J. Am. Chem. Soc. **1984**, *106*, 3913–3916

Stabilities and Hydrogen Bonding in Complexes of H_3O^+ and $CH_3OH_2^+$ with Crown Ethers, from Measurements of Gas-Phase Ion–Molecule Equilibria

Ram B. Sharma and Paul Kebarle*

Contribution from the Chemistry Department, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. *Received November 2, 1983*

Abstract: Enthalpy (kcal/mol) and entropy (eu) changes were obtained for the complexation of H_3O^+ and $CH_3OH_2^+$ by crown ethers: 18-crown-6 (Cr6), 15-crown-5 (Cr5), and 12-crown-4 (Cr4). These are as follows: $Cr6 + H_3O^+ = Cr6{\cdot}H_3O^+$, $\Delta H = -88.5$, $\Delta S = -55.8$; $Cr5 + H_3O^+ = Cr5{\cdot}H_3O^+$, $\Delta H = -76.9$, $\Delta S = -43$; $Cr6 + CH_3OH_2^+ = Cr6{\cdot}CH_3OH_2^+$, $\Delta H = -67.6$, $\Delta S = -50$; $Cr5 + CH_3OH_2^+ = Cr5{\cdot}CH_3OH_2^+$, $\Delta H = 60.8$, $\Delta S = -37.6$; $Cr4 + CH_3OH_2^+ = Cr4{\cdot}CH_3OH_2^+$, $\Delta H = -58.3$, $\Delta S = -40.6$ (standard state 1 atm). The very large exothermicity and large entropy loss for the formation of $Cr6{\cdot}H_3O^+$ is consistent only with the formation of a triply hydrogen bonded complex in which the H_3O^+ interacts with three oxygens of the Cr6 and there is additional stabilization of the central charge by the remaining three CH_2OCH_2 dipoles in Cr6. The bonding in the remaining complexes is also examined. The data were obtained by measuring ion–molecule equilibria in the gas phase with a pulsed electron, high-pressure mass spectrometer.

Polyethers like glymes, crown ethers, and cryptands can be very effective and specific complexing agents for cations in solution, and these properties are of great chemical and biological significance.[1-5] Determinations of the complexing energies of cations with polyethers in the gas phase are possible in principle and would be of some relevance since such measurements provide the complexing power in the absence of solvent and counterion and thus facilitate understanding of the effect of the solvent environment and ion pairing.

An earlier study from this laboratory dealt with the gas-phase basicities of glymes and crown ethers, i.e., the complexing of the proton by these multidentate ligands.[6] Meot-Ner[7] has also reported gas-phase basicity measurements of a number of open- and closed-chain polyethers. The present work is a sequel to these studies and deals with the complexing of the oxonium ion H_3O^+ and methoxonium ion $CH_3OH_2^+$ with the crown ethers 12-Cr-4 (Cr4) 15-Cr-5 (Cr5), and 18-Cr-6 (Cr6). The crown ethers are cyclic ethers made up of $-CH_2OCH_2$ subunits. It will prove meaningful to examine hydrogen bonds of H_3O^+ (and $CH_3OH_2^+$) to the crown ethers by comparing them to the hydrogen bonds of H_3O^+ to separated CH_2OCH_2 groups, i.e., to dimethyl ether molecules, CH_3OCH_3.

The preparation of a stable complex between H_3O^+ and dicyclohexyl-18-crown-6 (I) in the condensed phase was reported in 1972 by Izatt et al.[8] The crystalline $[H_3O^+{\cdot}I][ClO_4^-]$ complex was obtained by adding an excess of the acid $HClO_4$ to an aqueous solution of I. Infrared absorption spectra of mulls of the solid were consistent with a structure where H_3O^+ is triply hydrogen bonded to three oxygens and is essentially inside the ring of I. These findings are not surprising since the structure of Cr6 ethers allows for appropriate distances between the O atoms such that an essentially unstrained triply hydrogen bonded complex, $Cr6{\cdot}H_3O^+$ (see structure II of Figure 3 in the Discussion), can be formed. On the other hand the geometry of Cr5 and Cr4 ethers does not allow for an unstrained triply hydrogen bonded complex but only for essentially a doubly bonded one. Thus, the complexing powers of these smaller crowns toward H_3O^+ are expected to be significantly weaker. The methoxonium ion $CH_3OH_2^+$ cannot form a triply hydrogen bonded complex with Cr6 or the lower cyclic analogues. The present gas-phase complexation studies of H_3O^+ and CH_3OH^+ with Cr6, Cr5, and Cr4 explore these expected trends. The experimental determinations are based on the measurement of gas-phase ion–molecule equilibria with a pulsed electron-beam, high-pressure mass spectrometer.

