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ION ASSOCIATION AND REACTIVITY OF THE ALKALI METAL SALTS OF ALKANOIC ACIDS IN DIPOLAR APROTIC SOLVENTS

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The effect of added alkali metal perchlorates on the rate of lactonization of ω-bromoalkanoate ions was investigated in 99% dimethyl sulphoxide (four-membered ring formation) and in dimethylformamide (DMF) (four- and sixteen-membered ring formation). In all cases the effect of the added metal salts is rate depressing, as a result of the lower reactivity of metal ion-associated species relative to the free ions. Ion-pairing association constants were determined, but the reactivity of ion pairs were so low as to elude direct measurement in most cases. Evidence was also obtained for the formation of ion triplets with Li^+ in DMF. The relevance of the present results in connection with the 'caesium effect' is briefly discussed.

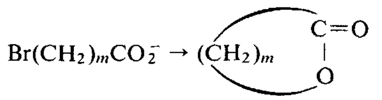
INTRODUCTION

The notion that the reactivity of anionic nucleophiles can be considerably affected by association with metal ions is widespread,[1] but much of the evidence on which such a notion is based is still qualitative in nature, or semiquantitative at best. In recent years we have started a programme devoted to a physico-organic investigation of the phenomenon. We have studied the effect of metal ion association on the rates of alkylation of aryloxide ions[2,3] and of β-ketoenolate ions derived from malonic[4] and acetoacetic[5] esters. We have shown that under a suitable set of conditions a self-consistent analysis can lead to a meaningful subdivision of reactivity data into contributions from free ions and ion pairs, and to reliable estimates of ion-pair association constants.

In view of our continuing interest in this field, and with the aim of extending the scope of the self-consistent approach, we have now undertaken an investigation of the effect of added alkali metal salts on the rates of alkylation of alkanoate ions.

RESULTS

Because of the inherent slowness of intermolecular alkylations of alkanoate ions with primary alkyl bromides,[6] and of the problems linked to the 'spontaneous' reaction of the latter with dimethyl sulphoxide (Me_2SO),[2] we chose as a probe reaction the lactonization of 3-bromopropanoate anion (four-membered ring formation) [equation (1)], which has been reported to occur smoothly in Me_2SO solution at room temperature.[7] Its rate, lying in the stopped-flow range, is still conveniently fast for extensive rate measurements both in dimethylformamide (DMF) and 99% Me_2SO at 25 °C in the presence of rate-retarding added salts. Further, in view of our long-standing interest in macrolactonization reactions, we have also studied the cyclization of 15-bromopentadecanoate anion (16-membered ring formation) [equation (1)] in DMF. For the latter substrate, rate measurements were carried out at 45 °C for experimental convenience.



(1)

$m = 2$ and 14

Since little or no change in absorbance accompanies the transformation of carboxylate into a lactone function, a visual acid–base indicator (InH) was matched to the reactions concerned, so that the kinetics could be simply followed by monitoring the disappearance of the basic form In^- either by stopped-flow or conventional spectrophotometry, depending on the time-scale of the experiment. Details on the spectrophotometric method with the visual indicator have been reported elsewhere.[7,8] Briefly, the concentration of In^- is bound to that of the reacting substrate $Br(CH_2)_mCO_2^-$ through equation (2), in which K_{InH} and K_m are the acidity

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constants.

$$[\mathrm{In}^-] = \frac{K_{\mathrm{InH}}[\mathrm{InH}]}{K_{\mathrm{m}}[\mathrm{Br(CH_2)}_m\mathrm{CO_2H}]}[\mathrm{Br(CH_2)}_m\mathrm{CO_2^-}] \quad (2)$$

