Mechanistic Studies in Strongly Basic Media. Part IX.[1] Patterns of Reactivity of Sodium Salts of 9-Substituted Fluorenes with Molecular Oxygen and with Acrylic Esters

By **Donald Bethell,* Colin S. Fairclough, Robert J. E. Talbot, and Rodney G. Wilkinson**, The Robert Robinson Laboratories, The University, P.O. Box 147, Liverpool L69 3BX

The kinetics of autoxidation and of Michael addition to methyl acrylate, methacrylate, and crotonate of sodium salts of three 9-substituted fluorenes, FlHX (X = CN, CO_2Me, or SO_2Ph) in t-butyl alcohol solution have been studied. The effect on the rate of changing the concentration of free sodium ions in the solution, by dilution and by addition of the common-ion salts sodium perchlorate and sodium tetraphenylborate, has been examined in an attempt separately to evaluate the reactivities of the free and associated carbanions. In autoxidation reactions, the kinetic effect is small and the common-ion effect cannot be distinguished with certainty from the medium effect of the added salt. Much larger effects arise in t-butyl alcohol containing dimethyl sulphoxide and these suggest that, for sodium 9-phenylsulphonylfluorenide, the free carbanion is more reactive than the ion pair, while, for sodium 9-cyanofluorenide, the reverse is the case. In Michael additions in which methyl acrylate is the acceptor or in which 9-cyanofluorene is the addend, no common-ion effect is detectable, suggesting that free and paired anions are equally reactive in these systems. In all other cases studied, the free ion was 10—100 times more reactive than the ion-pair. Some of the more important factors relevant to the interpretation of this complex pattern of behaviour are indicated.

IN earlier Parts,[2,3] the importance of ion association in reactions taking place in t-butyl alcohol solutions of alkali-metal t-butoxides was explored. In Part VIII [1] we examined in detail the effect of ion association on the reactivity of alkali-metal 9-substituted fluorenides in the displacement of halide ions from benzyl halides. It was shown that substantial differences in reactivity between the free carbanion and the corresponding associated form were only detectable with the salts of 9-methoxycarbonylfluorene. The biggest influence on overall reactivity was provided by the benzyl halide. We now describe a series of studies aimed to throw light on the way that the pattern of behaviour of these carbanion salts is influenced by the nature of the chemical reaction. The reactions studied were the base-induced autoxidation of 9-substituted fluorenes, where the rate-limiting process is believed to be electron transfer from the carbanion to a ground state oxygen molecule,[2e,3,4] and carbanion addition to the activated carbon–carbon double

---

[1] Part VIII, D. Bethell, C. S. Fairclough, and R. G. Wilkinson, *J.C.S. Perkin II*, 1975, 1090.

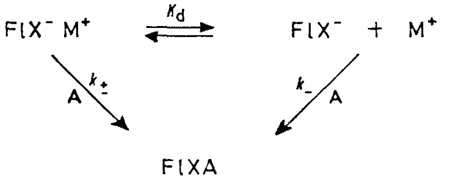
[2] D. Bethell and A. F. Cockerill, *J. Chem. Soc.* (*B*), 1966, (*a*) 913; (*b*) 917; (*c*) 920; (*d*) D. Bethell, A. F. Cockerill, and D. B. Frankham, *ibid.*, 1967, 1287; (*e*) D. Bethell and R. J. E. Talbot, *ibid.*, 1968, 638; (*f*) D. Bethell, A. F. Cockerill, and D. B. Frankham, *ibid.*, 1970, 1271.

[3] See also D. Bethell, R. J. E. Talbot, and R. G. Wilkinson, *Chem. Comm.*, 1968, 1528 for a preliminary account.

[4] G. A. Russell, A. G. Bemis, E. J. Geels, and E. G. Janzen, ' Oxidation of Organic Compounds,' Amer. Chem. Soc. Advances in Chemistry Series, No. 75, 1968, vol. 1, p. 174.

bond in acrylic esters (Michael addition).[5] In both reactions, the 9-substituted fluorenes chosen were those in which the 9-substituent (CN, CO_2Me,SO_2Ph) rendered the molecule sufficiently acidic to be formed quantitatively from the parent carbon acid by dilute solutions of sodium or potassium t-butoxide in t-butyl alcohol.

As before, our initial objective was to analyse the overall kinetic behaviour into contributions from the free carbanion and the ion pair with the sodium counter-ion as set out in the Scheme.



SCHEME

It is easily shown that under conditions where the ion-pair dissociation equilibrium is established rapidly compared with the steps in which the reagent A is involved, the rate of disappearance, v, of the carbanion, both free and associated combined, is given by equation (1). In

$$v = \frac{k_\pm[M^+] + k_-K_d}{K_d + [M^+]}[\mathrm{MFlX}]_{\mathrm{total}}[A] \qquad (1)$$

order to evaluate the equilibrium and rate constants in (1), the equation can be transformed into (2) or (3). Using (2), plots of $k_{obs}(K_d + [M^+])$ against $[M^+]$, the

$$k_{obs}\,(K_d + [M^+]) = k_\pm[M^+] + k_-\,K_d \qquad (2)$$

$$k_{obs} = k_\pm + \frac{K_d\,(k_- - k_\pm)}{K_d + [M^+]} \qquad (3)$$

calculable concentration of free counter-ion which can easily be varied by dilution of the carbanion or by addition of common-ion salts, should be linear and yield $k_\pm$ from the slope and k_- from the intercept if the value of K_d, the ion-pair dissociation constant of the carbanion salt is known. The correlation using equation (2) is generally very good, especially if $[M^+] > K_d$, but the intercept is often small with poorly dissociated carbanion salts and frequently cannot be distinguished from zero. Equation (3) yields $k_\pm$ from the intercept and $(k_- - k_\pm)$ from the slope of plots of k_{obs} against $(K_d + [M^+])^{-1}$. Because it involves a reciprocal plot, the procedure is very sensitive to errors and curvature can readily be caused by, for example, systematic errors in the estimation of $[M^+]$. Correlation coefficients from linear regression analysis are generally poorer with equation (3) than with (2). However, equation (3) was used wherever possible in the present study.