Experimental Section

Apparatus and Methods of Measurement. The measurements of the ion–molecule equilibria were performed with a pulsed electron beam high ion source pressure mass spectrometer. The same instrument was used as in the basicity measurement of the polyethers.[6] The experimental techniques and conditions were also very similar. The reagents were squirted as a liquid solution into the 1-atm flowing methane carrier gas, by means of a motor-driven syringe, as was done in the earlier work.[6] In the present case the liquid solution consisted of the given crown dissolved in water, resp. methanol. The molar ratios Cr/H_2O and Cr/CH_3OH were typically $^1/_{10}$–$^1/_{50}$. Typical experimental conditions in the ion source were as follows: methane, 4 torr; H_2O (or CH_3OH) at a known pressure in the 5–100-mtorr range.

The major reaction sequence under the above conditions, written for H_2O, is as follows: CH_5^+ and $C_2H_5^+$, the ultimate stable ions produced when methane is irradiated by electrons, engage in rapid proton transfer to water (reaction 1). This is followed by rapid clustering of the H_3O^+ (reactions 2 and 3) and proton or H_3O^+ transfer to the crown (reactions 4 and 5).

$$CH_5^+ \text{ (and } C_2H_5^+\text{)} + H_2O \rightarrow H_3O^+ + CH_4 \text{ (and } C_2H_4\text{)} \tag{1}$$

$$H_3O^+ + H_2O \rightarrow H_3O^+{\cdot}H_2O \tag{2}$$

$$H_3O^+(H_2O)_{n-1} + H_2O \rightarrow H_3O^+(H_2O)_n \tag{3}$$

$$H_3O^+(H_2O)_n + Cr \rightarrow CrH^+ + (n+1)H_2O \tag{4}$$

$$\rightarrow CrH_3O^+ + nH_2O \tag{5}$$

$$CrH^+ + H_2O \rightarrow CrH_3O^+ \tag{6}$$

At the chosen concentrations and ion source temperatures, reaction 1 is complete in a few microseconds and reactions 2 and 3 and 4 and 5 in tens of microseconds; i.e., the CH_5^+ and $C_2H_5^+$ ions disappear within microseconds while the oxonium hydrates $H_3O^+(H_2O)_n$ disappear within tens of microseconds after the electron pulse. The equilibrium that was measured was reaction 6. The reactant ions CrH^+ and $Cr{\cdot}H_3O^+$ reached equilibrium rapidly, within less than 200 μs. Evidence for this was the observed time independent ion ratio CrH^+/CrH_3O^+ which becomes established in 100–200 μs after the ionizing electron pulse. The stationary ion ratio could be observed over 2000–3000 μs.

Results

The enthalpy (ΔH°), entropy (ΔS°), and free energy changes (ΔG°) for reactions 7 and 8 are given in Table I. The significance of these data will be examined in the Discussion. Here we note that the reactions are very exothermic; for example ΔH_7° for Cr6

$$Cr + H_3O^+ \rightarrow CrH_3O^+ \tag{7}$$

$$Cr + CH_3OH_2^+ \rightarrow CrCH_3OH_2^+ \tag{8}$$

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Table I. Thermochemical Data for Complex Formation between H_3O^+ and Crowns and $CH_3OH_2^+$ and Crowns and Related Reactions[a]

