Influence of Multiple Hydrogen Bonding on Reactivity: Ion/Molecule Reactions of Proton-Bound 12-Crown-4 Ether and Its Mixed Clusters with Ammonia and Methanol

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Abstract: Reactions of protonated 12-crown-4 ether (Cr4·H$^+$) and its ammonium (Cr4·AH$^+$) and methoxonium (Cr4·MH$^+$) ion complexes with a series of base molecules were studied using a selected ion flow tube. Reaction efficiencies are enhanced for base molecules capable of forming multiple hydrogen bonded structures. The association kinetics of Cr4·H$^+$ were compared with those of the protonated dimer of 1,2-dimethoxyethane ((G1)$_2$H$^+$). Insertion of ammonia into Cr4·H$^+$ is 8.8 times more efficient than its insertion into (G1)$_2$H$^+$. The preferred reaction channel of Cr4·MH$^+$ reactions is switching, while Cr4·AH$^+$ undergoes association as well as switching reactions. The reactivity and reaction patterns of Cr4·H$^+$ and Cr4·MH$^+$ are comparable to those of alkyl-blocked protonated dimers and trimers studied previously, while Cr4·AH$^+$ has a different reactivity due to its hydrogen-bonding capabilities.

We have studied recently[1−5] gas phase ion/molecule reactions of proton-bound dimers and trimers. Reactions observed depended on the proton affinity (PA) and gas phase basicity (GB) of the neutral reagent, ranging from association, through ligand switching and switching with solvent evaporation, to proton transfer. The reaction efficiencies and types of reaction products observed for alkyl-blocked clusters such as $(CH_3CN)_2H^+$ [2] and $(CH_3CN)_2(C_2H_5OH)H^+$ [4] were found to be different than for unblocked ones capable of further hydrogen bonding, e.g. $(HCOOH)_2H^+$ [3] and $(C_2H_5OH)_3H^+$.[4]

An intramolecular hydrogen bond can form when multiple functional groups are present in an ion. Internal hydrogen bonds as strong as 30 kcal/mol were observed for polyethers such as crown ethers and glymes.[6] The intramolecular hydrogen bond stabilizes the ion and thereby increases the PA of the molecule.[7] The cyclic structures also lead to large negative entropies of protonation of up to ~19 cal/(mol·K).[6] The hydrogen bonding of polyfunctional molecules with polyprotonic ions forms multiply hydrogen bonded structures.[6,8] This leads to stabilization of the ion/molecule complexes[6] as was observed for ammonia ion−crown ether[8a] and methoxonium ion $(CH_3OH_2)^+$−crown ether complexes.[8b]

The complexing properties of crown ethers have biological as well as chemical significance.[8,9] Hydrogen-bonded cluster ions can serve as models for bioenergetics[10] such as interactions with active enzyme centers[11] and water wires which transport protons in biomembranes.[12] The importance of determining thermochemical properties for complexing of cations by polyethers, in the absence of solvent and counterions, has been pointed out.[8] This has been done through pulsed high-pressure mass spectrometry by Meot-Ner[8a] and Kebarle[8b] and co-workers. The thermochemistry of internal hydrogen bonds[7] and of multiple hydrogen bonding[8] was estimated by comparisons between polyfunctional and analogous monofunctional ions.

The kinetics of reactions of multiply hydrogen bonded systems is of great interest. We have carried out a study along these lines using our selected ion flow tube (SIFT), in which the influence of multiple hydrogen bonding on reactivity has been investigated. We report here on the kinetics and reactivity of protonated 12-crown-4 ether (Cr4), $(c\text{-}C_8H_{16}O_4)H^+$, and its ammonium and methoxonium ion complexes, $(c\text{-}C_8H_{16}O_4)(NH_3)H^+$(Cr4·AH$^+$) and $(c\text{-}C_8H_{16}O_4)(CH_3OH)H^+$(Cr4·MH$^+$). The results can be compared with reactions of ordinary proton-bound dimers and trimers which we have studied previously.[1−5] Furthermore, some of the clusters which we and others have studied recently were proposed to have cage, crown ether-like, structures, for example, $(RCOOH)_nH^+$ and $(RCOOH)_n(H_2O)H^+$ (R = H, CH_3)[13,14] and $(ROH)_n(H_2O)H^+$,[15,16] and a comparison with the crown ethers is of interest.

Experimental Section

The SIFT (selected ion flow tube) apparatus employed has been described in detail elsewhere.[17] Briefly, reactant ions are generated in a suitable ion source, are mass selected by a quadrupole mass filter, and are injected into a flow tube by a helium carrier gas via a Venturi inlet. A neutral reactant is introduced into the flow tube at an appropriate distance downstream to ensure laminar flow. A detector quadrupole filter analyzes the reactant and product ions.

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Table 1. Association Reactions of $(Cr4)H^+$ and $(G1)_2H^+$ [a]

reaction	k_{exp} (cm^3/(molecule•s))	k_f[b] (cm^3/(molecule•s))	product ion distribution (%)
$(Cr4)H^+ + CH_3OH$ PA = 181.9 [c]	5.3×10^{-11}	1.76×10^{-9}	$(Cr4)(CH_3OH)H^+$ (100)
$(G1)_2H^+ + CH_3OH$	4.1×10^{-11}	1.76×10^{-9}	$(G1)_2(CH_3OH)H^+$ (94) $(G1)(CH_3OH)H^+$(6)
$(Cr4)H^+ + C_2H_5OH$ PA = 188.3	2.0×10^{-10}	1.63×10^{-9}	$(Cr4)(C_2H_5OH)H^+$ (100)
$(Cr4)H^+ + CH_3CN$ PA = 188.4	no reaction		
$(Cr4)H^+ + NH_3$ PA = 204.0	2.4×10^{-10}	2.01×10^{-9}	$(Cr4)(NH_3)H^+$ (100)
$(G1)_2H^+ + NH_3$	3.1×10^{-11}	2.01×10^{-9}	$(G1)_2(NH_3)H^+$ (84) $(G1)(NH_3)H^+$ (16)
$(Cr4)H^+ + G1$ PA = 204.9	2.9×10^{-11}		$(Cr4)(G1)H^+$ (100)

[a] Cr4, 12-crown-4 ether; G1, dimethoxyethane (glyme 1). [b] Bimolecular gas kinetic collision rate constant for formation of the energized complex (see text). [c] PA in kcal/mol.

