from an alcohol or ether.[50] The α-C–H bond energy in methyl amine[51] now appears to be similar to that in methanol[52] (94 kcal/mol), and the values would be decreased somewhat in both cases for secondary and tertiary α-C–H to values substantially less than those for N–H and O–H bonds. The direct abstraction might be more rapid from α-C–H of amines than from alcohols due to greater polar contribution to the transition state. However the much higher rate constants indicate initial charge transfer (process a of eq 16).

Reaction of a triplet with a primary or secondary amine that contains both N–H and α-C–H may also begin by reversible charge transfer which channels to two transition states, one in which the N–H bond is stretched, as in step a of eq 15, and one in which the α-C–H is stretched, as in step a of eq 16, leading to abstraction from N and α-C, respectively. Alternatively two independent reactions may occur, one starting by abstraction from N, as in eq 15b, the other from α-C as in process b of eq 16. However, abstraction from N in these systems, which contain α-CH, need not lead essentially entirely back to starting materials as it does with *tert*-butyl amine. These aminyl radicals may be oxidized to imines by ground-state ketone (eq 4), and the efficiency of the reduction would be determined by the relative rates of this to that of disproportionation (eq 5).

The very high rate constants, the general effectiveness of reduction by amines, the observation of radical ions in the benzophenone–*tert*-butylamine system in hydroxylic solvents,[6] and the occurrence of the k_e process in aminoketones[53,54] and in reactions with Dabco[36,37] and quinuclidine[41] support the initial charge-transfer mechanisms, a processes of eq 15 and 16, over initial attack on N–H and α-C–H, b processes of eq 15 and 16. Support for the initial charge-transfer mechanism is also found in photoreduction by methionine.[55] In this system a high value of k_{ir} indicates that the reaction starts by charge transfer with S, a process which normally leads to low radical yield and to little reduction.[56] High quantum yield is then best explained by subsequent charge transfer from N to $S^{+\cdot}$ and reaction of the $N^{+\cdot}$ species.

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Solvent Dependence of the Kinetics of Formation and Dissociation of Cryptate Complexes

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Abstract: The rates of dissociation of a variety of alkali metal cations and Ca^{2+} cryptates have been measured in several solvents. These have been combined with measured stability constants to give the corresponding formation rates. The dissociation rates are very sensitive to solvent variation, covering a range of more than 9 orders of magnitude. Except for (2,1,1) cryptates, formation rates are all within the range 10^6–10^9 M^{-1} s^{-1}. Changes in stability constants, whether from a change in the cation, ligand, or solvent, are largely reflected in changes in dissociation rates. The properties of the transition state, particularly with respect to solvent variation, most closely resemble those of the reactants, suggesting that the transition state lies close to the reactants. The dissociation rates increase sharply with increasing donor number of the solvent, whereas the formation rates decrease but are much less sensitive to solvent variation. On the basis of these correlations, formation rates in water are much lower than expected and dissociation rates much higher than expected. It is suggested that this is due to the H-bonded interactions between water and the electronegative atoms (O and N) of the ligands.

Introduction

Most of the applications of the synthetic macrocyclic ligands are based on their ability to form stable complexes with metal ions and their selectivity toward metal cations. These equilibrium properties, however, only give information about the initial and final states of the system. From both a practical and mechanistic point of view, the dynamic characteristics of the process of complexation and decomplexation are important. Of particular interest are the kinetic origin of the ligand selectivities and also the mechanism by which the solvent molecules associated with the uncomplexed cations are replaced during complexation.

Caldin and Bennetto[1,2] have considered the influence of solvent on ligand substitution reactions at some divalent transition-metal cations in terms of the Eigen–Wilkins[3] mechanism for ligand substitution and found evidence of a strong influence of solvent structure on the relative rates of ligand substitution and solvent exchange. The effects are particularly marked when bidentate or tridentate ligands are involved. To date, however, there have been no systematic studies of the effect of solvent on the formation and dissociation rates of complexes formed between alkali and alkaline earth cations and macrocyclic ligands. These systems are of interest both in relation to the general problem of ligand exchange and substitution at metal centers and to ligand-facilitated transport of ions through membranes.[4-6] In addition, there now

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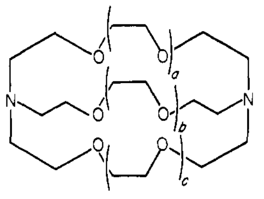
Table I. Rates of Dissociation of Cryptates in Several Solvents at 25 °C

