# Gas Phase Ion Equilibria Studies of the Solvation of the Hydrogen Ion by Methanol, Dimethyl Ether, and Water. Effect of Hydrogen Bonding

**Eric P. Grimsrud and Paul Kebarle***

*Contribution from the Chemistry Department, University of Alberta, Edmonton, Alberta, Canada. Received July 9, 1973*

**Abstract:** The equilibria $H^+(CH_3OH)_n = H^+(CH_3OH)_{n-1} + CH_3OH$ and $H^+(CH_3OCH_3)_n = H^+(CH_3OCH_3)_{n-1} + CH_3OCH_3$ were measured in the gas phase for $n = 2$ to 8 (methanol) and $n = 2$ to 3 (dimethyl ether). A pulsed electron beam high pressure ion source mass spectrometer was used. Temperature dependence of $K_{n,n-1}$ led to evaluation of $\Delta H_{n,n-1}$, $\Delta G°_{n,n-1}$, and $\Delta S°_{n,n-1}$. The present results were compared with earlier determinations for the proton hydrates $H^+(H_2O)_n$. The initial interaction (2,1) is nearly equally strong for the three systems. For water and methanol the energies $\Delta H_{n,n-1}$ and $\Delta G_{n,n-1}$ decrease quite regulary with $n$. There is a dramatic drop for dimethyl ether between $n = 2$ and 3. This must be due to blocking of H bonding past structure $H^+(CH_3OCH_3)_2$. Small discontinuities in values for water and methanol indicate somewhat more stable structures for $H^+(CH_3OH)_3$ and $H^+(H_2O)_4$. The formation of $(CH_3)_2OH^+$ in methanol and $(CH_3)_3O^+$ in dimethyl ether was observed at high temperatures.

Several years ago a study[1] of the gas phase equilibria $(n,n-1)$ was made in our laboratory. Determination of the temperature dependence of the equilibrium constants $K_{n,n-1}$ permitted the evaluation of $\Delta G°_{n,n-1}$, $\Delta H°_{n,n-1}$, and $\Delta S°_{n,n-1}$ for $n = 1$ to 8. A later study,[2] with improved apparatus, of the kinetics of the above reaction, confirmed the thermodynamic values for the reactions with $n > 4$ but led to somewhat lower $\Delta H_{2,1}$ and $\Delta H_{3,2}$ and somewhat higher $\Delta G°_{4,3}$.

$$H^+(H_2O)_n = H^+(H_2O)_{n-1} + H_2O \qquad (n,n-1)$$

The above determinations provided the first experimental values for the dissociation energies of the strongly hydrogen-bonded clusters $H^+(H_2O)_n$. The results showed a large $D(H_3O^+ - H_2O) \approx \Delta H_{2,1} = 32$ kcal/mol. The successive $\Delta H_{n,n-1}$ decreased initially rapidly and then more slowly leading to $\Delta H_{8,7} = 10.3$ kcal for the last step that could be measured. The $\Delta H°_{n,n-1}$ and $\Delta G°_{n,n-1}$ plotted *vs.* $n$ presented a rather smooth curve. This result was to a certain extent surprising since the symmetric Eigen structure[3,4] $H_3O^+(H_2O)_3$ (see IVb, Figure 1) had been expected to be of high stability and thus lead to large discontinuity in the changes in the $\Delta G°_{n,n-1}$ and $\Delta H°_{n,n-1}$ values. No such large effect was evident, but a close examination of the data (Figure 5, ref 1) did show a small break between the $\Delta G°_{4,3}$ and $\Delta G°_{5,4}$, which could be due to a somewhat more stable configuration for the cluster $n = 4$, *i.e.*, the cluster which could have the Eigen structure.

Several theoretical studies[5-8] of the proton hydrates were published after the experimental energy determinations.[1] Most of the treatments dealt with the lowest cluster, *i.e.*, $H_2OH^+OH_2$. The calculated values for the dissociation energy to $H_3O^+$ and $H_2O$ were somewhat scattered but were in general agreement with a value for $\Delta H_{2,1}$ between 32 and 38 kcal/mol. The study by Newton and Ehrenson[8] dealt also with higher clusters. These calculations were made with less extensive basic Gaussian orbital sets and are therefore of lower accuracy. Nevertheless, the relative energies of the structures are probably significant. Ehrenson's calculations showed that the lowest energy structure of $H^+(H_2O)_4$ is indeed the Eigen structure IVb. The chain structure IVa (Figure 1) was only 0.007 au (4.4 kcal) of higher energy. The actual difference between the two structures is probably even smaller, since the method tends to lead to energy values that are too high.

