{A})) +$$
$$\beta_2\beta_1 + \beta_2 k_1(\text{A}) + k_1 k_2(\text{A})^2 = 0 \quad (22)$$

In the hydrated proton reactions the number of sequential equilibria involved is large (eight equilibria have been identified so far) and a lower hydrate of the proton such as $\text{H}_5\text{O}_2{}^+$ can be converted to many higher species. However, because of mathematical complexities, we must approximate the system, and we think that the most realistic approximation is to consider all the higher equilibria to constitute a sink which will consume a lower species of interest. Thus we consider the case

$$\text{H}_3\text{O}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_5\text{O}_2{}^+ \quad (23)$$

$$\text{H}_5\text{O}_2{}^+ + \text{H}_2\text{O} \longrightarrow \text{irreversible higher hydrates} \quad (24)$$

Reactions 23 and 24 are specific examples of reactions 14, and we can treat this case mathematically by taking, in (14)–(22), $\beta_2 = 0$, $\text{AH}^+ = \text{H}_3\text{O}^+$, $\text{A}_2\text{H}^+ = \text{H}_5\text{O}_2{}^+$, and $\text{A} = \text{H}_2\text{O}$.

We make the same type of numerical calculation as we made in the case of chemical ionization followed by one equilibrium reaction; namely, we vary the values of the various experimental quantities appearing in (19)–(22) and calculate the corresponding values of the ratios of the apparent and true equilibrium constants, K^a and K^t, respectively, for reaction 23. Specifically, we calculate the effect of allowing the concentration of water in (23) and (24) to vary (the same concentration applying to both reactions), taking fixed values of the other parameters. The results of this calculation are given in Table II.

We take water concentrations between 10^{12} and 10^{15} molecules/cm³ (0.00005–0.050 Torr) for β_1 values of 10^5 and 10^6 sec⁻¹, and we also treat the case where k_2 is larger (by an arbitrarily assumed factor of 5) than k_1. We obtain the result that in all cases as $k_1(\text{H}_2\text{O})$ increases, the value of K^a/K^t decreases. The decrease is slow at first, but when significant consumption of H_3O^+ sets in, the decrease in the equilibrium constant ratio becomes more marked. In the case where the reaction to form the higher hydrates occurs at a faster rate ($k_1 = 0.2k_2$), the decrease in the equilibrium con-

Table II. Mathematical Model Calculations. Equilibrium and Sink[a,b]

	β_1	$(H_3O^+)^d$	$(H_5O_2^+)$	Higher hydrates	K^a/K^t
$k_1(H_2O) = k_2(H_2O)^c$					
10^3	10^5	0.99	0.006	4×10^{-4}	0.63
10^4		0.94	0.058	0.003	0.62
10^5		0.51	0.27	0.21	0.53
10^6		4×10^{-4}	0.001	1.0	0.27
10^3	10^6	1	1×10^{-3}	9×10^{-6}	1.0
10^4		0.99	0.010	9×10^{-4}	0.99
10^5		0.85	0.077	0.074	0.92
10^6		0.02	0.01	0.97	0.62
$k_1(H_2O) = $ $1/5\ k_2(H_2O)$					
10^3	10^6	1.0	1×10^{-3}	4×10^{-5}	1.0
10^4		0.99	0.009	4×10^{-3}	0.95
10^5		0.70	0.047	0.26	0.68
10^6		3×10^{-4}	6×10^{-5}	1.0	0.19

[a] $H_3O^+ + H_2O \rightleftarrows H_5O_2^+$ (k_1, forward; β_1, reverse); $H_5O_2^+ + H_2O \xrightarrow{k_2}$ higher hydrates. [b] $t = 10^{-5}$ sec. [c] $k_1 = k_2 = 10^{-9}$ cm³/(molecule sec) or $k_1 = 10^{-9}$, $k_2 = 5 \times 10^{-9}$. [d] $(H_3O^+)_0 = 1$.

stant ratio is more marked. We make this calculation for illustrative purposes, and because of the several approximations used a strict, quantitative representation of the experimentally observed data is not to be expected. However, the experimental fact is that the decrease in the equilibrium constants resulting from an increase in pressure is generally in the range 2–5 for an increase in water pressure by a factor of 10–100, and it is gratifying that the calculated changes in K^a/K^t given in Table II are comparable. We think that the agreement between the behavior of our mathematical model and the experimental behavior is evidence that the experimentally observed decrease in equilibrium constants with pressure is the result of time limitations on the establishment of equilibrium in sequential reversible reactions.

