Effect of Metal-ion Complexation on the Rate of the Alkaline Ester Hydrolysis and the Carbon Acid Dissociation of Crown Malonates in Ethanol–Water Mixtures

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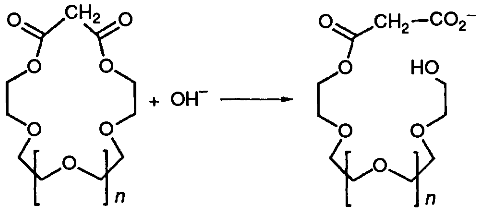
The initial rates of the alkaline hydrolysis of 19-crown-6 malonate (**1**) and 16-crown-5 malonate (**2**) in ethanol–water mixtures are increased to limiting values by the addition of NaCl and KCl. For **1** in 76% (w/w) ethanol–water the addition of 0.015 mol dm^{-3} KCl produces a 65-fold increase in the rate compared with that in the absence of metal ions. The results are compatible with the formation of metal ion–crown malonate complexes which undergo hydrolysis more rapidly than the uncomplexed ligands. Values of the equilibrium constants (K) for complex formation and values of the rate coefficients for hydrolysis of the complexes at hypothetical zero ionic strength (k_c°) are derived. For the K$^+$–19-crown-6 malonate complex the values of K and k_c°/k_f, where k_f is the rate coefficient for hydrolysis of the uncomplexed ligand, increase as the relative permittivity (ε_r) of the solvent mixture decreases. The magnitude of the k_c°/k_f values indicate that the relative permittivity of the space between the bound cation and the reaction centre is about twofold lower than the value of ε_r for the bulk solvent. Spectrophotometric results for the formation of carbanions from **1** and **2** permit qualitative conclusions to be reached about the effect of cation binding on the dissociation of the crown malonates as carbon acids.

The ability of crown compounds to form stable complexes with a wide range of metal cations, protonated amines and neutral molecules is well known.[1] The binding constants are dependent on parameters such as the cavity size and flexibility, the number of donor heteroatoms and the nature of substituents. Cation binding by crown compounds containing functional groups may affect the acid dissociation constant,[2] conformation[3] and spectrum[4] of the functional group.

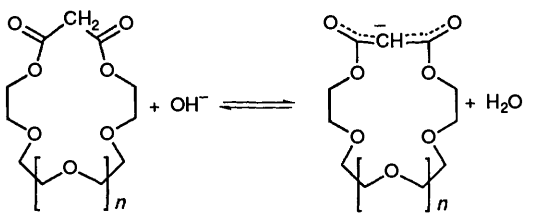
There has also been limited study[5] of the effect of cation binding on the chemical reactivity of functional groups attached to crown ethers. For example we have found[6] that the rate coefficient for the hydroxide-ion promoted hydrolysis of 4′-(4-nitrophenoxycarbonyl)benzo-15-crown-5 is increased in the presence of Na$^+$, K$^+$, Rb$^+$ and Cs$^+$. From measurements in 39, 49 and 54% (w/w) ethanol–water it was found that the value of the ratio of the rate coefficient for reaction of the complexed crown ester (k_c°) at hypothetical zero ionic strength to the rate coefficient for reaction of the uncomplexed ester (k_f) increased as the relative permittivity (ε_r) of the solvent decreased. However, the effects of cations on the rate were too small to permit detailed discussion of the solvent effect on the magnitude of k_c°/k_f. It was found in previous work that cation binding brings about larger rate effects when the functional group is incorporated into the crown ether ring, as, for example, in the alkaline hydrolysis of 19-crown-6 malonate which was studied[7] in 60% (v/v) dioxane–water. We have therefore studied the effect of Na$^+$ and K$^+$ on the hydrolysis of 19-crown-6 malonate (**1**), eqn. (1), in a range of ethanol–water mixtures with varying values of ε_r so as to provide more reliable data for the effect of solvent on k_c°/k_f. The results are used to estimate values of the relative permittivity of the space between the cation and the reactive ester carbonyl and to compare these with the values of ε_r for the bulk solvent. We have also studied the hydrolysis of 16-crown-5 malonate **2** in 76% (w/w) ethanol–water in the presence of K$^+$ and Na$^+$.

