Electron Nuclear Double Resonance and Electron Spin Resonance Studies of Anion-radicals derived from *p*-Benzoquinone [1]

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Solutions of *p*-benzoquinone and quinol in alkaline propan-2-ol and [$^2H_8$]propan-2-ol have been studied using e.s.r. and ENDOR. Four secondary radicals, anions of quinones formed by reaction of the solvent with the substrate, have been identified. Proton hyperfine coupling constants for the radical-anions of 3-alkoxy-2,6-dimethyl-*p*-benzoquinones, formed from 2,6-dimethyl-*p*-benzoquinone in alkaline methanol, ethanol, and propan-2-ol, are reported.

Electron nuclear double resonance (ENDOR) spectroscopy is well established as a method for making very precise measurements of the hyperfine coupling constants in free radicals in solution. Like all double resonance techniques ENDOR is particularly useful when the spectra of different species overlap, for the double resonance spectrum of each contributing species can often be obtained individually. However, so far this particular potential of ENDOR has hardly been exploited for solutions. Allendoerfer and Papez [2] have used a variant of ENDOR to distinguish free duroquinone anion from its ion pair with sodium, while in previous work in this laboratory secondary radicals formed in alkaline alcoholic solutions of *p*-benzoquinone or its 2,5-dimethyl derivative were distinguished from the radical anion of the original solute using conventional ENDOR.[3] This work was independently duplicated, to some extent, by Kotake and Kuwata.[4] The work reported here is an extension of the earlier study.[3]

Originally the solvents used were methanol and ethanol and the secondary radicals reported were the anions of the *p*-dialkoxy-derivatives of the original quinones.[3] Here we have studied *p*-benzoquinone in propan-2-ol and have detected four secondary radicals, measured the proton hyperfine coupling constants using ENDOR, and we suggest identities for the radicals. Fully deuteriated propan-2-ol was used to aid the assignment of the coupling constants and the identification of the radicals. Secondary radicals formed from 2,6-dimethyl-*p*-benzoquinone in alkaline methanol, ethanol, and propan-2-ol have also been studied.

EXPERIMENTAL

All experiments were carried out in air. Ordinary alcohols were Laboratory Reagent grade. Perdeuteriated propan-2-ol was obtained from Anderton and Company and was exposed to air as little as possible to minimise deuteron–proton exchange with atmospheric moisture. Quinol, *p*-benzoquinone, and 2,6-dimethyl-*p*-benzoquinone were obtained commercially and used without further purification.

E.s.r. spectra were run on a Varian E-3 spectrometer and ENDOR spectra on a Varian E-700 operating in conjunction with a V-4500 series e.s.r. spectrometer. ENDOR Spectra were generally recorded at 273 K, e.s.r. spectra at room temperature. In the ENDOR measurements the free proton frequency was always *ca.* 14·3 MHz. Many spectra were recorded over several months and the coupling constants reported are averages: they are precise to better than ±0·02 MHz.

RESULTS AND DISCUSSION

No obvious differences of behaviour between *p*-benzoquinone and quinol were observed and most experiments were done with quinol. The radical-anion of *p*-benzoquinone (I) forms immediately when quinol is dissolved in alkaline propan-2-ol. This radical is long-lived in very dilute alkali, but in more concentrated alkali the e.s.r. spectra of secondary radicals can be seen within minutes of making up the solution. An example is shown in Figure 1a. The e.s.r. spectrum of (I), which is indicated schematically in Figure 1a, can still be discerned in the more complex e.s.r. spectrum. ENDOR Spectra were obtained for saturation of various features of the e.s.r. spectrum and these established the presence of two secondary radicals (II) and (III). Their ENDOR spectra, obtained by saturating at the points marked (II) and (III) in Figure 1a, are shown

