Inorganica Chimica Acta, *147* (1988) 9–15

Kinetic Studies and Thermodynamic Results for Complex Formation and Solvation of Thallium(I) Cryptates in Acetonitrile and in Acetonitrile–Water Mixtures

B. G. COX

Department of Chemistry, University of Stirling, Stirling FK9 4LA, U.K.

J. STROKA

University of Warsaw, Institute of Fundamental Problems of Chemistry, Warsaw, Poland

and H. SCHNEIDER

Max-Planck-Institut für biophysikalische Chemie, D-3400 Göttingen, F.R.G.

(Received October 7, 1987)

Abstract

Stability constants and dissociation rate constants of a range of thallium(I) cryptates in acetonitrile and of the cryptate $Tl(2,2,2)^+$ in water–acetonitrile mixtures have been measured at 25 °C. Solvation free energies of transfer for Tl^+ from water to acetonitrile and to water–acetonitrile mixtures have been estimated from polarographic measurements using the ferrocene assumption. The results allow the calculation of transfer free energy data for the stable cryptate, $TlCry^+$, and for the transition state $(Tl^+...Cry)^{\ddagger}$.

In mixtures of water and acetonitrile the stability constant of $Tl(2,2,2)^+$ increases substantially with increasing acetonitrile content. This variation arises almost equally from an increase in the formation rate constant and a decrease in dissociation rate constant. Alternatively, the increase of stability constants for $Tl(2,2,2)^+$ with increasing mole fraction of acetonitrile results from a strongly decreasing transfer free energy of the cryptate which surpasses in magnitude the increasing transfer free energies of the reactants.

Introduction

The cryptands, first synthesised by Lehn and Sauvage [1], are now well known for their ability to form stable complexes (cryptates) with alkali metal ions in water [2] and in polar organic solvents [3]. The stability constants, K_s, depend strongly upon the size of the cations in relation to the cavity size of the ligands [2, 3] and are also sensitive to ligand variation. K_s increases as the solvent interaction between the cations, M^{n+}, and the solvent molecules decreases [3]. Rate measurements on cryptate complexes have shown that among non-aqueous solvents the dissociation rate constants are influenced more strongly by solvent variation than the formation rate constants [4].

In water–organic solvent mixtures the influence of solvent upon the complexation equilibrium (1) is more complicated. The formation and dissociation

$$M^{n+} + Cry \xrightleftharpoons{K_s} MCry^{n+} \tag{1}$$

rate constants are both sensitive to the water content of the solvent and depend upon preferential solvation of the free cation, the ligand, and the complex by water or the organic component of the mixtures [5–10]. This is true also of complexes of the naturally occurring macrocyclic antibiotics such as valinomycin [11] and calcimycin [12] and is indicative of a strong involvement of water molecules in the complexation reactions.

We have previously investigated reactions of K^+ and Ag^+ with cryptands in mixtures of water and acetonitrile [5–8], these systems being of particular interest because of the strongly contrasting solvation behaviour of the two cations in the mixtures [13]. In this paper we extend this work to include a study of the kinetics and equilibria of the thallium cryptate, $Tl(2,2,2)^+$, in water–acetonitrile mixtures, and of a range of thallium cryptates in acetonitrile (AN). A comparison between the results for Tl^+ and K^+ cryptates is very relevant because the thallium(I) ion is often used as a probe for the potassium cation in biological systems. It may replace K^+ in cells and activate K^+-activated enzymes, and may be monitored much more readily by a variety of spectroscopic and electrochemical techniques [14].

