Salt Effects in Some Nucleophilic Substitution Reactions of Ethoxide Ions

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Kinetic studies (in anhydrous ethanol at 25 °C) are reported for the reactions:

$$RX + MOEt \longrightarrow ROEt + MX$$

where R = Et, X = I, M = Li, Na, or K;
R = 2,4-dinitrophenyl, X = Cl, M = Li, Na, K, or Cs;
and R = 2,4-dinitrophenyl, X = I, M = Li, Na, or K.

Measurements were made over a range of metal ethoxide concentrations extending down to 3×10^{-3} mol l^{-1}, so that kinetic behaviour may be compared with conductimetric data for metal ethoxide ' ion-pair ' association. The major salt effects observed are consistent with the postulate that the total reaction rate contains separate contributions from ' free ' ethoxide ions and metal–ethoxide ' ion-pairs '. Additional kinetic complexity arises from: (*a*) influence of the product salt on the association of metal ethoxides; (*b*) an effect at higher concentrations which is either a salt effect on the ' free ' ion + substrate reaction, or which reflects an inadequacy in the assessment of metal ethoxide association from conductimetric data.

With ethyl iodide, ' ion pairs ' are unreactive but with the aromatic substrates both the ' free ' ethoxide ion and the ' ion-pair ' react. The observed reactivity patterns are explicable in terms of different transition-state geometries and trends in strengths as electrolytes of metal halides and ethoxides in ethanol.

THE Bjerrum concept of ' ion pairing ' has proved invaluable in the development of descriptions of the equilibrium properties of solutions of electrolytes at finite concentrations, in spite of the rather arbitrary nature of the model and doubts concerning the significance of the association ' constants ' which derive from it. The model has had some success in rationalising specific salt effects observed in a variety of reactions, and kinetic measurements have indeed been used for the evaluation of ion-association constants. The utility of the ' ion-pairing ' concept in reaction kinetics has been discussed by Davies [1] for reactions in aqueous solution. Winstein and his co-workers [2] have shown the value of ' ion-pairing ' concepts in rationalising kinetic data from studies of unimolecular solvolyses proceeding *via* carbocation ion formation.

Complexity in the kinetic form of the bimolecular reactions of alkyl iodides with ethoxides in ethanolic solution was first studied by Hecht, Conrad, and Bruckner,[3] who found that second-order rate constants for reactions with sodium ethoxide increased with increasing dilution of the reactants. Similar effects were found with other cations; the magnitude of the effect, at a particular concentration, depended on the nature of the cation used. Acree [4] suggested that the observed rate constant could be regarded as composite, with distinct contributions to the total reaction rate from free ethoxide ion and a metal–ethoxide ' ion-pair '.

Acree's view which was based on the Arrhenius concept of separate molecules and ions, may be regarded as the extreme of simplification in applying the ' ion-pairing ' concept to the rationalization of salt effects. The metal ion of the reactant salt may interact, not only with the ethoxide ion, but also with the substrate, intermediates and transition states. Thus the total kinetic effect may not be related in a simple way to the ' ion-pair ' association constant for the salt. A view, which is at the opposite extreme to that taken by Acree, was presented by Ingold and his co-workers in a discussion of Finkelstein reactions in anhydrous acetone.[5] They consider it . . . ' impossible that the functions of the salt can be accurately described in terms of two sharply differentiated but inherently uniform species, called ' associated ' and ' dissociated ' . . .,' but suggest that Acree's model might be justified as the simplest approach to a broad comparison.

Acree's own analysis of his results cannot be regarded as satisfactory, nor can the subsequent re-evaluation of the same kinetic data by Brandstrom.[6] Although the latter author used a more sophisticated conductance equation for the calculation of the degree of dissociation of the salt, the real problem is that the kinetic data refer to a range of salt concentration, for which satisfactory analysis of conductance data is not, at present, possible, particularly in a solvent such as ethanol.

The objective of the present work has been to obtain precise kinetic data at metal ethoxide concentrations where modern conductivity theory will give more reliable values of the degree of dissociation of salts. Kinetic studies of the following reactions are reported:

$$RX + MOEt \longrightarrow ROEt + MX$$

where R = Et, X = I, M = Li, Na, K
R = 2,4-dinitrophenyl, X = Cl, M = Li, Na, K, Cs
R = 2,4-dinitrophenyl, X = I, M = Li, Na, K

EXPERIMENTAL

Materials.—Ethanol. Re-rectified absolute alcohol was fractionated onto Drierite which had previously been dried at 270 °C for 1 h. The alcohol was then re-fractionated and was collected and stored under nitrogen with protection against contamination from moisture and CO_2. Constant boiling hydrochloric acid was used as primary acidimetric standard. Sodium hydroxide solutions were B.D.H. volumetric reagent (carbonate free).

