The decomposition of diazo-compounds induced by nucleophiles. The decomposition of 9-diazofluorene in the presence of hydroxide or alkoxide ions

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9-Diazofluorene, on treatment with stoichiometric or substoichiometric amounts of quaternary ammonium hydroxide or methoxide or of potassium *t*-butoxide in solution in aqueous or alcoholic dimethyl sulfoxide or acetonitrile at 30 °C, decomposes with evolution of nitrogen to yield fluorenone azine [bis(fluorenylidene)hydrazine] in almost quantitative yield. Studies are reported of the identity of the minor by-products, together with an examination of the kinetics of the reactions and additional spectroscopic experiments. The general rate equation is $v = k[FlN_2]^{3/2}[Nu^-]^{1/2}$, where Nu^- represents the nucleophile. It is concluded that the oxyanions, most probably after nucleophilic attack on 9-diazofluorene under these basic conditions to generate a new anionic species, are capable of transferring an electron to the diazo-compound. This initiates decomposition of further diazo-molecules in a process of electron-transfer chain catalysis that bears some similarities to, but has also some differences from, that encountered using cathodic initiation. In support of this interpretation it is found that reactions can be accelerated by the introduction of carbon acids (fluorene, 9-phenylfluorene) into the reaction mixtures. The nature of the initiation, propagation and termination steps of the chain mechanism are discussed

Introduction

In 1953 Beringer and co-workers[1] reported that 9-diazofluorene, on treatment with fluorenyl lithium in tetrahydrofuran, was converted into fluorenone azine [bis(fluorenylidene)hydrazine] which they believed arose by simple nucleophilic attack of the carbanion on the terminal nitrogen atom of the diazo-compound. This interpretation was later revived by McDonald and Lin.[2] It is well known that phosphorus-centred nucleophiles do indeed react in this way, forming stable adducts (phospha-zines),[3] but the carbanion adducts are negatively charged and cannot yield the azine without loss of a negatively charged entity (*e.g.* electron, hydride ion). This prompted publication of an alternative view that the interaction was not one between nucleophile and electrophile, but rather involved initial electron transfer from the carbanion to the diazo-compound.[4] Thus complete decomposition of the diazo-compound could be induced by substoichiometric quantities of the carbanion, although labelling revealed that the carbanion could be incorporated to some extent into the azine product. Sub-sequently, Handoo *et al.*[5] presented additional evidence, including EPR results that indicated that odd-electron species were generated when 9-diazofluorene was treated with meth-anolic KOH in DMSO solution. It had been established that conversion of 9-diazofluorene into fluorenone azine could also be initiated by cathodic reduction[6] in acetonitrile solution in a process often referred to as electron transfer chain (ETC) catalysis.[7] The kinetics of this process in a stirred reactor have been studied;[8] while it proved possible to establish the kinetic behaviour in terms of ETC catalysis, the identity of the chain carrier involved in the critical electron transfer could not be determined unambiguously. Although the transformation of 9-diazofluorene into the azine is of limited synthetical importance, the reaction provides a valuable test system for elucidating the sorts of reactive intermediates that can be generated from diazoalkanes or diazoketones in the presence of nucleophiles. Accordingly we report here on kinetic studies of the decomposition of 9-diazofluorene brought about by

solutions of quaternary ammonium hydroxide or methoxide and of potassium *t*-butoxide usually in dimethyl sulfoxide con-taining water, methanol or *t*-butyl alcohol respectively. A few experiments were also conducted in acetonitrile for comparison with the earlier electrochemical studies. In the course of the work it became necessary to re-examine the role of carbanions as part of a chain initiation process. Accordingly the kinetic effect of introducing carbon acids such as fluorene and 9-phenylfluorene into the highly basic reaction mixtures was investigated.

Results

Reactions in the presence of tetraethylammonium hydroxide

Treatment in an atmosphere of oxygen-free nitrogen of 9-diazofluorene in solution in either dimethyl sulfoxide or acetonitrile with a small amount of a 20% aqueous solution of tetraethylammonium hydroxide at 30 °C led to formation of a deep purple colouration (λ_{max} = 570 nm) and smooth and rapid evolution of nitrogen, accompanied by precipitation in high yield of fluorenone azine. Essentially complete conversion could be achieved with as little as 0.5 mol% hydroxide with respect to the diazo-compound; a small amount of the diazo-compound was trapped unchanged within particles of the azine during the precipitation. The progress of the reaction could be followed either by infrared spectrophotometry of the diazo-compound at 2050 cm^{-1} on samples of the reaction mixture, or, more conveniently by determining the increase in pressure in the closed reaction vessel arising from the nitrogen evolution; the results were kinetically equivalent. At a given hydroxide concentration, reactions in DMSO were almost an order of magnitude faster than those in acetonitrile. The reaction products when nitrogen evolution ceased were determined quantitatively by hplc (Table 1) and indicated that in general more than 95% of the diazofluorene had been converted into the azine. Pressure changes in the system were consistent with this. In addition to the azine, small amounts of fluorene and a few of its derivatives (9-fluorenone, its hydrazone and 9-fluorenol) were also present, especially when relatively high hydroxide concentrations were used.

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Table 1 Products of the reaction of 9-diazofluorene with tetraethylammonium hydroxide at 30 °C[a]

| Solvent	DMSO[b]				CH$_3$CN[b]		
10^3[Et$_4$NOH]/M	1.0	2.5	5.0	10.0	2.5	5.0	10.0
Products (%)[c]							
Fl=N–N=Fl	96.1	95.9	95.8	94.2	99.1	97.5	96.4
Fl=N–NH$_2$	0.1	0.3	0.2	1.6	nd	nd	0.2
Fl=O	0.3	1.1	0.8	3.1	0.9	2.3	2.8
FlH–OH	1.0	0.5	1.5	2.0	nd	nd	0.3
FlH$_2$	0.1	1.3	0.6	1.5	nd	0.1	0.2
FlN$_2$ Conversion(%)	97.9	97.5	98.9	99.0	99.8	99.3	99.1

[a] Fl = 9-fluorenylidene; nd = not detected. [b] Containing 1.0 M water. [c] Percentage of 9-diazofluorene (initially 0.05 M) converted into each product.

