Kinetic Deuterium Solvent Isotope Effects on the General Acid-catalysed Dissociation of Metal Cryptates

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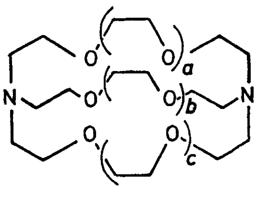
The dissociation of metal ions from cryptate complexes is subject to general acid catalysis in a number of cases. The dissociation of $Ca(2,2,2)^{2+}$ has been studied in the presence of HCl and several carboxylic acids as catalysts, and kinetic solvent isotope effects measured for the HCl- and CH_3CO_2H-catalysed dissociation. The observation of general acid catalysis, combined with relatively large isotope effects (2.4 and 2.7, respectively), are consistent with a rate-determining proton transfer in the dissociation reaction. The H^+-catalysed dissociation of $Ag(2,2,2)^+$ shows a lower, but still significant, isotope effect (1.9) and most likely also involves a rate-determining proton transfer step. $Li(2,1,1)^+$ shows somewhat different behaviour in that the apparent catalytic constant for acid catalysed dissociation decreases with increasing buffer concentration. The results are shown to be in quantitative accord with a reaction scheme involving protonation of $Li(2,1,1)^+$ followed by competitive dissociation of Li^+ from $Li(2,1,1)H^{2+}$ and deprotonation by A^- of $Li(2,1,1)H^{2+}$ to give $(2,1,1)H^+$ or regenerate $Li(2,1,1)^+$, respectively. Kinetic solvent deuterium isotope effects for the protonation and deprotonation–dissociation steps are close to unity.

THE dissociation of metal ions from complexes (cryptates) formed between cations and macrobicyclic ligands (cryptands) of the type (1)—(3) [1] has been shown in a number of cases to be subject to catalysis by strong acids,[2-5] and by general acids, HA, in a variety of solvents.[6-8] The susceptibility to catalysis decreases as the size of the metal ion increases relative to that of the ligand cavity, and as the conformational flexibility of the ligand is decreased.[1,4,7,8] Catalysis is particularly marked in solvents such as propylene carbonate,[7] in which the uncatalysed dissociation rates of the complexes are very low. Catalysis presumably involves the interaction between a proton or acid HA and the lone pair of one of the nitrogen atoms in an *exo*-conformation. The final product of the reaction is the protonated cryptand.



(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)

Recent work by Bergman *et al.*[9] and Cox and Jencks [10] has established that significant kinetic isotope effects may be observed for proton transfer between oxygen and nitrogen bases (k^H/k^D values of up to *ca.* 3.8). Such proton-transfer reactions are normally very fast, but may become rate-determining if they occur after an unfavourable equilibrium, as part of a complex reaction scheme. Maximum isotope effects were observed when the pK_a values of the proton donor and the protonated proton acceptor were similar. This latter conclusion, however, does not appear to hold if the proton is involved in strong intramolecular hydrogen bonding.[11]

In this paper we present a full account of a study of the general acid catalysed dissociation of $Ca(2,2,2)^{2+}$ and $Li(2,1,1)^+$ cryptates,[6] together with a study of the kinetic solvent deuterium isotope effects on the dissociation of $K(2,2,2)^+$, $Ag(2,2,2)^+$, $Ca(2,2,2)^{2+}$, and $Li(2,1,1)^+$ cryptates.

EXPERIMENTAL AND RESULTS

Cryptands (2,2,2) and (2,1,1) were commercial samples (Merck) used without further purification. The salts $LiClO_4$, LiCl, KCl, $CaCl_2$, $Ca(NO_3)_2$, $AgNO_3$, and NaOAc (Merck or B.D.H.) were used without further purification. NEt_4Br, used to maintain constant ionic strength where appropriate, was purified by recrystallisation from 95% $EtOH-H_2O$. Buffer solutions were prepared by partial neutralisation of the acid with aqueous NEt_4OH solutions (except for buffers in D_2O).

DCl and $DClO_4$ solutions in D_2O were prepared by diluting concentrated aqueous solutions of the acids (*ca.* 10—12M) with D_2O (Fluorochem Ltd., 99.9%). As the acid concentrations used in kinetic measurements were $\leqslant 3 \times 10^{-3}$M, the amounts of H_2O introduced in this way were negligible. CH_3CO_2D solutions in D_2O were prepared by adding glacial acetic acid to D_2O. In the most concentrated acetic acid solutions used in D_2O (0.2M) this corresponds to only 0.2% ^1H. The ^1H content of D_2O solutions used was checked by n.m.r., using internal references such as the CH_3 group in $CH_3CO_2D-CH_3CO_2^-$ and were found to be always <1%. $CH_3CO_2D-CH_3CO_2^-$ buffers in D_2O were prepared from appropriate mixtures of CH_3CO_2D and $Na[CH_3CO_2]$ solutions. It was shown by comparative studies in H_2O using buffers prepared both from $CH_3CO_2H + NEt_4OH$ and $CH_3CO_2H + Na[CH_3CO_2]$ that the presence of Na^+ (which could, in principle, interfere in the reactions by competitive complexation) had no effect on the observed rates.

Reactions were initiated in a stopped-flow apparatus (Durrum–Gibson or instrument constructed at M.P.I., Göttingen) by mixing an excess of acid with the appropriate cryptate salt [equations (1) and (2) where HA represents a

$$MCry^{2+} + 2H^+ \longrightarrow CryH_2^{2+} + M^{2+} \quad (1)$$

$$MCry^{2+} + 2HA \longrightarrow CryH_2^{2+} + M^{2+} + 2A^- \quad (2)$$

general acid]. An excess of at least 10-fold in acid concentration was normally used in order to ensure pseudo-first order conditions. Where necessary, corrections were made to allow for any change in acid concentration (or buffer ratio, r = [HA]/[A$^-$]) that occurred during reaction. The reactions were followed conductimetrically as described earlier.[2,4,6] Reaction (1) is accompanied by a decrease in conductance because of the loss of (highly mobile) protons, reaction (2) is accompanied by a significant increase in conductance. All reactions were carried out at 25.0 (±0.1) °C.