2,4-*Dinitrochlorobenzene* (DNCB). Hopkin and Williams

Micro Analytical Standard DNCB was recrystallized from ether and dried in a vacuum oven at 40 °C.

2,4-Dinitroidobenzene (DNIB). This was prepared following the procedure of Bunnett.[7] The lemon-yellow crystals had m.p. 89 °C, (lit.,[7] 89 °C).

Ethyl Iodide. Laboratory grade ethyl iodide was purified according to the method described by Gand.[8] The purified material was stored in a darkened flask in a P_2O_5 desiccator.

Lithium ethoxide. Solutions of this compound were prepared from pure lithium metal (Grade 3N, L. Light & Co.). A piece of lithium of approximately the required size was cut and then pierced with a glass rod. The superficial impurities were removed by holding the metal under ethanol. The bright metallic lithium was then quickly transferred to pure ethanol in which it dissolves at a convenient rate to form a clear solution of lithium ethoxide.

Sodium ethoxide solutions. Metallic sodium was melted under xylene and transferred by means of a heated safety pipette, to more xylene at 110 °C. The molten sodium was drawn up into glass tubes (4 mm i.d.) and allowed to solidify, the tubes then being stored under xylene. Sodium ethoxide solutions were prepared by cutting an appropriate length of sodium filled tubing and transferring it to a flask containing pure ethanol.

Potassium ethoxide solutions. The procedure for sodium ethoxide wes followed except that the xylene was heated only to 80 °C.

Caesium ethoxide solutions. Pure caesium metal, sealed in glass ampoules was obtained from I.R.D. Co. Ltd. The ampoules were opened in a glove box filled with pure dry argon and the metal dissolved in pure ethanol.

Lithium chloride. B.D.H. laboratory reagent was recrystallised from ethanol and dried at 110 °C.

Apparatus and Procedures.—Three types of reaction vessel were used. For reactions at concentrations $>10^{-2}$M and of short half-lives the reaction vessel was a three-necked flask, one limb of which carried a sealed stirrer. The second limb carried an outlet pipe for sampling of the reaction solution *via* a B–D Cornwall continuous pipetting outfit. The outlet was protected against CO_2 ingress by a Sofnolite guard tube. The third limb carried a reservoir for storage of metal ethoxide solution prior to reaction initiation, the organic substrate solution being placed directly in the reaction flask. The reservoir was connected to the reaction flask *via* a ground-glass plug which could be withdrawn to allow mixing of the reactants.

For reactions at lower concentrations a similar flask was used except that the third limb carried a serum cap through which reactants were injected. For reactions with half-lives >1 day a sealed bulb technique was used. Reaction vessels were 50 ml conical flasks closed by serum caps through which reactants were injected. In the preparation and manipulation of reactant solutions rigorous precautions were taken against moisture and CO_2 contamination.

Reactions were followed by measurement of the change in ethoxide concentrations with time. This was done by quenching samples of the reaction solution with an excess of aqueous hydrochloric acid and back titrating with sodium hydroxide. At sufficiently high ethoxide concentrations the titrations were carried out using Bromothymol Blue as indicator. The titrations were performed under nitrogen to avoid fading of the end-point. At lower ethoxide concentrations more satisfactory end-points were obtained using conductimetric titrations; the two methods gave results in excellent agreement in the overlap range.

All experiments were carried out in a water thermostat at 25 ± 0.002 °C. Volumetric apparatus was calibrated. Time was measured with a Favag precision timing unit. Experiments with ethyl iodide solutions were carried out in the dark.

RESULTS AND DISCUSSION

Degree of Dissociation (α) *Values for Metal Ethoxides.*—Attempts were made to apply the Fuoss–Onsager–Pitts equation [9,10] to the conductivity data of Jones and Hughes [11] and of Ogston [12] for alkali-metal ethoxide solutions in order to obtain α-values. The computer program, which was tested using conductivity data for lithium chloride [13] in ethanol and gave α-values in agreement with those obtained by Kay,[14] did not yield convergent solutions with the metal ethoxide data. It seems likely, either that the conductivity data are not sufficiently accurate, or that the equation is unsuitable for use with the ethoxide–ethanol system. Fuoss [15] has stated that this equation requires extremely accurate conductivity data for salts with p*K* *ca.* 2.

Brandstrom [6] has used the Marshall and Grundwald empirical extension of the Onsager equation [16] to calculate α-values of metal ethoxides over a very wide concentration range. At low concentrations the values obtained are almost identical with those obtained from the Onsager equation. In the present work we have used the α-values reported by Brandstrom.

