

E.S.R. Studies of Diazirine Anion Radicals

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A new class of anion radicals of alkylphenyldiazirines has been prepared and characterized by e.s.r. spectroscopy; the added electron was localized primarily on the two nitrogen atoms of the C-N-N ring.

Diazirines, the cyclic isomers of diazoalkanes, are well-known for their ability to yield carbenes.¹ In contrast, the electrochemical behaviour of diazirine in aprotic solvent has not been reported until recently.² This paper reports the finding of the e.s.r. spectrum of a new class of nitrogen-containing radicals, the anion radicals of diazirines.

The two compounds studied were 3-n-butyl-3-phenyldiazirine³ (**1**) and 3-trifluoromethyl-3-phenyldiazirine⁴ (**2**). The cyclic voltammetric behaviour of (**1**) underwent a one electron reversible reduction at -2.55 V (E_{p_c})² and the cyclic voltammograms of (**2**) demonstrated similar behaviour at -1.94 V (E_{p_c}). The electrode process was diffusion controlled

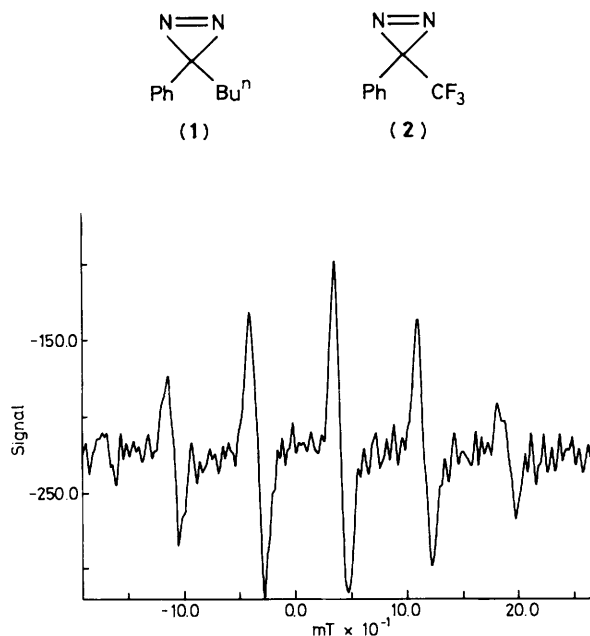


Figure 1. E.s.r. spectrum of 3-n-butyl-3-phenyldiazirine anion radical ($1^{\bullet-}$) at 10 °C in MeCN-Et₄NClO₄ (0.1 M).

and at 16 °C the ratio of the anodic peak current to cathodic peak current was unity for a range of switching potentials and therefore, the reduced form of (2) was assumed to be the anion radical ($2^{\bullet-}$). The difference in cathodic peak potentials between (1) and (2) was approximately -0.6 V, which means that ($2^{\bullet-}$) was a considerably weaker reducing agent than ($1^{\bullet-}$).

Upon initiating controlled potential electrolyses at 8 °C in the same electrolyte mixture, the initially colourless solutions of (1) and (2) quickly turned purple and yellow-brown, respectively. These highly coloured species were assumed to be the anion radicals. Since they persisted in solution for several minutes during the early stages of electrolysis, their e.s.r. spectra were recorded. The e.s.r. spectrometer was a modified Varian E-4, controlled by a PDP11/23 computer and capable of generating a magnetic field⁵ sweep rate of 0.4 mT s⁻¹ over 5 mT. Radicals produced in the water-jacketed electrolysis cell were drawn by vacuum through cooled glass tubing into a Varian E-231 e.s.r. cavity at an estimated temperature of 10 °C. The d.c. magnetic field was quickly swept and the signal recorded and stored in the computer. The spectra of ($1^{\bullet-}$) and ($2^{\bullet-}$) are shown in Figures 1 and 2, respectively.