From the first two groups of calculated results in Table II ($\beta_2 = 10^5$ and 10^6 sec⁻¹) it may be seen that as the rate of the reverse reaction increases, *i.e.*, as the temperature increases and the point of equilibrium lies more to the reactant, the apparent equilibrium constant approaches the true constant. This is the result obtained previously for the mathematical model for chemical ionization followed by one equilibrium.

The conclusion we draw from our calculations is that in our system involving chemical ionization followed by sequential reversible reactions at the experimental conditions obtaining ($t = 10^{-5}$–10^{-4} sec, $P = 0.0005$–0.050 Torr), equilibria will not be established in all the reversible reactions simultaneously, but under certain conditions it will be established completely or to a significant degree in some of the reactions. The conditions must be such that not much reaction to form product occurs, and satisfactory results for lower reactions in the series can be obtained only in the absence of significant amounts of reactions higher in the sequence. In addition, we have made calculations similar to those given above that indicate that equilibrium can be established for reactions higher in the sequence, but then the accompanying lower reactions will not be at equilibrium. We assert that when the proper precautions are taken, a mass spectrometer operated in the chemical ionization mode can give meaningful information about reversible gaseous ionic reactions.

B. Experimental Study of the System Propane–Water. Hydrated Proton Equilibria. The experiments made in the propane–water system consisted of an extended temperature–pressure study wherein the spectra were determined at 40° intervals between 0 and 250° using water pressures of 0.0007 and 0.015, 0.045 and 0.070 Torr at each temperature. In addition, an extended-temperature study (between 0 and 250°) was made using water pressures such that the 1,2 equilibrium of reactions 2 could be closely examined. Since our previous work with neat water[6] and methane–water[2] and the work of Kebarle and coworkers[3] all agree for the higher proton hydrate equilibria, in the propane–water investigation more emphasis was placed on the lower equilibria.

We give in Table III the spectra obtained in the propane–water system at four values of the ionization chamber temperature. The spectra are quite com-

Table III. Spectra Obtained in the Propane–Water System[a]

m/e	Ion	40°	120°	200°	260°
19	H_3O^+	0.005	0.010	0.071	0.072
28	$C_2H_4^+$			0.002	0.002
29	$C_2H_5^+$			0.003	0.007
37	$H(H_2O)_2^+$	0.025	0.026	0.008	0.002
39	$C_3H_3^+$	0.024	0.025	0.024	0.028
42	$C_3H_6^+$	0.012	0.019	0.059	0.057
43	$C_3H_7^+$	0.156	0.228	0.701	0.740
44	$C_3H_8^+$	0.011	0.016	0.039	0.044
55	$H(H_2O)_3^+$, $C_4H_7^+$	0.043	0.044	0.010	0.008
56	$C_4H_8^+$	0.031	0.025	0.006	0.003
57	$C_4H_9^+$	0.373	0.467	0.040	0.021
58	$C_4H_{10}^+$	0.025	0.028	0.004	0.002
61	$C_3H_7^+ \cdot H_2O^+$	0.014	0.015	0.005	0.001
71	$C_5H_{11}^+$	0.003	0.006	0.007	0.005
73	$H(H_2O)_4^+$	0.083	0.004		
79	$C_3H_7 \cdot 2H_2O^+$	0.031	0.031	0.001	
85	$C_6H_{13}^+$	0.031	0.045	0.015	0.007
86	$C_6H_{14}^+$	0.011	0.007	0.002	0.001
87	$C_6H_{15}^+$	0.003			
88	$C_6H_{16}^+$	0.002			
91	$H(H_2O)_5^+$	0.003			
97	$C_3H_7 \cdot 3H_2O^+$	0.099	0.004		
111	$C_8H_{15}^+$	0.013			