Influence of the Product Salts on the Kinetics of the Reactions.—Most of our experiments were carried out with equal concentrations of reactants. From individual experiments, excellent integrated second-order law kinetic plots were obtained, implying that the second-order rate constant, *k*, did not vary (standard deviation ⩽ ±2%) in a reaction followed for >2 half-lives. Examples are shown in Figure 1. However, experiments with different initial reactant concentrations yielded *different* values for the rate constant, *e.g.* for the reaction of DNCB with LiOEt:

Initial [DNCB] = Initial [LiOEt]/mol l^{-1}	k/l mol^{-1} min^{-1}
(1) 0.012 32	3.50
(2) 0.003 07	4.40

The initial conditions in (2) correspond to the reactant concentrations in (1) after *ca.* 2 half-lives. However, the rate constant in (1) did not approach 4.40 but remained constant at 3.50.

The only difference in the reaction solutions is that (1) after 2 half-lives contains the reaction products, and the experimental data in Table 1 show that the effect arises from an influence of the product salt (LiCl) on the reaction of DNCB with LiOEt.

It is probable that this effect arises because the alkali-metal ethoxides are weaker electrolytes than the corresponding halides in ethanol; thus during a reaction the production of LiCl results in an increase in free Li^+ concentration, an effect which would in turn lead to a repression of LiOEt dissociation and a decrease in free ethoxide-ion concentration. Support for this view comes from the observation that the rate constants for

Finkelstein reactions have been found to vary in the course of reaction.[17] In the present case the apparent invariance of the rate constants must arise from a near perfect cancellation. The rate constants quoted in this paper although determined from integrated second-order plots, are taken as referring to the initial reaction conditions. The results for all the reactions are collected in Table 2. Figure 2 shows graphs of the second-order rate constants against the stoicheiometric metal ethoxide concentration.

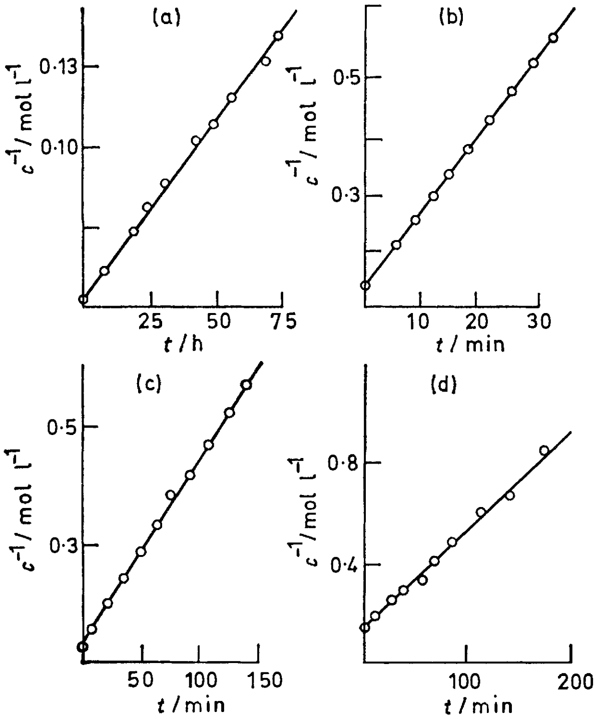


FIGURE 1 Typical integrated second-order plots for the reactions: (a) EtI + KOEt, (b) DNCB + KOEt, (c) DNCB + LiOEt, and (d) DNCB + NaOEt

TABLE 1

Effect of LiCl on the rate constant for the reaction of DNCB with LiOEt at 25.0 °C

[DCNB] = [LiOEt]/mol l^{-1}	[LiCl]/mol l^{-1}	k/l mol^{-1} min^{-1}		
		(1)	(2)	(3)
0.009 920	0.027 97	3.66	2.80	2.95
0.024 61	0.006 32	3.16	3.00	3.07
0.005 89	0.014 67	4.00	3.19	3.26
0.007 63	0.012 64	3.84	3.16	3.26
0.012 47	0.005 31	3.50	3.25	3.30
0.005 45	0.009 21	4.06	3.24	3.40
0.003 25	0.005 50	4.36	3.72	3.78

(1) k In absence of initial LiCl. First column shows initial concentrations of reactants. (2) k With added initial LiCl. First column shows initial concentrations of reactants. (3) k in reaction solution with LiCl present. Reaction solution prepared by partial decomposition of a more concentrated solution.

