105. *Kinetics and Mechanism of the Formation of Bifluorenylidene from 9-Bromofluorene in t-Butyl Alcohol.*

By D. BETHELL.

Benzyltrimethylammonium hydroxide and potassium t-butoxide in t-butyl alcohol convert 9-bromofluorene into bifluorenylidene by a mechanism involving rate-determining nucleophilic displacement of bromide ion from the organic halide by the rapidly formed 9-bromo-9-fluorenyl anion. Kinetic results are correlated with indicator measurements on *p*-nitroaniline in the same media and possible interpretations of the results are discussed.

A NUMBER of organic halides characterised by the absence of β-hydrogen, *e.g.*, 2-methylallyl chloride and 9-bromoanthrone, under the influence of base (B) undergo an apparent α-elimination of the type:

$$2{>}CHX + 2B \longrightarrow {>}C{:}C{<} + 2BH^+ + 2X^-$$

The mechanism of formation of the dimeric olefin has been of interest for many years and two types of mechanism have been suggested, namely:

(i) *Carbene mechanism* (*α-elimination*).

$${>}CHX + B \rightleftharpoons {>}CX^- + BH^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (a)$$

$${>}CX^- \longrightarrow {>}C{:} + X^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (b)$$

$${>}C{:} + {>}C{:}\left\{\begin{array}{l}\text{or } {>}CX^- \\ \text{or } {>}CHX\end{array}\right. \longrightarrow {>}C{:}C{<} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (c)$$

The operation of this mechanism in the 4-nitrobenzyl series has recently been proved by using kinetic methods.[1,2]

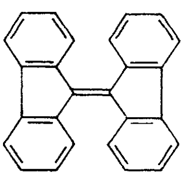
(ii) *Bimolecular displacement mechanism.*

$${>}CHX + B \rightleftharpoons {>}CX^- + BH^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (a)$$

$${>}CX^- + {>}CHX \longrightarrow X^- + {>}CX{\cdot}CH{<} \text{ (I)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (b)$$

$${>}CX{\cdot}CH{<} + B \longrightarrow {>}C{:}C{<} + BH^+ + X^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (c)$$

Isolation of the intermediate "dimeric" halide (I) at low temperatures constitutes evidence for the occurrence of this mechanism in the benzyl and the diphenylmethyl series.[3]



(II)

9-Halogenofluorenes also undergo this type of elimination, forming the scarlet hydrocarbon, 9,9′-bifluorenylidene (II).[4] Both mechanisms, (i) and (ii), have been suggested at various times[3,5,6] without compelling evidence for either. Now, provided that proton transfers occur rapidly, the slow steps for the two mechanisms would be expected to be (i*b*) and (ii*b*), steps which are respectively uni- and bi-molecular. Determination of the kinetic order of the reaction in the concentration of 9-bromofluorene thus provides a method of distinguishing the operative mechanism.

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[1] Hanna, Iskander, and Riad, *J.*, 1961, 217.

[2] Swain and Thornton, *J. Amer. Chem. Soc.*, 1961, **83**, 4033.

[3] Hauser, Brasen, Skell, Kantor, and Brodhag, *J. Amer. Chem. Soc.*, 1956, **78**, 1653.

[4] (*a*) Thiele and Wanscheidt, *Annalen*, 1910, **376**, 278; (*b*) Kliegl, Wünsch, and Weigele, *Ber.*, 1926, **59**, 631; (*c*) Bavin, *Canad. J. Chem.*, 1960, **38**, 882.

[5] Bergmann and Hervey, *Ber.*, 1929, **62**, 893.

[6] Kleucker, *Ber.*, 1929, **62**, 2587.

In this paper will be presented kinetic evidence that 9-bromofluorene yields bifluorenylidene on treatment with benzyltrimethylammonium hydroxide or potassium t-butoxide in t-butyl alcohol by bimolecular displacement. Since the molecularity of the rate-determining step is known, the reaction has also been used to examine the validity of another, less certain, criterion of reaction mechanism, namely, the correlation of velocity constants with indicator-ionisation ratios in media of low dielectric constant.

