Protonation of Polyethers, Glymes and Crown Ethers, in the Gas Phase

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Abstract: The gas-phase basicities of several glymes and crown ethers were determined by measuring proton-transfer equilibria with a pulsed electron beam high ion source pressure mass spectrometer. Determinations of the equilibrium constants at different temperature led, via van't Hoff plots, to the $\Delta G°$, $\Delta H°$, and $\Delta S°$ changes. It was found that the proton affinity can be correlated with the possibility of bringing two oxygens within the optimal O---H$^+$---O bonding distance of 2.4 Å and aligning the corresponding two CH_2OCH_2 dipoles to be coaxial with the OHO axis. While the above stabilization by dicoordination is most important, significant additional stabilization is obtained when the dipoles of a third and fourth CH_2OCH_2 group can be brought near the proton and placed in favorable dipole orientation. The measured proton affinities, in kcal/mol, based on PA(NH_3) = 204 kcal/mol are Me_2O (191), glyme-1 (204), glyme-2 (218), glyme-3 (224), Glyme-4 (227), 12-crown-4 (221), 15-crown-5 (223), 18-crown-6 (230), 1,4-dimethoxybutane (221), and 1,5-dimethoxypentane (221). Proton affinities higher than 221, e.g., higher than those of the two diethers, are believed to be mostly due to the above-mentioned participation of a third and fourth CH_2OCH_2 dipole in the stabilization of the proton. Loss of freedom due to proton-induced cyclizations of the glymes and stiffening of the ring structures of the crowns is deduced from measured negative entropy changes for the protonation of these compounds. Glyme-1 is the polyether with the lowest proton complexing power. This compound is also the only one that leads to noticeable clustering. The equilibrium $G1H^+ + G1 = (G1)_2H^+$ (G = glyme) was measured and led to a $\Delta H°$ = −23 kcal/mol and $\Delta S°$ = −25 cal/(deg mol) (standard state, 1 atm).

Introduction

The ability of polyethers—glymes, crown ethers, and cryptands—to act as very effective complexing agents for cations is well established and represents a field of great chemical and biological significance.[1-5] Studies of the complexing energies of positive ions in the gas phase, like the alkali ions, with the above ethers are possible at least in principle[6] and would be of some relevance since such measurements can provide the complexing power in the absence of a solvent and a counterion and thus facilitate understanding of the effects of the solvent environment and ion pairing.

The present study, which deals with the protonation of polyethers, may be considered as a start in such a gas-phase complexation study. The proton, being very small, is dicoordinated in the condensed phase.[7] Dicoordination in solution is often achieved by interaction of the protonated base BH^+ with a solvent molecule, as, for example, BH^+--OH_2. Additional hydrogen-bonding interactions of that solvent molecule with neighboring solvent molecules make this a very effective stabilization. Dicoordination can also be achieved by suitable disubstituted ligands. However, in basic solvents, intramolecular dicoordination is often less effective than the solvent stabilization mentioned above, and a substantial increase of basicity may not result from the introduction of a second basic group. Dicoordination by the same ligand should be much more important in very weakly basic solvents like lipids, halohydrocarbons, and hydrocarbons. At the extreme end of this scale is the gas phase, i.e., the complete absence of solvent. In the gas phase, the presence of a suitably placed second basic group on the same molecule always leads to a large increase of basicity. Thus, in terminal straight chain diammines and diethers, protonation of the first group is followed by cyclization, i.e., formation of an internal hydrogen bond in which the proton is dicoordinated by the two basic groups. This can be clearly demonstrated by measurement of proton transfer equilibria (eq 1) in the gas phase. Measurements of the equilibrium constants

$$B_0H^+ + B = B_0 + BH^+ \qquad (1)$$

stants K_1 at different temperatures lead, via van't Hoff plots, to $\Delta G_1°$, $\Delta H_1°$, and $\Delta S_1°$. The presence of two basic groups in the ligand B leads not only to a large increase of basicity, i.e., large $-\Delta G_1°$ and $-\Delta H_1°$, but also to a large loss of entropy due to loss of freedom caused by the proton-induced cyclization.[9-11]

In the presence of more than two basic groups, there is the possibility for additional stabilization by tri- and tetracoordination. It is of considerable interest to establish by gas-phase measurements whether such coordination does occur. Such gas-phase results should have some relevance also for protonation in weakly basic solvents where stabilization by tri- and tetracoordination is also a possibility. Studies of the protonation of glymes and crown ethers in chloroform and dichloroethane have been performed by J. Jagur-Grodzinski and co-workers.[12] The results were interpreted by assuming that dicoordination of the proton is the only significant interaction. The authors also found that the six-oxygen-containing 18-crown-6 had much higher basicity than the five- or four-oxygen crown ethers. As will be shown herein, gas-phase studies provide an amplified and somewhat different picture of the stabilization in the protonated polyethers in the absence of a (basic) solvent.

Experimental Section

The measurements of the proton-transfer equilibria were performed with a pulsed electron beam high ion source pressure mass spectrometer that has been described previously.[13]

A gas mixture was passed slowly through the ion source at known pressures in the 3–5-torr range. The major gas, methane, carried known partial pressures of the two bases B_1 and B_2. Short electron pulses produce CH_5^+ and $C_2H_5^+$ as final ions in CH_4. These protonate the bases

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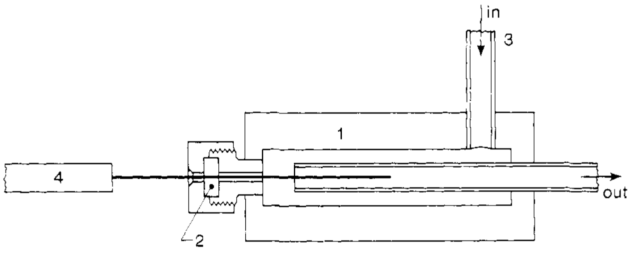


Figure 1. Device for adding controlled partial pressures of bases B_1 and B_2 to methane carrier gas flow: (1) metal block containing heaters and thermocouple (not shown), (2) elastomer septum, (3) methane flow in, (4) motor-driven syringe. Syringe delivers known volume/minute solution of $B_1 + B_2$ to flowing carrier gas. Temperature of block adjusted to obtain complete evaporation of B_1 and B_2.