	k_d/s^{-1} [a]						
cryptate	H_2O[b]	MeOH[c]	EtOH	Me_2SO	DMF	NMP	PC[d]
$Li(2,1,1)^+$	2.5×10^{-2}	4.4×10^{-3}	6.0×10^{-4}	2.12×10^{-2} [e]	1.40×10^{-2} [f]	4.81×10^{-3}	$<10^{-5}$
$Na(2,1,1)^+$	1.4×10^{2}	2.50	7.1×10^{-1}	ca. 5		4.7×10^{-1}	3.6×10^{-2}
$Ca(2,1,1)^{2+}$	8.2×10^{-1}				ca. 2×10^{-1}		
$Li(2,2,1)^+$		7.5×10	ca. 1.3×10				
$Na(2,2,1)^+$	1.45×10	2.35×10^{-2}	2.62×10^{-3}	7.5×10^{-1}	2.5×10^{-1}	1.67×10^{-1}	$<10^{-2}$
$K(2,2,1)^+$	2.0×10^{3}	1.09	1.35×10^{-1}		ca. 2.6	1.35	3.7×10^{-2}
$Rb(2,2,1)^+$		7.5×10	1.1×10				7.5
Cs(2,2,1)		ca. 2.3×10^{4}	ca. 2×10^{3}				ca. 4×10^{2}
$Ca(2,2,1)^+$	6.1×10^{-4}				8.0×10^{-4}		
$Na(2,2,2)^+$	1.47×10^{2}	2.87	3.0×10^{-1}			5.68	<1
$K(2,2,2)^+$	7.5	1.8×10^{-2}	4.08×10^{-3}	2.68	4.0×10^{-1}	1.33×10^{-1}	3×10^{-3}
$Rb(2,2,2)^+$	1.4×10^{2}	8.0×10^{-1}	9.17×10^{-2}			5.0×10^{-1}	1.7×10^{-1}
$Cs(2,2,2)^+$		ca. 4×10^{4}					ca. 3×10^{2}
$Ca(2,2,2)^{2+}$	2.1×10^{-1}				4.4×10^{-2}		

[a] k_d values to ±5% unless otherwise stated. [b] Values from ref 9-13. [c] Values from ref 14. [d] Values from ref 15. [e] Cf. ref 20 gives $k_d = 2.32\ (\pm 0.54) \times 10^{-2}\ s^{-1}$. [f] Cf. values of $k_d = 1.30\ (\pm 0.33) \times 10^{-2}$ [20] and $k_d = 1.53\ (\pm 0.08) \times 10^{-2}$.[23]

exists a considerable amount of thermodynamic data on the interactions between alkali metal cations and a variety of solvents.[7,8]

In this paper we report a study of the solvent dependence of the rates of formation and dissociation of cryptate complexes,[4] formed between the macrobicyclic cryptand ligands **1**-**3** (Cry)[4] and various alkali metal cations and Ca^{2+}. In addition to results already available in water,[9-13] methanol,[14] and propylene carbonate (PC),[15] we have obtained results in ethanol, *N*-methylpropionamide (NMP), dimethyl sulfoxide (Me_2SO), and dimethylformamide (DMF). Dissociation rates k_d have been measured by using a conductimetric technique described earlier[11,14,15] and the corresponding formation rates k_f obtained by combining the k_d values with stability constants K_s ($=k_f/k_d$) measured in the various solvents.[16]



1, $a = 1, b = c = 0$ (2,1,1)
2, $a = b = 1, c = 0$ (2,2,1)
3, $a = b = c = 1$ (2,2,2)

Experimental Section and Results

(a) Materials. Cryptands (2,1,1), (2,2,1), and (2,2,2) were purchased from Merck and used without further purification. Their purities have been checked by pH-metric, conductimetric, and NMR methods.

The preparation, where appropriate, and purification of the solvents have been described previously.[16]

Inorganic salts were as previously used,[16] except for the following: in EtOH, LiCl (BDH, LR), KI (M & B Pronalys, AR), and RbCl (JMC, Specpure); in Me_2SO, KNO_3 (Fisons, AR).

Dichloroacetic acid (DCA) solutions were prepared by dissolving the neat liquid (BDH LR) in the appropriate solvent. The resulting solutions were analyzed by titration against standard alkali.

Hydrochloric acid solutions were prepared by bubbling HCl gas (BOC) into the solvent (DMF) or by adding concentrated aqueous HCl (Fisons, AR, specific gravity 1.18) to the solvent (EtOH). In the latter case, the amount of water introduced to the solvent was less than 0.1%, even in the most concentrated HCl solutions used ($\leq 10^{-2}$ M). The HCl solutions were standardized against standard alkali.

(b) Kinetic Measurements. The reactions were followed conductimetrically by using a Durrum-Gibson stopped-flow apparatus with conductance detection for faster reactions or a conventional conductance cell. Earlier studies in water,[11,17] methanol[14] and propylene carbonate[15] have shown that the dissociation rates may be conveniently measured by following the conductance changes after the addition of excess acid (either H^+ or HA) to an equilibrium cation–cryptand mixture.

