Reduction of 9-Diazofluorene at a Platinum Cathode: a Re-examination

By Donald Bethell,* Peter J Galsworthy, and Kishan L Handoo
(*The Robert Robinson Laboratories, The University, P O Box* 147, *Liverpool* L69 3BX)
and Vernon D Parker*
(*Laboratory of Organic Chemistry, Norwegian Institute of Technology, N*-7034, *Trondheim*)

Summary Low temperature cyclic voltammetry shows that the reduction of 9-diazofluorene at a platinum cathode to give fluorenone azine probably does not involve the intermediate formation of a carbene radical anion.

RECENTLY McDonald, Hawley, and their co-workers[1] have presented evidence that the reduction of 9-diazofluorene and diazodiphenylmethane in dimethylformamide (DMF) at a platinum cathode, which leads predominantly to the production of the corresponding symmetrical azines, is a radical anion chain process. On the basis of a cyclic voltammetric investigation they have further proposed that the initially formed diazoalkane radical anion rapidly loses nitrogen in a unimolecular process giving the related carbene radical anion[2] ($R_2C:)^{\bullet -}$, which then either attacks a further molecule of diazoalkane or abstracts a hydrogen atom from the medium. A further proposal is that the carbene radical anion from diazofluorene is stable enough to undergo reversible oxidation and reduction during cyclic voltammetry at modest scan rates (75 mV s^{-1}). We regard the last interpretation as unreasonable in view of what is known about the lifetime of diarylmethylenes in solution; for example, the elegant flash photolytic experiments of Closs and Rabinow[3] show that dimerisation of a series of diarylmethylenes occurs with rate constants close to the diffusion-controlled limit. With this in mind, and in the light of our studies of the chemical reduction of 9-diazofluorenes,[4] we have re-examined the question of carbene radical anion formation in the electrochemical reaction.

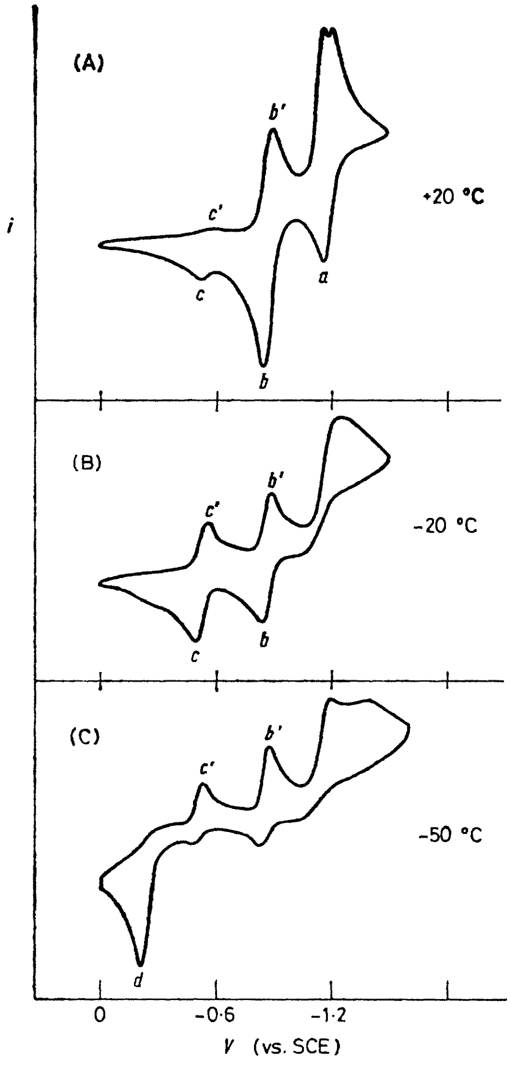
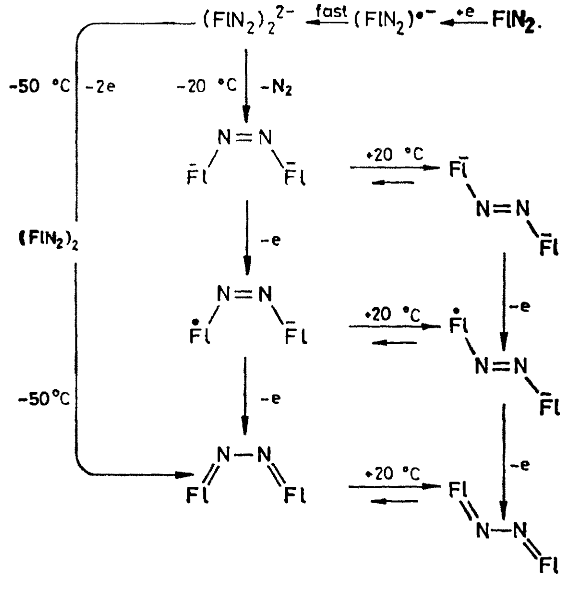


FIGURE. Cyclic voltammograms of 9-diazofluorene (5 mM) in DMF at (A) +20 °C; (B) −20 °C, and (C) −50 °C. [Bu_4NBF_4] = 0·1 M. Voltage sweep rate = 1000 mV s^{-1}.

