Does Nitrogen Elimination follow One-electron Reduction of Diazofluorene? A Radiation Chemical Study

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Rapid nitrogen elimination on one-electron reduction of 9-diazofluorene, FlN_2, does not occur, and the parent radical anion, $FlN_2{\cdot}^-$, can undergo electron transfer reactions.

Recently there has been disagreement in the literature on the lifetime and fate of the electron adducts of the diazoalkanes, diazodiphenylmethane and 9-diazofluorene (FlN_2), produced electrochemically in aprotic solvents. McDonald, Hawley, and co-workers maintain that the electron adduct undergoes unimolecular loss of nitrogen to give the corresponding carbene radical anion too fast for it to be reoxidised on the return sweep in cyclic voltammetry and that subsequently observed reactions have the carbene radical anion as precursor.[1–6] In contrast, Bethell and Parker believe that the parent electron adduct does not lose nitrogen rapidly and is sufficiently long-lived to participate in further chemical and electrochemical events.[7–9]

We have now studied the one-electron reduction of 9-diazofluorene (FlN_2) in 3 : 2 : 1 v/v water–propan-2-ol–acetone solvent mixture by pulse and ^{60}Co-γ radiolysis. Radiolysis of this solvent system under nitrogen results in the formation of the radicals $Me_2\dot{C}OH$ at neutral pH and its conjugate base $Me_2\dot{C}O^-$ at high pH, both of which are strong one-electron reducing agents.[10] Figure 1 shows the electronic spectra of the transient species produced in 2.5×10^{-3} M FlN_2 solutions following a 0.2 μs pulse of 4 MeV electrons[10] delivering a dose of 10 J dm^{-3} under neutral conditions and in the presence of 0.1 M sodium hydroxide. The rate constants for the formation of these species measured by following their rate of grow-in were 4.6×10^8 and 6.2×10^8 dm^3 mol^{-1} s^{-1} in neutral and alkaline solution respectively. At intermediate hydroxide ion concentrations contributions to the observed spectra from both species are evident, and it is concluded the species are an acid–base conjugate pair with pK_a *ca.* 11.

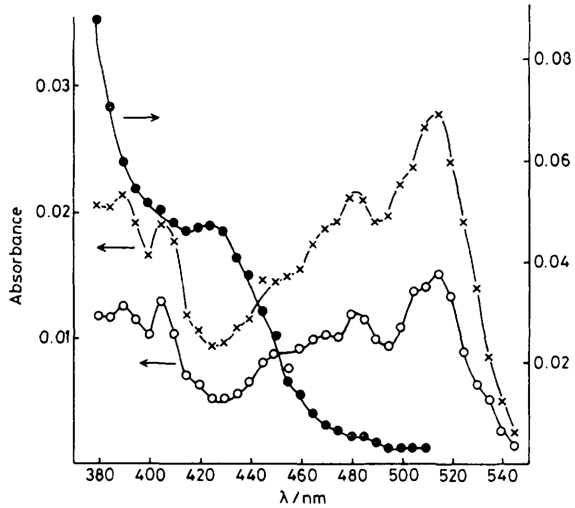
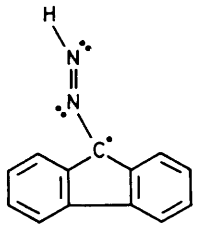


Figure 1. The electronic spectra of products detected in a 1.5 cm cell following a 10 J dm^{-3} pulse of 4 MeV electrons to a solution of 2.5×10^{-3} M diazofluorene in 3 : 2 : 1 v/v water–propan-2-ol–acetone under an atmosphere of nitrogen. Neutral solution × after 10 μs, ○ after 400 μs; 0.1 M NaOH solution ● after 10 μs and 400 μs. Arrows indicate which scale of absorbance to apply.

The radical formed in neutral solution decayed by second-order kinetics, with $2k = 3.7 \times 10^8$ dm^3 mol^{-1} s^{-1}, while that in alkaline solution was completely stable over 400 μs. The presence of a small amount of oxygen had no effect on the decay of the radical in neutral solution, but it caused the



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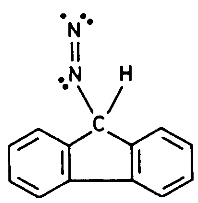

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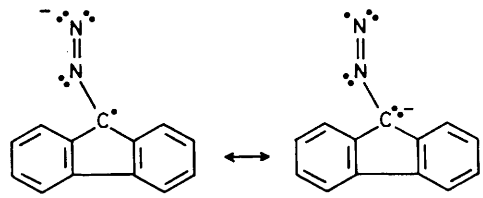

(3)

species in alkaline solution to decay completely in a few microseconds. The species in alkaline solution also transferred an electron to *p*-nitroacetophenone to give the electron adduct of the latter[10] with a rate constant of 4.3×10^8 dm^3 mol^{-1} s^{-1}.

Although the electronic spectrum of the transient species in neutral solution is similar to that of the 9-fluorenyl radical recently reported,[11] that we are not observing the 9-fluorenyl radical in neutral pH, and its conjugate base, the carbene radical anion, in alkaline solution is shown by ^{60}Co-γ radiation studies. When 1×10^{-3} M FlN_2 in alkaline solution is irradiated under nitrogen for 30 min at a dose rate of 0.34 J dm^{-3} s^{-1}, over 65% of the FlN_2 is lost (implying more than one FlN_2 molecule reacts per $Me_2\dot{C}O^-$ radical) and there is spectral evidence for a new product. However when the experiment is repeated under the same irradiation conditions but while a 95:5 v/v N_2–O_2 gas mixture is bubbled gently through the solution no loss of FlN_2 occurs, the spectrum of the solution after irradiation being identical with that before. This means that the long-lived species observed on pulse radiolysis regenerates FlN_2 on electron transfer to oxygen, and therefore has not undergone fast unimolecular elimination of nitrogen, in agreement with the interpretations of Bethell and Parker.

In view of the similarity in the spectrum of our transient species in neutral solution to that of the 9-fluorenyl radical we suggest that its structure is that shown in (**1**), with little delocalisation of charge on to the nitrogens, rather than that of its tautomer, (**2**). This is in agreement with the views of McDonald and Hawley for diazodiphenylmethane who claim from their electrochemical evidence that $Ph_2CN_2^{\bullet -}$ can protonate on the terminal nitrogen rather than on carbon prior to nitrogen elimination.[4] The long-lived radical we detect in alkaline solution must be (**3**), the conjugate base of (**1**), and not the carbene radical anion.

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