The solvation of $Tl(2,2,2)^+$ in the mixtures has also been studied by combining the complex stability constants with measurements on the solvation of the thallium(I) ions. The results indicate that whereas the Gibbs free energy of transfer of Tl^+, $\Delta G_{tr}(Tl^+)$, from water to water–acetonitrile changes from zero to

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TABLE I. Stability Constants (log K_s) and Gibbs Free Energies of Transfer of Tl^+ and $Tl(2,2,2)^+$ from Water to Water–Acetonitrile Mixtures at 25 °C

$x_{AN} = 1 - x_{H_2O}$	log K_s	$\Delta G_{tr}(Tl^+)$ (kJ mol^{-1})	$-\Delta G_{tr}(Tl(2,2,2)^+)$ (kJ mol^{-1})
0.0	6.6(4)[e] 6.4(0)[a]; 6.3(0)[b]; 6.5[c]	0	0
0.1	7.6(0)[e]	0	8.3
0.3	8.4(6)[f]	0	13.3
0.52	9.2(5)[f]	0	16.0
0.7	9.8(3)[f]	0.7	17.5
0.8	10.9(0)[f]	1.8	20.7
0.9	11.5(5)[f]	3.8	21.2
1.0	12.3(2)[f]; 12.4(7)[f]	9.2[d]	18.5

[a] Ref. 16. [b] Ref. 17. [c] Ref. 18. [d] Ref. 19. [e] Potentiometric determination. [f] Spectroscopic determination.

TABLE II. Stability Constants of Thallium(I) Cryptates in Acetonitrile and Water, and Gibbs Free Energies of Transfer from Water to Acetonitrile at 25 °C[a]

Ligand	log K_s(AN)	log $K_s(H_2O)$[e]	$-[\Delta G_{tr}(Tl(Cry)^+) - \Delta G_{tr}(Cry)]$ (kJ/mol)
(2,1,1)	7.0(2)[b]	3.1(9)	12.7
(2,2,1)	11.9(2)[c]	6.8	20.2
(2,2,2)	12.3(2)[c] 12.4(7)[d]	6.6(4)	23.2
$(2_B,2,2)$	10.3(0)[b]	5.8(4)	16.3
$(2_B,2_B,2)$	10.2(3)[b]	4.6(1)	22.9

[a] $\Delta G_{tr}(Tl^+)$ = 9.2 kJ/mol, ref. 19. [b] Potentiometric determination. [c] Spectroscopic determination against Ag^+. [d] Spectroscopic determination against K^+. [e] Ref. 14.

positive at around $x_{AN} = 0.6$ (preferential solvation by water), the corresponding free energies of transfer of the complex are strongly negative across the whole range of solvent compositions.

The observed variations in the stability constants, the formation rate constants, k_f, and the dissociation rate constants, k_d, are very similar for the K^+- and Tl^+-(2,2,2) complexes, but there are some differences in the absolute values. Thus the K_s and k_f values are in all cases higher for the Tl^+ complexes.

Experimental

The cryptands (2,1,1), (2,2,1), (2,2,2), $(2_B,2,2)$, and $(2_B,2_B,2)$, acetonitrile, trifluoroacetic acid (all from Merck), and $HClO_4$ (Baker 70–72 vol%) were used without further purification. $TlClO_4$ and $TlCF_3CO_2$ salts were prepared by reacting Tl_2CO_3 with $HClO_4$ or CF_3CO_2H, respectively. The resulting salts were twice recrystallised from water and dried under vacuum. The solvent mixtures were prepared by weight.

The stability constants for complexation of Tl^+ with the various ligands were determined by pAg potentiometric titrations, unless otherwise indicated, according to the procedure described earlier [15]. In cases where $K_s(TlCry^+)$ were significantly higher than $K_s(AgCry^+)$, thus rendering the potentiometric method unreliable, the stability constants were determined spectroscopically. Fortunately in a competitive reaction between Tl^+ and K^+ or Ag^+ for a cryptand only the Tl^+-cryptates absorb in the UV region. We determined the stability constants of $Tl(2,2,2)^+$ in solutions with $x_{AN} \geqslant 0.3$ and of $Tl(2,2,1)^+$ in acetonitrile at 250 nm ($\epsilon \sim 3000$ M^{-1} cm^{-1}) and 243 nm ($\epsilon \sim 5500$ M^{-1} cm^{-1}) respectively using the stability constants of $AgCry^+$ and $KCry^+$ [3]. At $x_{AN} = 0.30$ the stability constant of $Tl(2,2,2)^+$ from spectroscopic measurements in solutions with Ag^+ and K^+ is in good agreement with the result from potentiometric titrations. The results obtained are presented in Tables I and II.