For reactions carried out in buffer solutions [equation (2)] the ionic strength was maintained at a constant value by the addition of NEt_4Br. This was necessary in order to maintain constant hydrogen-ion concentration in buffer solutions of varying concentration. Reactions involving $HClO_4$ or HCl solutions [equation (1)] were carried out in the absence of added NEt_4Br in order to maximise the conductance changes (<10%) being measured. The observed rates were corrected to zero ionic strength as described below.

In all cases the rate law shown in equation (3) was obeyed, in which k_e is the observed first-order rate constant.

$$-d[MCry^{2+}]/dt = k_e[MCry^{2+}] \qquad (3)$$

Rates of dissociation of K(2,2,2)$^+$, Ag(2,2,2)$^+$, Ca(2,2,2)$^{2+}$, and Li(2,1,1)$^+$ were measured under a variety of conditions as described below.

K(2,2,2)$^+$. Earlier studies in aqueous solution have shown that the rate of dissociation of K(2,2,2)$^+$ is independent of H$^+$ concentration (up to 2.5 × 10^{-3}M)[2] and CH_3CO_2H concentration (up to 0.1M).[6] Acid-catalysed dissociation has, however, been observed in more concentrated aqueous H$^+$ solutions,[5] and the dissociation is strongly catalysed by acids in propylene carbonate.[7] In the present study, the uncatalysed dissociation rate constant, k_d, has been determined in H_2O and D_2O from measurements in HCl (or DCl) solutions [equation (1)]. Concentrations of HCl(DCl), KCl, and (2,2,2) were in the range (0.2—2) × 10^{-3}M, 1.0 × 10^{-3}M, and (0.7—1.0) × 10^{-4}, respectively. The results obtained were $k_d(H_2O)$ 7.5 (±0.3) and $k_d(D_2O)$ 6.5 (±0.3) s^{-1}.

Ag(2,2,2)$^+$. The dissociation of Ag(2,2,2)$^+$ is very strongly acid-catalysed. Measurements were carried out in H_2O and D_2O, and the results and experimental conditions are reported in Table 1. The observed rate constant in H_2O and D_2O had the form shown in equations (4) and (5) respectively. Values of k_e, calculated from equations (4) and (5), using activity coefficients $\gamma_\pm$ obtained from the

$$k_e(H_2O/s^{-1} = 0.4\ (\pm0.2) + 5.27\ (\pm0.25) \times 10^3\ [H^+]/\gamma^2_\pm \qquad (4)$$

$$k_e(D_2O)_4s^{-1} = 0.12(\pm0.1) + 2.74\ (\pm.14) \times 10^3[D^+]/\gamma^2_\pm \qquad (5)$$

Davies equation (6), are included in Table 1 for comparison with experimental values. In equation (6), I represents the

$$\log \gamma_\pm = -AI^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) + AI/3 \qquad (6)$$

ionic strength, and A the Debye–Hückel parameter. Earlier measurements on the dissociation rates of several Ag$^+$ cryptates gave a slightly lower value (4.70 × 10^3 dm^3 mol^{-1} s^{-1}) for the H$^+$-catalysed dissociation of Ag(2,2,2)$^+$.[12] However, for the purposes of comparison with the results in D_2O the present results are more appropriate as the results summarised in equations (4) and (5) were measured under identical conditions, thus minimising the relative errors in the two solvents.

TABLE 1

Acid-catalysed dissociation of Ag(2,2,2)$^+$ in H_2O and D_2O at 25 °C

(i) $HClO_4$ in H_2O, [$AgClO_4$] (1—5) × 10^{-4}M, [2,2,2] (0.25—1) × 10^{-4}M

10^3[$HClO_4$]/M	0.141	0.169	0.496	0.675	0.860
k_e/s^{-1}	0.78	0.89	2.97	3.88	5.25
k_e(calc)/s^{-1} [a]	0.80	1.25	2.60	4.00	5.08
10^3[$HClO_4$]/M	1.25	1.45	1.64	2.02	2.23
k_e/s^{-1}	7.42	7.93	9.84	12.4	13.3
k_e(calc)/s^{-1} [a]	7.36	8.59	9.69	12.1	13.4

(ii) $DClO_4$ in D_2O, [$AgClO_4$] (0.2—2) × 10^{-3}M, [2,2,2] (0.25—1.1) × 10^{-4}M

10^3[$DClO_4$]/M	0.172	0.19	0.36	0.43	0.76
k_e/s^{-1}	0.203	0.90	0.60	1.40	2.27
k_e(calc)/s^{-1} [b]	0.56	0.64	1.10	1.21	2.30
10^3[$DClO_4$]/M	1.25	1.52	1.63	1.92	2.02
k_e/s^{-1}	4.06	4.64	4.90	5.50	6.09
k_e(calc)/s^{-1} [b]	3.73	4.60	4.90	5.81	6.09
10^3[$DClO_4$]/M	0.86	1.15	2.36		
k_e/s^{-1}	2.64	3.45	7.28		
k_e(calc)/s^{-1} [b]	2.51	3.47	7.10		

[a] Calculated from equation (4). [b] Calculated from equation (5).