no.[b]	reaction	$-\Delta H$, kcal/mol	$-\Delta S$, eu	no.	reaction	$-\Delta H$, kcal/mol	$-\Delta S$, eu
7[c]	$Cr6 + WH^+ \rightarrow Cr6WH^+$	88.5	55.8	6[e]	$Cr6{\cdot}H^+ + W \rightarrow Cr6{\cdot}WH^+$	26.4	34.6
7[c]	$Cr5 + WH^+ \rightarrow Cr5WH^+$	76.9	43.2	6[e]	$Cr5{\cdot}H^+ + W \rightarrow Cr5{\cdot}WH^+$	21.6	33.0
7[c]	$Cr4 + WH^+ \rightarrow Cr4WH^+$	g	g	6[e]	$Cr4{\cdot}H + W \rightarrow Cr4{\cdot}WH^+$	g	g
8[c]	$Cr6 + MH^+ \rightarrow Cr6MH^+$	67.6	50.0	6[e]	$Cr6{\cdot}H^+ + M \rightarrow Cr6{\cdot}MH^+$	20.0	29.5
8[c]	$Cr5 + MH^+ \rightarrow Cr5MH^+$	60.8	37.6	6[e]	$Cr5{\cdot}H^+ + M \rightarrow Cr5{\cdot}MH^+$	20.0	28.0
8[c]	$Cr4 + MH^+ \rightarrow Cr4MH^+$	58.3	40.6	6[e]	$Cr4{\cdot}H^+ + M \rightarrow Cr4{\cdot}MH^+$	19.5	34.0
10[d]	$E + WH^+ \rightarrow EWH^+$	49.8	30.0	9[f]	$WH^+ + Cr6 \rightarrow W + Cr6{\cdot}H^+$	62.1	21.2
11[d]	$2E + WH^+ \rightarrow E_2WH^+$	63.3	56.3	9[f]	$WH^+ + Cr5 \rightarrow W + Cr5{\cdot}H^+$	55.3	10.2
12[d]	$3E + WH^+ \rightarrow E_3WH^+$	80.0	82.9	9[f]	$WH^+ + Cr4 \rightarrow W + Cr4{\cdot}H^+$	53.3	7.2
13[d]	$E + MH^+ \rightarrow EMH^+$	35.0	24.7	9[f]	$MH^+ + Cr6 \rightarrow M + Cr6{\cdot}H^+$	47.6	20.6
14[d]	$2E + MH^+ \rightarrow E_2NH^+$	55.0	54.5	9[f]	$MH^+ + Cr5 \rightarrow M + Cr5{\cdot}H^+$	40.8	9.6
	$Cr6 + c\text{-}C_6H_{11}NH_3^+ \rightarrow Cr6{\cdot}C_6H_{11}NH_3^+$	46.0[h]	38.0[h]	9[f]	$MH^+ + Cr4 \rightarrow M + Cr4{\cdot}H^+$	38.8	6.6
	$Cr5 + c\text{-}C_6H_{11}NH_3^+ \rightarrow Cr5{\cdot}C_6H_{11}NH_3^+$	42.3[h]	36.5[h]				

[a] The following notation has been used: $W = H_2O$, $WH^+ = H_3O^+$, $M = CH_3OH$, $E = CH_3OCH_3$, Cr6 = 18-crown-6, Cr5 = 15-crown-5, Cr4 = 12-crown-4. [b] Numbers by which reactions are identified in text. [c] Evaluated from thermodynamic cycle: (7) = (6) + (9) where (6) and (9) involve W, (8) = (6) + (9) where (6) + (9) involve M. $\Delta H_7°$ and $\Delta H_8°$ values believed reliable to ±3 kcal/mol, $\Delta S_7°$ and $\Delta S_8°$ to ±4 eu. [d] From earlier measurements in this laboratory.[11] [e] From measurement of equilibrium constants for reactions 6 at different temperatures (see Figure 1) and corresponding van't Hoff plots (see Figure 2). Present experimental work: $\Delta H° = \pm 2$ kcal/mol, $\Delta S° = \pm 3$ eu. [f] From proton affinities of Cr6 (229.4), Cr5 (222.6), Cr4 (220.6) (Sharma[6], H_2O (167.3), CH_3OH (181.8) (Kebarle[9]. Above values based on NH_3 (203.6), H_2O (167.3), and Ceyer[9], used as anchoring points. All values in kcal/mol; see also Rosenstock[9]. [g] Exact values for the equilibria $WH^+ + Cr4 \rightarrow Cr4{\cdot}WH^+$ could not be obtained. The tendency for the formation of the $Cr4{\cdot}WH^+$ complex was weaker than was the case with $Cr4{\cdot}MH^+$. At the lower temperatures required to observe $Cr4{\cdot}WH^+$ interference by the equilibrium, $Cr4{\cdot}H^+ + Cr4 \rightarrow (Cr4)_2H^+$ was encountered. [h] From Meot-Ner, ref 18.