Protonated Cr4, $(c\text{-}C_8H_{16}O_4)H^+$, was injected from the ion source into the flow tube. Ninety percent of the ions remained intact, while 10% underwent collision-induced decomposition. The major reactions were consecutive losses of C_2H_4O units as observed before in a triple-quadrupole mass spectrometer[18] with additional minor products as follows: 90% $(c\text{-}C_8H_{16}O_4)H^+$ (m/z = 177), 0.1% $C_6H_{13}O_4^+$ (m/z = 149), 5.3% $C_6H_{13}O_3^+$ (m/z = 133), 0.7% $C_4H_{11}O_3^+$ (m/z = 107), 3.5% $C_4H_9O_2^+$ (m/z = 89), and 0.4% $C_2H_4OH^+$ (m/z = 45).

Mixed dimer reactant ions $(c\text{-}C_8H_{16}O_4)(NH_3)H^+$ ($Cr4\cdot AH^+$) and $(c\text{-}C_8H_{16}O_4)(CH_3OH)H^+$ ($Cr4\cdot MH^+$) were prepared by collision-stabilized association reactions of $(c\text{-}C_8H_{16}O_4)H^+$ with NH_3 and CH_3OH, respectively. This was achieved by introducing neutral ammonia or methanol into the flow tube through an inlet port which follows very closely in space the Venturi inlet.[1] Ninety two percent of the injected $(c\text{-}C_8H_{16}O_4)H^+$ can be converted to $(c\text{-}C_8H_{16}O_4)(CH_3OH)H^+$ at a methanol flow rate of 5 cm^3/min, leaving 2% unreacted and the rest appearing as minor impurity ions: 1% $C_6H_{13}O_3^+(CH_3OH)_2$, 1% $C_4H_9O_2^+(CH_3OH)_2$, 2% $C_6H_{13}O_3^+$, and 2% $(CH_3OH)_3H^+$. The impurity ions do not interfere with the rate measurements of the methoxonium ion—crown ether complex with various base molecules to be described below. The protonated methanol trimer $(CH_3OH)_3H^+$ may react with the base molecules of high PA to produce the protonated base, but this can be corrected for on the basis of its known reactivity patterns.[1] Ninety four percent conversion of the protonated ether to the ammonium complex could be achieved at an ammonia flow rate of 1.6 cm^3/min, leaving no unreacted protonated ether but forming in addition other ions at minor concentrations: 1% $C_6H_{13}O_3^+\cdot NH_3$, 4% $C_6H_{13}O_3^+$, 0.5% $C_4H_9O_2^+(NH_3)_2$, and 0.5% $C_4H_9O_2^+\cdot NH_3$. These impurity ions do not interfere with the rate measurements of the ammonium ion—crown ether complex to be reported. We observed no detectable product ions which could be due to the impurity ions.

The protonated dimer of 1,2-dimethoxyethane (glyme, G1) was prepared by association of $G1\cdot H^+$ injected from the ion source into the flow tube with neutral G1 at a 1.5 cm^3/min flow rate, introduced at the first port close to the Venturi inlet. Protonated ammonia was injected from the ion source to produce with G1 the corresponding ammonium complex, $(G1)_2AH^+$, as a reactant ion.

Second-order rate coefficients of the protonated crown ether and its ammonium and methoxomium ion complexes were obtained by monitoring the intensity of the primary ion decay as a function of the neutral reactant gas B concentration introduced downstream from the ammonia or methanol inlet. Rate coefficients were similarly measured for the protonated dimer glyme and its ammonium complex. Product ion distributions were obtained by plotting the percentage of each product ion as a function of the gas B flow rate and extrapolating the resulting curves to zero flow rate. The product ion distributions for very slow reactions were estimated approximately at the minimum base flow rate of 0.1 cm^3/min, without extrapolation. All product ion distributions were corrected via the measured mass discrimination factor of the detector quadrupole mass filter. The error limits for the rate coefficients are ±5—20% depending on the magnitude of the rate coefficient. The product ion percentage yields are accurate to ±3%.

Typical reaction conditions were as follows: helium flow rate, 7 L/min; helium pressure in the flow tube, 0.31 Torr; reaction temperature, 300 K.

The 12-crown-4 ether was a sample from Aldrich Co. (98% pure) which was employed without further purification.

Results and Discussion

Experimental rate constants and product ion distributions are summarized in Tables 1, 2, and 3 for reactions of $Cr4\cdot H^+$, $Cr4\cdot AH^+$, and $Cr4\cdot MH^+$, respectively. The experimental rate constants, k_{exp}, are compared with gas kinetic collision rate constants. The latter were calculated using the parametrized expression of Su and Chesnavich.[19] Table 1 includes reactions of the protonated dimer of 1,2-dimethoxyethane (glyme, G1).

The reaction efficiencies, $r = k_{exp}/k_c$, and the product branching ratios will be demonstrated to depend on the PAs of the neutral base reactants, i.e. on the reaction thermochemistry. This behavior has been observed before for proton-bound dimer and trimer reactions with neutral bases.[1-5] In general, association reactions are favored for bases of low proton affinity, switching reactions for bases of intermediate PA and proton