RESULTS

The Reaction of Carbanions with Molecular Oxygen.—Products. On a preparative scale (*ca.* 5 mmol) the three 9-substituted fluorenes (HFlX; X = CN, CO_2Me, or SO_2Ph) on treatment with an oxygen-saturated solution of sodium t-butoxide were converted into fluorenone (*ca.* 85% of the theoretical yield of crystalline material). During the course of the oxidation, white solids were precipitated (70—85% of theory) and in two of the cases these were shown to be the sodium salts of OX^-, *i.e.* sodium cyanate and sodium benzenesulphonate for X = CN and SO_2Ph respectively. When reactions were conducted at the dilutions appropriate to spectrophotometric estimation of the carbanion concentration (*ca.* 10^{-4}M) essentially quantitative formation of fluorenone was observed and the product sodium salt was not precipitated.

Experiments on the sodium salt of 9-methoxycarbonylfluorene showed that the disappearance of the carbanion was *ca.* 50 times faster than the appearance of fluorenone. An ether extract of the quenched reaction mixture immediately after the disappearance of the carbanion showed the presence of an unstable intermediate which liberated iodine from iodide ion, but this could not be isolated. We take this to be the hydroperoxide resulting from collapse of the radical pair formed in the rate-limiting step of the reaction

$$\begin{tikzcd}[column sep=large] \mathrm{MeO_2CFl^-Na^+} \arrow[r, "O_2", "\text{slow}"'] & \mathrm{MeO_2CFl{\cdot}O_2^{-}{\cdot}Na^+} \arrow[r, "\text{fast}"] & {} \\ & & \mathrm{MeO_2CFlO_2^-Na^+} \arrow[d, "\text{very slow}"] \\ & & \mathrm{Fl{=}O + CO_2 + Na^+OMe^-} \end{tikzcd} \qquad (4)$$

Kinetics. All reactions were followed spectrophotometrically by the disappearance of the visible absorption of the carbanion. The presence of fluorenone in the appropriate concentration was confirmed at the completion of each reaction. In a few cases fluorenone formation was monitored spectrophotometrically during kinetic runs. In all cases reaction mixtures were saturated with dry air or oxygen at atmospheric pressure, the gas being passed through the solution throughout the course of the oxidation.

The disappearance of the carbanion salt followed a strict first-order kinetic law over 1—4 half-lives under these reaction conditions, indicating that there was little variation of k_{obs} with carbanion concentration. The kinetic effect of changing the oxygen and (excess) base concentration in the solution and of adding dimethyl sulphoxide to the reaction mixture is shown in Table 1. Changing the saturating gas from pure oxygen to air reduced k_{obs} by a factor of *ca.* 4.8 confirming a first-order dependence of the reaction on oxygen concentration. Although all the carbanion salts are fully formed under the reaction conditions, as indicated by the invariance with increasing base concentration of the extrapolated absorbance at zero time, the observed velocity constant changes with base concentration. Thus k_{obs} increases with increasing [NaOBu] for sodium 9-cyanofluorenide, but decreases for sodium 9-phenylsulphonylfluorenide, the value for the 9-methoxycarbonyl derivative remaining apparently unchanged over a fairly wide range of t-butoxide concentration. A similar pattern of behaviour resulted when potassium t-butoxide was used to generate the carbanion salt.

The kinetic effect of adding the common ion salts sodium

---

[5] For reviews, see E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, 1959, **10**, 179; H. O. House, 'Modern Synthetic Reactions,' Benjamin, Menlo Park, 1972, 2nd edn., p. 595.

perchlorate and sodium tetraphenylborate is given in Table 2, together with the concentration of free sodium ion in the solution obtained by iterative calculation from the known [1] ion-pair dissociation constants of the salts present. Again, the presence of the common ion salt changed k_{obs} in the same direction but to a larger extent than occurred on changing the concentration of sodium t-butoxide. Thus the added sodium salts accelerated slightly the oxidation of 9-cyanofluorene, retarded the oxidation of 9-phenylsulphonylfluorene and left k_{obs} for sodium 9-methoxycarbonylfluorenide unchanged. The added salts had no effect on the quantitative nature of conversion of the carbanion salt into fluorenone. They did not change the basicity of the reaction solutions, as measured by the weakly acidic indicator 4-chloro-2-nitroaniline, and they had no effect on the saturation concentration of oxygen in the solutions as monitored using a Rank electrode.

TABLE 1

Kinetics of oxidation of sodium 9-substituted fluorenides (NaFlX) by oxygen and air in t-butyl alcohol at 30° in the presence of excess of sodium t-butoxide.

X	[NaFlX]/M	10^3[NaOBu]$_0$/M	$10^3k_{\mathrm{obs}}/\mathrm{s}^{-1}$ Oxygen	$10^3k_{\mathrm{obs}}/\mathrm{s}^{-1}$ Air	$(\overset{+}{\mathrm{Na}})_{\mathrm{total}}$
CN	3.33×10^{-4}	1.0	5.30 (6.7) [a]	1.10	4.81×10^{-5}
		5.0	5.40		4.81×10^{-5}
		10.0	5.50 (7.5) [a]	1.16	4.81×10^{-5}
		20.0	5.60	1.20	4.82×10^{-5}
		50.0	5.80 (8.7) [a]		4.85×10^{-5}
		113.0	6.30 (0.25) [b]		4.90×10^{-5}
SO_2Ph	6.67×10^{-5}	1.0	0.164 (0.176) [a]		4.74×10^{-6}
		5.0	0.119		5.06×10^{-6}
		10.0	0.103 (0.148) [a]		5.43×10^{-6}
		11.3	0.101 (0.073) [b]		5.53×10^{-6}
		20.0	0.092		6.11×10^{-6}
CO_2Me	6.62×10^{-4}	3.0	15.8 (0.30) [c]		2.87×10^{-5}
		6.0	15.6		2.88×10^{-5}
		10.0	16.4 (11.2) [a]		2.88×10^{-5}
		20.0	16.1 (11.1) [a]	(2.08) [a]	2.90×10^{-5}

[a] Interpolated from more extensive measurements using potassium t-butoxide. [b] Dimethyl sulphoxide (1.0M) present; rates determined both by carbanion disappearance and fluorenone formarion. [c] Determined by fluorenone formation.