The dissociation rate constants of the $TlCry^+$ complexes were obtained from measurements on the reactions of the cryptates with excess acid, monitored using an all-glass stopped-flow apparatus with conductometric detection. When an excess of perchloric acid ($x_{AN} \leqslant 0.8$) or trifluoroacetic acid ($x_{AN} \geqslant 0.8$) was mixed rapidly with a cryptate solution, a pseudo-first

$$\mathrm{TlCry^+ + 2H^+(2CF_3CO_2H)} \xrightarrow{k_e} \mathrm{Tl^+ + CryH_2{}^{2+} (+ 2CF_3CO_2{}^-)} \qquad (2)$$

order reaction, eqn. (2), was found, with the observed first order rate constant, k_e being linearly dependent on the acid concentration, as in eqns. (3) and (4).

$$k_e = k_d + k_H[H^+] \qquad (3)$$

$$k_e = k_d + k_{HA}[CF_3CO_2H] \qquad (4)$$

Cryptand concentrations were in the range 10^{-4} – 10^{-3} mol dm^{-3}, and the metal ion concentration always 2–5 times higher to ensure that the proportion of uncomplexed ligand was low. The acid was in 2–100 fold excess over the cryptand.

For the reactions studied using perchloric acid as scavenger, k_d and k_H were determined from the intercepts ($[H^+] = 0$) and slopes, respectively, of plots of k_e against acid concentration, after appropriate correction to zero ionic strength [15, 20] using activity coefficients, $\gamma_\pm$, calculated using the Davies equation [21]. Where CF_3CO_2H was used as scavenger, eqns. (2) and (4), k_d values were obtained by extrapolating k_e to zero acid concentration, using the average concentration of CF_3CO_2H during the reaction (CF_3CO_2H is a weak acid in solutions for which $x_{AN} \geqslant 0.8$), as illustrated in Fig. 1

The formation rate constants were obtained by combining the stability constants with k_d values ($K_s = k_f/k_d$). The dissociation and formation rate constants are listed in Tables III and IV.

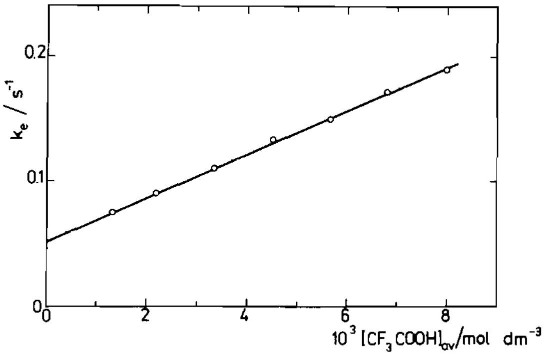

Fig. 1. Dissociation rate of $Tl(2_B,2_B,2)^+$ as a function of acid concentration in acetonitrile solution at 25 °C.

The Gibbs free energies of transfer of thallium(I) from water to water–acetonitrile mixtures were estimated from the difference, ΔE_f, between the formal potentials of the $Tl^+/Tl(Hg)$ electrode in water and in the solvent mixtures in question, relative to the ferrocinium/ferrocene electrode as reference, eqn. (5). It was assumed that the potential of the

$$\Delta G_{tr}(Tl^+) = -zF\Delta E_f(Tl^+/Tl(Hg)) \qquad (5)$$

latter is independent of the solvent [22]. The formal potentials of $Tl^+/Tl(Hg)$ in the mixtures were determined polarographically according to the procedure described [23] using a PAR electrochemical system (model 174). The concentration of Tl^+ was 2×10^{-3} M, and tetraethylammonium perchlorate (0.1 M) was

