

73. *Aryloxy-radicals. Part II.*¹ *Application of Electron Spin Resonance in the Elucidation of Reaction Mechanisms.*

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The identification of free aryloxy radicals by means of their electron spin resonance spectra helps to elucidate the course of oxidation of pyrocatechol and of reduction of 2-*o*-hydroxyphenyl-1,4-benzoquinone.

It is well known that alkaline solutions of quinol are easily oxidised in air to *p*-benzosemiquinone and that 4,4'-dihydroxybiphenyl is oxidised to 4,4'-diphenoquinone, but the corresponding stages of oxidation of aqueous solutions of pyrocatechol and of 2,2'-dihydroxybiphenyl are unknown. We have found that the examination of the electron spin resonance (e.s.r.) spectra of alkaline solutions of dihydric phenols helps considerably to clarify autoxidation mechanisms since thereby it is possible to detect and identify radical intermediates.

A solution of pyrocatechol in alkaline ethanol gives the e.s.r. spectrum of *o*-benzosemiquinone (I) first reported by Hoskins² who obtained coupling constants $a(3,6\text{-H}) = 1.0$, $a(4,5\text{-H}) = 4.0$ Oe. Our coupling constants are 0.95 and 3.65 Oe, respectively, which

¹ Part I, *J.*, 1964, 213.

² Hoskins, *J. Phys. Chem.*, 1955, **23**, 1975.

are similar to those obtained by Adams and his colleagues³ in later work. In dimethylformamide the coupling constants are 1.16 and 3.55 Oe, respectively (Fig. 1a). Solvent effects of this type have already been discussed by Stone and Maki.⁴

While recording the spectrum of *o*-benzosemiquinone in alkaline dimethylformamide we observed the gradual appearance of a triplet superimposed on the centre of the original spectrum (Fig. 1b). This triplet, which decayed with time much less rapidly than did the triplet of triplets characteristic of *o*-benzosemiquinone, had a coupling constant of 0.64 Oe. A triplet e.s.r. spectrum corresponds to a radical having only two equivalent hydrogen atoms which can interact with the free electron of a radical. Of the known oxidation

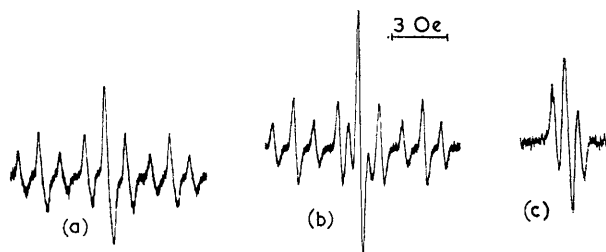
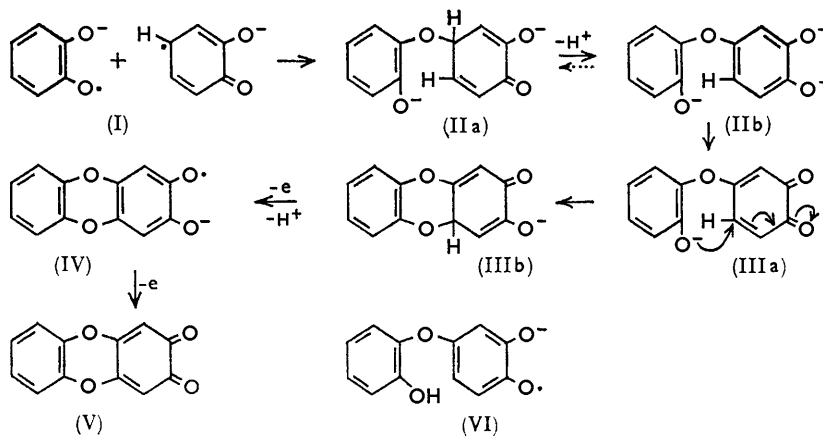


FIG. 1. E.s.r. spectra of (a) *o*-benzosemiquinone alone, (b) *o*-benzosemiquinone showing appearance of secondary radical, and (c) semiquinone (IV).