Equation (2) shows that $[\mathrm{In}^-]$ is simply proportional to $[\mathrm{Br(CH_2)}_m\mathrm{CO_2^-}]$ when the ratio $[\mathrm{InH}]/[\mathrm{Br(CH_2)}_m\mathrm{CO_2H}]$ is constant. Such a condition was fulfilled (i) by running the cyclization of a given alkanoate anion in the presence of a significant amount of the parent bromoacid and (ii) by choosing InH in such a way that only a very small fraction is converted into the basic form under the reaction conditions. The indicators of choice were 2,6-dichlorophenol for 3-bromopropanoic acid and *m*-nitrophenol for 15-bromopentadecanoic acid. The kinetics were started by the fast addition of a calculated amount of 0·04 M Bu_4NOH stock solution to a mixture of the parent bromoacid and InH in the proper solvent. The amount of base was calculated in order to neutralize approximately half of the bromo acid. Typical concentrations in the kinetic runs were $[\mathrm{Br(CH_2)}_m\mathrm{CO_2^-}] \approx [\mathrm{Br(CH_2)}_m\mathrm{CO_2H}]$ $2{\cdot}5\times10^{-4}$–5×10^{-4} M, $[\mathrm{In}^-]2\times10^{-5}$–$4\times10^{-5}$ M and

Table 1. Salts effects on lactonization of ω-bromoalkanoates[a]

Salt	Concentration (M)	$k_{obs}(s^{-1})$	Salt	Concentration (M)	$k_{obs}(s^{-1})$
		$Br(CH_2)_2CO_2^-$ in 99% Me_2SO at 25·0 °C			
None		0·068	$NaClO_4$	$2{\cdot}7\times10^{-3}$	0·051
				0·010	0·031
Et_4NBr	0·089	0·063		0·039	0·022
				0·100	0·013
$CsClO_4$	0·010	0·065			
	0·090	0·041	$LiClO_4$	0·010	0·043
				0·020	0·035
$KClO_4$	$3{\cdot}0\times10^{-3}$	0·063		0·031	0·029
	0·010	0·060		0·054	0·023
	0·032	0·048		0·097	0·020
	0·094	0·036			
		$Br(CH_2)_2CO_2^-$ in DMF at 25·0 °C			
None		0·073	$NaClO_4$	0·020	0·018
				0·033	0·012
Et_4NBr	0·095	0·063		0·049	$8{\cdot}0\times10^{-3}$
				0·099	$5{\cdot}1\times10^{-3}$
$CsClO_4$	0·010	0·060		0·170	$4{\cdot}3\times10^{-3}$
$KClO_4$	$5{\cdot}2\times10^{-3}$	0·064	$LiClO_4$	0·010	0·037
	0·013	0·059		0·018	0·027
				0·031	0·018
				0·049	0·011
				0·098	$5{\cdot}7\times10^{-3}$
				0·160	$3{\cdot}7\times10^{-3}$
		$Br(CH_2)_{14}CO_2^-$ in DMF at 45·0 °C			
None		$3{\cdot}8\times10^{-3}$	$NaClO_4$	$7{\cdot}2\times10^{-3}$	$6{\cdot}6\times10^{-4}$
				0·014	$4{\cdot}3\times10^{-4}$
Et_4NBr	0·054	$3{\cdot}5\times10^{-3}$		0·025	$3{\cdot}0\times10^{-4}$
	0·144	$2{\cdot}8\times10^{-3}$		0·020	$3{\cdot}5\times10^{-4}$
				0·050	$2{\cdot}0\times10^{-4}$
$KClO_4$	0·010	$1{\cdot}8\times10^{-3}$		0·059	$2{\cdot}0\times10^{-4}$
				0·184	$1{\cdot}0\times10^{-4}$
$CsClO_4$	$8{\cdot}0\times10^{-3}$	$2{\cdot}9\times10^{-3}$			
	0·021	$2{\cdot}2\times10^{-3}$	$LiClO_4$	$1{\cdot}5\times10^{-3}$	$1{\cdot}1\times10^{-3}$
	0·048	$1{\cdot}6\times10^{-3}$		$4{\cdot}3\times10^{-3}$	$5{\cdot}2\times10^{-4}$
	0·078	$1{\cdot}3\times10^{-3}$		$8{\cdot}9\times10^{-3}$	$3{\cdot}0\times10^{-4}$
	0·107	$1{\cdot}0\times10^{-3}$		0·018	$2{\cdot}3\times10^{-4}$
	0·209	$7{\cdot}8\times10^{-4}$		0·045	$8{\cdot}1\times10^{-5}$
				0·091	$5{\cdot}0\times10^{-5}$
				0·167	$2{\cdot}4\times10^{-5}$

[a] Reproducibility of rate constants within ±5%.

