Anion Effect on the Dissociation of Metal Cryptates in Methanol

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Studies of the dissociation reactions of complexes of the macrobicyclic polyether diamine cryptands (Cry) with alkali [1] and alkaline-earth metal [2] ions, as well as with transition metal [3] and lanthanide ions [4], have been carried out by several authors. The variation of the dissociation rates with the size and charge of the complexed cation have often been discussed [1, 2, 4]. The influence of the solvent on the rate constants [1] as well as that of the addition of substituents in the ligand molecule [5] have been the subject of previous investigations. The influence of the anion on the dissociation rates of the cryptand complexes has been much less studied [4, 6]. The role of the anion in complexation–decomplexation reactions with neutral macrocyclic ligands is important in relation to the transport of ions through membranes by neutral naturally-occurring carriers (*e.g.* valinomycin, monactin, *etc.*) [7–9]. In this case, the anion has to be transported alongside the complex to fulfil the electroneutrality condition. Weaver *et al.* [4] have observed that the dissociation of trivalent lanthanide cryptates is accelerated remarkably by OH^- and F^-. However, Schwing *et al.* [6], in a study of the dissociation mechanism of a potassium cryptate, report a negligible influence of the anion (Cl^-, Br^-, I^-) in the dissociation rate constant of the complex. In this work we wish to report a kinetic study of the effect of the anions ClO_4^-, Cl^- and Br^- on the dissociation rates of calcium (2_B, 2, 2) and (2_B, 2_B, 2) cryptates in methanol. We have chosen these ligands since it is possible to measure their dissociation rate constants by spectrophotometry, as will be seen below.

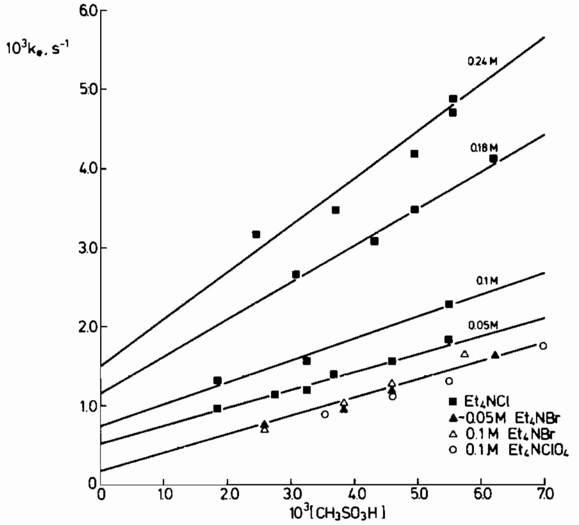

Fig. 1. Observed rate constants for the dissociation of Ca(2_B, 2, 2)$^{2+}$ in the presence of various supporting electrolytes in methanol.

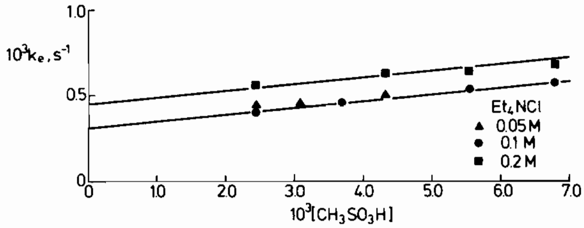

Fig. 2. Observed rate constants for the dissociation of Ca(2_B, 2_B, 2)$^{2+}$ in the presence of Et_4NCl in methanol.

Experimental and Results

Cryptands (2_B, 2, 2) and (2_B, 2_B, 2) were purchased from Merck and used without further purification. The salts were all Analytical Grade. Methanol was from Merck (dried AR, max. 0.01% H_2O).

The dissociation rates of the calcium (2_B, 2, 2) and (2_B, 2_B, 2) complexes in methanol were determined in different supporting electrolytes at 25 °C using methanesulphonic acid as scavenger, eqn. (1). The reactions could be followed spectrophotometrically

$$CaCry^{2+} + 2H^+ \xrightarrow{k_e} Ca^{2+} + H_2Cry^{2+} \qquad (1)$$

(λ = 280 nm) because of the difference in optical density between complexed and protonated ligand. The observed rate constant k_e is given by eqn. (2), as has been shown in previous papers [2b]. In eqn.