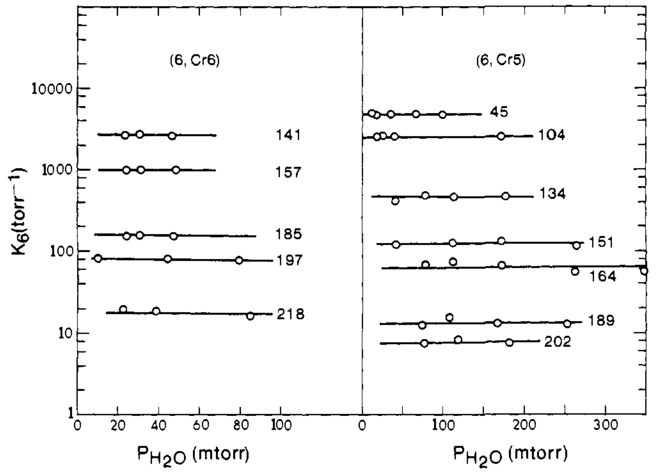

Figure 1. Measured equilibrium constants K_6 (torr^{-1}) for reactions (6, Cr6) $Cr6{\cdot}H^+ + H_2O \rightarrow Cr6{\cdot}H_3O^+$ and (6, Cr5) $Cr5{\cdot}H^+ + H_2O \rightarrow Cr5{\cdot}H_3O^+$. Numbers given beside pressure plots give ion source temperature in °C.

is exothermic by a whole 88 kcal/mol. Due to the strong bonding indicated by this value, a direct measurement of this equilibrium would have been impossible. However thermochemical values for reactions 7 and 8 can be obtained from a thermodynamic cycle. The cycle uses reactions 6 and 9 (written for the systems involving H_2O). It is evident that $\Delta H_7 = \Delta H_6 + \Delta H_9$. The conditions

$$CrH^+ + H_2O \rightarrow CrH_3O^+ \qquad (6)$$

$$Cr + H_3O^+ \rightarrow CrH^+ + H_2O \qquad (9)$$

$$Cr + H_3O^+ \rightarrow CrH_3O^+ \qquad (7)$$

used for the measurement of reaction 6 were described in the Experimental Section. Reaction 9 represents the proton transfer from H_3O^+ to the respective crown. The thermochemical values required for (9) involve the proton affinities and gas-phase basicities of the crowns, water (and methanol). The data for the crowns were taken from our earlier study of the basicities of the crowns,[6] while those for water and methanol are available from the literature.[9-11] The equilibrium constants and the van't Hoff plots for reaction 6 measured in the present work are shown in Figures 1 and 2, and all the thermochemical data involved in the cycles (6) + (9) = (7) are given in Table I.