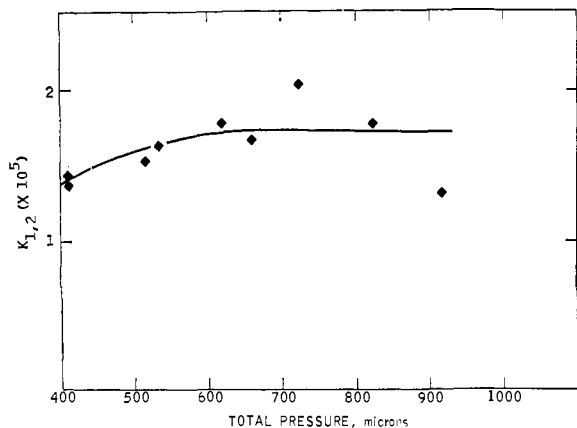[a] $P_{H_2O} = 0.015$ Torr, $P_{C_3H_8} = 0.80$ Torr, approximate field-free conditions.

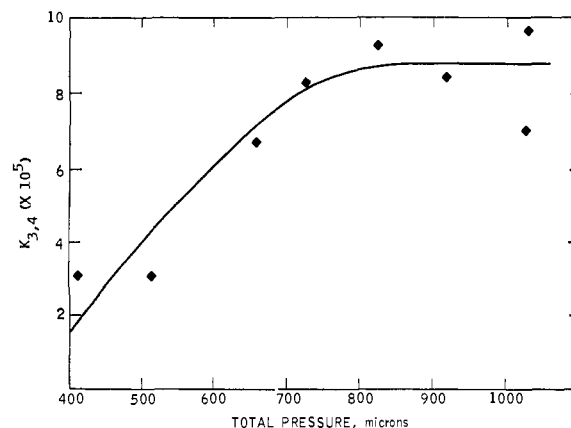Figure 1. $K_{1,2}$ vs. total pressure; $P_{H_2O} = 0.0007$ Torr, $P_{C_3H_8} =$ variable, source temperature $= 42°$.

Figure 2. $K_{3,4}$ vs. total pressure; $P_{H_2O} = 0.0007$ Torr, $P_{C_3H_8} =$ variable, source temperature $= 42°$.

plicated, and several different kinds of ions are present. These are the ions from propane such as those with m/e 39, 42, 43, 44, 55, and 71. In addition, we point out that the propane spectrum at low temperatures contains ions with m/e 85, 86, 87, and 88, and these are interesting, new hydrocarbon association ions. They will be considered in a later report. Another type of ion is the proton hydrates at m/e 19, 37, 55, 73, and 91; a third type is the ions formed by association of propyl ion (sec-$C_3H_7^+$) with varying numbers of water molecules, m/e 61, 79, and 97. The identification of this last type of ion is based on the correspondence between the observed m/e values and the calculated molecular weights of the ions and also upon the fact that the intensities of the ions vary appropriately with the pressures of both water and propane. Finally, the ion with m/e 57 exists and has a large intensity in the lower portion of the temperature range. We assign this ion the formula $tert$-$C_4H_9^+$, and we think that it is formed by the chemical ionization of isobutane impurity by sec-$C_3H_7^+$ from the propane. We know from our previous chemical ionization studies using isobutane as reactant[6] that $tert$-butyl ion does not react with water, and thus the $tert$-butyl is an inert ion in the propane–water system. The variations of the relative intensities of the several types of ions with temperature are complicated, since a number of competing reactions are involved in the production of the observed spectra. We shall not attempt to sort out and classify the total behavior of the system; rather we shall treat only the hydrated proton equilibria (this section) and the hydrated propyl ion equilibria (next section).

The effect of water pressure upon the equilibrium constants for the hydrated proton equilibria is the same as that described in our study of the methane–water system;[2] namely, for the higher equilibria and higher temperatures the equilibrium constants are independent of water pressure, but for the lower equilibria and lower temperatures the calculated values of the equilibrium constants decrease as the pressure increases. The behavior is depicted in Figures 6 and 7 of ref 2, and a mathematical rationalization of the behavior has been given in section A, above.