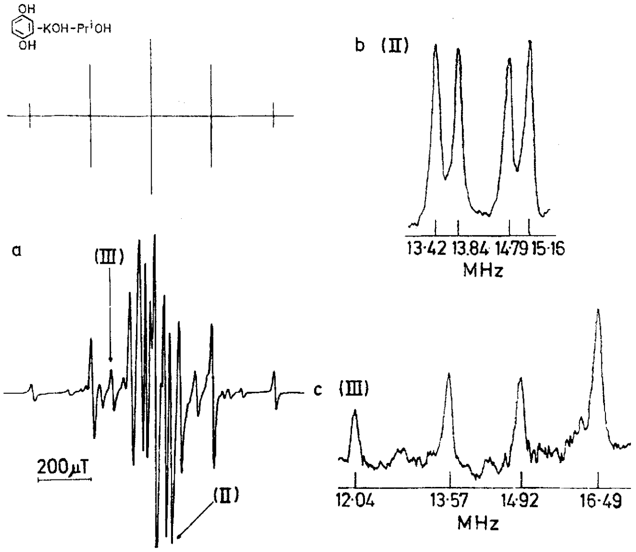

FIGURE 1 a, E.s.r. spectrum obtained from a solution of quinol in alkaline propan-2-ol. The quintet of *p*-benzoquinone radical-anion, indicated schematically above the observed spectrum, can be discerned. b and c, ENDOR spectra of secondary radicals (II) and (III), obtained by saturating at points (II) and (III) in the e.s.r. spectrum a

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[1] A brief account of this work was presented to the International Symposium on Organic Free Radicals, Sirmione, 1974.

[2] R. D. Allendoerfer and R. J. Papez, *J. Amer. Chem. Soc.*, 1970, **92**, 6971.

[3] N. M. Atherton and A. J. Blackhurst, *J.C.S. Faraday II*, 1972, **68**, 470.

[4] Y. Kotake and K. Kuwata, *Bull. Chem. Soc. Japan*, 1972, **45**, 2663.

in Figures 1b and c respectively. The coupling constants are shown in Table 1 and given their magnitudes it is straightforward to interpret the e.s.r. spectra: each radical has hyperfine coupling to two pairs of equivalent protons. Repeating the experiments in [$^2H_8$]propan-2-ol established that in each radical one pair of protons originated in the solvent.

TABLE 1

Proton hyperfine coupling constants (J/MHz) in secondary radicals formed from *p*-benzoquinone in alkaline propan-2-ol

Radical	Parent compound	Ring	Propoxy (CH)
(II)	2,5-Dipropoxy-*p*-benzoquinone	0·95	1·74
(III)	2,6-Dipropoxy-*p*-benzoquinone	4·40	1·37
(IV)	2-Hydroxy-5-propoxy-*p*-benzoquinone	0·56(3),[a] 1·81(6)[a]	1·98
(V)	2-Hydroxy-6-propoxy-*p*-benzoquinone	0·52(5),[a] 7·88(3)[a]	1·24

[a] Assigned to the ring-position indicated in parentheses on the basis of the Hückel calculation described in the text.

It is clear that (II) and (III) are the radical anions of dipropoxy-*p*-benzoquinones. The earlier work[3] gave values for the coupling constants in the 2,5-dimethoxy- and 2,5-diethoxy-anions and these compare very well with those in radical (II). Accordingly we take (II) to be the radical-anion of 2,5-dipropoxy-*p*-benzoquinone. Comparison of the coupling constants for the alkoxy-protons in the 2,5-dimethoxy-, 2,5-diethoxy, and 2,5-dipropoxy anions is of some interest. The coupling constant in the methoxy anion is not temperature dependent while that to the methylene protons in the ethoxy anion is quite strongly so.[3] We now observe that the coupling to the methine proton in the propoxy anion is not markedly temperature dependent. This suggests that the barrier to rotation of the alkyl group is higher in the propoxy anion than the ethoxy, as would be expected from models. Further the relative magnitudes of the coupling constants in the ethoxy and propoxy anions indicate that in the former the methylene protons have an average position well out of the plane of the aromatic ring, while in the latter the average position of the methine proton is closer to the plane of the ring. Again, this conclusion correlates with studies of models. The pattern in these compounds parallels that in the radical-cations of the dialkoxybenzenes, which have been studied by Forbes *et al.*[5]