Reaction of Ethyl Iodide.—For this system all the metal ethoxides studied shown substantial negative specific salt effects. The magnitude of the effect at similar concentrations increases in the series $K^+ < Na^+ < Li^+$, which is also the sequence of decreasing strengths of the alkali-metal ethoxide salts. The problem is to examine the nature of the relationship between the kinetic effect and the degree of ion association of the salt. The simplest form of the Acree model yields equations (1) and (2), where k_i and k_m are regarded as concentration independent second-order rate constants for the ion and ion-pair respectively and α is the degree of dissociation of the metal ethoxide. Thus this model

$$k_{obs} = k_i\alpha + k_m(1 - \alpha) \qquad (1)$$

or

$$k_{obs} = (k_i - k_m)\alpha + k_m \qquad (2)$$

ascribes the salt effect entirely to the influence of total concentration on the distribution of free ions and ion-pairs in the reactant salt. According to this model, if

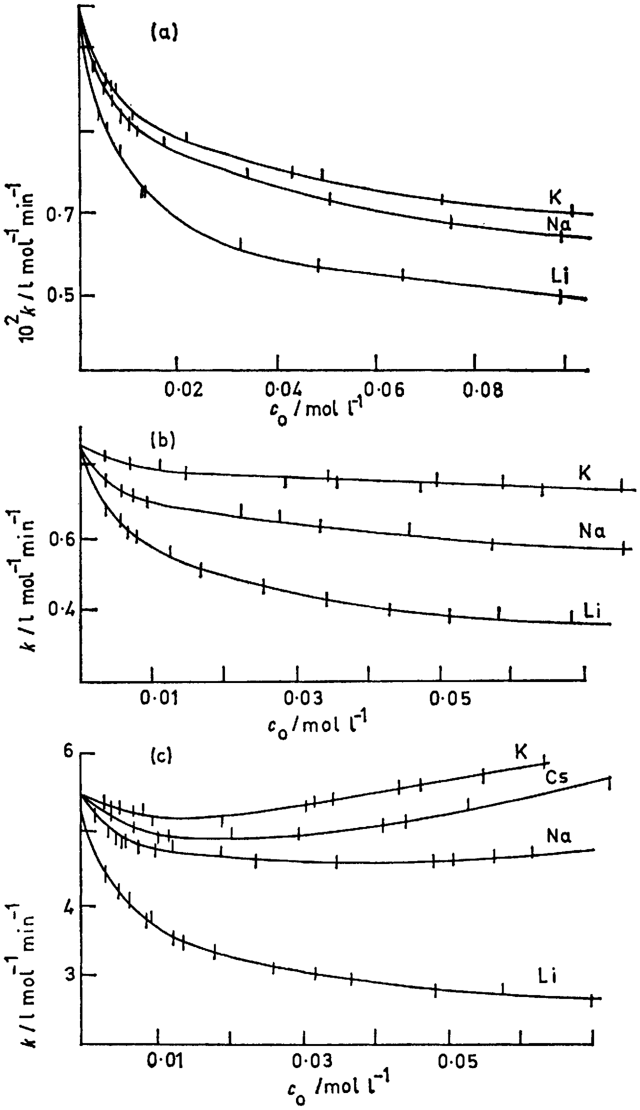


FIGURE 2 Dependence of second-order rate constant, k (l mol^{-1} min^{-1}), on initial reactant concentration, c_0 (mol^{-1}), at 25 °C, for reactions of alkali-metal ethoxides with (e) EtI, (b) DNIB, and (c) DNCB

the ion-pair is totally unreactive (k_{obs}/α) should be a constant. Applying the Brandstrom[6] α values to the data for ethyl iodide reaction yields values of k_{obs}/α which increase systematically with increasing concentration for all three reactants salts as shown in Table 2. The increase is 10—15% in the concentration range 3×10^{-3}—10^{-1}M. We consider two possible explanations for this behaviour.

TABLE 2

Second-order rate constants (k/l mol^{-1} min^{-1}) at 25 °C for the reactions of alkali ethoxides with alkyl and aryl halides (equal initial reactant concentrations, c_0/mol l^{-1})

c_0	10^2k	k/α
	LiOEt + EtI	
0.096 7	0.513	0.013 9
0.064 5	0.558	0.013 1
0.048 0	0.575	0.012 8
0.032 0	0.618	0.012 3
0.013 22	0.750	0.012 0
0.012 43	0.750	0.011 8
0.008 29	0.830	0.012 0
0.005 75	0.890	0.012 2
0.003 83	0.930	0.011 8
	NaOEt + EtI	
0.096 0	0.681	0.013 3
0.074 0	0.682	0.012 7
0.049 3	0.751	0.012 8
0.033 2	0.813	0.013 0
0.016 58	0.884	0.012 6
0.011 75	0.895	0.012 4
0.009 25	0.918	0.012 0
0.008 25	0.929	0.012 1
0.006 16	0.979	0.012 2
0.004 75	1.01	0.012 0
0.002 96	1.05	0.012 4
	KOEt + EtI	
0.097 9	0.715	0.013 7
0.072 0	0.749	0.013 5
0.048 0	0.805	0.013 4
0.042 4	0.810	0.013 2
0.021 18	0.862	0.013 1
0.010 62	0.932	0.012 4
0.007 08	0.975	0.012 4
0.005 79	0.998	0.012 3
0.005 27	1.01	0.011 8
0.003 01	1.06	0.012 0