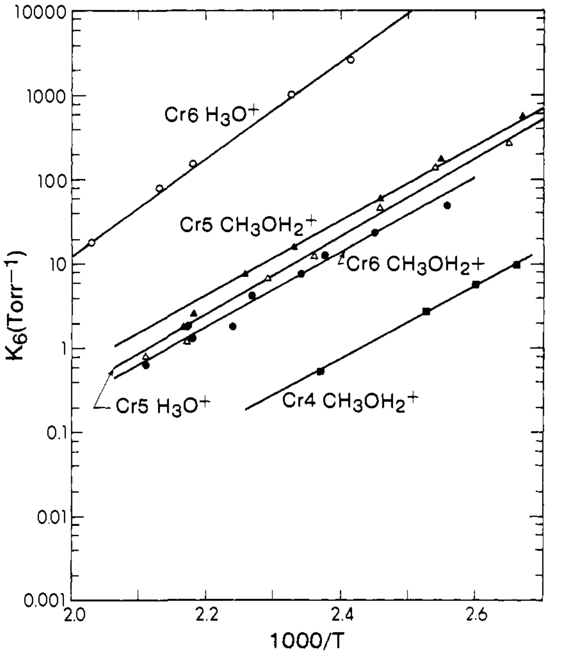

Figure 2. van't Hoff plots of equilibrium constants for reactions 6: (⊙) $Cr6{\cdot}H^+ + H_2O \rightarrow Cr6{\cdot}H_3O^+$, (▲) $Cr5{\cdot}H^+ + CH_3OH \rightarrow Cr5{\cdot}CH_3OH_2^+$, (△) $Cr5{\cdot}H^+ + H_2O \rightarrow Cr5{\cdot}H_3O^+$, (●) $Cr6{\cdot}H^+ + CH_3OH \rightarrow Cr6{\cdot}CH_3OH_2^+$, (■) $Cr4{\cdot}H^+ + CH_3OH \rightarrow Cr4{\cdot}CH_3OH_2^+$. Enthalpy and entropy changes ΔH_6 and ΔS_6 obtained from van't Hoff plots are given in Table I; these values were used in a thermodynamic cycle to evaluate the data for reactions 7 and 8, i.e., $Cr6 + H_3O^+ \rightarrow Cr6{\cdot}H_3O^+$, etc.

Discussion

The enthalpy changes for the complexation of H_3O^+ (and $CH_3OH_2^+$) with the crowns, i.e., reactions 7 and 8, are given in Table I. The most exothermic reaction, as expected (see introduction), is the complexing of H_3O^+ to Cr6. The enthalpy change

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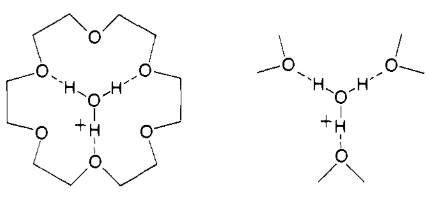

II III

Figure 3. Structures of $Cr6{\cdot}H_3O^+$ and $(CH_3OCH_3)_3H_3O^+$.

for this reaction is −88 kcal/mol. This is a very large exothermicity for a reaction that involves only hydrogen bonding. We shall first examine whether this result makes sense. An approximately to scale, planar representation of the $Cr6{\cdot}H_3O^+$ complex is given in Figure 3. If the Cr6 is put in a configuration where the six oxygens are essentially coplanar, a molcule of H_3O^+ can be fitted inside the cavity such that three hydrogen bonds are formed with three of the crown oxygens. The OHO distance of each bond is slightly smaller than the optimal distance of 2.4 Å occurring in $O{\cdot\cdot}H^+{\cdot\cdot}O$ hydrogen bonds[12] if the H_3O^+ molecule is assumed planar and its O atom is placed in a coplanar position with the Cr6 oxygens. Actually, H_3O^+ when alone or hydrogen bonded to three oxygens as in $H_3O^+(H_2O)_3$ is probably a shallow pyramide, H–O–H angle in H_3O^+ ~112°.[13] When such a geometry is assumed and the known relative ease for changes of this angle are considered, it is possible to fit an H_3O^+ molecule to the Cr6, such that the central O atom of H_3O^+ is slightly above the plane of the crown oxygens. This can occur with minimum strain and yield $O{\cdot\cdot}H^+{\cdot\cdot}O$ distances of 2.4 Å or even somewhat larger.