[InH] 3×10^{-4}–6×10^{-4} M. The decrease in the absorption of the basic form of the indicator was followed in the range 320–335 nm for 2,6-dichlorophenol and 470–490 nm for *m*-nitrophenol. The alkali metal ions were added as perchlorates, which are likely to behave as strong electrolytes in the given solvents[9] in the concentration range used, namely 10^{-3}–10^{-1} M. Any possible association of In^- with the metal ions, apart from presumably being small,[3] had no appreciable influence on the fulfillment of the proportionality conditions expressed by equation (2). The effect of tetraethylammonium bromide was also studied. Strict first-order behaviour was observed in all cases.

The observed rate constants are listed in Table 1 and are plotted as a function of the concentration of added salt in Figure 1.

Treatment of rate data

It is apparent that Et_4NBr exerts only a small effect on the given reactions, which can be interpreted as indicative of a negligible association between the alkanoate ions and the tetraalkylammonium ion.[2–5] Accordingly, the k_{obs} values obtained in the presence of the Bu_4N^+ ion, as the sole counter ion accompanying

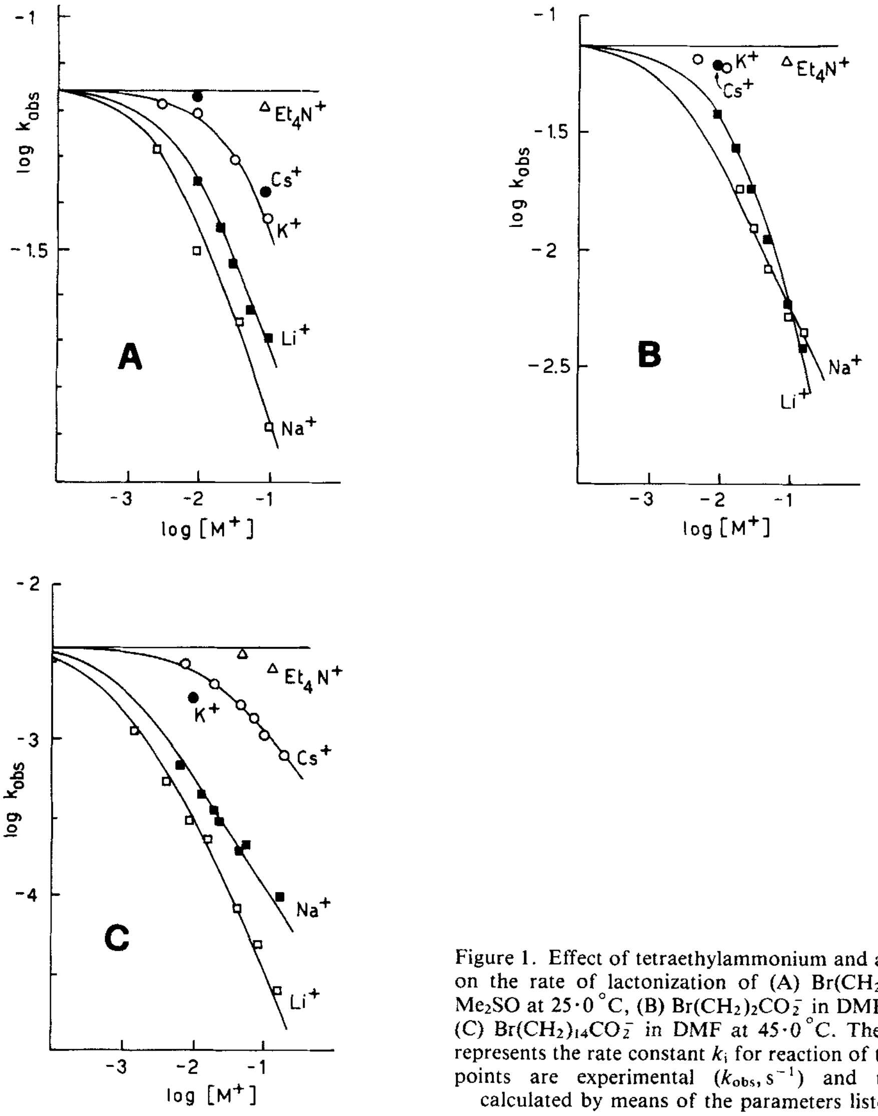
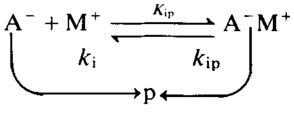


