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KINETICS OF COMPLEXATION BETWEEN TERT-BUTYLAMMONIUM HEXAFLUOROPHOSPHATE AND CROWN ETHERS

F. de Jong, D.N. Reinhoudt and R. Huis
Koninklijke/Shell-Laboratorium, Amsterdam
Shell Research B.V., The Netherlands

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Recently we reported a simple ^1H NMR method to determine the rate of decomplexation of t-$BuNH_3PF_6$ (AM) complexes of crown ethers[1]. By this method the rate of cation exchange between a kinetically stable (IAM) and a kinetically unstable (IIAM) complex is determined from the exchange broadening of the tert-butyl signal.

$$\mathrm{IAM} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{I} + \mathrm{AM} \tag{1}$$

$$\mathrm{IIAM} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{II} + \mathrm{AM} \tag{2}$$

$$\mathrm{IAM} + \mathrm{AM}^{*} \xrightarrow{k_3} \mathrm{IAM}^{*} + \mathrm{AM} \tag{3}$$

When $k_2 \gg k_1$ the observed rate of exchange equals the rate of exchange between IAM and free t-$BuNH_3PF_6$ (AM), the reciprocal lifetime of IAM being given by

$$\tau^{-1}_{\mathrm{IAM}} = k_1 + k_3[\mathrm{AM}] . \tag{4}$$

We have now used this method to determine the rates of decomplexation of the t-$BuNH_3PF_6$ complexes of a series of crown ethers. The measurements were carried out with equimolar solutions (0.01 M) of IAM, IIAM and uncomplexed II, under which conditions the bimolecular exchange can be neglected[1] and $\tau^{-1}_{\mathrm{IAM}} = k_1$.

The rates and activation parameters of crown ethers **1**-**10** (see Table I) were determined with the usual formulae for a two-site system[2]. Relative association constants were determined from competition experiments, as described previously[3]. The absolute values were then calculated using the known value[1] of 2.2×10^5 M^{-1} at 20 °C for the complex of crown ether **5**. The rates of complex formation were obtained from $k_{-1} = k_1 . K_1$.

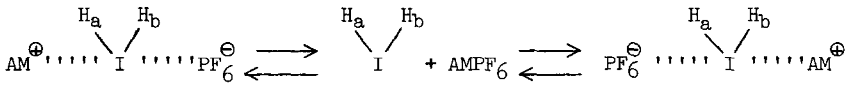
The results (Table I) show that the rates of complex formation are almost constant ($k_{-1} = (0.8 - 1.6) \times 10^9$ M^{-1} s^{-1}) over the whole series of crown ethers and are most probably diffusion controlled[4]. Consequently, the observed differences in thermodynamic complex stability are fully reflected in the different rates of decomplexation[5], which range from 10^2 to 10^4 s^{-1} at 20 °C.

For the decomplexation the Arrhenius energies of activation (E_a) follow the same order as the free energies of activation ($\Delta G_1^{\neq}$), being high (19.3 ± 1 kcal/mol for **1**) for thermodynamically stable complexes and low (9.9 ± 1 kcal/mol for **7**) for the weaker complexes.

In some cases the rates of decomplexation were also obtained from two other types of exchange process as indicated below.

A. Exhange between the "back" and "face" sides of the complex[6]

The C_2 axis of symmetry present in the free crown ether is absent in the complex. If the cation and anion are located on opposite sides of the crown ether, there may be an exchange between the back and face sides (eq.5), the rate of which can be determined at the coalescence temperature



(5)

(T_c) for the signals of H_a and H_b with the aid of the usual formulas[2]. The results obtained using the benzylic protons in the complexes of crown ethers **5**-**10** are given in Table II.