Table 2. Rate Constants and Branching Ratios for Reactions of $Cr4\cdot NH_3H^+ + B$ at 300 K

neutral B	PA (kcal/mol)	k_{exp} (cm^3/(molecule•s))	k_c (10^{-9} cm^3/(molecule•s))	branching ratio (%)
CH_3CHO	186.6	1.23×10^{-11}	2.25	$\xrightarrow{AS}$ $Cr4\cdot(CH_3CHO)(NH_3)H^+$(100)
C_2H_5OH	188.3	3.16×10^{-11}	1.61	$\xrightarrow{AS}$ $Cr4\cdot(NH_3)(C_2H_5OH)H^+$ (2) $\xrightarrow{SW}$ $Cr4\cdot(C_2H_5OH)H^+$ (98)
CH_3CN	188.4	4.55×10^{-11}	3.12	$\xrightarrow{AS}$ $Cr4\cdot(NH_3)(CH_3CN)H^+$ (97) $\xrightarrow{SW}$ $Cr4\cdot(CH_3CN)H^+$ (3)
CH_3OCH_3	192.1	1.19×10^{-11}	1.36	$\xrightarrow{AS}$ $Cr4\cdot(CH_3OCH_3)(NH_3)H^+$ (100)
CH_3COCH_3	198.4	3.04×10^{-11}	2.21	$\xrightarrow{AS}$ $Cr4\cdot(CH_3COCH_3)(NH_3)H^+$ (100)
$CH_3COOC_2H_5$	200.7	7.47×10^{-11}	1.46	$\xrightarrow{AS}$ $Cr4\cdot(CH_3COOC_2H_5)(NH_3)H^+$ (100)
$CH_3OCH_2CH_2OCH_3$	204.9	3.26×10^{-10}		$\xrightarrow{AS}$ $Cr4\cdot(CH_3OCH_2CH_2OCH_3)(NH_3)H^+$ (100)
CH_3NH_2	214.1	1.43×10^{-9}	1.56	$\xrightarrow{SW}$ $Cr4\cdot(CH_3NH_2)H^+$ (100)
$(CH_3)_2NH$	220.6	1.28×10^{-9}	1.29	$\xrightarrow{SW}$ $Cr4\cdot(Me_2NH)H^+$ (100)
$(CH_3)_3N$	225.1	1.07×10^{-9}	1.11	$\xrightarrow{SW}$ $Cr4\cdot(Me_3N)H^+$ (100)
$(C_2H_5)_3N$	232.3	1.27×10^{-9}	1.14	$\xrightarrow{SW}$ $Cr4\cdot(Et_3N)H^+$ (98.7) $\xrightarrow{PT}$ $(Et_3N)H^+$ (1.3)

Table 3. Rate Constants and Branching Ratios for Reactions of Cr4·MH$^+$ + B at 300 K

neutral B	PA (kcal/mol)	k_{exp} (cm^3/(molecule·s))	k_c (10^9 cm^3/(molecule·s))	branching ratios (%)	$\Delta H°$ (kcal/mol)	$\Delta G°$ (kcal/mol)
CH_3CHO	186.6	no reaction				
C_2H_5OH	188.3	3.29×10^{-10}	1.60	$\xrightarrow{SW}$ Cr4·(C_2H_5OH)H$^+$ (100)		
CH_3CN	188.4	3.84×10^{-11}	3.10	$\xrightarrow{AS}$ Cr4·(CH_3OH)(CH_3CN)H$^+$ (80)		
				$\xrightarrow{SW}$ Cr4·(CH_3CN)H$^+$ (20)		
CH_3OCH_3	192.1	3.16×10^{-11}	1.36	$\xrightarrow{SW}$ Cr4·(CH_3OCH_3)H$^+$ (100)		
CH_3COCH_3	198.4	2.00×10^{-11}	2.19	$\xrightarrow{SW}$ Cr4·(CH_3COCH_3)H$^+$ (100)		
$CH_3COOC_2H_5$	200.7	4.29×10^{-11}	1.44	$\xrightarrow{SW}$ Cr4·($CH_3COOC_2H_5$)H$^+$ (100)		
NH_3	204.0	3.27×10^{-10}	1.99	$\xrightarrow{SW}$ Cr4·(NH_3)H$^+$ (100)		
$CH_3OCH_2CH_2OCH_3$	204.9	4.07×10^{-11}		$\xrightarrow{SW}$ Cr4·($CH_3OCH_2CH_2OCH_3$)H$^+$ (100)		
CH_3NH_2	214.1	4.81×10^{-10}	1.55	$\xrightarrow{SW}$ Cr4·(CH_3NH_2)H$^+$ (100)		
$(CH_3)_2NH$	220.6	4.51×10^{-10}	1.28	$\xrightarrow{SW}$ Cr4·(Me_2NH)H$^+$ (100)		
$(CH_3)_3N$	225.1	2.29×10^{-10}	1.10	$\xrightarrow{SW}$ Cr4·(Me_3N)H$^+$ (97)	−19.8[a]	−20.1[a]
				$\xrightarrow{PT}$ (Me_3N)H$^+$ (3)	+16.0	+3.3
$(C_2H_5)_3N$	232.3	8.51×10^{-10}	1.12	$\xrightarrow{SW}$ Cr4·(Et_3N)H$^+$ (90)		
				$\xrightarrow{PT}$ (Et_3N)H$^+$ (10)	+8.8	−3.9

[a] Reference 8.

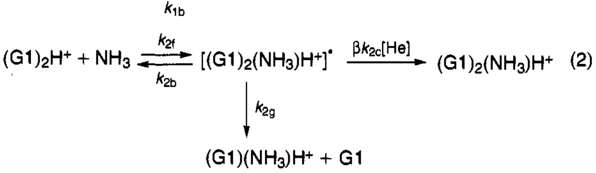
transfer for bases of high PA. However, proton-bearing bases such as CH_3OH and R_2NH (R = H, CH_3) undergo unique insertion reactions with alkyl-blocked dimers[2] such as $(CH_3CN)_2H^+$ by forming $CH_3OH_2^+$, NH_4^+, $CH_3NH_3^+$, or $(CH_3)_2NH_2^+$ as the core ion. These core ions are of special interest as guests in crown ether host compounds.[8,9] We plan to demonstrate the analogous behavior of the protonated crown ether and the alkyl-blocked dimers. The same types of base molecules, ROH and R_2NH, undergo switching reactions with alkyl-blocked trimers, e.g. in reactions with ammonia, methylamine, and i-C_3H_7OH of $(CH_3CN)_2(C_2H_5OH)H^+$ the protonated ethanol core ion is exchanged by the protonated core ions of the three bases, respectively.[4] We plan to demonstrate that the methoxonium and ammonium complexes of the crown ether behave in fashions similar to those of the alkyl-blocked trimers but that the ammonium complex has additional attributes due to its hydrogen-bonding capabilities.