TABLE 2

Effect of added sodium perchlorate and sodium tetraphenylborate on the kinetics of oxidation of sodium 9-substituted fluorenides by oxygen in t-butyl alcohol at 30° [a]

(a) Sodium 9-cyanofluorenide (3.33×10^{-4}M)						
10^3[NaClO$_4$]/M	0.0	0.57	1.16	2.18	3.28	4.42
$10^3k_{\mathrm{obs}}/\mathrm{s}^{-1}$	5.5	6.5	6.6	6.7	6.8	7.2
10^5[Na$^+$]/M	4.80	5.30	5.76	6.47	7.15	7.79
10^3[NaBPh$_4$]/M	0.67	1.64	3.33	6.67	7.20	8.00
$10^3k_{\mathrm{obs}}/\mathrm{s}^{-1}$	6.8	7.2	7.4	7.8	8.0	8.1
10^5[Na$^+$]/M	43.4	80.9	127	192	201	214
(b) Sodium 9-phenylsulphonylfluorenide (6.67×10^{-5}M)						
10^3[NaClO$_4$]/M	0.0	0.78	1.16	2.18	3.28	4.42
$10^3k_{\mathrm{obs}}/\mathrm{s}^{-1}$	0.103	0.101	0.097	0.094	0.090	0.086
10^5[Na$^+$]/M	0.54	2.55	3.10	4.24	5.20	6.03
10^3[NaBPh$_4$]/M	0.67	1.67	3.33	6.67	9.00	
$10^3k_{\mathrm{obs}}/\mathrm{s}^{-1}$	0.102	0.093	0.087	0.078	0.074	
10^5[Na$^+$]/M	43.0	81.6	127	192	229	
(c) Sodium 9-methoxycarbonylfluorenide (6.62×10^{-4}M)						
10^3[NaBPh$_4$]/M	0.0	0.83	8.33			
$10^3k_{\mathrm{obs}}/\mathrm{s}^{-1}$	16.4	16.1	16.3			
10^5[Na$^+$]/M	2.88	50.7	219			

[a] The carbanion salts were generated by use of 1×10^{-2}M-sodium t-butoxide in all cases.

The measured salt effects on the rates of autoxidation in t-butyl alcohol are quite small. It was felt that this might be a consequence of the low degree of dissociation of the carbanion salts in the solvent. Even sodium 9-cyanofluorenide, the most dissociated of the carbanion salts, exists in the free ion form to the extent of only *ca.* 20% at the lowest concentration employed. The salt effects were therefore re-examined in t-butyl alcohol to which the dipolar aprotic solvent dimethyl sulphoxide (1.0M) had been added. In this mixed solvent all the salts are very much more dissociated than in the pure alcohol as is shown in Table 3 by the conductimetric values of K_{d}, obtained by the procedure previously described. Autoxidation of sodium 9-cyano- and 9-phenylsulphonyl-fluorenides shows a number of significant kinetic features (Table 4). The presence of dimethyl sulphoxide slowed down autoxidation of both carbanion salts, but sodium 9-cyanofluorenide particularly. The common ion salts changed the rate in a manner qualitatively similar to their effect in t-butyl alcohol alone, but much more pronounced in absolute terms.

TABLE 3

Conductimetric ion-pair dissociation constants of some sodium salts at 30° in t-butyl alcohol containing 1.0M-dimethyl sulphoxide

Salt	$\Lambda_0/$ Ω^{-1} cm^2 [a]	F/Ω^2 cm^{-4} M^{-1} [b]	r [c]	K_{d}/mol l^{-1}
NaOBu	16.3 (3)	37,400	0.997	1.0×10^{-7}
NaClO$_4$ [d]	19.8 (15)	28.0	0.991	9.1×10^{-5}
NaBPh$_4$	13.8 (13)	2.70	0.994	1.9×10^{-3}
NaFlCN	14.5 (9)	45.0	0.994	1.1×10^{-4}
NaFlSO$_2$Ph	14.5 (10)	152	0.996	3.1×10^{-5}

[a] Obtained using Walden's rule. Observed values obtained from the Fuoss plot are in parentheses. [b] Slope of Fuoss plot by the method of least squares. [c] Correlation coefficient in Fuoss plot. [d] In pure t-butyl alcohol: $K_{\mathrm{d}} = 8.3 \times 10^{-7}$ l mol^{-1}.

Addition of Carbanions to Acrylic Esters.—Products. Large scale preparative experiments were carried out under nitrogen to provide samples of the products from addition of each of the three fluorenyl anions to the activated olefins methyl acrylate, methyl methacrylate, and methyl crotonate. By g.l.c. these addition products could be readily distinguished from fluorenone, the reaction product obtained if air is present. Kinetic solutions were checked to establish that the reaction rate observed was due to the formation of the addition product rather than due to oxidation.