EXPERIMENTAL

Materials.—*9-Bromofluorene.* This compound was prepared by bromination of fluorene with *N*-bromosuccinimide;[7] recrystallised from ligroin, it had m. p. 104°. 9-Bromo-9-deuterofluorene was obtained similarly by bromination of 9,9-dideuterofluorene.[8] The nuclear magnetic resonance spectrum indicated that it was $\sim$95% isotopically pure. The infrared spectrum, determined for a solution in carbon disulphide, showed marked differences from that of undeuterated material in the 11—14 μ region, *viz.*: 9-bromofluorene 11·65ms, 12·81s, 13·60vs; 9-bromo-9-deuterofluorene 11·08m, 13·24s, 13·52s, 13·79s μ.

Benzyltrimethylammonium hydroxide. A commercial preparation (40% aqueous solution) was used without purification. Stock solutions for kinetic and indicator measurements were prepared by diluting this solution with freshly distilled t-butyl alcohol. The water content of these solutions was determined by Karl Fischer titration. Other benzyltrimethylammonium salts were prepared by neutralisation of the hydroxide with the appropriate aqueous acid, followed by removal of water under reduced pressure and recrystallisation.

Indicators. *o*- and *p*-Nitroaniline were recrystallised from alcohol and had m. p.s in agreement with the literature.

t-Butyl alcohol. The solvent was purified by distillation from potassium through a 12-in. helix-packed column immediately before use. Karl Fischer titration indicated that it contained 0·05% w/w of water.

Potassium t-butoxide. Solutions of potassium t-butoxide in t-butyl alcohol were prepared by dilution of portions of a saturated solution obtained by dissolving clean potassium in freshly distilled t-butyl alcohol. Solutions prepared by dilution of a fresh, saturated solution gave different kinetic and indicator results from those in which an " aged " saturated solution was used. Saturated solutions of potassium t-butoxide in t-butyl alcohol less than three days old were used in all the later experiments, the solutions being stored in stoppered flasks in a desiccator over magnesium perchlorate and soda-lime. Concentrations of potassium t-butoxide in the diluted solutions were determined by titration with standard hydrochloric acid to Bromothymol Blue.

Preparative Experiments.—On a preparative scale (*ca.* 0·02 mole) it was established that the conversion of 9-bromofluorene into bifluorenylidene was essentially quantitative in the reaction media chosen, provided that oxygen was rigorously excluded. The crystalline product, m. p. 189—190°, was isolated in 95% yield together with 3% of an amorphous brown solid of indefinite m. p. (*ca.* 240°), which was not examined further. When preparative reactions were carried out in the presence of air the yield of bifluorenylidene fell to 80—85% (cf. ref. 4*c*). Attempted separation of the by-products on alumina yielded a small quantity of fluorenone and uncharacterised red-brown gums.

Exchange Experiments.—Both mechanisms (i) and (ii) have as their first step a reversible proton-removal from 9-bromofluorene by the base. To establish whether this was rate-determining, exchange experiments were carried out on 9-bromo-9-deuterofluorene, under conditions similar to those of the kinetic measurements on the formation of bifluorenylidene at low base concentrations ($9{\cdot}4 \times 10^{-4}$M-benzyltrimethylammonium hydroxide and $1{\cdot}2 \times 10^{-2}$M-potassium t-butoxide). The reactions were arrested after partial conversion of 9-bromofluorene into bifluorenylidene by addition of a large excess of 5% aqueous hydrobromic acid to the reaction solution. The product and unchanged 9-bromofluorene were extracted with ether and separated by chromatography on alumina. The infrared spectrum of the recovered 9-bromofluorene indicated that exchange of the 9-hydrogen was complete in the reaction in which potassium t-butoxide was used and at least 80% complete (less than 2% conversion

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[7] Wittig and Felletschin, *Annalen*, 1944, **555**, 133.

[8] Scherf and Brown, *Canad. J. Chem.*, 1960, **38**, 697.

into bifluorenylidene) in the experiment with benzyltrimethylammonium hydroxide. It was established in a separate experiment that no appreciable exchange occurred during quenching of the reaction mixture and subsequent recovery of unchanged 9-bromofluorene.