Because of the method used to follow the reaction, it has also been possible to investigate the effect of metal-ion binding on the carbon acid dissociation of the crown malonates, eqn. (2).



(1)

1 $n = 2$
2 $n = 1$



(2)

Experimental

16-Crown-5 malonate (**2**) was prepared using a method reported in the literature[8] and 19-crown-6 malonate (**1**) was available from an earlier study.[7]

The hydrolysis of **1** and **2**, eqn. (1), was observed by means of the method used previously.[7] Hydrolysis of the second ester group does not interfere with observation of reaction (1) providing initial rates of reaction are studied. On mixing **1** and **2** with hydroxide ion, the ionisation of the crown malonates produces low concentrations of the carbanions, eqn. (2). These anions show an intense absorbance at 262 nm, thus allowing the concentration of crown malonate to be monitored. The products of hydrolysis contain α-hydrogen atoms which are much less acidic than those of the crown malonate and so do not absorb strongly in this region of the spectrum.

The hydrolysis was followed in ethanol–water mixtures in the presence of lithium hydroxide and with NaCl, KCl, LiCl or

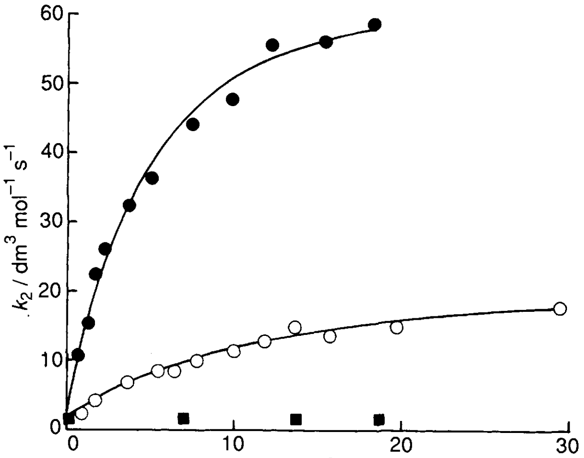


Fig. 1 Effect of metal chlorides (M^+Cl^-) on the initial second-order rate coefficient (k_2) for hydrolysis of 19-crown-6 malonate in ethanol-water mixtures: ●, KCl in 76% ethanol-water; ○, KCl in 54% ethanol-water; ■, LiCl in 54% ethanol-water

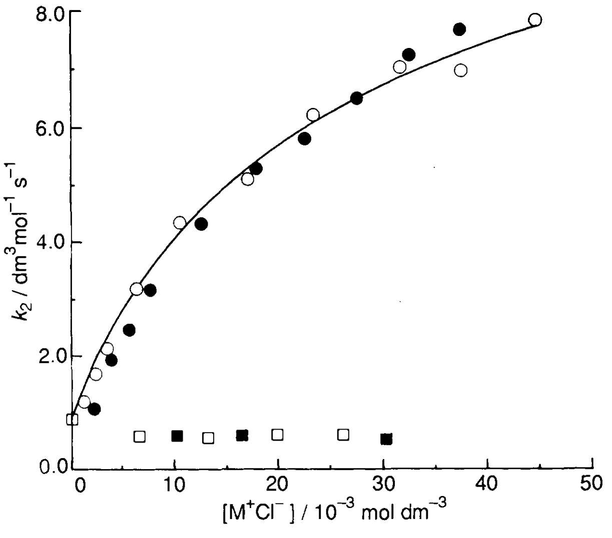


Fig. 2 Effect of metal chlorides (M^+Cl^-) on the initial second-order rate coefficient (k_2) for hydrolysis of 16-crown-5 malonate in 76% ethanol-water: ○, KCl and ●, NaCl; □, LiCl and ■, Me_4NCl

Me_4NCl. Aqueous ethanol mixtures were prepared in 2 dm^3 batches by mixing appropriate weights of distilled water and 99.7% ethanol (James Burroughs AR quality). Tetramethylammonium chloride, lithium chloride and lithium hydroxide were dried under vacuum. Stock solutions of the crown malonates and of the alkali-metal chlorides were made up in ethanol-water mixtures, and the concentrations of stock aqueous LiOH solutions were checked by titration with hydrochloric acid.

