Mechanistic Studies in Strongly Basic Media. Part VIII.[1] Kinetic Studies on the Displacement of Halide from Benzyl Halides by Alkali-metal Salts of 9-Substituted Fluorenes in t-Butyl Alcohol Solution

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The kinetics of the displacement of halide from benzyl fluoride, chloride, and bromide by alkali-metal 9-cyano-, 9-methoxycarbonyl-, and 9-phenylsulphonylfluorenides have been studied in t-butyl alcohol solution in which the salts have been shown to exist largely in the form of ion pairs. The effects of variation in the reactant concentrations and of the addition of a common cation salt, sodium tetraphenylborate, on the kinetic form and reaction rate have been examined. The reaction of sodium 9-cyano- and 9-phenylsulphonyl-fluorenides with the three halides show essentially clean second-order kinetics with rate constants little affected by dilution of the carbanion salt or addition of the common ion. Reactions involving 9-methoxycarbonylfluorenide, however, display an increase in the second-order velocity constant as the reactions progress, and sodium tetraphenylborate retards the reaction; both observations indicate that the free carbanion is substantially more reactive than the associated form(s). Since sodium 9-cyanofluorenide is more dissociated than the 9-methoxycarbonyl salt, the absence of these kinetic effects implies that the free ion and ion pair are of equal reactivity in this system.

THE phenomenon of ion association influences almost all aspects of carbanion chemistry.[2] Not only are the physical properties (*e.g.* conductance, spectroscopy) of solutions of stable carbanions affected, but the association also profoundly influences the reactivity of carbanions, including their overall reaction rate, partitioning between alternative reaction sites using ambident partners, and stereochemistry. The effects are further complicated by the existence of different types of association complex, contact and solvent-separated ion pairs and oligomers, as well as the free carbanions, and each species has its own physical and chemical properties.

In previous papers we have shown that ion association has an important role in the strongly basic system alkali-metal t-butoxide–t-butyl alcohol. Thus the basicity of such systems is dependent on the nature of the alkali metal,[3] and this in turn influences the relative rates of competing reactions of carbanion intermediates generated in this solvent, *e.g.*, in base-catalysed autoxidation of fluorene.[4] Investigations on the oxidation of sodium salts of certain 9-substituted fluorenes in t-butyl alcohol permitted the reactivities of the free and associated carbanions to be evaluated.[5] A striking feature of these results was the observation that, contrary to expectation, for sodium 9-cyanofluorenide the free ion appeared to be perceptibly less reactive than the ion pair. For sodium 9-phenylsulphonylfluorenide the free ion was substantially the more reactive form, but even here the reactivity difference was much smaller than had been generally observed in other carbanion reactions, particularly the anionic polymerisation of styrene in ethereal solvents [2b,c] (see, however, ref. 6).

There have been other reports of ion pairs having greater reactivity than free ions. Examples are (i) the Dieckmann cyclisation of ethyl *o*-ethoxycarbonylphenoxyacetate to 2-ethoxycarbonyl-3-hydroxybenzofuran by alkali-metal ethoxides in ethanol where second-order velocity constants decreased with decreasing ethoxide concentration in proportion to the degree of dissociation of the catalyst;[7] (ii) the proton transfer

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[1] Part VII, D. Bethell, A. F. Cockerill, and D. B. Frankham, *J. Chem. Soc.* (*B*), 1970, 1271.

[2] For reviews, see (*a*) D. J. Cram, ' Fundamentals of Carbanion Chemistry, 'Academic Press, New York and London, 1964; (*b*) M. Szwarc, ' Carbanions, Living Polymers and Electron Transfer Processes,' Wiley, New York, 1969; (*c*) ' Ions and Ion Pairs in Organic Reactions,' ed. M. Szwarc, Wiley, New York, vol. I, 1973; (*d*) J. R. Jones, ' The Ionization of Carbon Acids,' Academic Press, London and New York, 1973.

[3] D. Bethell and A. F. Cockerill, *J. Chem. Soc.* (*B*), 1966, 913, 920.

[4] (*a*) D. Bethell and R. J. E. Talbot, *J. Chem. Soc.* (*B*), 1968, 638; (*b*) see also D. Bethell, A. F. Cockerill, and D. B. Frankham, *J. Chem. Soc.* (*B*), 1967, 1267.

[5] D. Bethell, R. J. E. Talbot, and R. G. Wilkinson, *Chem. Comm.*, 1968, 1528.

[6] T. Shimomura, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, 1967, **89**, 5743.

[7] A. Brändstrom, *Arkiv Kemi*, 1957, **11**, 527, 567.

from 1,2-benzofluorene to sodium fluorenide in tetrahydrofuran or 1,2-dimethoxyethane where rate constants decrease with dilution and added sodium ions accelerate the reaction rate.[8] No satisfactory explanation of these unusual effects has yet been given.

In an attempt to throw further light on the reactivity of 9-substituted fluorenides in t-butyl alcohol, we have undertaken kinetic experiments on a simpler reaction than the autoxidation previously examined, namely, the bimolecular displacement of halide ion from benzyl halides.[9] In this reaction we believe that we are dealing with a one-step process [10] between the benzyl halide and the carbanion. The carbanion salts used, alkali-metal 9-cyano-, 9-methoxycarbonyl-, and 9-phenylsulphonyl-fluorenides (MFlX), can all be produced quantitatively from the parent fluorene (HFlX) by the action of low concentrations of the appropriate t-butoxide in t-butyl alcohol solution. Their conductance behaviour can be conveniently studied in the absence of oxygen, yielding values for their ion-pair dissociation constants (K_d), and their disappearance can be readily monitored spectrophotometrically. As we shall see, the results of the present study again indicate at most quite small differences in reactivity between the free carbanion and the alkali metal–carbanion ion pair.

