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Oxidation and Reduction of Diazofluorene. A Pulse-radiolysis Study

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In neutral solution the radical $Me_2\dot{C}OH$ reduces diazofluorene (FlN_2) to $FlN_2H\cdot$ with k 4.6 × 10^8 dm^3 mol^{-1} s^{-1} and this *N*-protonated radical (ϵ 3 850 dm^3 mol^{-1} cm^{-1}) decays in a second-order reaction with $2k$ 3.7 × 10^8 dm^3 mol^{-1} s^{-1}. $FlN_2H\cdot$ does not react with oxygen. In the presence of NaOH $FlN_2^{-\bullet}$ is formed and this radical is long lived but rapidly transfers an electron to oxygen and to *p*-nitroacetophenone. Trichloromethylperoxyl, $Cl_3COO\cdot$, oxidises FlN_2 with k 1.2 × 10^7 dm^3 mol^{-1} s^{-1}.

Diazoalkanes and diazonium ions are reactive species which have been widely used as sources of reactive intermediates such as carbenes, radicals, and carbocations.[1] Many years ago free radical chain mechanisms were postulated for the reactions of arenediazonium ions with phosphites[2] and alcohols[3] which result in the replacement of the diazo group by hydrogen (hydrodediazoniation), and direct evidence for radical involvement came somewhat later from e.s.r. studies.[4] The first really quantitative measurements on these chain reactions came from radiation studies, as radiolysis provides a simple way of initiating the reactions at a known rate.[5] Details of kinetic chain lengths, the nature of propagation and termination steps, and the effects of substituent groups were obtained together with the values of some rate constant ratios. Some absolute rate constants for the one-electron reduction of the diazonium ions were measured using the technique of pulse radiolysis.[6]

Much more recently it has been reported that radical-ion chain reactions can occur on one-electron reduction or oxidation of diazoalkanes in aprotic solvents. From chemical[7] and electrochemical[8] studies of 9-diazofluorene (FlN_2), reactions (1) and (2) were postulated to account for high yields of difluoren-9-ylidenehydrazine (fluorenone azine) obtained, and from the

$$\mathrm{FlN_2^{-\bullet} + FlN_2 \longrightarrow FlNNFl^{-\bullet} + N_2} \tag{1}$$

$$\mathrm{FlNNFl^{-\bullet} + FlN_2 \longrightarrow FlN\text{-}NFl + FlN_2^{-\bullet}} \tag{2}$$

electrochemical studies the rate of loss of the electron adduct $FlN_2^{-\bullet}$ was found to be second order in $FlN_2^{-\bullet}$ with a rate constant *ca.* 10^5 dm^3 mol^{-1} s^{-1}, the actual value varying with supporting electrolyte. An analogous reaction has been postulated for electrochemical reduction of diazodiphenylmethane, but here the chain length is much shorter as a chain-terminating reaction involving hydrogen abstraction by $Ph_2CN_2^{-\bullet}$ from acetonitrile solvent also occurs.[9] It has been reported that addition of a proton donor in electrochemical reductions of FlN_2 and Ph_2CN_2 lowers the yield of the azine with the corresponding ketone hydrazone becoming a significant product.[10]

A rather similar reaction sequence, (3) and (4), is postulated to account for azine formation following chemical one-electron oxidation of diazodiphenylmethane.[11]

$$\mathrm{Ph_2CN_2^{+\bullet} + Ph_2CN_2 \longrightarrow Ph_2CNNCPh_2^{+\bullet} + N_2} \tag{3}$$

$$\mathrm{Ph_2CNNCPh_2^{+\bullet} + Ph_2CN_2 \longrightarrow Ph_2C{=}N\text{-}N{=}CPh_2 + Ph_2CN_2^{+\bullet}} \tag{4}$$

We have initiated a study of the radiation chemistry of these diazoalkanes, and in this paper we report the results of a pulse radiolysis study of diazofluorene. One conclusion from this study has already been reported.[12]

