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# Kinetics of Dissociation of Potassium and Thallium Cryptates

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Abstract: The kinetics of dissociation of thallium cryptates $(222Tl)^+$ and $(221Tl)^+$ was studied in water and in methanol-water (90:10) over the range of temperatures 5–35 °C. The kinetic behaviors of $(222Tl)^+$ and $(222K)^+$ in water were compared. For the *direct dissociation* process the kinetic results have shown a similar behavior of $(222K)^+$ and $(222Tl)^+$ in water. A less solvating medium (methanol-water) than water leads to slower dissociation rates of the thallium cryptates studied. The *acid-catalyzed dissociation* path differentiates significantly, in terms of rate constants and activation parameters, the behavior of $(222K)^+$ and $(222Tl)^+$ in acidic aqueous medium.

Introduction

The macrocyclic diamines or "cryptands" synthesized by Lehn et al.[1] are now well known for their ability to form stable complexes with alkali metal ions.[2-6]

(2,1,1) $m = 0; n = 1$
(2,2,1) $m = 1; n = 0$
(2,2,2) $m = n = 1$
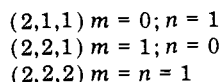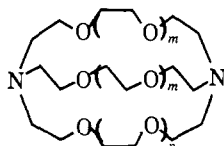
Dynamic aspects of these new complexes were first studied by NMR measurements[7-9] and by relaxation methods.[10,11] Flow methods were used by Wilkins et al.[12,13] for the kinetic study of the dissociation of several calcium cryptates in water and by Schneider et al.[14,15] for the study of the acid-catalyzed dissociation and formation rates of some alkali earth and alkali metal cryptates.

In this paper, we report on the influence of the solvent and of the temperature on the kinetics of dissociation of potassium and thallium cryptates. The kinetic behavior of Tl^+ and K^+ cryptates will be compared. K^+ is a cation of prime importance in biochemistry, but its spectroscopic properties are very poor. Tl^+ is now used as a physical probe in biological systems; it replaces K^+ and is easily measured by various techniques (NMR, UV, etc.).[5,16]

For the acid dissociation of a metallic cryptate, the overall reaction can be written

$$(CryM)^{n+} + 2H^+ \rightarrow M^{n+} + (CryH_2)^{2+} \quad (1)$$
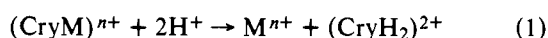
with $(CryM)^{n+}$ = metallic cryptate and $(CryH_2)^{2+}$ = protonated cryptand. We found the same rate law as that observed by Schneider et al.:[14]

$$v = \{k_D + k_H[H^+]\}[(CryM)^{n+}] \quad (2)$$

with k_D = rate constant for the direct dissociation and k_H = rate constant for the acid-catalyzed dissociation of the cryptate.

Experimental Section

Kinetics Procedure. The rates of reaction 1 for potassium and thallium cryptates were measured with a Durrum-Gibson stopped-flow spectrophotometer. The kinetic data were recorded by a transient recorder Datalab and treated on-line with a desk computer Olivetti P652.

Earlier we studied the dissociation kinetics of the potassium cryptate $(222K)^+$ in water and in acidic medium.[17] At 440 nm, with a pH indicator (2,6-dinitrophenol), the variations of the pH vs. time were obtained for reaction 1.

For the thallium cryptates, the experimental conditions were much easier: the dissociation of the complexes was directly observed with the stopped-flow spectrophotometer at 253 nm for $(222Tl)^+$, at 246 nm for $(221Tl)^+$, and at 250 nm for $(211Tl)^+$. Preliminary spectra were measured on a spectrophotometer Cary 17.