c_0	k
LiOEt + DNIB	
0.067 8	0.408
0.057 5	0.415
0.050 8	0.415
0.042 5	0.430
0.033 9	0.445
0.025 0	0.480
0.016 44	0.526
0.012 33	0.556
0.007 61	0.594
0.006 21	0.615
0.005 15	0.660
0.003 39	0.688
NaOEt + DNIB	
0.074 2	0.615
0.056 0	0.625
0.044 0	0.650
0.032 8	0.646
0.027 0	0.660
0.020 2	0.672
0.008 79	0.700
0.007 05	0.731
0.005 42	0.745
0.003 57	0.764
KOEt + DNIB	
0.002 4	0.775
0.057 4	0.790
0.047 8	0.790
0.040 6	0.790
0.038 1	0.776
0.028 1	0.777
0.015 20	0.789
0.011 01	0.795
0.006 93	0.781
0.004 71	0.810
0.003 31	0.834

c_0	k
LiOEt + DNCB	
0.069 5	2.71
0.055 8	2.80
0.046 8	2.86
0.035 5	2.97
0.031 3	3.08
0.026 0	3.12
0.018 0	3.30
0.013 42	3.47
0.012 32	3.50
0.009 11	3.75
0.008 40	3.78
0.006 35	4.00
0.006 20	3.95
0.004 71	4.18
0.003 07	4.40
KOEt + DNCB	
0.061 2	5.99
0.053 2	5.80
0.044 5	5.63
0.041 9	5.66
0.033 3	5.55
0.031 2	5.41
0.029 8	5.37
0.018 5	5.21
0.009 34	5.28
0.008 02	5.28
0.006 97	5.27
0.005 19	5.30
0.003 46	5.36
0.003 39	5.38

c_0	k
NaOEt + DNCB	
0.060 4	4.75
0.055 2	4.72
0.049 8	4.68
0.047 0	4.64
0.034 0	4.65
0.023 0	4.65
0.018 4	4.71
0.011 98	4.77
0.010 46	4.70
0.007 45	4.81
0.005 89	4.79
0.005 54	4.74
0.005 43	4.79
0.004 78	4.75
0.004 55	4.92
0.003 85	4.88
0.003 76	4.91
0.001 71	5.13
CsOEt + DNCB	
0.070 0	5.74
0.051 3	5.45
0.043 0	5.27
0.041 4	5.09
0.028 5	5.03
0.019 8	5.08
0.011 57	4.91
0.010 30	4.91
0.008 13	5.02
0.007 23	5.10
0.003 84	5.28

(i) If both the model and the α-values are accepted then the origin of this effect could be assigned to a salt effect on the bimolecular reaction of the free ion with the substrate. Figure 3 shows appropriate linear salt-effect plots of k/α against ionic strength ($c\alpha$). Although there is considerable scatter this concept could account for the observed results.

Brandstrom[6] has pointed out that a more suitable form of equation (1) for graphical evaluation of kinetic data is given by equation (3). Appropriate plots of

$$\frac{k_{obs}}{1-\alpha} = k_i \frac{(\alpha)}{(1-\alpha)} + k_m \qquad (3)$$

the data are shown in Figure 4. At low concentrations the data conform to linear curves which pass accurately through the origin, implying that $k_m = 0$, and yield $k_i = 0.012\,1$ l mol^{-1} min^{-1}. The deviations from linearity could be ascribed to a linear salt effect, as discussed above.

(ii) It must be admitted that the conductimetric α-values become progressively less certain as the concentration increases and it is possible that the Brandstrom calculation of α-values may underestimate the degree of dissociation of the salt at high concentrations. If it is accepted that $k_m = 0$, then the kinetic data may be used to calculate α-values (α_k) on the assumption that no primary salt effect operates. This calculation is purely formal when applied to the reactions of one substrate only, but the utility of this approach is considered below in the evaluation of data for the other systems studied.