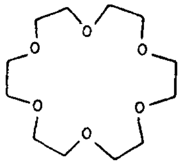
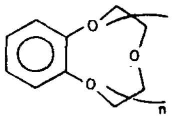
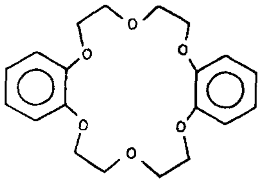
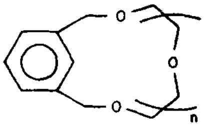
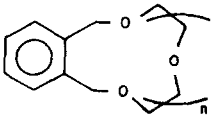
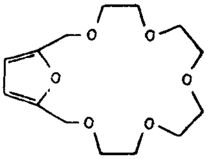
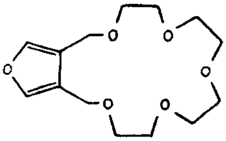
B. Exchange between free and complexed crown ether

At low concentrations cation exchange between free and complexed crown ether only occurs via decomplexation (eq.1). For only a few crown ethers (**4**, **5** and **10**) different chemical shifts for the free and complexed forms were observed. The results for equimolar (0.01 M) solutions of free crown ether and complex in chloroform are shown in Table II.

The agreement between the three methods is very satisfactory, particularly in view of the inaccuracy introduced by the use of the rather small differences in chemical shift in methods A and B. The cation exchange between complexes of different crown ethers (Method C in Table II) offers the possibility to maximize shift differences by a proper choice of complexes and to use uncoupled sites of exchange. The last method has a wider scope and gives more accurate data.

TABLE I

KINETIC, THERMODYNAMIC AND SPECTRAL DATA OF $t\text{-BuNH}_3\text{PF}_6$ COMPLEXES OF VARIOUS CROWN ETHERS IN CDCl_3 AT 20 °C

Crown ether		δ_{Bu} (ppm)	k_1 (s^{-1})	$\Delta G^{\neq}_1$ (kcal/mol)	E_a (kcal/mol)	K (M^{-1})	$-\Delta G_0$ (kcal/mol)
	1	1.356	65	14.7(a)	19.3	2.3×10^7	9.8
	2, n=3	1.287				8.2×10^3	
	3, n=4	1.155	155	14.2(a)	18.0	5.0×10^6	8.9
	4	0.849	850	13.2(b)	13.0	1.2×10^6	8.1
	5, n=3	0.824	5400	12.1(b)	12.2	2.2×10^5	7.1
	6, n=4	1.051				2.9×10^4	5.9
	7, n=3	0.842	9000	11.8(b)	9.9	1.4×10^5	6.9
	8, n=4	1.062				1.6×10^5	7.0
	9	1.172	1100	13.0(a)	15.2	1.3×10^6	8.2
	10	1.070	7000	12.0(b)	10.5	1.1×10^5	6.7

(a) from cation exchange with the complex of crown ether 5.

(b) from cation exchange with the complex of crown ether 2.

TABLE II

COMPARISON OF KINETIC DATA OBTAINED FROM CATION EXCHANGE BETWEEN BACK AND FACE SIDES OF THE COMPLEX (METHOD A), FREE AND COMPLEXED CROWN ETHER (METHOD B) AND COMPLEXES OF DIFFERENT CROWN ETHERS (METHOD C)

Crown ether	Method	T_c (^oC)	$\Delta\nu$(Hz)	J(Hz)	$\Delta G_c^{\neq}$ (kcal/mol)		
					A	B	C
4	B	$-20^{(a)}$	10			13.1	12.8
5	A	$-28^{(b)}$	15.4	9.5	12.3		12.0
	B	$-50^{(c)}$	10			11.5	11.8
6	A	$<-70^{(b)}$					
7	A	$-34^{(b)}$	36	10.1	11.7		11.4
8	A	$-48^{(b)}$	13.2	12.2	11.1		
9	A	$-14^{(b)}$	14.6	11.2	12.9		13.2
10	A	$<-70^{(b)}$					
	B	$-50^{(a)}$	14		11.4	11.4	11.4

(a) aromatic protons (b) benzylic protons (c) aromatic proton at the 2 position.

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