Ca(2,2,2)$^{2+}$. Rates of dissociation of Ca(2,2,2)$^{2+}$ were measured in dilute HCl solutions (H_2O and D_2O) and in buffers prepared from iodoacetic acid, formic acid, 3-chloropropionic acid, and acetic acid (H_2O and D_2O). Results and experimental conditions are listed in Table 2. In all cases the observed rate constants were found to conform to equation (7), $\gamma_\pm^4$ being the appropriate activity

$$k_e = k_d + k_H[H^+]/\gamma_\pm^4 + k_{HA}[HA] \qquad (7)$$

coefficient correction for reaction between species of charge 2+ and 1+. In solutions used to determine k_H (*i.e.* in the absence of HA), ionic strengths were low (<0.003M), so that activity coefficient corrections were relatively small. In buffer solutions, k_e was strictly linear with [HA], and independent of buffer ratio (after due allowance for H$^+$ catalysis). This is illustrated in Figure 1, which shows results obtained in CH_3CO_2H–$CH_3CO_2^-$ buffers after correction for the small contribution from H$^+$ catalysis at these pH values (*ca.* 4.0—4.5).

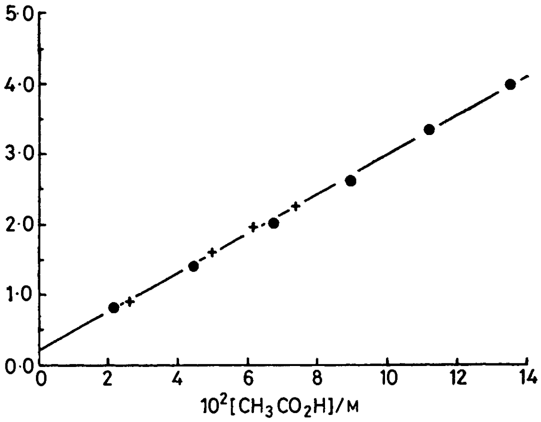


FIGURE 1 Acetic acid catalysed dissociation of Ca(2,2,2)$^{2+}$: ● [HOAc]/[OAc$^-$] 2.75; + [HOAc]/[OAc$^-$] 1.49

TABLE 2

General acid-catalysed dissociation of $\mathrm{Ca(2,2,2)^{2+}}$ in $\mathrm{H_2O}$ and $\mathrm{D_2O}$ at 25 °C

(i) HCl in $\mathrm{H_2O}$, $[\mathrm{CaCl_2}]$ 5 × 10^{-4}M, [2,2,2] 5 × 10^{-5}—2 × 10^{-4}M

$10^3[\mathrm{HCl}]/\mathrm{M}$	0.35	0.75	1.00	1.10	1.50
$k_e/\mathrm{s^{-1}}$	0.415	0.636	0.867	1.00	1.29
$k_e(\mathrm{calc})/\mathrm{s^{-1}}$ [a]	0.415	0.695	0.832	0.490	1.25
$10^3[\mathrm{HCl}]/\mathrm{M}$	1.80	2.80			
$k_e/\mathrm{s^{-1}}$	1.34	2.25			
$k_e(\mathrm{calc})/\mathrm{s^{-1}}$ [a]	1.43	2.23			

(ii) DCl in $\mathrm{D_2O}$, $[\mathrm{CaCl_2}]$ 1 × 10^{-3}M, [2,2,2] 5 × 10^{-5}—1 × 10^{-4}M

$10^3[\mathrm{DCl}]/\mathrm{M}$	0.29	0.63	0.92	1.26	1.60
$k_e/\mathrm{s^{-1}}$	0.169	0.248	0.353	0.430	0.577
$k_e(\mathrm{calc})/\mathrm{s^{-1}}$ [a]	0.159	0.261	0.341	0.450	0.562

(iii) $\mathrm{CH_2ICO_2H}$ in $\mathrm{H_2O}$, [HA] 0.87 $[\mathrm{A^-}]$, *I* 0.06M, [2,2,2] 7.5 × 10^{-4}M, $[\mathrm{CaCl_2}]$ 5 × 10^{-3}M

$10^2[\mathrm{CH_2ICO_2H}]/\mathrm{M}$	1.35	2.06	2.77	3.48	4.19
$k_e/\mathrm{s^{-1}}$	2.13	2.68	3.14	4.03	4.73
$k_e(\mathrm{calc})/\mathrm{s^{-1}}$ [a]	2.19	2.77	3.39	3.98	4.52

(iv) $\mathrm{HCO_2H}$ in $\mathrm{H_2O}$, [HA] = $[\mathrm{A^-}]$, *I* 0.06M, [2,2,2] 7.5 × 10^{-4}M, $[\mathrm{CaCl_2}]$ 5 × 10^{-3}M

$10^2[\mathrm{HCO_2H}]/\mathrm{M}$	0.78	1.64	2.50	3.35	4.21
$k_e/\mathrm{s^{-1}}$	0.735	1.11	1.46	1.83	2.21
$k_e(\mathrm{calc})/\mathrm{s^{-1}}$ [a]	0.740	1.12	1.44	1.85	2.20
$10^2[\mathrm{HCO_2H}]/\mathrm{M}$	5.07				
$k_e/\mathrm{s^{-1}}$	2.58				
$k_e(\mathrm{calc})/\mathrm{s^{-1}}$ [a]	2.54				

(v) $\mathrm{CH_2ClCH_2CO_2H}$ in $\mathrm{H_2O}$, [HA] 1.83 $[\mathrm{A^-}]$, *I* 0.06M, [2,2,2] 7 × 10^{-4}M, $[\mathrm{CaCl_2}]$ 5 × 10^{-3}M