An experimental way to explore further the significance of hydrogen-bonded structures is to use compounds similar to water but with one or two of the hydrogen-bonding positions blocked by inactive groups. For this purpose in the present study we have used methanol and dimethyl ether. A study of mixed water and methanol proton clusters was made earlier in our laboratory.[9] These experiments were conducted with water–methanol vapor mixtures at a single temperature. Thus only a limited set of $\Delta G°$ values could be obtained. These results showed that methanol is taken up preferentially in clusters of small $n$. Increase of cluster size led to a decrease of preference for methanol. These results could be easily understood. Methanol because of the electron donating property of the methyl group has a higher proton affinity than water.[10,11] The preference for methanol in clusters with small $n$ must be a carry-over of this effect. At higher $n$ the non-hydrogen-bonding $CH_3$ group leads to looser structures and becomes a hindrance.

Although the study of water–methanol proton clus-

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(2) A. J. Cunningham, J. D. Payzant, and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 7627 (1972).

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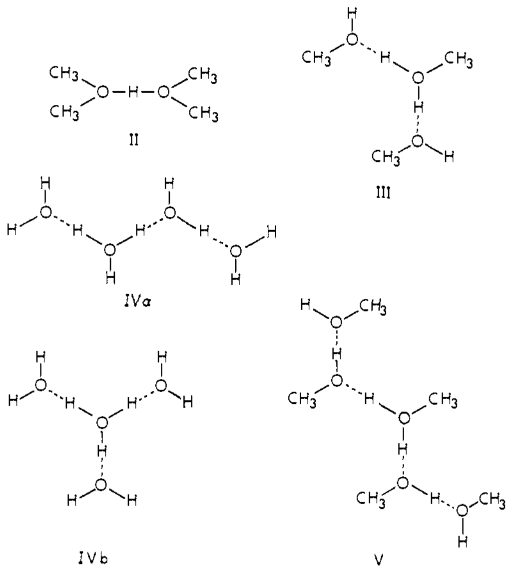

Figure 1. Structures of protonated clusters of water, methanol, and dimethyl ether.

ters[9] was useful, it was based on a limited set of experiments and the interpretation of the data suffered from an approach (the preference factor $\gamma$)[9] which was misleading.[12,13] The present work undertaken with the improved pulsed ion source is more extensive and yields new information and insights.

## Experimental Section

The ion-molecule reaction ion source and mass spectrometer were described earlier;[2] therefore, only a brief description of the procedures used in the present work will be given here.

Methane buffer gas at pressures of 4–5 Torr containing known amounts of either water (25–100 mTorr), methanol (10–250 mTorr), or dimethyl ether (6–400 mTorr) was flowed (~0.3 l. sec$^{-1}$) through the thermostated stainless steel ion source. The 2000-eV electron beam ($5 \times 10^{-9}$ A) was pulsed "on" for 4 to 180 $\mu$sec and "off" for 2–4 msec. The longer "on" times were used in cases where higher ion intensity was required. The low electron current is a deliberate choice. The low electron current taken together with the short duration of the pulses results in low ion density. We believe that high ionizing currents lead to a positive space charge build-up because of the fast diffusion of the secondary electrons to the walls. The space charge leads to a reduced ion source residence time of the average positive ion.

The ions escaping from the field free ion source during the "off" period (2–4 msec) were magnetically mass analyzed. Ions of a given mass were collected in a multichannel analyzer as a function of their time of arrival after the electron "on" pulse. Collection of some $10^4$ pulses at a given mass gave a satisfactory temporal profile of the ion with a channel dwell time of 20–30 $\mu$sec. Ratios of the ion intensities of two cluster ions were examined as a function of time. Generally these became stationary some 100–300 $\mu$sec after the pulse. Experiments at elevated ion source temperatures were made by heating the ion source with an electrically heated stainless steel jacket. The experiments below room temperature were made with a separate ion source having otherwise identical dimensions but with coolant circulation cavities milled out in the ion source block. Chilled liquid methanol was pumped through the cavities. Excellent temperature stability was obtained with the heated ion source. Temperature stability at low temperatures was more difficult to maintain.