One of the criteria we use to indicate whether equilibrium is achieved is that of the effect of the pressure of reactant gas upon the equilibrium constants. This was done for the propane–water system, and we give in

Figures 1 and 2 plots of the effect of propane pressure upon the 1,2 and 3,4 proton hydrate equilibria, respectively. Rather different behavior is observed for the two reactions: $K_{1,2}$ is constant over the whole pressure range investigated, but $K_{3,4}$ rises at first before reaching constancy at about 0.7 Torr. One can speculate about the reasons for this difference in behavior, but we shall restrict ourselves to making the observation that for the reactions represented in Figures 1 and 2, and for all the other equilibria observed in the propane–water system, the equilibrium constants are sensibly independent of propane pressure at 0.80 Torr, the pressure at which our thermodynamic studies were carried out.

Equilibrium constants were determined for the several proton hydrate equilibria (reactions 2) at various temperatures and pressures. The restrictions necessary for obtaining meaningful results as discussed in section A were observed; in particular the temperature and water pressure were adjusted so as to hold the relative amount of product to less than 10%, and usually much less than this amount. It was still possible to vary the water pressure somewhat without changing the value of the equilibrium constant, and at higher temperatures, pressures between 0.007 and 0.200 Torr of water could be used without significantly affecting the value of the equilibrium constant obtained.

We give in Figures 3–5 the van't Hoff plots for the 1,2, 2,3, and 3,4 hydrated proton equilibria, where the equilibrium constants are calculated by eq 3. Different symbols are used for different water pressures in the plot for the 1,2 equilibrium (Figure 3); clearly the equilibrium constants are independent of pressure. The same independence is found for the other equilibria, but for simplicity different pressures are not distinguished on the plots. The lines in the figures are fitted by least squares using points along the length of the line as drawn. The plots of Figures 3–5 all have a linear portion at higher temperatures and a nonlinear, downward-curving portion at low temperatures. The curved portion in Figure 5 is not pronounced. These low-temperature deviations from linearity are identical with those described earlier for the methane–water system[2] and rationalized mathematically in section A. The linear portions of the plots extend over three to four decades of K values and about 200° of temperature.

The thermodynamic values for the first three hydrated proton equilibria calculated from the van't Hoff

Table IV. Experimental Thermodynamic Values for Hydrated Proton Equilibria $H(H_2O)_n^+ + H_2O \rightleftharpoons H(H_2O)_{n+1}$

| $n, n+1$ | $-\Delta G_{300}$, kcal/mol | | | $K_{300}{}^a$ | | | $-\Delta H$, kcal/mol | | | $-\Delta S$, cal/(deg mol) | | |
	K^b	$B + F^c$	d	K	$B + F$	d	K	$B + F$	d	K	$B + F$	d
1, 2	25	7.7	11.2	1.8×10^{18}	4.2×10^6	1.5×10^8	36	7	16.3	33.3	-1	17.2
2, 3	13.6	9.3	9.7	8.7×10^9	6.3×10^6	1.2×10^7	22.3	13	14.8	29	14	16.9
3, 4	8.5	8.4	8.6	1.6×10^6	1.6×10^6	1.9×10^6	17	16.8	17.6	28.3	28	20.0

^{a} Standard state = 1 atm. ^{b} Kebarle and coworkers, ref 3. ^{c} Beggs and Field, ref 2; methane reactant. ^{d} This work.

plots given in Figures 3–5 are listed in Table IV. For comparison we include the values obtained by Kebarle and coworkers[3] and the values obtained in this laboratory in the methane–water system.[2] We shall defer

Figure 3. van't Hoff plot for $H_3O^+ + H_2O \rightleftharpoons H_5O_2^+$, P_{H_2O} = variable. Pressure key: ◆, 0.0007 Torr; ●, 0.0070 Torr; ▼, 0.015 Torr; ■, 0.045 Torr; □, miscellaneous, 0.070–0.200 Torr.
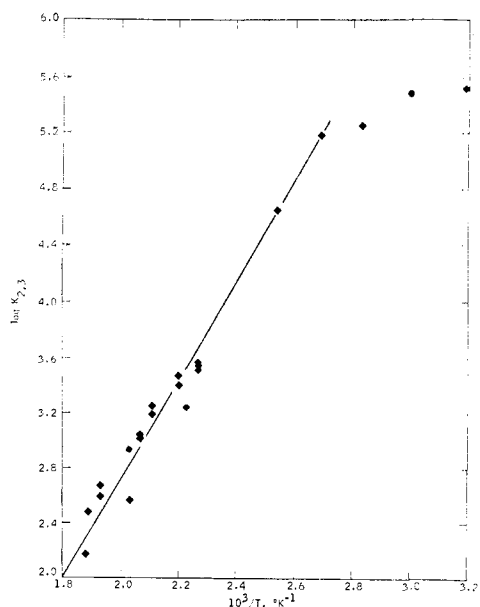
Figure 4. van't Hoff plot for $H_5O_2^+ + H_2O \rightleftharpoons H_7O_3^+$; P_{H_2O} = 0.0007–0.050 Torr.