Figure 1. Effect of tetraethylammonium and alkali metal salts on the rate of lactonization of (A) $Br(CH_2)_2CO_2^-$ in 99% Me_2SO at 25·0 °C, (B) $Br(CH_2)_2CO_2^-$ in DMF at 25·0 °C and (C) $Br(CH_2)_{14}CO_2^-$ in DMF at 45·0 °C. The horizontal line represents the rate constant k_i for reaction of the free ion. The points are experimental (k_{obs}, s^{-1}) and the curves are calculated by means of the parameters listed in Table 2

the added base, were taken as reliable measures of the reactivity of the free ions (k_i).

On the other hand, the rate-depressing effects exerted by the added metal salts are diagnostic of significant associations, the reactivity of the associated species being lower than that of unassociated reactants.



Scheme 1

The simplest scheme (Scheme 1) that can accommodate rate-retarding effects from ion association is one involving independent and additive contributions from the free ion and from the ion pair [equation (3)] with $k_{ip} < k_i$, whose relative proportions are ruled by the equilibrium constant K_{ip} for ion pairing [equation (4)]. Combination of equations (3) and (4), with the additional assumption of a negligible primary salt

$$v = k_i[\mathrm{Br(CH_2)}_m\mathrm{CO_2^-}] + k_{ip}[\mathrm{Br(CH_2)}_m\mathrm{CO_2^-M^+}] \qquad (3)$$

$$K_{ip} = \frac{[\mathrm{Br(CH_2)}_m\mathrm{CO_2^-M^+}]}{[\mathrm{Br(CH_2)}_m\mathrm{CO_2^-}]\,[\mathrm{M^+}]\gamma_\pm^2} \qquad (4)$$

effect,[5] leads to equation (5), which relates the measured quantities k_{obs}/k_i to $[\mathrm{M^+}]$ through a functional relationship containing only two adjustable parameters (k_{ip} and K_{ip}), provided that a suitable expression for the activity coefficient is available.

$$\frac{k_{obs}}{k_i} = \frac{1 + (k_{ip}/k_i)K_{ip}\gamma_\pm^2\,[\mathrm{M^+}]}{1 + K_{ip}\gamma_\pm^2\,[\mathrm{M^+}]} \qquad (5)$$

$$\frac{k_{obs}}{k_i} = \frac{1 + K_{T^\ddagger}\gamma_\pm^2\,[\mathrm{M^+}]}{1 + K_{ip}\gamma_\pm^2\,[\mathrm{M^+}]} \qquad (6)$$

In terms of transition state theory, the equivalent equation (6) is obtained,[10] where the quantity $K_{T^\ddagger} = (k_{ip}/k_i)K_{ip}$ has the meaning of the equilibrium constant for the formal conversion of the transition state $T^\ddagger$, which does not contain M^+, into one which contains M^+ [equation (7)].

$$T^\ddagger + M^+ \overset{K_{T^\ddagger}}{\rightleftharpoons} T^\ddagger M^+ \qquad (7)$$