The reaction mixtures were measured out into quartz cuvettes using graduated syringes, and the hydrolysis was initiated by adding a small amount of lithium hydroxide solution. The concentration of the carbanion derived from each crown malonate was monitored at 262 nm using a Hewlett-Packard 8451A diode-array spectrophotometer. The carbanions are generated rapidly on mixing **1** or **2** with hydroxide ion and are removed as the hydrolysis proceeds. Typical concentrations of lithium hydroxide and 19-crown-6 malonate in the cuvette were 9.8 × 10^{-4} and 1.4 × 10^{-3} mol dm^{-3}, respectively. Both malonate (C) and hydroxide ion are consumed as the reaction in eqn. (3) occurs. As neither reactant was present in large excess, the decrease in absorbance due to removal of the carbanion was only approximately proportional to the decrease in concentration of hydroxide ion. The approximation shown in eqn. (4) was therefore used, where A denotes absorbance, and the time is indicated as a subscript. The integrated rate equation for reaction (3) can be arranged[9] in the form of eqn. (5), where k_2 is the second-order rate coefficient for the reaction and $\Delta_0 = [C]_0 - [OH^-]_0$. For a simple ester hydrolysis a plot of $\ln(1 + \Delta_0/[OH^-]_t)$ *versus* time (t) will yield a straight line of gradient $\Delta_0 k_2$. For the malonate hydrolysis such plots are curved, because hydroxide ion is consumed in the subsequent hydrolysis of the monoester anion. Since eqns. (4) and (5) are only exact at $t = 0$, initial values of k_2 ($t \longrightarrow 0$) were calculated by fitting values of $\ln(1 + \Delta_0/[OH^-]_t)$ to a polynomial function of time, eqn. (6), using a least-squares method. The number of statistically significant terms in eqn. (6) (usually 2 or 3) was determined by use of Snedecor's *F*-test.[10] The initial value of the second-order rate coefficient is given by eqn. (7).

$$C + OH^- \longrightarrow \text{Products} \quad (3)$$

$$[OH^-]_t = [OH^-]_0\{(A_t - A_\infty)/(A_0 - A_\infty)\} \quad (4)$$

$$\ln(1 + \Delta_0/[OH^-]_t) = \Delta_0 k_2 t + \ln([C]_0/[OH^-]_0) \quad (5)$$

$$\ln(1 + \Delta_0/[OH^-]_t) = a_0 + a_1 t + a_2 t^2 + \ldots \quad (6)$$

$$k_2 = a_1/\Delta_0 \quad (7)$$

For the fastest reactions a significant decrease in absorbance occurred between the addition of base to the reaction mixture and the measurement of the first absorbance value. However, values of the rate coefficient calculated using an estimated value of the initial absorbance differed by less than 6% from values calculated using the standard procedure. The variance of k_2 gives a measure of the error associated with fitting the data to a polynomial curve and this was typically *ca.* 2%. The validity of this procedure for measuring rate coefficients was checked by determining the rate coefficient for the alkaline hydrolysis of diethyl malonate in 60% (v/v) dioxane-water at 35 °C for which a value for the rate coefficient has been measured previously. The value of 1.20 dm^3 mol^{-1} s^{-1} obtained compares favourably with the result of 1.19 dm^3 mol^{-1} s^{-1} obtained previously by a titration method.[11]

In solutions containing lithium chloride or tetramethylammonium chloride, a short induction period was observed during which the absorbance increased prior to the decrease in absorbance accompanying hydrolysis. In such cases the absorbance values obtained in this period were discarded and an estimated value for the initial absorbance was used to calculate values of k_2. The induction period is thought to arise because the carbon acid dissociation and the ester hydrolysis occur at similar rates. The initial rapid increase in absorbance due to formation of the carbanion is therefore overlapped by a gradual decrease in absorbance as crown malonate is consumed. It is possible that this effect is not observed in the presence of Na^+ and K^+ because these ions strongly accelerate the carbon acid ionisation.