B by the fast reactions: $CH_5^+ + B = CH_4 + BH^+$ and $C_2H_5^+ + B = C_2H_4 + BH^+$. The protonated bases BH^+ then reach proton transfer equilibrium (eq 1). The partial pressures of the bases B in the ion source were in the 0.01–0.1-torr range. At these concentrations, the observed ion intensity ratio B_1H^+/B_2H^+ became constant some 100 μs after the short (10 μs) electron pulse. The ratio remained constant for 2000 μs, i.e., the duration over which the ion concentrations were observed. B_1H^+ and B_2H^+ were the only two major ions in the mass spectrum after the initial kinetic stage of 100 μs was over. Only for glyme-1 (G1) was an appreciable concentration of a proton-held dimer, $(G1)_2H^+$, observed.

In general, the measurements were similar to other proton equilibria measurements performed in this laboratory. However, two points need mention. The molecular mass of most of the bases was relatively high, compared to earlier work. Since a magnetic mass analyzer was used, an adverse effect known to occur to a minor extent in previous work became more serious. Since the electron gun is placed at a considerable distance from the ion source,[13] the electron path to the ion source is rather long and even very weak stray magnetic fields from the magnet can deflect the electron beam before it enters the ion source. The stray field increases with increase of the magnetic field, which means that the electron beam deflection changes with the mass of the ions that are collected. Therefore, a mass-dependent change of the ion intensity can be present. To minimize this effect, the electron gun and the space containing the electron-beam path to the ion source is heavily shielded with high μ material (Netic-Conetic). However, at relatively high mass, this shielding is not sufficient to ensure complete absence of electron-beam deflection. Therefore, where possible B_1 and B_2 were chosen to have a minimal difference in mass. Furthermore, at each given mass, the electron beam was refocussed by means of the X and Y deflection plates (see Figure 1, ref 13) to maximize the ion intensity. The gain of intensity on refocussing depended on the mass difference between th B_1H^+ and B_2H^+ ions. In general, that gain was less than 30% for the B_1,B_2 pairs used.

In previous work,[13] the gas mixture of carrier gas methane and B_1 and B_2 was mixed in a thermostated 5-L bulb at atmospheric pressure, and constant flow through the ion source was maintained by means of a variable valve between bulb and ion source. In the present work, it was found more convenient to use a motor-driven microsyringe (syringe pump Model 341A SAGE instruments). A solution of B_1 and B_2 of known molar ratio was delivered from the syringe needle, which was stuck through a septum, into the heated, 1-atm methane carrier gas flow as shown in Figure 1. Very constant signals of B_1H^+ and B_2H^+ were obtained with this method. The desired ratio B_1/B_2 could be changed relatively rapidly by substituting new microsyringes filled with solution with a different B_1/B_2 ratio. Some of the bases B are solids at room temperature. Only pairs of B_1 and B_2 were selected that gave liquid solutions.

The relative partial pressures of a given base B in the ion source could be monitored with an auxiliary quadrupole mass spectrometer. This mass spectrometer was mounted in the vacuum housing near the ion source such that gases escaping from the ion source into the vacuum housing could be detected. Checks that the crown ethers do not pyrolyze at the ion source temperatures used for the equilibria measurements were made by following the intensity of the molecular ion at different ion source temperatures.

When monobasic ligands B are used, the proton-held dimers $(B)_2H^+$ are often stable under the conditions of the high-pressure mass spectrometer and are observed in equilibrium with the monomers BH^+. The proton-transfer equilibria (eq 1) between the monomers can be reliably measured only when the monomers represent more than about 20% of the total $(B)_2H^+$ and BH^+ ions. Since the ratio $(B)_2H^+/BH^+$ increases as the temperature is lowered, often the temperature-range available for the proton-transfer measurements is limited. Fortunately, the glymes and crowns did not tend to form proton-held dimers because the proton could be well complexes by a single molecule. By choosing base pairs that were both glymes or crowns, an extension of the measurements to lower temperatures was achieved.

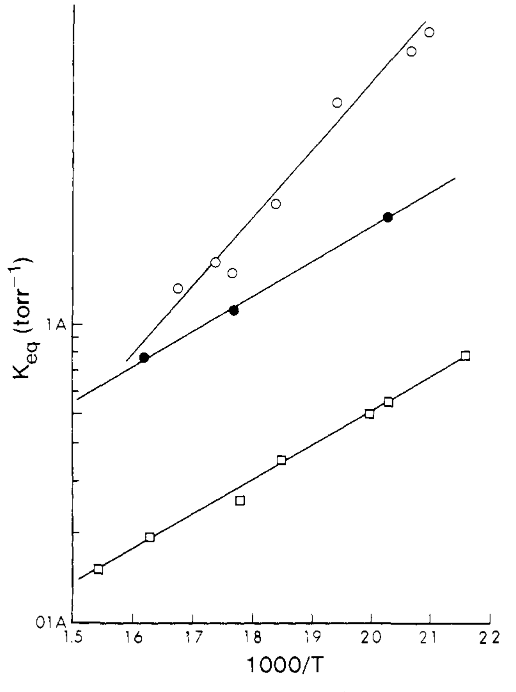


Figure 2. van't Hoff plots of equilibria $B_1H^+ + B_2 = B_1 + B_2H^+$: (○) B_1 = G3, B_2 = 2Cl, pyridine; (●) B_1 = 2Clpy, B_2 = G2; (□) B_1 = G2, B_2 = G3. Three different values must be assigned to log scale: A = 1 for ○, A = 0.1 for ●, and A = 100 for □.

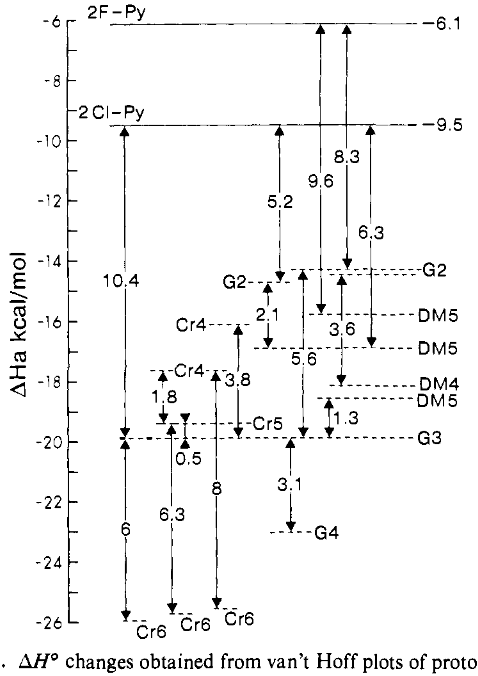


Figure 3. $\Delta H°$ changes obtained from van't Hoff plots of proton-transfer equilibria (see Figure 2). Values given between arrows are measured ΔH changes in kcal/mol. These are put on an absolute scale using ΔH_a for 2F and pyridine = −6.1 and 2Cl and pyridine = −9.5 kcal/mol. ΔH_a corresponds to enthalpy change for reaction $NH_4^+ + B = NH_3 + BH^+$. Averaged ΔH_a obtained from present figure are given in Table I.