Kinetic Experiments.—The distinctive colour of bifluorenylidene made a spectrophotometric procedure for the kinetic measurements attractive. Unfortunately, the low concentrations required in such experiments accentuate interference by traces of oxygen. Indeed, at spectroscopic concentrations of 9-bromofluorene (10^{-5}—10^{-4}M) practically no bifluorenylidene is formed if the reaction with base is carried out in air, and the conversion is far from quantitative at considerably higher concentrations. To overcome this difficulty a special reaction cell was designed (Fig. 1) which enabled solutions of the reactants to be virtually freed from oxygen before mixing, by successive cycles of freezing, pumping out, flushing with oxygen-free nitrogen, and melting. The reactants in an atmosphere of pure nitrogen could then be mixed and, by inversion of the apparatus, transferred to an optical cell in which changes in the optical density of the solution could be determined. The apparatus was designed to fit into the thermostat-controlled cell-holder of a Unicam S.P. 500 quartz spectrophotometer, a modified lid for the cell compartment being necessary to accommodate the upper part of the reaction cell.

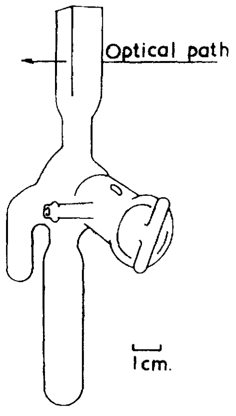

FIG. 1. Reaction cell.

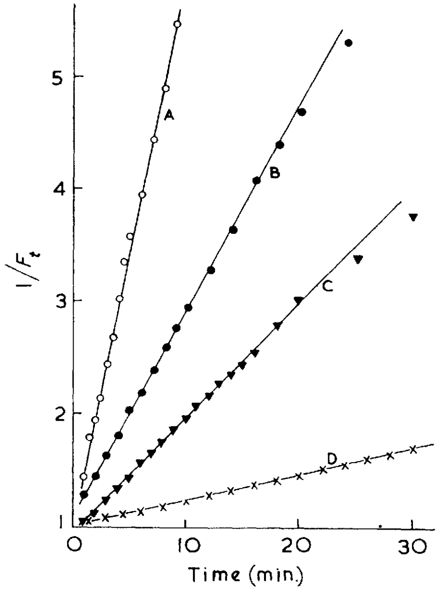

FIG. 2. Specimen second-order plots: (A) 0·0050M-Benzyltrimethylammonium hydroxide + 0·0049M-benzyltrimethylammonium bromide; (B) 0·0049M-benzyltrimethylammonium hydroxide; (C) 0·18M- and (D) 0·040M-potassium t-butoxide.

Only in the faster reactions was 9-bromofluorene converted quantitatively into bifluorenylidene. In the slower reactions the optical density of the reaction mixture, when it became constant, was less than that calculated from the known extinction coefficient of bifluorenylidene for 100% reaction, indicating that some 9-bromofluorene had been converted into non-absorbing products. The cause of this was presumably incomplete removal of oxygen from the reaction cell. However, 70% conversion was usual in the worst cases, and even then rates of reaction over the first 30—50% of reaction were generally reproducible within 10%. Reproducibility was poorest in concentrated solutions of potassium t-butoxide (>0·2M).

Procedure.—Appropriate quantities of stock solutions of 9-bromofluorene and base in t-butyl alcohol were weighed into the two lower arms of the reaction cell and oxygen removed from the apparatus as described above. The concentrations of the reactants in the final solution were determined from the known concentrations and densities of the stock solutions (made up at 30°), a small correction being necessary to allow for the solvent lost during removal of oxygen (usually *ca.* 1%). The reactants were brought to thermostat-temperature (30·0° ± 0·1° in all cases), mixed, and transferred to the optical cell. The optical density of the solution was determined at appropriate times, the wavelength used being chosen according to the initial concentration of 9-bromofluorene. In most cases a wavelength of 450 mμ was used, this being close to the maximum of absorption by bifluorenylidene in the visible region.

The kinetic order of the reaction in 9-bromofluorene was determined by measuring the initial rate of the reaction at different initial concentrations of 9-bromofluorene, and by applying integrated rate equations to the results of those runs in which there was quantitative conversion of the reactant into bifluorenylidene. In all experiments the fraction (F_t) of unchanged 9-bromofluorene at time t was taken to be $F_t = (D_\infty - D_t)/D_\infty$, where D_∞ is the final value of the optical density of the reaction mixture at the appropriate wavelength, calculated from the known extinction coefficient of bifluorenylidene, and D_t is the observed optical density at time t. Rate constants were evaluated graphically, typical (second-order) plots being shown in Fig. 2.