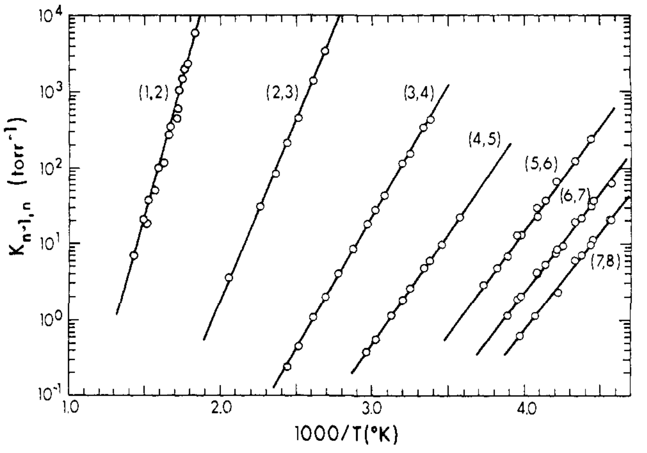

Figure 2. van't Hoff plots for gas phase equilibria ($n-1,n$): $H^+(CH_3OH)_{n-1} + CH_3OH = H^+(CH_3OH)_n$.

The methanol and water pressure in the ion source was determined by weight loss experiments.[2] Since dimethyl ether is gaseous at STP, a 3-l. reservoir was used for storage of the gas and the moles per second flowing out were calculated by measuring the small pressure drop in the reservoir.

The protonated ions $H_3O^+$, $CH_3OH_2^+$, and $(CH_3)_2OH^+$ are probably formed by proton transfer from the ultimate ions, $CH_5^+$ and $C_2H_5^+$, of methane. These very fast proton transfer reactions are followed by the third body dependent clustering reactions. The rate constants for these reactions decrease with temperature. The rate constants for the proton water cluster reactions measured earlier[2] were used for estimates of the concentrations of methanol or dimethyl ether required for the achievement of clustering equilibrium. The high range of pressures 100–400 mTorr for methanol and dimethyl ether were used at the high temperature range where the clustering rate constants are low. The time required for equilibrium calculated on the basis of the water values was 100–300 $\mu$sec. For the lower temperatures the concentrations were correspondingly reduced. Since the observed cluster intensity ratios became constant after some 100–300 sec, it was assumed that equilibrium had been achieved. The equilibrium constants for the reactions $n,n-1$ were calculated from the expression

$$K_{n,n-1} = I_{n-1}P_s/I_n$$

or

$$K_{n-1,n} = I_n/I_{n-1}P_s$$

where $I_n/I_{n-1}$ is the stationary intensity ratio of the corresponding clusters and $P_s$ is the solvent (water, methanol, ethanol) pressure.

At temperatures above normal, where temperature stability was good, generally three measurements at different solvent pressures varying by a factor of 5 led to equilibrium constants differing by no more than 20%. At low temperatures where the temperature stability of the source was not as good, some checks were made to show that the equilibrium constants are independent of pressure. However, most measurements in this temperature range were done at a single solvent pressure.

## Results and Discussion

### (a) Hydrogen Bonding in Protonated Clusters of Water, Methanol, and Dimethyl Ether.

The van't Hoff plots obtained for the methanol equilibria are

$$H^+(CH_3OH)_n = H^+(CH_3OH)_{n-1} + CH_3OH$$

shown in Figure 2. The methanol equilibria plots are compared with the earlier determined[1,2] water equilibria in Figure 3.

$$H^+(H_2O)_n = H^+(H_2O)_{n-1} + H_2O$$

The van't Hoff plots for the dimethyl equilibria are shown in Figure 4. The water equilibria data are

$$H^+(CH_3OCH_3)_n = H^+(CH_3OCH_3)_{n-1} + CH_3OCH_3$$

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(12) The proportions of water and methanol molecules in a cluster with fixed total number of ligands had appeared[9] to follow a statistical distribution weighed by a preference factor $\gamma$ for methanol molecules. In retrospect we realize that the statistical fits depended on a certain averaging out of the data. The result[9] that the preference for methanol in a cluster does not depend on the number of methanol molecules already present in the cluster is incorrect.[13]

(13) Eric P. Grimsrud and P. Kebarle, submitted for publication.