$$MCry^{n+} + 2H^+ \xrightarrow{k_e} M^{n+} + CryH_2^{2+} \tag{1}$$

$$MCry^{n+} + 2HA \xrightarrow{k_e} M^{n+} + CryH_2^{2+} + 2A^- \tag{2}$$

The very high mobility of H^+ in water, methanol, and ethanol means that a significant decrease in conductance accompanies reaction 1 in these solvents. In other nonaqueous solvents, it is generally more convenient to follow the increase in conductance accompanying reaction 2 in which a weak acid HA (dichloroacetic acid in this study) is used. Details of the use of both strong and weak acids in the dissociation of cryptates have been given previously.[11,17] It can be readily shown that for a reaction path represented in Scheme I,[18] i.e., the acid is acting as a scavenger for the free Cry in equilibrium with $MCry^{n+}$, the observed rate law is given by eq 3 and 4. Provided $k[HA] \gg k_f[M^{n+}]$, eq 4 simplifies to eq 5; i.e.,

$$-\frac{d[MCry^{n+}]}{dt} = k_e[MCry^{n+}] \tag{3}$$

$$k_e = \frac{k_d k[HA]}{k_f[M^{n+}] + k[HA]} \tag{4}$$

$$k_e = k_d \tag{5}$$

the dissociation of the cryptate is the rate determining step in the overall reaction. Under such circumstances the observed rate is independent of the [HA] and $[M^{n+}]$. When particularly rapid rates of complex formation (k_f very large) occur, k_d may be obtained from the intercepts of plots of k_e^{-1} against $[M^{n+}]$ at constant [HA]. Values of k_f may be

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[18] In Scheme I, the second protonation step (to give CrH^{2+}) has been ignored. This may be investigated independently and, except where otherwise stated, occurs rapidly compared with the overall rate of reactions 1 and 2, and simply affects the magnitude of the overall conductance change.

Table II. Rates of Formation of Cryptates in Several Solvents at 25 °C

	$k_f{}^a$/M^{-1} s^{-1}						
cryptate	H_2O	MeOH	EtOH	Me_2SO	DMF	NMP	PC
$Li(2,1,1)^+$	8.0×10^3	4.8×10^5	1.8×10^5	1.5×10^4	1.4×10^5	1.3×10^4	$<3 \times 10^7$
$Na(2,1,1)^+$	2.2×10^5	3.1×10^6	8.8×10^6	ca. 2×10^5		5.4×10^4	2.1×10^7
$Ca(2,1,1)^{2+}$	2.6×10^2				ca. 2.4×10^2		
$Li(2,2,1)^+$		1.8×10^7	ca. 3×10^6				
$Na(2,2,1)^+$	3.6×10^6	1.7×10^8	4.2×10^7	7.2×10^6	1.8×10^7	5.9×10^5	
$K(2,2,1)^+$	1.8×10^7	3.8×10^8	4.9×10^7		ca. 1.3×10^7	1.7×10^6	2.8×10^8
$Rb(2,2,1)^+$		4.1×10^8	8.3×10^7				8.0×10^7
$Cs(2,2,1)^+$		ca. 5×10^8	ca. 1×10^8				ca. 3.3×10^7
$Ca(2,2,1)^{2+}$	5.4×10^3				3.7×10^3		
$Na(2,2,2)^+$	1.2×10^6	2.7×10^8	1.1×10^8			3.8×10^6	
$K(2,2,2)^+$	2.0×10^6	4.7×10^8	1.3×10^8	3.5×10^7	3.8×10^7	ca. 1×10^7	4.6×10^8
$Rb(2,2,2)^+$	3.1×10^6	7.6×10^8	1.7×10^8			9.5×10^6	1.8×10^8
$Cs(2,2,2)^+$		ca. 9×10^8					ca. 5×10^6
$Ca(2,2,2)^{2+}$	5.4×10^3				3.1×10^2		

[a] k_f values obtained from $k_f = k_d K_s$, using K_s values from ref 16 and k_d values from Table I.

obtained by combining k_d values, measured as described above, with stability constants, K_s ($=k_f/k_d$), for complex formation.

Scheme I

$$MCry^{n+} \underset{k_f}{\overset{k_d}{\rightleftharpoons}} M^{n+} + Cry$$

$$Cry + HA \xrightarrow{k} CryH^+ + A^-$$

In addition to the mechanism shown in Scheme I, it has been shown previously that both H^+[11,14,19] and general acids[17] catalyze the dissociation of some cryptates. Under these circumstances, k_e has the form shown in eq 6, where HA is used to represent any acid that may be

$$k_e = k_d + k_{HA}[HA] \qquad (6)$$

present, and k_d and k_{HA} values may be obtained from the variation of k_e with [HA].

Dissociation rates (k_d/s^{-1}) and formation rates (k_f/M^{-1} s^{-1}) for the cryptates in the various solvents are listed in Tables I and II. Individual comments on the methods and conditions used in the various solvents are given below.

Ethanol. Metal ion and hydrochloric acid concentrations varied between 5×10^{-4} M and 10^{-2} M. Cryptand concentrations were ca. 10^{-4}–5×10^{-4} M and a factor of 5–20 lower than [HCl]. The observed rates were independent of [M^+], except for $K(2,2,2)^+$ and $Rb(2,2,2)^+$; in these cases the variation could be quantitatively accounted for in terms of eq 4. The dissociations of $Li(2,1,1)^+$, $Na(2,2,1)^+$, and $Na(2,2,2)^+$ were subject to catalysis by HCl, and k_d values were obtained from eq 6. The value obtained for $Rb(2,2,1)^+$ is approximate only because of interference to the observed rates by the second protonation step.[18]

