Solvents Effects on the Rates of Alkylation of Some Fluorenyl Carbanions

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Summary Depending on the substituents present, the addition of dimethyl sulphoxide to t-butyl alcohol can either increase or decrease the nucleophilic reactivity of fluorenyl carbanions.

THE rates of bimolecular nucleophilic substitution reactions involving small highly localised anions are greatly increased by a change in reaction medium from a protic to a dipolar aprotic solvent.[1] The rate increase arises from a reduction in the energy level between the reactants and transition state. Small anions are highly solvated in protic solvents due to hydrogen-bonding interactions, but in dipolar aprotic solvents they are essentially desolvated. On the other hand, charge-dispersed transition states are probably more solvated in dipolar aprotic solvents.[2] Recently, it has been reported that the rate of the Menchutkin reaction of benzyl chloride with the uncharged nucleophile, pyridine, differs little in methanol from that observed in dimethyl formamide.[3] A third category of nucleophilic reagent, on which kinetic studies are few, is that of highly delocalised carbanions. These have a lesser tendency than smaller anions to hydrogen-bond with protic solvents and with changes in the reaction medium little variation in nucleophilic reactivity might be reasonably predicted.[1] In fact, if the increased acidity of certain hydrocarbons in dimethyl sulphoxide relative to protic solvents[4] is due to enhanced stabilisation of the carbanion, carbanion reactivity may even be decreased in dipolar aprotic relative to protic media. Our results show that it is unsound to generalise on the variation in nucleophilic reactivity of highly delocalised carbanions with changes in the reaction medium.

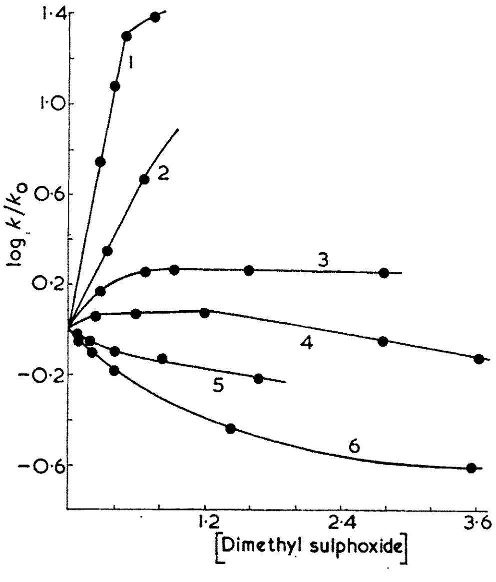

FIGURE. *The dependence of the rate of alkylation of some carbanions on the concentration of dimethyl sulphoxide in t-butyl alcohol at* 30°.

k_0 *refers to the second order rate constant in t-butyl alcohol.*
1. *Rate of conversion of* 2-*methoxy*-9-*bromofluorene into* 2,2′-*dimethoxybifluorenylidene with* KOBu^t. *The rate determining step is the displacement of bromide from the substrate by its carbanion, which is present as a small steady-state concentration. To allow for the change in this with increasing dimethyl sulphoxide, the rate constants have been divided by the medium basicity as measured by the ionisation of* 4-*amino*-4′-*nitro-azobenzene* (D. Bethell, A. F. Cockerill and D. B. Frankcum, *J. Chem. Soc.* (*B*), 1967, 1287).
2. *Alkylation of fluoradene anion by* 9-*chlorofluorene*. 3. *Alkylation of* 3-*nitro*-9-*chlorofluorene anion by benzyl bromide*. 4. *Alkylation of* 3-*nitro*-9-*chlorofluorene anion by* p-*bromobenzyl bromide*. 5. *Alkylation of methylfluorene*-9-*carboxylate anion by* 9-*chlorofluorene*. 6. *Alkylation of* 9-*cyanofluorene anion by* 9-*chlorofluorene*.