On radiolysis of water, $HO\cdot$ and e_{aq}^- radicals are produced, and these species have often been used to carry out one-electron oxidation or reduction of substrates in pulse radiolysis experiments. This simple approach is not possible with diazofluorene because this compound is not soluble in water. We have shown recently that one-electron oxidation of a number of water-insoluble but alcohol-soluble compounds of biological significance, such as α-tocopherol, occurs when an aqueous solution containing propan-2-ol, acetone, carbon tetrachloride, and air are pulse irradiated.[13] The oxidising radical trichloromethylperoxyl, is formed by reactions (5)—(10)

$$\mathrm{H_2O \longrightarrow HO\cdot + e_{aq}^-} \tag{5}$$

$$\mathrm{HO\cdot + Me_2CHOH \longrightarrow H_2O + Me_2\dot{C}OH} \tag{6}$$

$$\mathrm{e_{aq}^- + Me_2CO \longrightarrow Me_2CO^{-\bullet}} \tag{7}$$

$$\mathrm{Me_2CO^{-\bullet} + H_2O \longrightarrow Me_2\dot{C}OH + OH^-} \tag{8}$$

$$\mathrm{Me_2\dot{C}OH + CCl_4 \longrightarrow Me_2CO + H^+ + Cl^- + Cl_3C\cdot} \tag{9}$$

$$\mathrm{Cl_3C\cdot + O_2 \longrightarrow Cl_3COO\cdot} \tag{10}$$

and this oxidises the substrate, allowing detection of the product formed. In the absence of carbon tetrachloride and oxygen, $Me_2\dot{C}OH$ can directly reduce the substrate of interest.[14] A solvent containing 3:2:1 v/v water–propan-2-ol–acetone has been used for all experiments reported in this paper.

Experimental

Pulse-radiolysis experiments were done on the Brunel University 4 MeV linear accelerator with associated equipment for kinetic spectroscopy and computer analysis.[14] 0.2 μs pulses producing doses in the range 5—20 J kg^{-1} (Gy) (0.5—2 krad) in a 1.5 cm optical path-length cell were used. Dosimetry was carried out by simultaneously measuring the absorbance at 500 nm due to $(SCN)_2^{-\bullet}$ produced in an aerated 0.01M-KSCN solution, taking $\Gamma\varepsilon$ 2.12 × 10^{-4} m^2 J^{-1}, and the charge collected on a plate behind the cell.

The diazofluorene was given to us by Dr. D. Bethell. In all experiments the solvent was 3:2:1 v/v water (doubly distilled or Millipore filtered)–propan-2-ol–acetone (B.D.H. AnalaR). CCl_4 was B.D.H. (AnalaR) and benzoquinone was freshly sublimed. The pH was controlled with analytical grade sodium

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hydroxide. Solutions were saturated with nitrogen (British Oxygen Ltd.) using the syringe-bubbling technique,[15] or with air. All measurements were carried out at room temperature.

Results

Oxidation.—Diazofluorene absorbs strongly at wavelengths below 365 nm, limiting detection of transient species to wavelengths longer than this. When an air-saturated solution containing 0.1M-CCl_4 and 5×10^{-4}M-FlN_2 was pulsed only a very weak absorption at 370 nm was detected. In the absence of an easily detectable transient intermediate we looked for a possible reaction between $Cl_3COO\cdot$ and FlN_2 using a competition technique. We have shown recently that the anion 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) is readily oxidised by a number of radicals including $Cl_3COO\cdot$ to give a long lived radical product with a molar absorptivity of 36,000 $dm^3\ mol^{-1}\ cm^{-1}$ at 415 nm, and that this compound is an excellent marker for pulse-radiolysis studies.[16] Figure 1 shows the results of increasing the concentration of FlN_2 on the absorbance at 415 nm following pulse radiolysis of an air-saturated solution containing 0.1M-CCl_4 and 5×10^{-5}M-ABTS. Increasing FlN_2 lowered the absorption. No slower grow-in or decay of the $ABTS^{+\cdot}$ radical due to possible electron transfer from ABTS to the oxidation product of FlN_2, or from FlN_2 to $ABTS^{+\cdot}$, was detectable. By monitoring the rate of growth of $ABTS^{+\cdot}$ in the absence of FlN_2 the rate constant of reaction (11) was found to be $1.2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ for this

$$Cl_3COO\cdot + ABTS \longrightarrow Cl_3COO\cdot^{-\cdot} + ABTS^{+\cdot} \quad (11)$$

solvent composition. The slope of the plot $A°/A$ against $[FlN_2]/[ABTS]$ shown in Figure 1 is 0.01, from which we obtain a value of $1.2 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ for k_{12}. All our studies[13,17] on the reactions of $Cl_3COO\cdot$ indicated that it oxidises by an electron-transfer mechanism and we assume the initial product is $FlN_2^{+\cdot}$.