Results and Discussion

The effect of adding KCl on the initial rate of reaction between hydroxide ion and 19-crown-6 malonate in 76 and 54% (w/w) ethanol-water and the effect of LiCl in 54% (w/w) ethanol-water are shown in Fig. 1. Data for 16-crown-5 malonate in 76% ethanol-water in the presence of KCl, NaCl, LiCl and Me_4NCl are shown in Fig. 2. Concentrations of LiCl and Me_4NCl up to 0.03 mol dm^{-3} have no significant influence on the rate of hydrolysis of either crown malonate. The addition of KCl and

NaCl, however, produces an increase in the value of k_2 for the hydrolysis of **1** and **2** which approaches a limiting value. The size of the effect depends on the ligand and on the composition of the solvent. Potassium chloride has a larger influence on the rate of hydrolysis of 19-crown-6 malonate than does sodium chloride. For example, in the presence of 0.025 mol dm^{-3} of NaCl, the value of k_2 in 76% (w/w) ethanol–water is about eight times larger than when no salt is present, whereas 0.015 mol dm^{-3} KCl produces a 65-fold increase in the rate. In 54% (w/w) ethanol–water the addition of 0.03 mol dm^{-3} NaCl increases the value of k_2 by a factor of 2.5 whereas a similar concentration of KCl produces a *ca.* eleven-fold increase.

The effect of KCl on the hydrolysis of **1** is much greater in 76% (w/w) ethanol–water than in 54% (w/w) ethanol–water as shown in Fig. 1. A steady decrease in the effect of KCl is observed with increasing polarity of the solvent in the order 76% > 65% > 54% > 39% (w/w) ethanol–water.

In the hydrolysis of **2** in 76% (w/w) ethanol–water the effect of KCl is similar to that of NaCl but much smaller than the effect of KCl on the hydrolysis of **1** in the same solvent.

Sodium and potassium ions are known to form complexes in solution with 19-crown-6 malonate,[8] and with polyethers of similar size and structure. The enhancement in the rate of hydrolysis of **1** and **2** arises because the crown malonates and the metal ion form a complex which is more reactive than the uncomplexed ligand. In contrast, the rate of hydrolysis in 65% ethanol–water of diethyl malonate, which does not form complexes with metal ions, was found to be unaffected by concentrations of KCl in the range 0.007–0.03 mol dm^{-3} and the average value of the rate coefficient at four different concentrations was 0.33 ± 0.01 dm^3 mol^{-1} s^{-1}. The small effect of LiCl and Me_4NCl on the rate of hydrolysis of **1** and **2** is compatible with the absence of complex formation in these cases. The size of Me_4N^+ and the strong solvation of Li^+ inhibit complexation of these ions.

The hydrolysis of crown malonate (C) in the presence of metal ions (M^+) that form 1:1 complexes with the ligand may occur *via* one of two routes: the reaction of uncomplexed (or 'free') crown malonate, eqn. (8), or the reaction of the metal-ion-complexed species (CM^+), eqn. (11), the rate coefficients for which are k_f and k_c, respectively. The ratio of complexed to uncomplexed substrate is governed by the equilibrium for cation binding, eqn. (9). The effect of a positive charge close to the reaction centre may be gauged by comparing the values of k_f and k_c.

$$\mathrm{C} + \mathrm{OH}^- \xrightarrow{k_f} \text{Products} \qquad (8)$$

$$\mathrm{C} + \mathrm{M}^+ \rightleftharpoons \mathrm{CM}^+ \qquad (9)$$

$$K = [\mathrm{CM}^+]/[\mathrm{C}][\mathrm{M}^+] \qquad (10)$$

$$\mathrm{CM}^+ + \mathrm{OH}^- \xrightarrow{k_c} \text{Products} \qquad (11)$$

The stoichiometric concentration of substrate (C_{st}) at zero time of reaction is given by eqn. (12), and the rate of its disappearance expressed in terms of k_f and k_c is given by eqn. (13). The initial second-order rate coefficient (k_2) may therefore be written as in eqn. (14). Eqn. (15) which is obtained by combining eqns. (10), (12) and (14) is qualitatively consistent with the observed variation of k_2 with metal chloride concentration shown in Figs. 1 and 2.