RESULTS

Conductimetric Ion-pair Dissociation Constants (K_d).—The conductance studies will be reported in detail elsewhere. Here, we give only a summary of our findings on ion association in salts of interest to the kinetic studies. The values of K_d reported in Table 1 were obtained from measurements of equivalent conductance as a function of concentration using a simplified version of Fuoss' method.[11] In this, values of the equivalent conductance at infinite dilution (Λ_0) were obtained using Walden's rule [12] and these were then used to derive K_d from the least squares slope of the Fuoss plot (F). This procedure was necessary because in t-butyl alcohol the Λ_0 value cannot be accurately obtained by extrapolation of the equivalent conductance–concentration curves owing to its steep slope at high dilution, nor from the intercept of the Fuoss plot because, being small, this is subject to large uncertainties.

TABLE 1

Conductimetric ion-pair dissociation constants of some sodium salts in t-butyl alcohol at 30°

Salt	Λ_0/ Ω^{-1} cm^2 [a]	F/Ω^2 l cm^{-4} mol^{-1}	r [f]	K_d/l mol^{-1}
NaOBu	14.15 [b]	6.60×10^6	0.959	7.6×10^{-10} [g]
NaCl	13.8 [c]	2.53×10^5	0.987	2.1×10^{-8}
$NaBPh_4$	12.2 [d]	8.62	0.930	7.8×10^{-4}
NaFlCN	12.6 [e]	0.78×10^3	0.997	8.1×10^{-6}
$NaFlCO_2Me$	12.6 [e]	4.89×10^3	0.976	1.3×10^{-6}
$NaFlSO_2Ph$	12.6 [e]	18.2×10^3	0.981	0.35×10^{-6}

[a] From Walden's rule. [b] Using sodium ethoxide in ethanol as the reference system. [c] Using ethanol as the reference solvent. [d] Using tetrahydrofuran as the reference solvent. [e] Applying Walden's rule to sodium fluorenide in tetrahydrofuran [12] predicts $\Lambda_0 = 13.6$; an intuitive correction has been applied in an attempt to allow for the effect of the 9-substituent. [f] Correlation coefficient in the Fuoss plot. [g] For potassium t-butoxide, $K_d = 8.4 \times 10^{-10}$ l mol^{-1}.

The important points to note in the results of Table 1 are (i) the wide variation of K_d for the salts studied, even among the closely related carbanion salts, which indicates that the weakly hydrogen bonding t-butyl alcohol is a discriminating solvent for anions as well as cations; (ii) the very small values of K_d for sodium and potassium t-butoxides which means that, in the kinetic studies, the alkoxides can be ignored as sources of free alkali-metal cations compared with sodium tetraphenylborate and the carbanion salts. The salt produced in the displacement reaction, sodium chloride (and presumably also the bromide and fluoride), is also much less dissociated than the carbanion salts and contributes little to the concentration of free sodium ions in the kinetic experiments.

Product Analyses.—The reaction of the three 9-substituted fluorenides with benzyl fluoride, chloride, or bromide takes place virtually quantitatively in an oxygen-free atmosphere. Preparative experiments using benzyl chloride gave isolated yields of the 9-substituted 9-benzylfluorene not less than 95% of the theoretical. For reactions using the other benzyl halides, the essentially quantitative formation of the 9-alkylated product was established by analytical g.l.c. Products from the kinetic runs were checked from time to time to estimate the extent to which fluorenone, the oxidation product of the carbanions, had been formed. While this can be done by g.l.c., spectrophotometry at 256 nm is more sensitive. In the few cases where fluorenone was detected in the product the kinetic result was rejected.

Kinetics.—Procedure. Reactions were followed spectrophotometrically at the wavelength of maximum absorption of the carbanion in t-butyl alcohol using a reaction cell from which oxygen could be excluded.[13] The carbanions were generated from the parent 9-substituted fluorene by treatment with an excess of the appropriate alkali-metal t-butoxide. It was established that the excess alkoxide had no detectable effect on the kinetics of the reaction of the carbanion with the benzyl halide. No evidence of appreciable direct reaction between the t-butoxides and benzyl halides was discernible. Reactions using benzyl chloride and fluoride were conducted with a large excess of halide over the carbanion. Benzyl bromide is too reactive for such a procedure and kinetic studies with it were carried out using the reactants in more nearly equal concentration.

Reactions with benzyl chloride. Reactions of sodium 9-cyano- and 9-phenylsulphonyl-fluorenide with excess of benzyl chloride at 30° followed precisely a first-order kinetic

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[8] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1967, **89**, 2764.

[9] K. Bowden, and R. S. Cook, *J. Chem. Soc.* (*B*), 1968, 1529; A. F. Cockerill and R. T. Hargreaves, *Chem. Comm.*, 1969, 915.

[10] For a recent account of such displacements, see S. R. Hartshorn, 'Nucleophilic Aliphatic Substitution,' Cambridge University Press, London, 1973; but see also R. A. Sneen, *Accounts Chem. Res.*, 1973, **6**, 46.