We have measured the rate constants for the alkylation of a number of fluorenyl carbanions by benzyl, diphenylmethyl, and 9-fluorenyl halides in t-butyl alcohol containing varying amounts of dimethyl sulphoxide at 30°. All reactions were run under an atmosphere of nitrogen, in the absence of light. The hydrocarbons were completely ionised to their corresponding carbanions by KOBu^t, which was always present in at least a ten-fold excess. In the absence of added substrate, all carbanions were stable for at least twice the time required for the alkylation reaction. None of the substrates was consumed by the base during the time of the alkylation reaction and the reaction products were those predicted from a simple alkylation of the carbanion by the substrate (3-nitro-9-chlorofluorene anion[5] and benzyl halides eventually give 3-nitro-9-benzylidenefluorene). Reactions, which were strictly first order in both the substrate and the carbanion, were followed spectrophotometrically by monitoring the absorption due to the highly coloured carbanions. The Table lists the rate constants for the reactions in t-butyl alcohol, and the Figure illustrates the influence of added dimethyl sulphoxide.

The lack of correlation between nucleophilic reactivity of the carbanion and the pK_a of the parent hydrocarbon for the reactions in t-butyl alcohol is not surprising as the rate of the displacement reactions will be considerably influenced by steric interactions. Of interest is the greater reactivity of the secondary halide, 9-chlorofluorene, than benzyl chloride towards all the carbanions (possibly attributable to some cyclopentadienyl anion character in the transition state for substitution of 9-chlorofluorene), and the reactivity of fluoradene anion.

Rate constants for the alkylation of some fluorenyl carbanions in t-butyl alcohol at 30°

Anion precursors	9-Cyanofluorene	Methylfluorene 9-carboxylate	3-Nitro-9-chlorofluorene	Fluoradene
pK_a	11·41(ethanol)[6]	13·88(ethanol)[6]	<14 (Bu^{t}OH)	10(Me$_2$SO) 13·5(methanol)[7]
$\lambda_{\max}^{\text{anion}}$ ($\epsilon_{\max}$) Bu^{t}OH	410(2250)	395(3610)	574(16,300)	546(4440)
Bu^{t}OH–1M-DMSO	410(2250)	405(3190)	600(19,800)	555(4500)
Substrates (k_2 in l. mole^{-1} min.$^{-1}$ [a])				
9-Chlorofluorene	246 ± 11[b]	80·5 ± 1·6	—	4260[d]
Benzyl chloride	13·2 ± 0·06	9·60 ± 0·27	—	—
Diphenylmethyl chloride	1·63 ± 0·06	0·556 ± 0·084	—	—
Benzyl bromide	917 ± 168[c]	—	8·17 ± 0·46	—
p-Bromobenzyl bromide	—	—	34·2 ± 2·6	—

[a] Unless stated, determined from pseudo-first-order rate constants divided by [substrate]; [b] average deviation of the mean; [c] determined from second order plot; [d] determined from second order plot with equal concentration of both reactants.

The spectral characteristics of 9-cyanofluorene anion were unaffected by a change in the solvent. However, for the other carbanions, the position of maximum absorption was shifted to a longer wavelength as the concentration of dimethyl sulphoxide was increased to about 1M, further increases causing no additional change. Such spectral variations indicate a change from predominantly ion associated carbanions (contact ion pairs) in t-butyl alcohol to more dissociated carbanions (solvent separated or free ions) in the presence of the better cation-solvating dimethyl sulphoxide. The latter type of carbanion should have greater nucleophilicity as the need for the substrate to displace a cation before attaining the transition state is removed. The alkylation reactions involve charge dispersal in attaining the transition state, and as dimethyl sulphoxide has a greater dielectric constant than t-butyl alcoho ,[8] a rate retardation is predicted in accordance with the Hughes–Ingold theory[9] as the medium is enriched in dimethyl sulphoxide.

The influence of changing solvent on the rate constant for the alkylation reactions can be explained by varying contributions arising from the Hughes–Ingold medium effect and changes in ion association. Fluorenyl carbanions in which delocalisation of the negative charge by the α-substituent is mainly by the mesomeric effect (CN, CO_2Me) show little tendency to form contact ion pairs in t-butyl alcohol. However, for cases in which delocalisation is controlled mainly by the inductive effect (Br, Cl), ion pairing is more pronounced.

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