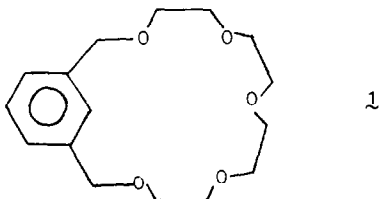


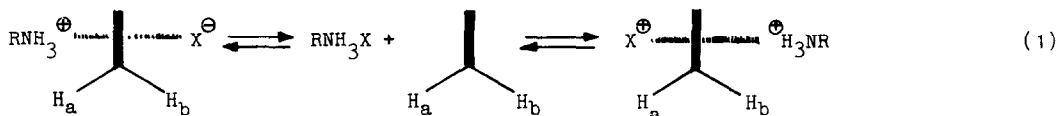
KINETICS OF COMPLEXATION BETWEEN CROWN ETHERS  
 AND PROTONATED AMINES

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The ability of crown ethers to recognize alkylammonium cations by their shape, forms the basis of a vast body of "host-guest" chemistry. The degree of molecular recognition was found to be strongly dependent on — among other things — the structure of the cation and the nature of the anion<sup>1</sup>. Since the effects of these parameters on the stability of crown ether complexes in apolar solutions are largely unknown, we have studied the stability of  $\text{RNH}_3^+\text{X}^-$  complexes of 1,3-xylyl-18-crown-5 (1) in chloroform solution.



Previously<sup>2,3</sup> we demonstrated that dynamic <sup>1</sup>H NMR spectroscopy yields valuable information about the kinetic stability of  $t\text{-BuNH}_3^+\text{PF}_6^-$  complexes of crown ethers. For example, it was found that the rate of cation exchange between the front and back faces of the host (eq. 1) can be



determined from the exchange broadening of the signals of  $\text{H}_a$  and  $\text{H}_b$ , and that simple formulas<sup>4</sup> can be used to obtain the free energies of activation at the coalescence temperature. The kinetic data obtained by this method proved to correlate fairly well with the results of other cation

exchange methods<sup>3</sup>. In  $\text{RNH}_3 \cdot \text{X}$  complexes<sup>5</sup> of **1** in chloroform solution, the benzylic protons can serve as the NMR probes  $\text{H}_a$  and  $\text{H}_b$  (eq. 1), the singlet observed at +30 °C separating into an AB system at low temperature. The free host gave a temperature-independent  $^1\text{H}$  NMR spectrum.

#### A. The effect of cation structure

The data in Table I show that the free energies of activation ( $\Delta G_c^\ddagger$ ) for the decomplexation step of the complexes with 1,3-xylyl-18-crown-5 (**1**), increase in the order  $\text{CH}_3\text{NH}_3^+ < \text{CH}_3\text{CH}_2\text{NH}_3^+ < (\text{CH}_3)_2\text{CHNH}_3^+$ , while the iso-propyl- and tert-butylammonium complexes are kinetically equally stable. This result indicates that  $\alpha$ -methyl substituents induce hardly any steric repulsion in the complex, if at all. This is also evident from a comparison of the isopropyl- and cyclopropylammonium complexes, the latter being only slightly more stable than the former. Steric hindrance in  $\beta$ -substituted ethyl-ammonium complexes does not seem to be significant either, the kinetic stability increasing in the order:  $\text{CH}_3\text{CH}_2\text{NH}_3^+ < \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3^+ < (\text{CH}_3)_3\text{CCH}_2\text{NH}_3^+$ . Only for  $(\text{CH}_3\text{CH}_2)_2\text{CHNH}_3^+$  does the effect of steric hindrance become clearly visible, since both iso-propyl- and cyclopentylammonium complexes are kinetically more stable. The benzylammonium complex was found to be the most stable alkylammonium complex, while anilinium complexes gave the lowest rates of decomplexation of ammonium complexes of **1** observed so far.