The kinetics of the reaction in both DMSO and in acetonitrile were followed at 30 °C by pressure change in a stirred, closed system incorporating a pressure transducer. Some typical pressure time curves are shown in Fig. 1 to illustrate their form, the dependence of rate on hydroxide concentration and the relative rates in DMSO and acetonitrile solutions. Addition of a second aliquot of 9-diazofluorene to a reaction mixture in which decomposition of a first aliquot was complete gave a pressure/time curve that was indistinguishable from the first provided that the solutions were not exposed to air. It was also established that increase of the concentration of water in the reaction mixture at constant hydroxide concentration led to a roughly proportionate increase in the time to 50% reaction. In most experiments the water concentration was held at 1.0 M.
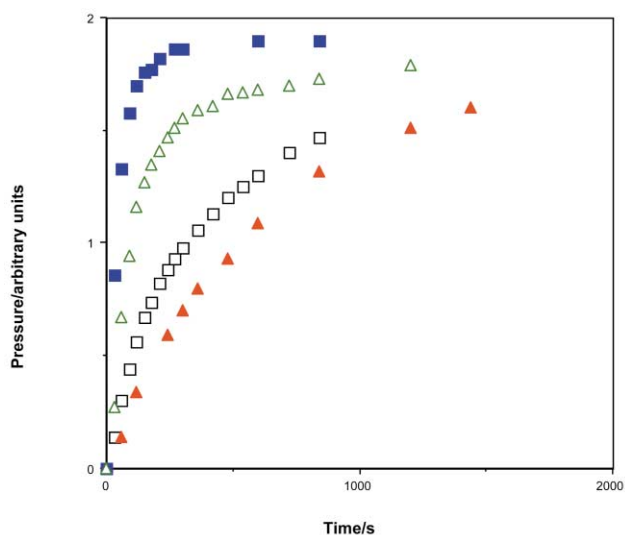
Fig. 1 Pressure/time curves for the decomposition of 9-diazofluorene (50 mM) induced by tetraethylammonium hydroxide in 1 M aqueous DMSO or CH$_3$CN at 30 °C. Hydroxide concentrations: ■ 5 mM; ▲ 2.5 mM; □ 1 mM in DMSO; ▲ 2.5 mM in CH$_3$CN.

Curves of the type shown in Fig. 1 were used to determine the reaction order in 9-diazofluorene. It was evident by inspection that the order was higher than one since successive half-lives of pressure build-up during each experiment were not constant, and, in separate experiments, values increased with decreasing initial concentration of the diazo-compound. The inference was confirmed by the curvature of plots of $\ln (p_\infty - p_t)/(p_\infty - p_0) = \ln$ [FlN$_2$]/[FlN$_2$]$_0$ versus time. Linear plots with excellent correlation coefficients, typically over 2 to 3 half-lives, were, however, achieved by plotting [FlN$_2$]$^{-1/2}$ against time, and this implies that the reaction is of 3/2 order in diazofluorene, the resultant rate coefficients being independent of the initial concentration of the diazo-compound. Table 2 is a compilation of the values of the corresponding rate coefficients. Although a plot (Fig. 2; main graph) of the rate coefficients against the
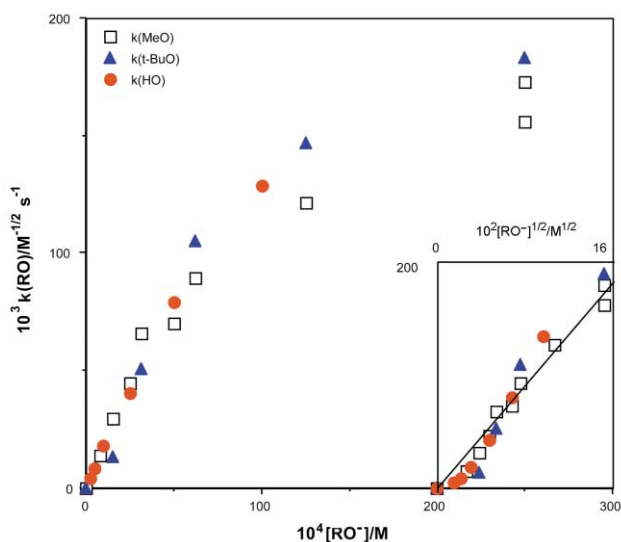
Fig. 2 Dependence of 3/2-order rate coefficients for the decomposition of 9-diazofluorene at 30 °C on the hydroxide or alkoxide concentration.

concentration of quaternary ammonium hydroxide suggests an apparent order in hydroxide ion close to unity in DMSO, the results fit into a broader pattern of results with other bases and over a wider concentration range that suggest an order closer to 1/2 (see below).

The results in Table 2 indicate that the rate of reaction is unaffected by the presence of fluorenone azine (at saturation level at the start of reaction) or by fluorenone. The presence of p-dinitrobenzene (at a concentration one half of that of the hydroxide), however, caused inhibition of the decomposition; this was total at low hydroxide concentration, but led to a halving of the observed rate coefficient at a higher base concentration. The presence of diazodiphenylmethane in the reaction mixture had no effect on the decomposition of 9-diazofluorene; the additional diazo-compound was unchanged after all the diazofluorene had been transformed into the azine and the reaction rate was unchanged. This finding is analogous to our previous observation on the reaction of diazofluorene and diazodiphenylmethane with potassium t-butoxide in t-butyl alcohol/DMSO (9:1 v/v).[4]

Reactions in the presence of benzyltrimethylammonium methoxide or potassium t-butoxide in DMSO solution

Treatment of 9-diazofluorene in DMSO solution with sub-stoichiometric amounts of benzyltrimethylammonium methoxide (as a solution in methanol) or potassium t-butoxide (as a solution in t-butyl alcohol) in an atmosphere of nitrogen at 30 °C led to transformation of the diazo-compound into fluorenone azine in high (>90%) yield (Table 3). By-products were 9-fluorenone together, in the case of the methoxide reactions, with two unidentified products having m/z-values of 224 and 226. When reactions were conducted in the presence of

Table 2 Observed rate coefficients for the reaction of 9-diazofluorene with tetraethylammonium hydroxide at 30 °C[a]

$10^3[FlN_2]$/M	$10^3[HO^-]$/M	Additive[a](conc/M)	$10^3k(HO)/M^{-1/2}\,s^{-1}$	r
Reactions in DMSO[b]				
50	0.25		4.53 ± 0.04	0.9993
50	0.50		8.66 ± 0.14	0.9979
100	1.00		16.99 ± 0.45	0.9969
50	1.00		18.32 ± 0.30	0.9981
25	1.00		16.86 ± 0.17	0.9994
10	1.00		18.38 ± 0.46	0.9946
50	1.00	Fl=N–N=Fl (sat.)	17.06 ± 0.31	0.9981
50	1.00	Fl=O (10 mM)	20.73 ± 0.32	0.9988
50	1.00	PDNB (0.5 mM)	No reaction[c]	
50	1.00	Ph$_2$CN$_2$ (50 mM)	18.36 ± 0.29	0.9986
50	2.50		40.72 ± 0.89	0.9986
50	5.00		79.14 ± 6.82	0.9912
50	10.0		129.0 ± 7.9	0.9907
50	10.0	PDNB (5 mM)	58.60 ± 4.47	0.9886
Reactions in CH$_3$CN[b]				
50	2.50		6.16 ± 0.20	0.9924
100	5.00		10.48 ± 0.22	0.9975
50	5.00		10.98 ± 0.35	0.9931
25	5.00		9.65 ± 0.50	0.9777
100	10.0		24.67 ± 0.71	0.9975
50	10.0		25.61 ± 0.47	0.9985
25	10.0		24.80 ± 1.63	0.9791
50	25.0		74.08 ± 6.20	0.9897

[a] Additives: Fl=N–N=Fl, fluorenone azine; Fl=O, 9-fluorenone; PDNB, *p*-dinitrobenzene; Ph$_2$CN$_2$, diazodiphenylmethane. [b] Containing 1.0 M water.