$10^2[\mathrm{CH_2ClCH_2CO_2H}]/\mathrm{M}$	1.52	3.05	4.63	6.20	7.80
$k_e/\mathrm{s^{-1}}$	1.13	1.90	2.87	3.53	4.41
$k_e(\mathrm{calc})/\mathrm{s^{-1}}$ [a]	1.19	1.95	2.77	3.58	4.41
$10^2[\mathrm{CH_2ClCH_2CO_2H}]/\mathrm{M}$	9.35				
$k_e/\mathrm{s^{-1}}$	5.35				
$k_e(\mathrm{calc})/\mathrm{s^{-1}}$ [a]	5.25				

(vi) $\mathrm{CH_3CO_2H}$ in $\mathrm{H_2O}$, [HA] 3.8 $[\mathrm{A^-}]$, *I* 0.032M, [2,2,2] 7 × 10^{-4}M, $[\mathrm{CaCl_2}]$ 2.0 × 10^{-3}M

$10^2[\mathrm{CH_3CO_2H}]/\mathrm{M}$	0.019	0.029	0.049	0.069	0.099
$k_e/\mathrm{s^{-1}}$	0.761	1.11	1.66	2.26	3.17
$k_e(\mathrm{calc})/\mathrm{s^{-1}}$ [a]	0.770	1.07	1.75	2.25	3.18

(vii) $\mathrm{CH_3CO_2D}$ in $\mathrm{D_2O}$ [DA] 3.8 $[\mathrm{A^-}]$, *I* 0.032M, [2,2,2] 7 × 10^{-4}M, $[\mathrm{CaCl_2}]$ 2.0 × 10^{-3}M

$10^2[\mathrm{CH_3CO_2D}]/\mathrm{M}$	0.019	0.029	0.049	0.069	0.099
$k_e/\mathrm{s^{-1}}$	0.329	0.423	0.642	0.831	1.21
$k_e(\mathrm{calc})/\mathrm{s^{-1}}$ [a]	0.315	0.433	0.667	0.841	1.20

[a] Results calculated from equation (7) using catalytic constants listed in Table 3.

TABLE 3

Catalytic constants [a] for the general acid-catalysed dissociation of $\mathrm{Ca(2,2,2)^{2+}}$ in $\mathrm{H_2O}$ and $\mathrm{D_2O}$ at 25 °C

Acid	Solvent	$k_d/\mathrm{s^{-1}}$	$k_{\mathrm{HA}}/\mathrm{mol^{-1}\ dm^3\ s^{-1}}$	$I/\mathrm{mol\ dm^{-3}}$ [b]
	$\mathrm{H_2O}$	0.17		0.00
	$\mathrm{D_2O}$	0.09		0.00
$\mathrm{H^+}$	$\mathrm{H_2O}$		564	0.00
$\mathrm{D^+}$	$\mathrm{D_2O}$		231	0.00
$\mathrm{CH_2ICO_2H}$	$\mathrm{H_2O}$		82.8	0.06
$\mathrm{HCO_2H}$	$\mathrm{H_2O}$		40.0	0.06
$\mathrm{CH_2ClCH_2CO_2H}$	$\mathrm{H_2O}$		50.8	0.06
$\mathrm{CH_3CO_2H}$	$\mathrm{H_2O}$		29.6	0.032
$\mathrm{CH_3CO_2D}$	$\mathrm{D_2O}$		10.8	0.032

[a] Catalytic constants [equation (7)] ±5% except for k_d values ±10%. [b] Ionic strength.

Catalytic constants obtained by fitting the experimental results in the various solutions to equation (7) are collected in Table 3. Rate constants calculated from equation (7) using catalytic constants from Table 3 are included in Table 2 for comparison with experimental values.

$\mathrm{Li(2,1,1)^+}$. The dissociation of $\mathrm{Li(2,1,1)^+}$ was studied in dilute HCl ($\mathrm{H_2O}$ and $\mathrm{D_2O}$) and in a variety of buffers: chloroacetic acid, iodoacetic acid, formic acid, 3-chloropropionic acid, acetic acid, mono-oxalate ($\mathrm{HO_2C{\cdot}CO_2^-}$), and anilinium ion. The results are listed in Table 4, together with experimental conditions. The reaction has previously

TABLE 4

General acid-catalysed dissociation of $\mathrm{Li(2,1,1)^+}$ in $\mathrm{H_2O}$ and $\mathrm{D_2O}$ at 25 °C

(i) HCl in $\mathrm{H_2O}$, [LiCl] 9 × 10^{-4}M, [2,1,1] (0.5—1.0) × 10^{-4}M

$10^3[\mathrm{HCl}]/\mathrm{M}$	0.45	0.75	1.10	1.50	2.40
$10^2k_e/\mathrm{s^{-1}}$	3.64	4.58	5.24	6.30	8.26
$10^2k_e(\mathrm{calc})/\mathrm{s^{-1}}$	3.68	4.39	5.18	6.13	8.36

(ii) DCl in $\mathrm{D_2O}$, [LiCl] 1.0 × 10^{-3}M, [2,1,1] (0.5—1.0) × 10^{-4}M

$10^3[\mathrm{DCl}]/\mathrm{M}$	0.46	0.80	1.09	1.60	2.45
$10^2k_e/\mathrm{s^{-1}}$	3.00	3.50	3.94	5.08	5.89
$10^2k_e(\mathrm{calc})/\mathrm{s^{-1}}$	2.98	3.51	3.95	4.77	5.92

(iii) $\mathrm{CH_2ClCO_2H}$ in $\mathrm{H_2O}$, [HA] 0.40 $[\mathrm{A^-}]$, *I* 0.13M, $[\mathrm{LiClO_4}]$ 1 × 10^{-3}M, [2,1,1] 8 × 10^{-4}M

