

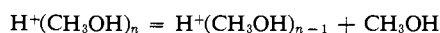
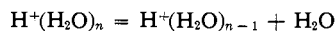
Gas Phase Ion Equilibria Studies of the Hydrogen Ion in Water-Dimethyl Ether and Methanol-Dimethyl Ether Mixtures

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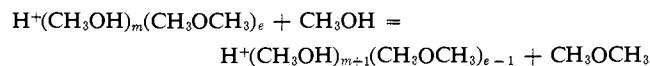
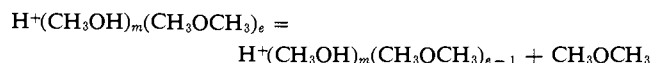
Abstract: Gas phase ion equilibria involving clusters $W_wE_eH^+$ and $M_mE_eH^+$, where W, M and E are water, methanol and dimethyl ether molecules, were measured with a high-pressure pulsed mass spectrometer. The temperature dependence of the equilibrium constants for equilibria of the types $W_wEH^+ + E = W_wE_2H^+$ (addition) and $M_mE_eH^+ + E = M_{m-1}E_{e+1} + M$ (exchange) permitted evaluation of the corresponding ΔG° , ΔH° , and ΔS° changes. Data involving many possible combinations of W and E and M and E were obtained for a total of up to five molecules in the cluster. These detailed results can be utilized in several ways. The proton affinity difference between E and W was determined to be 23 kcal/mol by means of thermodynamic cycles involving mixed clusters. The proton affinity difference of 9 kcal/mol between E and M was determined by direct proton transfer and thermodynamic cycles involving mixed clusters. Comparing clusters of the types W_nEH^+ and W_nWH^+ one finds that the difference between their basicities decreases rapidly with increase of n . These results suggest that the basicity of W might be higher than that of E in aqueous solution. The decrease of relative basicity of the cluster W_nEH^+ is due to two factors: weaker hydrogen bonding of W to EH^+ and removal of two H bonding positions by the methyl groups present in E. The energy changes observed on build-up of clusters like $W_wE_eH^+$ and $M_mE_eH^+$ show that hydrogen bonding is dominant. Clusters where the last molecule cannot hydrogen bond since all positions are blocked by methyl are very unstable. The preference for the more methyl substituted molecule decreases with cluster size. More energy is released if the incoming molecule can hydrogen bond to a position close to the (expected) location of positive charge.

Gas phase ion equilibria studies comparing the reactions



were published recently.¹ These studies showed that the stabilities of the proton held dimers B_2H^+ were quite similar, the ΔG° for dissociation to $BH^+ + B$ decreasing slightly in the order $B = H_2O, CH_3OH, (CH_3)_2O$. The protonated water and methanol species could form stable clusters containing more than two molecules. In contrast, the $(CH_3OCH_3)_3H^+$ and higher ether clusters were very unstable. This confirmed the expected importance of hydrogen bonding. Study of equilibria of the higher clusters of protonated water and methanol indicated that some structures like the symmetric structure $H_3O^+(H_2O)_3$ have somewhat higher stability. This showed that in H bonded structures a symmetric build-up of molecules around a center (a proton or a protonated molecule) leads to greatest stability.

The present work deals with mixtures of water and dimethyl ether and methanol and dimethyl ether. In mixtures of water and dimethyl ether the clusters $H^+(H_2O)_w(CH_3OCH_3)_e$ are observed in equilibria with water and dimethyl ether molecules. Mixtures of methanol and dimethyl ether lead to the observation of the mixed $H^+(CH_3OH)_m(CH_3OCH_3)_e$ species. Study of these equilibria as a function of temperature leads to determination of ΔG° , ΔH° , and ΔS° for dissociation and exchange reactions of the type shown below.



The thermodynamic quantities obtained provide information on stability changes with composition of the cluster, effect of hydrogen bonding, changes of basicities of methanol and dimethyl ether in the presence of water molecules, and other related properties.

Experimental Section

The high-pressure ion source mass spectrometer with which the measurements were done was described earlier.² Only a brief account of the procedures followed will be given here.

Methane buffer gas at a pressure of 4 Torr containing known amounts of water (130–320 mTorr) and dimethyl ether (2–8 mTorr), for water-dimethyl ether system, and of methanol (160–300 mTorr) and dimethyl ether (6–30 mTorr), for methanol-dimethyl ether studies, was passed (~ 1 m/sec⁻¹ measured at STP) through the thermostated ion source.

The 2000-V ionizing electron beam (5×10^{-8} A) was pulsed "on" for 150 μ sec and off for 2–4 msec. The ions escaping from the field free ion source into an evacuated region were magnetically mass analyzed and collected in a multichannel analyzer as a function of their arrival time after the electron pulse.

A good temporal profile for ions of a given mass can be obtained after some 10^4 electron pulses. The ratios of the ion intensities become constant some 100 μ sec after the electron pulse. These constant ratios were assumed equal to the ion concentration ratios at equilibrium.

Experiments at elevated ion source temperatures were made by heating the ion source block with an electrically heated jacket. Experiments below room temperature were made with an ion source of otherwise identical dimensions but with channels in the ion source block through which a cooling liquid (ethanol) was circulated.