In general the measured equilibrium constants for proton transfer at a given constant temperature changed by less than 20% for a change of the concentration ratio of the bases by a factor of 3–5.

Results and Discussion

(a) Thermochemical Data. Results from the proton-transfer equilibria (eq 1) measured in the present work are shown in

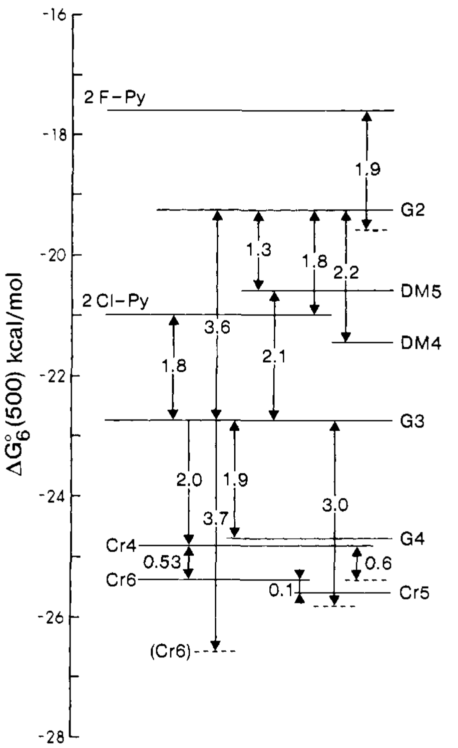


Figure 4. Free energy changes obtained from van't Hoff plots of proton-transfer equilibria (see Figure 2). Values given between arrows give ΔG° for proton transfer between the two bases at 500 K. The ordinate scale relates to ΔG_0°; $Me_2OH^+ + B = Me_2O + BH^+$. 2F–pyridine and 2Cl–pyridine were used as standards (see Table I).

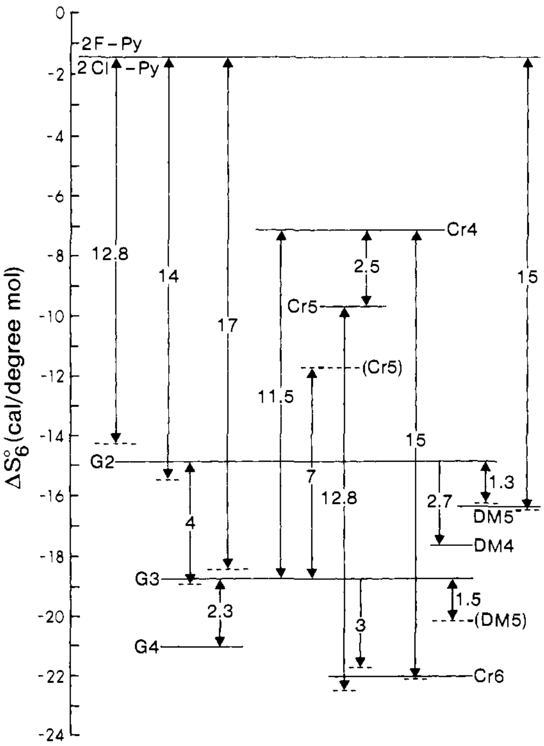


Figure 5. Entropy changes obtained from van't Hoff plots of proton transfer equilibria (see Figure 2). Values between arrows give measured ΔS change in cal/(deg mol). The absolute scale shown relates to ΔS_0°: $Me_2OH^+ + B = Me_2O + BH^+$ (see Table I).

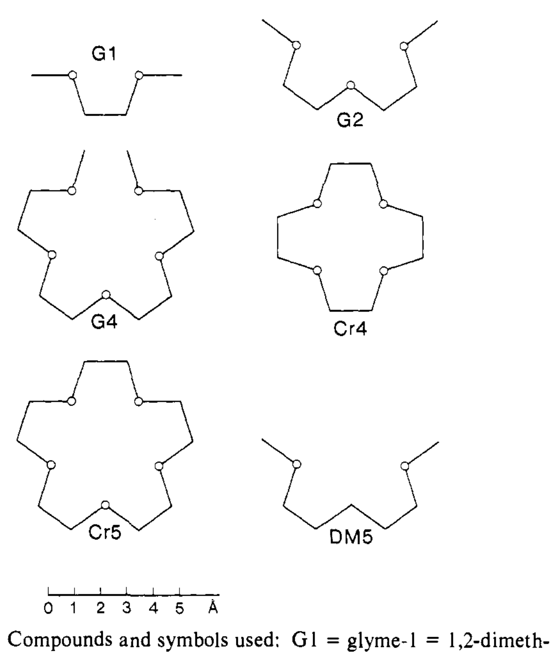


Figure 6. Compounds and symbols used: G1 = glyme-1 = 1,2-dimethoxyethane, Cr4 = 12-crown-4, DM5 = 1,5-dimethoxypentane. Bond distances and bond angles drawn approximately to scale. C–C 1.54 Å, C–O 1.43 Å.