Table 3 Products of the reaction of 9-diazofluorene with benzyltrimethylammonium methoxide in methanolic DMSO and with potassium *t*-butoxide in DMSO/*t*-butyl alcohol at 30 °C[a]

$10^3[FlN_2]$/M	$10^3[RO^-]$/M	Conversion/%	Products (%)			
			Fl=N–N=Fl	Fl=O	*m/z* 224[b]	*m/z* 226[c]
Methoxide reactions						
25	25	96.4	90.9	2.8	2.2	1.2
25	12.5	98.5	95.1	2.4	0.8	0.15
25	5.0	97.9	96.2	0.8	0.9	0.1
12.5	12.5	98.0	91.3	3.0	2.0	0.7
12.5[d]	12.5	100	62.5	28.9	7.7	1.7
12.5[e]	12.5	100	48.6	39.0	8.7	3.6
t-Butoxide reactions						
25	25	100	98.2	1.7		
25	12.5	100	97.7	2.2		
25	5.0	100	96.5	3.1		

[a] [ROH] = 1.0 M. [b] Fragmentation: *m/z* 224 (8%), 207 (21), 195 (22), 181 (52), 180 (80), 178 (79), 165 (20), 152 (39), 82 (52), 57 (80), 44 (100). [c] Fragmentation: *m/z* 226 (6%), 208 (6), 194 (3), 181 (100), 165 (12), 152 (19), 82 (14), 57 (14), 44 (18). [d] In air-saturated solution. [e] In oxygen-saturated solution.

air or oxygen, the yield of azine was drastically reduced with corresponding increases mainly in the yield of fluorenone but also of the two unidentified products.

Reactions were again followed by the increase in pressure as a function of time. Again the results fitted a 3/2 order law with respect to the diazo-compound for both alkoxides, and the order with respect to the alkoxide was close to 1/2 over the whole range of concentrations examined, as demonstrated in the inset in Fig. 2. Interestingly, the points in the plot in Fig. 2 suggest that the rate is dependent on the alkoxide concentration but not evidently its identity; hydroxide, methoxide and *t*-butoxide at a given concentration give roughly the same rate coefficient. It would seem that matters such as basicity and size of the initiating base make little difference to the kinetically important processes.

As with hydroxide-induced reactions, the addition of *p*-dinitrobenzene had an inhibiting effect, reducing the observed 3/2-order rate coefficient by some 30–40% depending on the concentration (Table 4). The addition of a spin trap, phenyl *t*-butyl nitrone (PBN) had a negligible effect, as did the long-lived radical di-*t*-butyl nitroxide (DTBN).

The reactions of 9-diazofluorene with sodium borohydride in DMSO and the influence of carbon acids on the kinetics of base-induced decomposition

Previous investigations of the transformation of the diazoketone azibenzil (benzoyl phenyl diazomethane) into the corresponding azine showed that the reaction could be initiated cathodically in acetonitrile solution,[9] and by sodium borohydride in DMSO solution.[10] An anionic chain mechanism was proposed for the borohydride reaction in which a key step is the transfer of a hydride ion to the diazo-carbon atom of the diazoketone. Products were the corresponding azine plus deoxybenzoin, the result of conversion of the diazo-function into a methylene group. In order to establish whether an

Table 4 Effects of additives on observed rate coefficients for the reaction of 9-diazofluorene with benzyltrimethylammonium methoxide in DMSO at 30 °C[a]

$10^3[FlN_2]/M$	$10^3[MeO^{···}]/M$	Additive[a] (conc/M)	$10^3k(MeO)/M^{-1/2}\,s^{-1}$	r
25	6.25		89.3	0.9966
25	6.25	PBN (2.5×10^{-3}M)	80.4	0.9991
25	6.25	DTBN (3.25×10^{-3}M)	87.1	0.9962
25	5.00		69.9	0.9967
25	5.00	PDNB (2.5×10^{-3}M)	40.8	0.9967
25	5.00	MDNB (2.5×10^{-3}M)	1.70	0.9996
25	2.50		44.7	0.9993
25	2.50	PDNB (1.25×10^{-3}M)	31.6	0.9975

analogous hydride transfer pathway was possible for 9-diazofluorene, similar experiments with sodium borohydride in DMSO were carried out, but these gave a somewhat different pattern of behaviour than that seen with azibenzil. The products were fluorenone azine and fluorenone hydrazone, the latter being formed in an amount roughly corresponding to the mol percent of sodium borohydride used. For example, with reaction mixtures 0.05 M in diazofluorene, yields of hydrazone were 23% and 14% when the sodium borohydride concentrations were 0.01 and 0.005 M respectively. Reaction mixtures remained red for a short period after mixing the reagents, during which nitrogen evolution was rather slow, and this was followed by a colour change to purple (λ_{max} 570 nm), as observed in the base-induced decompositions, and this was accompanied by much more rapid gas evolution. The timescale for completion of the reaction was much shorter than comparable reactions of azibenzil, but much longer than observed for base-induced reaction of diazofluorene at the same reactant concentrations. Furthermore it was found, using sodium borodeuteride, that, although the induction period was extended, once rapid nitrogen evolution started, the rate was little changed from that observed in reactions using NaBH₄.

It has previously been reported that transformation of azibenzil into the corresponding azine could be induced by carbanions,[10] for example that formed by deprotonation of deoxybenzoin, and it has been argued that the reaction follows the same hydride-transfer chain mechanism as that induced by sodium borohydride. Preliminary experiments had suggested that diazofluorene decomposition was not promoted by added carbanions generated from carbon acids by tetraethylammonium hydroxide in slightly aqueous DMSO. Subsequent study[5] showed that this was not generally true. The present work is concerned with the effect of carbon acids on reactions in DMSO in the presence of potassium *t*-butoxide. The presence of, for example, fluorene had a dramatic accelerating effect on the reaction rate. It was necessary to work in a solvent consisting of a mixture of DMSO and *t*-butyl alcohol in a ratio of 1:9 by volume in which solvent the 3/2 order rate coefficient for the transformation of the diazofluorene (25 mM) into azine by potassium *t*-butoxide (12.5 mM) alone was rather slow $[k(BuO) = 1.0 \times 10^{-3}\ M^{-1/2}\ s^{-1}$ at 30 °C]. In this reaction medium, the reactions in the presence of fluorene were all accelerated and afforded the azine in more than 98% yield. 9,9′-Bifluorenyl could be identified among the products; for example, in a reaction of diazofluorene (25 mM) with potassium *t*-butoxide (12.5 mM) in the presence of fluorene (6.25 mM), 4.5% of the fluorene was converted into bifluorenyl. No corresponding dimeric product was detected in the reactions in which the added carbon acid was 9-phenylfluorene. The kinetics of the reactions followed the 3/2-order dependence on diazofluorene concentration described earlier but the fit to a first order dependence was almost equally good. The kinetic effects of carbon acid addition on the observed rate coefficients are in Table 5. It can be seen that the order of effectiveness of the C-acids in promoting the formation of the azine is 9-phenylfluorene (p*K* in DMSO 17.9)[11] > fluorene (p*K* 22.6)[11] >> 9-*t*-butylfluorene (p*K* 24.4)[12] > 9-methoxyfluorene (pK 22.1)[13] >>