Indicator Measurements.—Solutions of indicators in the various alkaline media were prepared in an analogous manner to the solutions for kinetic experiments except that oxygen was not excluded. Ionisation ratios ($R = [\text{ArNH}^-]/[\text{ArNH}_2]$) were determined by spectrophotometric measurements at the absorption maximum of the indicator anion, corrections being applied for the small absorption of the un-ionised indicator at this wavelength. *p*-Nitroaniline was found to be completely ionised in a 6×10^{-2}M-solution of (solid) benzyltrimethylammonium hydroxide in t-butyl alcohol and in a saturated solution of potassium t-butoxide in the same alcohol. The position and shape of the long-wavelength absorption band of the anion derived from *p*-nitroaniline varied when different bases were used (see Table 1). For solutions of potassium t-butoxide, a small hypsochromic shift was observed with increasing base concentration. The band maximum, however, is rather broad and flat and little error is introduced by calculating ionisation ratios from results obtained at a constant wavelength.

TABLE 1.

Effect of different bases on the visible absorption spectrum of anions derived from *o*- and *p*-nitroaniline in t-butyl alcohol.

		p-$O_2N{\cdot}C_6H_4{\cdot}NH^-$		o-$O_2N{\cdot}C_6H_4{\cdot}NH^-$
Base	Cation	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)
OH^-	$Ph{\cdot}CH_2{\cdot}NMe_3^+$	462	28,060	485
Bu^tO^-	K^+	430	25,260	482
$CMe_2Et{-}O^-$*	Na^+	420	23,800	475

* In t-pentyl alcohol.[9]

Ionisation ratios were reproducible within 10% within the range of values from 0·1 to 10. Since adventitious moisture has a marked effect on the extent of ionisation, indicator measurements on a given alkali solution were carried out immediately before or after the corresponding kinetic run. For the systematic study of the influence of water on the ionisation ratio, the water concentration was determined by Karl Fischer titration on either the stock alkali solution or on the actual alkaline indicator solution immediately after the spectrophotometric measurements.

RESULTS AND DISCUSSION

Mechanism of the Reaction in the Presence of Benzyltrimethylammonium Hydroxide.—Exchange experiments have shown that the conversion of 9-bromofluorene into bifluorenylidene is much slower than the proton transfers to and from the 9-carbon atom. Consequently, as previously indicated, distinction between mechanisms (i) and (ii) is possible by determination of the kinetic order of the reaction in 9-bromofluorene. The results given in Table 2 indicate that the initial rate of formation of bifluorenylidene is proportional to the square of the concentration of 9-bromofluorene and this is confirmed by the kinetic form of quantitative reactions (see Fig. 2). This result enables us to rule

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[9] Jacquinot-Vermesse, Schaal, and Souchay, *Bull. Soc. chim. France*, 1960, 141.

out mechanism (i) immediately and suggests strongly the operation of the bimolecular displacement mechanism.

TABLE 2.

Initial rates (v) of disappearance of 9-bromofluorene in t-butyl alcohol at 30°.

Run no.	Base	[Base] (M)	$[FlHBr_0]$ (10^{-4}M)	v (10^{-5} mole l.$^{-1}$ min.$^{-1}$)	$v/[FlHBr]_0^2$	$v/[FlHBr]_0$
87	OH^-	0·0049	0·84	0·96	1290	0·112
92	,,	,,	1·55	2·84	1180	0·183
115	Bu^tO^-	0·14	1·66	0·35	127	0·021
116	,,	,,	4·30	2·62	142	0·061
124	,,	0·45	1·63	0·38	143	0·023
125	,,	,,	4·01	2·39	149	0·060

TABLE 3.

Influence of the concentrations of benzyltrimethylammonium hydroxide and water on the rate of disappearance of 9-bromofluorene and on the ionisation ratio of *p*-nitroaniline in t-butyl alcohol at 30°.