Figures 2–5. The structures and the symbols used for the glymes and crowns are given in Figure 6. The equilibrium constants K_1 for a given pair of bases were determined over as wide a temperature range as could be conveniently measured and van't Hoff plots of these determinations were made. The ΔH values given in Figure 3 were obtained from the slopes of such van't Hoff plots. Examples of the van't Hoff plots are shown in Figure 2. The

$$G2H^+ + 2\text{-ClPy} = G2 + 2\text{-ClPyH}^+ \quad \Delta H = +5.2 \text{ kcal/mol} \tag{2}$$

$$2\text{-ClPyH}^+ + G3 = 2\text{-ClPy} + G3H^+ \quad \Delta H = -10.4 \text{ kcal/mol} \tag{3}$$

$$G2H^+ + G3 = G2 + G3H^+ \quad \Delta H = -5.6\ (-5.2) \text{ kcal/mol} \tag{4}$$

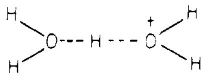
three plots of Figure 2 involving the equilibria (2)–(4) are quite typical of the data obtained. Since eq 2 + 3 = 4, $\Delta H_2 + \Delta H_3$ should equal ΔH_4. The directly determined ΔH_4 equals −5.6, while that from the cycle is −5.2 kcal/mol. The ΔH_1°, ΔG_1°, and ΔS_1° results, obtained from all van't Hoff plots, are shown in Figures 3–5. In these Figures there are many examples of multiple thermodynamic cycles. Generally somewhat more consistent results are observed for ΔG°_{500}, Figure 4. The ΔG°_{500} correspond mostly to direct determinations, since 500 K was a temperature used in practically all equilibria measurements. The ΔH° and ΔS° values, derived from the slopes and intercepts of the van't Hoff plots, lead to somewhat less consistent multiple cycles. From the consistency of the cycles, we estimate an error of ±1 kcal/mol for the $\Delta G(300)$ ± 1.5 kcal/mol for the ΔH determinations and ±3 cal/degree for ΔS°. The ΔG°, ΔH°, and ΔS° values deduced from averaging the results in Figures 3–5 are given in Table I. Three sets of values are quoted. The first set are values relative to ammonia, while the second set gives absolute proton affinities, and the third set gives values relative to dimethyl ether.

(b) Discussion of the Basicities of Glymes and Crown Ethers. As mentioned in the introduction, the proton is generally dicoordinated in solution.[7,8] The role of additional weaker coordination by the involvement of a third or fourth basic group is not well established and generally not invoked.[12] Gas-phase measurements of the clustering equilibria (eq 5) provide some in-

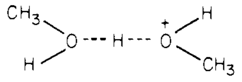
$$(B)_{n-1}H^+ + B = (B)_nH^+ \ (n-1, n) \tag{5}$$

$$B = H_2O,\ CH_3OH,\ CH_3OCH_3,\ CH_3COCH_3$$

formation on the stabilization that can be obtained beyond dicoordination. It was found that the binding energies of the proton-held dimers (dicoordinated protons) I–IV are remarkably



I



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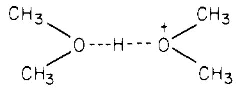
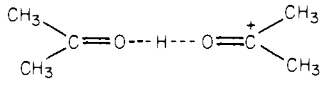


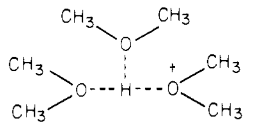
III



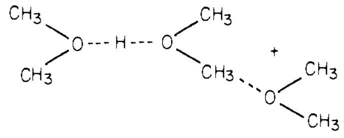
IV

similar ($-\Delta H_{1,2}$ between 30 and 32 kcal/mol).[14,15] The bonding for the higher clusters of H_2O and CH_3OH decreases gradually ($-\Delta H_{2,3}$ = 20 kcal/mol) while a much more abrupt fall off is observed for dimethyl ether and acetone, $-\Delta H_{2,3}(Me_2O)$ = 10 kcal/mol. The difference in behavior between I and II vs. III and IV is clearly due to the fact that I and II can grow by forming new periferal hydrogen bonds with incoming molecules while III and IV cannot because there are no protic hydrogens; i.e., the hydrogens have been replaced by methyl groups.

While the bonding decreases abruptly past the structures III and IV, still the 10 kcal/mol binding energy observed for the formation of the trimers is not a negligible quantity. Two possible structures can be considered for the trimer. In V the proton can be said to be tricoordinated, while in VI a weak hydrogen bond is formed via one of the methyl hydrogens. Hirao et al.,[16] in an interesting theoretical study (SCF computations with 4.31G basis set) of the protonated clusters in methanol and dimethyl ether, have found that the stabilities of V and VI are comparable. As could be expected, the first two Me_2O molecules in V engaged in the true hydrogen bond were found much closer to the proton (O- - -H distance 1.2 Å) while the third molecule was much farther away (O- - -H distance 3.5 Å). Thus we can envisage V as a dicoordinated proton in which a third molecule contributes to the stabilization of the ion through its permanent dipole and more weakly through its polarizability, the situation for the third molecule being similar to what may be expected in the interaction of a dimethyl ether molecule with a large ion like Cs^+. Stabilization by a third molecule as in V can occur also in the chained $-CH_2OCH_2-$ polymers, i.e., the glymes and the crowns. Use of this type of stabilization will be made in the interpretation of the observed basicities of these compounds.



V



VI

The $\Delta H_6°$, $\Delta G_6°$, and $\Delta S_6°$ values, corresponding to proton transfer from Me_2OH^+ to the various polyethers (Table I) provide a measure the the relative stabilization of the proton by multicoordination on the basis of the following reasoning. Glyme-1 (G1) represents two Me_2O molecules joined in an open chain, G2 represents three such molecules, and G*n* represents *n* such molecules. Similarly Crown 4 represents four Me_2O molecules joined in a cyclic structure, Cr5 five such molecules, and so on.

$$Me_2OH^+ + B = Me_2O + BH^+ \qquad (6)$$

The energy lowering with successive introduction of CH_2OCH_2 groups is examined in Figure 7. Data for Me_2O, glymes G1–G4, crowns Cr4–Cr6, and the terminal dimethoxy alkanes, dimethoxy butane DM4 and pentane DM5, are given. For the Me_2O series the clustering enthalpies $\Delta H_{1,2}°$ and $\Delta H_{2,3}°$, see eq 5, were plotted, while for the other compounds, the ΔH_6 (resp ΔG_6) for proton transfer from Me_2OH^+ (Table I) was used.