Dimethyl Sulfoxide. The rate of the second protonation step[18] in Me_2SO was sufficiently slow to interfere with the dissociation of all but the most stable (lowest dissociation rates) of the cryptates: $Li(2,1,1)^+$, $Na(2,2,1)^+$, and $K(2,2,2)^+$. An estimate of k_d for $Na(2,1,1)^+$ was also obtained. Dichloroacetic acid concentrations were ca. 10^{-3}–4×10^{-2} M, [M^+] ca. 5×10^{-4}–3×10^{-3} M, and [Cry] ca. 10^{-4}–5×10^{-4} M. In all cases, the rates were independent of both acid and metal ion concentration. Cahen, Dye, and Popov's[20] value of $k_d = 2.32\ (\pm 0.54) \times 10^{-2}$ s^{-1} for $Li(2,1,1)^+$, obtained by lithium-7 NMR, is in good agreement with the present value of $k_d = 2.12\ (\pm 0.1) \times 10^{-2}$ s^{-1} (see below).

***N*-Methylpropionamide.** There was no evidence of acid-catalyzed dissociation in any of the systems studied, even with dichloroacetic acid concentrations up to 2×10^{-2} M. Observed rates for $Na(2,2,1)^+$, $K(2,2,1)^+$, $K(2,2,2)^+$, and $Rb(2,2,2)^+$ showed some dependence on [M^+], but again this could be quantitatively accounted for in terms of eq 4. Metal ion concentrations used were ca. 10^{-3}–10^{-2} M, [dichloroacetic acid] ca. 10^{-3}–2×10^{-2} M, and [Cry] ca. 2×10^{-4}–10^{-3} M.

Dimethylformamide. For the most stable complexes, $Li(2,1,1)^+$, $Na(2,2,1)^+$, and $K(2,2,2)^+$, two acids were used for the measurements: dichloroacetic acid whose pK_a in DMF is 7.2[21] and HCl whose pK_a = 3.4.[22] At the acid concentrations used, DCA is essentially undissociated whereas HCl is significantly dissociated. When DCA was used to displace the metals from these cryptates, it was found that (a) the observed rates decreased with increasing acid concentration, with the rate constants levelling off to a constant value at higher DCA concentrations, and (b) the observed increase in conductance during the reaction was smaller at lower DCA concentrations. Both of these observations suggest that, at lower [DCA], the protonation reaction (eq 2) is not going to completion and that the observed rates represented the rate of approach to equilibrium. At higher [DCA] when the equilibrium is displaced almost completely to the right, the measured rates should correspond to the true dissociation rate. We have therefore used the rates extrapolated to high [DCA] ($>5 \times 10^{-2}$ M). In order to check these values, we also carried out the reactions using the much stronger acid HCl. For each of the systems, k_d values were obtained by using eq 4 as described earlier. There was no evidence of acid catalysis for [HCl] up to 10^{-2} M. Results for the two acids were the same within experimental error. Furthermore, it is possible to compare the results for $Li(2,1,1)^+$ with those obtained earlier by Cahen et al.[20] from ^{7}Li NMR studies and Gutknecht[23] by using methanesulfonic acid. The results obtained are as follows: (i) present values, k_d/s^{-1} = $1.4\ (\pm 0.1) \times 10^{-2}$ (DCA), $k_d = 1.56\ (\pm 0.06) \times 10^2$ (HCl); (ii) Cahen et al.[20] k_d/s^{-1} = $1.30\ (\pm 0.33) \times 10^{-2}$; (iii) Gutknecht,[23] k_d/s^{-1} = $1.53\ (\pm 0.08) \times 10^{-2}$. For the other cryptates studied, HCl was used as a scavenging acid. For $Ca(2,2,1)^{2+}$ and $Ca(2,2,2)^{2+}$, the rates were independent of acid and metal ion concentrations. The reactions of $K(2,2,1)^+$ and $Ca(2,2,1)^{2+}$ were studied over a range of acid and metal ion concentrations, and the results analyzed according to eq 4. The results obtained for $Ca(2,1,1)^{2+}$ and $K(2,2,1)^+$ are subject to larger uncertainties as the measured rates are close to those of the second protonation step.[18] The concentration ranges used in DMF were as follows: [HCl] = 10^{-3}–10^{-2} M, [DCA] = 10^{-3}–6×10^{-2} M, [M^{n+}] = 7×10^{-4}–10^{-2} M, [Cry] = 10^{-4}–5×10^{-4} M.

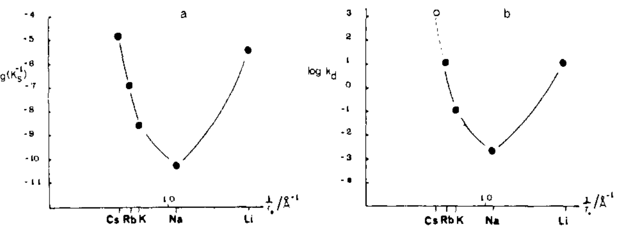

Figure 1. Variation of stability constants (a) and dissociation rates (b) with cation size of (2,2,1) cryptates in ethanol.

