

Reversible Reactions of Gaseous Ions. IV. Further Studies on the Equilibrium $\text{H}_3\text{O}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}(\text{H}_2\text{O})_2^+$

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Abstract: The first hydrated proton equilibrium has been reinvestigated by the chemical ionization technique in the propane–water system at high propane pressure. The results are essentially identical with those obtained at low propane pressure.¹ We concluded that the discrepancy with Kebarle, *et al.*,² does not result from the existence of nonequilibrium conditions in our ionization chamber.

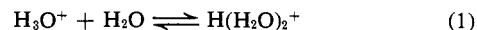
The thermodynamics of the hydrated proton equilibria have been obtained by Field and Beggs^{1,3,4} by the chemical ionization technique. In the methane–water study,³ and in experiments on neat water,⁴ the results for the higher hydrated proton equilibria were in agreement with those of the prior study by Kebarle and coworkers,² while the results for the 1,2 and 2,3 equilibria were in serious disagreement. Using propane as reactant gas,¹ the values of the equilibrium constants for the lower equilibria increased somewhat, but serious disagreement with Kebarle's results remained. For the 1,2 equilibria the equilibrium constant obtained in this laboratory was ten orders of magnitude smaller (at 300°K) than the Kebarle value, and our enthalpy was -16.3 kcal/mol compared with the Kebarle value of -36 kcal/mol.

De Paz, Leventhal, and Friedman⁵ have determined the heats of hydration of the proton hydrates from the determination of the thresholds for the collision-induced detachment of D_2O from D_5O_2^+ , D_7O_3^+ , and higher clusters. The derived heats of hydration were found to be in good agreement with the Kebarle values, although their relative ion abundances did not agree with the ion distributions deduced from the Kebarle free energy data.

Recently several theoretical calculations have been made of the energy of the reaction $\text{H}_3\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}(\text{H}_2\text{O})_2^+$. Kraemer and Dierksen,⁶ Kollman and Allen,⁷ and Newton and Ehrenson⁸ have obtained 32.2, 35, and 37 kcal/mol, respectively.

The question of dominating importance in mass spectrometric studies of reversible gaseous ionic reactions is whether thermodynamic equilibrium is achieved in the ionization chamber and whether the ion intensities measured with the mass spectrometer accurately represent the equilibrium ion concentrations present in the ionization chamber. The question has been considered by De Paz, Leventhal, and Friedman,⁵ Kebarle,⁹ Friedman,¹⁰ and Beggs and Field,¹ but no unanimity of

opinion exists. We recently upgraded our mass spectrometer by increasing its pumping capacity, which enables us to operate at significantly higher pressures than was previously possible. In the presence of higher pressures of an inert gas, a reversible gaseous ionic reaction in a mass spectrometer ionization chamber may be expected to approach equilibrium more closely. Consequently, we have reinvestigated the 1,2 reaction in water, *i.e.*



over the wider range of pressure now possible in our instrument in the hope of reducing any nonequilibrium component of our previous results.¹ The previous study of the propane–water system was performed at propane pressures of *ca.* 0.80 Torr. In this study we have again used propane as the reactant gas but at higher pressures.

Experimental Section

In order to operate the Esso Chemical Physics mass spectrometer at higher reactant pressures, two modifications were made. The existing ion source diffusion pump was replaced with a Norton Vacuum VHS-4 pump which has a pumping speed of 1200 l./sec. The electron acceleration energy was increased from 220 to 600 V. The latter modification increased the penetration of the electrons into the ionization chamber, which was required in order to have sufficient ion intensity at higher source pressures. With these modifications the instrument could be operated at source pressures up to 4 Torr.

The remainder of the apparatus and technique have been described in previous papers.^{1,3} In particular a fine mesh screen was present between the focus electrodes and the analyzer entrance slit, and only 5 V was maintained between the source and focus electrodes. Both of these conditions were used to reduce the likelihood of collision-induced dissociations in the region just outside the source ion exit slit. If such dissociations did occur, fragment ions would appear as a satellite on the low mass side of the true fragment ion of the same *m/e* value formed in the ionization chamber. Special attention has been paid to the forms of the peaks at *m/e* 19 and 37; no satellite peaks have been observed, and all peaks had the proper shape.