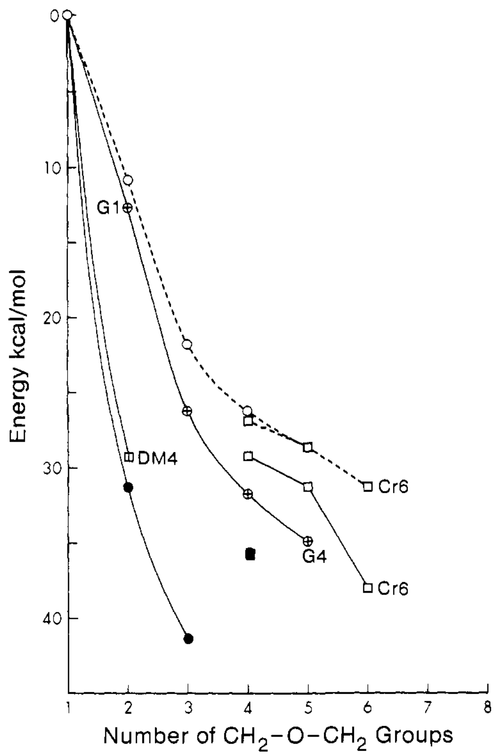


Figure 7. Energy of stabilization of proton by multiple-CH_2OCH_2- groups. Zero energy corresponds to protonated dimethyl eether Me_2OH^+. Proton in all other compounds is additionally stabilized by energy given in ordinate. (●) Stabilization by additional Me_2O molecules. ΔH values from previous work[14] on $(Me_2O)_nH^+$ clusters: (□) DM4 and DM5, (⊕) G1–G4, (□) Cr4–Cr6, (■) $(G1)_2H^+$; (—) ΔH changes, (- - - -) ΔG changes. Greatest stabilization (ΔH) observed for Me_2O clustering, since Me_2O molecules free to assume most favorable positions, lesser stabilization for open chain glymes, and least stabilization for closed chain crowns: Cr4 and Cr5. Cr6 has sufficient flexibility to be as good as the equivalent glyme (G5). The dimethoxybutane and -pentane, DM4 and DM5, which can only dicoordinate, give efficient stabilization due to flexibility of relatively long hydrocarbon chain. Presence of more than two CH_2OCH_2 groups is stabilizing if dipoles can orient favorably (G4, Cr6) and destabilizing if dipoles are forced in unfavorable orientation (G2).

The Me_2O clustering enthalpy values represent stabilization by $-CH_2OCH_2-$ groups that are free, apart from steric repulsions, to assume positions leading to maximum stabilization of the proton. The energy lowering for the Me_2O series should therefore be greater than that for the glymes and crowns, where the CH_2OCH_2 groups are connected in a chain and thus less free. This expectation is confirmed by the experimental results in Figure 7, which show largest stabilization for the Me_2O series, lesser stabilization for the open-chain glyme series, and least stabilization for the most constrained closed-chain crown series. The energy lowering for the dicoordinated $G1H^+$ is only about half of that for $(Me_2O)_2H^+$. The structure of G1 is shown in Figure 6. The distance between the two O atoms can be reduced to about 2.4 Å without introducing strain in the molecule. This is the optimal binding distance in the O--H--O hydrogen bond calculated by Kraemer and Diercksen[17] for the H_2O-H--OH_2^+ and Hirao[16] for structure I of $(CH_3)_2O$--H--$O(CH_3)_2^+$, as well as the distance for dicoordinated protons observed in the solid state.[7] Thus, the stabilization in $G1H^+$ is lower not because the optimum distance cannot be reached but because the two CH_2OCH_2 dipoles cannot achieve the optimum orientation, i.e., to be in line with the O--H--O bond. This results in a weaker, bent hydrogen bond in $G1H^+$. An additional but probably less important weakening of the stabilization is due to the inability of $G1H^+$ to achieve the staggered

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Table I. Proton Affinities and Relative Gas-Phase Basicities of Polyethers, Glymes and Crowns

compd B[d]	ΔH_a[a]	PA[b]	ΔH_6[c]	ΔG_a[a]	ΔG_6-(500)[c]	ΔG_6-(300)[c]	$\Delta S_6°$[c]
Me_2O[e]	+12.2	191.4	0.0	+11.0	0.0	0.0	0.0
1,4-dioxane[e]	+11.4	192.6	−1.2	+10.6	−0.5	−0.8	−1.4
THF[e]	+5.9	198.1	−6.3	+4.7	−6.3	−6.3	0.0
		(198.9)					
Et_2O[e]	+4.9	199.1	−7.3	+3.7	−7.3	−7.3	0.0
		(200.0)					
anisole[e]	+4.3	199.7	−8.3	+3.5	−7.9	−7.6	−1.4
G1[g]	−0.5	204.4	−12.7	+0.3	−9.5	−10.8	−6.4
		(204.7)					(−4.3)
2-fluoropyridine[e]	−6.1	210.1	−18.3	−6.9	−17.6	−17.9	−1.4
2-chloropyridine[e]	−9.5	213.5	−21.7	−10.3	−21.0	−21.3	−1.4
G2	−14.0	218.0	−26.2	−10.9	−19.1	−21.9	−14.3
		(218.9)					(−15.2)
G3	−19.5	223.5	−31.7	−15.2	−22.6	−26.2	−18.3
		(226.0)					(−20.0)
G4	−22.6	226.6	−34.8	−17.6	−24.5	−28.6	−20.7
Cr4	−17.0	221.0	−29.2	−15.7	−25.1	−26.7	−8.3
		(219.6)					(−3.2)
Cr5	−19.0	223.0	−31.2	−16.9	−25.7	−27.9	−11.1
		(220.9)					
Cr6	−25.8	229.8	−38.0	−20.1	−26.5	−31.4	−22.0
		(220.6)					
DM4	−17.2	221.2	−29.4	−13.4	−21.2	−24.4	−16.8
DM5	−17.2	221.2	−29.4	−13.2	−20.8	−24.2	−17.3
1,3-diaminobenzene[f]				−19.7			
Me_3N[f]				−21.0			
N,N,N′,N′-tetramethyl-1,8-diaminonaphthalene[f]				−39.2			