Most measurements were done at a single solvent pressure. Occasional checks were made in which a variation of the solvent pressure by a factor of 10 led to an equilibrium constant differing by less than 20%.

(1) E. P. Grimsrud and P. Kebarle, *J. Amer. Chem. Soc.*, **95**, 7939 (1973).

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

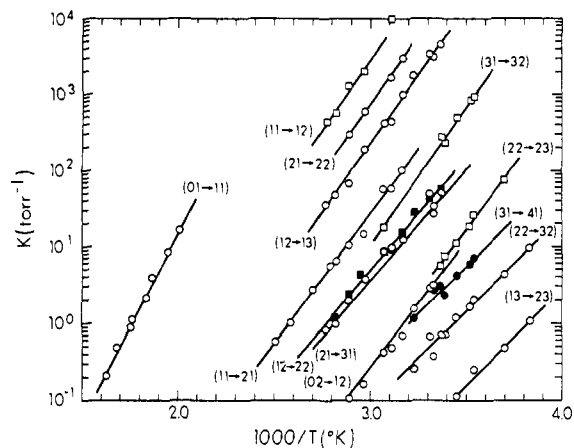


Figure 1. Van't Hoff plots for water (W) and dimethyl ether (E) equilibria: $W_w E_e H^+ + E = W_w E_{e+1} H^+$ or $W_w E_e H^+ + W = W_{w+1} E_e H^+$. The Van't Hoff lines are identified by the subscripts corresponding to number of water and dimethyl ether molecules in ion on left and right side of equation, i.e. ($w, e \rightarrow w, e + 1$) and ($w, e \rightarrow w + 1, e$) for the above two equations.

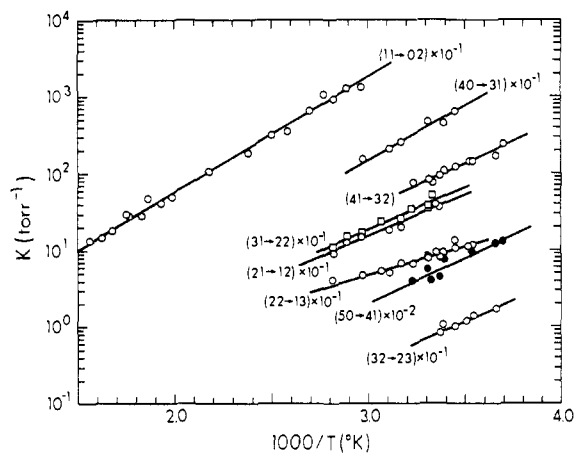


Figure 2. Van't Hoff plots for water (W) and dimethyl ether (E) exchange reactions of the type $W_w E_e H^+ + E = W_{w-1} E_{e+1} H^+ + W$. Van't Hoff lines identified by the same notation as used in Figure 1.

Results and Discussion

(1) Results. The experimentally obtained Van't Hoff plots for the water–dimethyl ether mixtures and methanol–dimethyl ether mixtures are shown in Figures 1–4. The corresponding ΔG , ΔH , and ΔS values are summarized in Figures 5 and 6 and Tables I and II. Included are results obtained earlier for the pure protonated water,² methanol,¹ and dimethyl ether¹ clusters.

Some of the values shown in Figures 5 and 6 are marked by an asterisk. Such values were obtained not by direct measurement of the equilibrium but by the application of thermodynamic cycles. This was necessary when the direct measurement of the equilibrium was difficult. An interesting example of such a situation is given in the following section.

The thermodynamic data obtained from direct equilibria measurements are amenable to cross checks by application of thermodynamic cycles. As can be verified in Figures 5 and 6 the ΔG° values in most cases do cancel within 1 kcal for a complete cycle. The direct measurements in general involve different conditions of concentration and temperature such that thermody-

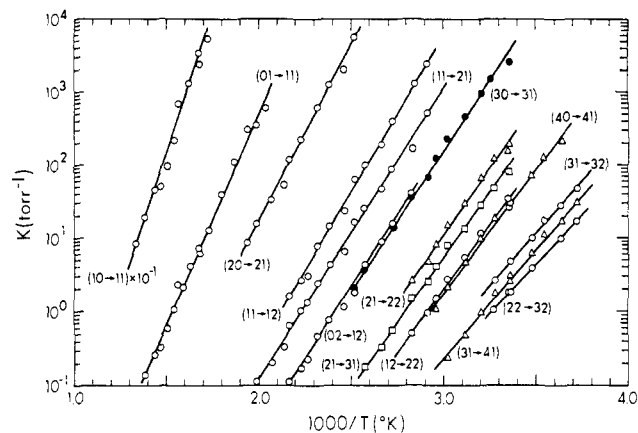


Figure 3. Van't Hoff plots for methanol (M) and dimethyl ether (E) equilibria of type $M_m E_e H^+ + E = M_m E_{e+1} H^+$ and $M_m E_e H^+ + M = M_{m+1} E_e H^+$. Van't Hoff lines identified by the same notation as used in Figure 1.