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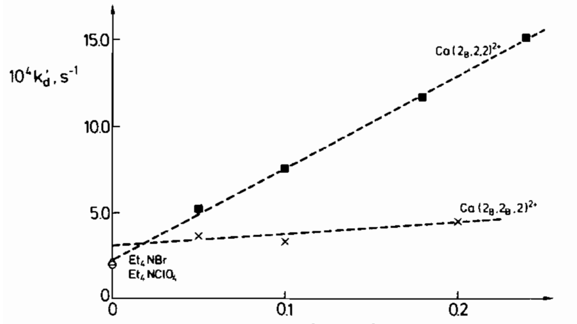

Fig. 3. Dissociation rate constants of $Ca(2_B, 2, 2)^{2+}$ and $Ca(2_B, 2_B, 2)^{2+}$ as a function of the concentration of Et_4NCl.

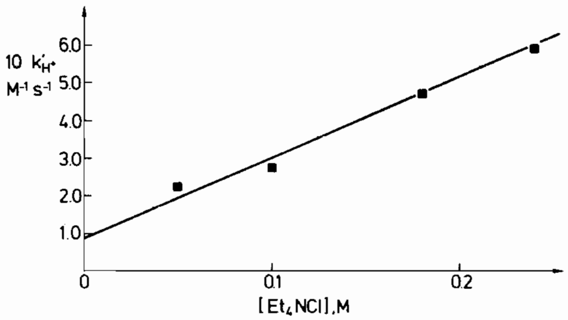

Fig. 4. The acid-catalysed dissociation rate constant of $Ca(2_B, 2, 2)^{2+}$ as a function of the concentration of Et_4NCl.

$$k_e = k'_d + k'_{H^+} [H^+] \quad (2)$$

(2) k'_d is the rate constant for the dissociation of the complex in the absence of acid and k_{H^+} is the rate constant for the acid-catalysed dissociation, both at a given concentration of supporting electrolyte. Figure 1 shows a plot of k_e against [acid] for the dissociation reaction of $Ca(2_B, 2, 2)^{2+}$ at different concentrations of electrolytes: 0.1 *M* Et_4NClO_4, 0.05 *M* and 0.1 *M* Et_4NBr, and 0.05 *M*, 0.1 *M*, 0.18 *M* and 0.24 *M* Et_4NCl. In Fig. 2 a plot of k_e against [acid] for the dissociation of $Ca(2_B, 2_B, 2)^{2+}$ in 0.05 *M*, 0.1 *M* and 0.2 *M* Et_4NCl is shown.

Discussion

Dissociation of $Ca(2_B, 2, 2)^{2+}$

Our results show that the observed rates for the dissociation of $Ca(2_B, 2, 2)^{2+}$ are practically independent of the supporting electrolyte when this is Et_4NBr or Et_4NClO_4. However, the dissociation rates increase with increasing concentration of Et_4NCl. Both the acid-independent dissociation rate constant k'_d (the intercept at [acid] = 0, Fig. 1) and the acid-catalysed dissociation rate constant k'_{H^+} (the slope of the k_e *vs.* [acid] curves, Fig. 1) take higher values at higher Et_4NCl concentrations. This means that the Cl^- ion is catalysing the dissociation reactions, both for the acid-catalysed and the acid-independent dissociation reactions. Conductivity studies of tetraalkylammonium halides suggest little or no association of Et_4Cl in methanol (the association constants for Me_4NCl and Bu_4NCl in methanol are 7 and 0, respectively) [10]. Plots of k'_d against $[Et_4NCl]$ (Fig. 3) and k'_{H^+} against $[Et_4NCl]$ (Fig. 4) show a linear correlation between the rate constants (k'_d or k'_{H^+}) and the concentration of Cl^- ion. The overall observed rate constant k_e (eqn. 2) for a dissociation mechanism which includes the dissociation reactions catalysed by an anion A^-, eqns. (3) and (4), is given by eqn. (5). In eqn. (5) k_d, k_{H^+} are the dissociation and acid-catalysed dissociation rate constants in the absence of A^-, respectively. Extrapolation of k'_d (Fig. 3) and k'_{H^+} (Fig. 4) to $[Et_4NCl]$ = 0 leads to values of the intercepts of $(2.2 \pm 0.2) \times 10^{-4}$ s^{-1} and $(8 \pm 3) \times 10^{-2}$ M^{-1} s^{-1} respectively. These values are comparable to the values of k_d and k_{H^+} obtained in the absence of supporting electrolyte [11]. From the slope of Fig. 3 we obtain $k_{A^-} = (5.5 \pm 0.3) \times 10^{-3}$ M^{-1} s^{-1} and from Fig. 4 $k_{H^+,A^-} = 2.1 \pm 0.2$ M^{-2} s^{-1} when $A^- = Cl^-$.