[a] Enthalpy change and free energy change (300 K) for proton transfer from ammonium ion: $NH_4^+ + B = NH_3 + BH^+$ in kcal/mol, $\Delta G°_a(NH_3) = 0$, $\Delta H°_a(NH_3) = 0$. [b] Proton affinity based on $PA(NH_3) = 204$ kcal/mol, Rosenstock et al.[20] This number is probably uncertain to ±1 kcal/mol. Errors in the present relative determinations of ΔH estimated at ±2 kcal/mol (see Figure 3). Numbers in brackets below respective compound from Meot-Ner.[24] [c] $\Delta H_6°$ and $\Delta G_6°$ at 300 and 500 K in kcal/mol, $\Delta S_6°$ in cal/(deg mol). For reaction $Me_2OH^+ + B = Me_2O + BH^+$. Based on present experimental results, Figures 3–5, and literature values for standard bases: dimethyl ether, anisole, 2-F-pyridine, and 2-Cl-pyridine, Kebarle[21] and Wolf[22]. Numbers in brackets below respective compound in ΔS_6 column are based on measurements of Meot-Ner.[24] [d] Symbols for compounds given in Figure 6. [e] Standards from ref 21 and 22. [f] Basicity of some nitrogen bases used for comparisons, from Lau.[19] [g] Results for G1 obtained from measurements of temperature dependence of equilibrium: anisole-H^+ + G1 = anisole + $G1H^+$; $\Delta H = -4.8$ kcal/mol, $\Delta S° = -5$ cal/(deg mol).

configuration of the two CH_2OCH_2 groups relative to the O--H--O axis which is present[17] in the H_2O--H--OH_2 and also in the $(CH_3)_2O$--H--$O(CH_3)_2^+$ species.[16]

It is interesting to note that the observed stabilization reflected in the enthalpy changes of the diethers $DM4H^+$ and $DM5H^+$ is almost as good as that observed for $(CH_3)_2OHO(CH_3)_2^+$ (Figure 7). Evidently, the flexibility of the long $(CH_2)_4$ and $(CH_2)_5$ chain permits the achievement of near optimum O--H--O distance *and* dipole alignment. The staggered configuration cannot be achieved, but this is partially compensated by the stabilizing effect due to the polarizability of the alkyl chains.

1,4-Dioxane, whose proton affinity is much lower than that of G1 and even lower than that of Et_2O (Table I), illustrates what happens when the second CH_2OCH_2 group is part of the very contrained six-membered ring. In unprotonated dioxane, the chair configuration is known to be more stable than the boat form by at least 20 kcal/mol.[18] Protonation of one of the oxygens probably leads to a flip over to the boat form since the dipolar repulsion between the two oxygens present in the neutral has disappeared and since in the boat form the dipole of the second CH_2OCH_2 group is less destabilizing to the positive charge than is the case for the chair form. Nevertheless, even in the boat form that dipole is in a quite unfavorable orientation, and it must be largely this effect that leads to the low proton affinity of dioxane.

The big increase of stabilization (enthalpy) observed when one moves from $G1H^+$ to $G2H^+$ (Figure 7) must be largely attributed to the lengthening of the chain between the two terminal oxygens. The increased flexibility of the chain helps in the dicoordination just as was the case for DM4 and DM5. It should be noted that the stabilization in $G2H^+$ is somewhat less than that in $DM4H^+$ and $DM5H^+$, see Figure 7 and Table I. Thus, the middle oxygen in G2 does not help but hinders the stabilization. Molecular models show that in order for the two terminal oxygens in $G2H^+$ to achieve the optimum O-H-O bonding distance of 2.4 Å, the chain connecting them must be puckered in a manner that causes the central C–O–C to assume a somewhat destabilizing orientation. Thus, the situation with regard to the central CH_2OCH_2 group in $G2H^+$ is somewhat similar to that in 1,4-dioxane.

The proton affinities are seen to increase in the order G2, G3, G4, Figure 7. The nature of the stabilization can be deduced from an examination of molecular models. For example in $G4H^+$ the two terminal CH_2OCH_2 groups can be easily brought within hydrogen-bonding distance and optimal dipole alignment, such that good dicoordination of the proton is obtained. Furthermore, the remaining three CH_3OCH_2 groups, while farther removed from the protonic area, are still relatively free to assume favorable dipole orientations in a variety of rotational conformers.

The stabilizations of the protonated crowns (Figure 7) are also very interesting. The proton affinities of Cr4 and Cr5 are somewhat lower than those of the corresponding G3 and G4. In $Cr4H^+$, two opposing oxygens in the ring can achieve good dicoordination with respect to distance and dipole orientation. The two other oxygens are forced to be at a larger distance from the proton and are constrained in a dipole orientation that is essentially perpendicular to the ring, i.e., neutral with regard to stabilization of the centrally located charge (see structures in Figure 8). Cr5 permits somewhat more flexibility and thus somewhat better secondary dipole orientations; however, a significant change occurs only with the introduction of the sixth group, i.e., for Cr6. The molecular model of Cr6 shows that when two opposing oxygens are brought together to give good dicoordination, two more dipoles can be brought relatively close to the charge in a favorable orientation. The puckering of the ring required to achieve this favorable configuration forces the remaining two dipoles into a partially unfavorable orientation; however, these dipoles are much farther away from the charge center. The ability of Cr6 to achieve

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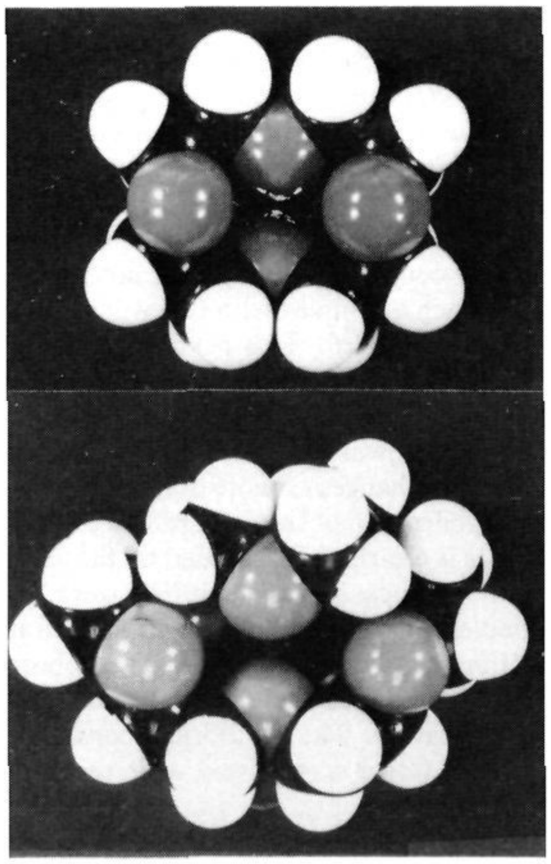