9-*t*-butoxyfluorene (pK 21.3;[13] no observable reaction): clearly there is no simple relation between activity and strength of the carbon acid. As shown in Fig. 3, the observed 3/2-order rate coefficients increase linearly with the square root of the concentration of the C-acid, a dependence more strictly adhered to with fluorene than with 9-phenylfluorene. It is to be noted that the fluorene line in Fig. 3 extends into a region where the fluorene concentration exceeds the concentration of potassium *t*-butoxide. The effect of increasing the (excess) butoxide concentration at a fixed concentration of carbon acid was less than proportional and close to a square root dependence, although the scatter of data points is substantial.
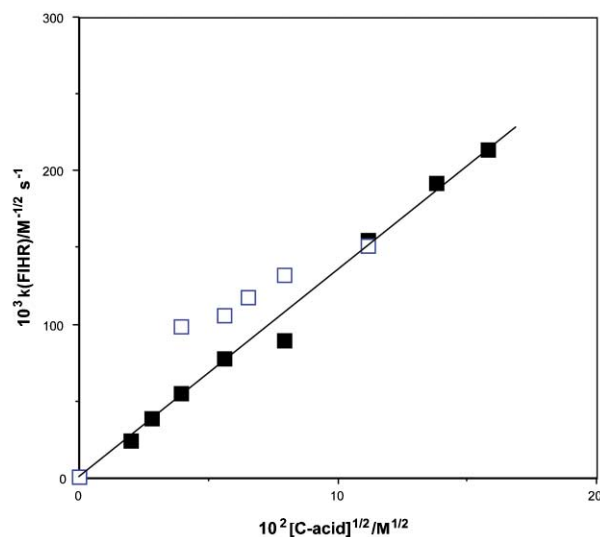
Fig. 3 Dependence of the rate coefficients for 9-diazofluorene decomposition on the concentration of carbon acid: ■ fluorene; □ 9-phenylfluorene.

Electron paramagnetic resonance and uv/visible spectroscopy

During and after completion of decomposition of 9-diazofluorene induced by hydroxide or alkoxide ions in DMSO or by potassium *t*-butoxide in conjunction with fluorene in 9:1 *t*-butyl alcohol/DMSO, the reaction mixtures displayed strong EPR signals. In each case the spectrum consisted of a single very broad signal upon which was superimposed an envelope spanning about 13 G and comprising some 39 lines with a uniform hyperfine splitting of 0.31 G. Fig. 4 shows a typical spectrum from the reaction of the diazo-compound with benzyltrimethylammonium methoxide. The appearance of the 39-line spectrum was rather similar to that reported by others[5] and ascribed to the azine anion radical.[14] Such differences as there are can be ascribed[15] to the somewhat higher temperature (*ca.* 25 °C) at which the present spectra were recorded. In all cases the radical species had slightly different *g*-values when generated using different bases: tetraethylammonium hydroxide, 2.00270; benzyltrimethylammonium methoxide, 2.00277; potassium *t*-butoxide, 2.00273. In the diazofluorene reactions, the radical concentration was estimated roughly to correspond

Table 5 Effects of carbon acids on observed rate coefficients for the reaction of 9-diazofluorene (25 mM) with potassium *t*-butoxide in DMSO-*t*-butyl alcohol (1:9 v/v) at 30 °C

[BuO⁻]/mM	Additive[a]	Conc/mM	$10^3 k(\text{FlHR})/\text{M}^{-1/2}\,\text{s}^{-1}$	r
12.5			1.00	0.9376
12.5	FlH₂	0.39	24.7	0.9838
12.5	FlH₂	0.78	38.8	0.9823
12.5	FlH₂	1.56	55.4	0.9828
12.5	FlH₂	3.12	78.1	0.9916
12.5	FlH₂	6.25	90.0	0.9788
12.5	FlH₂	12.5	155	0.9858
12.5	FlH₂	19.0	192	0.9656
12.5	FlH₂	25.0	214	0.9891
6.25	FlH₂	6.25	46.3	0.9889
19.0	FlH₂	6.25	101	0.9891
25.0	FlH₂	6.25	91.3	0.9901
37.5	FlH₂	6.25	98.0	0.9738
40.0	FlH₂	6.25	110	0.9970
12.5	FlHPh	1.56	98.5	0.9805
12.5	FlHPh	3.12	106.4	0.9929
12.5	FlHPh	4.25	118	0.9900
12.5	FlHPh	6.25	110	0.9900
12.5	FlHCMe₃	6.25	0.54	0.9993
12.5	FlHOMe	6.25	0.05	0.9009
12.5	FlHOCMe₃	6.25	No reaction	
12.5	FlHPh	12.5	151	0.9929
6.25	FlHPh	6.25	94.8	0.9910
19.0	FlHPh	6.25	106	0.9955
25.0	FlHPh	6.25	119	0.9954
31.3	FlHPh	6.25	125	0.9878

[a] Carbon acids: FlH₂ fluorene; FlHPh 9-phenylfluorene; FlHCMe₃ 9-*t*-butylfluorene; FlOMe 9-methoxyfluorene; FlOCMe₃ 9-*t*-butoxyfluorene.
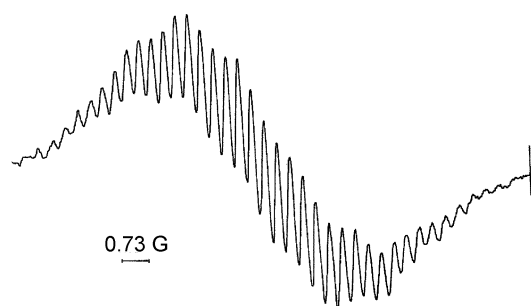
Fig. 4 EPR spectrum of a reaction mixture containing 9-diazo-fluorene (5 mM) and benzyltrimethylammonium methoxide (2 mM) in DMSO solution at ambient temperature.
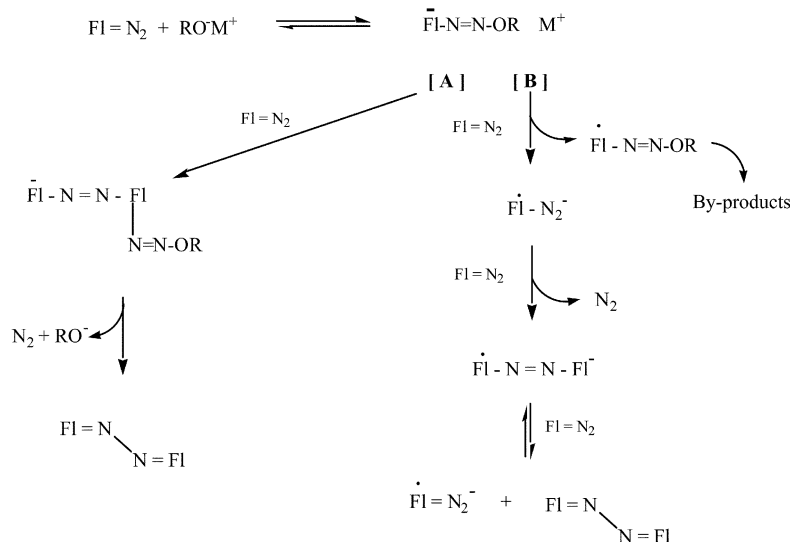
0.73 G