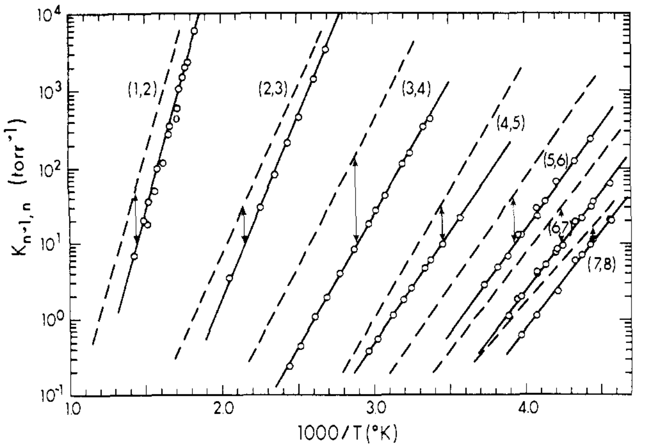

Figure 3. Comparison of van't Hoff plots for $H^+(H_2O)_n$ and $H^+(CH_3OH)_n$ equilibria: methanol (——), water (---). The double arrow indicates the temperature at which equilibrium constants for water and methanol were compared (see Figure 6).

included in the plot for comparison. In order to check that the present method is in agreement with the earlier measurements[1] some water equilibria measurements were repeated. These new experimental points shown in Figure 4 are in substantial agreement with the earlier results.

The $\Delta G°_{n,n-1}$, $\Delta H°_{n,n-1}$, and $\Delta S°_{n,n-1}$ resulting from these determinations and the earlier water[1,2] data are summarized in Table I.

Table I. Thermochemical Data from Protonated Clusters in Equilibria: Water, Methanol, and Dimethyl Ether Vapors[a]

| $n,n-1$ | $\Delta H$ | $\Delta G°$ [b] | $\Delta S°$ [b] | $\Delta H$ | $\Delta G°$ [b] | $\Delta S°$ [b] |
|---|---|---|---|---|---|---|
| | $H^+(H_2O)_n =$ $H^+(H_2O)_{n-1} + H_2O$[c] | | | $H^+(CH_3OH)_n =$ $H^+(CH_3OH)_{n-1} + CH_3OH$ | | |
| 2,1 | 31.6 | 24.3 | 24.3 | 33.1 | 24.0 | 30.5 |
| 3,2 | 19.5 | 13.0 | 21.9 | 21.3 | 12.9 | 28.2 |
| 4,3 | 17.5 | 9.3 | 27.3 | 16.1 | 7.5 | 28.9 |
| 5,4 | 15.3 | 5.5 | 32.6 | 13.5 | 4.9 | 28.7 |
| 6,5 | 13.0 | 3.9 | 30.3 | 12.5 | 3.2 | 31.1 |
| 7,6 | 11.7 | 2.8 | 29.6 | 11.9 | 2.1 | 32.9 |
| 8,7 | 10.3 | 2.2 | 27.0 | 12.0 | 1.4 | 35.7 |
| | $H^+(CH_3OCH_3)_n = H^+(CH_3OCH_3)_{n-1} + CH_3OCH_3$ | | | | | |
| 2,1 | 30.7 | 21.9 | 29.6 | | | |
| 3,2 | 10.1 | 1.9 | 27.6 | | | |

[a] Energy values in kcal/mol. The $\Delta H$ and $\Delta G$ values are estimated to be accurate within 10%; the $\Delta S$ values could have somewhat larger error. [b] 300°K, standard state 1 atm, entropy in cal deg$^{-1}$. [c] The 2,1; 3,2; and 4,3 equilibria data for the water system were taken from ref 2; the remaining values are from ref 1.

The 2,1 interactions for water, methanol, and dimethyl ether are seen to be quite similar. The $\Delta G°_{2,1}$ values decrease in the order water, methanol, and dimethyl ether. This order parallels the order observed[14] with methyl substitution in ammonia, where it was found that the $\Delta G°$ values decreased in the order ammonia, methylamine, dimethylamine, and trimethylamine. These regularities may be rationalized as follows. The proton affinities of the monomers increase with methyl substitution because the charge is internally stabilized by the introduction of the substituents.