Figure 8. Possible conformations for protonated crowns: $Cr4H^+$ (top) and $Cr6H^+$ (bottom). Proton not shown but two opposing oxygens (north and south oxygen in both pictures) are brought within O--H--O bonding distance (2.4 Å). In the rigid $Cr4H^+$ the remaining two CH_2OCH_2 dipoles are forced in an orientation that is perpendicular to the plane of the O--H--O bond such that no stabilization is provided. In the much more flexible $Cr6H^+$, two of the remaining four CH_2OCH_2 dipoles can come fairly close to the O--H--O charge center and assume partially favorable orientations.

such favorable conformation explains the observed high proton affinity for this compound. Cr6 falls on the extension of the curve for the glymes, i.e., in the expected position for the six-oxygen-containing G5 (see Figure 7). This means that the closed chain of the Cr6 happens to be able to assume as favorable a configuration as the much more free, open-chain G5.

The entropy changes given in Table I are consistent with the ΔH changes and attending conformations discussed above. The formation of $G1H^+$ leads to a ΔS change of −6.5 cal/deg. The magnitude of this value is in the expected range for a hydrogen-bonding cyclization involving a five-membered ring. Thus Meot-Ner et al.[10] observed −5.8 cal/deg and Yamdagni and Kebarle[9] observed −12.7 cal/deg for proton transfer from dimethylamine to 1,2-diaminoethane, a similar reaction in which a hydrogen-bonded five-membered ring is formed. Unfortunately the discrepancy between the two literature values[9,10] is unusually large; nevertheless these results support a magnitude of −6 cal/deg for the cyclization in $G1H^+$. The diethers DM4 and DM5 have cyclization entropies of −17 cal/deg (Table I). The values observed for the similar 1,4-diaminopentane are −20[9] and −14 cal/deg.[10] Thus the present result is in the expected range. The ΔS values for $G2H^+$, $G3H^+$, and $G4H^+$ are −14, −18, and −21 cal/deg. The value for $G2H^+$ appears somewhat low considering that a seven-membered hydrogen-bonded ring is formed, the formation of $DM5H^+$ led to a $\Delta S° = -17$ cal/deg. However, the hydrogen bond in $G2H^+$ is weaker than that formed in $DM5H^+$, and a weaker bond should lead to a somewhat lower $-\Delta S°$. The increases of $-\Delta S°$ from $G2H^+$ to $G4H^+$ are consistent with the loss of freedom due to stabilization of the two coordinated proton by favorable orientation of additional CH_2OCH_2 dipoles, indicated by the ΔH changes discussed above.

The observed ΔS changes for the crown ethers are −8 (Cr4), −11 (Cr5), and −22 (Cr6) cal/deg (Table I). The entropy loss for Cr4 and Cr5 is considerably smaller than that for the oxygen equivalent G3 and G4, a difference to be expected since the crowns are already cyclic before protonation. The entropy losses in the crowns are consistent with the discussed loss of freedom, i.e., stiffening of the soft, ring-puckering vibrations due to coordination of the proton. The $\Delta S_6 = -22$ cal/deg for Cr6 seems much too large at first glance. However, the molecular model of $Cr6H^+$ (Figure 8) shows that a very stiff structure is required to explain the observed large stabilization of the proton indicated by the ΔH changes. Since Cr6 is an 18-membered ring, it has a large number of soft, ring-puckering vibrations. One can estimate[23] that there should be some 15 soft vibrations in the 150-cm^{-1} range. At $T = 300$ K, the entropy of one such vibration is ~2.8 cal/(deg mol). If half of these vibrations disappeared on protonation there would be an entropy loss of some 20 cal/(deg mol). On this basis, the experimentally obtained $\Delta S_6°$ of −22 cal/(deg mol) appears quite reasonable. The ΔS_6 results for Cr6 and G4 are −22 and −21 cal/deg (Table I). Considering that G4 has five CH_2OCH_2 groups and is initially an open chain that cyclizes on protonation to a relatively stiff structure in which there is additional dipolar assistance to the dicoordinated proton, one would have expected that $-\Delta S_6(G4)$ should be somewhat larger than $-\Delta S_6(Cr6)$. This could indeed be the case. A reversed order is within the estimated error of the $\Delta S°$ measurements (± 3 cal/deg).

The $\Delta G_6°$ changes at 300 K for the glymes and crowns are also shown in Figure 3. An increase of stabilization of the proton is observed as one moves from G1 to G4. The ΔH stabilization of G3 was higher than that for the Cr4; however, also the loss of entropy was larger for the glyme. These two effects mutually balance each other such that the free energy change comes out to be almost the same for these two compounds. The same is true for G4 and Cr5. Cr6, the most basic polyether measured, has a $\Delta G_6°$ stabilization relative to Me_2O of as much as 31 kcal/mol. It is found to fit quite well on the curve of the glymes. The diethers DM4 and DM5 have $\Delta G_6° = -24$ kcal/mol. This is considerably less than the values for G3, Cr4, G4, Cr5, and Cr6, which provides a clear demonstration that additional stabilization, beyong dicoordination, is provided by the dipoles of the large polyethers. While the basicity of Cr6 is very high for an oxygen base it is not higher than that of many nitrogen bases. Thus, Me_3N has a ~3 kcal/mol higher basicity and the proton sponge *N*,*N*-dimethyl-1,8-diaminonaphthalene[19] has a gas-phase basicity that is some 19 kcal/mol higher than that of Cr6. These and a few other nitrogen bases are included for comparison purposes in Table I.