The next sections will describe and discuss the results for Cr4·H$^+$, Cr·AH$^+$, and Cr4·MH$^+$. In the first section we will expand the discussion on the efficiency of forming the ammonium and ethoxonium Cr4 guest−host complexes by comparing the reactivity of Cr4·H$^+$ with ethanol and ammonia with its reactivity with other base molecules and by comparing the reactivity of Cr4·H$^+$ and $(G1)_2H^+$ with similar base molecules.

Reactions of Protonated Cr4. We were interested in learning about the reactivity pattern of Cr4·H$^+$ with several base molecules having different properties, as well as comparing the reactivities of Cr4·H$^+$ and $(G1)_2H^+$ with the same base.

Reactions of the protonated Cr4 with two pairs of base molecules, C_2H_5OH/CH_3CN and $NH_3/CH_3OCH_2CH_2OCH_3$, respectively, were studied in order to determine the effect of multiple hydrogen bonding capability on reactivity. Ethanol and acetonitrile have nearly the same PAs yet their reactivities are quite different (Table 1); a similar conclusion holds for the ammonia−G1 pair. Ethanol and ammonia, which can form polyprotonic ions $C_2H_5OH_2^+$ and NH_4^+, respectively, react at an ~0.1 collision rate to produce the corresponding ethoxonium or ammonium ion complex. Dimethoxyethane (G1) reacts much more slowly than ammonia, while acetonitrile is totally unreactive.

Meot-Ner has compared the thermochemistry of association reactions of ammonium ions with monoethers, polyethers, and crown ethers.[8a] In Table 1 we compare the reactivity of NH_3 with the proton-bound dimer of G1 and with the protonated crown ether. The reaction efficiency with the crown ether Cr4·H$^+$ is almost 1 order of magnitude higher than with $(G1)_2H^+$. The kinetics of the association reactions can be analyzed by the following schemes:[20−22]



$$\begin{tikzcd}(Cr4)\bullet H^+ + NH_3 \arrow[r, shift left, "k_{1f}"] & \left[(Cr4)(NH_3)H^+\right]^{\bullet} \arrow[l, shift left, "k_{1b}"] \arrow[r, "\beta k_{1c}[He]"] & (Cr4)(NH_3)H^+ \end{tikzcd} \quad (1)$$

$$\begin{tikzcd}(G1)_2H^+ + NH_3 \arrow[r, shift left, "k_{2f}"] & \left[(G1)_2(NH_3)H^+\right]^{\bullet} \arrow[l, shift left, "k_{2b}"] \arrow[r, "\beta k_{2c}[He]"] \arrow[d, "k_{2g}"] & (G1)_2(NH_3)H^+ \\ & (G1)(NH_3)H^+ + G1 & \end{tikzcd} \quad (2)$$

Making the steady state assumption concerning the concentration of the energized complexes gives the following expressions for the apparent second-order rate constants:

$$k_{1,\mathrm{app}} = \frac{k_{1f}\cdot\beta k_{1c}[\mathrm{He}]}{k_{1b} + \beta k_{1c}[\mathrm{He}]} \tag{3}$$

$$k_{2,\mathrm{app}} = \frac{k_{2f}\cdot\beta k_{2c}[\mathrm{He}]}{k_{2b} + k_{2g} + \beta k_{2c}[\mathrm{He}]} \tag{4}$$

The apparent rate constants may be equated with the experimental ones from Table 1. The values for k_{1f}, k_{2f}, k_{1c}, and k_{2c} are calculated.[19] The efficiency for stabilization of the complex by collisions with He is assumed to be $\beta = 0.1$. The value for k_{2g} is derived from the experimental branching ratio between the collision-stabilized product ion (84%) and the product ion due to G1 evaporation (16%); see Table 1. This analysis gives the first-order rate constants for the back-reactions as follows: $k_{1b} = 3.87 \times 10^6$ s^{-1} and $k_{2b} = 3.42 \times 10^7$ s^{-1}. Clearly, the back-reaction of the glyme dimer complex with ammonia is 8.8 times faster than that of the crown ether complex with ammonia. This result is independent of the value assumed for

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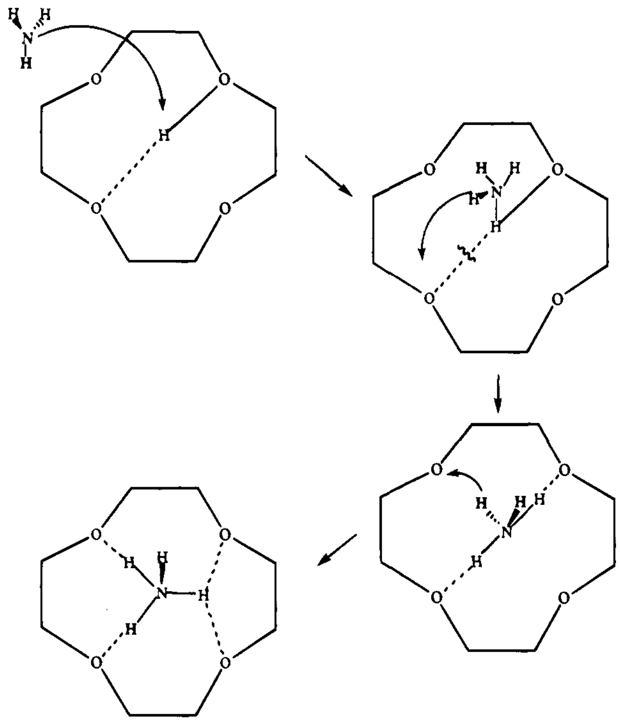
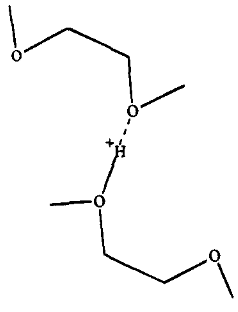
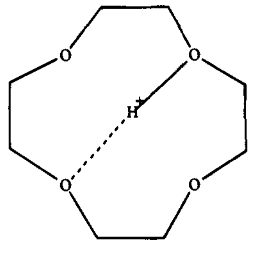
Scheme 1