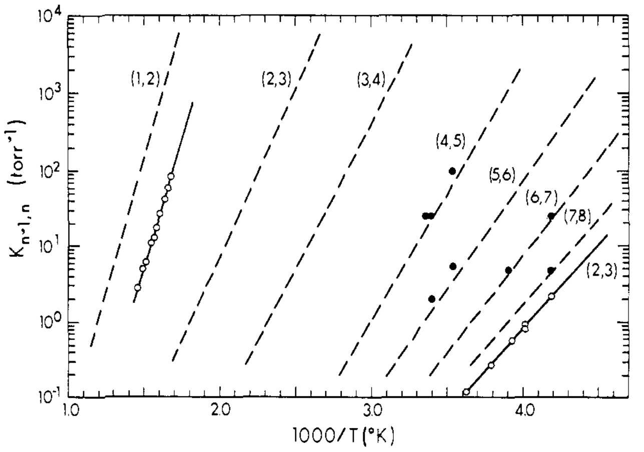

Figure 4. Comparison of van't Hoff plots for dimethyl ether (——) and water (---) for proton cluster equilibria. (●) The present experimental points for water. The very large difference between the $n = 2$ and 3 cluster of dimethyl ether is strikingly evident from the plot.

This internal stabilization leads to a diminishing return for the external stabilization obtained by dimerization. Some regularities for the formation of the mixed amine dimers were observed[14] which are reproduced also in the mixed (*i.e.*, water, methanol, etc.) dimers. These will be discussed in a future publication[13] dealing with structures of the mixed water, methanol, and dimethyl ether dimers.

The $\Delta H_{2,1}$ and $\Delta S_{2,1}$ do not show the same simple regularity with methyl substitution. Thus the measured $\Delta H_{2,1}$ for $CH_3OH$ is higher while the $CH_3OCH_3$ value is lower. The differences are small and not outside the experimental error.

The $\Delta H_{n,n-1}$ and the $\Delta G°_{n,n-1}$ for the higher clusters of water and methanol decrease fairly regularly. The $\Delta G°_{n,n-1}$ values are shown in Figure 5. The $\Delta S°_{n,n-1}$ values show a minimum at $\Delta S°_{2,3}$ after which they increase fairly regularly in both systems. This increase of entropy might reflect the gradual tightening of the clusters, *i.e.*, adjustments of *all* molecules in the growing cluster. The entropy changes for methanol are generally somewhat larger. It should be noted that the van't Hoff plots (Figures 2 and 3) for the last two equilibria cover a rather narrow temperature range and that the resulting $\Delta S°_{7,6}$ and $\Delta S°_{8,7}$ are quite uncertain. For $\Delta S°_{7,6}$ we expect a somewhat lower value which should lead to also a lower $\Delta H_{8,7}$ such that $\Delta H_{8,7} < \Delta H_{7,6}$.

The results for the dimethyl ether system are very different. The 3,2 interaction is dramatically weaker than the corresponding interactions for water and methanol. (See Table I and Figures 4 and 5.) Undoubtedly this is due to the complete blockage of hydrogen bonding by the methyl groups such that the more stable structure is $(CH_3)_2OH^+O(CH_3)_2$.

A more careful examination of the van't Hoff plots for water and methanol (Figures 2 and 3), the $n,n-1$ data of Table I and Figure 5, reveals that some more stable structures are revealed by specific $n,n-1$ changes.

Plotted in Figure 6 are the differences of successive $\Delta G°_{n,n-1}$ values corresponding to $\Delta\Delta G° = \Delta G°_{n,n-1} - \Delta G°_{n+1,n}$ for water and for methanol. The 300°K $\Delta G°_{n,n-1}$ values of Table I were used for the plot. The

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[14] R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **95**, 3504 (1973).