products of pyrocatechol, only dibenzo-[1,4]-dioxin-2,3-quinone (V) could yield a radical (IV) of this type. Accordingly the quinone (V) was synthesised by oxidising pyrocatechol by potassium iodate (cf. Forsyth, Quesnel, and Roberts⁵); reduction of this by alkaline dithionite in dimethylformamide immediately gave the triplet e.s.r. spectrum of Fig. 1c, with a coupling constant 0.65 Oe identical with that of the central triplet of Fig. 1b. The course of oxidation of pyrocatechol by air can thus be represented by the annexed reaction



scheme. Further evidence for this has been obtained by isolating a small amount of the quinone (V) on aerial oxidation of an alkaline solution of pyrocatechol in dimethyl sulphoxide.

We suggest that the dimer (IIa) from the initial radical (I) is rapidly oxidised to the *o*-quinone (IIIa) and that ring closure to (IIIb) is a fast heterolytic reaction, for homolytic oxidation of (IIb) should yield a radical (VI) which has three non-equivalent hydrogen

³ Adams, Blois, and Sands, *J. Chem. Phys.*, 1958, **28**, 774.

⁴ Stone and Maki, *J. Chem. Phys.*, 1962, **36**, 1944.

⁵ Forsyth, Quesnel, and Roberts, *Biochim. Biophys. Acta*, 1960, **37**, 322.

atoms and there was no sign of even the transient appearance of an e.s.r. spectrum of corresponding complexity. The reactions (IIIb) \longrightarrow (IV) \longrightarrow (V), however, evidently each involve removal of one-electron.

A transient free radical also seems to be involved in the reduction of 2-*o*-hydroxyphenyl-1,4-benzoquinone (VIII) and its analogues. Our first evidence for this was the observation of a doublet splitting of 2.64 Oe in a radical formed by dithionite reduction of the quinone (VII) which has recently been described by one of us,⁶ for the semiquinone of (VII) which has two non-identical hydrogen atoms on the semiquinone ring should have a hyperfine structure with a doublet of doublets. Moreover, the simple doublet spectrum was observed, with practically undiminished intensity, for samples which had been kept for more than 24 hours. Since this doublet spectrum would correspond to that of a radical formed by reduction of a dibenzofuranquinone, the course of reduction of 2-*o*-hydroxyphenyl-1,4-benzoquinone (VIII) by alkaline dithionite has been investigated by electron spin resonance; an improved method of preparation of this quinone is reported in the Experimental section.

In anhydrous dimethylformamide reduction of the quinone (VIII) gave a triplet of doublets corresponding to two equivalent hydrogens, with a coupling constant of 3.20

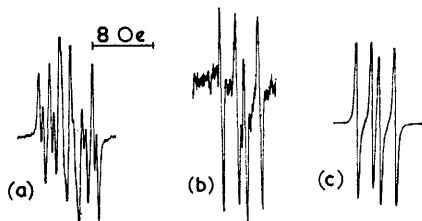
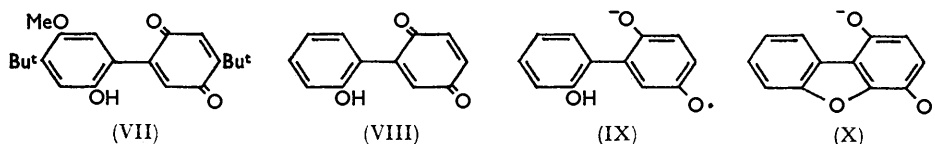


FIG. 2. E.s.r. spectra of (a) initial radical from (VIII), (b) radical from (VIII) after 15 min., and (c) semiquinone (X).

Oe, and one other hydrogen with a coupling constant of 1.60 Oe, which is consistent with the predicted e.s.r. spectrum of the semiquinone (IX). However, in aqueous dimethylformamide, although the initial spectrum (Fig. 2a) was too unsymmetrical for analysis, after about 15 min. the spectrum had changed to a doublet of doublets (Fig. 2b) corresponding to two non-equivalent hydrogen atoms with coupling constants of 3.41 and 2.25 Oe. Such a spectrum would correspond to dibenzofuran-1,4-semiquinone (X). Accordingly, dibenzofuran-1,4-quinone was prepared by oxidising 4-hydroxydibenzofuran with Frémy's salt, and on reduction it gave the e.s.r. spectrum shown in Fig. 2c with identical coupling constants.