to about 5% of the initial concentration of the diazo-compound (1.25 to 10 mM). Increasing the concentration of dia-zofluorene above this range, or using acetonitrile as the solvent led to much less well resolved spectra. Reactions carried out in DMSO with addition of PBN gave EPR spectra of slightly reduced intensity but with no evidence of the change in the appearance of the spectra that would indicate radical trapping and formation of nitroxyl species. Reactions in the presence of DTBN (1 mM) led to the disappearance of some 95% of the intensity of its characteristic triplet EPR signal; the 39-line sig-nal observed in reaction mixtures not containing DTBN was absent.

Within a few seconds of the initiation of all reactions, the mixtures took on a deep purple colouration, and spectroscopic investigation showed strong absorbance at 380, 545 (sh) and 580 nm, with much weaker bands at 742, 824 and 880 nm. The colour in all cases was discharged on exposure of reaction mixtures to the air. It was similar in appearance to that observed during preparative electrolysis of 9-diazofluorene at a platinum cathode in acetonitrile.[4] Significantly, the spectrum is identical to that resulting from spectroelectrochemical experiments on the reduction of fluorenone azine in the same solvent.[14] Indeed we have found that the same colour, and the same 39-line EPR spectrum as described above, could be generated by treatment of fluorenone azine (typically 5 mM in

DMSO) with an equimolar solution of hydroxide, methoxide or *t*-butoxide. The timescale of events was roughly the same as that of the decomposition of 9-diazofluorene; for example with equimolar (5 mM) azine and tetraethylammonium hydroxide the half-life of colour production was some 600 s.

Discussion

The decomposition of 9-diazofluorene induced by quaternary ammonium hydroxide and methoxide, and by potassium *t*-butoxide with or without the addition of carbon acids such as fluorene affords fluorenone azine which is precipitated in almost quantitative yield. Evolution of nitrogen occurs at a rate $d[N_2]/dt \propto [FlN_2]^{3/2}[RO^-]^{1/2}$. Free radicals are detectable in the reaction mixtures by EPR spectroscopy and the EPR signals and colour of the reaction mixtures are identical to those produced when 9-diazofluorene or the azine are subjected to cathodic reduction, or when the azine is treated with the bases mentioned above. The question then is whether the base-induced decomposition of the diazo-compound (with or without addi-tion of a carbon acid) is analogous to the cathodically induced reaction which is thought to involve electron transfer chain catalysis, or whether a non-radical, polar mechanism operates, with the radical formation a side reaction independent of the diazoalkane decomposition and involving perhaps only the more readily reduced azine and the base solution. In order to illustrate the problem, we present possible, but by no means unique, pathways of these two types in Scheme 1. They are formulated in terms of a common first step, involving diazo-fluorene and the nucleophile. Attack of the nucleophile on the diazo-carbon atom would be expected to generate nitrogen and a 9-substituted fluorenyl anion; since fluorenyl alkyl ethers in the presence of potassium *t*-butoxide do not appear to promote efficient decomposition of diazofluorene, this pathway seems unlikely, even though a 9-methoxy-substituent in fluorene is reported to have a strongly radical-stabilising effect as judged from its effect on the acidity-oxidation potential.[16] Reversible nucleophilic addition to the terminal nitrogen of the diazo-compound could, however, afford a carbanion which could attack a further molecule of 9-diazofluorene either by nucleo-
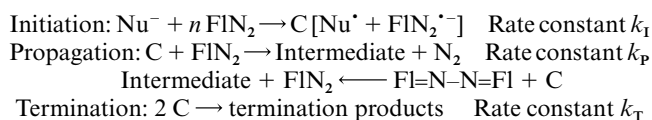
Fl = N$_2$ + RO$^-$M$^+$ $\rightleftharpoons$ $\overset{-}{\text{Fl}}$-N=N-OR   M$^+$

[A]   [B]

Fl = N$_2$

$\overset{-}{\text{Fl}}$ - N = N - Fl
$|$
N=N-OR

Fl = N$_2$ Fl - N=N-OR   By-products

$\overset{\cdot}{\text{Fl}}$ - N$_2$$^-$

N$_2$ + RO$^-$

Fl = N$_2$ N$_2$

Fl = N
   $\diagdown$
      N = Fl

$\overset{\cdot}{\text{Fl}}$ - N = N - Fl$^-$

Fl = N$_2$

$\overset{\cdot}{\text{Fl}}$ = N$_2$$^-$ +   Fl = N
                          $\diagdown$
                             N = Fl

Scheme 1

philic addition to the terminal nitrogen atom, followed by loss of the original nucleophile and a molecule of nitrogen (Pathway A) or by electron transfer to the second molecule of the diazo-compound (Pathway B).

On the basis of Pathway A, the azine yield should be high, and indeed, in all cases, was found to be greater than 90%, even when the oxyanion concentration was equal to the initial concentration of 9-diazofluorene. Using hydroxide ion as the nucleophile, 9-fluorenol was detected in yields that increased with the hydroxide concentration, but the amounts were small and could be attributed to a side reaction in which the nucleophile attacked the diazo-carbon. One of the unidentified products from reactions in the presence of methoxide ions has $m/z =$ 224 corresponding to FlH–N=N–OMe. The other by-products cannot be rationalised in terms of the mechanism, and, along with the observed free radicals, would have to be attributed to separate side-reactions. Turning to the kinetic form expected for Pathway A, it is possible that the rate-limiting step would be the initial attack of the nucleophile on the diazo-compound, the subsequent reaction with a second diazo-molecule being rapid and producing an adduct whose fragmentation would be irreversible. If this were so, then the observed rate law would be $d[N_2]/dt \propto [FlN_2][RO^-]$, which is not observed. Rate-limiting attack by 9-hydroxydiazenyl- or alkoxydiazenyl-fluorenyl anion, rapidly formed in low equilibrium concentration, on a second molecule of diazofluorene or fragmentation of the resultant adduct cannot be rate-determining since this would lead to a kinetic law second order in the diazo-compound and first order in alkoxide ion. These kinetic features have not been observed, and we believe that the nucleophilic addition/elimination mechanism (Pathway A) can therefore be ruled out.