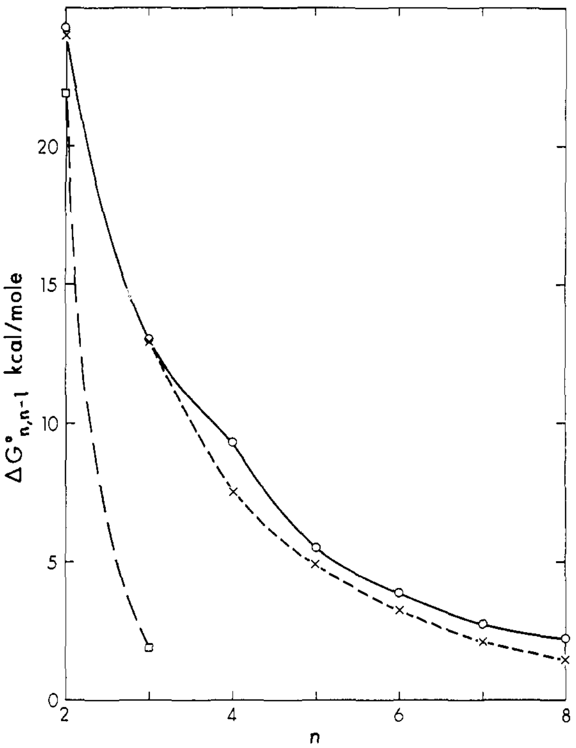


Figure 5. Comparison of $\Delta G°_{n,n-1}$ *vs.* $n$ for water (○), methanol (×), and dimethyl ether (□) at 300°K.

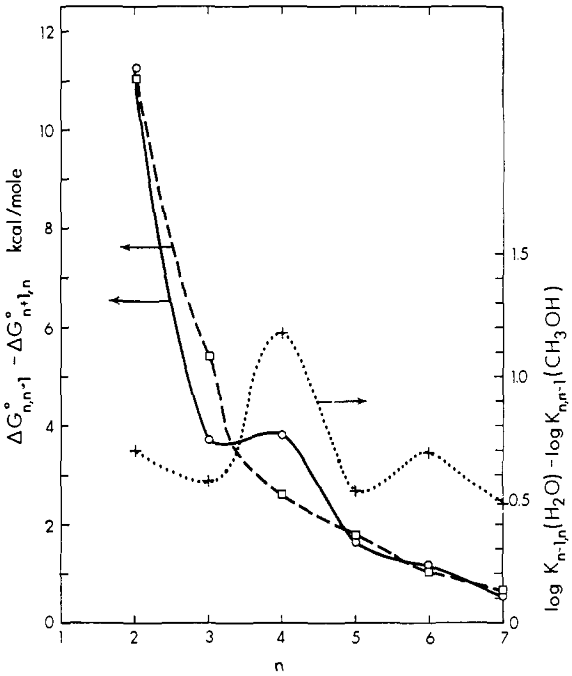


Figure 6. $\Delta\Delta G°$ plot of water (——) and methanol (---). The higher stability of the $n = 3$ relative to the $n = 4$ cluster in methanol is seen by the "bump" at $n = 3$ in the methanol curve. A larger maximum indicates higher stability of the $n = 4$ relative to the $n = 5$ cluster in water. The ordinate on the right gives the comparison between the stabilities of $H^+(H_2O)_n$ and $H^+(CH_3OH)_n$ clusters obtained by comparing log $K_{n,n-1}$ for water and methanol (see Figure 3). The first maximum at $n = 4$ indicates the higher stability of the $H^+(H_2O)_4$ cluster (Eigen structure) over $H^+(CH_3OH)_4$. The second small maximum at $n = 6$ might indicate another more stable water structure (see text).

$\Delta\Delta G°$ values correspond to the difference between the free energy lost when one molecule is taken from the cluster $n$ and the free energy gained when one molecule is added to the cluster. One expects (in the absence of specific stable configurations) that the $\Delta\Delta G°$ function will be high at low $n$ and decrease rapidly approaching zero for high $n$ where the successive clusters are very similar to each other. In the low $n$ range clusters with favorable structures should lead to a relatively large $\Delta\Delta G°$ value at some specific $n$. The plot shows stable structures for $n = 2$ both for water and methanol corresponding to the proton held dimers. The water curve shows a definite maximum at $n = 4$ which corresponds to the Eigen structure IVb (Figure 1). It is also interesting to note that the $n = 3$ value for methanol is considerably higher than that for water. Since the $n = 3$ structures for water and methanol are similar, this must mean that the $n = 4$ structure for methanol is not favorable. The favorable $n = 3$ structure for methanol should correspond to structure III (Figure 1). In the formation of the $n = 4$ cluster, the new methanol molecule must go to an outer position leading to a relatively small $\Delta G°_{n,n-1}$.