discussion of the results until after the results on the hydrated propyl ion have been presented.

C. Experimental Study of the System Propane–Water. Hydrated Propyl Ion Equilibria. As may be seen from Table III, ions with the formula and behavior of hydrated propyl ions appear in the spectra of propane–water mixtures. Their intensities change with
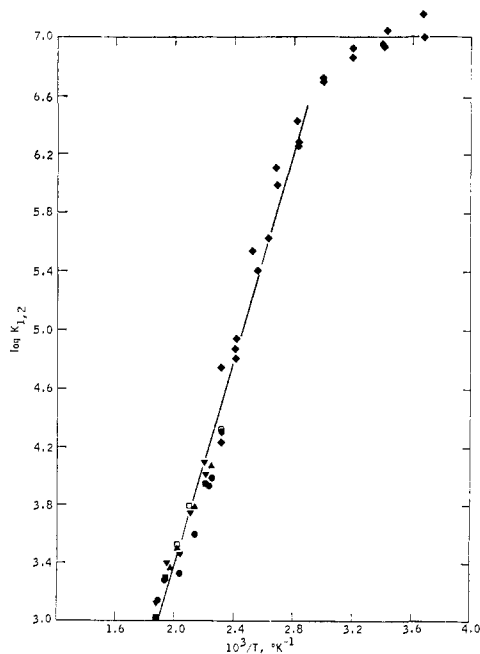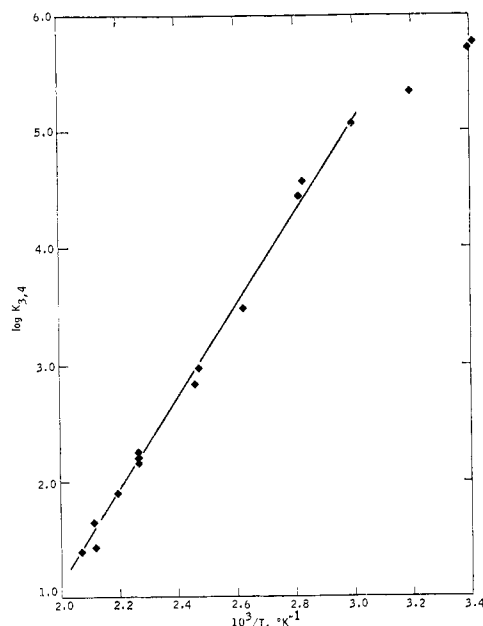

Figure 5. van't Hoff plot for $H_7O_3^+ + H_2O \rightleftharpoons H_9O_4^+$; P_{H_2O} = 0.0007–0.050 Torr.

temperature in ways that suggest that they are formed by reversible reactions, and thus we write

$$C_3H_7(H_2O)_{n-1} + H_2O \rightleftharpoons C_3H_7(H_2O)_n^+ \qquad (25)$$
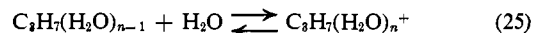
The equilibrium constant expressions for these reactions are

$$K_n = (I_{C_3H_7(H_2O)_n^+}/I_{C_3H_7(H_2O)_{n-1}^+})(1/P)_{H_2O} \qquad (26)$$

To conserve space we shall not give plots for K vs. P for the propyl hydrate equilibria, but we state that the behavior of the equilibrium constants with variations in water pressure is identical in form with the behavior shown for the proton hydrate equilibria in Figures 6 and 7 of ref 2, and furthermore, the variation of K with propane pressure is identical in form with that shown for the proton hydrate equilibria in Figures 1 and 2 of this paper. We believe that the propyl hydrate reactions achieve equilibrium to the same extent and with the same limitations as the proton hydrate reactions.