Reactions of 2,4-Dinitroiodobenzene.—These reactions show a pattern of negative specific salt effects very similar to those found for ethyl iodide. Again the magnitude of the effect at similar concentrations increases in the series $K^+ < Na^+ < Li^+$. The K^+ effect is only apparent at low concentrations; at concentration >0.02M the rate constant of the reaction with potassium ethoxide is independent of concentration within the experimental error. For the reaction with LiOEt, k_{obs}/α increases by *ca.* 15% between concentrations of 3×10^{-3} and 7×10^{-2}M. A plot of these data according to equation (3) gives a good straight line at lower concentrations which yields a positive intercept (finite k_m value) on the ordinate. Figure 5(a) compares the variation of the rate constant with conductimetric α-values and the values of α_k computed from the kinetic data for the reaction of ethyl iodide. The deviation of the rate constant data at high concentrations from a simple dependence on α are similar to those observed in the ethyl iodide reaction and these deviations are removed if the α_k values are employed.

The rate constants for the DNIB + NaOEt reaction vary with concentration to a much smaller extent than the previously discussed reactions; k/α shows a correspondingly larger change. Plots of the data according to equation (3) yield a straight line at lower concentrations with a substantial positive intercept. Figure 5(b) shows that the use of α_k values again removed the deviations at high concentrations. The rate constant in the reaction of DNIB + KOEt is independent of concentration except at very low concentration. This can arise if $k_m \approx k_i$ and analysis of the data using equation (3) is consistent with this view. Again the use of α_k values removes deviations from linearity in plots according to equation (3). The rate constants obtained, using α_k as an index of the degree of dissociation of the salts are as follows:

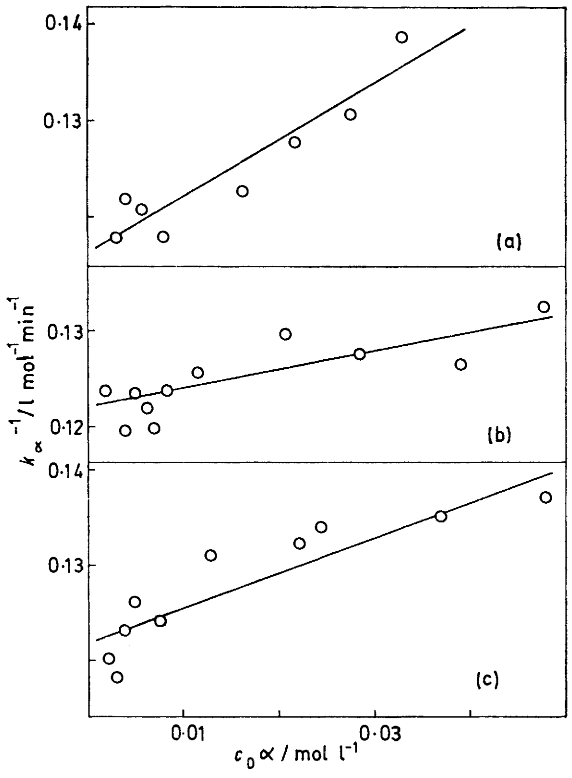


FIGURE 3 Dependence of k/α on ionic strength ($c_0\alpha$) for the reactions of ethyl iodide with: (a) LiOEt, (b) NaOEt, and (c) KOEt

Reaction	k_i/l mol^{-1} min^{-1}	k_m/l mol^{-1} min^{-1}
LiOEt + DNIB	0.84	0.06
NaOEt + DNIB	0.84	0.30
KOEt + DNIB	0.84	0.65

The three metal ethoxides all yield the same value for k_i [as determined from the slopes of plots according to equation (3)], as required by the model.

Reactions of 2,4-Dinitrochlorobenzene.—A significantly different pattern of behaviour emerges in these reactions. LiOEt shows a substantial negative salt effect but for the other salts, although the rate constant at first decreases with increasing concentration, it then passes through at minimum and at higher concentrations slowly increases with concentration.

For the LiOEt reaction analysis of the data conforms to the pattern of the reactions previously discussed. k/α Increases with concentration but this deviation is removed if α_k values are employed, as shown in Figure 5(c). Plots according to equation (3) are accurately linear when α_k values are used and yield $k_i = 5.3$ l mol^{-1} min^{-1} and $k_m = 0.55$ l mol^{-1} min^{-1}.