Discussion

The alkali metal cryptates in the solvents studied show very wide variations in stability constants and dissociation rates—K_s values vary by some 11 orders of magnitude[16] and k_d values by over 9 orders of magnitude (Table I). However, formation rates vary over a much smaller range, and, with the exception of $Li(2,1,1)^+$ and $Na(2,1,1)^+$, k_f values are all within the range 10^6–10^9

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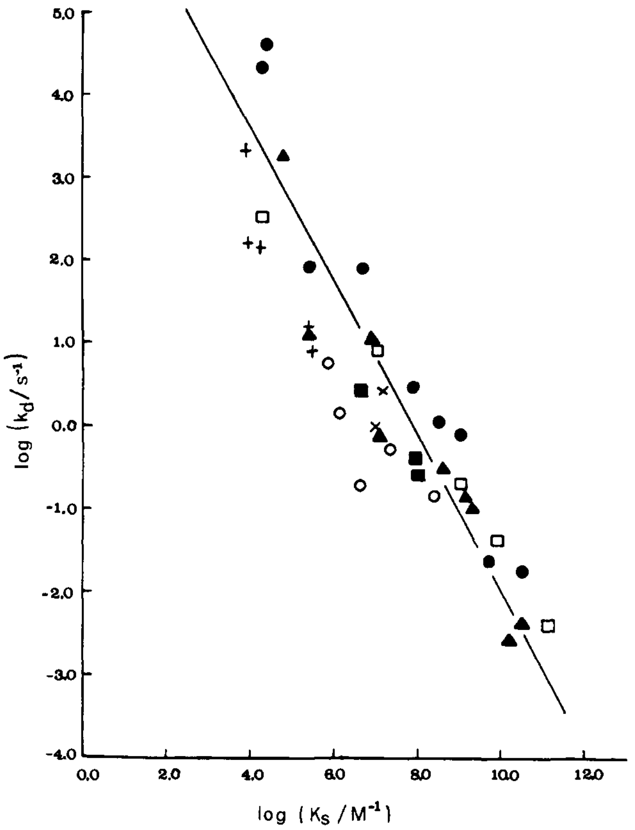

Figure 2. Dissociation rates and stability constants of (2,2,2) and (2,2,1) cryptates in several solvents: (+) H_2O; (●) MeOH; (▲) EtOH; (×) Me_2SO; (■) DMF; (○) NMP; (□) PC.

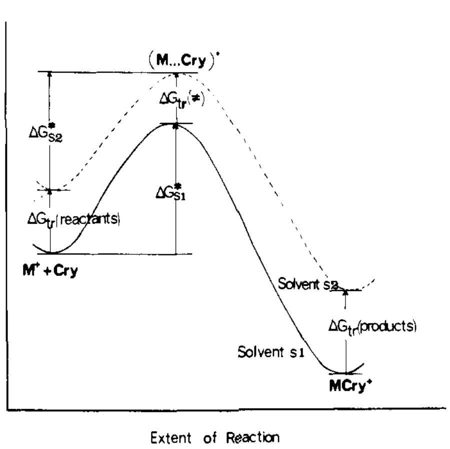

Figure 3. Solvent effect upon reactants, transition state, and products for cryptate formation.

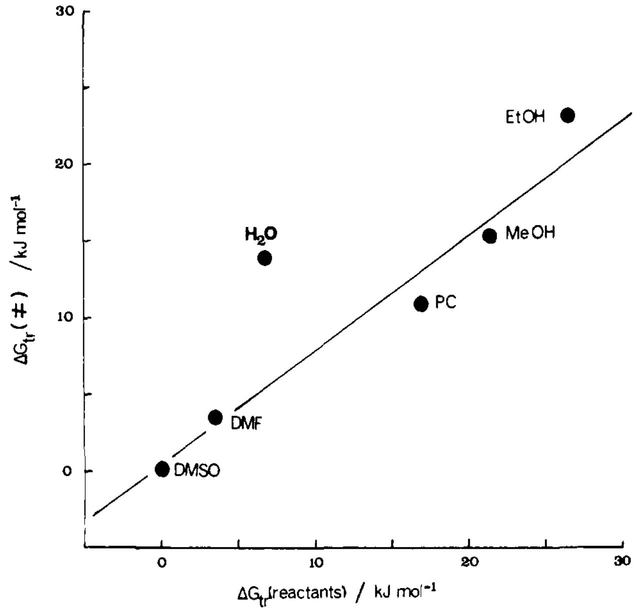

Figure 4. Comparison between the variation in the free energies of the reactants and the transition state for $K(2,2,2)^+$ formation in different solvents.

$mol^{-1}\ dm^3\ s^{-1}$. Within a single solvent, the variations in k_d values almost exactly mirror those in the corresponding K_s values. This is illustrated in Figure 1, in which log (K_s^{-1}) and log k_d values for (2,2,1) cryptates in ethanol are shown. It is apparent from the results in Table I that similar trends exist in all solvents, with the most stable complex of each of the ligands (i.e., Li^+ for (2,1,1), Na^+ for (2,2,1), and K^+ for (2,2,2)) having the lowest dissociation rates. On the other hand, the corresponding log k_f values are essentially independent of complex stabilities, and in several solvents there is an excellent linear correlation between log k_f and r_m^{-1}, where r_m is the ionic radius of the cation concerned. Thus within a given solvent, variations in stability constants are essentially reflected in the rates of dissociation of the complexes.

