ENDOR Spectra of Some Semiquinone Radical-Anions

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The proton ENDOR spectra of the radical-anions of several semiquinones in alkaline ethanol solution are reported. p-Benzosemiquinone and 2,5-dimethyl-p-benzosemiquinone are converted to di-alkoxy substituted derivatives through reaction with the solvent. When this happens the e.s.r. spectra become complicated because the spectra of the primary and secondary radicals overlap: the power of ENDOR for analyzing overlapping e.s.r. spectra is illustrated.

Hyde and Maki¹ reported the first proton electron nuclear double resonance (ENDOR) spectrum of a free radical in solution and the number of applications of the technique is now increasing, although the instrumentation is not simple and progress has been relatively slow. One of the main applications of the method is to obtain accurate measurements of hyperfine coupling constants in radicals which have poorly resolved e.s.r. spectra, for example the work by Hyde² on triphenyl-phenoxy radicals and that by Maki *et al.*³ on triarylmethyl radicals. In general the best results have often been obtained with neutral free radicals: these dissolve in non-polar solvents so that large sample volumes can be used. It has proved more difficult to obtain spectra of radical-ions. For example, if they are prepared by alkali metal reduction in ethers it seems that ENDOR spectra can usually only be obtained at temperatures very close to the freezing point of the solution.⁴ In this paper we report ENDOR spectra of some semiquinone radical ions. These are quite easy to obtain in alcohol solution.

Semiquinone radical-ions were among the first radicals to be studied by e.s.r.,⁵ and there have also been some ENDOR studies. Hyde ⁶ reported the spectra of p-benzosemiquinone and 2,5-di-t-butyl-p-benzosemiquinone, prepared by reduction of the quinones in ethanol. Das, Connor, Leniart, and Freed ⁷ have studied the spectra of several semiquinones related to Vitamin K : the radicals were prepared either by alkali metal reduction of the parent quinone in dimethoxyethane, which was then pumped off and replaced by ethanol, or by electrolytic reduction in dimethoxyethane and ethanol. Allendoerfer and Papez ⁸ have obtained good spectra at low temperature of both the free durosemiquinone anion radical and an ion-paired species after alkali metal reduction in dimethoxyethane. In this work we have found that good proton ENDOR spectra can be obtained when the radicals are formed by spontaneous reduction of the parent quinone in degassed alkaline methanol or ethanol under high vacuum.

EXPERIMENTAL

Quinones were obtained commercially and used without further purification. The alcohols were dried using molecular sieves. Sample tubes were made with an e.s.r./ENDOR cell consisting of a 4 mm o.d. quartz tube and a solvent side-arm. To make up a sample, a small amount of the dry quinone was put into the cell and 2-3 ml of dry alcohol, which

had been in contact with potassium hydroxide, were put in the side arm. The solvent was degassed by several freeze-pump-thaw cycles and the whole assembly sealed off from the high vacuum line. The radical generally formed immediately the alcohol and the quinone were mixed.

E.s.r. spectra were monitored as a matter of routine using a Varian E-3 spectrometer and ENDOR spectra recorded using a Varian E-700 instrument operating in conjunction with a V-4502 X-band e.s.r. spectrometer. Sample concentrations were adjusted to be in the range 10^{-3} - 10^{-4} M, and temperatures were controlled with a Varian V-4557 accessory. Hyperfine coupling constants measured from ENDOR spectra are believed to be accurate to ± 0.01 MHz. Free proton frequencies were close to 14.5 MHz.

RESULTS

PRIMARY RADICALS

Table 1 summarizes the ENDOR data for the primary radicals from seven quinones in ethanol. For comparison, e.s.r. data are also quoted, and these are the basis of the assignments. ENDOR spectra were obtained over the temperature range 213-293 K and in general the optimum temperature for ENDOR was not sharply peaked. The relative intensity of the t-butyl proton ENDOR signal from 2,5-di-t-butyl-p-benzosemiquinone varied dramatically with temperature, as we have observed for other t-butyl proton signals, but for radicals with larger couplings the relative intensities of the α -proton ENDOR lines did not show such marked variation with temperature.