Table 4

Effect of added sodium perchlorate and sodium tetraphenylborate on the kinetics of oxidation of sodium 9-substituted fluorenides in t-butyl alcohol containing 1.0M-dimethyl sulphoxide at 23° [a]

(a) Sodium 9-cyanofluorenide (3.33 × 10^{-4}M)

10^3[NaClO$_4$]/M	0.0	0.37	1.72	2.86	3.80
$10^3k_{obs}/s^{-1}$	0.250	0.270	0.295	0.314	0.320
10^4[Na$^+$]/M	1.44	2.20	3.95	5.00	5.74

10^3[NaBPh$_4$]/M	0.96	1.92	2.89	3.75	4.81	5.77	6.73
$10^3k_{obs}/s^{-1}$	0.325	0.354	0.365	0.380	0.384	0.400	0.420
10^4[Na$^+$]/M	7.35	12.0	15.9	19.0	22.3	25.0	27.6

(b) Sodium 9-phenylsulphonylfluorenide (6.67 × 10^{-5}M)

10^3[NaClO$_4$]/M	0.00	1.72	10^3[NaBPh$_4$]/M	2.89	4.81
$10^3k_{obs}/s^{-1}$	0.073	0.032		0.019	0.014
10^4[Na$^+$]/M	0.35	3.56		15.8	22.2

[a] Carbanions generated using 1.13 × 10^{-3}M-sodium t-butoxide.

Kinetics. The rate of addition of the carbanions to the acrylic esters under nitrogen were determined spectrophotometrically following the decrease in absorbance of the fluorenide anion. Under the conditions used the addition proceeds to completion. A first-order kinetic law was obeyed over the first 80% of reaction, whereafter instantaneous rate coefficients tended to decrease. Curvature was more pronounced at the lower acrylate ester concentrations and is presumably due to consumption of the ester in the absence of the carbanion. The rate coefficients recorded in Tables 5—7 were therefore determined graphically from the linear part of the first-order plots of the absorbance data observed at a standard initial concentration of the unsaturated ester. Values of k_2 were determined from the slopes by dividing by the average ester concentration. Reactions in which sodium 9-phenylsulphonylfluorenide was added to methyl methacrylate or crotonate also showed increasing instantaneous rate coefficients during the first 5—10% of reaction. Such curvature was not observed when the carbanion reacted with methyl acrylate or when other carbanions were used. The curvature appeared to be unaffected by changes in the concentration of reactants, the addition of sodium salts, or the exclusion from reaction mixtures of light. The origin of this initial curvature is not known, and, when it occurred, was ignored in the determination of rate coefficients.

Table 5

Effects of concentration and added sodium tetraphenylborate on the addition of 9-substituted fluorenes to methyl acrylate in t-butyl alcohol at 30°

$[\mathrm{NaOBu^t}]_0 = 3.33 \times 10^{-3}\mathrm{M}$, $[\mathrm{CH_2{:}CH{\cdot}CO_2Me}]_0 = 4.1 \times 10^{-3}\mathrm{M}$

(a) 9-Cyanofluorene

10^4[NaFlCN]$_0$/M	6.50	3.25	1.63
k_2/l mol^{-1} s^{-1}	0.77	0.74	0.75
10^5[Na$^+$]/M	6.86	4.74	3.25

(b) 9-Methoxycarbonylfluorene

10^4[NaFlCO$_2$Me]$_0$ /M	7.20	7.20	3.60	3.60	1.80	1.80
10^5[NaBPh$_4$]/M			358	358		5.96
k_2/l mol^{-1} s^{-1}	1.70	1.89	1.82	2.10	1.67	1.78
10^5[Na$^+$]/M	3.00	133	2.10	133	1.47	5.93

10^4[NaFlCO$_2$Me]$_0$ /M	1.80	1.80	1.80	1.80	1.80	1.80
10^5[NaBPh$_4$]/M	17.9	35.8	80.0	119	239	298
k_2/l mol^{-1} s^{-1}	1.84	1.88	2.03	2.06	2.10	2.17
10^5[Na$^+$]/M	15.1	26.7	49.1	19.1	103	118

(c) 9-Phenylsulphonylfluorene

10^4[NaFlSO$_2$Ph]$_0$ /M	4.00	2.00	1.00
k_2/l mol^{-1} s^{-1}	1.61	1.60	1.66
10^5[Na$^+$]/M	1.17	0.82	0.57

Table 6

Effect of concentration on the addition of 9-substituted fluorenes to methyl methacrylate in t-butyl alcohol at 30°

$[\mathrm{NaOBu^t}]_0 = 3.33 \times 10^{-3}\mathrm{M}$, $[\mathrm{CH_2{:}CMe{\cdot}CO_2Me}]_0 = 0.083\mathrm{M}$

(a) 9-Cyanofluorene

10^4[NaFlCN]$_0$/M	6.50	1.63
10^3k_2/l mol^{-1} s^{-1}	8.70	8.40
10^5[Na$^+$]/M	6.86	3.25

(b) 9-Methoxycarbonylfluorene

10^4[NaFlCO$_2$Me]$_0$/M	7.40	3.70	1.85	0.93
10^3k_2/l mol^{-1} s^{-1}	26.9	31.8	41.0	54.2
10^5[Na$^+$]/M	3.04	2.13	1.49	1.03

(c) 9-Phenylsulphonylfluorene

10^4[NaFlSO$_2$Ph]$_0$/M	4.00	2.00	1.00
10^3k_2/l mol^{-1} s^{-1}	91.3	132	156
10^5[Na$^+$]/M	1.17	0.82	0.57

Table 7

Effect of concentration on the addition of 9-substituted fluorenes to methyl crotonate in t-butyl alcohol at 30°

$[\mathrm{NaOBu^t}]_0 = 3.33 \times 10^{-3}\mathrm{M}$, $[\mathrm{CH_3CH{:}CH{\cdot}CO_2Me}]_0 = 0.107\mathrm{M}$

(a) 9-Cyanofluorene

10^4[NaFlCN]$_0$/M	6.50	3.25	1.63
10^3k_2/l mol^{-1} s^{-1}	5.17	5.38	5.01
10^5[Na$^+$]/M	6.86	4.74	3.25