[11] R. M. Fuoss, *J. Amer. Chem. Soc.*, 1935, **57**, 488; R. M. Fuoss and F. Accascina, 'Electrolytic Conductance,' Wiley-Interscience, New York, 1959.

[12] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1966, **88**, 318.

[13] D. Bethell, *J. Chem. Soc.*, 1963, 666.

law [equation (1)] to at least 90% completion. Variation

$$-\mathrm{d}[\mathrm{MFlX}]_{\mathrm{total}}/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{MFlX}]_{\mathrm{total}} \qquad (1)$$

of the excess of benzyl chloride established that the rate is directly proportional to the chloride concentration, at least up to 3×10^{-2}M (Tables 2 and 3), whereafter, presumably as a consequence of a medium effect, values of k_2 [equation (2)] fell somewhat. Addition of sodium tetraphenylborate

$$k_{\mathrm{obs}} = k_2[\mathrm{PhCH_2Y}] \qquad (2)$$

had a scarcely perceptible rate-retarding effect on the reactions of both carbanions, and, consistently, dilution of the carbanions had little effect on the observed rate coefficients.

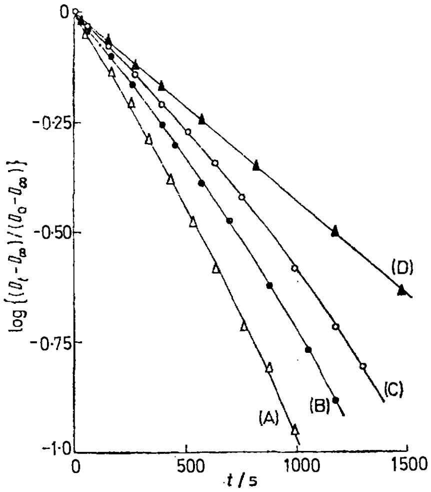


FIGURE 1 Kinetic form of the disappearance of sodium 9-methoxycarbonylfluorenide in the reaction with benzyl chloride (4.04×10^{-3}M) in t-butyl alcohol at 30°. Initial concentrations of carbanion salt are 1.50×10^{-4}M (A), 3.00×10^{-4}M (B), 6.00×10^{-4}M (C), and 6.00×10^{-4}M in the presence of 1.07×10^{-4}M $\mathrm{NaBPh_4}$ (D)

TABLE 2

Counter-ion and concentration effects on the displacement of chloride ion from benzyl chloride by alkali-metal 9-cyanofluorenides in t-butyl alcohol at 30°

Counter-ion, M	10^4[MFlCN]/M	$10^3[\mathrm{PhCH_2Cl}]$/M	$10^3[\mathrm{NaBPh_4}]$/M	$10^3k_{\mathrm{obs}}/\mathrm{s}^{-1}$	k_2/l mol^{-1} s^{-1}
Na [a]	6.50	4.04		1.22	0.30_2
	6.50	4.04	4.65	1.22	0.30_2
	6.50	12.1		3.66	0.30_2
	6.50	12.1	4.65	3.71	0.30_7
	6.50	15.2		4.79	0.31_6
	6.50	24.2		7.62	0.31_5
	6.50	24.2	3.10	7.06	0.29_2
	3.25	15.2		5.03	0.33_2
	1.63	15.2		4.97	0.32_8
K [b]	6.50	8.08		1.77	0.21_9
	3.25	8.08		1.90	0.23_6
	1.63	8.08		2.00	0.24_3

[a] $[\mathrm{NaOBu}]_0 = 3.33 \times 10^{-3}$M. [b] $[\mathrm{KOBu}]_0 = 2.50 \times 10^{-3}$M.

The disappearance of sodium 9-methoxycarbonylfluorenide under the standard conditions did not adhere strictly to the first-order law of equation (1). After some 50% reaction, a progressive increase in instantaneous rate coefficients became detectable (Figure 1). The effect was most marked in reactions in which the initial carbanion concentration was the lowest, and it was also detectable using lithium and potassium salts of the carbanion. Deviation from linearity in first-order kinetic plots was less marked in reaction mixtures to which sodium tetraphenylborate had been added (see Figure 1). Despite these deviations from simple behaviour, kinetic results were processed using equations (1) and (2). The values of the rate coefficients are in Tables 4 and 5, and, except where otherwise specified, refer to average values for the first 50% reaction. In cases where k_2 was evaluated over the second half-life of the carbanion, its higher value corresponded very closely with that measured over the first half-life in experiments using half the initial concentration of sodium 9-methoxycarbonylfluorenide. Clearly the deviations from equation (1) are in this instance a consequence solely of the carbanion concentration and do not arise from the build-up of a by-product which promotes the reaction.

Addition of sodium tetraphenylborate to the reaction mixture brought about a progressive decrease in k_2. The deviations from equation (1) were no longer detectable when the added salt reached 10^{-4}M (Table 5), a concentration at which it is still largely dissociated in t-butyl alcohol. Further increase in the concentration of added salt beyond this point decreased k_2 further but the effect was extremely small above 10^{-3}M.

The influence of the counter-ion on the reactivity of salts of 9-methoxycarbonylfluorene is similar to that observed in the case of 9-cyanofluorene (Tables 2 and 4). Values of k_2 fall in the sequence Li > Na > K, thus demonstrating the ability of t-butyl alcohol differentially to solvate cations and ion pairs (*cf.* the differential solvating ability towards anions and ion-pairs revealed by the conductance work).