$$[\mathrm{C_{st}}]_0 = [\mathrm{C}]_0 + [\mathrm{CM}^+]_0 \qquad (12)$$

$$-\mathrm{d}[\mathrm{C_{st}}]_0/\mathrm{d}t = (k_f[\mathrm{C}]_0 + k_c[\mathrm{CM}^+]_0)[\mathrm{OH}^-]_0 \qquad (13)$$

$$k_2 = (k_f[\mathrm{C}]_0 + k_c[\mathrm{CM}^+]_0)/[\mathrm{C_{st}}]_0 \qquad (14)$$

$$k_2 = (k_f + k_cK[\mathrm{M}^+]_0)/(1 + K[\mathrm{M}^+]_0) \qquad (15)$$

Since the reaction between the metal ion–crown malonate complex and hydroxide ion, eqn. (11), involves two charged species it is subject to a primary kinetic electrolyte effect. The value of k_c at finite ionic strength (I) is related to the value at zero ionic strength (k_c°) by eqn. (16), where the activity coefficients (y) refer to CM^+ and OH^-, and to the transition-state (#). The Debye–Hückel approximation,[12] eqn. (17), allows eqn. (16) to be expressed in the form of eqn. (18). The parameters A and B are dependent on the relative permittivity of the reaction mixture (ε_r) and were calculated from eqns. (19) and (20).[12] An estimated value for the ion-size parameter of $\mathring{a} = 400$ pm was used for both metal chlorides. The effect of ionic strength on the value of k_f is assumed to be negligible, an assumption that is justified by the observation that the rate coefficient for hydrolysis of diethyl malonate in 65% (w/w) ethanol–water is independent of the concentration of KCl up to 0.03 mol dm^{-3}.

$$k_c = k_c^\circ\{y_{\mathrm{CM}^+}y_{\mathrm{OH}^-}/y_{\#}\} \qquad (16)$$

$$\log y_i = -A(Z_i)^2(I)^{1/2}/[1 + B\mathring{a}(I)^{1/2}] \qquad (17)$$

$$\log(k_c/k_c^\circ) = -2A(I)^{1/2}/[1 + B\mathring{a}(I)^{1/2}] \qquad (18)$$

$$A/\mathrm{mol}^{-1/2}\,\mathrm{dm}^{3/2}\,K^{3/2} = 1.825 \times 10^6/(\varepsilon_rT)^{3/2} \qquad (19)$$

$$B/\mathrm{m}^{-1}\,\mathrm{mol}^{-1/2}\,\mathrm{dm}^{3/2}\,K^{1/2} = 50.29 \times 10^{10}/(\varepsilon_rT)^{1/2} \qquad (20)$$

The concentration of 'free' metal ions, and the ionic strength of the reaction solutions, will be reduced by the formation of ion pairs between metal ions and chloride or hydroxide ions, eqns. (21) and (22), and corrections were applied to account for this. The values of K_{pair} for (M^+Cl^-) were interpolated from literature values,[13] and those for (M^+OH^-) were assumed to be the same as those of the corresponding metal chloride. Whilst better fits to the data are obtained when ion pairing is taken into account, the effects of ion pairing at the concentrations used in the present work are small.

$$\mathrm{M}^+ + \mathrm{Cl}^- \rightleftharpoons (\mathrm{M}^+\mathrm{Cl}^-) \qquad (21)$$

$$K_{\mathrm{pair}} = [(\mathrm{M}^+\mathrm{Cl}^-)]/[\mathrm{M}^+][\mathrm{Cl}^-] \qquad (22)$$