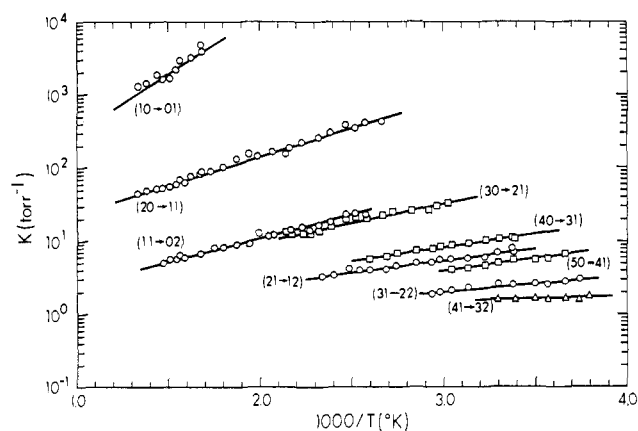
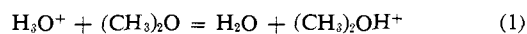


Figure 4. Van't Hoff plots for methanol (M) and dimethyl ether (E). Exchange reactions of the type $M_m E_e H^+ + M = M_{m+1} E_{e-1} H^+ + E$. Van't Hoff lines identified by the same notation as used in Figure 1.

namic consistency is not automatic. The errors observed in cycles involving the ΔH and ΔS data, Table I, are generally larger. They reflect the larger uncertainty of these determinations, particularly in cases where the temperature interval covered was comparatively narrow.

(2) Proton Affinity Differences between Water, Methanol, and Dimethyl Ether. Shown in Figures 5 and 6 are the ΔG° values for the proton transfer $W \rightarrow E$ and $M \rightarrow E$, corresponding to reactions 1 and 2. $\Delta G_1^\circ =$



23.3 kcal/mol was obtained indirectly following the path I outlined in Table III. A partly independent path II, Table III, leads to 22.3 kcal. Values for ΔG_2° can be obtained from the direct determination of K_2 since the basicity difference between methanol and dimethyl ether is much smaller. In addition to the direct value of 8.7 kcal/mol a number of indirect values can be obtained. Thus paths IV–VI, Table III, lead to values of 9.3, 9.1, and 8.7 kcal/mol.

Munson³ has summarized available proton affinities of oxygenated compounds. The "best values" given³

(3) J. Long and B. Munson, *J. Amer. Chem. Soc.*, **95**, 2427 (1973).

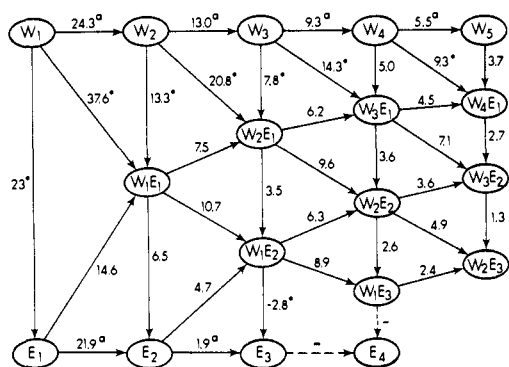


Figure 5. Free energy changes for addition and exchange reactions of protonated clusters containing water (W) and dimethyl ether (E) molecules. The value in parentheses gives $-\Delta G^{\circ}_{300}$ (kcal/mol) for the reaction leading from one to the other cluster. The proton is omitted from the clusters. Example: $W_1 \rightarrow W_2$ (24.3) means $\Delta G^{\circ} = -24.3$ kcal for reaction $W_1H^+ + W = W_2H^+$. Values with a star were obtained indirectly from cycles involving directly measured values. Standard state 1 atm. Values from ref 1 and 2 have "a" as a superscript.

Table I. Thermochemical Data from Protonated Mixed Clusters in Equilibria (Water and Dimethyl Ether)^a

Reaction	$-\Delta H^{\circ}$	$-\Delta G^{\circ}$	$-\Delta S^{\circ}$
(1) Addition Reactions			
$WEH^+ + E = WE_2H^+$	18.5 ± 2	10.7 ± 2	26.3 ± 4
$WE_2H^+ + E = WE_3H^+$	16.8 ± 1	8.9 ± 1	26.6 ± 2
$W_2EH^+ + E = W_2E_2H^+$	16.4 ± 1	9.6 ± 1	22.8 ± 2
$W_2E_2H^+ + E = W_2E_3H^+$	15.8 ± 1	4.9 ± 1	36.5 ± 3
$W_3EH^+ + E = W_3E_2H^+$	16.9 ± 1	7.1 ± 1	32.9 ± 2
$EH^+ + W = WEH^+$	22.6 ± 1	14.6 ± 1	26.5 ± 1
$WEH^+ + W + W_2EH^+$	15.3 ± 1	7.5 ± 1	26.3 ± 2
$W_2EH^+ + W = W_3EH^+$	13.8 ± 1	6.2 ± 1	25.4 ± 2
$W_3EH^+ + W = W_4EH^+$	10.2 ± 2	4.5 ± 2	19.0 ± 6
$E_2H^+ + W = WE_2H^+$	16.3 ± 1	4.7 ± 1	38.8 ± 2
$WE_2H^+ + W = W_2E_2H^+$	13.6 ± 1	6.3 ± 1	24.6 ± 2
$W_2E_2H^+ + W = W_3E_2H^+$	11.6 ± 1	3.6 ± 1	26.8 ± 3
$W_1E_3H^+ + W = W_2E_3H^+$	11.4 ± 1	2.4 ± 1	30.3 ± 3
(2) Exchange Reactions			
$WEH^+ + E = E_2H^+ + W$	6.8 ± 0.5	6.5 ± 0.5	1.0 ± 0.5
$W_2EH^+ + E = WE_2H^+ + W$	5.0 ± 1	3.5 ± 1	5.1 ± 1
$W_4EH^+ + E = W_3EH^+ + W$	5.9 ± 1	5.0 ± 1	2.9 ± 2
$W_3EH^+ + E = W_2E_2H^+ + W$	4.8 ± 0.5	3.6 ± 0.5	4.0 ± 1
$W_2E_2H^+ + E = WE_3H^+ + W$	3.4 ± 0.3	2.6 ± 0.5	2.4 ± 1
$W_3H^+ + E = W_4EH^+ + W$	5.2 ± 1.0	3.7 ± 1	5.0 ± 3
$W_4EH^+ + E = W_3E_2H^+ + W$	4.8 ± 1	2.7 ± 1	7.0 ± 2
$W_3E_2H^+ + E = W_2E_3H^+ + W$	4.4 ± 1	1.3 ± 1	10.5 ± 3