TABLE III. Rate Constants of Dissociation (k_d), Formation (k_f) and Catalysis (k_H) for the Cryptate $Tl(2,2,2)^+$ in Water–Acetonitrile Mixtures at 25 °C

$x_{AN} = 1 - x_{H_2O}$	$k_d{}^a$ (s^{-1})	$10^{-8} \times k_f$ ($M^{-1}\ s^{-1}$)	$k_H{}^b$ ($M^{-1}\ s^{-1}$)	k_H/k_d
0.0	5.5^c	0.24	2200^c	400
0.1	2.55	1.02	844	331
0.3	0.751	2.17	281	374
0.52	0.325	5.78	170	523
0.7	0.194	13.1	127	655
0.8	0.0605	48.1	136	225
0.9	0.00919	32.6	119^d	12950
1.0	0.00116	24.2	13.2^d	11400

$^a\Delta k_d = \pm 10\%$. $^b\Delta k_H = \pm 3\%$. ^{c}Ref. 16. $^d k_{HA}$ values.

TABLE IV. Formation and Dissociation Rate Constants of Thallium Cryptates in Acetonitrile at 25 °C

Ligand	k_d (s^{-1})	k_f ($M^{-1}\ s^{-1}$)	k_{HA} ($M^{-1}\ s^{-1}$)	k_{HA}/k_d (M^{-1})
(2,2,1)	0.000427	3.55×10^8	8.98	21030
(2,2,2)	0.00116	2.42×10^9	13.2	11400
(2_B,2,2)	0.00262	4.52×10^7	45.08	17206
(2_B,2_B,2)	0.05326	9.10×10^8	17.05	320

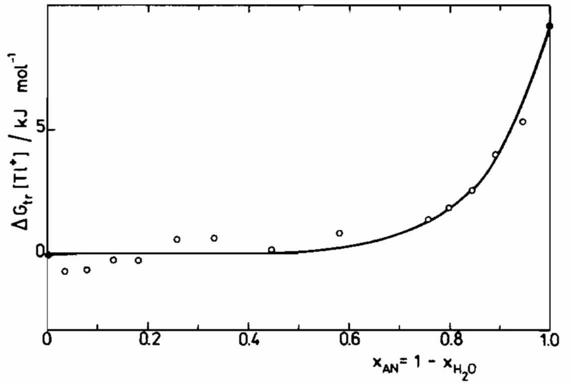

Fig. 2. Free energies of transfer of Tl^+ ion as a function of x_{AN} in water–acetonitrile mixtures at 25 °C. ●, $\Delta G_{tr}(Tl)^+$ from ref. 19.

used as supporting electrolyte. The reduction wave of the thallium(I) was reversible in all of the solutions investigated. The values of $\Delta G_{tr}(Tl^+)$ evaluated in this way are shown in Fig. 2.

Discussion

The stability constants of the $Tl(2,2,2)^+$ complex increase substantially and steadily with increasing acetonitrile content of the solvent (Table I). The observed variation in K_s for $Tl(2,2,2)^+$ with solvent composition is very similar to that of $K(2,2,2)^+$ in the same mixtures, as illustrated in Fig. 3, where log $K_s(x_{AN})/K_s(H_2O)$ is plotted against x_{AN}. The absolute values of the Tl^+ stability constants are, however, about one order of magnitude larger than those of K^+. These changes in stability constants with x_{AN} arise almost equally from an increase in the formation rate constant (about 2.5 orders of magnitude over the whole range) and a decrease in dissociation rate constant (about 3 orders of magnitude), Table III.

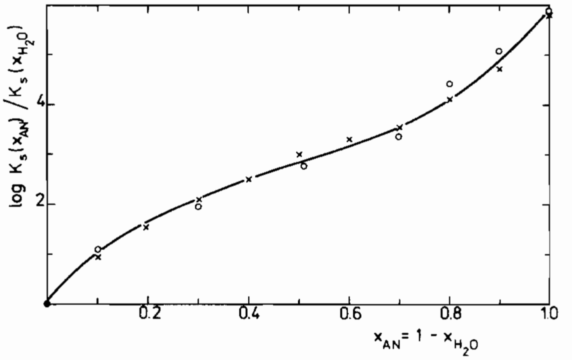

Fig. 3. Stability constant of ○, $Tl(2,2,2)^+$ and x, $K(2,2,2)^+$ in acetonitrile + water mixtures at 25 °C.

