Electrochemistry of Azobenzene in Dimethylformamide

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IN tetraethylammonium perchlorate (Et_4NClO_4, 0·1M) supporting electrolyte, *trans*-azobenzene reduces in two diffusion-controlled one-electron steps at polarographic half-wave potentials ($E_{\frac{1}{2}}$) of $-1·81$ v and $-2·29$ v [against the $Ag/AgNO_3$ (0·1M), Et_4NClO_4(0·1M) reference electrode]. The first reduction step is reversible and the second step is an irreversible electron-transfer. Coulometric reduction at $-2·0$ v yields a dark red-brown monoanion which gives a reasonably well resolved electron spin resonance spectrum which contains over 200 lines making the measurement and assignment of proton coupling constants virtually impossible without studies on deuterated azobenzenes. The monoanion of fully deuterated azobenzene gives the five line e.s.r. spectrum of an electron interacting with two equivalent nitrogen nuclei with a coupling constant of 4·96 gauss. Further reduction at $-2·8$ v yields a diamagnetic product which is probably a dianion. The colour of the dianion could not be determined due to traces of the intensely coloured monoanion remaining in solution but was either pale yellow or colourless. Both the dianion and the monoanion readily oxidise back to azobenzene in the presence of oxygen.

In potassium perchlorate (0·1M) and sodium perchlorate (0·1M) supporting electrolytes, azobenzene reduces in single one-electron steps at $E_{\frac{1}{2}} = -1·82$ and $-1·80$ v respectively. The second step in each case is obscured by discharge of the supporting electrolyte. The monoanions of the sodium and potassium salts give identical e.s.r. spectra to that of the tetraethylammonium salt.

In lithium chloride (0·1M) or lithium perchlorate (0·1M) supporting electrolytes, azobenzene gives a single two-electron reduction step at $E_{\frac{1}{2}} = -1·77$ v. Controlled-potential reduction at $-2·0$ v produces a colourless product which is very slowly oxidised back to azobenzene with oxygen. The reduction product does not give an e.s.r. spectrum and we assume it to be a dianion. Addition of a greater than ten times excess of lithium ions to the monoanion immediately discharges the intense red–brown colour of the monoanion forming a yellow diamagnetic solution. Reduction of this solution at $-2·0$ v requires approx. one mole of electrons per mole of azobenzene originally present and a colourless product is formed.

The reduction products of azobenzene were studied by ultraviolet and visible spectrophotometry. The spectra were obtained using a quartz e.s.r. aqueous sample cell (path-length 0·35 mm.) sealed into the cell housing of an Unicam SP 500 spectrophotometer. The electrolysis cell was mounted on top of the e.s.r. cell and, by using a mercury reservoir, the e.s.r. cell was filled with mercury to form the cathode in the electrolysis cell. The reservoir was then lowered to bring the reduction products into the e.s.r. cell.

Azobenzene, and its mono- and di-anion show characteristic electronic absorption spectra (Figures 1 and 2). The monoanion, produced in Et_4NClO_4 supporting electrolyte, gives an intense $\pi \rightarrow \pi^*$ transition at $\lambda_{max} = 425$ mμ and weaker bands at $\lambda_{max} = 295$ and 320 mμ. The band at 320 mμ arises from the same electronic transition as the band at 320 mμ observed in azobenzene but is less intense in the monoanion. The dianions, produced in Et_4NClO_4 or lithium salts as supporting electrolytes, exhibit a band at $\lambda_{max} = 295$ mμ and also an intense new band appears at $\lambda_{max} < 260$ mμ. Only a portion of this band can be observed as DMF absorbs strongly below 260 mμ.

The spectra of the dianions are very similar to that of hydrazobenzene in ethanol.[1] Hydrazobenzene gives two bands in the region 220—500 mμ at $\lambda_{max} = 245$ mμ ($\epsilon = 20{,}000$) and $\lambda_{max} = 291$ mμ ($\epsilon = 4{,}000$).

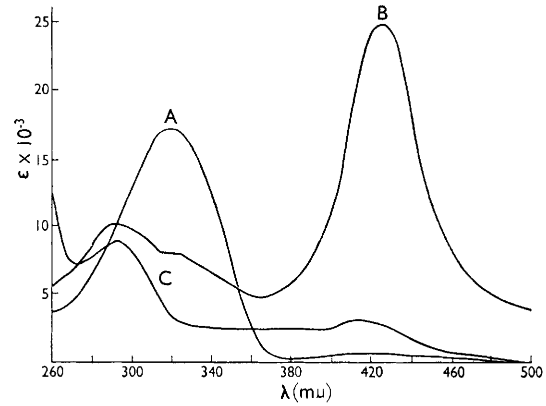

FIGURE 1. *Electronic spectra of azobenzene radical anions in DMF.* (A) *Azobenzene,* (B) *Monoanion in* Et_4NClO_4 *supporting electrolyte,* (C) *Dianion in* Et_4NClO_4 *supporting electrolyte.*

Addition of solid lithium chloride to the monoanion produced in Et_4NClO_4 supporting electrolyte leads to an increase in the band at $\lambda_{max} = 320$ mμ and also the band at $\lambda_{max} < 260$ mμ appears although its extinction at 260 mμ is less than with the dianion. This suggests that a mixture of azobenzene and the dianion is formed by a disproportionation reaction when lithium ions are added to the monoanion. It is proposed that disproportionation occurs in the presence of lithium ions due to stabilisation of the dianion by the formation of a dilithium adduct. The abnormal polarographic behaviour of azobenzene in lithium salts as supporting electrolytes can be interpreted in terms of a rapid disproportionation of the monoanion.

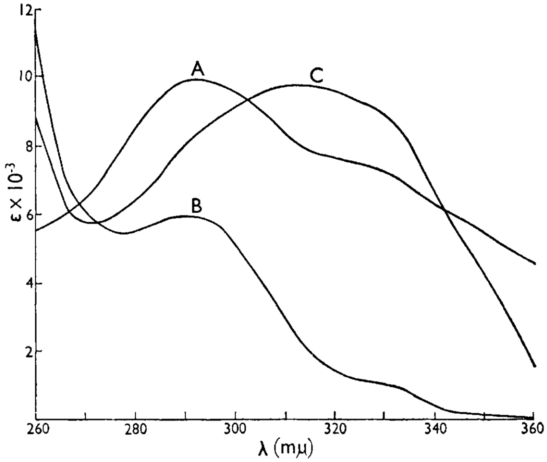

FIGURE 2. *Electronic spectra of azobenzene radical anions in DMF.* (A) *Monoanion in* Et_4NClO_4 *supporting electrolyte,* (B) *Dianion in* LiCl *supporting electrolyte,* (C) *Monoanion in* Et_4NClO_4 *supporting electrolyte* + LiCl *added.*

The electronic transitions in azobenzene radical anions have been interpreted in terms of molecular orbital theory and this will be discussed in a later publication.

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[1] R. C. Carlin, R. G. Nelb, and R. C. Odioso, *J. Amer. Chem. Soc.*, 1951, **73**, 1002.