$[OH^-]$ * (10^{-3}M)	$[H_2O]$ † (M)	$[FlHBr]_0$ (10^{-4}M)	$k_{obs.}$ (l. mole^{-1} min.$^{-1}$)	R	$R[H_2O]^2/[OH^-]$
0·49	(0·08$_3$)	—	—	0·41	5·8
0·90 ‡	0·14	1·60	53·2	0·13$_5$	2·9
1·99	0·08$_5$	1·52	566	1·35	4·9
2·28 ‡	—	1·60	663	1·01	—
3·34	(0·09$_0$)	1·67	1080	2·50	6·1
4·84	0·74	8·17	27·7	0·08$_0$	9·0
4·86 ‡	0·08$_7$	1·60	2480	4·92	7·7
4·89	0·21	0·82	539	0·94	8·5
4·90	0·35	4·07	161	0·37$_5$	9·4
4·90	1·34	—	—	0·02$_0$	7·3
4·93	0·08$_4$	0·80	1960	4·55	6·5
4·93	0·08$_9$	0·82	2220	4·55	7·3
4·95	—	1·62	2090	4·27	—
5·00 §	—	1·68	2910	5·91	—
24·1	~1·0	4·12	89·7	0·20	8·3
24·3		4·15	88·9		
					Average 7·0 ± 1·9

* Each entry, except the last two, refers to a different solution of benzyltrimethylammonium hydroxide in t-butyl alcohol. † Determined by Karl Fischer titration of aliquot parts of the stock alkali solutions, except for the values in parentheses which were determined on the indicator or kinetic solution itself. ‡ 4·0 × 10^{-3}M-Benzyltrimethylammonium toluene-*p*-sulphonate present. § 4·9 × 10^{-3}M-Benzyltrimethylammonium bromide present.

This assignment has been confirmed by examining the dependence of the reaction rate on the basicity of the medium. The ionisation of substituted aromatic amines in basic media measures the ability of a given medium to remove a proton from an electrically neutral molecule.[10] In the present work observed second-order velocity constants (k_{obs}) for the formation of bifluorenylidene in the presence of a variety of concentrations of benzyltrimethylammonium hydroxide and of water have been correlated with the ionisation ratio (R) of *p*-nitroaniline under similar conditions. The experimental results are assembled in Table 3. A graph of log k_{obs} against log R yields a straight line having a slope, 1·05, close enough to unity for us to write *

$$v = k_{obs}[FlHBr]^2 = kR[FlHBr]^2. \qquad (1)$$

A systematic study has been carried out of the dependence of R on the concentrations of water and hydroxide ion. Measurements of R were made for a 15-fold variation in the water concentration and 10-fold variation in hydroxide ion. The results given in Table 3

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* In the subsequent discussion, the symbol Fl has been used to denote the fluorenylidene group.

[10] See, for example, Stewart and O'Donnell, *J. Amer. Chem. Soc.*, 1962, **84**, 493; Langford and Burwell, *J. Amer. Chem. Soc.*, 1960, **82**, 1503.

show that $R[\mathrm{H_2O}]^2/[\mathrm{OH^-}]$ remains constant within the experimental error over the whole range of concentrations. Thus we may write

$$R = K[\mathrm{OH^-}]/[\mathrm{H_2O}]^2. \tag{2}$$

The square term in the denominator is somewhat surprising at first sight, in view of the conventional formulation of the indicator ionisation equilibrium. It is explained by assuming that hydroxide ion retains its identity in t-butyl alcohol and by ascribing specific hydration numbers to the anionic species present in solution, *e.g.*:

$$\mathrm{Ar{\cdot}NH_2 + OH^-,3H_2O \rightleftharpoons Ar{\cdot}NH^-,2H_2O + 2H_2O}$$

$$\mathrm{Ar{\cdot}NH_2 + OH^-,H_2O \rightleftharpoons Ar{\cdot}NH^- + 2H_2O}$$

Combining equations (1) and (2) gives the complete kinetic equation:

$$v = kK[\mathrm{FlHBr}]^2[\mathrm{OH^-}]/[\mathrm{H_2O}]^2. \tag{3}$$

This equation is consistent with mechanism (ii) which, for 9-bromofluorene, may be written:

$$\mathrm{FlHBr + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FlBr^- + (2)H_2O} \qquad \text{Fast}$$

$$\mathrm{FlBr^- + FlHBr \xrightarrow{k_2} FlBr{-}FlH + Br^-} \qquad \text{Slow}$$

$$\mathrm{FlBr{-}FlH + OH^- \longrightarrow Fl{=}Fl + Br^- + H_2O} \qquad \text{Fast}$$