Reactions with benzyl fluoride. Reactions were carried out with large excess concentrations of the halide over the carbanion so as to give conveniently measurable rates. In all cases the disappearance of the carbanion was fitted to equation (1). The linearity of first-order kinetic plots was good over 2—3 half-lives at the lower initial carbanion concentrations, but at the highest ($\geqslant 6 \times 10^{-4}$M) instantaneous rate coefficients decreased after some 50% of reaction. The values of k_{obs} and k_2 in Table 6 are averages over the first half-life of the carbanion. At the relatively high concentrations of benzyl fluoride used, k_{obs} values were not directly proportional to the halide concentration, presumably owing to a medium effect. Kinetic results

TABLE 3

Effects of concentration and added sodium tetraphenylborate on the kinetics of chloride-ion displacement from benzyl chloride by sodium 9-phenylsulphonylfluorenide in t-butyl alcohol at 30°

10^4[NaFlSO$_2$Ph]/M	10^3[PhCH$_2$Cl]/M	10^5[NaBPh$_4$]/M	10^3k_{obs}/s^{-1}	k_2/l mol^{-1} s^{-1}
1.00	20.2		5.01	0.24_8
2.00	20.2		4.93	0.24_4
4.00	5.05		1.02	0.20_2
4.00	5.05	4.65	0.94	0.18_6
4.00	10.1		2.26	0.22_4
4.00	10.1	4.65	2.06	0.20_4
4.00	10.1	760	1.94	0.19_2
4.00	15.2		3.38	0.22_3
4.00	20.2		4.41	0.21_8
4.00	20.2	62.0	3.91	0.19_4
4.00	20.2	155	3.99	0.19_8
4.00	20.2	760	3.90	0.19_4
4.00	20.2	1 030	3.88	0.19_2
4.00	30.3		6.26	0.20_7
4.00	30.3	465	6.24	0.20_6
4.00	50.5		9.55	0.18_9
4.00	50.5	30.5	9.32	0.18_5
4.00	50.5	183	9.60	0.19_0
4.00	50.5	610	9.25	0.18_4

TABLE 4

Counter-ion and concentration effects on the displacement of chloride ion from benzyl chloride by alkali-metal 9-methoxycarbonylfluorenides in t-butyl alcohol at 30°

Counter ion, M	10^4[MFlCO$_2$Me]/M	10^3[PhCH$_2$Cl]/M	10^3k_{obs}/s^{-1}	k_2/l mol^{-1} s^{-1}
Li [a]	6.00	4.04	1.74	0.43_1
	3.00	4.04	2.17	0.53_7
	1.50	4.04	2.74	0.67_8
Na [b]	6.00	4.04	1.22	0.30_2
	6.00	12.1	3.72	0.30_7
	6.00	20.2	6.03	0.29_9
	6.00	28.3	8.78	0.31_0
	3.00	4.04	1.52	0.37_6
	1.50	4.04	1.94	0.48_0
K [c]	6.00	8.08	1.19	0.14_7
	6.00	16.2	2.34	0.14_4
	3.00	8.08	1.35	0.16_7
	3.00	16.2	2.84	0.17_5
	1.50	8.08	1.58	0.19_6
	1.50	16.2	3.20	0.19_8

[a] [LiOBu]$_0$ = 5.00 × 10^{-3}M. [b] [NaOBu]$_0$ = 3.33 × 10^{-3}M. [c] [KOBu]$_0$ = 5.00 × 10^{-3}M.

TABLE 5

Influence of added sodium tetraphenylborate on the kinetics of chloride ion displacement from benzyl chloride by sodium 9-methoxycarbonylfluorenide [a] in t-butyl alcohol at 30°

10^3[PhCH$_2$Cl]/M	10^5[NaBPh$_4$]/M	10^3k_{obs}/s^{-1} [b]	k_2/l mol^{-1} s^{-1}
4.04		1.22 (1.52)	0.30_2 (0.37_6)
4.04	2.38	1.26 (1.39)	0.31_9 (0.34_4)
4.04	3.58	1.21 (1.30)	0.29_9 (0.32_2)
8.08	3.58	2.38	0.29_5
4.04	4.77	1.15 (1.22)	0.28_5 (0.30_2)
4.04	5.96	1.17 (1.19)	0.29_0 (0.29_5)
4.04	7.16	1.14 (1.14)	0.28_2 (0.28_2)
8.08	7.16	2.32	0.28_7
4.04	8.35	1.06	0.26_2
4.04	10.7	0.99	0.24_5
4.04	11.9	1.02	0.25_2
4.04	17.9	0.96	0.23_8
4.04	26.8	0.88	0.21_8
8.08	30.4	1.79	0.22_2
4.04	44.7	0.88	0.21_8
4.04	596	0.83	0.20_5

[a] [NaFlCN]$_0$ = 6.00 × 10^{-4}M; [NaOBu]$_0$ = 3.33 × 10^{-3}M. [b] Average value over the first 50% of carbanion disappearance; the figures in parentheses indicate the average value over the second half-life.

were therefore always compared at the same benzyl fluoride concentration.

Small additions of sodium tetraphenylborate to reaction mixtures containing sodium 9-cyanofluorenide had a negligible effect on the reaction rate or kinetic form. Very large salt concentrations, however, produced a substantial acceleration of rate, especially at low carbanion concentrations; indeed runs at low initial carbanion concentration and high sodium tetraphenylborate showed a slight increase in k_{obs} in the later stages. With the other carbanions, no kinetic effect was detectable on addition of large concentrations of the common-ion salt.