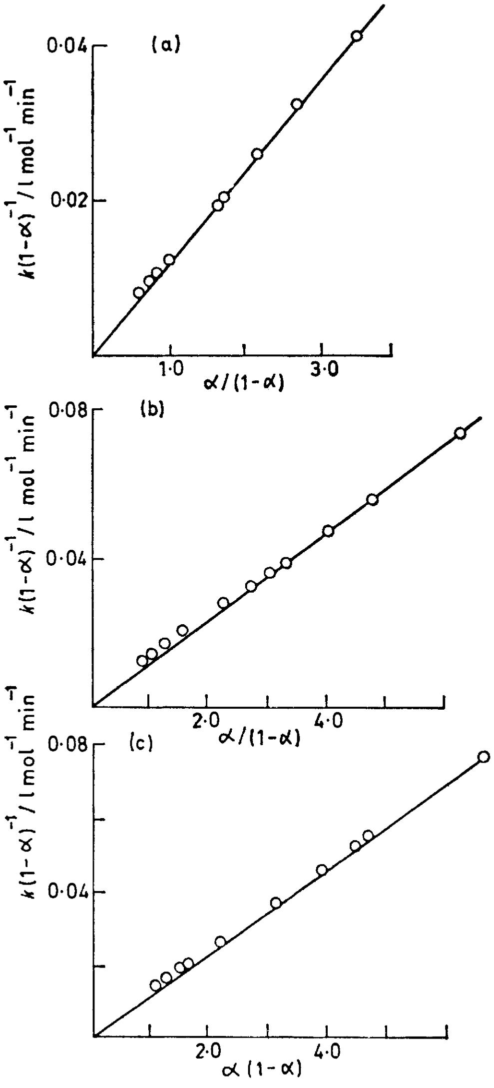


FIGURE 4 Dependence of $k/(1-\alpha)$ on $\alpha/(1-\alpha)$ for the reactions of ethyl iodide with : (a) LiOEt, (b) NaOEt, and (c) KOEt

The extremum behaviour shown by the remaining salts cannot be explained by the analysis used for the other reactions. However, in these reactions, a new factor enters, namely that the product salt in these reactions is insoluble and is precipitated in the course of the reaction. For all these reactions the behaviour at low concentrations parallels that found for the other reactions both in the direction and magnitude of the salt effect.

It is suggested that removal of the product salt into the solid phase as the reaction proceeds at high concentration results in an increase in the free ethoxide-ion concentrations and an increase in rate constant. The magnitude of the rate enhancement parallels the order of decreasing solubility of the metal chlorides (NaCl > CsCl > KCl). Although product salt precipitation cannot affect the initial reaction rate, the rate constants were obtained from integrated second-order plots. The influence of salt precipitation would be a progressive one and it seems possible that this results in an enhanced slope of the kinetic plots, but not to the extent that obvious deviations from linearity appear. The total effect is, of course, rather small. This hypothesis is certainly in accord with the explanation offered earlier for the rate depression, which is produced by the addition of soluble product salts.

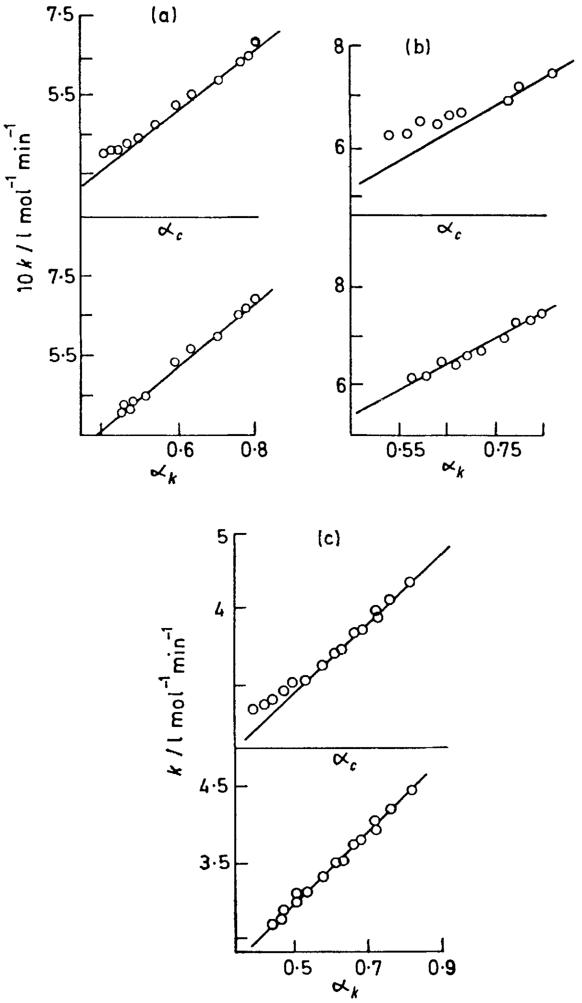


FIGURE 5 Comparison of dependence of k on α_c and α_k for the reactions: (a) DNIB + LiOEt, (b) DNIB + NaOEt, and (c) DCNB + LiOEt

Ignoring the rate constant increase at high concentrations the data for NaOEt and KOEt may be evaluated by making plots according to equation (3). The rate constants obtained for the reactions of DNCB are as follows:

Reaction	k_i/l mol^{-1} min^{-1}	k_m/l mol^{-1} min^{-1}
LiOEt + DCNB	5.3	0.55
NaOEt + DCNB	5.3	3.2
KOEt + DCNB	5.3	5.2

The agreement between the values of k_i obtained with three different reactant salts again supports the analysis of the data according to this model.