The theoretical rate expression for this mechanism, if one assumes $[\mathrm{FlBr^-}] \ll [\mathrm{FlHBr}]$ and neglects activity coefficients, is

$$v = (k_2k_1/k_{-1})[\mathrm{FlHBr}]^2[\mathrm{OH^-}]/[\mathrm{H_2O}]^2.$$

It is possible to write alternative mechanisms consistent with the second-order kinetic form and rapid exchange of 9-hydrogen. These involve rapid, reversible formation of a carbene from 9-bromofluorene with subsequent rate-determining attack on 9-bromofluorene, its conjugate base, or another carbene, *e.g.*:

$$\mathrm{FlHBr + OH^- \rightleftharpoons Fl\!: + Br^- + (2?)H_2O} \qquad \text{Fast}$$

$$\mathrm{Fl\!: + FlHBr,\ FlBr^-,\ or\ Fl\!: \longrightarrow \text{Products}} \qquad \text{Slow}$$

Slow reactions of a high-energy intermediate such as the carbene are most unlikely and can be discounted for the following reasons: (*a*) Added bromide ion has no effect on the rate of formation of bifluorenylidene other than that which it exerts on acid–base equilibria (*i.e.*, on *R*).[11] (*b*) Attack of carbene on the conjugate base of 9-bromofluorene or " dimerisation " of the carbene in the rate-determining step would require a higher dependence of the reaction rate on the basicity of the medium than that observed. It is concluded, therefore, that formation of bifluorenylidene occurs by bimolecular displacement (ii) under the conditions studied.

Mechanism of the Reaction in the Presence of Potassium t-Butoxide.—Exchange of the 9-hydrogen in 9-bromofluorene remains rapid compared with the formation of bifluorenylidene when potassium t-butoxide replaces benzyltrimethylammonium hydroxide as the base. Since the kinetic order in 9-bromofluorene is again two, it is concluded that in this system the mechanism is that involving a bimolecular displacement in the rate-determining step.

For solutions of potassium t-butoxide in t-butyl alcohol, *R* (*p*-nitroaniline as indicator)

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[11] Cf. Hine and Dowell, *J. Amer. Chem. Soc.*, 1954, **76**, 2688.

increases more rapidly than does the concentration of potassium t-butoxide (Table 4). It was the original intention to examine whether the rate of formation of bifluorenylidene parallels R or the base concentration, particularly since such a procedure has been suggested as a criterion of reaction mechanism in strongly basic media.[12] Since in this instance the mechanism is known independently to involve a bimolecular rate-determining step it was expected, by analogy with the Zucker–Hammett hypothesis,[13] that the reaction rate would not parallel R.

TABLE 4.

Influence of potassium t-butoxide concentration on the rate of disappearance of 9-bromofluorene and on the ionisation of *p*-nitroaniline in t-butyl alcohol at 30°.

[KOBu^t]		[FlHBr]$_0$	k_{obs} (l. mole^{-1} min.$^{-1}$)	
(M)	R	(10^{-4}M)	Expt.	Calc. (eqn. 6)
0·0021	0·09$_8$	—	—	—
0·0041	0·23	4·33	6·34	6·34
0·0066	0·33	—	—	—
0·0145	0·65	4·21	17·9	21·7
0·040	2·51	4·45	53·2	53·2
0·066	4·48	3·75	79·5	78·7
0·099	8·71	4·27	118	103
0·141	14·2	4·37	139	126
0·149	18·7	4·41	106	129
0·197	*ca.* 40	4·23	150	145
0·199	*ca.* 30	4·12	140	146
0·352	—	4·34	142	165
0·438	—	4·01	165	166

In the kinetic and indicator experiments (Table 4), as the base concentration increased, k_{obs} fell below proportionality to both R and the concentration of potassium t-butoxide.