Laboratory distilled water and Matheson CP propane were used. Traces of water in the propane were removed by passing the propane through a refrigerated bath at -70° .

Results

The spectra of the propane–water system at $P_{\text{C}_3\text{H}_8} = 0.80$ Torr, $P_{\text{H}_2\text{O}} = 0.015$ Torr, and source temperature = 473°K agreed with that given in Table III, ref 1. A replicate study of the temperature variation of the 1,2 equilibrium at a propane pressure of 0.80 Torr gave thermodynamic values which were also in good agreement with those given ref 1.

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- (10) L. Friedman, *ibid.*, **53**, 2130 (1970).

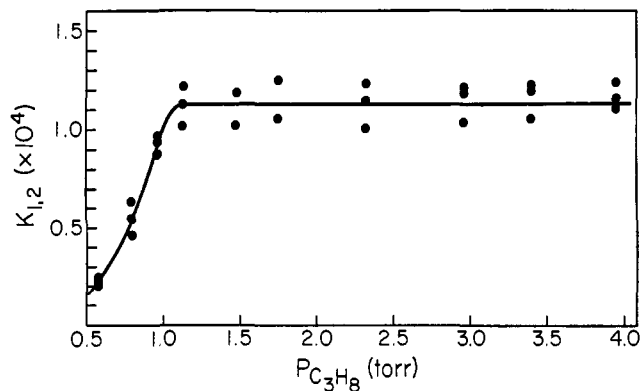


Figure 1. $K_{1,2}$ vs. propane pressure. $P_{H_2O} = 0.007$ Torr, $P_{C_3H_8}$ = variable, source temperature = 471 °K.

The effect of water pressure upon the apparent equilibrium constant at propane pressure of 2.5 Torr is essentially the same as that described in our previous studies; that is, it exhibited a decrease of a factor of 5 over a water pressure range of 0.0006–0.030 Torr at low temperatures but was essentially constant at higher temperatures. This has been ascribed¹ to time limitations on the achievement of equilibrium, which in turn limits the range of conditions over which equilibrium might be expected to exist. The experiments reported here were made with conditions lying within the equilibrium range.

Since the electron acceleration voltages used in this work were appreciably higher than has previously been the case in this laboratory, a study was made of the effect of this voltage on the value of $K_{1,2}$. No effect was observed.

The effect of the repeller voltage upon $K_{1,2}$ was reinvestigated at higher propane pressures. $K_{1,2}$ decreased essentially linearly from 2.3×10^4 at 2 V to 0.5×10^4 at 15 V (471 °K). In the quantitative experiments the repeller was maintained at a potential of 9.0 V, which is a compromise between the zero voltage desirable for thermodynamic reasons and the finite repeller needed with our machine to obtain a usable sensitivity. Operating at this potential lowers the absolute magnitude of $K_{1,2}$ by a factor of 2 compared with its maximum value.

We give in Figure 1 the effect of propane pressure upon the 1,2 equilibrium constant at constant temperature (471 °K) and water pressure (0.007 Torr). $K_{1,2}$ is independent of propane pressure from about 1.1 to 4.0 Torr.

Table I. Experimental Thermodynamic Values for the Equilibrium $H_3O^+ + H_2O \rightleftharpoons H(H_2O)_2^+$

	ΔG°_{300} , kcal/mol	K_{300}^a	ΔH° , kcal/mol	ΔS° , eu
Kearle, <i>et al.</i> , ref 2	-25	1.8×10^{18}	-36	-33.3
Beggs and Field, ref 1 ($P_{C_3H_8} = 0.80$ Torr)	-11.2	1.5×10^8	-16.3	-17.2
This work ($P_{C_3H_8} = 2.50$ Torr)	-11.7	3.0×10^8	-16.5	-16.3

^a Standard state = 1 atm.