Also shown in Figure 6 is a plot in which the stabilities of water and methanol clusters are compared at each $n$. The plot shows log $K_{n-1,n}$(water) − log $K_{n-1,n}$(methanol) as a function of $n$. The $K_{n-1,n}$ values were taken at temperatures corresponding to the middle of the temperature range for which the equilibrium constants were actually determined. This was done in order to obviate the uncertainties introduced by the long extrapolation required when the $\Delta G°$ data are compared at the same temperature. The points at which the equilibrium constants were compared are indicated on Figure 3. The plot in Figure 5 shows a large maximum at $n = 4$, which again indicates the higher stability of the Eigen water cluster relative to the $n = 4$ methanol cluster. Interestingly a second small maximum is indicated for $n = 6$. We believe this to be a real effect which is due to the relatively higher stability of the $n = 6$ water cluster compared with the $n = 6$ methanol cluster. The $n = 6$ methanol cluster corresponds to the species which has one more molecule than the structure V, Figure 1. This additional molecule must go in a far outer position. No such need exists for the corresponding water cluster. Therefore, the $n = 6$ water cluster should be relatively more stable than the $n = 6$ methanol cluster, which is in agreement with the data. The drop of stability between the $n = 5$ and 6 structure of methanol should have shown up also on the $\Delta\Delta G°$ plot for methanol. In fact the data suggest a somewhat bigger $\Delta\Delta G°$ at $n = 5$ for methanol. We believe that the effect might have been more pronounced if it were not for the uncertainties introduced by the long extrapolations to 300°K.

In conclusion we may summarize the results as follows. In protonated clusters containing molecules which permit continuous hydrogen bonding (HOH, $CH_3OH$) there is a fairly continuous decrease of the bonding energies. The decrease is initially rapid and then slow. The symmetric Eigen structure IVb (Figure 1) shows up as somewhat more stable than the "linear" structures IVa. The energies in the methanol clusters decrease more rapidly since the presence of the methyl group blocks available "near" positions and leads to the looser chain structuring like V, Figure 1. Introduction of two methyl groups as in dimethyl ether blocks hydrogen bonding completely and leads to drastic decreases of the clustering energies.

Results from experiments with mixtures of water and dimethyl ether and methanol–dimethyl ether extend the above results to a variety of structures. This work will be described in a separate publication.[13]

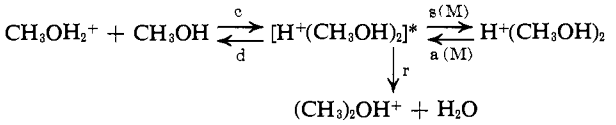
**(b) Formation of $(CH_3)_2OH^+$ and $(CH_3)_3O^+$ from the Proton Held Dimers of Methanol and Dimethyl Ether at High Temperatures.** The measurement of the (2,1) equilibria required temperatures in the 600–750°K

$$H^+(CH_3OH)_2 = CH_3OH_2^+ + CH_3OH \qquad (2,1)$$

$$(CH_3)_2OH^+O(CH_3)_2 = (CH_3)_2OH^+ + (CH_3)_2O \qquad (2,1)$$

range. In addition to the ions involved in the (2,1) equilibria, we observed the presence of $(CH_3)_2OH^+$ in the pure methanol experiments and in the pure dimethyl ether an ion of mass 61 which is probably the trimethyloxonium ion $(CH_3)_3O^+$. These ions became appreciable at ~620°K and dominant at 680°K.

We suspect that the $(CH_3)_2OH^+$ results from water elimination by some ionic reaction scheme like that shown below. A similar scheme but leading to the elimination of methanol can be written for the formation of the trimethyloxonium ion.



$$\begin{tikzcd} CH_3OH_2^+ + CH_3OH \arrow[r, shift left, "c"] & {[H^+(CH_3OH)_2]^*} \arrow[l, shift left, "d"] \arrow[r, shift left, "s(M)"] \arrow[d, "r"] & H^+(CH_3OH)_2 \arrow[l, shift left, "a(M)"] \\ & (CH_3)_2OH^+ + H_2O & \end{tikzcd}$$

The reaction path r could occur from an excited complex formed either by reaction c or the activation (a) of the proton held dimer. Both stabilization (s) and activation (a) are third body dependent.