We give in Figures 6 and 7 the van't Hoff plots for K_1, K_2, and K_3, that is, for the addition of water to propyl ion and the successive additions of two more

Table V. Experimental Thermodynamic Values for Hydrated Propyl Ion Equilibria and Hydrated Proton Equilibria

n	$-\Delta G_{300}$, kcal/mol $(C_3H_7^+)$[b]	(H_3O^+)[c]	K_{300}^a $(C_3H_7^+)$	(H_3O^+)	$-\Delta H$, kcal/mol $(C_3H_7^+)$	(H_3O^+)	$-\Delta S$, g/mol $(C_3H_7^+)$	(H_3O^+)
1	9.2	11.2	5.3×10^6	1.5×10^8	17.6	16.3	27.7	17.2
2	9.7	9.7	1.2×10^7	1.2×10^7	13.5	14.3	12.7	16.9
3	8.5	8.6	1.6×10^6	1.9×10^6	14.9	17.6	21.5	30.0

[a] Standard state = 1 atm.   [b] Hydrated propyl ion equilibria: $(C_3H_7(H_2O)_{n-1})^+ + H_2O \rightleftharpoons (C_3H_7(H_2O)_n)^+$.   [c] Hydrated proton equilibria: $H(H_2O)_n^+ + H_2O \rightleftharpoons H(H_2O)_{n+1}^+$.

water molecules. These reactions also exhibit the low-temperature deviations from linearity which appear in Figures 3–5 for the proton hydrates, but the deviations are of little intrinsic interest and have been omitted from Figures 6 and 7.
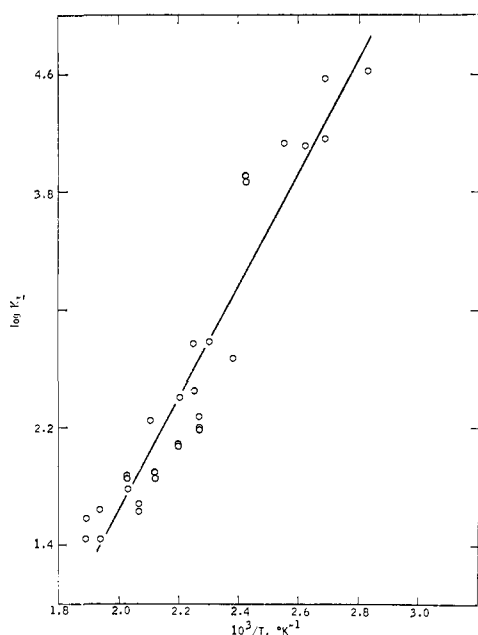
value listed in Table IV for the 2,3 equilibrium are slightly higher in the propane–water system than in the methane–water system, which may be looked upon as a manifestation of the same effect, although the magnitude of the differences is small and may well lie within the limits of experimental error.

Figure 6. van't Hoff plot for $sec\text{-}C_3H_7^+ + H_2O \rightleftharpoons C_3H_7 \cdot H_2O^+$; $P_{H_2O} = 0.0007\text{–}0.20$ Torr.
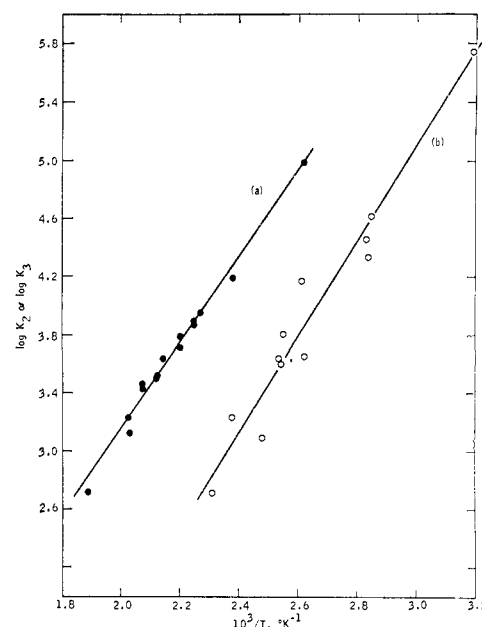

Figure 7. van't Hoff plot for (a) $C_3H_7 \cdot H_2O^+ + H_2O \rightleftharpoons C_3H_7 \cdot 2H_2O^+$, ●; and (b) $C_3H_7 \cdot 2H_2O^+ + H_2O \rightarrow C_3H_7 \cdot 3H_2O^+$, O.