Equilibrium constants were determined as a function of temperature at 2.5 Torr propane pressure. The

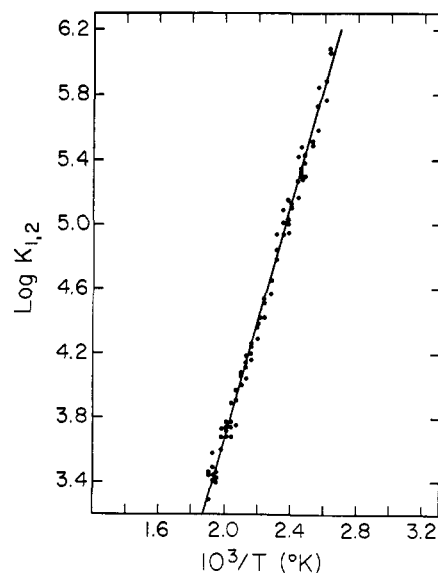


Figure 2. Van't Hoff plot for $H_3O^+ + H_2O \rightleftharpoons H(H_2O)_2^+$. $P_{H_2O} = 0.018$ – 0.0006 Torr, $P_{C_3H_8} = 2.50$ Torr.

restrictions necessary for obtaining meaningful results as discussed in ref 1 were observed. That is, the water pressure was adjusted so as to hold the product to reactant ion ratio to less than 10%. Duplicate measurements were made, and the agreement between them was excellent. The van't Hoff plot for one of these studies is shown in Figure 2. The thermodynamic values obtained from a least-squares fit of the experimental points are shown in Table I. For comparison we include the values obtained previously for the 1,2 reaction.

Discussion

Referring to Figure 1, the constancy of $K_{1,2}$ at propane pressures between about 1 and 4 Torr constitutes strong evidence that above 1 Torr equilibrium is achieved in our apparatus for reaction 1. However, it must be remembered that because of the repeller voltage, the ions contain a small component of energy derived from the electric field, and the effect of this is included in the equilibrium observed. Thus the experimental equilibrium constant is different from a purely thermal constant, but our experiments with the effect of repeller voltage indicate that the difference between the two is probably only about a factor of 2. In any event, the constancy of $K_{1,2}$ shows that no nonequilibrium factors which can be eliminated by the occurrence of a greater number of collisions are operating above about 1 Torr. In this regard it should be remembered that while the pressure range over which our $K_{1,2}$ value is constant is about a factor of 4, the corresponding range of the number of collisions undergone by an ion during its residence in the ionization chamber is 16. The reason is that the pressure variation was made at constant repeller voltage. The number of collisions per second experienced by an ion will increase linearly with the pressure, but since the ion drift velocity is proportional to field strength per unit of pressure, the ion residence time will also be proportional to pressure. Thus the total number of collisions an ion experiences will be proportional to the square of the pressure.

Table I gives the thermodynamic values we obtained for the 1,2 water equilibrium at propane pressure equal to 2.5 Torr, and for comparison we also give the values obtained in this laboratory previously at propane pressure equal to 0.8 Torr¹ and the values of Kebarle and coworkers.² The value of K_{300} obtained in the present work is a factor of 2 larger than our earlier value, and it is now clear that experimental limitations forced us to make our previous experiments at a propane pressure which was a little too low. Our new value for ΔG°_{300} reflects this increase in the value of K_{300} , but our new and old values of ΔH° and ΔS° are in effect identical. A very large discrepancy remains between

our thermodynamic values and those of Kebarle and coworkers. We have considered these discrepancies at some length previously,^{1,3} and the discussion will not be repeated. The present results enable us to add the statement that except for a trivial factor of 2 uncertainly coming from the effect of the repeller field, the discrepancy does not result from the existence of nonequilibrium conditions in our ionization chamber.