Thus, since the dibenzofuran ring closure seems to require the presence of aqueous alkali a probable mechanism for the formation of compound (X) is nucleophilic attack of the hydroxyl group of compound (VIII) on the adjacent free *ortho*-position in the *p*-quinonoid ring; this would lead heterolytically to the hydroquinone of radical (X). The production of a doublet spectrum even in anhydrous dimethylformamide from



compound (VII), and the failure to observe the spectrum of the simple semiquinone corresponding to (IX), can perhaps be attributed to the activating (+*M*) effect of the *p*-methoxy-group on the heterolytic ring closure.

⁶ Hewgill, *J.*, 1962. 4987.

EXPERIMENTAL

Electron spin resonance (e.s.r.) spectra were measured in the aqueous-solution cell of a 100 Kc./sec. Varian spectrometer, V4500.

Reductions.—Samples (5 mg.) of the quinones were vigorously shaken in a stoppered 4-ml. test tube with dimethylformamide (2 ml.) containing 10% v/v of water in the presence of an excess of solid sodium dithionite and a little sodium hydroxide, until a deeply coloured solution resulted. The solution was then poured into the sample cell and its e.s.r. spectrum was recorded at regular intervals.

Oxidations.—Pyrocatechol, in similar aqueous dimethylformamide containing sodium hydroxide, was shaken in air until the solution became coloured and the mixture was then transferred to the e.s.r. cell.

Materials.—Dibenzo-[1,4]-dioxin-2,3-quinone (V), red needles, m. p. 260—261° (lit., m. p. 260—261°) was prepared by the iodate oxidation of pyrocatechol;⁵ as previously reported,⁵ it gave, with *o*-phenylenediamine, a blue phenazine, m. p. >300°. 2-(2-Hydroxy-5-methoxy-4-*t*-butylphenyl)-5-*t*-butyl-1,4-benzoquinone was the sample described previously.⁶ 2-*o*-Hydroxyphenyl-1,4-benzoquinone, orange needles, m. p. 194—195° (lit.,⁷ m. p. 193°) was prepared by oxidising 2,2'-dihydroxybiphenyl with Frémy's salt.⁸

Oxidation of Pyrocatechol.—Air was drawn for 2 hr. through a solution of pyrocatechol (1 g.) in 9 : 1 dimethyl sulphoxide–water (50 ml.) in the presence of sodium hydroxide (1 g.). After 48 hr. the dark solution was passed through a column of powdered silica. The red-violet eluate was evaporated in a vacuum and the residue dissolved in water (100 ml.). This was extracted with chloroform (40 ml.), and the extract was dried (MgSO₄) and concentrated to 2 ml. Thin-layer chromatography on silica, by elution with 5 : 1 chloroform–acetic acid, gave a yellow spot with R_F 0.74, identical with that of dibenzo-[1,4]-dioxin-2,3-quinone (V).

Dibenzofuran-1,4-quinone.—4-Hydroxydibenzofuran (1.84 g.) in acetone (100 ml.) was added to a stirred solution of Frémy's salt (8 g.) in water (300 ml.) and *N*-sodium acetate (10 ml.) at 10°. After 1 hr. acetone (100 ml.) was added, and stirring continued for another hour. The suspension was extracted with chloroform (3 × 150 ml.), the extracts were washed with water and dried (MgSO₄), and the solvent was removed under reduced pressure leaving an orange, crystalline residue. Recrystallisation from aqueous acetone gave gold needles (0.85 g.), m. p. 189—190° (lit.,⁹ m. p. 187—188°).

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⁷ Grundman, *Ber.*, 1936, **69**, 1755.

⁸ Teuber and Rau, *Chem. Ber.*, 1953, **86**, 1036.

⁹ Adler and Magnusson, *Acta Chem. Scand.*, 1959, **13**, 505.