The experimental conditions chosen for the kinetic study of the cryptate $(222K)^+$ were already described.[17]

For the kinetic study of the dissociation of the thallium cryptates considered, a solution of acid in excess $(HClO_4)$ was mixed with a solution containing tetramethylammonium hydroxide $(10^{-2}$ mol $L^{-1})$, the cryptand $(\simeq 10^{-4}$ mol $l^{-1})$, and 10% excess of Tl^+. The experiments were done at various pH values over the range of 2–3. The ionic strength was controlled with tetraethylammonium perchlorate (0.1 mol $L^{-1})$.
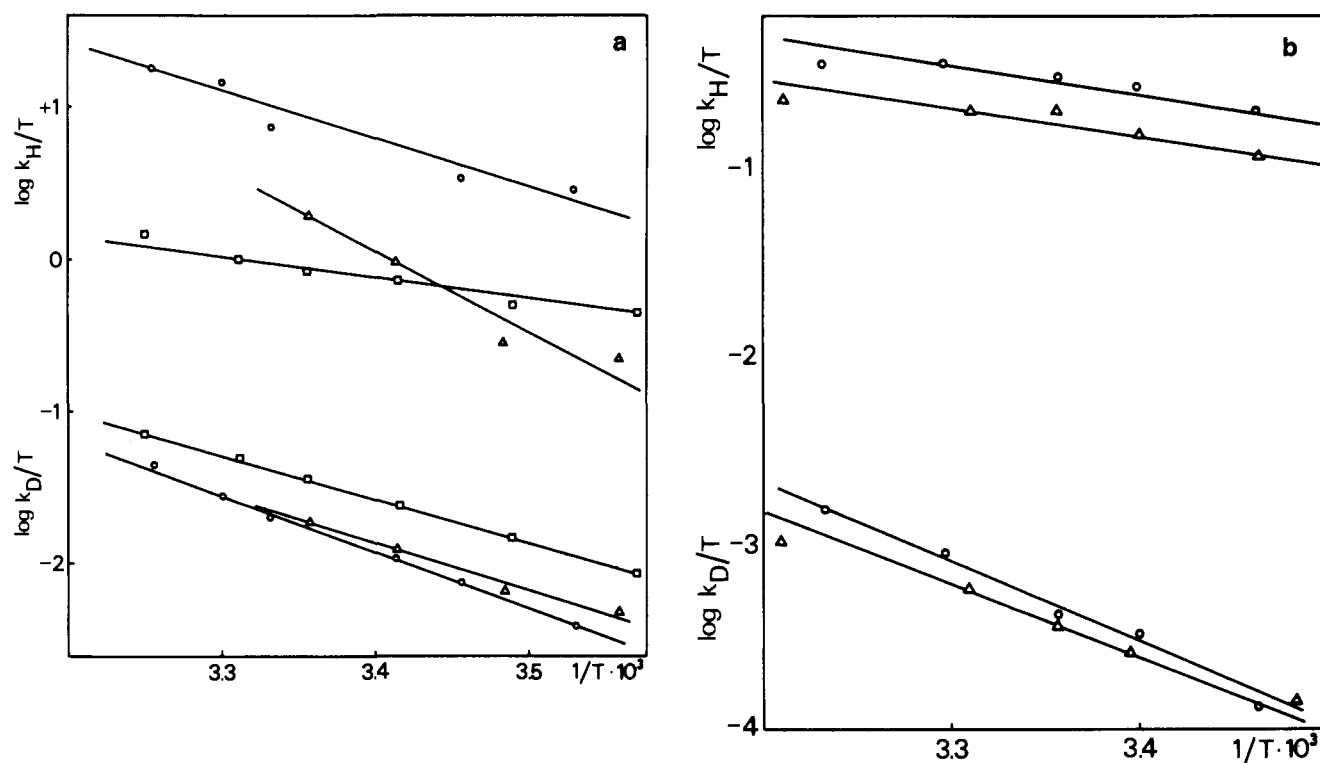
The activation parameters for both dissociation paths were determined from Eyring plots in the range of 5–35 °C (Figure 1).