TABLE 6

Effects of concentration and added sodium tetraphenylborate on the kinetics of fluoride-ion displacement from benzyl fluoride (0.128M) by sodium salts [a] of 9-substituted fluorenes in t-butyl alcohol at 30°

10^4[NaFlCN]/M	6.50	6.50	6.50	6.50	6.50	6.50	6.50
10^5[$NaBPh_4$]/M		2.98	5.96	18.0	59.6	298	596
$10^4k_{obs}/s^{-1}$	2.10	2.12	2.15	2.10	2.36	2.46	2.49
10^3k_2/l mol^{-1} s^{-1}	1.6_5	1.5_6	1.6_6	1.6_4	1.8_5	1.9_2	1.9_4

10^4[NaFlCN]/M	3.25	1.63	1.63
10^5[$NaBPh_4$]/M			343
$10^4k_{obs}/s^{-1}$	2.08	2.34	3.14
10^3k_2/l mol^{-1} s^{-1}	1.6_4	1.8_3	2.4_6

10^4[$NaFlCO_2Me$]/M	6.00	6.00	6.00	6.00
10^5[$NaBPh_4$]/M		298		119
$10^4k_{obs}/s^{-1}$	2.46	2.38	4.52 [b]	4.35 [b]
10^3k_2/l mol^{-1} s^{-1}	2.0_1	1.9_4	1.7_7	1.7_0

10^4[$NaFlSO_2Ph$]/M	4.00	4.00	4.00	4.00
10^5[$NaBPh_4$]/M		298		
$10^4k_{obs}/s^{-1}$	1.78	1.66	3.06 [b]	3.06 [b]
10^3k_2/l mol^{-1} s^{-1}	1.4_5	1.3_5	1.2_0	1.2_0

[a] Generated using $[NaOBu]_0 = 5.30 \times 10^{-3}$M. [b] $[PhCH_2F]_0 = 0.255$M.

Reactions with benzyl bromide. Because of the high reactivity of this halide, experiments were conducted with benzyl bromide present in only small excess. The reactions of the sodium salts of 9-cyano- and 9-phenylsulphonylfluorene obeyed the expected second-order kinetic law over at least 75% of the reaction. Decrease of the initial carbanion concentration had little or no effect on the observed rate coefficient, and, likewise, the effect of addition of sodium tetraphenylborate was negligible.

Most experiments were carried out using sodium 9-methoxycarbonylfluorenide, and here, as in the reactions with benzyl chloride, deviations from the expected kinetic behaviour were apparent. Indeed, it was not possible to derive values of k_2 from conventional second-order kinetic plots because the curvature was too marked, even in the initial stages of the reaction. In fact, the disappearance of the carbanion fitted with remarkable precision a first-order kinetic law [equation (1)], even when the carbanion salt and benzyl bromide were initially in almost equal concentration.

The following considerations make it clear that these reactions are also ones involving rate-limiting attack of the carbanion on benzyl bromide rather than a unimolecular process of the carbanion salt, such as, for example, ion-pair dissociation. (i) At high concentrations of benzyl bromide, the disappearance of the carbanion is too fast to measure by our technique. (ii) The observed ' first-order ' rate coefficients obtained using equation (1) increase markedly as the initial carbanion concentration is lowered, a finding inconsistent with a unimolecular reaction of an ion pair but one which parallels the kinetic observations in the benzyl chloride reaction. (iii) The apparent first-order behaviour is not maintained in the presence of added sodium tetraphenylborate which led to a partial, but never complete, reversion to second-order kinetics. The apparent first-order kinetics observed evidently arise from an accidental cancellation of the rate-retarding effect of the decreasing benzyl bromide concentration and the rate-accelerating effect of the decreasing carbanion concentration. The values of k_2 for the reactions of both sodium and potassium 9-methoxycarbonylfluorenides given in Table 7 were obtained from the slopes of first-order plots using equation (2).

TABLE 7

Effects of concentration and added sodium tetraphenylborate on the kinetics of bromide-ion displacement from benzyl bromide (6.88×10^{-4}M) by sodium salts [a] of 9-substituted fluorenes in t-butyl alcohol at 30°

10^4[NaFlCN]/M	6.50	6.50	6.50	3.25	3.25	3.25	1.68
10^5[$NaBPh_4$]/M		179	358		179	358	
k_2/l mol^{-1} s^{-1}	$23._6$	$19._5$	$21._7$	$23._2$	$22._8$	$23._4$	$23._2$

10^4[$NaFlCO_2Me$]/M	6.00	6.00 [b]	6.00	6.00	6.00	6.00	6.00
10^5[$NaBPh_4$]/M			3.58	4.77	5.96	9.54	17.9
k_2/l mol^{-1} s^{-1}	$23._4$	$9._4$	$22._7$	$20._8$	$20._9$	$17._2$	$14._1$

10^4[$NaFlCO_2Me$]/M	6.00	6.00	6.00	3.00	3.00	1.50	1.50 [b]
10^5[$NaBPh_4$]/M	59.6	179	238				
k_2/l mol^{-1} s^{-1}	$10._9$	$10._3$	$9._9$	$33._4$	$12._6$	$40._5$	$15._3$

10^4[$NaFlSO_2Ph$]/M	4.00	1.00
k_2/l mol^{-1} s^{-1}	6.6_7	7.2_3

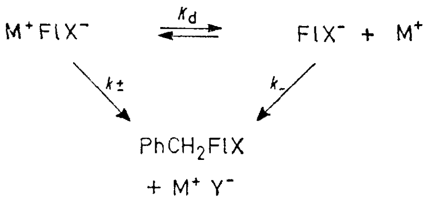
[a] Generated using $[NaOBu]_0 = 5.30 \times 10^{-3}$M. [b] Potassium salt.