The spectrum of ($1^{\bullet-}$) demonstrated a simple quintet which confirmed the electrochemical findings that the diazirine ring was retained in the radical. The quintet, therefore, arose from coupling of the added electron to the two equivalent nitrogen atoms ($S = 1$), $a^N = 0.755 \pm 0.001$ mT. The relatively large g value (2.0201) also implied that a large portion of the unpaired spin density resided on the nitrogen atoms; this agreed with Maeda and Ingold's work on diazirinyl radical.⁶ The disappearance of the anion radical caused the deviation of the peak intensity pattern from the theoretical 1:2:3:2:1 pattern. First-order rate constants, calculated from (i) the decrease in the peak to peak height of the line at the highest field compared with the height of the lowest field line of a single spectrum and (ii) the decrease of the integrated peak intensities of the same two lines, were 5.0×10^{-2} and $5.9 \times$

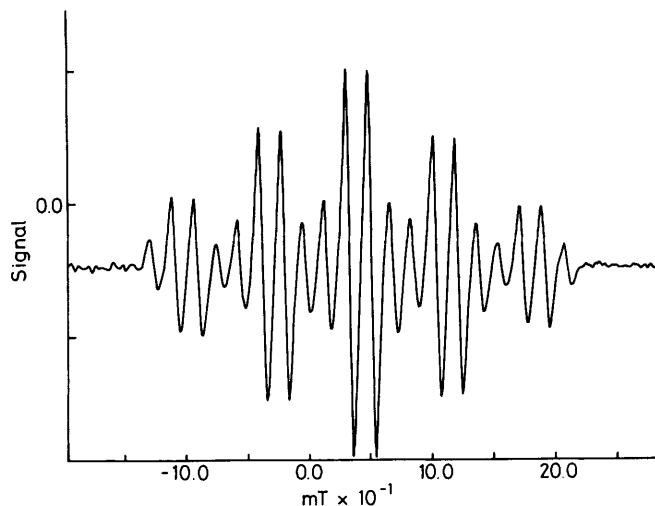


Figure 2. E.s.r. spectrum of 3-trifluoromethyl-3-phenyldiazirine anion radical ($2^{\bullet-}$) at 10 °C in MeCN-Et₄NClO₄ (0.1 M).

10^{-2} s⁻¹ at 10 °C (average $t_{1/2} = 13$ s). These values were consistent with the rate constant determined electrochemically at 16 °C for the reaction of ($1^{\bullet-}$) with the same medium.²

The spectrum of ($2^{\bullet-}$) also revealed a quintet pattern, but each line was further split into quartets. The quintet arose from coupling of the electron with the two equivalent nitrogens in the C-N-N ring, and then the three equivalent fluorines ($S = 1/2$) caused further splitting. This splitting requires a homohyperconjugative mechanism involving the trifluoromethyl radical which is less likely in ($1^{\bullet-}$). The hyperfine coupling constants were $a^N = 0.706 \pm 0.006$ and $a^F = 0.176 \pm 0.006$ mT. The peak intensity pattern closely approached theoretical behaviour: the difference in the average peak to peak heights of the two central lines of the first and fifth quartets was only 8%. For one sample, four spectra were recorded at intervals of one minute and the disappearance of the e.s.r. signal was clearly marked. The average peak to peak height of the central two lines of the four spectra which corresponded to the concentration of ($2^{\bullet-}$) was subjected to kinetic analysis. The data followed a first-order rate law and yielded a rate constant of 1.5×10^{-2} s⁻¹ at 10 °C ($t_{1/2} = 46$ s). These results were consistent with the electrochemical studies, because slow chemical reactions (*i.e.*, $t_{1/2} > 30$ s) that follow the electron transfer step do not cause the cyclic voltammetric behaviour to deviate from reversibility.⁷ The ($2^{\bullet-}$) radical has almost 4 times the half-life in solution of the ($1^{\bullet-}$) species.

The differences between the spectra of ($1^{\bullet-}$) and ($2^{\bullet-}$), apart from divergences in kinetic stability, were attributed to the presence of the three fluorine atoms in (2). The inductive effect of fluorines lowered the hyperfine splitting constants of the nitrogen centres by approximately 0.05 mT. Using the simple relationship, $a^x = Q^x e_x$ where x is the atom of interest, a is the observed splitting constant, Q is the theoretical hyperfine splitting constant ($Q^{FF} = 84.8$ and $Q^N = 2.5$ mT),^{8,9} and e is the unpaired electron spin density on x , the calculated electron density on each nitrogen of ($1^{\bullet-}$) was 0.302 and on ($2^{\bullet-}$) was 0.281. The unpaired electron spin density calculated for each fluorine was only 0.002, hence the change in electron spin density on the nitrogen centres in the presence of fluorines did not correspond to the increased density on the three fluorines. This suggests that the electron distribution has been rearranged in the C-N-N ring. Nevertheless, the

additional electron is localized mainly on the two nitrogens in both compounds in agreement with a simple valence bond picture of the molecules.

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