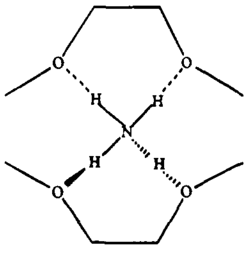




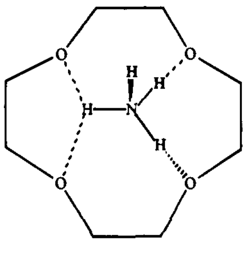
1. $(CH_3OCH_2CH_2OCH_3)_2H^+$



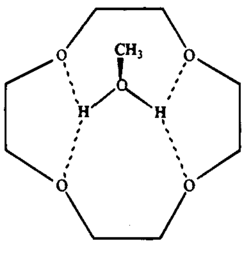
2. $(c\text{-}C_8H_{16}O_4)H^+$



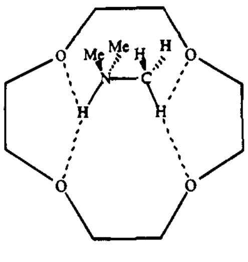
3. $(CH_3OCH_2CH_2OCH_3)_2(NH_3)H^+$



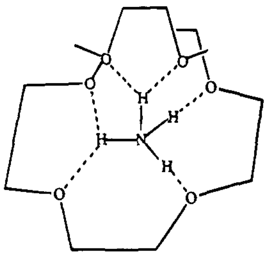
4. $(c\text{-}C_8H_{16}O_4)(NH_3)H^+$



5. $(c\text{-}C_8H_{16}O_4)(CH_3OH)H^+$



6. $(c\text{-}C_8H_{16}O_4)(N(CH_3)_3)H^+$



7. $(c\text{-}C_8H_{16}O_4)(NH_3)(CH_3OCH_2CH_2OCH_3)H^+$

Table 4. Thermochemical Data (298 K)

reaction	$\Delta H°$ (kcal/mol)	$\Delta S°$ (cal/(mol·K))	ref
$(Cr4)\cdot H^+ \rightarrow Cr4 + H^+$	221.6	34.3	24, 10
$(G1)_2H^+ \rightarrow 2G1 + H^+$	232.3	60.7	24, 10
$Cr4\cdot MH^+ \rightarrow Cr4\cdot H^+ + M^a$	19.5	34.0	8b
$Cr4\cdot MH^+ \rightarrow Cr4 + MH^+$	58.3	40.6	8b

[a] M = CH_3OH.

β. It reflects a higher critical energy of activation for the crown ether back-reaction and/or a lower activation entropy. There are suggested structures for the proton-bound glyme dimer,[10,23] **1**, and for the protonated crown ether,[7] **2**. $(G1)_2H^+$ has two freely rotating molecules according to Meot-Ner et al's suggested structure;[10] some of this free rotation is lost in the ammonia complex, **3**. There is no similar loss of free rotation upon association of **2** with ammonia to give the complex, whose suggested structure is **4**. In other words, the crown ether back-reaction does indeed have a lower activation entropy. Whether it also has a higher activation energy remains an open question, since the endothermicities of the two reactions are not known. The dissociation energy of $Cr4\cdot AH^+$ into ammonia and $Cr4\cdot H^+$ has not been determined, but is probably higher than the methanol binding energy in the methoxonium complex **5** (19.5 kcal/mol).[8b] The proton binding energy of the glyme dimer is ~11 kcal/mol higher than for the 12-crown-4 ether[10] (Table 4). It may quite safely be assumed that the endothermicity of the $Cr4\cdot AH^+$ back-reaction is higher than that of $(G1)_2AH^+$. Both of these attributes—a lower activation entropy and a higher activation energy—lead to a slower back-reaction and a higher experimental association rate constant for the ammonium complex (Table 1).

The association reactions undergone by $Cr4\cdot H^+$ with ammonia and methanol are viewed by us as insertion reactions by analogy with reactions of the alkyl-blocked dimers[2] $(CH_3CN)_2H^+$ and $(CH_3COCH_3)_2H^+$. The crown ether–amine host–guest complex structures are well established.[8,9] In the insertion reaction the internal $O—H^+\cdots O$ hydrogen bond of $Cr4\cdot H^+$ (see **2**) is broken and new hydrogen bonds are formed as in the ammonium complex **4** or in the methoxonium complex **5**. Scheme 1 presents a suggested mechanism for the insertion of ammonia. Acetonitrile or G1 cannot form such multiple hydrogen bonded systems. When they react with proton-bound dimers, such as $(CH_3COCH_3)_2H^+$ or $(CH_3OCH_3)_2H^+$, ligand switching is a possible reacton channel and does indeed occur. This is impossible when reacting with $Cr4\cdot H^+$. Furthermore, proton transfer is highly endothermic. As a result, CH_3CN is totally unreactive and G1 is much less reactive than ammonia.

Reactions of the Crown Ether Ammonium Complex $Cr4\cdot AH^+$. Table 2 summarizes the rate constants and branching ratios for reactions of $Cr4\cdot AH^+$ with a series of base molecules having PAs ranging from 186.6 kcal/mol (CH_3CHO) to 232.3 kcal/mol ($(C_2H_5)_3N$). The rate constants span a range of 2 orders of magnitude. Typical semilogarithmic plots of the reactant ion decays, from which the rate constants were derived, are represented in Figure 1. The dependence of the rate constants

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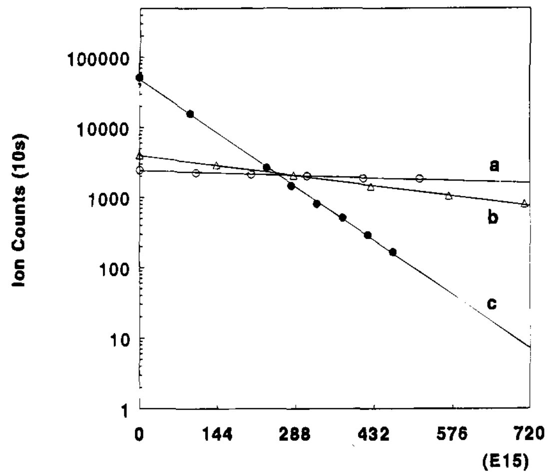


Figure 1. Semilogarithmic plot of the decay of the reactant ion as a function of the neutral flow rate for reactions of (Cr4)•AH^+ with (a) $CH_3COOC_2H_5$, (b) $CH_3OCH_2CH_2OCH_3$, and (c) CH_3NH_2.