$$Cl_3COO\cdot + FlN_2 \longrightarrow \text{Products} \quad (12)$$

Reduction.—On pulsing a neutral nitrogen-saturated solution containing 2.5×10^{-3}M FlN_2 strong absorptions at wavelengths >370 nm were observed, and the spectrum of the transient product 10 µs after the pulse is shown in Figure 2. A rapid grow-in to give a maximum absorption at *ca.* 10 µs was followed by a slower decay which was *ca.* 40% complete after 400 µs. The kinetics of both growth and decay were followed at 510 nm. The grow-in was exponential with the observed first-order rate constant being proportional to the FlN_2 concentration. From the slope of plot (a) of Figure 3, k^1 against FlN_2 concentration, the rate constant for the reduction of FlN_2 by the propan-2-ol radical was found to be $4.6 \times 10^8\ dm^3\ mol^{-1}$

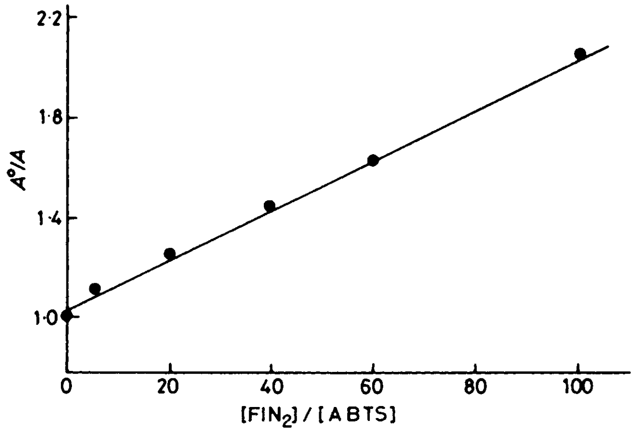


Figure 1. Competition plot showing the effect of increasing diazofluorene concentration on the absorbance at 415 nm due to $ABTS^{+\cdot}$ formed by the reaction of ABTS with $Cl_3COO\cdot$: [ABTS] 5×10^{-5}M (see text)

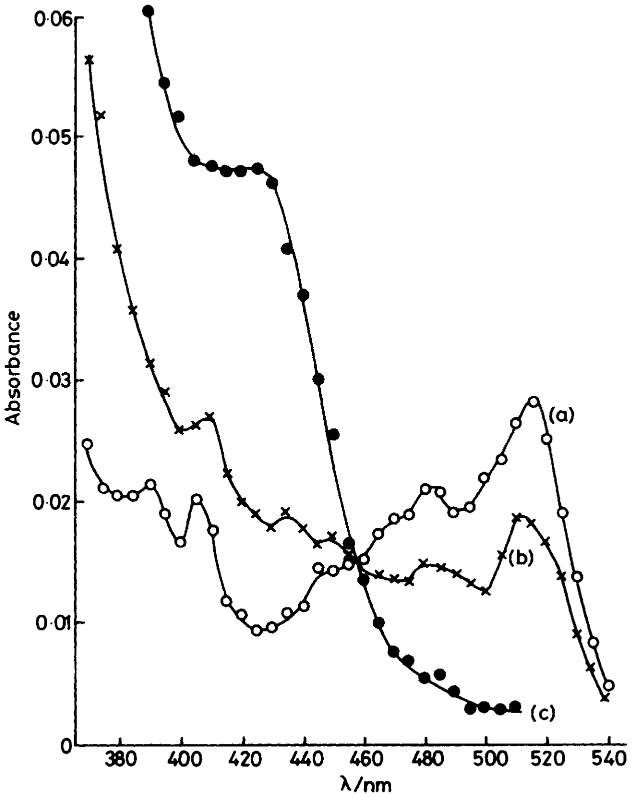


Figure 2. Optical absorption spectra of transient species 10 µs after a 10 Gy pulse for nitrogen-saturated 2.5×10^{-3}M-diazofluorene: (a) neutral solution, ○; (b) 4×10^{-3}M-NaOH, ×; (c) 0.1M-NaOH, ●