$10^2[\mathrm{CH_2ClCO_2H}]/\mathrm{M}$	0.76	1.55	2.38	3.20	4.03
$10^2k_e/\mathrm{s^{-1}}$	8.90	12.7	15.8	18.3	20.8

(iv) $\mathrm{CH_2ICO_2H}$ in $\mathrm{H_2O}$, [HA] 0.99 $[\mathrm{A^-}]$, *I* 0.05M, $[\mathrm{LiClO_4}]$ 5 × 10^{-3}M, [2,1,1] 5 × 10^{-4}M

$10^2[\mathrm{CH_2ICO_2H}]/\mathrm{M}$	0.76	1.57	2.38	3.20	4.01	4.82
$10^2k_e/\mathrm{s^{-1}}$	6.98	10.1	11.9	14.2	15.9	17.9

(v) $\mathrm{HCO_2H}$ in $\mathrm{H_2O}$, [HA] 1.03 $[\mathrm{A^-}]$, *I* 0.06M, $[\mathrm{LiClO_4}]$ 4.9 × 10^{-3}M, [2,1,1] 8.0 × 10^{-4}M

$10^2[\mathrm{HCO_2H}]/\mathrm{M}$	1.01	1.55	2.10	2.64	3.19	4.27
$10^2k_e/\mathrm{s^{-1}}$	4.68	5.37	5.99	6.40	7.20	7.98
$10^2[\mathrm{HCO_2H}]/\mathrm{M}$	5.36					
$10^2k_e/\mathrm{s^{-1}}$	8.82					

(vi) $\mathrm{CH_2ClCH_2CO_2H}$ in $\mathrm{H_2O}$, [HA] 1.85 $[\mathrm{A^-}]$, *I* 0.05M, $[\mathrm{LiClO_4}]$ 4.5 × 10^{-3}M, [2,1,1] 6 × 10^{-4}M

$10^2[\mathrm{CH_2ClCH_2CO_2H}]/\mathrm{M}$	1.53	3.06	4.64	6.21	7.81	9.36
$10^2k_e/\mathrm{s^{-1}}$	4.68	5.71	6.62	7.26	7.84	8.40

(vii) $\mathrm{CH_2CO_2H}$ in $\mathrm{H_2O}$, $[\mathrm{LiClO_4}]$ 4—8 × 10^{-3}M, *I* 0.03M, [2,1,1] 4—6 × 10^{-4}M

(a) $[\mathrm{CH_2CO_2H}]$ 4.4 $[\mathrm{CH_2CO_2^-}]$

$10^2[\mathrm{CH_3CO_2H}]/\mathrm{M}$	1.06	2.12	3.18	4.24	8.49	12.8
$10^2k_e/\mathrm{s^{-1}}$	3.43	3.80	4.09	4.31	5.14	5.60
$10^2[\mathrm{CH_3CO_2H}]/\mathrm{M}$	21.3					
$10^2k_e/\mathrm{s^{-1}}$	6.48					

(b) $[\mathrm{CH_3CO_2H}]$ 8.8 $[\mathrm{CH_3CO_2^-}]$

$10^2[\mathrm{CH_3CO_2H}]/\mathrm{M}$	2.11	4.21	6.32	8.42	10.5	13.6
$10^2k_e/\mathrm{s^{-1}}$	3.70	4.44	4.98	5.47	5.92	6.39
$10^2[\mathrm{CH_3CO_2H}]/\mathrm{M}$	18.1					
$10^2k_d/\mathrm{s^{-1}}$	6.94					

(c) $[\mathrm{CH_3CO_2H}]$ 20.5 $[\mathrm{CH_3CO_2^-}]$

$10^2[\mathrm{CH_3CO_2H}]/\mathrm{M}$	9.25	14.0	18.5	23.2
$10^2k_e/\mathrm{s^{-1}}$	6.41	7.52	8.70	9.61

(viii) $\mathrm{HO_2CCO_2^-}$ in $\mathrm{H_2O}$, $[\mathrm{HA^-}]$ 3.0 $[\mathrm{A^{2-}}]$, *I* 0.133M, $[\mathrm{LiClO_4}]$ 5 × 10^{-3}M, [2,1,1] 7 × 10^{-4}M

$10^2[\mathrm{HO_2CCO_2^-}]/\mathrm{M}$	0.74	1.54	2.34	3.15	3.96	4.77
$10^2k_e/\mathrm{s^{-1}}$	5.15	6.76	8.88	10.1	11.9	12.9

(ix) $\mathrm{C_6H_5NH_3^+}$ in $\mathrm{H_2O}$, $[\mathrm{HA^+}]$ 0.9 [A], $[\mathrm{LiClO_4}]$ 4 × 10^{-3}M, [2,1,1] 0.7—3 × 10^{-3}M, *I* 0.06M

$10^2[\mathrm{C_6H_5NH_3^+}]/\mathrm{M}$	1.13	2.28	3.41	4.57	5.70
$10^3k_e/\mathrm{s^{-1}}$	2.67	2.80	2.76	2.89	2.87

(i) $k_e(\mathrm{calc})/\mathrm{s^{-1}} = 0.027 + 20.6\,[\mathrm{H^+}]/\gamma_\pm{}^2$.