General Conclusions.—A model of the substitution reactions studied which assigns distinct kinetic behaviour to free ethoxide-ion and metal–ethoxide ion pairs can comprehend the results obtained; secondary effects upon the free-ion–ion pair distribution can account for a number of complicating features. If the partitioning of the observed rate constant into two distinct contributions is accepted, it only remains necessary to assess the pattern of reactivity which derives from this analysis.

For the reactions of ethyl iodide this pattern is strikingly simple in that it appears that ion-pair formation yields a totally unreactive species. The nature of bimolecular nucleophilic substitution at saturated carbon centres is well-characterised, in particular the configuration of the transition rate as a trigonal bipyramid. In this situation the counter cation of the reactant salt and the electrophilic centre of the substrate are essentially involved in a quite unequal competition for the nucleophilic anion.

For the reaction of the dinitrohalogenobenzenes a more complex reactivity pattern emerges. This has the following features:

(i) Substrate reactivities
DNCB > DNIB

(ii) Ion-pair reactivities
$K^+ > Na^+ > Li^+$

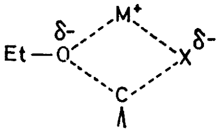
The observation that ethoxide substitution in DNCB occurs *ca.* 10 times faster than in DNIB is in striking contrast to Bunnett's observations [18] on the reactions of piperidine with 1-substituted 2,4-dinitrobenzenes. This indicates that, in the reactions that we have studied, carbon–halogen bond breaking is significantly important in the transition state. It seems likely that the essential reaction mechanism remains the same but that the weight of kinetic significance is shifted to a different stage in the reaction, that is intermediate complex formation is substantially rate limiting in the process studied by Bunnett, but intermediate complex breakdown is important in our own studies.

In the present work we have made some direct qualitative observations relevant to this point. In the reactions of DNCB and DNIB with metal ethoxides the reaction solutions became coloured, the colour varying from deep orange-red with reactant concentrations of 0.1M to pale yellow at 0.003M. This colour was not due to the main products of the reaction. Spectrophotometric studies showed the colour intensity increased at first, passed through a flat maximum and then decreased towards the end of the reaction. In t.l.c. experiments on the reaction mixture in benzene the coloured component remained on the base-line although the reactant and main product moved up the plate. When the chromatogram was run in ethanol the coloured material moved up the plate, indicating that the material was probably either highly polar or a salt. When a separation was attempted the material extracted was 2,4-dinitrophenol, although this could not have been the species responsible for the deep orange-red colour of the original reaction solution, and was probably formed by hydrolysis. These observations suggest that an intensely coloured reaction intermediate which may be a salt is formed in these reactions. A Meisenheimer complex intermediate would be consistent with these results.

The difference in reactivity of the ion-pairs that we find suggests that the cation in some way influences the lability of the halogen. Useful quantities for the analysis of these effects would be the strengths of the various metal halide salts in alcohol; unfortunately few of the required data are available. However, a number of trends in salt strength are apparent[1]:

Iodides > Chlorides
Lithium halides > Sodium halides > Potassium halides
Potassium ethoxide > Sodium ethoxide > Lithium ethoxide

If the transition states in these reactions are tetrahedral at the electrophilic carbon centre then, in the reactions *via* ion-pairs, the metal ion may be involved in a cyclic transition state of the form (A).



(A)

Thus, whereas in the reactions of ethyl iodide the influence of the metal ion is totally inhibitory, in the aromatic systems, this can be alleviated to some extent depending on the ability of the potential halide ion to interact with the metal. This ability would be expected to be related to the relative stabilities of the metal ethoxides and metal halides. The observed reactivity patterns are entirely consistent with the salt-strength sequences shown above.

It appears that the best available conductimetric α-values for metal ethoxide solutions may not be entirely adequate for analysis of the relative reactivities of free ions and ion-pairs except at very low concentrations. This does not necessarily imply that the conductimetric values at higher concentrations are incorrect, but may mean that a different assignment of the distribution of 'free' ions and 'ion pairs' may be appropriate to nucleophilicity than that applicable to mobility. Although the internal consistency that is achieved by the use of kinetic α_k values makes this approach to data analysis at higher concentrations attractive, the alternative possibility, that complexity arises from a small ion + molecule salt effect (which is of similar magnitude for all reactions of the same salt), cannot be excluded.

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