(b) 9-Methoxycarbonylfluorene

10^4[NaFlCO$_2$Me]$_0$/M	7.40	3.70	2.78	1.85
10^3k_2/l mol^{-1} s^{-1}	9.87	11.6	12.7	14.5
10^5[Na$^+$]/M	3.04	2.13	1.84	1.49

(c) 9-Phenylsulphonylfluorene

10^4[NaFlSO$_2$Ph]$_0$/M	4.00	2.00	1.00
10^3k_2/l mol^{-1} s^{-1}	26.4	34.9	46.3
10^5[Na$^+$]/M	1.17	0.82	0.57

As for our work on the displacement of halide ion from benzyl halides using 9-substituted fluorenide anions, evidence for ion association was sought by examining the kinetic effect of reducing the initial concentration of the carbanion and also of adding sodium tetraphenylborate. Using methyl acrylate, the effect of reducing the initial carbanion concentration was barely detectable with all three carbanion salts. Addition of sodium tetraphenylborate, however, gave a small rate increase which amounted to *ca.* 30% acceleration at the highest salt concentrations used, and was therefore substantially in excess of the experimental uncertainty. For methyl methacrylate and methyl crotonate, dilution of the carbanion had little kinetic effect on the addition of sodium 9-cyanofluorenide, but considerable increases in k_2 were found for the other carbanions.

DISCUSSION

Origin of Salt Effects in Autoxidation of 9-Fluorenide Anions.—Although it is tempting to interpret the changes in k_{obs} with changing concentration of free alkali cations in terms of the Scheme, an alternative explanation must also be examined. This stems from the fact that t-butyl alcohol is a solvent of low polarity and solvating power (dielectric constant 11.23 at 30°,[6] E_T 43.9 [7]). Addition of salts, which may themselves be partly dissociated, will thus have a pronounced effect on the ability of the solution to promote the generation of polar transition states from less polar reactants. Rate changes resulting from addition of common-ion salts could thus arise from a medium effect as well as from an equilibrium effect and these will be difficult to differentiate, especially when the total rate change is small.

We have endeavoured to distinguish the common-ion and medium effects of added salts by a number of experimental means, *viz.*, (i) deviations from linearity at high salt concentrations in plots according to equations (2) and (3); (ii) comparison of the kinetic effects of common-ion salts of widely different degrees of dissociation used at about the same concentration; (iii) continuance of salt effects even after the dissociation of the carbanion salt has been suppressed well below 1%. These procedures are illustrated using the data obtained on salt effects on the autoxidation of sodium 9-cyano- and 9-phenylsulphonyl-fluorenides.

It is likely that a large proportion of the rate changes given in Table 1 are a consequence of medium effects rather than ion-pairing since there is little change in the free sodium ion concentration. Nevertheless, ion association must have some bearing since, in all cases, small but significant changes in rate result when the counter-ion is changed from sodium to potassium. Another highly significant observation is that dimethyl sulphoxide (1M) has a very marked (25-fold) rate retarding effect on the oxidation of sodium 9-cyanofluorenide but a relatively small (28%) retarding effect on sodium 9-phenylsulphonylfluorenide. Dimethyl sulphoxide too will have a medium effect on reaction velocities in addition to its influence on the ion-pair dissociation equilibrium (see below).

The rate changes induced by added $NaClO_4$ and $NaBPh_4$ seem attributable to the effects of increased ion association in a system in which the associated carbanion is more reactive than the free ion in the case of sodium 9-cyanofluorenide, but less reactive for the 9-phenylsulphonylfluorenide. No significant change was observed in the autoxidation of sodium 9-methoxycarbonylfluorenide when the free sodium ion concentration was changed by a factor of over 70 and the proportion of free carbanion was reduced from *ca.* 4% to *ca* 0.06%. The implication here is that the free carbanion and the ion pair are equally reactive.

Although plausible in a qualitative sense, the interpretation of these results in terms of ion association alone does not bear quantitative examination. In Tables 2(a) and (b), it is evident that the rate of autoxidation is not simply a function of the free sodium ion concentration; for example sodium perchlorate (4.42×10^{-3}M) has a similar kinetic effect to sodium tetraphenylborate (1.64×10^{-3}M) although the free counter ion concentration is 10 times greater in the latter case. Clearly the undissociated salt must also play a role. Further, when the free sodium ion concentration exceeds 8×10^{-4}M, the degree of dissociation of sodium 9-cyanofluorenide falls below 1%; yet, further addition of sodium tetraphenylborate up to 8×10^{-3}M increases the observed rate coefficient by > 10%. Even if the free ion were totally unreactive, the maximum rate increase from suppression of dissociation would be 1%. Similar arguments could be applied to the results for the autoxidation of sodium 9-phenylsulphonylfluorenide. The conclusion to be reached therefore is that, because the medium effects of added salts are of similar or perhaps even greater magnitude compared with their effects on ion association, the results in t-butyl alcohol cannot be unambiguously interpreted quantitatively.*

The addition of dimethyl sulphoxide (1.0M) to t-butyl alcohol produces a solvent in which the carbanion salts are quite highly dissociated at the concentrations used in the kinetic studies (sodium 9-cyanofluorenide, 3—30%; sodium 9-phenylsulphonylfluorenide, 1—49%); this wider variation in the ratio of free to associated carbanions enables the effect of ion association to be more clearly discerned. Correlation according to equation (3) is linear at low concentrations of added salt, but at the highest salt concentration, k_{obs} shows an upward curvature suggesting a rate-enhancing medium effect. For the purpose of deriving values of $k_{\pm}$ and k_{-}, the linear regression analysis was applied only to data obtained at at concentrations of added salt $<3 \times 10^{-3}$M; the results are summarised in Table 8.

For sodium 9-phenylsulphonylfluorenide the free ion appears to be some eight times more reactive than the ion pair, a relatively small difference but nevertheless in line with intuitive expectation. For sodium 9-cyanofluorenide, the reverse is true; the ion pair is now some five times more reactive than the free ion. We attempt to explain this behaviour in a later section.