Again, dilution of the carbanion increases k_2 for both the sodium and potassium salts, the sodium salt being substantially the more reactive at all the concentrations examined. Addition of sodium tetraphenylborate had a marked retarding effect up to concentrations of *ca.* 10^{-3}M, whereafter further additions caused only minor deceleration.

DISCUSSION

The general pattern of results for the reaction of alkali-metal 9-methoxycarbonylfluorenides with the benzyl halides, namely (i) deviations from simple kinetic laws, (ii) the increase of rate coefficients with decreasing initial concentration of the carbanion salt, (iii) the variation of rate with changing counter ion, and (iv) the rate-retarding effect of added sodium tetraphenylborate, all indicate that the carbanion is involved both in the free state and in the form of ion pairs in t-butyl alcohol. The simplest formulation of the reaction is that shown in the Scheme, but clearly more complex reaction networks can be envisaged in which the roles of different types of ion pair are explicitly distinguished. That the interpretation of the reactions in the Scheme is reasonable may be judged from the fact that sodium

9-methoxycarbonylfluorenide (6×10^{-4}M) in t-butyl alcohol at 30°, for which $K_d = 1.3 \times 10^{-6}$M, exists to the extent of *ca.* 3.6% as free ions. There is thus ample scope for manipulating the degree of dissociation of the carbanion salt and hence, provided that the free ion reacts substantially faster than the paired ion, the reaction rate.



SCHEME

Representing the sum of the concentrations of the free and paired carbanions by [MC], the experimental value of k_2 on the basis of the Scheme is given by equation (3),[14] where α represents the degree of dissociation of the carbanion salt. The equilibrium between the free and paired ions is controlled by the concentration of kinetically free counter ions, M⁺. In reaction mixtures without added common-ion salt, possible sources of free counter ion at any instant are the carbanion salt itself, the product alkali-metal halide, MY, and the excess butoxide remaining after generation of the carbanion salt. The conductance studies on sodium salts summarised in Table 1 permit us to exclude the last two as principal sources of free sodium ions. Under the present reaction conditions then, the carbanion salt itself is the only source that need be considered. For $[\mathrm{MC}] \gg K_d$, as it is in all cases, α may be replaced by $(K_d/[\mathrm{MC}])^{\frac{1}{2}}$, whence equation (3) becomes (4). Clearly k_2 should vary as the total carbanion concentration is changed, with a sensitivity determined by both the magnitudes of the velocity constants and the dissociation constant. The value of k_2 would be expected to increase with dilution in general since k_- is likely to exceed $k_{\pm}$; the reverse situation, k_2 decreasing with dilution as a consequence of $k_{\pm}$ exceeding k_-, would be difficult to detect for a feebly dissociated carbanion salt such as sodium 9-methoxycarbonylfluorenide. Invariance of k_2 with dilution can result from a number of different circumstances: (i) $k_- = k_{\pm}$, (ii) $K_d^{\frac{1}{2}}$ is very small, so that $k_{\pm} \gg (k_- - k_{\pm})K_d^{\frac{1}{2}}$, (iii) K_d is so large that the carbanion salt is essentially completely dissociated over the whole range of concentrations studied.

$$k_2 = \frac{-1}{[\mathrm{MC}][\mathrm{PhCH_2Y}]} \cdot \frac{d[\mathrm{MC}]}{dt} = k_{\pm} + (k_- - k_{\pm})\alpha \quad (3)$$

$$k_2 = k_{\pm} + (k_- - k_{\pm})K_d^{\frac{1}{2}}/[\mathrm{MC}]^{\frac{1}{2}} \quad (4)$$

For reactions in the presence of added sodium tetraphenylborate, the added salt provides most of the free sodium ions except at very low concentrations. For a weakly dissociated carbanion salt, $\alpha = K_d/[\mathrm{Na}^+]$, where $[\mathrm{Na}^+]$ is the concentration of free sodium ions calculated from the dissociation constant of the added salt (7.8×10^{-4}M in the present experiments). Equation (3) is now transformed into (5) which predicts a linear dependence of k_2 on $[\mathrm{Na}^+]^{-1}$. As others have pointed out,[25] the ratios of the slopes of plots of kinetic data according to equations (5) and (4) gives $K_d^{\frac{1}{2}}$ for the carbanion salt by a non-conductimetric method.

$$k_2 = k_{\pm} + (k_- - k_{\pm})K_d/[\mathrm{Na}^+] \quad (5)$$

The kinetic data for reactions of alkali-metal salts of 9-methoxycarbonylfluorene with benzyl chloride and bromide have been fitted to equations (4) and (5). Excellent linear correlations were found with equation (4); the intercepts ($k_{\pm}$) and slopes $[(k_- - k_{\pm})K_d^{\frac{1}{2}}]$ from least squares calculations are in Table 8. The intercepts and slopes according to equation (5) refer only to the linear part of the plot (see Figure 2 for the full correlations); points corresponding to very low concentrations of added sodium tetraphenylborate were not used where the concentration of free sodium ions arising from dissociation of the carbanion salt itself exceeded *ca.* 10% of that resulting from the added salt. Clearly, by calculating the total free sodium ion concentration using the conductimetric K_d value for the carbanion salt, all the data could be fitted to one straight line. However, we wished to obtain K_d by the non-conductimetric method for purposes of comparison.