The thermodynamic values for the propyl hydrate equilibria calculated from these van't Hoff plots are listed in Table V. For comparison we include the values for the analogous proton hydrate equilibria obtained from the present study of the propane–water system.

Discussion

From the various thermodynamic values given in Table IV for the 1,2 equilibrium, we see that a significant change in our results is effected by using propane as the reactant gas rather than methane. In particular, the value of the K_{300} is about 400 times larger with propane than with methane, which is a reflection of the fact that the free energy change has become 3.5 kcal/mol more negative. The enthalpy and entropy changes have also become correspondingly more negative. These changes are in the direction that would be expected if the lower hydrate ions are in a higher state of excitation in the methane–water system than in the propane–water system, and thus these results comprise support for the exothermicity thesis of DePaz, Leventhal, and Friedman.[4] The K_{300} value and the ΔG_{300}

On the other hand, for the 3,4 equilibrium the agreement between the propane–water results and the methane–water results is excellent for all four thermodynamic quantities, and in addition the agreement with Kebarle's result is equally good. We mentioned previously that our results on neat water[6] agreed with Kebarle's for this equilibrium, and thus four separate studies involving different experimental conditions give the same thermodynamic quantities for this equilibrium. We also found[2] that our values for the 4,5 and 5,6 equilibria in the methane–water system were in agreement with Kebarle's. These results suggest strongly that the DePaz, Leventhal, and Friedman exothermicity thesis is not valid for the higher proton hydrate equilibria, and we retain the concept that thermodynamic equilibrium is established. We are of the opinion that it should be neither impossible nor logically inconsistent for the exothermicity thesis to be applicable for the lower equilibria but inapplicable for higher equilibria.

However, we wish to make a comment upon the DePaz, Leventhal, and Friedman thesis. Their experiments involve the determination of the internal energy

content of various proton hydrate ions by measuring the energy dependence of the collision-induced dissociation of these ions. For many ions they find evidence of the presence of significant amounts of internal energy, and because of this they question whether equilibrium is established in experiments such as Kebarle's (and, by extension, ours). We cannot concur in the interpretation of these workers. We assert that if indeed the ions in the ionization chamber are in thermal equilibrium, ions of all degrees of excitation must needs be present, and some must be so excited that the dissociations required for dynamic equilibrium occur. The question is not whether excited ions are present; rather the question is whether the energy distribution of the ions has the proper form, namely, the Boltzmann form. This need not necessarily be the case, and thus the basic question raised by DePaz, Leventhal, and Friedman has substance.
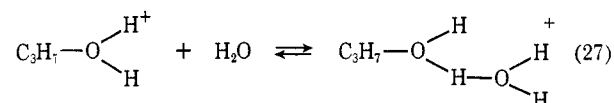
We found in our methane–water study that the agreement of our result with those of Kebarle[3] were poor for the 2,3 equilibrium and extremely bad for the 1,2 equilibrium. As may be seen from Table IV, since the equilibrium constants for these equilibria are higher for the propane–water system, the disagreements are not as bad but still egregious—10 orders of magnitude for the 1,2 equilibrium in propane–water instead of 13 orders of magnitude in methane–water. For the 2,3 equilibrium the Kebarle value is 700 times larger than our propane–water value. We can offer no reasonable explanation for these differences. In view of the various considerations we have presented, we have no reason seriously to question our results, and indeed, the excellent linearity over a long range for the van't Hoff plot given in Figure 3 is evidence against the presence of any but perhaps the most subtle of systematic errors. Since our value of $K_{1,2}$ rose appreciably in changing reactant gas from methane to propane, one can wonder whether our values are low because of the presence of much excitation energy in spite of our expectations for the propane–water system. We feel that this is not the case, but solid evidence on the point is not available.