Materials. The cryptands (222), (221), and (211) were commercial samples (Merck) used without further purification. Tetramethylammonium hydroxide was obtained as 10% aqueous solutions from Merck.

Results and Discussion

A. Direct Dissociation. As shown in Table I, the cryptates $(222K)^+$ and $(222Tl)^+$ have a similar behavior in their direct dissociation in water: the values of the rate constants are equal.

When we compare $(222Tl)^+$ and $(221Tl)^+$ in water, the dissociation rate becomes larger for $(221Tl)^+$; in methanol-water (90:10), the cryptates $(222Tl)^+$ and $(221Tl)^+$ dissociate at the same rate in the limits of the experimental uncertainties (Table I). It is worth noting that, in the cases of $(221K)^{+\ 11,18}$ and $(221Tl)^+$, respectively, compared with $(222K)^+$ and $(222Tl)^+$ in water, the loss of a binding site and a cavity of the ligand smaller than the ionic radius of the cation lead to larger

Figure 1. Eyring plots. k_D, direct dissociation rate constant, and k_H, acid-catalyzed dissociation rate constant. (a) $\triangle$ $(222K)^+$; $\bigcirc$ $(222Tl)^+$; $\square$ $(221Tl)^+$ in water. (b) $\bigcirc$ $(222Tl)^+$; $\triangle$ $(221Tl)^+$ in methanol-water (90:10).

Table I. Dissociation Rate Constants and Activation Parameters at 25 °C[a]

	uncatalyzed dissociation			acid-catalyzed dissociation			
cryptates	k_D, s^{-1} (t = 25 °C)	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	k_H, L mol^{-1} s^{-1} (t = 25 °C)	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	solvent
$(222K)^+$	5.5 ± 0.3	14 ± 2	−6 ± 4	590 ± 120	22 ± 5	28 ± 10	water
$(222Tl)^+$	5.5 ± 0.5	17 ± 1	1 ± 2	2200 ± 150	13 ± 1	1 ± 5	
$(221Tl)^+$	10.5 ± 0.5	13.5 ± 1.0	−9 ± 2	250 ± 20	7.5 ± 1.0	−23 ± 5	
$(222Tl)^+$	0.12 ± 0.01	18.5 ± 1.0	0 ± 3	92 ± 5	7 ± 2	−32 ± 5	methanol-water
$(221Tl)^+$	0.10 ± 0.01	15 ± 1	−12 ± 4	60 ± 5	5.5 ± 2.0	−33 ± 6	(90:10)
$(211Tl)^+$	31 ± 3			$(4 ± 0.4) \times 10^4$			

[a] For $(222K)^+$: I = 0.2 M with tetraethylammonium chloride. For all thallium cryptates: I = 0.1 M with tetraethylammonium perchlorate.

values of the dissociation rate constant (Table II). This effect is much smaller for the thallium cryptates and was not observed in methanol-water going from $(222Tl)^+$ to $(221Tl)^+$. Structural data[19] showed that the cation Tl^+ lies in the cavity of the cryptand 222; no structural data are available for $(221Tl)^+$. However, recent NMR measurements showed that chemical shifts of $(221Tl)^+$ were independent of the solvent;[20] the authors concluded that the cation was completely shielded by the cryptand as expected from an "inclusive" complex defined by Popov et al.[21] These results agree well with the observed values of k_D in the direct dissociation path of $(222Tl)^+$ and $(221Tl)^+$ and also with very close values of the stability constants[2] (Table II).

The high value of k_D determined for the cryptate $(211Tl)^+$ (Table I) in methanol-water can be easily explained by the lability of this complex in which the size of the cavity (0.8 Å) is too small for the cation Tl^+. No structural or thermodynamic data are available for this complex.

The dissociation rate constants become smaller going from water to a mixed solvent (methanol-water, 90:10) as expected from a less solvating medium (Table I).