Cyclic voltammetry of 9-diazofluorene (5 mM) in DMF at 20 °C gave results (see Figure A) identical to those already reported.[1b] However, a closer analysis of the relative currents at the peaks previously assigned[1b] to oxidation of the fluorenone azine dianion (peak *a*), to oxidation of the fluorenone azine anion radical (*b*), and to oxidation of the carbene anion radical (*c*) indicated that the peak current ratios, *a* : *b*, were not 1 : 1, as required by that assignment, but that *b* was significantly greater than *a*. The reason for this discrepancy became apparent when the voltammogram was recorded at −20 °C (Figure B), showing only peaks *b* and *c* in the ratio 1 : 1. Thus the current at peak *b* at the higher temperature is due to two different redox systems, *a* + *b* and *b* + *c*. If *c* were due to the oxidation of the carbene anion radical then, at the lower temperature, *b* would be due only to the oxidation of the carbene dianion. At −50 °C, an irreversible peak (*d*), not hitherto reported, appears as the only oxidation peak on the first cycle and gives rise to reductions corresponding to the redox system, *b* + *c* (Figure C). The current at *d* shows a marked decrease on (i) decreasing the concentration of 9-diazofluorene in the range 5—0·5 mM, and (ii) decreasing the scan rate in the range 1000—100 mV s^{-1}. Increasing the temperature in the range −50 to +20 °C leads, during the oxidation phase of the first cycle, to progressive replacement of *d* by *b* + *c* and finally to the *a* + *b* plus *b* + *c* pattern.

Constant potential electrolysis, at 25 °C, of 9-diazofluorene (5 mM) at 1·3 V [*vs.* standard calomel electrode (SCE)] showed fluorenone azine as the only product. Under the same conditions, electrolysis of a 1 : 1 mixture of diazofluorene and diazodiphenylmethane (which is not directly reduced at this potential) gave no detectable mixed benzophenone fluorenone azine and even when the ratio was



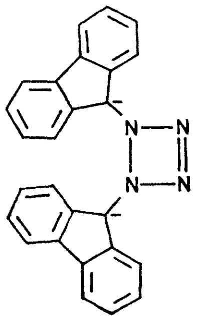
SCHEME. Fl = fluoren-9-yl.

increased to 1:5, the mixed azine was barely detectable by t.l.c. This result contrasts with the formation of substantial amounts of mixed azine which occurs in the carbanion-induced reaction.

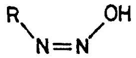
On this basis we tentatively suggest the interpretation shown in the Scheme, the key step of which is the dimerisation of the initially formed 9-diazofluorene radical anion. The dimer is thought to be sufficiently stable at −50 °C to survive until it is re-oxidised (*d*) whereupon it decomposes to the *cisoid*-azine. At −20 °C, nitrogen is lost before the re-oxidation giving the *cis*-azine dianion which is re-oxidised in two one-electron steps ($b + c$).

However, at +20 °C, the *cis*-azine dianion is shorter-lived, undergoing conversion into the *trans*-azine dianion with a half-time of the order of seconds. A *possible* structure of the intermediate dimeric dianion is (**1**), formed by head-to-head dimerization of the initial reduction product. An analogy, relating to the *cis–trans*-conversion, is found in structures (**2**) and (**3**) which are interconverted slowly at −50 °C.[5] Examples of intermediates, thermodynamically unstable with respect to stereochemical isomers, formed during electrode processes have previously been reported.[6]

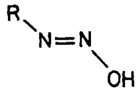
Experiments using 9-diazofluorene, ^{15}N-labelled at N$^{\alpha}$, showed that on constant potential electrolysis at room temperature the azine formed was mainly monolabelled, but $(8 \pm 4)\%$ of the material contained two ^{15}N atoms. This is consistent with the initial electrochemical generation of dimers of structure (**1**) yielding the doubly labelled azine dianion, which then initiates the homogeneous chain decomposition of diazofluorene, previously described,[1] a process known[4] to lead to the singly labelled product. The reaction product from preparative electrolysis is formed predominantly by this latter process while on the time scale of cyclic voltammetry the reaction proceeds *via* the dimer.



(1)



(2)



(3)

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[1] (a) R. N. McDonald, J. R. January, K. J. Borhani, and M. D. Hawley, *J. Am. Chem. Soc.*, 1977, **99**, 1268; (b) R. N. McDonald, K. J. Borhani, and M. D. Hawley, *ibid.*, 1978, **100**, 995; (c) R. N. McDonald and K.-W. Lin, *ibid.*, 1978, **100**, 8028.

[2] G. D. Sargent, C. M. Tatum, and R. P. Scott, *J. Am. Chem. Soc.*, 1974, **96**, 1602.

[3] G. L. Closs and B. E. Rabinow, *J. Am. Chem. Soc.*, 1976, **98**, 8190.

[4] J. M. Bakke, D. Bethell, P. J. Galsworthy, K. L. Handoo, and D. Jackson, *J. Chem. Soc., Chem. Commun.*, 1979, 890.

[5] R. A. Moss, *Acc. Chem. Res.*, 1974, **7**, 421.

[6] V. D. Parker, *Pure Appl. Chem.*, 1979, **51**, 1021; B. S. Jensen, R. Lines, P. Pagsberg, and V. D. Parker, *Acta Chem. Scand., Ser. B*, 1977, **31**, 707; R. Dietz and M. E. Peover, *Discuss. Faraday Soc.*, 1968, **45**, 154; R. D. Rieke, H. Kojima, and K. Ofele, *J. Am. Chem. Soc.*, 1976, **98**, 6735.

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