---

* In a preliminary report,[3] some results were interpreted in terms of ion association effects alone, using plots according to equation (2). We have since obtained more reliable values of K_d both for the carbanions and for the various sodium salts whose dissociation controls the free sodium ion concentration. Using these, the linear correlation according to equation (2), though good, yields reliable values only for $k_{\pm}$ (NaFlCN, 7.4×10^{-3} s^{-1}; $NaFlSO_2Ph$, 8.4×10^{-5} s^{-1}; $NaFlCO_2Me$, 1.6×10^{-2} s^{-1}). Correlation according to equation (3) is poor (correlation coefficients from least squares analysis are *ca.* 0.7).

[6] Landolt-Bornstein, 'Zahlenwerte und Functionen,' Part 6 (I), p. 635.

[7] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Annalen*, 1963, **661**, 1.

TABLE 8

Analysis of the correlation of kinetic data on the autoxidation of sodium 9-substituted fluorenides in t-butyl alcohol–dimethyl sulphoxide at 30°

Equation		NaFlCN		$NaFlSO_2Ph$	
		All data	Low salt data	All data	Low salt data
(2)	Slope, $k_\pm$	4.27×10^{-4}	3.92×10^{-4}	1.26×10^{-5}	1.62×10^{-5}
	Intercept	-2.76×10^{-8}	-6.38×10^{-9}	6.66×10^{-9}	5.31×10^{-9}
	k_-			2.15×10^{-4}	1.71×10^{-4}
	r	0.998	0.999	0.969	0.996
(3)	Slope	-4.32×10^{-8}	-3.35×10^{-8}	3.75×10^{-9}	3.54×10^{-9}
	Intercept, $k_\pm$	3.98×10^{-4}	3.73×10^{-4}	1.69×10^{-5}	1.96×10^{-5}
	k_-	0.05×10^{-4}	0.69×10^{-4}	1.38×10^{-4}	1.34×10^{-4}
	r	0.939	0.976	0.988	0.994

Ion Association in Michael Addition of 9-*Fluorenide Anions to Acrylic Esters.*—The problems associated with the interpretation of the kinetic effects of added common-ion salts on carbanion reactions in t-butyl alcohol extend to Michael addition. Thus, while correlation of the results in Table 5(b) according to equation (2) is very good ($k_\pm$, 1.86 l mol^{-1} s^{-1}; intercept too small to give k_-; r 0.9999), the more sensitive plot according to equation (3) shows very pronounced curvature suggesting that over the whole range of salt concentrations employed, the small rate changes are largely due to a medium effect. The variation of the second-order velocity constant k_2 with with changing initial concentration of the carbanion salt was previously shown [1] to be a sensitive procedure in the reaction of the carbanion salts with benzyl halide. Linear regression data, using equation (3) for all the Michael additions studied are given in Table 9. Values of the ratio of velocity constants for the free ion and ion pair are also included.

TABLE 9

Analysis of the kinetics of Michael addition of sodium 9-substituted fluorenides according to equation (3)

Acceptor [a]	Carbanion salt	$10^3k_\pm$ [b]	10^3k_- [b]	r	$k_-/k_\pm$
	NaFlCN	(760)	(760)		(*ca.* 1)
MA	$NaFlCO_2Me$	(1 700)	(1 700)		(*ca.* 1)
	$MaFlSO_2Ph$	(1 600)	(1 600)		(*ca.* 1)
	NaFlCN	8.6)	(8.6)		(*ca.* 1)
MMA	$NaFlCO_2Me$	10	400	0.998	40
	$NaFlSO_2Ph$	34	2 200	0.969	65
	NaFlCN	(5.2)	(5.2)		(*ca.* 1)
MC	$NaFlCO_2Me$	7.6	70	0.988	9
	$NaFlSO_2Ph$	6.7	690	0.999	103

[a] MA, methyl acrylate; MMA, methyl methacrylate; MC, methyl crotonate. [b] In l mol^{-1} s^{-1}; figures in parentheses refer to values deduced from the absence of a dilution effect.

The pattern of results is very clear. Sodium 9-cyanofluorenide with all three acrylic acceptors shows no dilution effect indicating approximate equality of $k_\pm$ and k_-. Methyl acrylate with all three carbanion salts likewise shows no effect. For methyl methacrylate and methyl crotonate, the free ion is 10—100 times more reactive than the ion pair. Thus, while very little variation is observed between the ion-pair reactivities of the three carbanion salts with a given acceptor, the free ion reactivity varies much more for methyl methacrylate and methyl crotonate. For methyl acrylate, however, the free ion reactivity varies little and, in part, this must be a consequence of the low k_- value of 9-phenylsulphonylfluorenyl anion, which is less than with methyl methacrylate, expected to be a less reactive acceptor for both polar and steric reasons by virtue of the methyl group attached to the double bond.

Patterns of Reactivity in Reactions of 9-*Substituted Fluorenide Anions.*—Combining the present results with those on nucleophilic displacement of halide from benzyl halides reported in Part VIII,* we now have information on a range of carbanion reactions. The pattern of behaviour is fairly complex but two general features stand out. (i) In all the reactions studied, sodium 9-cyanofluorenide shows behaviour indicating that $k_- \leqslant k_\pm$, whereas for the other two carbanion salts $k_- > k_\pm$ usually. (ii) The value of the ratio $k_- : k_\pm$ is generally lower with reaction partners, A, in which the reaction site has the less bulky groups around it.

Without further experimentation, a complete interpretation of our results is not possible. However, we offer here some tentative suggestions concerning some of the relevant factors.