The values of the activation enthalpy for the direct dissociation path of the cryptates of K^+ and Tl^+ studied in water and in methanol-water are between 13.5 and 18.5 kcal mol^{-1}

(Table I). The values of the activation entropy determined for the direct dissociation of the potassium and thallium cryptates in water and in methanol-water are generally negative or slightly positive (Table I). The negative sign of this parameter is probably due to the recoordination of solvent molecules to the metal atom which is still bound to the cryptand in the transition state, as already suggested by Wilkins et al.[13] for alkali earth cryptates.

B. Acid-Catalyzed Dissociation. There is a significant difference in the behavior of $(222K)^+$ and $(222Tl)^+$ in the acid-catalyzed dissociation path. The catalytic rate constant k_H is much larger for $(222Tl)^+$ than for $(222K)^+$ in water (Table I): the attack of a proton on a nitrogen atom has a more destabilizing effect on the transition state of the thallium cryptate than on that of the potassium cryptate. Weiss et al.[19] have observed a shortened Tl-N bond in the crystal structure of $(222Tl)^+$ in agreement with the fact that the cation Tl^+ is a good acceptor for nitrogen atoms and suggesting that this bond has slight covalent character.

A high value of activation enthalpy and a quite positive activation entropy were determined for the acid-catalyzed dissociation of $(222K)^+$ in water (Table I). Lower values of activation enthalpy and negative (or slightly positive) activation entropies were obtained for the thallium cryptates in water

Table II. Thermodynamic and Kinetic Determinations of Stability Constants in Water and at 25 °C

cryptates	no. of binding sites	ionic radius, Å/ radius of the cavity of the ligand, Å	kinetic determinations			equilibrium determinations $\log K_s$
			direct dissociation rate constant k_D, s^{-1}	formation rate constant k_F, L mol^{-1} s^{-1}	$\log K_s$ $K_s = k_F/k_D$	
(222K)$^+$	8	1.33/1.40	7.5 (14) 9 (11) 5.5 ± 0.3	2 × 10^6 (14) 2 × 10^6 (11)	5.4 (14) 5.4 (11)	5.58 (22) 5.3 (2)
(221K)$^+$	7	1.33/1.15	2 × 10^3 (11) 66 (18)	3 × 10^7 (11) 6 × 10^5 (18)	4.2 (11) 4 (18)	3.95 (2)
(222Tl)$^+$	8	1.40/1.40	5.5 ± 0.5	(1.4 ± 0.1) × 10^7 [a]	6.4 ± 0.1	5.5 (22) 6.6 (2)
(221Tl)$^+$	7	1.40/1.15	10.5 ± 0.5	(6.7 ± 0.8) × 10^7 [a]	6.8 ± 0.1	6.5 (2)

[a] Preliminary results.

(Table I). These results show a large difference between the behavior of (222K)$^+$ and thallium cryptates on going to the transition state in the acid-catalyzed dissociation process. Loss of more water molecules by the proton and a larger increase in ligand internal entropy could explain the higher activation entropy observed for (222K)$^+$ than for (222Tl)$^+$ in water. The slightly covalent character of the Tl–N bond,[19] the difference in size of the Tl$^+$ and K$^+$ cations, or the orientation of the 6s lone pair of Tl$^+$ are important features which could play a major role in making the kinetic behavior of (222K)$^+$ different from that of (222Tl)$^+$ in the acid-catalyzed path.

We observe a great solvent effect on the catalyzed dissociation of (222Tl)$^+$: the catalyzed dissociation rate is much slower in methanol–water than in water (Table I). The entropic contribution becomes larger (quite negative entropy) in the mixed solvent than in water; this effect could be explained by considering a reaction between two charged species H$^+$ and CryTl$^+$ in a medium having a lower dielectric constant than water.

The kinetic results for the direct dissociation of potassium and thallium cryptates show that they behave in a very similar manner. However, it is of interest to observe that, in terms of rate constants and activation parameters, the acid-catalyzed dissociation process is significantly different for thallium and potassium 222 cryptates in water.

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