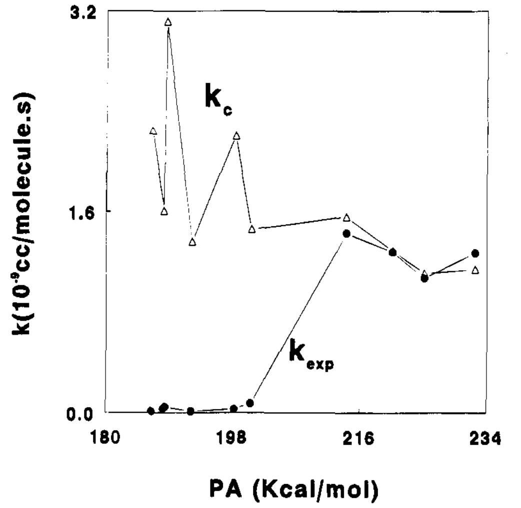
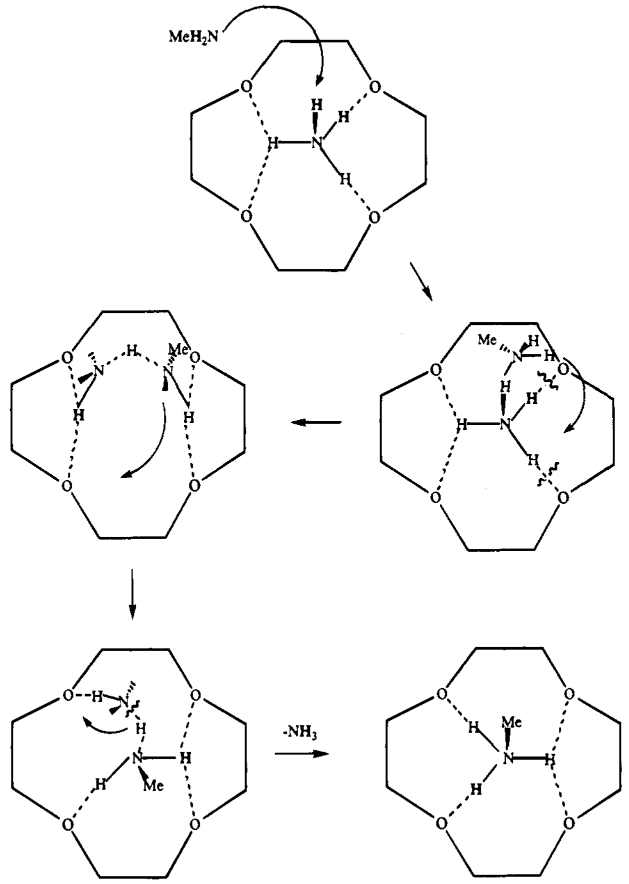


Figure 2. Reaction rate constants for reactions of (Cr4)•AH^+ with a series of base molecules, B, as a function of their proton affinity, PA: k_{exp}, experimental; k_c, calculated.

on PA is represented in Figure 2. There is a clear rise in the experimental rate constants toward gas kinetic collision rate constants for the amines, which have higher PAs than ammonia. These reactions are exothermic, and as a result, their reaction efficiencies are near unity. The reactions of the amines are clean ligand-switching reactions except for triethylamine, which has the highest PA of the amines studied, for which there is 1.3% proton transfer. These ligand-switching reactions are analogous to the ones occurring in alkyl-blocked trimers[4] such as $(CH_3CN)_2(C_2H_5OH)H^+$. One may speculate on the mechanism, and there are at least two possible alternatives: (1) The alkylamine attacks from the back side of the crown ether plane forming a complex adduct, proton transfer takes place in this adduct, and the ammonia molecule is released. (2) The alkylamine attacks the peripheral proton of the ammonium complex; this leads to cleavage of the N···H bond in ammonia; the protonated alkylamine which is formed within the collison complex attaches itself to the crown ether and ammonia is released (Scheme 2).

Trialkylamines do not react by switching out the core ion[4] of $(CH_3CN)_2(C_2H_5OH)H^+$, presumably because they are incapable of forming multiple hydrogen bonded systems. However, $(CH_3)_3N$ and $(C_2H_5)_3N$ do react with Cr4•AH^+ by efficient ligand switching. Fast reactions with $(CH_3)_3N$ and $(C_2H_5)_3N$ mean that their product ions Cr4•Me_3NH^+ and Cr4•Et_3NH^+ have

Scheme 2



stable structures even though they appear to provide only one hydrogen-bonding site. The occurrence of carbon−hydrogen−oxygen bonds, as in **6**, has been suggested before.[8]

Ligand switching occurs, irrespective of the PA, for proton-bearing hydrogen-bonding molecules such as ethanol. Ethanol reacts at a much slower rate than gas collision rate because of its low PA compared to the PA of ammonia. However, its ability to form a polyprotonic ion reflects itself in the product branching ratio which gives 98% ligand switching. Endothermic reactions do take place in the SIFT, albeit at considerably lower rates than collision rates, as is indeed the case for the ethanol reaction. The exact endothermicity of the reaction is unknown. As noted earlier, the methanol binding energy in the methoxonium complex **5** is 19.5 kcal/mol (Table 4); that for ethanol in the ethoxonium complex is most probably higher. The multiple hydrogen bonding capabilities of ammonia are also present in ethanol, particularly in view of the probable occurrence of carbon−hydrogen−oxygen bonds as has been suggested for the alkylamines, by analogy to structure **6**. It would be desirable to study these endothermic switching reactions on a more quantitative basis in the future.