It is possible to extend this generalization further, at least for 2,2,1 and 2,2,2 cryptates. For these ligands there is a good correlation between log k_d and log K_s extending over all of the alkali metal cations and solvents studied (Figure 2). Thus, although there is some scatter, variations in stability constants, whether resulting from changes in solvent, cation, or ligand, may be identified primarily with variations in k_d values. The results for (2,1,1) cryptates show a similar correlation, but the log k_d values, particularly for $Li(2,1,1)^+$ complexes, are between 3 and 4 orders of magnitude below the line drawn in Figure 2. This suggests that the smaller, and presumably less flexible, (2,1,1) ligand presents a significantly higher steric barrier to the dissociation of the enclosed cation. The low formation rates of (2,1,1) cryptates compared with those of the other ligands are also consistent with this explanation.

The results strongly suggest that the transition state for complex formation lies very close to the reactants. This can be considered more quantitatively, however, by comparing the solvent dependence of the free energy of the transition state for a given reaction ($(M...Cry)^+$, $\ddagger^+$) with that of the reactants (M^+, Cry). It can be readily shown (Figure 3) that the free energy of transfer of the transition state from solvent S1 to solvent S2, $\Delta G_{tr}(\ddagger^+)$, may be calculated from the free energies of transfer of the reactants, $\Delta G_{tr}(M^+) + \Delta G_{tr}(Cry)$, and the free energies of activation of the formation reactions in the two solvents, $\Delta G_{S1}^\ddagger$ and $\Delta G_{S2}^\ddagger$, by using eq 7. Values of $\Delta G_{S1}^\ddagger$ and $\Delta G_{S2}^\ddagger$ may be simply obtained from

$$\Delta G_{tr}(\ddagger^+) = \Delta G_{tr}(M^+) + \Delta G_{tr}(Cry) + \Delta G_{S2}^\ddagger - \Delta G_{S1}^\ddagger \quad (7)$$

the respective formation rates by using eq 8, in which k_B is

$$\Delta G_s^\ddagger = RT \ln [k_BT/hk_f(S)] \quad (8)$$

Boltzmann's constant and h is Plank's constant. (Figure 3 should not be taken to imply that the formation reaction is necessarily a single-step reaction. Substitution of the solvent molecules presumably occurs in a stepwise fashion, and there may be one or more preequilibria between reactants and transition state.[1-3] The present kinetic data and discussion refer to the difference between the reactants (separate M^+ and Cry in solution) and the transition state for the overall formation reaction (similarly for the dissociation reaction).) These may be then combined with $\Delta G_{tr}(M^+)$ values estimated from ion solvation studies in the various solvents[7,8] and ΔG_{tr}(Cry) values[16] according to eq 6 to give $\Delta G_{tr}(\ddagger^+)$ values. Figure 4 shows a plot of $\Delta G_{tr}(\ddagger^+)$ against ΔG_{tr}(reactants) for $K(2,2,2)^+$ in a variety of solvents, by using Me_2SO as a reference solvent. There is quite a good correlation between the two terms, except for the results in water, which will be discussed further below. The free energy of the transition state is slightly less sensitive to solvent variation than that of the reactants (the line shown in Figure 4 has a slope of 0.75) but

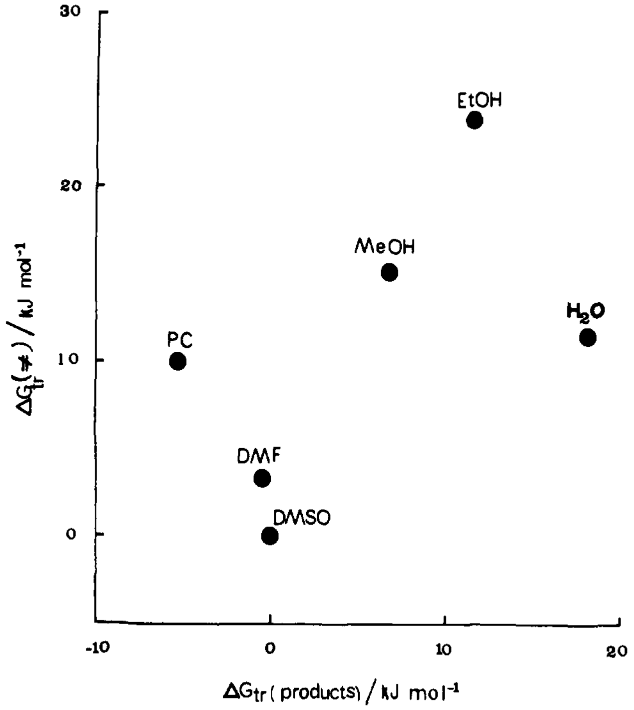

Figure 5. Comparison between the variation in the free energies of the products and the transition state for $K(2,2,2)^+$ formation in different solvents.

otherwise has a very similar solvent dependence. Analogous behavior is observed for other cryptates such as $Na(2,2,1)^+$ and $Li(2,1,1)^+$ including a positive, although smaller, deviation of the water values. In contrast to this, there is no correlation between the free energies of transfer of the transition state and that of the products ($MCry^+$). For example, the results for $K(2,2,2)^+$ in Figure 5 show a large random variation of $\Delta G_{tr}(\ddagger^+)$ with $\Delta G_{tr}(MCry^+)$, the changes in the two terms between some pairs of solvents even having opposite sign (e.g., PC, Me_2SO). These results again suggest that only a small amount of desolvation of the cation has occurred on formation of the transition state and that at least in its response to solvent variation, the transition state closely resembles the reactants and not the products.