The exothermicity $\Delta H_7(Cr6) = -88$ kcal/mol can be compared with the energy released when H_3O^+ forms three hydrogen bonds with three dimethyl ether molecules, i.e., reaction 12. The enthalpy changes for reactions 10–13 were obtained in earlier measurements from this laboratory, reactions 10–12 from ref 11, and reaction 13 from ref 14. Reaction 13 involving three H_2O molecules rather than dimethyl ether molecules is given for comparison. The exothermicity of (13) is considerably smaller than that of (12). We believe that (12) is much more suitable for comparisons with the hydrogen bonding in the Cr6 ether. The complex presumed to result from reaction 12 is also shown in Figure 3. The exothermicity of the H_3O^+ complexation with Cr6 is some 8 kcal/mol larger than the exothermicity of (12). When comparing the two systems one needs to consider that while the dimethyl ether molecules should represent quite well the local molecular environment for the three hydrogen bonds in the $Cr6{\cdot}H_3O^+$ complex, the geometry of the methyl ether complex will be quite different since the ether molecules are free to assume the most favorable configuration. On this basis one expects that the hydrogen bonds in that complex should be stronger than those in $Cr6{\cdot}H_3O^+$. On the other hand, for the $Cr6{\cdot}H_3O^+$ species one may expect additional stabilization of the positive charge by the favorably oriented dipoles of the three remaining CH_2OCH_2 groups, i.e., the groups not directly engaged in hydrogen bonding (see II, Figure 3). Our previous results on the proton affinities of crown ethers[6] gave strong evidence for the existence of such dipolar stabilization. The observation that the formation of $Cr6{\cdot}H_3O^+$ is more exothermic by 8 kcal/mol than that of the methyl ether complex shows that the stabilization due to aligned dipoles is more important than the inability of the three hydrogen bonding CH_2OCH_2 groups to assume the most favorable orientation. While the dipolar alignment in $Cr6{\cdot}H_3O^+$ should be the principle source of additional stabilization, the greater polarizability of Cr6 as compared to that of three ether molecules should be another contributing factor.

$$H_3O^+ + (CH_3)_2O \rightarrow H_3O^+{\cdot}O(CH_3)_2 \qquad \Delta H_{10} = -44.8\ \text{kcal/mol} \quad (10)$$

$$H_3O^+ + 2(CH_3)_2O \rightarrow H_3O^+(O(CH_3)_2)_2 \qquad \Delta H_{11} = -63\ \text{kcal/mol} \quad (11)$$

$$H_3O^+ + 3(CH_3)_2O \rightarrow H_3O^+(O(CH_3)_2)_3 \qquad \Delta H_{12} = -80\ \text{kcal/mol} \quad (12)$$

$$H_3O^+ + 3H_2O \rightarrow H_3O^+(OH_2)_3 \qquad \Delta H_{13} = -69.4\ \text{kcal/mol} \quad (13)$$

The 88 kcal/mol exothermicity of the complexation of H_3O^+ with Cr6 is of a similar order of magnitude as total single ion hydration energies in liquid water. This is illustrated by reactions 14–16 which give data for the H_3O^+, Na^+, and K^+ ions.[15] Thus,

$$H_3O^+(g) + H_2O(l) = H_3O^+(aq) \qquad -\Delta H_{14} \approx 101\ \text{kcal/mol} \quad (14)$$

$$Na^+(g) + H_2O(l) = Na^+(aq) \qquad -\Delta H_{13} \approx 106\ \text{kcal/mol} \quad (15)$$

$$K^+(g) + H_2O(l) = K^+(aq) \qquad -\Delta H_{14} \approx 86\ \text{kcal/mol} \quad (16)$$

the Cr6 can in a single blow provide almost all the solvation enthalpy which is otherwise provided by the complete solvent environment.

The entropy loss for the formation of $Cr6{\cdot}H_3O^+$, $-\Delta S_7(Cr6) = 56$ eu, is very large; however, a result of that magnitude can be expected when one considers that in reaction 7 there is a loss of 35 eu of translational entropy and in addition a considerable rotational *and* vibrational entropy loss. The latter is considerable in the present case since the formation of $Cr6{\cdot}H_3O^+$ should cause the stiffening of a large number of soft puckering vibrations that are present in Cr6 (see ref 6).