A non-linear least-squares procedure[5] was used to fit the data to equation (5) or (6) with the mean activity coefficient $\gamma_\pm$ calculated as previously[2,3] from the extended Debye–Hückel equation. It is worth stressing that neglect of activity coefficients leads to a totally meaningless fit of rate data. As an example, in $\mathrm{Me_2SO}$ at 25 °C we estimate the quantity $\gamma_\pm^2$ to be 0·722 and 0·418 at 5×10^{-3} and 1×10^{-1} M ionic strength, respectively. In view of the adaptability of equations containing two adjustable parameters, and of the obvious difficulty in accounting with acceptable precision for the non-ideal behaviour of relatively concentrated electrolyte solutions, caution is needed in the interpretation of the results of the curve-fitting procedure. This is particularly so in the case of $K_{T^\ddagger}$ [or $K_{ip}(k_{ip}/k_i)$], which turned out to be very small for all of the systems investigated.

In fact, for many reactions [$\mathrm{Na^+}$, $\mathrm{Br(CH_2)_2CO_2^-}$, DMF; $\mathrm{K^+}$, $\mathrm{Br(CH_2)_2CO_2^-}$, 99% $\mathrm{Me_2SO}$; $\mathrm{Na^+}$ and $\mathrm{Cs^+}$, $\mathrm{Br(CH_2)_{14}CO_2^-}$, DMF] $K_{T^\ddagger}$ was so small (i.e. < 10) that the quantity $1 + K_{T^\ddagger}\gamma_\pm^2\,[\mathrm{M^+}]$ is not significantly larger than 1 in the investigated concentration range. In the above cases a satisfactory fit of the data was also obtained with the simple equation (8), which contains the quantity K_{ip} as the sole adjustable parameter and holds for the case where the ion pair is totally unreactive. In only two cases, i.e. $\mathrm{Li^+}$ and $\mathrm{Na^+}$ in the cyclization of $\mathrm{Br(CH_2)_2CO_2^-}$ in 99% $\mathrm{Me_2SO}$, were the $K_{T^\ddagger}$ values large enough to support the existence of small but definite contributions from the ion-pair path to the overall rate.

$$\frac{k_{obs}}{k_i} = \frac{1}{1 + K_{ip}\gamma_\pm^2\,[\mathrm{M^+}]} \qquad (8)$$

The situation is more complicated with the $\mathrm{Li^+}$ salts in DMF. The least-squares treatment of the data according to equation (6) afforded negative values for the quantities $K_{T^\ddagger}$, which is clearly devoid of physical significance. The simple equation (8) gave a poor fit to the data, with a definite tendency for the k_{obs} values in the high concentration region to be significantly lower than those calculated. The situation is closely reminiscent of that exhibited by $\mathrm{Li^+}$ aryloxides,[3] for which the occurrence of ion triplets of the type + − + was shown[3] to be more significant in DMF than in 99% $\mathrm{Me_2SO}$. Accordingly, the rate-depressing effects on lactone formation exerted by $\mathrm{Li^+}$ in DMF were well accounted for quantitatively in terms of equation (9), which is an expansion of equation (8) to include triple-ion formation [equation (10)], and holds when both ion pairs and ion triplets are unreactive.[3]

$$\frac{k_{obs}}{k_i} = \frac{1}{1 + K_{ip}\gamma_\pm^2\,[\mathrm{M^+}]\,(1 + K_{it}[\mathrm{M^+}])} \qquad (9)$$

$$\mathrm{Br(CH_2)}_m\mathrm{CO_2^-M^+} + \mathrm{M^+} \overset{K_{it}}{\rightleftharpoons} \mathrm{Br(CH_2)}_m\mathrm{CO_2^-(M^+)_2} \qquad (10)$$