^a All values are in kcal/mol, ΔG° values for 300°K, ΔS° in eu, standard state 1 atm. Only data from directly measured equilibria are shown. Data for related reactions can be obtained from thermodynamic cycles as shown in Figure 5 and Table III.

are: $PA(H_2O) = 165 \pm 3$, $PA(CH_3OH) = 182 \pm 3$, and $PA(CH_3OCH_3) = 190 \pm 5$ kcal/mol. The differences between these values give 25 for reaction 1 and 8 kcal/mol for reaction 2 with a probable error of some 5 kcal. This is close to the average values of about 23 and 9 kcal shown in Table III. It should be noted that

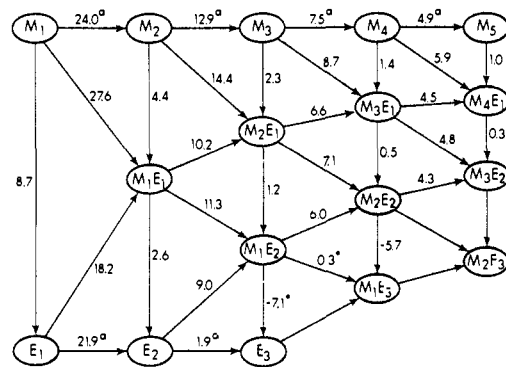


Figure 6. Free energy changes for addition and exchange reactions of protonated clusters containing methanol (M) and dimethyl ether (E) molecules. Same conventions as in Figure 5. Values from ref 1 and 2 have "a" as a superscript.

Table II. Thermochemical Data from Protonated Mixed Clusters in Equilibria (Methanol and Dimethyl Ether)^a

Reaction	$-\Delta H^{\circ}$	$-\Delta G^{\circ}_{300}$	$-\Delta S^{\circ}$
(1) Addition Reactions			
$MH^+ + E = MEH^+$	35.0 ± 2	27.6 ± 2	24.7 ± 3
$MEH^+ + E = ME_2H^+$	20.2 ± 0.5	11.3 ± 1	29.8 ± 2
$M_2H^+ + E = M_2EH^+$	21.9 ± 0.5	14.4 ± 1	25.2 ± 2
$M_2EH^+ + E = M_2E_2H^+$	16.6 ± 0.5	7.1 ± 1	31.8 ± 2
$M_3H^+ + E = M_3EH^+$	17.2 ± 0.5	8.7 ± 1	28.6 ± 1
$M_3EH^+ + E = M_3E_2H^+$	12.5 ± 0.5	4.8 ± 1	25.6 ± 2
$M_4H^+ + E = M_4EH^+$	15.3 ± 0.5	5.9 ± 1	31.5 ± 2
$EH^+ + M = MEH^+$	26.3 ± 0.5	18.2 ± 1	27.1 ± 1
$MEH^+ + M = M_2EH^+$	18.8 ± 0.3	10.2 ± 0.5	28.9 ± 1
$M_2EH^+ + M = M_3EH^+$	15.9 ± 0.3	6.6 ± 0.5	31.2 ± 1
$M_3EH^+ + M = M_4EH^+$	13.7 ± 0.3	4.5 ± 0.5	30.8 ± 1
$E_2H^+ + M = ME_2H^+$	18.1 ± 0.4	9.0 ± 1	30.6 ± 1
$ME_2H^+ + M = M_2E_2H^+$	15.1 ± 0.4	6.0 ± 1	30.6 ± 2
$M_2E_2H^+ + M = M_3E_2H^+$	12.2 ± 0.2	4.3 ± 0.5	26.5 ± 1
(2) Exchange Reactions			
$MH^+ + E = EH^+ + M$	7.6 ± 1	8.7 ± 0.7	-3.9 ± 1
$M_2H^+ + E = MEH^+ + M$	3.6 ± 0.2	4.4 ± 0.2	-2.8 ± 1
$M_1E_1H^+ + E = E_2H^+ + M$	2.9 ± 0.2	2.6 ± 0.2	1.0 ± 1
$M_3H^+ + E = M_2EH^+ + M$	2.2 ± 0.2	2.3 ± 0.2	-0.4 ± 1
$M_2EH^+ + E = M_1E_2H^+ + M$	1.4 ± 0.2	1.2 ± 0.2	0.9 ± 1
$M_4H^+ + E = M_3EH^+ + M$	1.6 ± 0.2	1.4 ± 0.2	0.6 ± 1
$M_3EH^+ + E = M_2E_2H^+ + M$	0.9 ± 0.2	0.5 ± 0.2	1.4 ± 1
$M_2E_2H^+ + E = ME_3H^+ + M$		-5.7^b	
$M_5H^+ + E = M_4EH^+ + M$	1.8 ± 0.5	1.0 ± 0.5	2.7 ± 1
$M_4EH^+ + E = M_3E_2H^+ + M$	0.0 ± 0.5	0.3 ± 0.5	-0.8 ± 1