In the discussion above, we have considered the observed changes in rate in terms of the solvent dependence of the free energies of the various species involved in the reactions. It would be useful, however, to be able to relate these rate variations to some property of the solvents. It is clear from the results in Tables I and II that neither the formation or dissociation rates are ranked in the same sequence as, for example, the dielectric constants of the solvents. An empirical parameter that has been used with some success to correlate kinetic as well as equilibrium properties of cations in various solvent is Gutmann's donor number (DN).[24] This is simply the heat of complex formation between solvent S and antimony pentachloride in 1,2-dichloroethane and represents an attempt to define quantitatively the electron donating ability of solvent S. Figure 6 shows a plot of log k_d against DN for the dissociation of $K(2,2,2)^+$ in various solvents. The corresponding plot for the formation rates is shown in Figure 7. The results are typical of those found for other cryptates. The dissociation rates increase sharply with increasing donor number of the solvent, and the formation rates decrease but with a slope only approximately one-third of that for the dissociation rates. Although the number of solvents involved in Figures 6 and 7 is limited, the correlation for the nonaqueous solvents, particularly for k_d values, is sufficiently good to suggest that donor numbers provide a reasonable means of estimating rates in other solvents from those given in Tables I and II. The lower sensitivity of the k_f values to solvent variation makes the significance of the correlation shown in Figure 7 less certain.

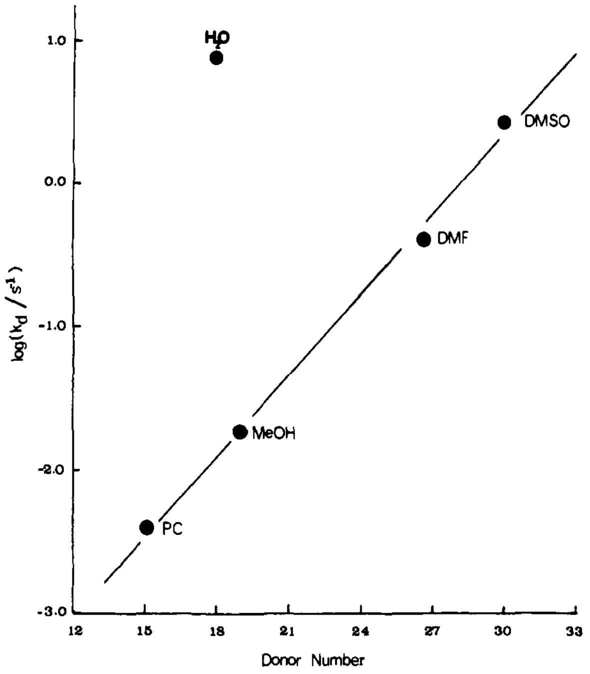

Figure 6. Variation of dissociation rates with solvent donor number for $K(2,2,2)^+$ cryptates in different solvents.

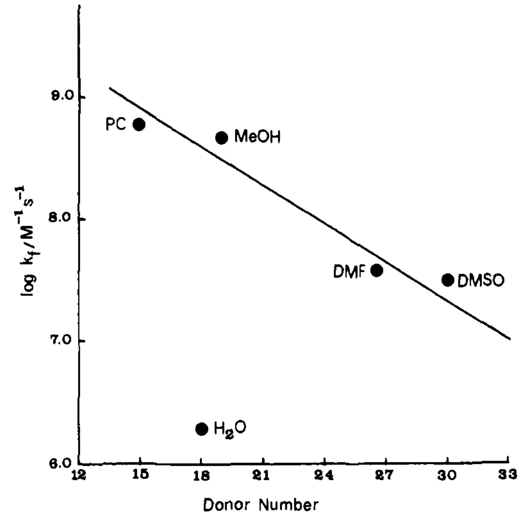

Figure 7. Variation of formation rates with solvent donor number for $K(2,2,2)^+$ cryptates in different solvents.

The results for water as solvent obviously differ quite drastically from those in other solvents, with k_d values much higher and k_f values much lower than those expected on the basis of the donor numbers of water. This may be related to the fact that donor numbers measure the ability of solvent molecules at infinite dilution in an inert medium to donate electrons, and the properties of water molecules in bulk water may be quite different from those under the former conditions. Another explanation, however, may be that water molecules are strong hydrogen bond donors and may interact quite strongly with the electronegative atoms (O and N) of the cryptand ligands. Such interactions with water molecules presumably account for the fact that, for example, the free energy of the (2,2,2) ligand increases by an average of ca. 5 kJ mol^{-1} on transfer from water to methanol[25] and various dipolar aprotic solvents,[16] despite the large number of hydrophobic groups in the ligand. Thus formation of cryptate in water would be expected

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to be relatively slow as it requires disruption of the interaction between water and the ligand, in addition to partial desolvation of the metal. Similarly, the dissociation process would be assisted by interaction between water molecules and the donor atoms of the ligand bridges. The deviation of the water values in Figure 4 presumably also has a common origin.

