The Effects of Solvents on the E.s.r. Spectra of the Radical-anions of Aromatic Dinitro-compounds

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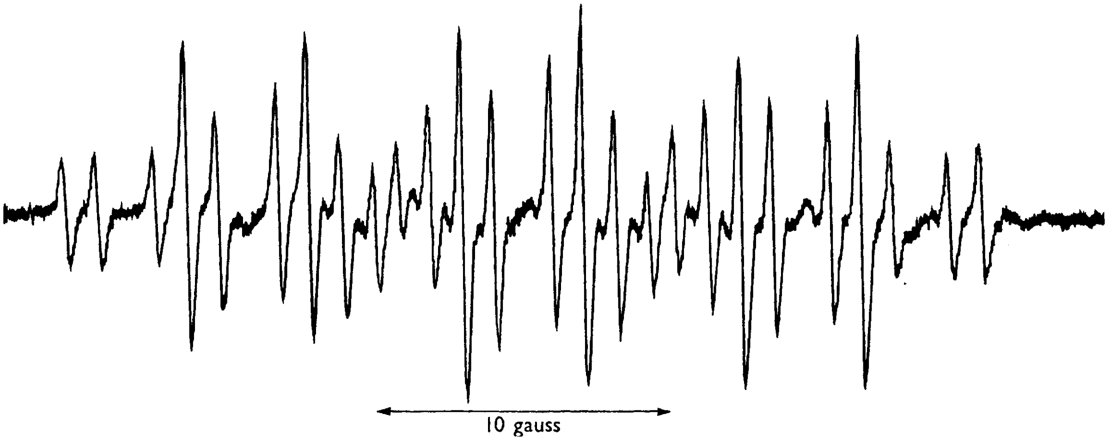
DURING a study of the reduction of aromatic nitro-compounds we have found that the reaction between sodium dithionite and *m*-dinitrobenzene in 40% aqueous alkaline acetone gives, in a flow system,[1] a free radical, the e.s.r. spectrum, *I*, of which analyses for only one nitrogen hyperfine interaction: $a_N = 12{\cdot}54$, $a_H\ (3) = 3{\cdot}52$, $a_H\ (1) = 1{\cdot}11$ gauss. If the solvent contains less than 40% acetone, or if aqueous ethanol is used, the spectra indicate the presence of a small amount of a secondary radical—possibly the radical anion of 3,3′-dinitroazoxybenzene.

A spectrum similar to *I* has been published by Russell, Janzen, and Strom[2] who obtained their radical by electron transfer from various donors to *m*-dinitrobenzene in ethanol and tentatively regarded it as the radical-anion of *m*-dinitrobenzene. Ayscough, Sargent, and Wilson[3] have obtained a spectrum with splitting constants very close to *I* by irradiating solutions of *m*-dinitrobenzene in methanolic sodium methoxide and ascribed this to the radical anion of *m*-nitroanisole. However, the displacement by MeO^- or OH^- of one nitro-group from *m*-dinitrobenzene is very unlikely and the coupling constants for the radical-anion of *m*-nitrophenol[4] are quite different from *I*.



A *E.s.r. spectrum obtained by study of electrolytic reduction of* m-*dinitrobenzene in* DMF–EtOH = 85/15 *v/v*.

We confirm that the e.s.r. spectrum *II* of the radical-anion obtained by the electrolytic reduction of *m*-dinitrobenzene in dimethylformamide[5] (DMF) shows the expected interaction with two equivalent nitrogen nuclei. Freed, Rieger, and Fraenkel[5,6] have reported that in DMF at −50° spectrum *II* shows an alternation in line-widths, the lines corresponding to $M_N = 0$ and ± 1 appearing to be less intense than expected (M_N is the total *z* component of the nitrogen nuclear spin angular momentum). Freed and Fraenkel[7] have pointed out that any time-dependent process which results in a momentary inequality of the two nitrogen couplings can lead to broadening of lines corresponding to $M_N = 0$ and ± 1 and have suggested that if sufficient broadening occurred those lines corresponding to $M_N = \pm 1$ would no longer be observed and that those corresponding to $M_N = 0$ and ± 2 would be of equal intensity. We consider that spectrum *I* is of this type.

We have reduced *m*-dinitrobenzene (10^{-3}M) electrolytically in DMF–ethanol mixtures with tetrabutylammonium perchlorate (0·1 M) as supporting electrolyte. As the percentage of ethanol is increased from 0 to 20% the $M_N = \pm 1$ interactions become progressively broader. In DMF containing 15% of ethanol the $M_N = \pm 1$ lines appear as weak satellites (Fig. A) and comparison with a spectrum (Fig. B) simulated by a computer‡ shows that the line-width of the $M_N = \pm 1$ lines is about 2·6 times that of the $M_N = \pm 2$ lines. Though slight secondary radical formation is also apparent in A we regard the concordance between A and B to support conclusively the Fraenkel theory.