Of the data processed in this way, those from the reactions with benzyl chloride are thought to be the

TABLE 8

Ion association and reactivity of alkali metal 9-methoxycarbonylfluorenides with benzyl chloride and bromide in t-butyl alcohol at 30°

		Equation (4)			Equation (5)			
M	$\mathrm{PhCH_2Y}$	$k_{\pm}$ [a]	10^3 Slope	k [a,b]	$k_{\pm}$	10^6 Slope	k_-	10^6K_d/ l mol⁻¹
Li	$\mathrm{PhCH_2Cl}$	0.185 ± 0.005	6.05 ± 0.07	(4.27)				2.19
Na	$\mathrm{PnCH_2Cl}$	0.124 ± 0.001	4.36 ± 0.08	4.27	0.202 ± 0.002	4.57 ± 0.28	4.35	1.10
K	$\mathrm{PhCH_2Cl}$	0.097 ± 0.005	1.24 ± 0.07	(4.27)				0.088
Na	$\mathrm{PhCH_2Br}$	7.76 ± 3.46	411 ± 55	256	9.34 ± 0.11	681 ± 17	258	2.74
K	$\mathrm{PhCH_2Br}$	3.88 ± 0.90	142 ± 14	(256)				

[a] l mol⁻¹ s⁻¹. [b] Figures in parentheses are the values derived for the sodium salt.

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[14] S. F. Acree, *Amer. Chem. J.*, 1912, **48**, 353.

more reliable principally because the fit to equation (4) showed less scatter. The value of K_d for the sodium salt of 9-methoxycarbonylfluorene so obtained is in good agreement with the conductimetric value. Agreement with the K_d value obtained from the benzyl bromide reactions was less good than was hoped, but is still fair. The correspondence between the values of $k_{\pm}$ from the dilution and sodium tetraphenylborate studies also left something to be desired. However, using the derived values of K_d and $k_{\pm}$, k_- was evaluated from the slopes of the plots of the data for the sodium salts according to equations (4) and (5). In conjunction with the slopes and intercepts obtained from plotting the results for the lithium and potassium salts according to equation (4), the k_- value afforded values of $k_{\pm}$ and K_d for these carbanion salts as shown in Table 8. These results indicate that the order of overall reactivity observed for the alkali-metal salts of 9-methoxycarbonylfluorene stems from the combination of $k_{\pm}$ and K_d values both of which decrease in the sequence Li > Na > K. The clear inference is that solvation of the alkali metal is the major determinant of the behaviour of these carbanion salts both as regards dissociation and reaction of ion pairs. Not surprisingly, the larger effect is on dissociation where solvation of free alkali-metal cations is involved.

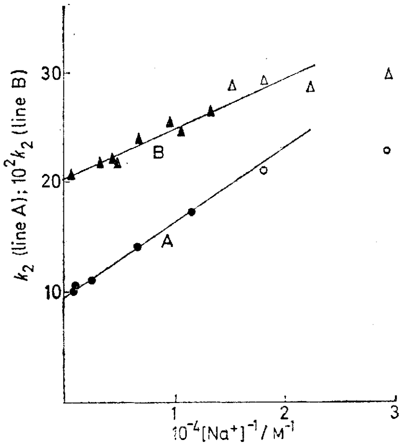

FIGURE 2 The kinetic effect of added sodium tetraphenylborate on the disappearance of sodium 9-methoxycarbonylfluorenide in t-butyl alcohol at 30° plotted according to equation (5). Curve A, reaction with benzyl bromide; curve B, benzyl chloride. The lines are those calculated by the method of least mean squares using the filled data points

The results for the reactions of the other two carbanions with the three benzyl halides all show rate constant changes on dilution of the carbanion or addition of sodium tetraphenylborate which are very much smaller than those found in the case of the salts of 9-methoxycarbonylfluorene and, indeed, are difficult to differentiate with certainty from experimental error. This absence of any marked effect is of particular significance in the reactions of sodium 9-cyanofluorenide. Our conductance results indicate that, of the three carbanion salts studied, this was the most dissociated (5—20% over the range of concentrations used in the kinetic experiments). Now, since the effects of ion association were detectable with 9-methoxycarbonylfluorenide salts, they should also have been detectable in this case if k_- differed significantly from $k_{\pm}$. That little or no effect was observed indicates then that $k_- \simeq k_{\pm}$. We note also that in the reaction of sodium 9-cyanofluorenide with benzyl fluoride, small *decreases* occur in k_2 on dilution of the carbanion salt and small *increases* occur on addition of the common-ion salt. This is the pattern of behaviour to be expected if $k_{\pm} > k_-$, but the effects are still fairly small, although, significantly, most pronounced at the lowest carbanion concentration, and there may be complications arising from the relatively high benzyl fluoride concentration. The absence of a significant rate retardation when sodium tetraphenylborate is added to reactions of sodium 9-methoxycarbonylfluorene with benzyl fluoride may be an indication that medium effects cancel common-ion rate depression or that benzyl fluoride is a substrate for which $k_{\pm}$ is always unusually high relative to k_-.