TABLE I. EFFECT OF CATION STRUCTURE ON THE KINETIC STABILITY

OF  $\text{RNH}_3^+ \cdot \text{1} \cdot \text{PF}_6^-$  COMPLEXES IN  $\text{CDCl}_3$  (0.025 M)

	$T_c$ (°C)	$\Delta\nu$ (Hz)	J (Hz)	$\Delta G_c^\ddagger$ (kJ/mol)
$\text{CH}_3$	-43	21.7	9.2	47.7
$\text{CH}_3\text{CH}_2$	-33	20.4	8.7	49.3
$(\text{CH}_3)_2\text{CH}$	-25	19.5	8.9	51.5
$(\text{CH}_3)_3\text{C}$	-27	16.3	9.5	51.5
$(\text{CH}_3)_3\text{CCH}_2$	-25	23.3	9.0	51.5
$(\text{CH}_3\text{CH}_2)_2\text{CH}$	-36	21.1	9.1	49.4
Cyclopropyl	-22	20.6	8.9	52.3
Cyclopentyl	-19	19.8	9.0	53.2
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$	-31	20.8	8.8	50.2
$\text{C}_6\text{H}_5\text{CH}_2$	-16	15.8	8.8	54.0
p- $\text{CH}_3\text{C}_6\text{H}_4$	-7	31.7	9.0	54.9
p- $(\text{CH}_3\text{O})\text{C}_6\text{H}_4$	-5	33.0	9.0	54.9

From our results we conclude that the cavity of 1,3-xyllyl-18-crown-5 is only slightly sterically shielded. Certain diaza-crown ethers show a much larger effect of the alkyl group on the  $\Delta G_c^\ddagger$  of alkylammonium complexes<sup>6</sup>. It is interesting to note that also 18-crown-6 showed a higher selectivity for alkylammonium ions in methanol<sup>7</sup>.

#### B. The effect of the anion

We have determined  $\Delta G_c^\ddagger$  for a number of complexes of **1** (Table II), with various anions. The order of kinetic stability,  $(\text{CH}_3)_3\text{CNH}_3^+ < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_3^+ < \text{p.CH}_3\text{C}_6\text{H}_4\text{NH}_3^+$ , was the same for  $\text{PF}_6^-$  and  $\text{ClO}_4^-$ . Apparently, the structure of the cation has little effect on the relative complex stabilities for different anions. Therefore, the order of decreasing kinetic stability  $\text{PF}_6^- > \text{ClO}_4^- > \text{BF}_4^- > \text{I}^- > \text{SCN}^- > \text{Cl}^-$  found for the benzylammonium cation, is probably valid for most protonated amines.

TABLE II. EFFECT OF ANION ON THE KINETIC STABILITY ( $\Delta G_c^\ddagger$ , kJ/mol at  $T_c$  (°C)) OF  $\text{RNH}_3^+ \cdot \mathbf{1} \cdot \text{X}^-$  COMPLEXES IN  $\text{CDCl}_3$  (0.025 M)

$\text{X}^- \backslash \text{R}$	$(\text{CH}_3)_3\text{C}$	$\text{C}_6\text{H}_5\text{CH}_2$	$\text{p.CH}_3\text{C}_6\text{H}_5$
$\text{PF}_6^-$	51.5 ( -27 °C)	54.0 ( -16 °C)	54.9 ( -7 °C)
$\text{ClO}_4^-$	46.1 ( -51 °C)	49.8 ( -35 °C)	51.1 ( -25 °C)
$\text{BF}_4^-$		49.0 ( -39 °C)	
$\text{I}^-$		46.8 ( -48 °C)	
$\text{SCN}^-$	<43 ( <-65 °C)	45.2 ( -56 °C)	<43 ( <-65 °C)
$\text{Cl}^-$	<43 ( <-65 °C)	<43 ( <-70 °C)	<43 ( <-65 °C)

We previously found<sup>3</sup> that differences in thermodynamic stability ( $\Delta G_0$ ) are fully reflected in the free energy of activation for decomplexation ( $\Delta G_c^\ddagger$ ). Therefore, the free energy of complex formation follows the order<sup>8</sup>  $\text{PF}_6^- < \text{ClO}_4^- < \text{BF}_4^- < \text{I}^- < \text{SCN}^- < \text{Cl}^-$ . This order is identical to that of the hydrogen bonding abilities of these anions in apolar solvents<sup>9</sup>. Since the hydrogen bonding between the anion and the protonated amine must be disrupted when the  $\text{RNH}_3^+ \cdot \text{X}^-$  ion pair is converted into the crown ether-separated ion pair  $\text{RNH}_3^+ \cdot \mathbf{1} \cdot \text{X}^-$ , it is readily understood that the most stable complexes are formed with anions that are essentially non-hydrogen bonding. Since both  $\Delta G_c^\ddagger$  and  $\Delta G_0$  show a good linear relationship with the hydration ratio (a measure of the free energy of hydration<sup>9</sup>) of the anions of Table II, it is expected that the effect of other anions, too, can be predicted on the basis of their known<sup>9</sup> affinity for H-bond donors.

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