The observation of fractional orders of reaction is often associated with radical chain reactions. In the present instance, all the reactions show an order in diazofluorene of 3/2 and in hydroxide/alkoxide of 1/2. In the case of reactions promoted by fluorene, the order of reaction with respect to the carbon acid is 1/2 and, at fixed fluorene concentration of 6.25 mM, increasing the t-butoxide concentration in the range 6.25 to 40 mM led to an increase in rate that showed a rough dependence on the square root of the butoxide concentration. These reaction orders can be fitted to the standard formulation of a chain reaction, analogous to Pathway B but including a chain-termination step, viz.,

Initiation: Nu$^-$ + n FlN$_2$ $\rightarrow$ C [Nu$^\cdot$ + FlN$_2$$^{\cdot-}$]   Rate constant k_I
Propagation: C + FlN$_2$ $\rightarrow$ Intermediate + N$_2$ Rate constant k_P
          Intermediate + FlN$_2$ $\longleftarrow$ Fl=N–N=Fl + C
Termination: 2 C $\rightarrow$ termination products   Rate constant k_T

On the basis of the establishment of a steady state for the concentration of the chain carrier C as formulated in eqn. (1) and (2),

$$d[C]/dt = k_I[Nu^-][FlN_2]^n - k_T[C]^2 = 0 \qquad (1)$$

whence

$$[C] = \{(k_I/k_T)[Nu^-][FlN_2]^n\}^{1/2} \qquad (2)$$

If the rate of propagation is much larger than the rate of initiation, then the rate of product formation is given by eqn. (3).
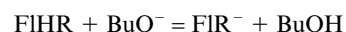
$$d[Fl{=}N{-}N{=}Fl]/dt = d[N_2]/dt = k_P[C][FlN_2] = \\ k_P(k_I/k_T)^{1/2}[Nu^-]^{1/2}[FlN_2]^{1 + n/2} \qquad (3)$$

For the reactions induced by hydroxide or alkoxide (Nu$^-$ = HO$^-$ or RO$^-$), the chain formulation fits the observed kinetic form if the number of 9-diazofluorene molecules (n) participating in the rate-limiting step of the initiation process is one. Note that in the propagation step it has been assumed that the two diazofluorene molecules which are converted by the chain carrier into azine are involved in two separate steps, the first of which determines the overall rate of propagation.

In the case of reactions promoted by added carbon acids in the presence of potassium t-butoxide, the nucleophile is presumed to be the related, rapidly formed carbanion, FlR$^-$, the concentration of which is given by eqn. (4),

$$[FlR^-] = [FlHR]_{total}[BuO^-]/([BuO^-] + \\ K_{equ}[BuOH]) = [Nu^-] \qquad (4)$$

where $[FlHR]_{total}$ is the total concentration of carbon acid added to the reaction mixture and K_{equ} is the equilibrium constant for the protonation of the carbanion according to:

$$FlHR + BuO^- = FlR^- + BuOH$$

In such cases, the rate expression becomes:

$$d[Fl{=}N{-}N{=}Fl]/dt = \\ k_P(k_I/k_T)^{1/2}\{[FlHR]_{total}[BuO^-]/([BuO^-] + \\ K_{equ}[BuOH])\}^{1/2}[FlN_2]^{3/2} \qquad (5)$$

and the apparent order in butoxide concentration will be one half for weak carbon acids or less for carbon acids that are substantially deprotonated under the reaction conditions.

Consistent with this, the plot of observed 3/2 order co-efficients against $[FlHR]_{total}^{1/2}$ is linear for fluorene, but shows downward curvature as the butoxide concentration increases, in the case of 9-phenylfluorene (Fig. 3).

Having established that the kinetic form of the reactions fits the chain model with second order termination in the chain carrier concentration, we need to consider the identity of the carrier, its formation and destruction. The observation that the hydroxide- and methoxide-induced reactions are inhibited by *p*-dinitrobenzene, a good one-electron acceptor, points to an electron-transfer chain mechanism, but it is necessary to explain why chain termination has a different kinetic form from that previously observed in electrochemically induced decomposition of 9-diazofluorene in a stirred, divided reactor.

The simplest formulation of the reaction in the absence of added carbon acids is that initiation of the reaction involves direct electron transfer from the hydroxide/alkoxide ion in DMSO solution to diazofluorene, generating a hydroxy- or alkoxy-radical and a diazofluorene anion radical, the chain carrier. In this model, propagation of the chain would be by attack of the carrier on a second diazofluorene molecule in the rate-limiting step, generating molecular nitrogen and a molecule of fluorenone azine as its anion radical. The latter would be involved in an electron-transfer equilibrium with a further molecule of diazofluorene, regenerating the chain carrier and giving azine which would precipitate. A significant concentration of the azine anion radical would remain in solution and would be detectable by EPR spectroscopy. Termination of the chains would be by dimerisation of the carrier species, a reaction we have previously identified and reported.[8a] In order to account for the by-products; fluorenone and 9-fluorenol, the oxygen centred radical produced in the initiation step would have to be trapped irreversibly by diazofluorene generating molecular nitrogen and 9-hydroxyfluorenyl radicals some of which might be expected to undergo disproportionation; N-protonation of diazofluorene anion radical would generate 9-diazenylfluorenyl radical, disproportionation of which would produce a molecule of fluorenone hydrazone and regenerate one of diazofluorene, as suggested in pulse radiolysis studies.[17] The addition of fluorene to reaction mixtures containing potassium *t*-butoxide accelerates the conversion of diazofluorene into fluorenone azine and this is consistent with the simple formulation if initiation of the chains is mediated by fluorenyl anions. Electron transfer from the carbanion would afford 9-fluorenyl radicals, leading to the corresponding radical dimer, 9,9′-bifluorenyl, as is indeed observed, and to the 1/2-order kinetic dependence on the fluorene concentration. Reactions in the presence of 9-phenylfluorene fit less well; the kinetic dependence on carbon acid concentration is somewhat less well defined and no products attributable to 9-phenylfluorenyl radicals were detected.