The results of the least-squares analysis of rate data are summarized in Table 2. It is worth noting that the log K_{ip} values for $\mathrm{Br(CH_2)_2CO_2^-}$ in 99% $\mathrm{Me_2SO}$ compare remarkably well with the corresponding values reported by Olmstead and Bordwell[11] for the benzoate anion in $\mathrm{Me_2SO}$ at 25 °C: 2·21 for $\mathrm{Li^+}$, 2·31 for $\mathrm{Na^+}$ and 1·68 for $\mathrm{K^+}$. The pK_a of benzoic acid in water is 4·20 and that of 3-bromopropanoic acid is 4·00.[12] It seems very likely that the acidities of the two acids should follow a comparable trend also in $\mathrm{Me_2SO}$. Thus,

Table 2. Rate and equilibrium parameters

Substrate/conditions	Metal ion	Log K_{ip}	Log K_{it}	Log $K_{T^{\neq}}$	k_{ip}/k_i
$Br(CH_2)_2CO_2^-$, 99% Me_2SO, 25·0 °C	Li^+	2·08	—	1·20	0·14
	Na^+	2·28	—	1·26	0·09
	K^+	1·40	—	—	—
	Cs^+	1·2[a]	—	—	—
$Br(CH_2)_2CO_2^-$, DMF, 25·0 °C	Li^+	2·21	1·18	—	—
	Na^+	2·60	—	—	—
$Br(CH_2)_{14}CO_2^-$, DMF, 45·0 °C	Li^+	3·24	1·00	—	—
	Na^+	2·98	—	—	—
	Cs^+	1·85	—	—	—

[a] Rough estimate from only two points, under the assumption that the ion pair is unreactive.

the similarities of the basicities of the corresponding carboxylate anions render meaningful a direct comparison of their ion-pairing tendencies, and point to the correctness of our analysis of rate data.

DISCUSSION

Stability of associated species

The log K_{ip} data in Table 2 provide useful information about some of the factors which govern ion-pairing phenomena, namely, the nature of the metal ion and of the solvent and basicity of the alkanoate ion.

The strongest associations are found for the smaller alkali metal ions, with a modest but nevertheless real reversal in the Li^+/Na^+ order on going from $Br(CH_2)_2CO_2^-$ ($Na^+ > Li^+$) to $Br(CH_2)_{14}CO_2^-$ ($Li^+ > Na^+$). When DMF replaces Me_2SO as the solvent, the ion-pairing tendency of $Br(CH_2)_2CO_2^-$ increases. The $K_{ip}(DMF)/K_{ip}(Me_2SO)$ ratio is 1·3 for Li^+ and 2·1 for Na^+. The observed trend is consistent with a greater cation–anion electrostatic interaction in the solvent with lower dielectric constant (Me_2SO 46·7; DMF 36·7), but the effects are modest. They are in fact much smaller than those observed for an *o*-alkoxy-substituted phenoxide ion,[3] for which the $K_{ip}(DMF)/K_{ip}(Me_2SO)$ ratio is 11 for Li^+ and 3·1 for Na^+.

Although the K_{ip} data for $Br(CH_2)_2CO_2^-$ and $Br(CH_2)_{14}CO_2^-$ in DMF were obtained at different temperatures, there seems to be little doubt that the greater ability of the latter anion to bind cations is a real phenomenon, which is understandable on the basis of its greater basicity.

The data collected in recent years on ion-pairing phenomena involving oxyanions, such as alkoxides,[13] aryloxides[2] and enolates,[4,5,11,14] mostly in Me_2SO solution, allow some of the factors which influence the formation of ion pairs in dipolar aprotic solvents to be delineated. When the negative charge is localized on oxygen, or when chelate interaction is allowed by geometrical factors, as in the β-ketoenolates which can adopt the U-type conformation,[11] large and widely spaced association constants are observed, decreasing in the order $Li^+ \gg Na^+ > K^+$. Whenever available,[2] K_{ip} data for the larger alkali metal ions show the expected trend, $K^+ > Rb^+ > Cs^+$, but the differences are very small. The situation is clearly one where the stability order is dominated by the stronger electrostatic interactions with the smaller cations, in spite of the fact that the latter suffer from a greater loss of solvation energy on contact pairing. However, when the negative charge of the anion is more spread, and its geometry is unsuitable for chelate interaction, much lower and less widely spaced K_{ip} values are observed as a result of an increase of the relative importance of solvation. This may even cause anomalous orders among cations, such as the order $Na^+ > Li^+ > K^+$ reported by Olmstead and Bordwell[11] for $CH_2{=}NO_2^-$ and $C_6H_5CO_2^-$. They reasoned that the oxygen–oxygen distance in $C_6H_5CO_2^-$ (and $CH_2{=}NO_2^-$) is not sufficient to permit chelation with Li^+, but that a certain degree of chelation is possible with the larger metal ions. Consistent with this suggestion, x-ray crystallographic data show that, unlike the larger alkali metal ions, the size of the Li^+ ion is not such as to permit interactions with both oxygens of carboxylate ions.[15]