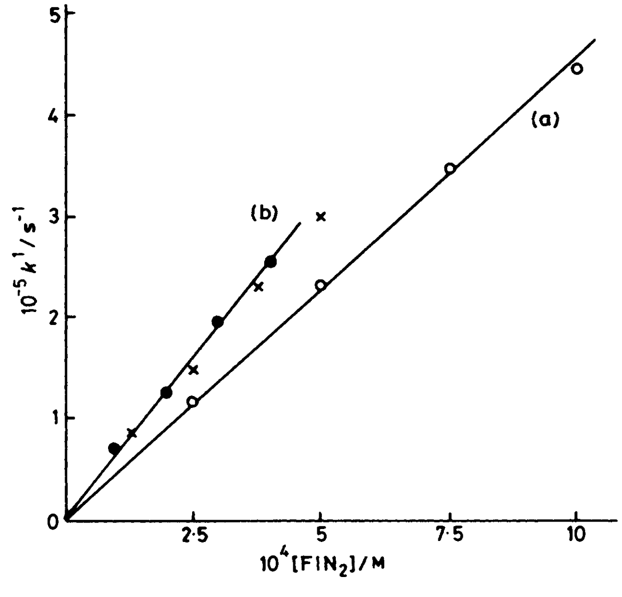
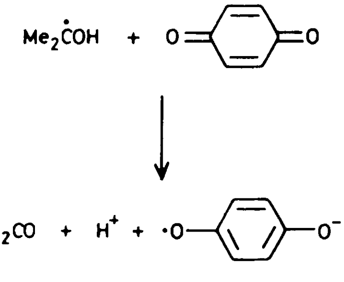


Figure 3. Plots of first-order rate constants for formation of absorption at 510 nm against diazofluorene concentration for nitrogen-saturated solution. Neutral solution, ○; 4×10^{-3}M-NaOH, ×; 0.1M-NaOH, ●

s^{-1}. The decay followed simple second-order kinetics, with the half-life increasing with decreasing dose per pulse. From the slopes of plots of $1/A$ against time for doses of 9 and 20 Gy, $2k/\varepsilon$ was found to be 9.60×10^3 cm s^{-1}, where ε is the molar absorptivity of the transient species at 510 nm. The value of ε can be determined in principle if the yield of $Me_2\dot{C}OH$ radicals, $\Gamma(Me_2\dot{C}OH)$, is known and all these radicals are scavenged by FlN_2. We determined $\Gamma(Me_2\dot{C}OH)$ by measuring the absorbance at 430 nm due to the benzosemiquinone radical anion ($BQ^{-\bullet}$) following a 10 Gy pulse of a nitrogen-saturated solution containing 1×10^{-3}M-benzoquinone. Reaction (13) is fast.[18] Using the published value[19] of $\varepsilon_{BQ^{-\bullet}}^{430nm}$ of 7 300 dm^3 mol^{-1} cm^{-1} $\Gamma(Me_2\dot{C}OH)$ was found to be 4.6×10^{-7} mol J^{-1}. This figure is very close to that determined from measuring the absorbance due to the ascorbate radical-anion produced by the oxidation of ascorbic acid by $Cl_3COO\bullet$ in aerated water–propan-2-ol–acetone solutions containing CCl_4 and ascorbic acid.[17] From this measured yield of $Me_2\dot{C}OH$, the molar absorptivity of the reduced diazofluorene transient species at 510 nm was 3 853 dm^3 mol^{-1} cm^{-1}, and hence $2k$ for the second-order decay of the transient was 3.7×10^8 dm^3 mol^{-1} s^{-1}.

When the pH of the solutions were raised by adding sodium hydroxide, the spectrum of the transient species changed. Figure 2 also shows the spectra obtained from solutions containing 4×10^{-3}M-NaOH, (b), and 0.1M-NaOH, (c). The species produced in 0.1M-NaOH was long lived, showing almost no decay over 400 μs. However, the mixed spectrum obtained at 4×10^{-3}M-NaOH did decay appreciably over 400 μs. Figure 4 shows the change in the maximum absorbance at 430 and 510 nm following a 10 Gy pulse as a function of sodium hydroxide concentration. From this plot it can be deduced that the transient formed in neutral solution is a weak acid with a pK_a of *ca.* 11—12. Figure 3 also shows the observed first-order constants for the grow-in at 510 nm in 4×10^{-3}M-NaOH solution and at 430 nm for 0.1M-NaOH solution. In water the pK_a of $Me_2\dot{C}OH$[20] is 12.1, and therefore at high concentration of NaOH the reducing radical is its conjugate base $Me_2CO^{-\bullet}$, the electron adduct of acetone. From the slope of plot (b) the second-order rate constant for the reduction of FlN_2 by $Me_2CO^{-\bullet}$ is 6.1×10^8 dm^3 mol^{-1} s^{-1}.