There are other more serious problems with the simple formulation, however, particularly in respect of the initiation process, the identity of the chain carrier so produced, and the termination process. There has been much discussion over the possibility of hydroxide and alkoxide ions taking part in outer sphere electron transfer reactions with organic acceptors. Eberson,[18] Sawyer and Roberts[19] and Djaasberg *et al.*[20] in particular have advanced compelling arguments based on Marcus theory that this should not be feasible and that alternative pathways involving the generation of better one-electron donors should be sought. In dipolar aprotic solvents in which anion solvation energies are much lower than in protic solvents, the situation should be more favourable, and reports continue to appear of outer sphere electron transfer from hydroxide ion, in some cases assisted by subsequent irreversible steps.[21] An alternative to direct electron transfer from oxyanions is that shown in Scheme 1 (Pathway B) in which the anionic diazofluorene/nucleophile adduct initiates the chain by transferring an electron to a second molecule of diazofluorene. Such an

initiation process has the additional virtue of rationalising the formation of the by-product having m/z = 224 observed in methoxide induced reactions as Fl=NNHOMe, but it would require that the rate-limiting step of initiation be the formation of the 9-(methoxydiazenyl)fluorenyl anion rather than the subsequent electron transfer if it is to be consistent with the overall fractional order in the diazo-compound. It should be noted, however, that the isomeric adduct formed by attachment of the oxyanion to C-9 of the diazo-compound, $Fl(OR)N_2^-$ could be the key intermediate, electron-transfer being facilitated by irreversible fragmentation: $Fl(OR)N_2^- + FlN_2 \longrightarrow FlN_2^{-\bullet} + FlOR^\bullet + N_2$. We cannot discount this possibility, but we suspect that $Fl(OR)N_2^-$ may not have a long enough lifetime. Although we cannot unambiguously rule out direct electron transfer from the oxyanions to the diazo-compound, we believe that a nucleophile/diazoalkane adduct is responsible. Our observation that electron transfer also takes place to fluorenone azine in hydroxide or alkoxide solutions in DMSO when no 9-diazofluorene is present might seem to suggest direct transfer from the oxyanions, but again the transfer might be mediated by an azine/oxyanion adduct, although we have no direct evidence for this.

The identity of the chain carrier as the diazofluorene anion radical needs further consideration. We have previously shown that, when generated electrochemically in dimethylformamide or acetonitrile solution, it rapidly dimerises forming a dianion which, at room temperature, rapidly loses molecular nitrogen to form fluorenone azine as its strongly basic dianion.[22] We have previously argued[8] that, in cathodically induced conversion of diazofluorene into fluorenone azine, which follows an electron-transfer chain catalysis mechanism, the diazofluorene anion radical is unlikely to be the chain carrier since it would dimerise in preference to propagating the chain by reaction with further diazoalkane molecules under the prevailing reaction conditions. It was suggested that the carrier was probably the s-*cis*-fluorenone azine anion radical. In the present experiments in a different solvent system, in which there is an appreciable concentration of water or alcohol to act as a proton source, the same considerations may not apply. Even though the kinetic form of the propagation step appears to be the same, that of the termination step is different, and it has to be a dimerisation or disproportionation in the base induced reactions. Moreover the rate of generation of the chain carriers is not under independent experimental control as is the case in electrolysis. For simplicity therefore we propose that the carrier is indeed the 9-diazofluorene anion radical, and that propagation involves attack on a molecule of diazofluorene, yielding after nitrogen loss the fluorenone azine anion radical (the intermediate in Scheme 1, Pathway B) which transfers its extra electron to a further diazo-molecule in a rapidly established electron-transfer equilibrium. Dimerisation of the carrier could terminate the chain but only if the dimer is inactivated as an electron transfer agent; in the present conditions that could be achieved by rapid protonation either before or after loss of a molecule of nitrogen, although no corresponding products were detected. On this basis the observed second-order rate constant estimated from the inset in Fig. 2 of 11.4×10^{-3} M^{-1} s^{-1} is equal to $k_P(k_I/k_T)^{1/2}$. The value of k_P from cathodically initiated reactions is 9.7 M^{-1} s^{-1} and k_T taken as the dimerisation of the carrier is 2×10^5 M^{-1} s^{-1}; hence the value of k_I would have to be 0.2 M^{-1} s^{-1}, which seems reasonable in the light of the rate of generation of the anion radical from fluorenone azine and tetraethylammonium hydroxide.

The effect of adding carbon acids to diazofluorene solutions containing potassium *t*-butoxide is to accelerate the conversion of diazofluorene into fluorenone azine. The kinetic form of the reactions indicates that the carbanion formed by deprotonation of the carbon acid facilitates electron transfer to diazofluorene, generating the chain carrier, as expected for a species much more readily oxidised than the oxyanions.[17,18] It would seem

that thereafter the behaviour is essentially the same as in reactions without added carbon acid. Our earlier experiments[4] have shown that the radicals formed after electron transfer from carbanions to diazofluorene can dimerise but can themselves attack diazo-molecules and generate azines.

In summary, we have shown that hydroxide and alkoxide anions can induce the transformation of 9-diazofluorene into fluorenone azine in high yield. This reaction is accelerated by the addition of carbon acids such as fluorene, but inhibited by *p*-dinitrobenzene, a good one-electron acceptor. Reaction mixtures exhibit EPR signals. The reaction shows fractional orders in the diazo-compound, the oxyanions and the carbon acid. It is argued that this is all consistent with an electron-transfer chain mechanism with second order termination. Suggestions have been made concerning the nature of the initiation step; although direct (outer sphere) electron transfer from the oxyanion to diazofluorene, generating the diazo-fluorene anion radical as the chain carrier, provides the simplest interpretation of the kinetics, redox-potential considerations make this unlikely. A diazofluorene/nucleophile adduct as the electron-transfer agent is a likely alternative.

Experimental

Materials

9-Diazofluorene, mp 94–5 °C [from petrol (bp 60–80°)], was prepared as previously described;[23] from hplc analysis, contamination by fluorenone (the only impurity) was less than 0.02%. Fluorenone azine was prepared from fluorenone and its hydrazone in the presence of acetic acid,[24] mp 273 °C (from *m*-xylene). Of the carbon acids used, fluorene, 9-*t*-butylfluorene and 9-phenylfluorene were recrystallised commercial samples while the 9-methoxy- and 9-*t*-butoxy-fluorenes were prepared by refluxing 9-bromofluorene with silver nitrate in the appropriate alcohol as solvent;[25] all had mp in agreement with literature values. Dimethyl sulfoxide was dried by standing overnight over calcium hydride, followed by distillation under reduced pressure, discarding the first 15% of the distillate. Acetonitrile (hplc grade) was passed through a short column of activated alumina immediately prior to use. Tetraethyl-ammonium hydroxide was a commercial 20% solution in water and benzyltrimethylammonium methoxide was a commercial 40% solution in methanol; both were used as supplied, and their concentrations determined by titration with standard hydrochloric acid. The stock solutions were diluted with water or methanol as appropriate before mixing with the dipolar aprotic solvent so as to have a concentration of the hydroxylic component of 1.0 M in all cases. Solutions of potassium *t*-butoxide in *t*-butyl alcohol were freshly prepared as previously described and then diluted with the alcohol where necessary before mixing with DMSO. Except in the experiments involving the addition of carbon acids, the concentration of *t*-butyl alcohol in the reaction mixtures was 1.0 M.

Instrumentation

Quantitative infrared measurements were made on a Perkin Elmer 1320 instrument using calcium fluoride cells. Hplc analyses were carried out on a Varian 5000 liquid chromatograph using a RP18-2776 reverse phase column and 85% aqueous acetonitrile as eluant; uv detection was at 254 nm. Mass spectra and GCMS data were obtained on a VG 7070E instrument using a capillary column with OV1 as the stationary phase.