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Reversible Reactions of Gaseous Ions. V. The Methane–Water System at Low Temperatures

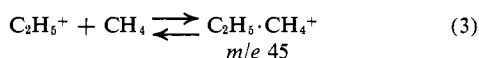
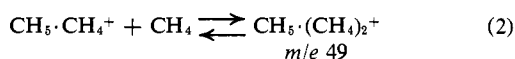
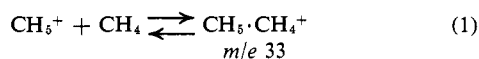
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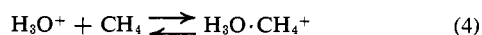
Abstract: The mass spectra of methane–water mixtures have been determined at several subambient temperatures. The $\text{H}_3\text{O}\cdot\text{CH}_4^+$ ion (m/e 35) is formed in an equilibrium reaction with H_3O^+ and CH_4 . The $\text{H}_3\text{O}\cdot(\text{CH}_4)_2^+$ ion (m/e 51) is formed in an equilibrium reaction between $\text{H}_3\text{O}\cdot\text{CH}_4^+$ and CH_4 . The equilibrium constants for these reactions were determined at several temperatures, and the following thermodynamic values were obtained. For the formation of $\text{H}_3\text{O}\cdot\text{CH}_4^+$, $K_{300} = 25$, $\Delta G^\circ_{300} = -1.9$ kcal/mol, $\Delta H^\circ = -8$ kcal/mol, and $\Delta S^\circ = -20.4$ eu. For the formation of $\text{H}_3\text{O}\cdot(\text{CH}_4)_2^+$ the corresponding values are 7, -1.2 kcal/mol, -3.4 kcal/mol, and -8.1 eu. Classical electrostatic calculations are made to determine the energy of interaction of the $\text{H}_3\text{O}\cdot\text{CH}_4^+$ ion and the $\text{CH}_5\cdot\text{CH}_4^+$ ion produced in pure methane at low temperatures. From these calculations we conclude that the experimentally observed interactions can be adequately accounted for in terms of ion-induced dipole interactions. Differences in the observed interactions in the $\text{H}_3\text{O}\cdot\text{CH}_4^+$ ion and the $\text{CH}_5\cdot\text{CH}_4^+$ ion are also accounted for by the calculations.

In a previous study in this laboratory of the gaseous ionic reactions in methane at subambient temperatures (down to liquid nitrogen temperature) we found¹ that the following reversible gaseous ionic reactions occur.



Equilibrium constants, free energies, enthalpies, and entropies were determined for the reactions.

It is virtually impossible completely to exclude water from a mass spectrometer, and in the course of this study ions with m/e 19 and 35 were always observed with small intensities. The m/e 19 ion is, of course, H_3O^+ , and in a system containing just methane and water the m/e 35 ion with little uncertainty may be taken as the association complex between H_3O^+ and methane formed by the reaction



We have undertaken to study the low temperature water–methane system, and in this paper we report our results. We have also made classical electrostatic calculations in an attempt to explain the binding in ions such as $\text{CH}_5\cdot\text{CH}_4^+$ and $\text{H}_3\text{O}\cdot\text{CH}_4^+$, and we also give the results of these calculations.

Experimental Section

The apparatus used for these studies was the Esso Chemical Physics mass spectrometer described previously.^{2,3} It was equipped with the ion source designated previously³ as source III, which can be heated to 270° and cooled to approximately liquid nitrogen temperature. A 200 line per in. wire screen (maintained at focus electrode potential) is located between the focus electrode and the analyzer entrance slit, and the distance between this screen and the ion exit slit of the source is relatively large (12 mm). Thus one is assured that little or no penetration of the ion acceleration voltage (3000 V) into the source region occurs. The repeller and the focus electrodes were maintained at minimum operating potentials (typically 5 V repeller and 5 V focus) needed to achieve a usable sensitivity. The electron collector electrode and the electrode in the electron gun immediately in front of the ionization chamber were both maintained at ionization chamber potential. These are the conditions previously referred to as approximate field-free conditions,³ and with them the ions in the ionization chamber and downstream of the ion exit slit for a distance of 12 mm are

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