The exothermicity (enthalpy) for the formation of $Cr5{\cdot}H_3O^+$ is a whole 12 kcal/mol lower than that for $Cr6{\cdot}H_3O^+$; i.e., $\Delta H_7(Cr5) = -76.9$ kcal/mol while $\Delta H_7(Cr6H_3O^+) = -88.5$ kcal/mol (Table I). The $Cr5{\cdot}H_3O^+$ complexation can be compared with reaction 11 where two strong hydrogen bonds to two dimethyl ether molecules are formed. We note that $\Delta H_7(Cr5)$ is significantly larger than $-\Delta H_{11}$. Furthermore, this difference is much larger than that found for the formation of $Cr6{\cdot}H_3O^+$ vs. $H_3O^+(CH_3OCH_3)_3$. This suggests that in $Cr5{\cdot}H_3O^+$ there are not just two strong hydrogen bonds and additional assistance from favorable CH_2OCH_2 dipole orientations, but also a third partial hydrogen bond; i.e., the hydrogen bonding involves three oxygens, but the last bond is weak because of strain. A slightly distorted $Cr5{\cdot}H_3O^+$ structure could also lead to three nearly equivalent, but somewhat weakened, hydrogen bonds. The entropy loss for the formation of $Cr5{\cdot}H_3O^+$, $-\Delta S_7(Cr5) = 43$ eu, is large in absolute terms but considerably smaller than $-\Delta S_7(Cr) = 56$ eu, in line with the bonding differences considered above.

$CH_3OH_2^+$ can form only two strong hydrogen bonds. This fact should be reflected in the binding enthalpies of the $CH_3OH_2^+{\cdot}Cr$ complexes and in particular the $Cr6{\cdot}CH_3OH_2^+$ vs. $Cr6{\cdot}H_3O^+$ complex. The corresponding enthalpies are as follows: $-\Delta H_8(Cr6) = 67.6$ kcal/mol and $-\Delta H_7(Cr6) = 88.5$ kcal/mol. As expected, the three hydrogen bond complex $Cr6{\cdot}H_3O^+$ has a much higher bonding enthalpy. However, not all of the difference should be attributed to the two vs. three hydrogen bond change. It has been shown[16–18] that when a hydrogen bond $AH^+ + B \rightarrow AHB^+$ is formed in the gas phase, the strength of the bond increases with the gas-phase acidity of AH^+ and basicity of B. The gas-phase acidity of AH^+ decreases with an increase of basicity of the conjugate base A. Methanol has a higher proton affinity than water ($PA(CH_3OH) = 181.8$ kcal/mol, $PA(H_2O) = 167.3$ kcal/mol; see Table I). This means the acidity of H_3O^+ is larger

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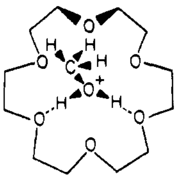
than that of $CH_3OH_2^+$, and, therefore, H_3O^+ should form stronger hydrogen bonds than $CH_3OH_2^+$. The enthalpies for reactions 13 and 14 are available from previous work.[11] Comparing (18) with

$$CH_3OH_2^+ + O(CH_3)_2 \rightarrow CH_3OH_2{\cdot}O(CH_3)_2^+ \qquad -\Delta H_{13} = 34 \text{ kcal/mol} \quad (17)$$

$$CH_3OH_2^+ + 2O(CH_3)_2 \rightarrow CH_3OH_2(O(CH_3)_2)_2^+ \qquad -\Delta H_{14} = 55 \text{ kcal/mol} \quad (18)$$

the analogous (11) we find that two hydrogen bonds formed by H_3O^+ provide an exothermicity of 63 kcal/mol while $CH_3OH_2^+$ gives only 55 kcal/mol. This supports the argument that only part of the difference of the enthalpies ΔH_7(Cr6) and ΔH_8(Cr6) is due to the presence of one less hydrogen bond in Cr6·$CH_3OH_2^+$.

The exothermicity for the formation of Cr6·$CH_3OH_2^+$ ($\Delta H_8 = -67.6$ kcal/mol) is much larger than that for the formation of the two ether complex with $CH_3OH_2^+$ ($\Delta H_{14} = -55$ kcal/mol). The total difference of 12.6 kcal/mol may be due to additional stabilization in the Cr6 complex by favorable CH_2OCH_2 dipole alignments and the higher polarizability of Cr6 relative to two dimethyl ether molecules. However considering that the difference is appreciably larger than that observed for Cr6·H_3O^+ and $H_3O^+(O(CH_3)_2)_3$ (8 kcal/mol), it is likely that a new factor is also involved. There could be some hydrogen bonding from the partially protic hydrogens of the methyl group of $CH_3OH_2^+$ to one of the oxygens of the Cr6 as shown schematically in structure IV. Space filling models show that it is sterically possible to form a third hydrogen bond in this manner. The occurrence of carbon–hydrogen–oxygen bonds of this type was suggested by Meot-Ner[18] in his recent study of ionic hydrogen bonds. The existence of such carbon–hydrogen bonds is supported also by theoretical calculations (Hirao,[12] and other work[19]).