We infer that (III) is the radical-anion of 2,6-dipropoxy-*p*-benzoquinone. Formation of the 2,3-disubstituted compound seems unlikely on steric grounds, but the rigorous identification of (III) can be made following the work of Fitzpatrick and Steelink.[6] They studied alkaline alcoholic solutions of 2,6-dimethoxy-*p*-benzoquinone and found that there was rapid replacement of the alkoxy-groups by those of the solvent. The coupling constants they report for a radical-anion identified as that of 2,6-dipropoxy-*p*-benzoquinone agree with those we find for (III). Further, we have repeated some of their experiments and we find that the radical first observed in freshly prepared solutions of 2,6-dimethoxy-*p*-benzoquinone in propan-2-ol is indeed radical (III).

At longer times the e.s.r. spectrum in Figure 2a appears. An ENDOR spectrum, Figure 2b, shows that there are at least two radicals. This spectrum is an interesting example of the power of ENDOR to discern that there are two species contributing to an e.s.r. spectrum: by saturating at a point in the e.s.r. which is close to a derivative peak for one species and a trough for the second the two ENDOR spectra appear with opposite phases. The up-going spectrum in Figure 2b is for the triplet of doublets in the centre of the e.s.r. spectrum of Figure 2a, while the down-going ENDOR is for the quartets at the wings of the e.s.r. spectrum. We label the radicals (IV) and (V) respectively.

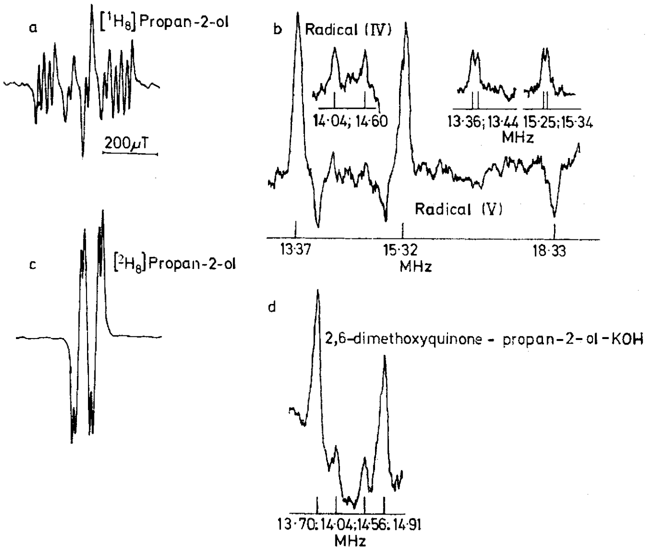

FIGURE 2 a, E.s.r. spectrum obtained from a solution of quinol in alkaline propan-2-ol at longer time than that of Figure 1a. b, ENDOR Spectrum of radicals (IV) and (V). The insets at the top show details of the spectrum of (IV). c, E.s.r. Spectrum obtained in [$^2H_8$]propan-2-ol at similar stage of reaction to that for a. d, ENDOR Spectrum of radical (V) obtained from solution of 2,6-dimethoxyquinone in alkaline propan-2-ol

Two part-ENDOR spectra for radical (IV) are shown as insets to Figure 2b. That for the region of the free proton frequency simply shows the ENDOR for the small proton coupling which gives the doublet structure to the e.s.r. triplet. The other inset, obtained from a more dilute solution, shows that the triplet splitting

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[5] W. F. Forbes, P. D. Sullivan, and H. M. Wang, *J. Amer. Chem. Soc.*, 1967, **89**, 2705.

[6] J. D. Fitzpatrick and C. Steelink, *J. Org. Chem.*, 1972, **37**, 762.

comes in fact from two almost-equivalent protons. This is illustrated dramatically by the e.s.r. spectrum of Figure 2c, obtained in [$^2H_8$]propan-2-ol: the triplet has collapsed to a doublet. Precise measurement of the hyperfine coupling of the remaining proton, using ENDOR, shows that, of the two near-equivalent protons in the fully protonated radical, the one with the larger coupling originates in the solvent. Radical (IV) thus has coupling to three inequivalent protons, one of which originates in the solvent.