TABLE 1.—ABSOLUTE VALUES OF THE COUPLING CON	nstants (MHz) in primary radicals
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	parent molecule	coupling from ENDOR	coupling from e.s.r. ^a	assignment ^b	no. of protons
Π	2.5-dimethyl-p-benzoquinone	6.38	6.29 c	methyl	6
	_,,, p	5.22	5.14 °	3,6	2
III	2,5-di-t-butyl-p-benzoquinone	6.13	5.96 d	3,6	2
		0.19	0.17 ^d	t-butyl	18
IV	1.4-naphthoguinone		9.04 ^c	2,3	2
		1.84	1.83 c	e	2
		1.51	1.44 °	е	2
v	2,3-dichloro-1,4-naphthoquinone	2.18		е	2
	, , <u> </u>	1.60		е	2
VI	9,10-anthraquinone	2.73	2.69 ^c	2,3,6,7	4
	, <u> </u>	1.50	1.56 °	1,4,5,8	4
VII	1,5-dichloro-9,10-anthraquinone	3.52		е	2
	, , , ,	2.24		е	2
		0.99		е	2
VIII	9,10-phenanthraquinone	4.91	4.68 ^c	3,6	2
		4.54	3.78 ^c	1,8	2
		1.19	1.18 °	4,5	2
		1.01	0.56 c	2,7	2

^a literature values. Quoted splittings in gauss converted to MHz assuming g = 2; ^b assignments based on e.s.r. spectra; ^c quoted in H. Fischer, Landolt-Bornstein, New Series. Group II, volume I, *Magnetic Properties of Free Radicals* (Springer-Verlag, Berlin, 1965); ^d G. K. Fraenkel, *Ann. N.Y. Acad. Sci.*, 1957, **67**, 553; ^e no assignment.

SECONDARY RADICALS

The e.s.r. spectra of the primary radicals from p-benzoquinone and 2,5-dimethylp-benzoquinone (compounds I and II respectively) changed fairly rapidly, becoming more complex. It was clear that a secondary radical was being formed and that the

ENDOR SPECTRA OF RADICAL-ANIONS

later spectra were superpositions of those of two species. E.s.r. spectra for compound II in ethanol are shown in fig. 1. ENDOR is ideal for situations of this sort because by saturating various features of the superposed spectra one can obtain the ENDOR spectra of either radical separately, or of both simultaneously. The point is illustrated



FIG. 1.--(i) E.s.r. spectrum of freshly prepared solution of II in ethanol. (ii) Spectrum some time later showing extra features due to the secondary radical. Both spectra taken at room temperature. Features marked (a), (b), (c) were saturated to obtain the ENDOR spectra in fig. 2.

by Fig. 2, which shows the ENDOR spectra obtained by saturating the three features marked in fig. 1b. Fig. 2a is the spectrum of the primary radical, and this is the spectrum observed when freshly prepared solutions are examined. Fig. 2b shows the spectrum of the secondary radical and 2c shows features due to both radicals. This sort of application of ENDOR, to sort out the species responsible for overlapping e.s.r. spectra, has to our knowledge previously been used only for solids.

We identify the secondary radicals from compounds I and II as the alkoxysubstituted semiquinone anions. Previous e.s.r. work ⁹ has indicated that alkoxy attack occurs in these systems and our present study confirms this on the following grounds. First, the coupling constants in the secondary radicals depend on the solvent; we have studied each compound in both methanol and ethanol. The coupling constants, which we will discuss later, are summarized in table 2. The second point is that the rate of formation of the secondary radicals depends on the alkali concentration. Thus at high KOH concentrations the secondary radical appears within a few minutes of dissolving the quinone and the final e.s.r. spectrum shows no sign of the primary radical, whereas at low concentration of KOH the spectrum of the primary radical can persist for hours with no sign of the secondary radical. The rate of formation of secondary radicals depends on the substituents in the original quinone : the rate is faster for I than II, and we have never observed a secondary



FIG. 2.—ENDOR spectra obtained by saturating features (a), (b), (c) of the e.s.r. spectrum fig. 1 (ii), 253 K. (a) is the primary radical II, (b) the secondary radical IIE, (c) shows features from both radicals.