Thus, it seems likely that differences between the results in water and those in the other solvents studied may be best interpreted in terms of specific hydrogen-bonded interactions between water and the ligands rather than effects arising from the bulk structure of water. That the effect is not simply an artifact due to an inappropriate DN for H_2O is supported by the observation that a "corrected" DN which fits the linear correlation in Figure 6 is not applicable in Figure 7.

In absolute terms the formation rates are high, particularly considering the relative inflexibility of the ligands, and the fact that during the overall process of complex formation all of the solvent molecules in the immediate vicinity (inner coordination sphere) of the cations must be replaced. The rates are also relatively independent of solvent and for (2,2,2) and (2,2,1) cryptates in poorly solvating media (e.g., MeOH, EtOH, Pc) are generally close to the rates of solvent exchange in the inner coordination sphere of the cations. Substantial variations in charge densities of the cations can, however, lead to somewhat more drastic variations in rate. This is particularly apparent from a comparison of Ca^{2+} and Na^+ rates and to a lesser extent from the rates of formation of Li^+ cryptates compared with those of the other alkali metal cations. Weaver and co-workers[26] have considered the effect of charge density on cryptate formation rates in water and find even larger effects for 3+ cations. It must be remembered, however, that the total solvation energy of Ca^{2+} is some 1000 kJ mol^{-1} higher than that of Na^+ and even that of Li^+ is more than 100 kJ mol^{-1} higher than Na^+.[27] Thus even a relatively small amount of desolvation of these high charge density cations on formation of the transition state can lead to quite large energy barriers.

Finally, it is of interest to see how the results for naturally occurring macrocyclic antibiotics such as valinomycin and the macrotetralides[5,28] compare with those of the cryptands. Many of the results for these systems have been obtained in methanol, because of problems of low solubility and low complex stability in water. High complex formation rates, of the order of 10^7–10^8 $M^{-1}\,s^{-1}$, have been found by using various relaxation techniques. It is quite possible, in view of the results for the cryptands, that these high rates may be at least partially due to the poor solvating ability of methanol and that significantly lower results might be expected in water. In water, as discussed above, not only more effective cation solvation but also H-bonded interactions with the ligands cause lower formation rates in the case of cryptates. Measurements of the formation rate constants for some valinomycin complexes of alkali metal ions in methanol–water mixtures[5] suggest that similar effects may be operating for these complexes. Thus the value of k_f for the K^+ complex of valinomycin in methanol is 3.5×10^7 $M^{-1}\,s^{-1}$, in 90% MeOH–H_2O is 1.3×10^7 $M^{-1}\,s^{-1}$, in 80% MeOH–H_2O is 5.5×10^6 $M^{-1}\,s^{-1}$, and in 70% MeOH–H_2O is 1.3×10^6 $M^{-1}\,s^{-1}$. There is a clear tendency to lower k_f values with increasing water content of the solvent.

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Storage of Electrons in Aqueous Solution: The Rates of Chemical Charging and Discharging the Colloidal Silver Microelectrode

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Abstract: Conductometric methods were applied to study the electron transfer from 1-hydroxy-1-methylethyl radicals, $(CH_3)_2COH$, to colloidal silver particles and the reduction of water by electrons stored on the silver particles. The charging reaction is diffusion controlled and takes place within milliseconds. The rate of the discharge reaction depends on the number of electrons stored on one silver particle. This reaction requires seconds or even minutes in solutions of pH 3.7. In the stationary state, up to 1 C of electrons (or 10^{-5} mol of electrons) could be stored per liter of solution, each silver particle carrying about 450 electrons under these conditions. The total electrical capacity of a 2.5×10^{-4} M colloidal silver solution was determined as about 1 F/L, the specific capacity of the silver particles as 43 $\mu F/cm^2$ of surface. The storage of electrons is also proven by their transfer to a compact mercury electrode in contact with the colloidal solution. Potential changes of about 0.3 V of this electrode were measured. A few properties of the microelectrode such as its absorption spectrum, its sensitivity toward oxygen, and its efficiency in combination with various stabilizers for catalyzing the reduction of water by radicals are also reported.

(1) Introduction

Colloidal silver[1-3] and colloidal gold[4-7] have recently been found to catalyze novel reactions of free radicals in aqueous solution. These reactions include the decomposition of water to yield hydrogen and the multielectron reduction of dissolved substances. The most important step in the postulated mechanism[1] is the storage of electrons on the colloidal particles as the free radicals transfer electrons to them. The stored electrons are then used to carry out the various reduction processes. Equations 1 and 2

$$m(CH_3)_2COH + Ag_n \rightarrow Ag_n^{m-} + m(CH_3)_2CO + mH^+ \tag{1}$$

$$Ag_n^{m-} + 2H_2O \rightarrow Ag_n^{(m-2)-} + H_2 + 2OH^- \tag{2}$$

describe the processes of charging colloidal silver particles by

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