It is interesting to note that the overall reaction 1 is

$$CH_3OH_2^+ + CH_3OH = (CH_3)_2OH^+ + H_2O \qquad (1)$$

slightly exothermic and occurs if the pressure is low ($p < 10^{-3}$ Torr) already at room temperature (Henis[15]). Miasek, McMahon, and Beauchamp[16] have determined recently $k_1 = 3 \times 10^{-11}$ molecule$^{-1}$ cm$^3$ sec$^{-1}$, at low pressure and room temperature. It is plausible to assume that $k_c \approx 10^{-9}$ molecule$^{-1}$ cm$^3$ sec$^{-1}$. Since $k_1 \ll k_c$ it follows that $k_r \ll k_d$, decomposition (d) being the only competitive path at low pressure. Evidently reaction 1 requires some free energy of activation. In the present work at room temperature and higher pressures ($p > 1$ Torr) the major ions were $(CH_3OH)_nH^+$. This means that stabilization (s) was dominant. This is consistent with the finding of Beauchamp that $k_1 \ll 10^{-9}$. The high-temperature, high-pressure formation of protonated ether observed in the present work should be due to activation (a) of the methanol proton dimer or to inefficient stabilization (s) of the complex at high temperatures.

Since the water and methanol elimination reactions were observed in the same range as the (2,1) equilibria, one could assign to them "conventional activation energies" of the same order as the energies for the $\Delta H_{2,1}$ reactions, *i.e.*, some ~35 kcal/mol.

Freeman[17] has proposed a similar ionic mechanism for the radiation-induced formation of diethyl ether from ethanol.

(15) J. M. S. Henis, *J. Amer. Chem. Soc.*, **90**, 844 (1968).

(16) J. L. Beauchamp, private communication based on the Ph.D. thesis of P. G. Miasek and T. B. McMahon, California Institute of Technology, Pasadena, Calif.

(17) K. M. Bansal and G. R. Freeman, *Radiat. Res. Rev.*, **3**, 209 (1971).

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# Hydrogen-Bond Patterns in Liquid Water[1]

**A. Rahman[1b] and F. H. Stillinger*[1c]**

*Contribution from the Argonne National Laboratory, Argonne, Illinois 60439, and Bell Laboratories, Murray Hill, New Jersey 07974.* *Received July 11, 1973*

**Abstract:** Distributions of non-short-circuited hydrogen-bond polygons in water have been constructed, using configurations generated by a molecular dynamics simulation for the liquid. The thermodynamic state analyzed has temperature 10° and mass density 1 g/cm$^3$. The distributions are broad and show nontrivial contributions from polygons with sizes greater than eight. The results seem to be inconsistent with the view of liquid water as a recognizably disrupted version of any known ice or hydrate crystal structure.

The capacity to form intermolecular hydrogen bonds is the single most important molecular feature underlying the properties of liquid and solid water. These bonds affect both macroscopic thermodynamic behavior as well as microscopic structure. They are furthermore decisive in explaining kinetic properties.

It is natural then that past "models" for liquid water and aqueous solutions should have forms strongly influenced by the demands of hydrogen bonding.[2a] In particular, there has been a tendency to rely on known ice or hydrate crystal structures to suggest which class of hydrogen-bond patterns might dominate in the liquid. Thus we have seen advocated for the liquid at various times a self-clathrate model,[2b] a distended ice Ih with interstitials,[3] ice-like "clusters" suspended in unbonded water,[4] or small aggregates bonded in the

(1) (a) Part of the work carried out at the Argonne National Laboratory was supported by the U. S. Atomic Energy Commission; (b) Argonne National Laboratory; (c) Bell Laboratories.

(2) (a) J. L. Kavenau, "Water and Solute-Water Interactions," Holden-Day, San Francisco, Calif., 1964. (b) L. Pauling, "Hydrogen Bonding," D. Hadzi and H. W. Thompson, Ed., Pergamon Press, London, 1959, pp 1-5.

(3) M. D. Danford and H. A. Levy, *J. Amer. Chem. Soc.*, **84**, 3965 (1962).

(4) H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).