(ii) $k_e(\mathrm{calc})/\mathrm{s^{-1}} = 0.023 + 14.2\,[\mathrm{D^+}]/\gamma_\pm{}^2$.

been shown to be strongly catalysed by H^+, and the results in Table 4 show that the rate is also dependent upon the concentration of general acids. However, in contrast to results for $Ca(2,2,2)^{2+}$, the observed rate constants do not show a simple linear dependence upon [HA] in any of the buffers studied. This is illustrated in Figure 2 in which results in CH_3CO_2H–$CH_3CO_2^-$ buffers (again corrected for the small contribution from H^+ catalysis) are shown. It is noticeable that at higher concentrations of acetic acid (and hence acetate ions) the results fall below those extrapolated from lower concentrations. Furthermore, the curvature becomes more pronounced as the buffer ratio is decreased. In order to study the effect more quantitatively, rates were measured at constant acetic acid concentration (0.2M) and a variety of acetate concentrations. The results (in H_2O and D_2O) are listed in Table 5. The rate constants corrected for the uncatalysed reaction, k_d and H^+ catalysed reaction, $[H^+]k_{H^+}/y_{\pm}^2$ using values obtained in dilute HCl solution, are also included in Table 5 (see below). The interpretation of these results is discussed below.

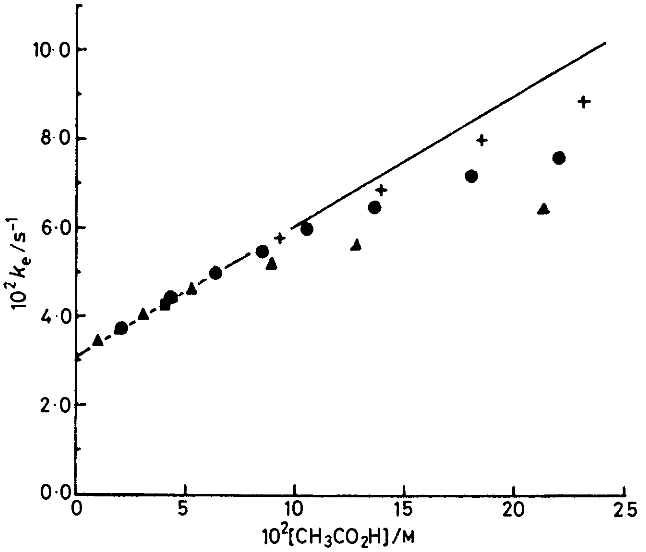


FIGURE 2 Acetic acid catalysed dissociation of $Li(2,1,1)^+$: + [HOAc]/[OAc⁻] 20; ● [HOAc]/[OAc⁻] 8.8; ▲ [HOAc]/[OAc⁻] 4.4; ■ [HOAc]/[OAc⁻] 2.3

TABLE 5

Effect of acetate on the acetic acid catalysed dissociation of $Li(2,1,1)^+$ in H_2O and D_2O at 25 °C [a]

[NaOAc]/M	k_e/s^{-1} [b]	k(corr)/s^{-1} [c]
$H_2O : [CH_3CO_2H] = 0.2$M		
0.010	0.109	0.069
0.015	0.098	0.062
0.025	0.087	0.054
0.045	0.072	0.041
0.065	0.060	0.030
0.085	0.056	0.027
0.105	0.050	0.021
$D_2O : [CH_3CO_2D] = 0.2$M		
0.015	0.088	0.063
0.025	0.083	0.059
0.045	0.069	0.045
0.065	0.059	0.036
0.085	0.054	0.031
0.105	0.048	0.025

[a] Ionic strength = 0.113 ($NaNO_3$). [b] Observed rate constant (±3%). [c] Rate constant corrected for uncatalysed, k_d, and H^+-catalysed, $[H^+]k_H/\gamma_{\pm}^2$ dissociation.

DISCUSSION

The dissociation reactions of $Ca(2,2,2)^{2+}$ with a variety of acids, and of $Ag(2,2,2)^+$ and $Li(2,1,1)^+$ with H^+, show a simple linear dependence of rate upon acid concentration. This is illustrated, for example, in Figure 1. The dissociation of $Li(2,1,1)^+$ is also catalysed by general acids (Table 4 and Figure 2), but the apparent catalytic effect of HA decreased with increasing concentrations of the basic component, A^-. Such an effect could be produced by competitive interaction between A^- and $Li(2,1,1)^+$ to form a complex that is relatively inert towards dissociation of Li^+. Weaver and his co-workers [13] have found evidence of strong interaction between lanthanide cryptates and the anions OH^- and F^-. However, this association was restricted to 3+ cryptates and furthermore, led to a more rapid dissociation of the complexes. Thus we present an alternative explanation of the present results in the form of the Scheme, in which $[Li(2,1,1)H^{2+}]$ is assumed to be low.

$$Li(2,1,1)^+ + H^+ \underset{k_{-1}}{\overset{k_H}{\rightleftharpoons}} Li(2,1,1)H^{2+} \qquad (8a)$$

$$Li(2,1,1)^+ + HA \underset{k_A}{\overset{k_{HA}}{\rightleftharpoons}} Li(2,1,1)H^{2+} + A^- \qquad (8b)$$

$$Li(2,1,1)H^{2+} \xrightarrow{k_2} (2,1,1)H^+ + Li^+ \qquad (9)$$

SCHEME

Application of the steady state approximation to $[Li(2,1,1)H^{2+}]$ leads to the rate law shown in equations (10) and (11). Thus in the presence of an excess of HA and A^- the reactions would be pseudo-first-order, but if k is plotted against [HA] at constant buffer ratio, curves concave to concentration axes are obtained instead of the usual straight lines. Such a scheme can be treated quantitatively in the general case [14] by making use of the fact that the various rate constants are not independendent, but are related through the equilibrium constant, $[Li(2,1,1)H^{2+}]/[H^+][Li(2,1,1)^+] = K$. However, in the CH_3CO_2H–$CH_3CO_2^-$ buffer system for which the most comprehensive set of results have been obtained, effects due to catalysis by H^+ are very small, contributing a maximum of 12% to the observed rates, and normally much less. Thus in order to simplify the treatment the observed rate constants have been corrected to allow for catalysis by H^+, using catalytic constants measured in dilute HCl solutions, and reactions (8b) and (9) only included in the kinetic scheme. Under these conditions, we obtain (12), in which $k = k_e\text{-}k_d\text{-}k_H[H^+]/y_{\pm}^2$. The