It is clear from the above considerations that the behaviour of $Br(CH_2)_2CO_2^-$ and $Br(CH_2)_{14}CO_2^-$ is typically that of anions with a substantially spread negative charge, and with a limited propensity for chelation with the alkali metal counter ions, as suggested by Olmstead and Bordwell. As a consequence, there is significant compensation of differences of contributions from electrostatic interactions and losses of solvation energy on ion pairing, which causes substantial flattening of cation effects on stability of ion pairs, and also of the effect of changing the solvent from Me_2SO to DMF. Such a compensation is almost exact for the Li^+/Na^+ pair. The fact that the stability order among these cations is reversed on going from the less basic $Br(CH_2)_2CO_2^-$ to the more basic $Br(CH_2)_{14}CO_2^-$ illustrates well how delicate is the balance among the factors underlying ion-pair formation.

Finally, evidence has been obtained that the formation of triple ions containing two Li^+ ions becomes significant in DMF, but not in 99% Me_2SO, which is in line with previous conclusions.[3]

Reactivity of ion pairs

All of the added alkali metal ions depress the carboxylate reactivity in the investigated lactonization reactions. The rate-depressing effect is larger the stronger is the interaction of the alkanoate ion with M^+. Analysis of rate data has shown that in the investigated concentration range contributions to the overall rate from associated species are in all cases very small, or even negligible, in comparison with contributions from free ions. Thus, on addition of alkali-metal salts, the overall rate is depressed to extents essentially reflecting the decrease in free anion concentration caused by the mass-law effect exerted by the added alkali metal ion. The present data are well in line with all of the available evidence[1] pointing to a low reactivity of ion pairs and higher aggregates in S_N2 reactions between anions and neutral molecules. Reduction of the cation interaction on going from a reactant anion to a transition state is easily understood on the basis of the widely accepted picture for the latter as a species with a spread negative charge and a geometry unsuitable for chelate interaction.

It is worth noting that in the present systems Cs^+ behaves exactly as would be expected from its position in the group. A strictly analogous situation has been reported for the effect of Cs^+ on the rates of intra- and inter-molecular alkylation of aryloxide ions with alkyl bromides.[2] These observations bear upon the question of the so-called 'caesium effect.'[16,17] As pointed out by Dijkstra *et al.*,[17] the term relates to the 'readiness with which caesium carboxylates in DMF can be alkylated with alkyl halides' in synthetically useful procedures, and to the high yields with which many macrocycles can be obtained via intramolecular anionic S_N2 processes because 'intermolecular substitution is suppressed relative to the intramolecular process.' Being aware of the limits involved in any extension of kinetic results to the more concentrated systems used in preparative experiments, especially to those carried out under heterogeneous conditions, we stress that nothing emerges from rate data, as obtained under homogeneous conditions, that points to a peculiar behaviour of caesium carboxylates (and aryloxides), as distinct from the other alkali metal salts. Caesium carboxylates are simply less associated, and consequently more reactive, than the carboxylates of the smaller alkali metal ions. Still, they are less reactive than the corresponding tetraalkylammonium salts, for which ion pairing is negligible, or nearly so.

The above considerations confirm our previous reservations[18] concerning the mere existence of a 'caesium effect' as an effect that can be unequivocally defined in model systems. This matter will be dealt with in greater detail in a forthcoming paper.