^a All energy values are in kcal/mol, ΔG° values for 300°K, ΔS° in eu, standard state 1 atm. Only data from directly measured equilibria are shown. Data for related reactions can be obtained from thermodynamic cycles as shown in Figure 6 and Table III.

^b Value obtained by measurements at a single temperature (300°K) using 4 Torr of dimethyl ether. The signal from the ME_3H^+ cluster was only slightly above noise level. Assuming possible error due to background ΔG° for reaction $ME_2H^+ + E = ME_3H^+$ probably larger than $+5.7$ kcal/mol.

the proton affinities quoted in the literature are often obtained by a bracketing technique involving gaseous proton transfer reactions.³ More recently proton

Table III. Thermodynamic Data for Proton Transfer Reactions between Water, Methanol, and Dimethyl Ether^a

Path of thermodynamic cycle ^b	(1) (CH ₃) ₂ OH ⁺ + H ₂ O = (CH ₃) ₂ O + H ₃ O ⁺		ΔS_1° , eu
	ΔG_1° , kcal/mol	ΔH_1° , kcal/mol	
(I) E ₁ , W ₁ E ₁ , W ₂ E ₁ , W ₃ E ₁ , W ₄ , W ₃ , W ₂ , W ₁	23.3	22.8	-1.8
(II) E ₁ , E ₂ , W ₁ E ₂ , W ₂ E ₂ , W ₃ E ₁ , W ₄ , W ₃ , W ₂ , W ₁	22.3	18.7	-7.2
(2) (CH ₃) ₂ OH ⁻ + CH ₃ OH = (CH ₃) ₂ O + CH ₃ OH ₂ ⁺			
	ΔG_2° , kcal/mol	ΔH_2° , kcal/mol	ΔS_2° , eu
(III) E ₁ , M ₁	8.7	7.6	-3.9
(IV) E ₁ , M ₁ E ₁ , M ₁	9.4	8.7	-2.4
(V) E ₁ , E ₂ , M ₁ E ₁ , M ₂ , M ₁	9.1	8.9	-0.9
(VI) E ₁ , E ₂ , M ₁ E ₂ , M ₂ E ₁ , M ₂ , M ₁	8.7	7.6	-3.6

^a Data obtained from Figures 5 and 6, Tables I and II, and ref 1. Values of ΔG° at 300°K, all energies in kcal/mol, ΔS in eu, standard state 1 atm. ^b For notation used see Figures 1, 5, and 6.

transfer ion equilibria have also been used.⁴⁻⁶ In both of these cases one obtains values corresponding to ΔG° for proton transfer. These are assumed to be close to the ΔH° values since the entropy change of the proton transfer reactions is generally small,⁶ *i.e.*, around 1-3 eu. The bracketing technique and the equilibrium technique depend on proton transfer studies involving many compounds with similar proton affinities such that each proton transfer step involves a relatively small ΔG change. The proton affinity difference between water and dimethyl ether of 23 kcal obtained in the present results also involves many steps since the direct measurement of the equilibrium constant K_1 is not possible. In the present case the intermediate compounds are mixed clusters whose proton affinities change more gradually. We do not think that the present technique necessarily gives more accurate results. The relatively good agreement with the literature data³ might also be due to fortuitous cancellations of errors in the values shown in Figure 5. Nevertheless, it is significant that the present completely independent determinations are close to those obtained by other methods. Obviously, the much lower ΔG and ΔH values obtained by Bennett, Beggs, and Field⁷ for the H⁺(H₂O)₂ and H⁺(H₂O)₃ formation (W₁ → W₂ → W₃) will not lead to proton affinity differences in agreement with literature data³ when substituted in the thermodynamic cycles of Figure 5 or 6.

The ΔH and ΔS values for reactions 1 and 2 can also be obtained from the present determinations. Unfortunately, the Van't Hoff plots for the clusters containing water and dimethyl ether were taken over a rather narrow temperature range. Furthermore, because of the large proton affinity difference between these two compounds several of the equilibria were difficult to measure. For this reason the ΔH and particularly the ΔS values are less reliable. The two

(4) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Amer. Chem. Soc.*, **93**, 4314 (1971).