(13)

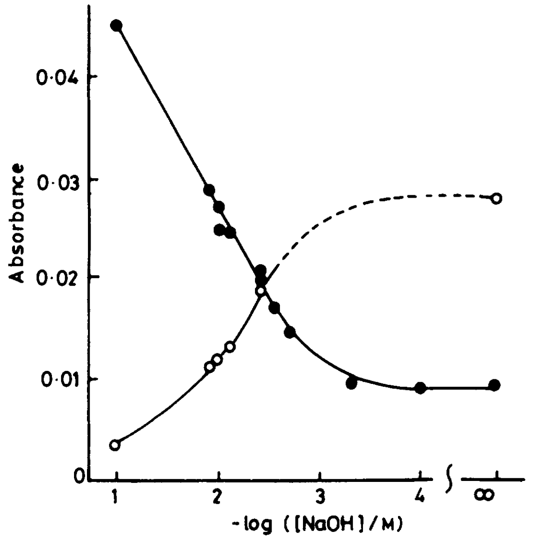


Figure 4. Maximum absorbance after a 10 Gy pulse of nitrogen-saturated 10^{-3}M-diazofluorene as a function of sodium hydroxide concentration: ●, 430 nm; ○, 510 nm

When air was admitted to the system under neutral conditions the yield of the transient product was lowered, but its rate of decay was not affected, showing the transient species did not react with oxygen, the decrease in yield being due to competition between O_2 and FlN_2 for $Me_2\dot{C}OH$. Experiments with mixtures of diazofluorene and benzoquinone also showed simple competition between BQ and FlN_2 for $Me_2\dot{C}OH$, but not further reaction between $BQ^{-\bullet}$ and FlN_2 or between BQ and the FlN_2 transient product. Similar experiments were done with mixtures of diazofluorene and *p*-nitroacetophenone (PNAP). The electron adduct of the latter compound is long lived and has an absorption peak at 550 nm, at which wavelength the FlN_2 product does not absorb.[21] Again there was simple competition between PNAP and FlN_2 for the reducing radical, the absorbance at 550 nm decreasing with increasing $[FlN_2]/[PNAP]$, with no evidence for reactions between $PNAP^{-\bullet}$ and FlN_2 or PNAP and the FlN_2 transient product, the absorbance at 550 nm remaining constant over 400 μs.

However, in the presence of 0.1M-NaOH, the absorbance at 430 nm decayed rapidly in the presence of oxygen. On pulsing solutions containing 2.5×10^{-3}M-FlN_2 and (1—10) $\times 10^{-4}$M-PNAP there was an exponential grow-in of $PNAP^{-\bullet}$, and the observed first-order rate constants monitored at 550 nm were proportional to PNAP concentration. From the slope of the plot shown in Figure 5, the second-order rate constant for the electron-transfer reaction from the FlN_2 transient species to PNAP was found to be 4.3×10^8 dm^3 mol^{-1} s^{-1}.

We carried out an experiment to see if the radical produced by reduction of FlN_2 in neutral solution could act as an oxidising agent, *i.e.* could be further reduced. As ABTS is readily oxidised to a radical with a very large molar absorptivity we pulsed a solution containing 2×10^{-3}M-FlN_2 and 5×10^{-4}M-ABTS. No $ABTS^{+\bullet}$ was formed and the rate of decay of