$$-d[Li(2,1,1)^+]/dt = k[Li(2,1,1)^+] \qquad (10)$$

$$k = k_e - k_d = \frac{k_H k_2[H^+] + k_{HA}k_2[HA]}{k_{-1} + k_A[A^-] + k_2} \qquad (11)$$

$$\frac{[HA]}{k} = \frac{1}{k_{HA}} + \frac{k_A[A^-]}{k_{HA}k_2} \qquad (12)$$

application of equation (12) to the results in Table 5 is shown in Figure 3, in which k^{-1} is plotted against $[A^-]$. The lines shown correspond to equations (13) and (14) for results in H_2O and D_2O respectively. These results (Figure 3) give $k_{HOAc}(H_2O)$ 0.476 and $k_{DOAc}(D_2O)$ 0.439

$$\frac{1}{k(H_2O)} = 10.5 + 330[OAc^-] \qquad (13)$$

$$\frac{1}{k(D_2O)} = 11.4 + 258[OAc^-] \qquad (14)$$

$mol^{-1}\ dm^3\ s^{-1}$, and values for $k_{OAc}/k_2 = 31.7$ and 22.7 $mol^{-1}\ dm^3$ in H_2O and D_2O, respectively. In the other buffer systems studied the concentrations of HA and A^- vary simultaneously and the kinetic measurements were carried out at low $[A^-]$ in order to obtain more accurate values of k_{HA}. However, the results may be analysed in a similar manner by plotting $[HA]/k$ against $[A^-]$, and the resulting values of k_{HA} are reported in Table 6. Values of k_A/k_2 for the various carboxylate anions obtained from the analysis of the results in Table 4 are k_A/k_2 = 4.9, 4.5, 9.0, 22.3, and 31 mol dm^{-3} for $A^- = CH_2ClCO_2^-, CH_2ICO_2^-, HCO_2^-, CH_2ClCH_2CO_2^-$, and $CH_3CO_2^-$, respectively. The values are subject to large uncertainties, but show a sensible increase in k_A/k_2 as the basic strength of A^- increases. Also included in Table 6 are catalytic constants for H^+ catalysis and rate constants for the uncatalysed dissociation, k_d, obtained from the measurements in the absence of added buffer.

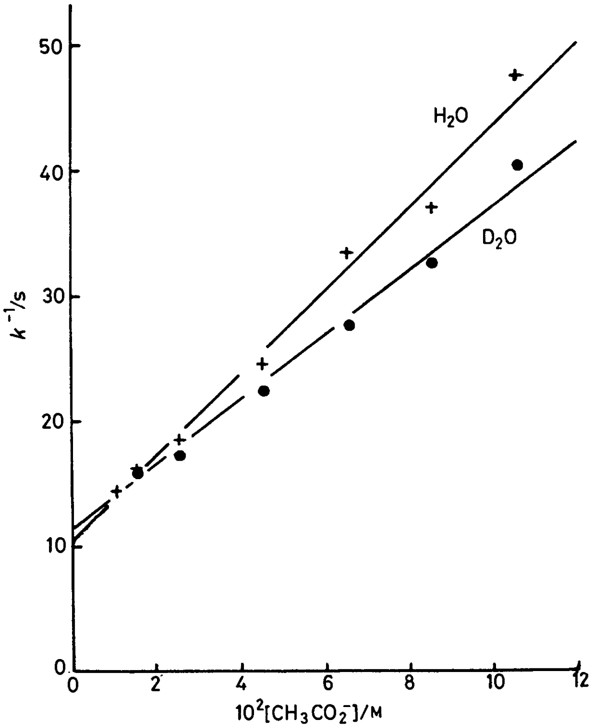


FIGURE 3 Effect of acetate on the acetic acid-catalysed dissociation of $Li(2,1,1)^+$ or H_2O + and D_2O ●

TABLE 6

Catalytic constants [a] for the general acid-catalysed dissociation of $Li(2,1,1)^+$ in H_2O and D_2O at 25 °C

Acid	Solvent	k_d/ s^{-1}	k_{HA}/mol^{-1} $dm^3\ s^{-1}$	pK_a (HA) [b]	I/mol dm^{-3} [c]
	H_2O	0.027			0.0
	D_2O	0.023			0.0
H^+	H_2O		20.6 [d]	−1.70	0.0
D^+	D_2O		14.2 [d]		0.0
CH_2ClCO_2H	H_2O		5.5	2.87	0.13
CH_2ICO_2H	H_2O		3.26	3.17	0.05
HCO_2H	H_2O		1.51	3.75	0.06
$CH_2ClCH_2CO_2H$	H_2O		0.87	4.10	0.05
CH_3CO_2H	H_2O		0.48	4.76	0.113
CH_3CO_2D	D_2O		0.44		0.113
$HO_2CCO_2^-$	H_2O		4.2 [d]	4.27	0.138
$C_6H_5NH_3^+$	H_2O		0.04 (±0.02) [d]	4.60	0.06

[a] k_{HA} ±5%. [b] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1965, 2nd edn. [c] Ionic strength. [d] Corrected to $I = 0$.