(5) E. M. Arnett, F. M. Jones III, M. Taagepera, W. G. Henderson, D. Holtz, J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).

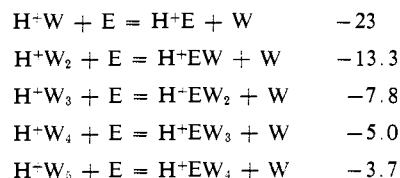
(6) J. P. Briggs, R. Yamdagni, and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 5128 (1972).

(7) D. P. Beggs and F. H. Field, *J. Amer. Chem. Soc.*, **93**, 1567 (1971); F. H. Field and D. P. Beggs, *ibid.*, **93**, 1576 (1971); L. Bennett and F. H. Field, *ibid.*, **94**, 5186 (1972).

major cycles available for ΔH_1 and ΔS_1 give for the enthalpy 22.8 and 18.7 kcal and the entropy -1.8 and -7.2 eu. We believe the first value to be more reliable since ΔS is expected to be small.

More consistent results are obtained for the proton transfer from dimethyl ether to methanol. The values for several paths are summarized in Table III. The ΔH values are between 7.6 and 8.9 kcal, while the ΔS values are in the range -1 to -3.9 eu.

(3) Changes of Basicities of Methanol and Dimethyl Ether with Increasing Hydration. A number of interesting relationships can be observed from a study of the data shown in Figures 5 and 6. One of these is the change of basicity of methanol and dimethyl ether with increasing hydration. As discussed in the preceding section, the basicities (or proton affinities) increase in the order H₂O, CH₃OH, and (CH₃)₂O. This is a consequence of the stabilizing effect of the methyl group on the positive charge in the protonated species. The basicity order in aqueous solution has been difficult to determine.⁸ Data from Figure 5 corresponding to the reaction H⁺W_{*n*} + E = H⁺EW_{*n-1*} + W are shown below.



The G° values (kilocalories per mole) demonstrate that the exothermicity in replacing a water by an ether molecule decreases progressively with increasing water content in the cluster. This means that the greater basicity of ethanol rapidly decreases with increasing water content of the cluster. An extrapolation of the present results to aqueous solution is not possible; however, the rapid fall off of the values does suggest that the ether is probably a weaker base than HOH in aqueous solution.

The reasons for the rapid decrease of basicity of the ether with water content are probably twofold. A big decrease is observed already between the first and second proton transfer reaction (W, E) and (W₂, WE). This decrease cannot be due to steric blockage of hydrogen bonding by the methyl groups since steric effects probably play only a minor role in the stability of the EWH⁺. The initial decrease from 23 to 13.3 kcal should be due to the fact that the stabilizing charge dispersion caused by the methyl groups in EH⁺ makes the additional stabilization by one water molecule less important than is the case for WH⁺. Earlier^{9,10} we had observed that the strength of hydrogen bonding in charged species increases with the acidity of the proton donor and basicity of the proton acceptor. Applying this to the present hydration reactions (EH⁺ + W = WEH⁺ and WH⁺ + W = W₂H⁺), we conclude that the smaller energy release in the first reaction is due to the lower acidity of EH⁺ when compared with WH⁺. Thus, the higher basicity of E relative to W automatically reduces the energy gain of the hydration reaction.

(8) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(9) R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **93**, 7139 (1971).

(10) J. D. Payzant, A. J. Cunningham, and P. Kebarle, *Can. J. Chem.*, **51**, 3242 (1973).

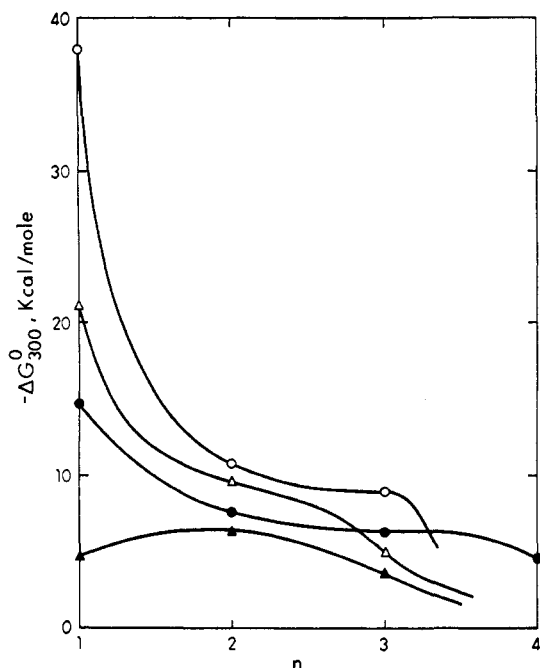


Figure 7. Free energy changes at 300°K (standard state 1 atm) for addition of water (W) or ether (E) to protonated clusters: (○) sequence a, $W_nE_{n-1}H^+ + E = W_nE_nH^+$; (●) sequence b, $W_{n-1}E_1H^+ + W = W_nE_1H^+$; (△) sequence c, $W_2E_{n-1}H^+ + E = W_2E_nH^+$; (▲) sequence d, $W_{n-1}E_2H^+ + W = W_nE_2H^+$.