Sodium 9-phenylsulphonylfluorenide is the least dissociated of the carbanion salts studied and this may be largely responsible for the absence of marked kinetic effects on dilution or addition of the common cation. Such effects as have been observed are in the direction expected for $k_- > k_{\pm}$.

The most striking feature of these results is the remarkable similarity in the reactivity of the free ions and ion pairs. Even with sodium 9-methoxycarbonylfluorenide, the maximum value of $k_-/k_{\pm}$ is only *ca.* 30, and with the other carbanion salts it is more nearly unity. Moreover, the associated carbanions show little variation in reactivity with changing 9-substituent even though this has a quite pronounced effect on pK_a (CN,[2d] 11.4; CO_2Me,[2d] 12.9; SO_2Ph,[15] 15.0). Thus values of $k_{\pm}$ for the three carbanions are all in the range 0.12—0.30 l mol^{-1} s^{-1}. If $k_{\pm} = k_-$ for sodium 9-cyanofluorenide, then a somewhat larger variation of k_- with structure is implied, as seems plausible in a protic solvent. The biggest structural influence on reactivity, however, is shown by the leaving halide where the sequence is Br (*ca.* 1 200) > Cl (*ca.* 150) > F (1.0). Together, these structural effects suggest that the transition state for displacement is one in which breaking of the carbon–halogen bond has progressed much further than formation of the new carbon–carbon bond.

EXPERIMENTAL

Materials.—t-Butyl alcohol was purified as previously described.[3] Solutions of alkali-metal t-butoxides were prepared and handled using methods developed earlier.[3] A commercial sample of sodium tetraphenylborate was recrystallised from aqueous alcohol and vacuum dried. The benzyl halides were all middle cuts from fractional distillations under reduced pressure.

The three 9-substituted fluorenes were prepared by literature methods,[15-18] and were analytically pure. All gave the spectrum of the corresponding carbanion salt on treatment with excess of alkali-metal t-butoxide in t-butyl alcohol: NaFlCN $\lambda_{max.}$ 406 nm ($\varepsilon_{max.}$ 2 040); NaFlCO$_2$Me $\lambda_{max.}$ 386 nm ($\varepsilon_{max.}$ 2 420); NaFlSO$_2$Ph $\lambda_{max.}$ 375 nm ($\varepsilon_{max.}$ 9 050). The rather broad peaks in t-butyl alcohol solution were little affected by changing the counter ion either in wavelength or intensity. It was established that Beer's law applies over the range of carbanion concentrations used.

Preparative benzylations of the carbanions were carried out as follows. The 9-substituted fluorene (1 mol) and benzyl chloride (5 mol) were dissolved in t-butyl alcohol and placed in one limb of a Y tube reactor and a solution of sodium t-butoxide (10 mol) was placed in another. The apparatus was freed of oxygen by several freeze–pump–thaw cycles with intermediate flushing with nitrogen. The solutions were then mixed at 30° and maintained at this temperature until the colour of the carbanion was discharged. After quenching with water, the product was extracted with ether and crystallised from hexane. M.p. and analytical data are as follows. 9-Benzyl-9-cyanofluorene had m.p. 111° (lit.,[9] 111—112°) (Found: C, 89.8; H, 5.5; N, 4.9. Calc. for $C_{21}H_{15}N$: C, 89.7; H, 5.4; N, 5.0%). *9-Benzyl-9-methoxycarbonylfluorene* had m.p. 65° (Found: C, 84.2; H, 5.6. $C_{22}H_{18}O_2$ requires C, 84.1; H, 5.8%). *9-Benzyl-9-phenylsulphonylfluorene* had m.p. 203° (Found: C, 78.6; H, 5.2; S, 8.3. $C_{26}H_{20}O_2S$ requires C, 78.8; H, 5.1; S, 8.1%). G.l.c. analyses were carried out using a 2 m × 6 mm o.d. column packed with 1% OV 17 on Gas Chrom Q (60—80 mesh) at 150°. Triphenylmethane was used as standard.

Kinetics.—The disappearance of the carbanions was followed using a Unicam SP 1800 spectrophotometer. Reactant solutions were separately free of oxygen as described above and then thermostatted at the reaction temperature. After mixing, the decreasing absorbance of the carbanion was monitored by repetitive scanning of the whole peak in slower reactions or by recording the optical density at $\lambda_{max.}$ for the carbanion as a function of time. Values of k_{obs} were obtained graphically from first-order plots as indicated in the Results section, and were in general reproducible to ±3%.

Conductance Measurements.—Measurements were made using one of two cells having cell constants of 1.30 and 0.039 cm^{-1}, in conjunction with a Wayne–Kerr type B221A ratio-arm bridge operating at 1 592 Hz, a more accurate combination than that used previously.[4b] The cells were calibrated using aqueous potassium chloride solution, and the calibrations were checked periodically. Both cells were equipped with detachable two-limb vessels for mixing and diluting solutions and a connector for degassing. Additionally the cell with the lower cell constant was attached to a 10 mm spectrophotometer cell so that the conductance of carbanion solutions could be related directly to the absorbance and hence the concentration of the carbanion. In Fuoss calculations on the equivalent conductance–concentration results, the dielectric constant of t-butyl alcohol at 30° was taken as 11.2 and its viscosity as 3.32 cP.

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[4/2647 *Received*, 19*th September*, 1974]

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