Our pattern of energy and entropy changes for the three equilibria given in Table IV is different from that of Kebarle. Both sets of free energy change values become less negative as one goes to higher equilibria, but the Kebarle decrease is much sharper than ours. Kebarle's enthalpy change values also become sharply less negative toward the higher equilibria, whereas ours are essentially constant. Intuitively we expect that less heat will be released for each additional water molecule added to the cluster, and thus Kebarle's results are more reasonable than ours. Also, we pointed out in the methane–water study[2] that our metastable ion results are more compatible with Kebarle's enthalpy change pattern than with ours. Our entropy changes of the 1,2 and 2,3 equilibria are much different from Kebarle's, and if our results are taken at face value they suggest that the clusters formed in these reactions are relatively loose and less highly organized.
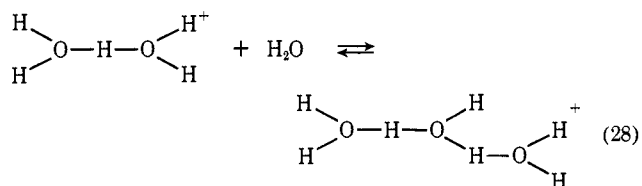
Turning to the propyl ion hydrates given in Table V, the value of K_1 and the corresponding free energy change show that $sec\text{-}C_3H_7^+$ adds to H_2O less readily

than does H_3O^+, as is quite obvious when running the spectra of propane–water mixtures from the relative intensities of the m/e-61 and m/e-37 ions. However, from Table V one notes that the smaller value of K_1 is the result of the entropy factor, since the enthalpy changes for the addition of propyl ion and hydronium ion to a water molecule are about the same. It is not surprising that the tendencies for the combination of water with two different kinds of ions are different. However, when we examine the values for K_2 and K_3 we see that these values are identical with those of the equilibrium constants for the corresponding hydrated proton equilibria. Free energy changes are of course also identical. Enthalpy changes are very similar, if not the same within experimental error, and differences in the entropy changes are to be observed.

The reactions corresponding to K_2 and $K_{2,3}$ are most likely

$$C_3H_7{-}O{\big\langle}^{\!H^+}_{\;H} + H_2O \;\rightleftarrows\; C_3H_7{-}O{\big\langle}^{\!H}_{\;H{-}O{\langle}^H_H} \quad (27)$$

and

$$\begin{array}{l} {}^{H}_{H}{\big\rangle}O{-}H{-}O{\big\langle}^{H^+}_{\;H} + H_2O \;\rightleftarrows\; \\[2mm] {}^{H}_{H}{\big\rangle}O{-}H{-}O{\big\langle}^{\;H}_{\;H{-}O{\langle}^H_H} \quad (28) \end{array}$$

In both cases the water molecule is presumably being added to a hydrogen atom to create a new ionic hydrogen bond. Similar mechanisms exist for the reactions corresponding to K_3 and $K_{3,4}$. The equality of the K values, the free energy change values, and the near equality of the enthalpy change values indicate that the energy released in forming a new ionic hydrogen bond is independent of whether the reactant ion contains a propyl group or an H_3O group. We would not have predicted this lack of substituent effect in advance.

The reaction corresponding to $n = 1$ in Table V is the association of sec-propyl ion with water to form $sec\text{-}C_3H_7OH_2^+$, and this entity may be looked upon as protonated 2-propanol. From the enthalpy change given in Table V and the known heats of formation for sec-propyl ion and water,[5a] we calculated that the heat of formation of protonated 2-propanol is 114 kcal/mol. From this value and the known heat of formation of 2-propanol and gaseous proton,[5a] we calculate that the proton affinity of 2-propanol is 190 kcal/mol. Beauchamp and Dunbar[12] give the value 13 ± 5 kcal/mol, which is presumably obtained by the ion–molecule bracketing technique. The agreement provides some confirmation of the quantitative accuracy of our gaseous ion equilibrium measurements. When the equilibrium method is well established we think that it will be the method of choice when it can be used to obtain ionic energies. This will probably be fairly frequently.

(12) J. L. Beauchamp and R. C. Dunbar, J. Amer. Chem. Soc., 92, 1477 (1970).