EPR spectra were recorded on a Varian E-4 X-band spectrometer using a two-legged glass arrangement fused to the EPR sample tube. A solution of the diazo-compound in DMSO was syringed into one leg of the apparatus and a solution of the base RO⁻/ROH in DMSO into the other and degassed by freeze–pump–thaw cycles; after bringing to room temperature under oxygen-free nitrogen, the solutions were mixed and, by inversion of the apparatus, the mixture transferred to the EPR tube for recording of the spectra. Where necessary, phenyl *t*-butyl nitrone or di-*t*-butyl nitroxide were introduced; both were commercial samples used as received.

Apart from a few experiments using infrared spectrophotometry, most kinetic studies were carried out in a thermostatted (30 °C), two-legged, modified Warburg apparatus that was equipped with a two way tap to permit degassing and flushing with oxygen-free nitrogen and a side arm housing a pressure transducer (R.S. Components Ltd., Type 303–337). The transducer response (mV), recorded on a chart recorder (Servoscribe 1S) or using a digital voltmeter and calibrated against a mercury manometer, was linear over the range of pressures generated during reaction. For a kinetic experiment, DMSO solutions of the diazo-compound and, where appropriate, other additives were syringed into one of the legs, the base solution in DMSO into the other. Using fixed volumes of reaction solutions, the pressure changes recorded corresponded closely with expectation based on the yield of azine when reaction was complete.

References

1 F. M. Beringer, J. A. Farr and S. Sands, *J. Am. Chem. Soc.*, 1953, **75**, 3984.
2 R. N. McDonald and K.-W. Lin, *J. Am. Chem. Soc.*, 1978, **100**, 8028.
3 H. Staudinger and J. Meyer, *Helv. Chim. Acta.*, 1919, **2**, 619,635; D. Bethell, S. F. C. Dunn, M. M. Khodaei and A. R. Newall, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1829; D. Bethell, M. P. Brown, M. M. Harding, C. A. Herbert, M. M. Khodaei, M. I. Rios and K. Woolstencroft, *Acta Crystallogr., Sect. B*, 1992, **48**, 683; D. Bethell, R. Bourne and M. Kazlan, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2081.
4 J. M. Bakke, D. Bethell, P. J. Galsworthy, K. L. Handoo and D. Jackson, *J. Chem. Soc., Chem. Commun.*, 1979, 890.
5 K. L. Handoo, K. Gadru and C. K. Jain, *Indian J. Chem., Sect. A*, 1983, **22B**, 526.
6 R. N. McDonald, K. J. Borhani and M. D. Hawley, *J. Am. Chem. Soc.*, 1978, **100**, 995, but see V. D. Parker and D. Bethell, *Acta Chem. Scand. Ser. B*, 1981, **B35**, 691 for an alternative interpretation of the electrochemistry.
7 See for example, M. Chanon and M. L. Tobe, *Angew. Chem. Int. Ed. Engl.*, 1982, **21**, 1.
8 (*a*) D. Bethell, L. J. McDowall and V. D. Parker, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1531; (*b*) D. Bethell, P. J. Galsworthy, K. L. Handoo and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 1980, 534; (*c*) D. Bethell and V. D. Parker, *J. Am. Chem. Soc.*, 1986, **108**, 895.
9 D. Bethell, L. J. McDowall and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 1984, 308.
10 D. Bethell and L. J. McDowall, *J. Chem. Soc., Chem. Commun.*, 1984, 1408.
11 W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum and N. R. Vanier, *J. Am. Chem. Soc.*, 1978, **97**, 7006.
12 F. G. Bordwell, G. E. Drucker and G. J. McCollum, *J. Org. Chem.*, 1982, **47**, 2504.
13 F. G. Bordwell, M. Van Der Puy and N. R. Vanier, *J. Org. Chem.*, 1976, **41**, 1885.
14 See Y. P. Kitaev, V. K. Ivanova, A. S. Mukhtarov and L. N. Orlova, *New Research on the Electrochemistry of Organic Compounds*, 8th All-Union Conference on the Electrochemistry of Organic Compounds, ed. L. G. Feoktistov, Zinatne, Riga, 1973, p. 168; Y. P. Kitaev, V. K. Ivanova, A. S. Mukhtarov, L. N. Orlova and A. Ladygin, *Akad. Nauk SSSR, Ser. Khim.*, 1974, **1**, 72.
15 K. M. White, PhD Thesis, Liverpool University, 1982.
16 F. G. Bordwell and M. J. Bausch, *J. Am. Chem. Soc.*, 1986, **108**, 1979.

17 J. E. Packer and R. L. Willson, *J. Chem. Soc., Chem. Commun.*, 1983, 733; J. E. Packer and R. L. Willson, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1415.

18 L. Eberson, *Acta Chem. Scand. Ser B*, 1982, **B36**, 533; L. Eberson, *Acta Chem. Scand. Ser. B*, 1984, **B38**, 439; L. Eberson, *Adv. Phys. Org. Chem.*, 1982, **18**, 79; L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer Verlag, Heidelberg, 1987.

19 D. T. Sawyer and J. L. Roberts, *Acc. Chem. Res.*, 1988, **21**, 469.

20 K. Djaasberg, S. R. Knudsen, K. N. Sonnichsen, A. R. Andrade and S. U. Pedersen, *Acta Chem. Scand.*, 1999, **53**, 938.

21 See, for example, S. M. Mattar and D. Sutherland, *J. Phys. Chem.*, 1991, **95**, 5129; J. M. Robinson, E. T. Flynn, T. L. McMahan, S. L. Simpson, J. C. Trisler and K. B. Conn, *J. Org. Chem.*, 1991, **56**, 6709; W. Y. Zhao and Y. C. Liu, *Acta Chim. Sinica.*, 1991, **49**, 1028; R. Bacaloglu, A. Blasko, C. A. Bunton, F. Ortega and C. Zucco, *J. Am. Chem. Soc.*, 1991, **113**, 238; R. Bacaloglu, A. Blasko, C. A. Bunton, F. Ortega and C. Zucco, *J. Am. Chem. Soc.*, 1992, **114**, 7708.

22 For a review of electrochemically generated bases including dianions, see J. H. P. Utley, *Topics in Current Chemistry*, Springer Verlag, Heidelberg, 1987, vol. 142, p. 133; J. H. P. Utley and M. F. Nielsen, in *Organic Electrochemistry*, 4th edn., ed. H. Lund and O. Hammerich, Marcel Dekker, New York, 2000, p. 1227.

23 H. Staudinger and O. Kupfer, *Chem. Ber.*, 1911, **44**, 2197.

24 S. Cohen, F. Cohen and C. Wang, *J. Org. Chem.*, 1963, **28**, 1479.

25 A. Kliegl, *Chem. Ber.*, 1929, **62**, 1327.