

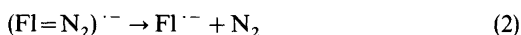
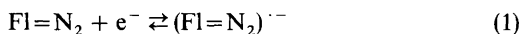
## On the Question of the Intermediate Formation of Carbene Anion Radicals during Cathodic Reduction of 9-Diazofluorene

VERNON D. PARKER<sup>a</sup> and DONALD BETHELL<sup>b</sup>

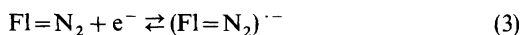
<sup>a</sup>Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway and <sup>b</sup>The Robert Robinson Laboratories, The University, P.O. Box 147, Liverpool L69 3BX, England

On the basis of low temperature cyclic voltammetry, we have recently concluded that the first observable intermediate during the electrochemical reduction of 9-diazofluorene results from the dimerization of the initially formed anion radicals.<sup>1</sup> Another intermediate, which had previously been suggested to be the fluorenylidene anion radical<sup>2,3</sup> was proposed to be the *cis*-azine in various oxidation states. We now report preliminary results of a kinetic study which support the dimerization mechanism previously proposed<sup>1</sup> and clearly rule out the intervention of fluorenylidene anion radical in the electrochemical synthesis of fluorenone azine.

Rate determining loss of nitrogen from the 9-diazofluorene anion radical (eqns. 1 and 2) is an example of an EC mechanism. The linear sweep voltammetric (LSV) wave for this mechanism is characterized



by the slopes,  $dE^p/d \log v = 29.6$  and  $dE^p/d \log C^\circ = 0$  mV/decade at 298 K, where  $E^p$  is the peak potential,  $v$  the sweep rate and  $C^\circ$  the concentration of the substrate.<sup>4</sup> On the other hand, dimerization of the diazofluorene anion radical is an example of the EC(dim) mechanism for which both the slopes are equal to 19.7 mV/decade at 298 K. Thus,



LSV offers a clear-cut distinction between the two mechanistic proposals, carbene anion radical<sup>2,3</sup> *contra* anion radical dimerization.

Attempts to conduct an LSV mechanistic analysis of the reduction of  $\text{Fl}=\text{N}_2$  in *N,N*-dimethylformamide (DMF) were inconclusive due to variations in the response, presumably due to filming on the electrode. Electrode potential measurements were found to be reproducible in acetonitrile (AN). Since the details of the cyclic voltammetric behaviour of  $\text{Fl}=\text{N}_2$  in AN have not been reported, it was necessary to verify that the electrode reaction is the same as in DMF. Cyclic voltammograms in AN at a platinum electrode were similar to those observed in DMF with the exception that a peak due to what we believe to be the *cis*-azine anion radical oxidation was not observed. The steady state voltammogram indicates that fluorenone azine is formed in high yield. That the oxidation peaks,  $O_1$  and  $O_2$ , are due to reactions of azine anion radical and dianion, respectively, was shown by a direct comparison. At  $-30^\circ\text{C}$ , the voltammogram for the reduction of 9-diazofluorene in acetonitrile is very similar to that reported earlier<sup>1</sup> for the low temperature reduction in DMF. Thus, the solvent change does not significantly affect the nature of the electrode process.

Results of an LSV study of the reduction of 9-diazofluorene in acetonitrile- $\text{Bu}_4\text{NBF}_4$  at  $23^\circ\text{C}$  are summarized in Table 1. The peak potential measurements were made by derivative cyclic voltammetry which has recently been shown to give a high degree of precision in peak potential measurements.<sup>5,6</sup> Each electrode potential is the mean value of 15 replicate determinations and standard deviations were in general about  $\pm 0.1$  mV. Because of the very high precision in the measurements, it was possible to obtain accurate values of the slopes using a relatively narrow sweep rate range. Holding  $v$  to values of  $1.0 \text{ V s}^{-1}$  or less avoided complications due to interference of charge transfer kinetics<sup>4</sup> and to uncertainties in the magnitude of the uncompensated resistance.<sup>7</sup> The values of  $dE/d \log v$  and  $dE/d \log C^\circ$ , 20.7 (1.7) and 19.2 (1.4) mV/decade, respectively, are within experimental error of those predicted by theory for the EC(dim) mechanism (eqns. 3 and 4). The fact that the EC mechanism (eqns. 1 and 2), previously proposed by McDonald, Hawley and co-workers,<sup>2,3</sup> predicts independence of substrate concentration is particularly significant and the observed slopes unequivocally rule out that mechanism.

While our data conclusively rule out the EC carbene anion radical mechanism, it does not prove the dimerization mechanism. Mechanism analysis by LSV can only be used to narrow the number of possibilities. What is indicated by our data is that the mechanism has a second order rate determining step. The simplicity of the cyclic

Table 1. Linear sweep voltammetric data for the reduction of 9-diazo fluorene in acetonitrile.<sup>a</sup>

(FIN <sub>2</sub> )/mM	-E <sup>p</sup> /mV				dE/d log v
	0.10 V s <sup>-1</sup>	0.20 V s <sup>-1</sup>	0.40 V s <sup>-1</sup>	1.00 V s <sup>-1</sup>	
0.20	218.0	221.0	227.3	238.2	20.6
0.40	211.4	216.6	222.3	232.4	21.0
0.80	205.1	210.9	218.7	(230.2) <sup>b</sup>	22.6
1.00	203.3	208.3	213.1	222.0	18.5
dE/d log C <sup>c</sup>	-21.0	-17.9	-18.3	-19.6	

<sup>a</sup> Measurements made at a platinum electrode at 23 °C with a supporting electrolyte (Bu<sub>4</sub>NBF<sub>4</sub>) concentration of 0.1 M. The analogue response was differentiated with a PAR model 189 selective amplifier<sup>5</sup> before conversion to digital form and processing with an on line computer. Measurement precision was better than ± 0.2 mV in the peak potentials. The E<sup>p</sup> values are the mean of 15 determinations and are referred to a bias setting of -1.50 V vs. an Ag/Ag<sup>+</sup> reference electrode in acetonitrile. <sup>b</sup> This value deviated substantially from the correlation line for the other three points and was not included in determining the slopes.

voltammetric response at low temperatures showed the presence of only one electroactive intermediate which undergoes irreversible oxidation to the fluorenone azine system. (LSV studies in DMF were attempted without success prior to submitting Ref. 1 for publication.) Since the dimerization mechanism is totally consistent with all of the experimental data, we are inclined to accept this mechanism until further definitive kinetic data are available.

*Acknowledgement.* We thank the Royal Norwegian Council for Scientific and Industrial Research for a visiting scientist grant to D.B.

- Bethell, D., Galsworthy, P. J., Handoo, K. L. and Parker, V. D. *J. Chem. Soc. Chem. Commun.* (1980) 534.
- McDonald, R. N., January, J. R., Borhani, K. J. and Hawley, M. D. *J. Am. Chem. Soc.* 99 (1977) 1268.
- McDonald, R. N., Borhani, K. J. and Hawley, M. D. *J. Am. Chem. Soc.* 100 (1978) 995.
- Nadjo, L. and Savéant, J. M. *J. Electroanal. Chem.* 48 (1973) 113.
- Ahlberg, E., Svensmark, B. and Parker, V. D. *Acta Chem. Scand. B* 24 (1980) 53.
- Ahlberg, E. and Parker, V. D. *J. Electroanal. Chem.* 106 (1980) 419.
- Ahlberg, E. and Parker, V. D. *J. Electroanal. Chem.* 107 (1980) 197.

Received July 18, 1980.