$$MCry^{2+} + A^- \xrightarrow{k_{A^-}} M^{2+} + Cry + A^- \quad (3)$$

$$MCry^{2+} + 2H^+ + A^- \xrightarrow{k_{H^+,A^-}} M^{2+} + H_2Cry^{2+} + A^- \quad (4)$$

$$k_e = (k_d + k_{A^-}[A^-]) + (k_{H^+} + k_{H^+,A^-}[A^-])[H^+] \quad (5)$$

It may be noted that no correction for ionic strength (I) has been included in eqn. (5), and the results should be taken to refer to an average ionic strength I ≅ 0.15 *M*. Our results with Cl^- show that both k'_d and k'_{H^+} are correlated with the stoichiometric concentrations of Et_4NCl (in the range I = 0.05 to 0.24 *M*). For reactions (3) and (4) one should expect ionic strength corrections proportional to $\gamma_\pm^4$ and $\gamma_\pm^2$ respectively (both tending to reduce observed k_{A^-} and k_{H^+,A^-} values as I increases). For example, if the activity coefficients are calculated using the Davies equation [12], we find for I = 0.1 *M*, $\gamma_\pm^2 = 0.159$ and $\gamma_\pm^4 = 0.025$ at 25 °C. Thus the absolute corrections relative to infinite dilution may be very large, although the variations of $\gamma_\pm$ over the ionic strength range used is much smaller. Inclusion of activity coefficient corrections in the relationship between the rate constants and concentrations, eqn. (5), based on calculated $\gamma_\pm$ values does not lead to reasonable conclusions. This may in part be due to the fact that at higher ionic strengths calculated activity coefficients based on Debye–Hückel theory are lower than observed values [13], but may also suggest that in the transition states, $MCry^{2+}\cdots A^-$ and $MCryH^{3+}\cdots A^-$, the individual ions, *i.e.* the cryptate and the anion, maintain their identity with respect to conserving their charges and forming individual ionic atmospheres. This behavior has been observed previously in the OH^- catalysed hydrolysis of ethyladipate where evidence has been presented that in sufficiently dilute solutions the transition state with a carboxylate ion and a hydroxyl ion at the opposite ends of the molecule behaves as a conventional doubly-charged ion. As the radius of the Debye–Hückel ionic atmosphere becomes comparable with the separation between the charges, each charge tends to build up its own atmopshere, and simulate independent ions [13b].

The anions Br^- and ClO_4^- (also presumably NO_3^-) do not catalyse the dissociation of $Ca(2_B, 2, 2)^{2+}$. There seems to exist a correlation between the ability of the anion to catalyse the dissociation of the complex and the ability to form ion pairs MA^+ with the metal ion. Lee and Wheaton [14] report an association constant of 410 M^{-1} for $CaCl^+$ in methanol. This significant association is reflected in the strong variation of the ^{43}Ca chemical shift with the total concentration of the $CaCl_2$ salt [15]. These authors also report a much smaller dependence of the chemical shift on the concentrations of $Ca(NO_3)_2$ or $Ca(ClO_4)_2$. Thus, in the reaction between cryptate and anion, direct interactions between the metal ion and the anion may facilitate the dissociation of the cryptate. In the most stable conformation of the complex, the endo–endo conformation [16], the metal ion is wrapped up in the ligand molecule. Thus, it is not possible for a large anion like Cl^- to interact directly with the complexed metal ion, as may be the case for smaller anions like F^- or OH^- which may penetrate through the polyether strands of the cryptate [4]. Therefore, in the transition state the complex may assume an endo–exo conformation in which the ligand adopts a crown-ether like structure leaving part of the metal ion exposed, thus allowing some interaction with the anion. A possible kinetic scheme (A) for the dissociation of the cryptate is shown below.