radical from 2,5-di-t-butyl-p-benzosemiquinone. It is clear from the e.s.r. spectra, and from ENDOR, that the secondary radicals are symmetrically di-substituted. We see no sign of the mono-substituted radicals, presumably because once an alkoxy group has gone in the second step follows very quickly. The spectroscopically-based arguments alone leave no doubt as to the identities of the secondary radicals but

TABLE 2.—ABSOLUTE VALUES OF THE COUPLING CONSTANTS (MHz) IN SECONDARY RADICALS

	radical	coupling constants	assignment a	no. of protons
IN	A 2,5-dimethoxy-p-benzosemiquinone	2.75	methyl	6
		0.87	3,6	2
IE	2,5-diethoxy-p-benzosemiquinone	3.35 ^b	ethoxy-methylene	4
		0.87	3,6	2
		0.17	ethoxy-methyl	6
IIM	3,6-dimethoxy-2,5-dimethyl-p- benzosemiquinone	4.06	ring methyl	6
IIE	3,6-diethoxy-2,5-dimethyl-p-	3.89	ring methyl	6
	benzosemiquinone	0.19	ethoxy-methylene	4

a assignments based on e.s.r. spectra; b temperature dependent. Reported value for 253 K.

confirmatory evidence was provided by product analysis in one case. The solutes resulting after long treatment of II with ethanol or methanol were put in a high resolution mass spectrometer : the mass spectra indicated the presence of 2,5-dimethyl-3,6-diethoxy-p-benzoquinone and 2,5-dimethyl-3,6-dimethoxy-p-benzoquinone respectively.

It is convenient to label the secondary radicals with a number (I or II) denoting the precursor, and a letter (M or E), denoting the substituent. Table 2 constitutes a

ENDOR SPECTRA OF RADICAL-ANIONS

key to the notation. It is interesting to compare the couplings in the various products. For example, the ring proton couplings in IM and IE are the same, indicating that the spin populations on the ring atoms are not sensitive to the alkoxy substituent. Thus one might have expected the methoxy-methyl and ethoxy-methylene couplings in IM and IE to be comparable, while in fact they turn out to be rather different. We find that the methylene proton coupling in IE is temperature dependent: it changes from 3.6 MHz at 213 K to 3.1 MHz at 273 K, and we ascribe this to hindered rotation of the ethoxy group. The difference between the methylene and methyl couplings in the two radicals may thus be ascribed to geometric factors. For example, for the methyl protons we may have rapid averaging over all possible orientations with respect to the ring, whereas for the methylene protons there may be rapid averaging over only a limited (temperature dependent) range of orientations such that the methylene carbon atom does not get into the plane of the ring. The averaging must be rapid for there are no signs of line broadening in e.s.r. or ENDOR spectra.

Another interesting comparison is between radicals IE and IIE. In so far as the ring proton and ring methyl proton couplings in the two radicals monitor the spin distribution in the rings, the spin distributions in the two radicals appear to be quite different. Presumably the differences could be described quantitatively in terms of the relative inductive and hyperconjugative parameters for the methyl and ethoxy groups although there are rather a lot of parameters available. The interpretation of the relative couplings to the methylene protons, which appear to reflect consistently the difference in spin distribution over the rings, may be complicated by their having different average orientations in the two radicals. This coupling in IIE is so small that a possible weak temperature dependence could not be accurately analyzed.

The ability to pick out the separate radicals in an overlapped spectrum could be one of the most useful potentials of ENDOR for chemical studies. However, one can envisage a situation where it might be difficult to apply. For example, if the spectra overlapped in such a way that there was no clear e.s.r. spectral feature from one of the radicals. In such a case, if the lines from the two species are of different widths, it may still be possible to detect the ENDOR of just one radical, the one with broader lines, even when saturating both spectra, by increasing the field modulation Thus the narrower e.s.r. line could be overmodulated and the ENDOR amplitude. signal from it greatly diminished in intensity. We have demonstrated that the method works with the radical IIE: saturating the central feature and using a fairly conservative field modulation amplitude enables us to observe both ENDOR spectra (fig. 2c), but when the modulation amplitude is increased only the ENDOR of the secondary radical is observed, if all the other operating conditions are preserved. It may also be possible to differentiate ENDOR spectra by varying the microwave power if the radicals have different T_1 values: an application of this in solution ENDOR remains to be illustrated.