This effect should carry over to some of the subsequent hydration steps. As the water content of the cluster increases a second effect, the hydrogen bonding blocking property of the methyl groups, should become important. Since H_3O^+ has three H bonding positions, further hydration leads to a symmetric growth of the cluster. $(CH_3)_2OH^+$ has only one H bonding position and must of necessity stay on the outer periphery of the cluster. This leads to clusters of lower stability and gradually, with growth of the number of water molecules, all the advantages of the stronger intrinsic basicity of dimethyl ether must become lost.

Some specific considerations on stabilities of mixed clusters are considered in the next section.

(4) Stabilities of Protonated Clusters Containing Water and Dimethyl Ether. Free energy changes for some selected addition reactions involving water and dimethyl ether are shown in Figure 7. The corresponding reactions and the resulting hydrogen bonded structures are shown in Figure 8. Structures were chosen which seemed to be of lowest energy and fitted the observed ΔG changes.

Sequence a gives the free energies for successive additions of ether molecules to H_3O^+ . The release of energy on addition of the first E is the largest observed in Figure 8. This is a consequence of the high basicity of E and the high acidity of H_3O^+ . The results show that the addition of a second molecule of E releases very much less energy (Figure 7). One expects that in the species $(EHW)^+$ more positive charge will be on E than on W. Since the second E molecule must go onto W if it is to hydrogen bond, the resulting species should be $(EH_3OE)^+$ (see Figure 8). The stabilizing effect of the second E thus might be expected to be relatively small, since it is going to a position which is far removed from the original charge distribution. The addition of a third E is found to release only a slightly lower amount

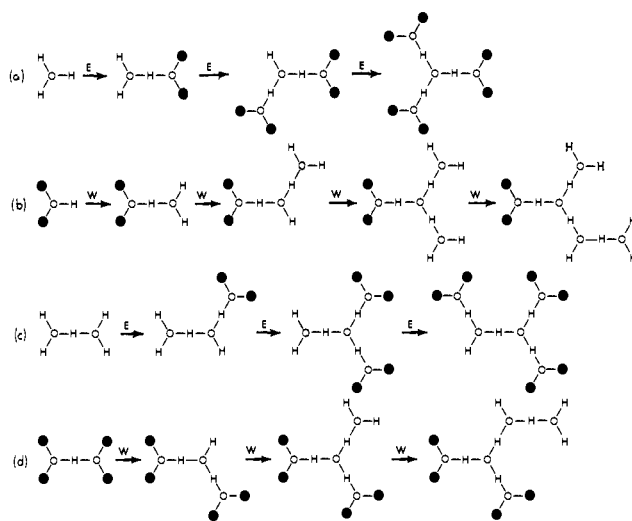


Figure 8. Structures assumed to be involved in reaction sequences a-d of Figure 7. Each structure contains one positive charge. (●) methyl.

of energy than the second E. This is not surprising. In $(EH_3OE)^+$ charge was dispersed to the two hydrogen bonded ends of the W molecule and the third E attaches to the last available position of the water molecule (Figure 8). The fourth E in WE_4H^+ cannot hydrogen bond. The cluster WE_4H^+ was not observed in experiments at concentration and temperature conditions where one would have seen it had it been as stable as some of the other H bonded species with the same total number of molecules. The low stability of WE_4H^+ indicates that the ion-dipole interaction by which the fourth E should be held is weak. This could be expected since the charge in the hydrogen bonded $(H_3O)-E_3^+$ ion must be very dispersed.

Sequence b (Figures 7 and 8) deals with successive additions of water to EH^+ . The first W releases much less energy than in the corresponding first step of sequence a. This is expected since in the present case EH^+ is the weaker acid and W the weaker base. The addition of a second water molecule releases considerably less energy than the first. Presumably this is caused by the fact that the second W must H bond in an outer position relative to the proton shared by W and E. The addition of a third W leads to an only slightly reduced energy interaction, since the second and third molecule occupy similar positions. A fourth water molecule can H bond. Therefore, a stable cluster W_4EH^+ is observed in contrast to the unstable WE_4H^+ of sequence a. The energy released in the addition of the fourth W molecule is significantly smaller than that for the third. This probably reflects the fact that the fourth molecule must go in a far outer position (see Figure 8).

In sequence c E is added to W_2H^+ . The first addition of E brings in a substantial energy release (Figure 7) because of the high basicity of E. The second E releases less energy. The resulting structure is probably one in which both E are attached to the same W (see Figure 8). Interestingly a larger than usual decrease is observed for the third E molecule. This probably results from the fact that the third E must be accommodated on the second W away from the original location of the charge (see Figure 8).