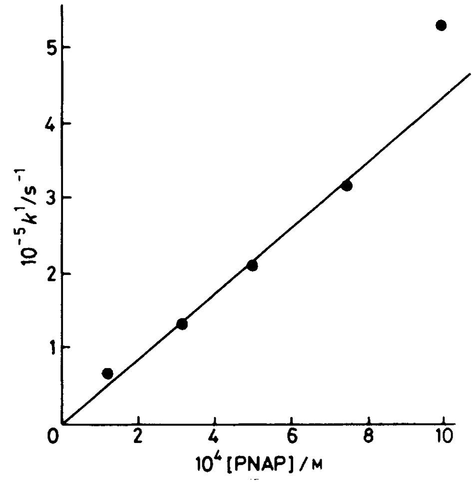


Figure 5. Plot of first-order rate constant for formation of absorbance at 550 nm due to $PNAP^{-\bullet}$ formed by electron transfer from $FlN_2^{-\bullet}$ as a function of *p*-nitroacetophenone concentration for nitrogen-saturated 2.5×10^{-3}M diazofluorene

the FlN_2 radical (followed at 510 nm) was the same as in the absence of ABTS, showing ABTS did not reduce the radical on the time scale of these experiments.

Discussion

At the time of these experiments the literature showed there was some doubt on the lifetime of the election adduct of FlN_2, $FlN_2^{-\bullet}$. Based on chemical and electrochemical experiments one group of workers considered it to be long lived[7,8] and the second group[22,23] considered nitrogen was rapidly lost to produce the fluorene carbene anion radical $Fl^{-\bullet}$. Thus we were uncertain as to whether the transient radicals we were detecting on reduction of FlN_2 were $FlN_2H\cdot$ and $FlN_2^{-\bullet}$ in neutral and alkaline solution respectively or $FlH\cdot$ and $Fl^{-\bullet}$. We have reported that we found a low concentration of oxygen protected FlN_2 on ^{60}Co γ-irradiation at high pH, and how this fact together with our pulse-radiolysis observation that the reduced radical produced at high pH reacts rapidly with oxygen shows conclusively that rapid loss of nitrogen does not occur.[11] After we had submitted that note the second group reported further electrochemical experiments which also now showed that $FlN_2^{-\bullet}$ in fact did not rapidly lose nitrogen.[24] Thus we need not consider the possibility of rapid nitrogen elimination further in this discussion.

At high pH the reduction of FlN_2 must proceed by electron transfer from the electron adduct of acetone to diazofluorene, reaction (14), with k_{14} 6.2×10^8 dm^3 mol^{-1} s^{-1}. Parker and

$$Me_2CO^{-\bullet} + FlN_2 \longrightarrow Me_2CO + FlN_2^{-\bullet} \quad (14)$$

Bethell[8] have measured the rate constant for the dimerisation of $FlN_2^{-\bullet}$ in acetonitrile, and found a value of the order of 1×10^5 dm^3 mol^{-1} s^{-1}, the actual value varying a little with the nature of the supporting electrolyte. If $FlN_2^{-\bullet}$ dimerised with this rate constant in our solvent system, under our pulse conditions where we produce $FlN_2^{-\bullet}$ with an initial concentration of *ca.* 4×10^{-6} mol dm^{-3}, the half-life would be *ca.* 2 s. Thus the fact that we see no decay over 400 μs is not inconsistent with the electrochemical data.

Both Bethell[7,8] and Hawley and McDonald[24] consider a reaction between $FlN_2^{-\bullet}$ and FlN_2 possible, in fact this being a key step in the mechanism of the chain reaction which leads to fluorenone azine. If such a reaction is occurring in our system we must consider three possibilities to explain our results.

(i) It is too slow to observe over 400 μs and therefore must have a rate constant much less than 10^5 dm^3 mol^{-1} s^{-1}.

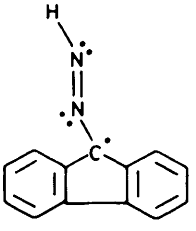
(ii) It is too fast to observe and the spectrum (c) of Figure 2 is not that of $FlN_2^{-\bullet}$ but that of $(FlN_2)_2^{-\bullet}$ the rate constant for reaction (15) being greater than 10^9 dm^3 mol^{-1} s^{-1}.

$$FlN_2^{-\bullet} + FlN_2 \longrightarrow (FlN_2)_2^{-\bullet} \quad (15)$$

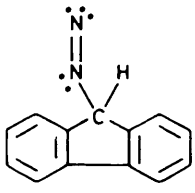
(iii) The reaction between $Me_2\dot{C}O$ and FlN_2 is very fast, $>10^9$ dm^3 mol^{-1} s^{-1}, and the kinetics we are measuring in Figure 3 at high pH are of reaction (15) and not (14).