All other molecules undergo association by virtue of hydrogen bonding via a free proton of the ammonia (see **4**). As noted earlier, acetonitrile is unreactive with Cr4•H^+—the internal hydrogen bond of the crown ether prevents association. However, Cr4•AH^+ undergoes association with acetonitrile. The suggested structure of Cr4•G1•AH^+ is **7**. The association reaction forming it from Cr4•AH^+ and G1 is 1 order of magnitude faster than the one forming Cr4•G1•H^+ (Tables 1 and 2). The high rate coefficients observed for some of the reactions of Cr4•AH^+ are due to the hydrogen-bonding capability of the peripheral proton of the ammonium complex. In this respect the crown ether ammonium complex behaves like other clusters with peripheral protons capable of hydrogen bonding

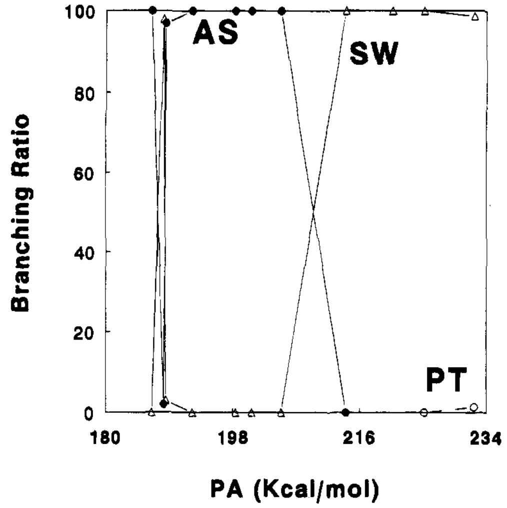
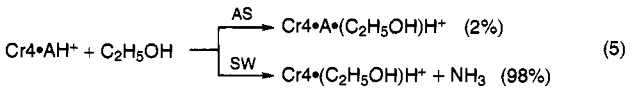


Figure 3. Branching ratios (%) as a function of PA(B) for reactions of $(Cr4){\cdot}AH^+ + B$: AS, association (●); SW, switching (△); PT, proton transfer (○). The exceptional point at low PA (PA = 188.3 kcal/mol) is due to ethanol.

such as $(CH_3OH)_3H^+$,[1] $(HCOOH)_nH^+$,[3] $(C_2H_5OH)_nH^+$,[4] and $(CH_3COOH)_nH^+$.[5]

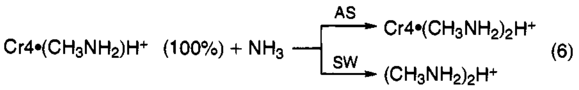
The branching ratios between association (AS), switching (SW), and proton transfer (PT) for reactions of $Cr4{\cdot}AH^+$ with various bases B as a function of PA(B) are represented in Figure 3. The dependence of the branching ratios on PA demonstrate quite clearly the superposition of thermochemical effects and mechanistic effects with the striking example of ethanol giving ligand switching as the major reaction channel in spite of its low PA. Some of the reactions, e.g.



$$\mathrm{Cr4{\bullet}AH^+ + C_2H_5OH}\begin{cases}\xrightarrow{AS}\mathrm{Cr4{\bullet}A{\bullet}(C_2H_5OH)H^+}\ (2\%)\\ \xrightarrow{SW}\mathrm{Cr4{\bullet}(C_2H_5OH)H^+ + NH_3}\ (98\%)\end{cases}\qquad(5)$$

were observed to proceed no further, while others, e.g.

$$\mathrm{Cr4{\bullet}AH^+ + CH_3NH_2}\xrightarrow{SW}$$



$$\mathrm{Cr4{\bullet}(CH_3NH_2)H^+\ (100\%) + NH_3}\begin{cases}\xrightarrow{AS}\mathrm{Cr4{\bullet}(CH_3NH_2)_2H^+}\\ \xrightarrow{SW}\mathrm{(CH_3NH_2)_2H^+}\end{cases}\qquad(6)$$

$$\mathrm{Cr4{\bullet}AH^+ + (CH_3)_3N}\xrightarrow{SW}$$

$$\mathrm{Cr4{\bullet}(CH_3)_3NH^+\ (100\%) + NH_3}\xrightarrow{SW}\mathrm{((CH_3)_3N)_2H^+}\qquad(7)$$

were observed to give secondary association or switching products. The $(G1)_2{\cdot}AH^+$ complex undergoes an analogous reaction to reaction 6 with methylamine, at near gas collison rate, 1.53 × 10^{-9} cm^3/(molecule·s). The primary products are $(G1)_2(CH_3NH_2)H^+$ (99.7%) and $(G1)(CH_3NH_2)H^+$ (0.3%).

Reactions of the Crown Ether Methoxonium Complex $Cr4{\cdot}MH^+$. Rate constants and branching ratios for reactions of $Cr4{\cdot}MH^+$ with various base molecules are presented in Table 3. The thermochemistry of the 12-crown-4 ether methoxonium complex is well established[8b] (Table 4). All the reactions are considerably slower than the ones of $Cr4{\cdot}AH^+$ (Table 2) and do not reach gas kinetic collision rates (see Figure 4). This reflects the substantial reactivity difference between $Cr4{\cdot}AH^+$, which is capable of hydrogen bonding as discussed earlier, and $Cr4{\cdot}MH^+$ (**5**), which is an alkyl-blocked dimer. Product ions having at least two hydrogen bonds are formed 1 order of magnitude faster than ions having only one hydrogen bond (Table 3). Reactions of $Cr4{\cdot}MH^+$ with $(CH_3)_3N$ and $(C_2H_5)_3N$ fall into the first category by virtue of forming a C—H- - -O hydrogen bond. There are two abrupt rises at C_2H_5OH (PA = 188.3 kcal/mol) and NH_3 (PA = 204.0 kcal/mol) in the plot of the rate constants as a function of proton affinity (Figure 4). This reflects multiple hydrogen bonded interactions in the product ions.