The dependence of the catalytic constant, k_{HA}, upon the strength of the acid HA for the two systems $Ca(2,2,2)^{2+}$ and $Li(2,1,1)^+$ may be seen more clearly in Figure 4, in which log k_{HA} is plotted against pK_a(HA). Also included in Figure 4 is the dependence of k_A/k_2 upon pK_a(HA) for the $Li(2,1,1)^+$ system. Catalytic constants for the dissociation of $Ca(2,2,2)^{2+}$ are considerably larger than for $Li(2,1,1)^+$ and significantly less sensitive to acid strength (Brønsted α values [15] are 0.27 and 0.57, respectively). A striking difference between the uncharged carboxylic acids and the charged acids (mono-oxalate ion, $HCO_2{\cdot}CO_2^-$, and anilinium ion, $C_6H_5NH_3^+$) when used as catalysts for the dissociation of $Li(2,1,1)^+$ is also apparent. Thus k_{HA} for $HCO_2CO_2^-$ is *ca.* 100 larger than that for $C_6H_5NH_3^+$, despite a difference of only 0.23 in their pK_a values (Table 6). Although the results are rather limited, it does seem that the relative charge of the complex and the catalysing acid plays an important part in determining the overall rate. This is despite the fact that the cation might be expected to be relatively insulated from the catalyst by the ligand.

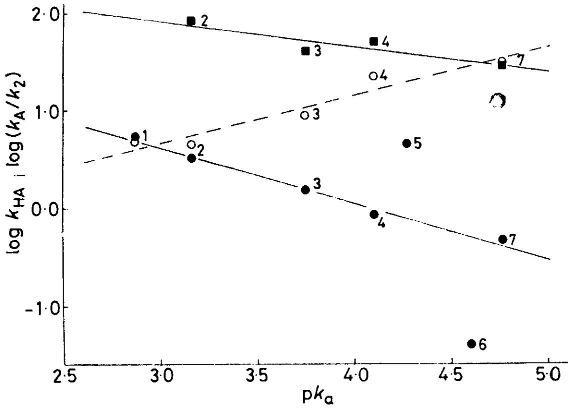


FIGURE 4 Brønsted plot for the general acid catalysed dissociation of $Ca(2,2,2)^{2+}$ ■ and for the protonation ● and deprotonation–dissociation, k_A/k_2 ○, of $Li(2,1,1)^+$. Catalysing acids are as follows: 1, CH_2ClCO_2H; 2, CH_2ICO_2H; 3, HCO_2H; 4, $CH_2ClCH_2CO_2H$; 5, $HO_2CCO_2^-$; 6, $C_6H_5NH_3^+$; 7, CH_3CO_2H

The solvent deuterium isotope effects for the various dissociation reactions are collected in Table 7. The results for the uncatalysed dissociation of $Li(2,1,1)^+$ and $K(2,2,2)^+$ show that as expected the change in solvent from H_2O to D_2O has little effect on reactions not involving proton transfer. The value for $Ag(2,2,2)^+$ catalysed by H^+ is sufficiently large to suggest a rate-determining proton transfer for this reaction. The dissociation of $Ag(2,2,2)^+$ in carboxylic acid buffers has not been studied because of problems with incomplete reaction for this very stable cryptate, but the reaction should be subject to general acid catalysis.

TABLE 7

Kinetic deuterium solvent isotope effects on the dissociation of metal cryptates at 25 °C

Cryptate	Catalyst	$k(H_2O)/k(D_2O)$ [a]
$K(2,2,2)^+$		1.15
$Ag(2,2,2)^+$	H^+	1.92
$Ca(2,2,2)^{2+}$		1.9 (±0.4)
$Ca(2,2,2)^{2+}$	H^+	2.42
$Ca(2,2,2)^{2+}$	CH_3CO_2H	2.74
$Li(2,1,1)^+$		1.17
$Li(2,1,1)^+$	H^+	1.45
$Li(2,1,1)^+$	CH_3CO_2H	1.09

[a] $k(H_2O)/k(D_2O)$ values ±10%.

Isotope effects are relatively large for each of the three reactions of $Ca(2,2,2)^{2+}$ studied. The observed isotope effects for the uncatalysed or spontaneous dissociation indicates that water may be assisting as a general acid catalyst in this reaction, but the large uncertainty in the value of $k(H_2O)/k(D_2O)$ makes this observation rather tentative. The results for H^+ and CH_3CO_2H as catalysts strongly support the conclusion that general acid catalysis of $Ca(2,2,2)^{2+}$ dissociation is due to a rate-determining proton transfer, rather than to an alternative mechanism involving, for example, a rate-determining dissociation of Ca^{2+} from a H-bonded $AH \cdots (2,2,2)Ca^{2+}$ complex formed in a pre-equilibrium step. Such a mechanism should lead to an inverse isotope effect.[16,17]

The results for the acetic acid-catalysed and to a lesser extent the H^+-catalysed dissociation of $Li(2,1,1)^+$ contrast quite sharply with those for $Ca(2,2,2)^{2+}$ and show an almost negligibly small isotope effect. Such a situation is indicative of a very unsymmetrical transition state for the transfer of the proton [9,18] and may be consistent with the observation of a competitive back reaction between $Li(2,1,1)H^{2+}$ and A^- as discussed earlier (Scheme). In the limit of a very fast back reaction ($k_A[A^-] \gg k_2$) (Scheme) and equations (10) and (11) would correspond to specific acid catalysis, and the overall reaction should show an inverse isotope effect.[15] Thus, depending upon the extent to which the transition state for the forward reaction lies close to $Li(2,1,1)H^+$, a low isotope effect is not unreasonable. It has been noted earlier [19] that transfer of a proton from H_2O (or D_2O) to the free ligand (2,1,1) shows quite a large kinetic isotope effect (k^H/k^D 3.9).

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