Similar kinetic behaviour has been observed recently by Streitwieser, Van Sickle, and Langworthy[14] for hydrogen-isotope exchange in toluene, catalysed by lithium cyclohexylamide in cyclohexylamine, and by Welch[15] for anionic polymerisation of styrene initiated by butyl-lithium in benzene solution. These authors explain the deviation of their observed rate constants from proportionality to the concentration of lithium derivative by assuming that the catalyst is in equilibrium with inactive dimers or higher polymers. By making a number of reasonable assumptions it is possible to derive a theoretical expression which can be made to fit the experimental results closely.

Such an explanation is not consistent with the present results. Even if potassium t-butoxide in t-butyl alcohol is appreciably associated at high concentrations, its ability to convert *p*-nitroaniline into the corresponding anion does not seem to be impaired. Similarly, proton-removal from 9-bromofluorene should not be affected. Association between reactants and/or intermediates does not lead to the prediction of the characteristic dependence of reaction rate on potassium t-butoxide concentration, save in one case. This exception is interaction between 9-bromofluorene and potassium t-butoxide, provided that an appreciable proportion of the total concentration of organic halide is removed as some species which is not attacked by the 9-bromo-9-fluorenyl anion.

The interaction could in fact be proton removal from 9-bromofluorene. Analysis of the experimental results suggests that, in a 0·2M-solution of potassium t-butoxide, the 9-bromofluorene present would have to be approximately 50% ionised in order to explain the observed reaction rate. Such a concentration of the 9-bromo-9-fluorenyl anion would be detectable spectroscopically since intense absorption in the visible region of the spectrum is observed with stable carbanions of somewhat similar constitution.[8,16] However, in the kinetic runs at high base concentrations, the spectrum of the reaction mixture immediately after mixing of the reactants differed little from that of 9-bromofluorene in pure t-butyl alcohol.

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[12] Allison, Bamford, and Ridd, *Chem. and Ind.*, 1958, 718.

[13] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791; Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

[14] Streitwieser, Van Sickle, and Langworthy, *J. Amer. Chem. Soc.*, 1962, **84**, 244.

[15] Welch, *J. Amer. Chem. Soc.*, 1959, **81**, 1345.

[16] Mason, *Quart. Rev.*, 1961, **15**, 287.

In view of this, the preferred scheme consists of rapid association and dissociation equilibria involving a loose, non-ionic complex:

$$\mathrm{FlHBr} + \mathrm{KOBu^t} \underset{\text{Rapid}}{\overset{K_A}{\rightleftharpoons}} \text{Complex} \underset{\text{Rapid}}{\overset{K_D}{\rightleftharpoons}} \mathrm{Bu^tOH} + \mathrm{FlBr^-,K^+} \xrightarrow[\text{Slow}]{k_2} \text{Products}$$

The active nucleophile, $\mathrm{FlBr^-}$, is formed in very small concentration and attacks the uncomplexed 9-bromofluorene in the rate-determining step.* The concentration of uncomplexed halide is given by:

$$[\mathrm{FlHBr}] = [\mathrm{FlHBr}]_{\mathrm{st}}/(1 + K_{\mathrm{A}}[\mathrm{KOBu^t}]) \qquad (4)$$

where $[\mathrm{FlHBr}]_{\mathrm{st}}$ is the stoicheiometric concentration of 9-bromofluorene. Then, if we assume that activities may be replaced by concentrations, the reaction rate is

$$v = k_2[\mathrm{FlBr^-,K^+}][\mathrm{FlHBr}] = k_2K_{\mathrm{A}}K_{\mathrm{D}}[\mathrm{FlHBr}]^2[\mathrm{KOBu^t}]/[\mathrm{Bu^tOH}]. \qquad (5)$$

Combining equations (4) and (5), we have:

$$k_{\mathrm{obs}} = \frac{v}{[\mathrm{FHBr}]_{\mathrm{st}}^2} = \frac{k_2K_{\mathrm{A}}K_{\mathrm{D}}}{(1 + K_{\mathrm{A}}[\mathrm{KOBu^t}])^2} \cdot \frac{[\mathrm{KOBu^t}]}{[\mathrm{Bu^tOH}]}. \qquad (6)$$

A graph of $([\mathrm{KOBu^t}]/k_{\mathrm{obs}})^{\frac{1}{2}}$ against $[\mathrm{KOBu^t}]$ was approximately linear and yielded the following values for the parameters of equation 6: $k_2K_{\mathrm{A}}K_{\mathrm{D}}/[\mathrm{Bu^tOH}] = 1600$ l.^{2} mole^{-2} min.$^{-1}$; $K_{\mathrm{A}} = 2{\cdot}4$ l. mole^{-1}. Second-order velocity constants calculated from equation 6 by using these values are included in Table 4 and agree satisfactorily with experiment.