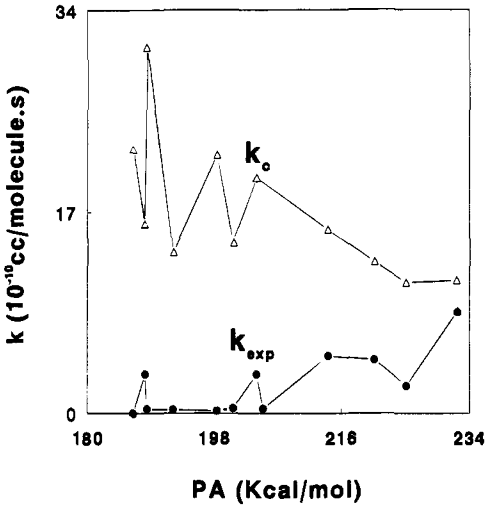
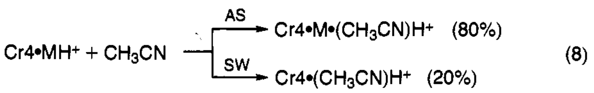


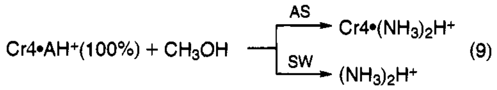
Figure 4. Reaction rate constants as a function of PA(B) for the reactions $(Cr4){\cdot}MH^+ + B$: k_{exp}, experimental; k_c, calculated.

All of the reactions studied demonstrate a single or substantial switching channel except for the reaction of $Cr4{\cdot}MH^+$ with acetonitrile for which association is more pronounced. Some reactions undergo secondary association or switching steps, as follows:

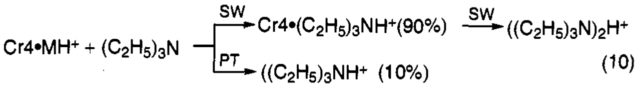


$$\mathrm{Cr4{\bullet}MH^+ + CH_3CN}\begin{cases}\xrightarrow{AS}\mathrm{Cr4{\bullet}M{\bullet}(CH_3CN)H^+}\ (80\%)\\ \xrightarrow{SW}\mathrm{Cr4{\bullet}(CH_3CN)H^+}\ (20\%)\end{cases}\qquad(8)$$

$$\mathrm{Cr4{\bullet}MH^+ + NH_3}\xrightarrow{SW}$$



$$\mathrm{Cr4{\bullet}AH^+(100\%) + CH_3OH}\begin{cases}\xrightarrow{AS}\mathrm{Cr4{\bullet}(NH_3)_2H^+}\\ \xrightarrow{SW}\mathrm{(NH_3)_2H^+}\end{cases}\qquad(9)$$



$$\mathrm{Cr4{\bullet}MH^+ + (C_2H_5)_3N}\begin{cases}\xrightarrow{SW}\mathrm{Cr4{\bullet}(C_2H_5)_3NH^+(90\%)}\xrightarrow{SW}\mathrm{((C_2H_5)_3N)_2H^+}\\ \xrightarrow{PT}\mathrm{((C_2H_5)_3NH^+}\ (10\%)\end{cases}\qquad(10)$$

The branching ratios between AS, SW, and PT for reactions of $Cr4{\cdot}MH^+$ with various bases B as a function of PA(B) are represented in Figure 5. The opening up of the PT channel observed for highest base PAs is due to the exergonic character of the reactions (see Table 3). The overall behavior demonstrates again a superposition of thermochemical and mechanistic effects with CH_3CN being a striking exception, as noted earlier.

Conclusion

The protonated crown ether, $Cr4{\cdot}H^+$, undergoes association–insertion reactions with ammonia and methanol. These reactions are analogous to reactions of alkyl-blocked dimers.[2] Non-proton-bearing molecules such as acetonitrile do not undergo association. The insertion reaction of ammonia into $Cr4{\cdot}H^+$ is nearly 1 order of magnitude more efficient than its insertion into the protonated diglyme, $(G1)_2H^+$, while insertion of methanol into $Cr4{\cdot}H^+$ and $(G1)_2H^+$ is about equally efficient.

The ammonium and methoxonium complexes of Cr4 undergo different reactions. The major reaction of $Cr{\cdot}MH^+$ is switching since it has no proton free for hydrogen bonding. Its reactions are analogous to those of alkyl-blocked trimers such as $(CH_3CN)_2(C_2H_5OH)H^+$.[4] The major reaction of $Cr4{\cdot}AH^+$ is association, except for reactions with hydrogen-containing mol-

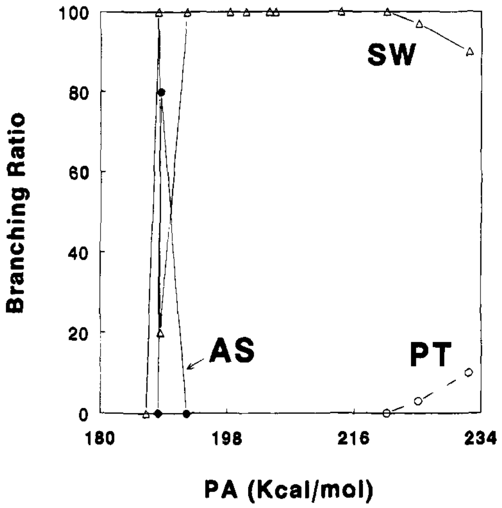


Figure 5. Branching ratios (%) as a function of PA(B) for reactions of (Cr4)·MH^+ + B: AS, association (●); SW, switching (△): PT, proton transfer (○). The exceptional point at low PA (PA = 188.4 kcal/mol) is due to acetonitrile.

ecules or very strong bases with which it undergoes switching. The tendency toward association reflects the hydrogen-bonding capability of the peripheral free proton of Cr4•AH^+. The reactions of Cr4•AH^+ are thus analogous to those of $(ROH)_nH^+$ [1,4] and $(RCOOH)_nH^+$.[3,5] All of the reaction rates of the methoxonium complex are slower than gas kinetic collision rates, while those of the ammonium complex with the amine series proceed at the collison rates. The slow rates of the methoxonium complex are due to the absence of a peripheral proton with hydrogen-bonding capabilities. Attack of the base is on the central proton leading to steric hindrance and to back-reactions.

Alcohols and amines are known[8,9] to possess special guest–host relationships with crown ethers. Their ability to form polyprotonic ions is the reason behind this attribute. This ability leads to the observation of their unique association–insertion reactions into alkyl-blocked proton-bound dimers reported before[2] and into protonated crown ethers. The same polyprotonic ions can be switched out in ligand-switching reactions by base molecules which have the similar capability of forming polyprotonic ions and multiple hydrogen bonded systems. The alkylamines do this with high reaction efficiencies because of their high PAs, while the alcohols do it with low efficiencies because of their low PAs.

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