When the corrections of eqns. (18) and (22) had been applied, eqn. (15) was fitted to the experimental results by the stepwise iterative adjustment of K and k_c° using the previously employed procedure.[7] The points in Figs. 1 and 2 are experimental results and the curves were generated using the derived values of K and k_c° given in Table 1. Good fits to the experimental data were obtained for 19-crown-6 malonate but in view of the assumptions required in the analysis, the values of K and k_c° in Table 1 are subject to some uncertainty. The effects of metal ions on the hydrolysis of 16-crown-5 malonate were smaller and kinetic studies were restricted to 76% ethanol–water for which the largest effects are obtained. Data in the presence of KCl, NaCl, LiCl and Me_4NCl are shown in Fig. 2. The curve is a fit of eqn. (15) to the results for KCl using the values of K and k_c° given in Table 1. The values of K and k_c° have large errors associated with them but it is obvious that the complexes formed between **2** and K^+ are weaker than the corresponding 19-crown-6 malonate complexes. Analysis of the rate data for the hydrolysis of 16-crown-5 malonate in the presence of NaCl failed to yield convergent values of K and k_c°, although, as can be seen from the results in Fig. 2, the data are quite similar to the results obtained in the presence of KCl.

Table 1 Parameters relating to cation binding by the crown malonates derived from the rate coefficients for hydrolysis

Malonate	Metal chloride	Solvent (w/w %) EtOH–H_2O	ε_r [a]	K/dm^3 mol^{-1}	k_c°/dm^3 mol^{-1} s^{-1}	k_c°/k_f	ε_r(eff) [b]
1	NaCl	76	35	42	34	39	24
1	KCl	76	35	81	230	270	16
1	KCl	65	41	49	95	77	21
1	KCl	54	47	31	72	45	24
1	KCl	39	55	13	59	31	26
2	KCl	76	35	6	*ca.* 120	*ca.* 150	

[a] ε_r is the relative permittivity of the solvent. [b] ε_r(eff) is the calculated value for the relative permittivity of the space between the centres of the metal cation and the carbonyl oxygen in the transition state for reaction of the crown malonate–cation complex with hydroxide ion.

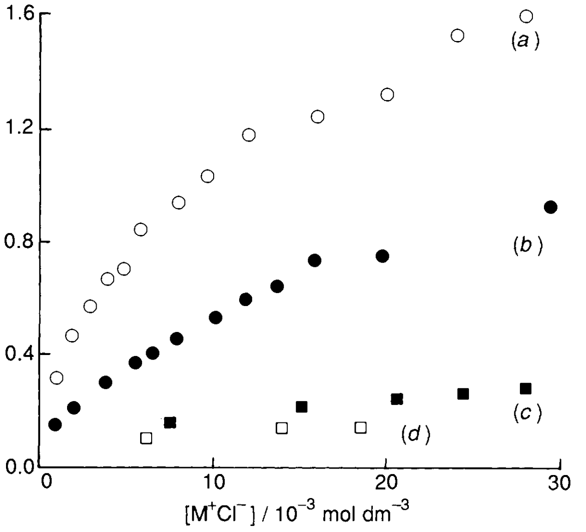


Fig. 3 Effect of metal chlorides (M^+Cl^-) on the overall change in absorbance (ΔA) accompanying hydrolysis of 19-crown-6 malonate: (*a*) with KCl in 65% (w/w) ethanol–water; (*b*) with KCl in 54% (w/w) ethanol–water; (*c*) with NaCl in 54% (w/w) ethanol–water; (*d*) with LiCl in 54% (w/w) ethanol–water

As expected, the largest values of K and k_c° are associated with systems in which low concentrations of metal chloride produce a large increase in the rate of hydrolysis and an attainment of a constant value of k_2 at low concentrations of the metal ion. The values of K show that in ethanol–water mixtures 19-crown-6 malonate binds potassium ions more strongly than sodium ions. The cation binding constant for the interaction of K^+ with 19-crown-6 malonate decreases as the water content, and therefore the relative permittivity of the solvent mixture, increases. Similar behaviour has been observed[14] for the complexes formed between sodium ions, and 18-crown-6 and benzo-15-crown-5 and is due to increased solvation of the reactants in the more polar solvent mixtures.