IV

The stabilization by dipolar alignments and additional C–H hydrogen bonding as in III introduces a greater rigidity in the $CH_3OH_2^+$·Cr6 complex, and this stiffening is probably responsible for the large entropy loss, $\Delta S_8°$(Cr6) = −50 eu, observed for the formation of the complex.

The exothermicity of the formation of the $CH_3OH_2^+$·Cr5 complex ($-\Delta H_8$(Cr5) = 60.8 kcal/mol) is 7 kcal/mol lower than that for the Cr6 complex (see Table I). This difference should be attributed mostly to the greater flexibility of the Cr6 which can better adjust to give maximum stabilization in the ion complex.

Meot-Ner[18] has recently published a comprehensive study of the complexing of ammonium ions with polyethers including Cr4, Cr5, and Cr6. Of interest in connection with the present work are his results for cyclohexylammonium (c-$C_6H_{11}NH_3^+$) and the crown ethers. These results are quoted in Table I. It is interesting to note that even though three hydrogen bonds are formed in c-$C_6H_{11}NH_3^+$·Cr6, the exothermicity of the complex formation ($\Delta H = -46$ kcal/mol) is very much smaller than that for the H_3O^+·Cr6 formation ($\Delta H = -88$ kcal/mol). The proton affinity of the nitrogen base is ~221 kcal/mol while that of H_2O is only 167 kcal/mol;[9] this means that the acidity and thus the hydrogen bonding ability of H_3O^+ is much larger than that of cyclohexylammonium (see preceding discussion). This tendency is directly demonstrated if one compares the hydrogen bond formed in reaction 10 with that in (19) (the value for ΔH_{19} is from Meot-Ner[18]). Taking into account that (10) would be somewhat

$$H_3O^+ + CH_3OCH_3 \rightarrow H_3O^+(CH_3OCH_3) \qquad \Delta H_{10} = -44.8 \text{ kcal/mol} \quad (10)$$

$$\text{c-}C_6H_{11}NH_3^+ + C_2H_5OC_2H_5 \rightarrow \text{c-}C_6H_{11}NH_3^+(C_2H_5OC_2H_5) \qquad \Delta H_{15} = -22 \text{ kcal/mol} \quad (19)$$

more exothermic had diethyl ether been involved, one concludes that the hydrogen bond formed by H_3O^+ is more than twice as strong as that formed by the ammonium ion. Seen in this light, the nearly twice higher complexation energy for H_3O^+Cr6 as compared to c-$C_6H_{11}NH_3^+$·Cr6 is not surprising.

The complexing of substituted ammonium ions with crown ethers in water and methanol has been subject to considerable study,[20] while no similar determinations for the H_3O^+ analogues seem to be available. Presumably this is because the complexation of H_3O^+ from aqueous solution is much weaker than that of ammonium ions. This must be due to a solvent effect; i.e., the much higher hydration energy of H_3O^+ relative to that for ammonium ions more than counterbalances the high exothermicity for the Cr6·H_3O^+ formation.

The very high complexation energy of H_3O^+·Cr6 observed in the gas phase could be of importance in the condensed phase in media which are not strongly hydrogen bonding, i.e., weak hydrogen accepting solvents like lipids and halohydrocarbons.

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(19) See references in Meot-Ner.[18] The similar hydrogen bonds in which the proton donor is a carbon acid and the proton acceptor an anion have been described by: French, M. A.; Ikuta, S.; Kebarle, P. *Can. J. Chem.* **1982**, *60*, 1907. Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, 105, 2944.

(20) Roberts, J. L.; McClintock, R. E.; El-Omrain, Y.; Larson, J. W. *J. Chem. Eng. Data* **1979**, *24*, 79. Izatt, R. M.; Terry, R. E.; Haymore, B. L.; Hansen, L. D.; Dalley, N. K.; Avondet, A. G.; Cristensen, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 7620.