In general we believe that k_- should be greater than $k_\pm$ in reactions which depend on the availability of the carbanion's electrons. This is because we believe that ion-association has the effect of 'binding' the carbanionic electron pair to a greater extent than solvation, at least in t-butyl alcohol as solvent; electron availability, whether singly in autoxidation or in pairs in substitut- and addition is thereby reduced in the ion pair, lowering the reactivity. There is n.m.r. evidence that the counter ion in lithium fluorenide when dissolved in ethereal solvents is located centrally over one face of the fluorenyl group; [8] any steric hindrance which the cation might exert will therefore be restricted to that face. Moreover, reaction of the ion pair at the exposed face has the effect of dissociating the salt, a disfavoured process in t-butyl alcohol. Electron-withdrawing groups at the 9-position

---

* Using equation (3) to calculate $k_\pm$ and k_- from the data of Part VIII in order to compare the results with those in this paper, we obtain the following velocity constants (l mol^{-1} s^{-1}). $NaFlCO_2Me$: with $PhCH_2Br$, $k_\pm$ 350, $k_\pm$ 11; with $PhCH_2Cl$, k_- 4.1, $k_\pm$ 0.20; with $PhCH_2F$, $k_- \simeq k_\pm = 1.9 \times 10^{-3}$.

[8] J. A. Dixon, P. A. Gwinner, and D. C. Lini, *J. Amer. Chem. Soc.*, 1965, **87**, 1379.

will clearly modify this picture, distorting the relative positions of the two ions and also introducing steric influences of their own as regards attack of external reagents on C-9. A further complication lies in the possibility of differences in the position of the equilibrium between contact and solvent separated ion pairs as the substituent is changed, with consequent changes in reactivity. We have little evidence on this last point except that, in tetrahydrofuran–t-butyl alcohol (30 : 1, v/v) sodium 9-methoxycarbonylfluorenide shows a long wavelength peak (418 nm) not present in solutions in t-butyl alcohol alone. This peak increases in intensity as the temperature is lowered, but it disappears on addition of small amounts of t-butyl alcohol.[9] At similar concentrations, sodium 9-cyanofluorenide shows a relatively much more intense long wavelength peak (436 nm) in tetrahydrofuran–t-butyl alcohol, while sodium 9-phenylsulphonylfluorenide shows no additional peak. The additional peak in ethereal solvents could be due to free carbanions only or to both free and solvent separated carbanions; however, these spectrophotometric results parallel those from conductivity in t-butyl alcohol concerning the degree of dissociation of the carbanion salts. At most they would suggest a parallelism between formation of solvent separated ion pairs and free ions.

t-Butyl alcohol shows great discrimination between anions for its solvating capacity as judged by ion-pair dissociation constants of sodium salts,[1] halide and alkoxide ions being poorly solvated, while large ions with well spread negative charge seem the more stable. Thus in this solvent interaction of the cation with a developing localised negative charge could be crucial. The activation energy of a reaction could therefore be substantially lowered if an attacking ion pair could lead to a transition state in which the counter-ion were placed so as to provide some stabilisation of the developing negative charge on, for example, a departing halide ion or a superoxide ion. Entropy considerations would, of course, tend to offset the advantage. An explanation of this type has been put forward in the case of proton transfer from benzo[*a*]fluorene to sodium fluorenide in ethereal solvents,[10] where rate decreases on dilution and common ion rate acceleration indicate $k_{\pm} > k_{-}$.

In the case of carbanion reactions involving reaction partners which can specifically solvate the countercation thereby increasing reactivity, kinetic features similar to those suggesting $k_{\pm} > k_{-}$ result; such a reaction is that between the sodium salt of fluoradene and ethylene oxide.[11] This latter interpretation of common-ion rate acceleration seems unlikely in the case of the displacement of halide from benzyl halides [1] and can be excluded in the case of the present autoxidation work since it has been established that the added common-ion salts do not influence the concentration of oxygen in the saturated solution as would be expected for a specific complex formation.

A third possible mechanism exists by which ion association could lead to low values of $k_{-}/k_{\pm}$. This is when an anionic intermediate is formed reversibly in the overall reaction, as shown in equation (5). The corresponding expression for the observed velocity constant k_{obs} is of

$$\begin{tikzcd}
\mathrm{M^+C^-} + \mathrm{A} \arrow[r, shift left, "k_1^{\pm}"] \arrow[d, shift right] & \mathrm{M^+CA^-} \arrow[l, shift left, "k_{-1}^{+}"] \arrow[r, "k_2^{\pm}"] & \text{products} \\
\mathrm{M^+} + \mathrm{C^-} + \mathrm{A} \arrow[r, shift left, "k_1^{-}"] \arrow[u, shift right] & \mathrm{CA^-} \arrow[l, shift left, "k_{-1}^{-}"] \arrow[r, "k_2^{-}"] & \text{products}
\end{tikzcd} \qquad (5)$$

the same form as equation (3), where $k_{\pm}$ is now replaced by $k_1^{\pm}/(k_{-1}^{\pm}/k_2^{\pm} + 1)$ and k_{-} by $k_1/(k_{-1}^{-}/k_2^{-} + 1)$. It can be demonstrated that even if the velocity constant for each step is greater for the free ion than for the ion pair, then both positive and negative slopes in plots according to equation (3) can result depending on whether $k_{-1}^{-}/k_2^{-} >$ =, or $< k_{-1}^{\pm}/k_2^{\pm}$. We have previously demonstrated [2c,e] that the partitioning of fluorenide anions between different reaction paths is strongly cation dependent which increases the plausibliity of this interpretation.