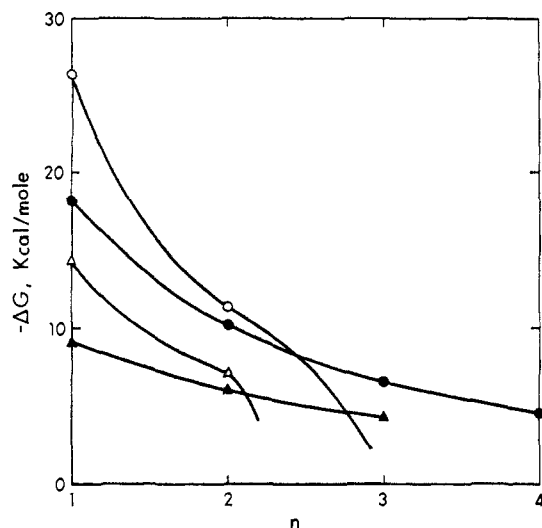


Figure 9. Free energy changes at 300°K (standard state 1 atm) for addition of methanol (M) or dimethyl ether (E) to protonated clusters: (○) sequence a, $M_1E_{n-1}H^+ + E = M_1E_nH^+$; (●) sequence b, $M_{n-1}E_1H^+ + M = M_nE_1H^+$; (△) sequence c, $M_2E_{n-1}H^+ + E = M_2E_nH^+$; (▲) sequence d, $M_{n-1}E_2H^+ + M = M_nE_2H^+$.

In sequence d water molecules are added to E_2H^+ . The energy released by the first water molecule is very low because the poor base W must insert itself and separate the strongly bonded E_2H^+ species (see Figure 9). Addition of the second water molecule is relatively favorable and leads to a larger free energy change since now a hydrogen bonding position close to the central H_3O is available. The third water molecule must go to an outer position with a less favorable interaction.

Some selected reaction sequences involving the protonated methanol and dimethyl ether clusters are shown in Figures 9 and 10. These results can be interpreted along the same lines as the results in Figures 7 and 8 involving water and dimethyl ether. Only in the methanol sequences one must take into account that the basicities of M and E are more similar and that methanol has one less H bonding position than water. For example, sequence a in Figure 10, which involves successive addition of E to MH^+ , can be compared with sequence a in Figure 8, which involved successive addition of E to WH^+ . The energy released on addition of the first E to MH^+ (Figure 9) is substantially lower than that for WH^+ , since MH^+ is a weaker acid. A second E goes on to the methanol cluster, but a third E leads to a species of low stability since no H bonding position is available.

Addition of M molecules to EH^+ in sequence b in Figures 9 and 10 leads to evenly decreasing free energy changes since, in contrast to sequence b with W, each successive M has only one position to go to.

Sequence c (Figure 10) corresponding to addition of E to M_2H^+ leads to an unstable cluster after addition of two ether molecules. The same could be expected for all M_nH^+ clusters since they have only two H bonding positions.

Sequence d (Figure 10) in which M is added to E_2H^+ shows distinctive differences from the analogous sequence d involving W. The methanol sequence shows a continuous decrease of released energy. This is not surprising since in this case every methanol molecule

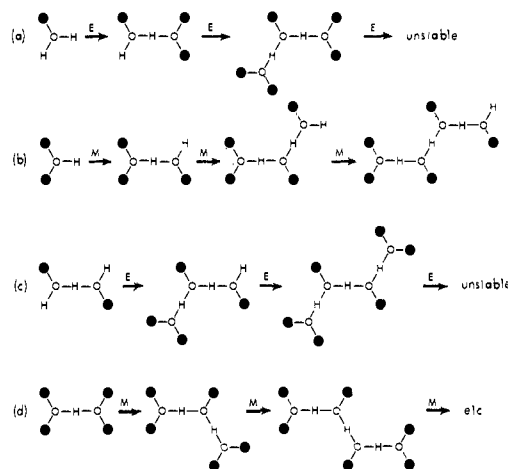


Figure 10. Structures assumed to be involved in reaction sequences a-d of Figure 9. Each structure carries one positive charge. (●) methyl.

must insert itself in a chain which is terminated on both sides by ether molecules.

Similar observations can be made regarding the free energy changes found for the exchange reactions. Since basically the same species are involved a detailed separate discussion of these reactions will not be given. In general the exchange data in Tables I and II show that the more highly methyl substituted compound is taken in with great preference (large negative ΔG) in small clusters. This preference decreases with an increase of cluster size.

The entropy changes of the exchange reactions are generally small. Exchange of E for W in the cluster is always accompanied by a negative ΔS (Table I) with most of the values ranging between 0 and 5 eu. The translational entropy change for these reactions can be easily evaluated by the Sackur-Tetrode equation and amounts to a constant term of about -2 eu. Several of the reactions show negative entropy changes which are numerically larger. This effect might be due to the more restrictive and thus unfavorable steric requirements of E.

The entropy changes in the exchange reactions between E and M shown in Table II are generally smaller than those between E and W as might have been expected due to the greater similarity between M and E. The changes are not always of the same sign, but it is not clear how much of this is due to experimental error.

The small values of ΔS for the exchange reactions require that the ΔS for the addition reactions should be similar. In general this is the case with most values lying in the range between 25 and 30 eu (Tables I and II).

In conclusion, the following three principles may be underlined as determining the diverse free energy changes depicted in Figures 7 and 9. Hydrogen bonding is dominant. The preference for the more methyl substituted base decreases with cluster size. More energy is released if the incoming base can hydrogen bond to a position close to the (expected) location of positive charge.

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