A series of spectra, identical to those obtained from electrolytic studies, can be obtained by reducing *m*-dinitrobenzene (2×10^{-3}M) with hydroxylamine (2×10^{-3} M) in DMF–ethanol mixtures made alkaline with tetrabutylammonium hydroxide. In this way we have generated the radical-anions without undue secondary radical formation in mixtures containing up to 50% ethanol, at which stage the broad components of

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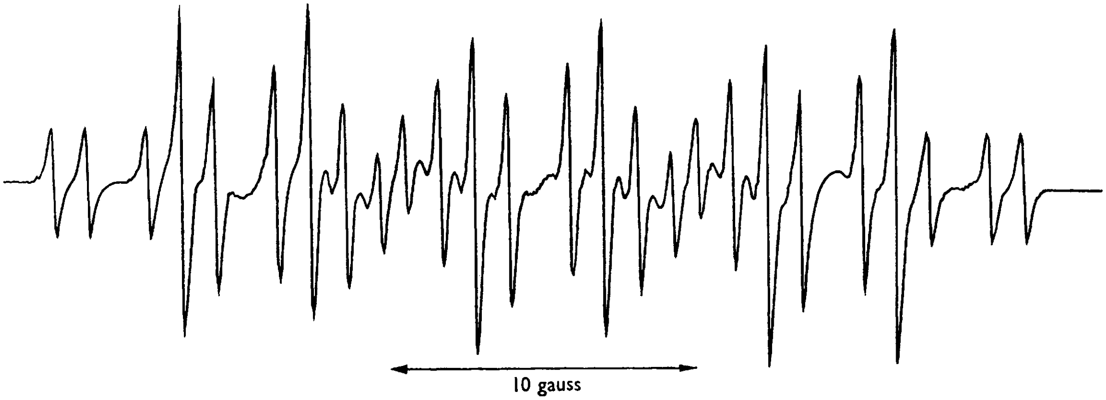
‡ Spectrum B was simulated by a Japan Electron Optics Co. Ltd. JNM-RA-1 computer. It is the sum of two spectra, B_1 and B_2. B_1 represents the sharp components ($M_N = \pm 2$ and one component of $M_N = 0$); B_2, twice the intensity of B_1, represents the broad components ($M_N = \pm 1$). The contribution of the broad components of $M_N = 0$ is assumed to be insignificant.

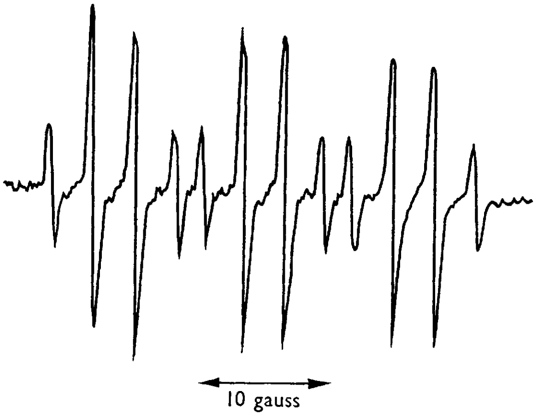
the spectrum can no longer be detected. Since in these experiments the concentration of counterions was $< 10^{-2}$ M it is most unlikely that our observations can be explained in terms of fluctuating ion-pair formation.[8]



B *Simulated spectrum using coupling constants*[7] $A_{N(1,3)} = 4{\cdot}68$, $A_{H(2)} = 3{\cdot}05$, $A_{H(4,6)} = 4{\cdot}11$, $A_{H(5)} = 1{\cdot}10$ *gauss. Sharp line-width (distance between derivative extrema)* = 0·21 *gauss. Broad line-width* = 0·55 *gauss.*

The observation that one-nitrogen spectra (*e.g.*, *I*) can be obtained from *m*-dinitrobenzene does not appear to depend on the use of a mixed solvent since the reduction ($Na_2S_2O_4$) in aqueous solution of 3,5-dinitrobenzoic acid gives a radical the e.s.r. spectrum of which (Fig. C) analyses unequivocally for one nitrogen, $a_N = 12{\cdot}87$ gauss and three equivalent hydrogens, $a_H = 3{\cdot}51$ gauss.

In aqueous acetone, spectra of type *II* (two equivalent nitrogen nuclei) are obtainable from *p*- and *o*-dinitrobenzenes and from 2,6-dinitrophenol. Freed and Fraenkel[9,10] observed no alternation of line widths in the spectra obtained by electrolytic reduction of these compounds in DMF solution. However, 2,6-dinitrotoluene, 2,6-dinitroanisole, 3,5-dinitroanisole, 3,5-dinitrophenol, and 3,5-dinitroaniline all give spectra of type *I* showing only one nitrogen interaction. Thus the e.s.r. spectral type is to be associated both with the solvent and with the structure of the dinitrocompound chosen. We are extending this study to the examination of other aromatic nitrocompounds.



C *E.s.r. spectrum obtained by* $Na_2S_2O_4$ *reduction of aqueous sodium* 3,5-*dinitrobenzoate.*

(*Received, December* 6*th*, 1965; *Com.* 761.)

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