We were unable to obtain a high-quality ENDOR spectrum of radical (V) alone from e.s.r. spectra like that of Figure 2a. However, we observed that the same radical was formed in solutions of 2,6-dimethoxy-*p*-benzoquinone in alkaline propan-2-ol. An ENDOR spectrum obtained from this system is shown in Figure 2d. The radical again has coupling to three inequivalent protons, one originally in the solvent. Fitzpatrick and Steelink observed this radical in their work,[6] and identified it as the anion of 2-hydroxy-6-propoxy-*p*-benzoquinone. Radical (V) thus relates to radical (III) through hydrolysis of an alkyl group. We assume that (IV) is analogously related to (II) and identify it as the anion-radical of 2-hydroxy-5-propoxy-*p*-benzoquinone.

The differences between the coupling to the two ring protons in each of the radicals (IV) and (V) are quite large so that one would hope to be able to achieve a correct assignment on the basis of a Hückel calculation. For the alkoxy-group we used the parameters suggested by Sullivan [7] for methoxy, since no gross changes in the pattern of spin distribution in the ring should occur for different alkoxy-groups. The parameters of Das and Fraenkel [8] were used for the quinone oxygen at the 1-position. In alkaline solution the radicals most probably exist as dianions and may equally well be regarded as arising from 2-hydroxy-*p*- or 4-hydroxy-*o*-benzoquinone. Accordingly we treated the oxygen atoms at the 2- and 4-positions equally, taking $\alpha_O = \alpha_C + 2\cdot2\beta_{CC}$, $\beta_{CO} = 1\cdot0\beta_{CC}$. Converting the Hückel spin populations to coupling constants using $|Q_{CH}{}^{H}| = 70$ MHz we find couplings of 5·49 and 0·04 MHz for the 3- and 5-positions in (V) and of $<0\cdot01$ and 0·09 MHz for the 3- and 6-positions in (IV), respectively. The result is clear-cut for (V), disappointing for (IV). However, the assignments indicated in Table 1 are based on these calculations. There are many parameters in the calculations and an attempt at optimisation would be a major undertaking for a minor result.

All four of the secondary radicals discussed should have a common ancestor in the monopropoxy-substituted quinone. The e.s.r. spectrum in Figure 1a does have some weak features discernible between the $|\Sigma M_I| = 2$ and the $|\Sigma M_I| = 1$ lines of the primary radical (I). We have never been able to obtain these lines with sufficient intensity to get an ENDOR spectrum of the radical. However the e.s.r. indicates that there are small couplings to two inequivalent protons, in addition to further splitting or splittings, and this is what would be expected for the radical-anion of 2-propoxy-*p*-benzoquinone. The e.s.r. indicates couplings of 1·3 and 2·0 MHz to two single protons, with the sum of the remaining couplings, or a third coupling to a single proton, being 15·2 MHz.

Secondary radicals containing a single alkoxy-group are formed in alkaline alcoholic solutions of 2,6-dimethyl-*p*-benzoquinone. We have studied methanol, ethanol, and propanol solutions. So far as we can discern the monoalkoxy-substituted derivatives are the only secondary radicals formed. For each solvent the coupling constants have been measured using ENDOR. The data are collected in Table 2. They illustrate again the relative insensitivity of the spin distribution to the alkoxy-substituent.

TABLE 2

Proton hyperfine coupling constants (J/MHz) in radical anions of 3-alkoxy-2,6-dimethyl-*p*-benzoquinones

	Coupling constants		
3-Substituent	Methyl	Ring	Alkoxy
Me	4·15, 7·27	4·81	
Et	3·95, 7·19	4·93	0·15(CH_2)
Pr^i	3·63, 7·12	5·06	

We thank the S.R.C. for an equipment grant and for the award of a research studentship to P. A. H.

[4/1760 *Received*, 21*st August*, 1974]

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[7] P. D. Sullivan, *J. Phys. Chem.*, 1970, **74**, 2563.

[8] M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **42**, 1350.