If either (ii) or (iii) is correct, then $(FlN_2)_2^{-\bullet}$ undergoes electron-transfer reaction to oxygen to give back $2FlN_2$, which is plausible, and the unimolecular decomposition of this species is a slow process with $t_{\frac{1}{2}} \gg 400$ μs. We can rule out the possibility that this unimolecular reaction is so fast that the species we are observing is $FlNNFl^{-\bullet}$ because electron transfer to oxygen from the latter species would not regenerate all the FlN_2.

However, we reject arguments (ii) and (iii) for the following reasons. The spectrum of the transient product in neutral solution, (a) of Figure 2, is very similar to that of the fluorenyl radical,[25] implying it is a carbon-centred radical and therefore (1) rather than its tautomer (2) in agreement with the views of Hawley and McDonald.[10,26] The radical $Me_2\dot{C}OH$ is considered to reduce by an electron-transfer pathway rather than by hydrogen-atom transfer. This means $FlN_2^{-\bullet}$ must be formed first and then undergo rapid protonation. The spectrum (b) of Figure 2 and its decay characteristics imply we are observing a rapidly maintained equilibrium [reaction (16)].



(1)



(2)

$$FlN_2H\cdot + OH^- \rightleftharpoons FlN_2^{-\bullet} + H_2O \quad (16)$$

If $FlN_2^{-\bullet}$ reacted fast with FlN_2, then at intermediate pH values sufficient to give some $FlN_2^{-\bullet}$, reaction (16) would be displaced to the right by reaction (15), and equilibrium would not be maintained during the second-order decay of $FlN_2H\cdot$.

Thus we consider the transient species with spectrum (c) of Figure 2 to be the electron adduct $FlN_2^{-\bullet}$ and that it is k_{14} which has the value 6.2×10^8 dm^3 mol^{-1} s^{-1}.

Hawley and McDonald have shown that the presence of the proton donor diethyl malonate during electroreduction of FlN_2 and Ph_2CN_2 in aprotic solvent leads to some formation of the corresponding ketone hydrazones $Fl{=}NNH_2$, and $Ph_2C{=}NNH_2$, respectively. Fluorenone hydrazone would be the product of disproportionation of $FlN_2H\cdot$ [reaction (17)]. However, in a preliminary experiment involving the ^{60}Co-γ-irradiation of FlN_2 in neutral propan-2-ol–water, we find the spectrum of the products and $\Gamma(FLN_2)$ are consistent with 9,9′-bifluorenyl being the major radiation product.[27]

$$2FlN_2H\cdot \longrightarrow Fl{=}NNH_2 + FlN_2 \quad (17)$$

The fact that we could not detect a reaction between $FlN_2^{-\bullet}$ and FlN_2, either reaction (1) or (15), over 400 μs implies the rate constant must be $<10^5$ dm^3 mol^{-1} s^{-1}. However, even if it is three powers of ten lower than this it could still be the propagating step in the chemically and electrochemically initiated chain reactions postulated by Bethell and Parker and by Hawley and McDonald.

That $FlN_2^{-\bullet}$ transfers an electron to *p*-nitroacetophenone implies $E^\ominus_{FlN_2 | FlN_2^{-\bullet}}$ is < -0.36 V, (NHE), the value of $E^\ominus_{PNAP | PNAP^{-\bullet}}$[14] ($E^\ominus_{O_2 | O_2^-}$ is -0.16 V).

Although Bethell and his co-workers[11] have published extensively on the one-electron oxidation of Ph_2CN_2 no similar experiments on FlN_2 have been reported. It was therefore of interest to see if FlN_2 could be oxidised by oxidising radicals known to be electron-transfer agents. As FlN_2 is water-insoluble $Cl_3COO\cdot$ was perhaps the only radical which could be used. Our competition kinetics results show clearly that FlN_2 is oxidised by this radical, but at a rate considerably lower than that for many other substrates such as for example ascorbate, phenothiazines, and phenolate ions.[17] If the rate of electron transfer is related to the redox potential, $E^\ominus_{FlN_2^{+\bullet} | FlN_2}$ (Marcus theory), onemight have expected $FlN_2^{+\bullet}$ to be reasonably strong oxidising radical and oxidise ABTS.

This clearly did not happen. Further work is required to decide whether this reaction is slow or whether $FlN_2^{+\cdot}$ reacts further with FlN_2 in a fast step.

Acknowledgements

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