EXPERIMENTAL

The alkali metal perchlorates and Et_4NBr were of analytical-reagent grade and were dried under vacuum. 3-Bromopropanoic acid, 15-bromopentadecanoic acid, 2,6-dichlorophenol and *m*-nitrophenol were available from previous investigations.[7,8] The mixed solvent 99% (v/v) aqueous Me_2SO was prepared as before.[8] Dimethylformamide was kept 48 h over anhydrous copper(II) sulphate, filtered, stirred overnight over potassium hydroxide pellets, filtered again and finally distilled from anhydrous copper(II) sulphate at reduced pressure, b.p. 60–62 °C at 40 mmHg. It was stored in an automatic burette under nitrogen.

Stock solutions of the base (0·04 M) were freshly prepared by placing 0·1 ml of a 0·8 M solution of Bu_4NOH in methanol (Fluka) and diluting to 2 ml with either 99% Me_2SO or DMF.

Stopped-flow spectrophotometric rate measurements were carried out on a Durrum Model 110 apparatus. Conventional spectrophotometric rate measurements were carried out on either a Cary 219 or a Varian DMS 90 spectrophotometer with a thermostatted cell compartment.

The low solubility of potassium salts in DMF prevented kinetic measurements at concentrations of added K^+ ion exceeding 0·01 M.

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REFERENCES

1. (a) J. E. Gordon, *The Organic Chemistry of Electrolyte Solution*, Chapt. 3. Wiley, New York (1975); (b) N. S. Isaacs, *Physical Organic Chemistry*, Chapt. 1. Longman, Harlow (1987).
2. G. Illuminati, L. Mandolini and B. Masci, *J. Am. Chem. Soc.* **105**, 555 (1983).
3. M. Crescenzi, C. Galli and L. Mandolini, *J. Chem. Soc., Chem. Commun.* 551 (1986).
4. C. Galli and L. Mandolini, *J. Chem. Soc., Perkin Trans. 2* 1435 (1984).
5. R. Cacciapaglia and L. Mandolini, *J. Org. Chem.* **53**, 2579 (1988).
6. C. Galli and L. Mandolini, *J. Chem. Soc., Perkin Trans. 2* 443 (1977).
7. L. Mandolini, *J. Am. Chem. Soc.* **100**, 550 (1978).

8. C. Galli, G. Illuminati, L. Mandolini and P. Tamborra, *J. Am. Chem. Soc.* **99**, 2591 (1977).
9. M. S. Grenberg and A. I. Popov, *J. Solution Chem.* **5**, 653 (1976).
10. L. P. Hammett, *Physical Organic Chemistry*, p. 213. McGraw-Hill, New York (1970).
11. W. N. Olmstead and F. G. Bordwell, *J. Org. Chem.* **45**, 3299 (1980).
12. G. Kortüm, W. Vogel and K. Andrussow, *Dissociation Constants of Organic Acids in Aqueous Solution.* Butterworths, London (1961).
13. J. H. Exner and E. C. Steiner, *J. Am. Chem. Soc.* **96**, 1782 (1974).
14. (a) E. M. Arnett, S. G. Maroldo, S. L. Schilling and J. A. Harrelson, *J. Am. Chem. Soc.* **106**, 6759 (1984); (b) E. M. Arnett and J. A. Harrelson, *Gazz. Chim. Ital.* **117**, 237 (1987).
15. C. J. Carrell, H. L. Carrell, J. Erlebacher and J. P. Glusker, *J. Am. Chem. Soc.* **110**, 8651 (1988).
16. B. Klieser, L. Rossa and F. Vögtle, *Kontakte (Darmstadt)*, 3 (1984).
17. G. Dijkstra, W. H. Kruizinga and R. M. Kellogg, *J. Org. Chem.* **52**, 4230 (1987).
18. C. Galli and L. Mandolini, *J. Chem. Soc., Chem. Commun.* 251 (1982).