Scheme (A)

$$\begin{tikzcd}
M(n,n)^{2+} \arrow[r, shift left, "K_c"] & M(n,x)^{2+} \arrow[l, shift left] \arrow[r, "k"] \arrow[d, shift left, "+A^-"'] & M^{2+} + \text{ligand} \\
 & (M(n,x)^{2+}\cdots A^-)^{\ddagger} \arrow[u, shift left, "K^{\ddagger}"'] \arrow[r, "k'"] & MA^+ + \text{ligand}
\end{tikzcd}$$

In this scheme $M(n,n)^{2+}$ and $M(n,x)^{2+}$ represent the endo–endo and endo–exo conformations of the complex respectively. It can easily be shown that the following relationships apply: $k_d = kK_c$ and $k_{A^-} = k'K^{\ddagger}K_c$. In the transition state both the metal cryptate and the anion should maintain their identity and charge (*e.g.* a solvent-separated ion pair), as discussed above. This general scheme is consistent with earlier studies on solvent effects of alkali metal cryptates [1] which suggest that in the transition state the metal ion is largely outside the ligand cavity and free to interact with solvent molecules and presumably other suitable ligands or anions. These interactions would of course stabilize the transition state and lead to an increase in the dissociation rate of the metal ion from the cryptate.

Dissociation of $Ca(2_B, 2_B, 2)^{2+}$

The results for the kinetics of dissociation of $Ca(2_B, 2_B, 2)^{2+}$ show a very small dependence of the observed rate constant k_e on the concentration of Et_4NCl (Fig. 2). Indeed, k'_d varies by only around 20% between $[Et_4NCl]$ = 0.05 *M* and $[Et_4NCl]$ = 0.2 *M*, and k'_{H^+} remains practically constant. From a plot of k'_d *vs.* $[Et_4NCl]$ (Fig. 3) we obtain from the slope a value of $k_{A^-} = (6.5 \pm 2) \times 10^{-4}\ M^{-1}\ s^{-1}$ ($A^- = Cl^-$) for $Ca(2_B, 2_B, 2)^{2+}$. The intercept $(3.1 \pm 0.5) \times 10^{-4}\ s^{-1}$ is close to the reported value of k_d determined in the absence of the supporting electrolyte, as expected from eqn. (5) [11]. The lower value of k_{A^-} ($A^- = Cl^-$) for the anion-catalysed dissociation of $Ca(2_B, 2_B, 2)^{2+}$ compared to that of $Ca(2_B, 2,2)^{2+}$ is to be expected since the dibenzo molecule is more rigid and therefore less able to attain a reactive endo–exo configuration in the complex. Moreover, the two benzo groups of the ligand molecule should diminish the possibilities of anion–complex interactions by making it sterically more difficult for the anion to approach the metal ion in the complex. Anions larger than Cl^-, like Br^- and ClO_4^-, should not be able to catalyse the dissociation of $Ca(2_B, 2_B, 2)^{2+}$ by analogy with the results for the dissociation of $Ca(2_B, 2, 2)^{2+}$.

Conclusions

The dissociation reactions of metal cryptates may be catalysed by some anions. The catalytic effect of the anion seems to be related to its ability to form ion pairs with the complexed metal ion. This suggests that in the dissociation reaction catalysed by the anion, the anion interacts directly with the central metal ion. However, if the structure of the ligand makes it sterically difficult for the anion to approach the metal cation, the degree of catalysis by the anion can be reduced or even suppressed.

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