ENDOR INTENSITIES

On the basis of a phenomenological description of ENDOR, Allendoerfer and Maki¹⁰ have shown how to correct the observed signal intensities for overlap of hyperfine lines. They deduce the equation

$$I_{\rm obs} = I_{\rm max} \left\{ \frac{(T_2 a_{\omega})^2}{(T_2 a_{\omega})^2 + 2.5} \right\}$$
(1)

where I_{obs} and I_{max} are the observed intensity and the intensity for large couplings,

475

 T_2 is the transverse relaxation time of the electron, and a_{ω} is the hyperfine coupling constant. This equation has been shown to give a satisfactory description of the relative ENDOR intensities in a variety of spectra.^{10, 11} We have attempted to apply it to the spectra obtained in this work.

The primary radicals from compounds IV, V, VI, VII and VIII (see table 1) each have equal numbers of protons of each type and as the coupling constants are relatively large all the ENDOR lines should be of equal intensity. This is what we observe experimentally. For the primary radical from III the observed ENDOR intensity ratio, in the spectra we consider optimum, for t-butyl/ring protons is 1.10 : 1 compared to the theoretical value of 9 : 1. If we choose $T_2 = 4.9 \times 10^{-7}$ s eqn (1) predicts a ratio of 1.09 : 1, which is good agreement with the experimental value. Again, for IIE (table 2) choosing $T_2 = 9 \times 10^{-7}$ s gives a theoretical intensity ratio of 9.45 : 2 for methyl/methylene protons, which is good agreement with the observed 9.41 : 2. However, there are also cases where the equation works less well. For example, for both IM and IE there are no values of T_2 which give the observed intensity ratios. In the case of the primary radical from II we observe an intensity ratio of 2 : 1 at 273 K for methyl/ring protons, which is rather far from the expected 3 : 1 considering that both couplings are relatively large.

Eqn (1) is derived for the condition of maximum ENDOR and this will only be achieved for all protons simultaneously if they all have the same relaxation times. There is no general reason why this should be the case and it seems to us that the success or failure of the equation may be a useful comment on the equality or otherwise of these relaxation times. The interesting problem then becomes that of understanding the relative magnitudes of the relaxation times.

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- ¹ J. S. Hyde and A. H. Maki, J. Chem. Phys., 1964, 40, 3117.
- ² J. S. Hyde, J. Phys. Chem., 1967, 71, 68.
- ³ A. H. Maki, R. D. Allendoerfer, J. C. Danner and R. T. Keys, J. Amer. Chem. Soc., 1968, 90, 4225.
- ⁴ A. Lagendijk, N. F. M. Tromp, M. Glasbeck and J. D. W. van Voorst., *Chem. Phys. Letters*, 1970, **6**, 152; R. D. Allendoerfer, personal communication; N. M. Atherton, A. J. Blackhurst, I. P. Cook and B. Day, unpublished observations.
- ⁵ B. Venkataraman and G. K. Fraenkel, J. Amer. Chem. Soc., 1955, 77, 2707.
- ⁶ J. S. Hyde, J. Chem. Phys., 1965, 43, 1806.
- ⁷ M. R. Das, H. D. Connor, D. S. Leniart and J. H. Freed, J. Amer. Chem. Soc., 1970, 92, 2258.
- ⁸ R. D. Allendoerfer and R. J. Papez, J. Amer. Chem. Soc., 1970, 92, 6971.
- ⁹ D. C. Reitz, J. R. Hollahan, F. Dravnieks and J. E. Wertz, J. Chem. Phys., 1961, 34, 1457.
- ¹⁰ R. D. Allendoerfer and A. H. Maki, J. Magn. Resonance, 1970, 3, 396.
- ¹¹ R. D. Allendoerfer and J. H. Engelmann, Mol. Phys., 1971, 20, 569.