In the present reactions, reversible intermediate formation is quite possible in the electron-transfer step of the autoxidation process, and has been demonstrated in certain Michael addition reactions.[12] Indeed in the latter reactions k_2 would refer to protonation of the adduct and this might well be facilitated in the ion pair by the heighted acidity of alcohol molecules solvating the positive ion. Such effects have been described by Cram in connection with hydrogen isotope exchange in t-butyl alcohol.[13] Intermediate formation cannot be a factor in halide displacement from benzyl halides. Cationic enhancement of the reactivity of the substrate through specific solvation seems unlikely with all three reactions. Electrostatic stabilisation of the developing negative charge by the counter-ion of an ion pair would be possible for all three reactions if the positive ion could be accommodated in the transition state between (or on a plane which passes between) the reactants. This would be particularly likely in autoxidation and perhaps less so but still likely in Michael addition provided that congestion by substituent groups were not too great. In halide displacement reactions, solvation of the leaving group by a counter-ion associated with the attacking nucleophile would only be possible in a fairly tight transition state resulting from attack by a relatively well separated ion pair. Such might well be the case with 9-cyanofluorenide but seems unlikely with a 9-phenylsulphonyl substituent.

---

[9] W. T. Ford, *J. Amer. Chem. Soc.*, 1970, **92**, 2857; T. E. Hogen-Esch, *ibid.*, 1973, **95**, 639.

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

[11] C. J. Chang, R. F. Kiesel, and T. E. Hogen-Esch, *J. Amer. Chem. Soc.*, 1973, **95**, 8446.

[12] L. A. Kaplan and H. B. Pickard, *J. Amer. Chem. Soc.*, 1971, **93**, 3447 and references therein.

[13] D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York and London, 1965; W. D. Kollmeyer and D. J. Cram, *J. Amer. Chem. Soc.*, 1968, **90**, 1779; D. J. Cram and L. Gosser, *ibid.*, 1964, **86**, 5445; J. N. Roitman and D. J. Cram, *ibid.*, 1971, **93**, 2231.

EXPERIMENTAL

Materials.—t-Butyl alcohol and solutions in it of alkali metal t-butoxides and of sodium tetraphenylborate were prepared as previously described.[1,2a] Dimethyl sulphoxide was distilled twice from calcium hydride and had m.p. 18.4°.

The carbanions were generated as before [1] from analytically pure specimens of the parent 9-substituted fluorene. Solutions were stable over long periods in the absence of oxygen. Acrylic esters were distilled twice at atmospheric pressure.

In autoxidation reactions oxygen (or air) was purified by passage through aqueous sodium hydroxide, concentrated sulphuric acid and then through two 12 in columns packed with soda lime and one 12 in column packed with magnesium perchlorate. The gas was finally bubbled through t-butyl alcohol at 30° to saturate it with solvent before it was introduced into the reaction vessel.

TABLE 10

Microanalytical data for Michael adducts

9-Substituted fluorene	Methyl ester	Found (%)				Required (%)			
		C	H	N	S	C	H	N	S
FlHCN	Acrylate	78.0	5.35	5.30		78.0	5.45	5.05	
	Methacrylate	78.1	5.6	4.70		78.3	5.9	4.81	
	Crotonate	78.5	6.0	4.60		78.3	5.9	4.81	
$FlHCO_2Me$	Acrylate	73.6	5.8			73.5	5.85		
	Methacrylate	73.6	6.3			74.1	6.2		
	Crotonate	74.3	6.5			74.1	6.2		
$FlHSO_2Ph$	Acrylate	70.2	5.1		8.3	70.4	5.15		8.15
	Methacrylate	71.2	5.55			70.9	5.45		
	Crotonate	70.8	5.55			70.9	5.45		

Kinetic Procedures.—*Autoxidation.* The reaction vessel was a twin-limbed glass apparatus with attached spectrophotometer cell similar to that previously described,[14] but with, in place of the tap, an orifice which was sealed by a serum cap. Through the cap passed two 1/32 in O.D. Teflon tubes attached to the oxygen supply, the ends dipping into the main reactant arm and the optical cell. A hypodermic needle provided an exit part for the gas stream. A small volume of a t-butyl alcohol solution of the 9-substituted fluorene was placed in the smaller arm of the apparatus, while the base solution was in the larger arm. The reactant solutions were presaturated with oxygen for 20 min at the reaction temperature before inverting the apparatus to mix the reagents. The apparatus was placed in the cell compartment of a Unicam SP 800 spectrometer and the carbanion absorbance (D_t) recorded by repetitive scans. Oxygen was bubbled slowly through the solution throughout the course of the reaction.* As the spectrometer scanned the absorbance maximum of the carbanion, however, the gas flow was interrupted by the operation of a micro-switch which actuated a solenoid-operated cut-off valve in the oxygen supply. Reactions were followed for 2—4 half-lives and rate coefficients were evaluated either graphically from plots of log (D_t—D_∞) against time, *t*, or by the method of least squares. Most experiments were run in duplicate, average values being given in the Tables. For each run, the yield of fluorenone was shown to be quantitative by dilution of a portion of the reaction mixture with alcohol and measuring the absorbance of the solution at 256 nm. In a few experiments, the reaction was monitored by estimation of the fluorenone formed using a similar procedure.

Michael addition. Kinetic runs were carried out under nitrogen in the presence of an excess (at least six-fold) of the acrylic ester using essentially the same techniques as for the halide displacement studies in Part VIII.[1] After completion of the reaction, the carbanion concentration was zero, as judged spectrophotometrically, indicating that the reaction was proceeding to completion. Reactions were followed for *ca.* 4 half-lives. When the addition was complete, reaction mixtures were checked for fluorenone formation; in the few instances when fluorenone was detected, the kinetic run was rejected. Rate coefficients were determined graphically from the linear portion of first-order plots. All reactions were carried out at least in duplicate. The values of k_2 in Tables 5—7 are averages; individual values differed from these by $<3\%$.

Larger scale experiments at 30° permitted the isolation and characterisation of the addition products. All were viscous uncrystallisable oils, purified for analysis by distillation. Analytical data are given in Table 10.

Financial support from the S.R.C. and from Unilever Research are gratefully acknowledged.

[5/1049 *Received, 2nd June*, 1975]

---

* It was established that the rate of autoxidation of the carbanion salts was independent of the oxygen flow rate in the range 10—100 ml min^{-1}. The flow rate usually employed was 10 ml min^{-1}.

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