The values of k_c°/k_f in Table 1 reflect the effect of metal ions on the reactivity of the malonate group. The relatively large values for this ratio are likely to arise from an electrostatic interaction between the positively charged metal ion and the developing negative charge on the carbonyl of the ester in the transition state for nucleophilic attack of hydroxide ion. The values of k_c°/k_f for reaction of 19-crown-6 malonate in the presence of K^+ decrease as the relative permittivity of the bulk solvent increases. This decrease in electrostatic stabilisation implies that the relative permittivity of the space between K^+ and the charge in the transition state increases as the bulk relative permittivity of the solvent is increased.

The effect of the charge of the metal ion on the value of k_c°/k_f for the hydrolysis of 19-crown-6 malonate in 60% (v/v) dioxane–water has been treated[7] by the model originally applied by Bjerrum[15] to the dissociation of dicarboxylic acids. This approach leads to expression (23) in which e_0 is the electronic

$$\ln(k_c^\circ/k_f) = e_0^2/[4\pi\varepsilon_0 kTr\varepsilon_r(\text{eff})] \qquad (22)$$

charge, ε is the vacuum permittivity and k is Boltzmann's constant. The charges on the metal ion and the carbonyl oxygen in the transition state are at a distance of r separated by a space of relative permittivity ε_r(eff). A value for r of 620 pm was used.

The values of ε_r(eff) calculated from eqn. (23) for the transition state for the reaction of the 19-crown-6 malonate–K^+ complex are given in Table 1 and are compared with the values of ε_r for the bulk solvent. The effect of the metal ion in stabilising the negative charge on the carbonyl oxygen in these reactions can be accounted for by an electrostatic interaction through space which has a relative permittivity which is about half that of the bulk solvent. The calculated values of ε_r(eff) decrease in parallel with ε_r for the bulk solvent but this is probably not significant in view of the assumptions involved in using eqn. (23). In calculations of the contribution of electrostatic interactions to the intramolecular substituent effects of charged groups, as for example in the dissociation of substituted benzoic acids, values of the relative permittivity of the medium through which the effect is transmitted ranging from that of the bulk solvent to the value of a hydrocarbon chain have been used.[16] In metal ion–crown ether acetal complexes it has been found that the use of the relative permittivity of the bulk solvent for ε_r(eff) provides good agreement with the experimental results.[17]

As was noted above, the crown malonates used in this study act as carbon acids, eqn. (2), and low concentrations of carbanions are produced under the reaction conditions. These species absorb strongly at 262 nm and since the products of hydrolysis and the unionised crown malonates absorb to a negligible extent at this wavelength, the overall absorbance change during the hydrolysis (ΔA) is proportional to the carbanion concentration at zero reaction time and hence provides a measure of the extent of dissociation of the crown malonates. The values of ΔA for the reactions of **1** and **2** were found to increase with the stoichiometric concentration of sodium and potassium ions in the solution as shown for **1** in Fig. 3. The shift in the position of equilibrium (2) to the right on adding complexable cations arises because the bound cation stabilises the carbanion through electrostatic interaction. Similar behaviour has been observed for the effect of metal ions on the dissociation of carboxylic acid groups attached to crown ethers.[2] The data in Fig. 3 show that the addition of increasing concentrations of lithium ions to the reaction solution produces a small increase in the value of ΔA which is likely to arise from ion pairing or a small electrolyte effect. Also, when the hydrolysis of diethyl malonate was studied in 65% ethanol–water it was found that the value of ΔA was independent of the concentration of potassium ions. This is compatible with the absence of a host–guest interaction in this system. From the changes in ΔA with concentration it can be concluded that potassium ions have a larger influence on the acid dissociation constant of 19-crown-6 malonate than do sodium ions, whereas the dissociation of 16-crown-5 malonate is affected to a similar extent by these ions. The size of the effects also increases with decreasing polarity of the solvent. This behaviour reflects the relative cation-binding constants of the ligands towards Na^+ and K^+ and parallels the conclusions reached from the kinetic results.

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