While the interpretation of the kinetic results in terms of appreciable association of 9-bromofluorene with potassium t-butoxide is favoured, the possibility of an alternative explanation cannot be ruled out. Such an explanation could lie in ion association phenomena or some other property of concentrated solutions of potassium t-butoxide in t-butyl alcohol. Further experimental investigation of this question is planned.

It is clear, however, that great care must be exercised in the application of correlations of kinetic and indicator measurements in these systems for the purpose of mechanistic distinction.

It is interesting that the velocity constant for the reaction in a dilute solution of potassium t-butoxide in t-butyl alcohol (where the rate constant still parallels the indicator ionisation ratio) is ~16 times smaller than the rate constant in a solution of benzyltrimethylammonium hydroxide having the same ability to convert *p*-nitroaniline into its conjugate base. This difference probably resides in the value of k_2. It seems too large to be a salt effect and arises possibly from the differing degrees of association between the 9-bromo-9-fluorenyl anion and the cation in the two instances. While, under both sets of conditions, the active nucleophile is likely to be an ion pair, the interaction of the carbanion with a potassium ion would be expected to be stronger than with the quaternary ammonium ion on account of the metal cation's smaller size. This would make the nucleophilic activity (*i.e.*, k_2) less in the presence of potassium than of benzyltrimethylammonium ions. Such interactions could also account for the considerable hypsochromic shift of the long-wavelength absorption band of the anion derived from *p*-nitroaniline when the base is changed. This is probably an effect of the changing cation. It is perhaps significant that Wittig and Stahnecker,[18] who observed no shift in the visible absorption maximum of the phenoxydiphenylmethyl anion with changing cation, employed tetrahydrofuran and

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* It is only necessary that a significant proportion of 9-bromofluorene be removed as complex. Complex formation has been written as a first stage in the ionisation of 9-bromofluorene by analogy with the association-dissociation equilibria observed in the interaction of bases with indicators in benzene solution.[17]

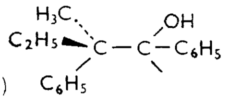
[17] Davis and Hetzer, *J. Res. Nat. Bur. Stand.*, 1952, **48**, 381.

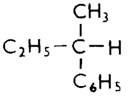
[18] Wittig and Stahnecker, *Annalen*, 1957, **605**, 69.

1,2-dimethoxyethane as solvents. These are solvents known to be capable of cation solvation [19] and would be expected to reduce interaction between the metal cation and organic anion.*

Rather similar interactions have been invoked by Cram and his co-workers [20] to explain changes in the stereochemical course of electrophilic aliphatic substitution in t-butyl alcohol when the cation accompanying the basic reagent was changed from potassium to benzyltrimethylammonium. Thus compound (III) was converted into s-butylbenzene (IV) by potassium t-butoxide with 84% net retention of configuration. When the base used was benzyltrimethylammonium hydroxide the same reaction was effected with 1% net inverson of configuration. It has been suggested that association between the carbanionic intermediate, the cation, and the electrophile (t-butyl alcohol) is weaker with the quaternary ammonium cation and makes possible readier formation of a symmetrically solvated carbanion.

(III)





$C_2H_5{-}\overset{CH_3}{\underset{C_6H_5}{C}}{-}H$

(IV)

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* In a qualitative experiment, 1,2-dimethoxyethane was found to accelerate formation of bifiuorenylidene from 9-bromofluorene in the presence of a high concentration of potassium t-butoxide.

[19] Zaugg, *J. Amer. Chem. Soc.*, 1961, **83**, 837.

[20] Cram, Mateos, Hauck, Langemann, Kopecky, Nielsen, and Allinger, *J. Amer. Chem. Soc.*, 1959, **81**, 5774.