In qualitative terms it is clear that the changes in K_s, k_f, and k_d cannot be attributed solely or largely to variations in the free energies of any one of the reactants or products separately, and that the transition state differs significantly in solvation from reactants and products. However, in the composition range $0.7 \leqslant x_{AN} \leqslant 1.0$ there is evidence of a significant influence of the solvation of Tl^+ on the reactions. Thus in this region there is a sharp increase in K_s and a corresponding decrease in k_d which parallels the decrease in solvation of Tl^+ (Fig. 2). These results are considered more quantitatively below.

The catalytic constant for the H^+ catalysed dissociation of $Tl(2,2,2)^+$ decreases quite strongly from pure water to $x_{AN} = 0.5$, and more slowly to $x_{AN} = 0.8$ (Table III). However, in comparison to the uncatalysed k_d value it remains relatively unchanged to about $x_{AN} = 0.7$; beyond this region k_H/k_d increases sharply (Fig. 4) as do the corresponding values for dissociation of $K(2,2,2)^+$ and $Ag(2,2,2)^+$ [6]. The increase in k_H/k_d at high mole fractions of acetonitrile probably arises predominantly from the increased reactivity of the proton as the water content of the mixtures decreases [6].

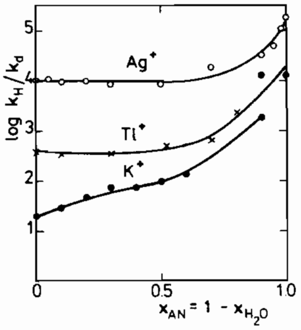

Fig. 4. Dependence of k_H/k_d *vs.* mole fraction of acetonitrile for $Tl(2,2,2)^+$, $K(2,2,2)^+$ and $Ag(2,2,2)^+$ cryptates at 25 °C. ⊗, denote k_{HA}/k_d values.

It is noticeable that the relative importance of the acid catalysed pathway for cryptate dissociation increases in the series $K(2,2,2)^+ < Tl(2,2,2)^+ < Ag(2,2,2)^+$, *i.e.* protonation of the nitrogen atom has a greater destabilising effect on the metal–ligand interaction energy in the transition state for Tl^+ and especially for Ag^+ than for K^+ complexes. The high stabilities of Ag^+ complexes of nitrogen-containing macrocycles have been attributed to a specific and at least partly covalent Ag^+–N interaction [2, 24], and the present results are indicative of a similar although weaker covalent Tl^+–N interaction [25].

Further support for a specific interaction between Tl^+ and the cryptand ligands comes from a comparison between the stability constants of Tl^+ and K^+ cryptates [3] in acetonitrile, both in terms of the absolute magnitudes and of the variations with cavity size. The K_s value for the Tl^+ complex of (2,2,2) in acetonitrile is 0.9 log units higher than that of K^+ [3], despite the larger size of Tl^+ ($r_{Tl} = 1.44$ Å, *cf.* $r_K = 1.33$ Å) [26]. In contrast, the stability constant of the Rb^+ complex ($r_{Rb} = 1.48$ Å) is almost 2 log units lower than that of K^+. Furthermore, the difference between the stabilities of Tl^+ and K^+ complexes increases to 2.4 and 4.2 log units on changing to the smaller ligands (2,2,1) and (2,1,1), respectively [3]. These trends are in exactly the opposite direction to those expected if the K_s values of the Tl^+ cryptates were determined to the same extent by the relationship between the sizes of the cation and ligand cavity as those of the alkali metal cations. The effects are considerably smaller than those for the corresponding Ag^+ complexes, but are nevertheless significant.