A study of the gas-phase protonation of polyethers by Meot-Ner[24] was published after the present work was submitted for publication. Several compounds dealt with in the present study were also studied by Meot-Ner. The results of Meot-Ner for compounds that were duplicated in the two studies are shown in Table I. The proton affinities of G1, G2, and Cr4 agree within less than 1 kcal/mol. G3 and Cr5 agree within about 2 kcal/mol. Somewhat similar small discrepancies are found for the corresponding ΔS_6 values. The only large disagreement is found for the proton affinity of Cr6 where the present value 229.8 kcal/mol is appreciably higher than the 220.6 kcal/mol of Meot-Ner. The latter is based on measurement of proton-transfer equilibria at a single temperature (600 K) and an assumed ΔS_6 of −5 cal/deg. This ΔS might have been considered a reasonable choice in the absence of experimental data. As was shown above, the present direct measurements based on van't Hoff plots lead to a very different result, i.e., $\Delta S_6° = -22$ cal/deg. It is interesting to note that Meot-Ners' proton-transfer measurement at 600 K leads to a $\Delta G_6°(600) = -26$ kcal/mol, while the present results (Table I) give −25 kcal/mol. Thus, the direct experimental data on Cr6 are in agreement, and it is only Meot-Ners assumed $\Delta S_6°$ that

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(23) Of the 120 normal vibrations for Cr6, there should be stiff vibrations, 24 C–H stretches, 48 CH_2 deformations, 12 CO stretches, 6 C–C stretches, and soft vibrations, 15 C–O–C deformations in the 300–500-cm^{-1} range and 15 out-of-plane C or O displacements 0–300 cm^{-1}. We are indebted for this information to Prof. J. E. Bertie, Chemistry Department, University of Alberta.

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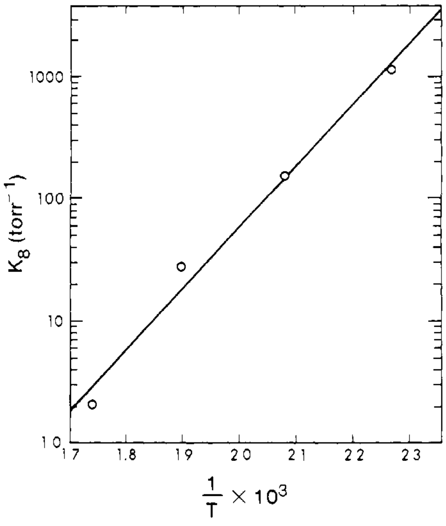

Figure 9. van't Hoff plot for the equilibrium: $G1H^+ + G1 = (G1)_2H^+$. $\Delta H = -22.8 \pm 2$ kcal/mol, $\Delta S = -24.5 \pm 5$ cal/(deg mol) (standard state 1 atm). The imperfectly dicoordinated $G1H^+$ was the only protonated glyme or crown ether for which significant dimer formation was observed.

is responsible for the very different ΔH_6 and proton affinities.

The rationalization of hydrogen bonding to polyethers provided by Meot-Ner[23] is fairly similar to that in the present work. However, Meot-Ner did not invoke stabilizing effects by the dipoles of favorably oriented third and fourth CH_2OCH_2 groups. We feel that the present work provides strong evidence for the existence of these latter effects and that therefore the present work provides a significant extension and amplification of Meot-Ner's analysis.

Jagur-Grodzinski et al.[12] have studied the basicities of glymes and crown ethers in chloroform and dichloroethane by spectroscopic and conductometric techniques. The glymes Cr4, benzo-13-crown-4, dibenzo-14-crown-4, and other Cr4 compounds were too weak to produce any significant increase of conductivity, but with Cr5 and Cr6 basicities could be measured. Relative basicities corresponding to the equilibrium constant K_7 for process 7 were

$$\mathrm{Cr} + \mathrm{AH} = \mathrm{A}^- + \mathrm{CrH}^+ \qquad (7)$$

evaluated.[12] For AH = paratoluenesulfonic acid the ratio of $K_7(\mathrm{Cr6})/K_7(\mathrm{Cr5})$ in dichloroethane was found equal to ~8000. Expressed as a free energy difference this ratio leads to $\delta\Delta G_7 = RT \ln 8000 = 5.4$ kcal/mol at 300 K. The observed basicity difference in the gas phase, $\delta\Delta G_6° = \Delta G_6°(\mathrm{Cr5}) - \Delta G_6°(\mathrm{Cr6}) = 3.5$ kcal/mol (Table I), is smaller. One might have expected the opposite, i.e., that in solution, effects of solvation or ion pairing might make the $\delta\Delta G_7°$ smaller than the gas-phase $\delta\Delta G_6°$. An experimental error in the gas phase result cannot be excluded, considering that the estimated error in the $\Delta G°(300)$ values is ±1 kcal/mol. However, it is also possible that the solution difference is in error. In the presence of traces of water, H_3O^+ can form a very stable complex with Cr6 but not with Cr5 (Izatt[3]). The formation of such a complex with Cr6 will lead to an apparent much higher basicity of Cr6. This possibility was considered by Nae and Grodzinski[12] but rejected as unlikely. In any case, since in the gas phase it is possible to measure the basicities of the weaker glymes and crowns, one obtains a more comprehensive picture of the basicity changes as more oxygens are made available. The additional stabilization of the dicoordinated proton by nearby CH_2OCH_2 dipoles is clearly demonstrated by the gas-phase results while this was not the case in the solution work.[12]

As mentioned earlier, abundant formation of dimers $(B)_2H^+$, among the protonated glymes and crowns, was observed only for G1, i.e., the system in which the proton is most imperfectly dicoordinated by cyclization. The equilibrium constants for reaction 8 could be measured over a relatively wide temperature range,

$$G1H^+ + G1 = (G1)_2H^+ \qquad (8)$$

and this allowed the construction of the van't Hoff plot shown in Figure 9. The resulting enthalpy change, $\Delta H_8 = -22.8$ kcal/mol, is substantial. It is actually larger than twice the ΔH for the clustering reaction in Me_2O considered earlier:

$$(Me_2O)_2H^+ + Me_2O = (Me_2O)_3H^+ \qquad \Delta H = -10 \text{ kcal/mol}$$

The stabilization of $(G1)_2H^+$ is shown in Figure 7. The observed stabilization is somewhat larger than that for the four-oxygen $G3H^+$. This is an expected result since the $(G1)_2H^+$ system has more freedom for coordination. One can envisage a structure in $(G1)_2H^+$ where the proton is quite effectively dicoordinated by one CH_2OCH_2 group from each G1 and where the two remaining dipoles provide additional stabilization. It should be noted that the stabilization in $(G1)_2H^+$ is still smaller than that for the trioxygen system $(Me_2O)_3H^+$; see Figure 7.

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Registry No. G1, 110-71-4; G2, 111-96-6; G3, 112-49-2; G4, 143-24-8; Cr4, 294-93-9; Cr5, 33100-27-5; Cr6, 17455-13-9; DM4, 13179-96-9; DM5, 111-89-7.