In order to discuss the variations of stability constants and rate constants with solvent in terms of the solvation of the reactants, products and transition states, we have calculated the Gibbs free energies of transfer of the various species from water to the solvent mixtures. These follow from eqn. (6) for the stable cryptates, and from eqn. (7) for the transition state.

$$\Delta G_{tr}(Tl(Cry)^+) = \Delta G_{tr}(Tl^+) + \Delta G_{tr}(Cry) - RT \ln K_s(x_{AN})/K_s(H_2O) \qquad (6)$$

$$\Delta G^{\ddagger}_{tr}(Tl^+ \ldots Cry) = \Delta G_{tr}(Tl^+) + \Delta G_{tr}(Cry) - RT \ln k_f(x_{AN})/k_f(H_2O) \qquad (7)$$

The results presented in Fig. 2 for $\Delta G_{tr}(Tl^+)$ are typical of those expected for a cation which is preferentially solvated by water in the mixtures [13, 23]. In solvent mixtures with high water content ($0 \leqslant x_{AN} \leqslant$ *ca.* 0.6), $\Delta G^{\circ}_{tr}(Tl^+)$ remains close to zero. It then increases sharply as the last few percent of water is removed ($0.8 \leqslant x_{AN} \leqslant 1.0$) and water molecules in the solvation shell of the Tl^+ ions are replaced by acetonitrile molecules.

The free energies of transfer of $Tl(2,2,2)^+$ are negative in all of the solvent mixtures and the decrease is especially marked at low mole fractions of acetonitrile. The results are qualitatively similar to those for $Ag(2,2,2)^+$, $K(2,2,2)^+$ [27], and large organic cations. For example $\Delta G_{tr}(Tl(2,2,2)^+)$ is comparable to that of Ph_4As^+ ($\Delta G_{tr} = -32.6$ kJ mol^{-1}) [19]. The most likely explanation for this behaviour is that the Tl^+ is encapsulated by the cryptand [28], with the strong interactions between Tl^+ and the ligand donor atoms ensuring that the organic sheath of the ligand is exposed to the solvent.

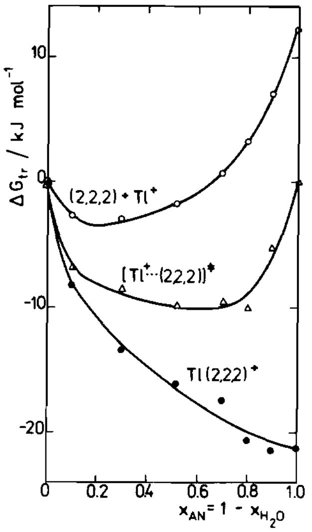

Fig. 5. The Gibbs free energies of transfer of reactants, transition states and products for the formation of $Tl(2,2,2)^+$ in water–acetonitrile mixtures at 25 °C.

The broad features of the results for the free energies of transfer of the transition state (Fig. 5) are similar to those of the reactants (Tl^+ and (2,2,2)) but the absolute values are substantially more negative, and intermediate between those of the reactants and products. In discussing these results we may consider three factors which will contribute to the solvation behaviour of the transition state: (i) the preferential hydration of the nitrogen and oxygen atoms of the ligand [5, 27], (ii) the preferential solvation of Tl^+ by water molecules [19], and (iii) the solvation of the hydrocarbon part of the ligand by acetonitrile. The relative importance of these factors will depend upon the extent to which Tl^+ has entered the ligand cavity in the transition state. The significant decrease of $\Delta G^{\ddagger}_{tr}(Tl^+ \ldots (2,2,2))$ at low x_{AN} suggests that in the transition state reorientation of the ligand has already occurred, such that more favourable interactions with acetonitrile may occur (*cf.* the stable complex). However, the rapid increase in ΔG_{tr} at $x_{AN} > 0.8$ is characteristic of the desolvation of Tl^+ and of the loss of any remaining hydration of the ligand donor atoms [5]. We conclude from this that in the transition state the Tl^+ cation remains largely outside the ligand cavity and still interacts directly with the solvent. But, unlike reactions confined to non-aqueous media, the hydration of the ligand donor atoms and its disruption during complex formation (or conversely its onset during dissociation) plays an important role in cryptand complexation reactions in water–acetonitrile mixtures. Similar comments are expected to apply to other ionophores, and other water–organic solvent mixtures.

The stability constants of all of the $Tl(Cry)^+$ complexes are markedly larger in acetonitrile than in water (Table II). The increase is almost four log units for (2,1,1) and between five and six log units for complexes of the other ligands. The increased stabilities are in agreement with the reduced solvation of Tl^+ in acetonitrile compared with water, but this does not seem to be the complete explanation. If the difference in the stability constants in the two solvents depends only on the solvation of Tl^+, then it follows from eqn. (6) that $\Delta G_{tr}(Tl(Cry)^+) - \Delta G_{tr}(Cry)$ should be independent of the ligand and also close to zero. The former requirement, which may be tested unambiguously, holds almost within experimental error (Table II) except for the (2,1,1) complex, for which there is the greatest difference between the cation and cavity size [2]. On the basis of the ΔG_{tr}-(Tl^+) values given in Fig. 2, however, $\Delta G_{tr}(Tl(Cry)^+)$ $- \Delta G_{tr}(Cry)$ differs considerably from zero, and thus the stabilities of the complexes are determined also by changes in the solvation of the complexes and ligands in water and in acetonitrile. This most likely results from specific interactions with the water molecules, as corresponding results for transfer among a range of non-aqueous solvents are consistent with the assumption that $\Delta G_{tr}(Tl(Cry)^+) = \Delta G_{tr}(Cry)$. Although water molecules may interact with the ligand donor atoms or with the cation through gaps in the ligand bridges, the cryptate is – like large organic ions – more strongly solvated by acetonitrile than by water.

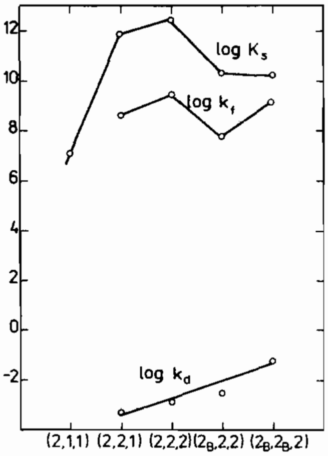

Fig. 6. Stability constant and rate constant for formation and dissociation of thallium cryptates in acetonitrile at 25 °C.

Finally, we conclude with some general observations with regard to the kinetics of the complexation reactions (Table IV). The k_f values are all high and relatively insensitive to the ligand. The k_d values increase steadily in the order $(2,2,1) < (2,2,2) < (2_B,2,2) < (2_B,2_B,2)$ and strongly from (2,2,1) to (2,1,1) (k_d for $Tl(2,1,1)^+$ was too large to measure by stopped flow), (Fig. 6). These variations of k_d with ligand are the same as those observed for Tl^+ cryptates in several non-aqueous solvents [14]. The high k_d value for $Tl(2,1,1)^+$ is almost certainly related to the fact that Tl^+ is much too large to fit properly into the cavity of (2,1,1), as discussed above.

One additional point which may be noted from the results in Table IV is the marked reduction in the sensitivity of the dissociation rate of the $(2_B,2_B,2)$ complex to acid catalysis. This results mainly from the decreased flexibility of the dibenzo ligand [2] which will hinder the formation of conformations in which the catalyst can interact with the nitrogen atoms. A similar effect was noted for the thallium cryptate in other solvents [14], and indeed for those of alkali metal cations [29]. However, unlike complexes of K^+ and Rb^+, the introduction of a single benzene ring in forming $(2_B,2,2)$ does not significantly alter the susceptibility to acid catalysis of the Tl^+ complex.

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