ENDOR Study of Radical Mixture Formed on the Reduction of *p*-Xyloquinone4)

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The central line of the ESR spectrum of a radical mixture may be very complicated when the spectra both contain odd numbers of lines centered at almost the same *g* value. But in this central line all the information of the system is contained. ENDOR is capable of extracting hyperfine splitting constants (hfsc) and the intensity change of the lines in both spectra independently because ENDOR detects the enhancement of an ESR line intensity when the radio frequency hits the NMR frequency of the proton in a radical. Only a couple of ENDOR lines above and below the NMR frequency of free proton appear for each group of equivalent protons. The assignment of the hfsc and the identification of the radical can be made clear from inspection of the ESR spectra. Moreover the kinetic behavior of the system may be studied much more easily than by using ESR technique.

Mixing C_2H_5ONa–C_2H_5OH with *p*-xyloquinone (2,5-dimethylbenzoquinone) produced radicals which showed ESR spectra as Figs. 1a—1c. In dilute ethanolic solution of C_2H_5ONa the spectrum was that of *p*-xylosemiquinone anion radical.1) In the case that C_2H_5ONa concentration was high the spectra changed with time.

The ENDOR spectra at several reaction stages measured at the top of the first derivative ESR spectrum for the center line at −10°C are shown in Figs. 1d, 1e, and 1f. The ENDOR spectrometer used was constructed in our laboratory which consists of ordinary ESR spectrometer with 200 Hz field modulation and high power ENDOR attachment. This unit delivers maximum output of peak 600 watts sinusoidally modulated radio frequency power and its modulation frequency can be varied from 5 to 15 kHz. The field frequency lock was also used.2) The comparison between Fig. 1b and 1e may show the advantage of ENDOR technique. Figure 1b consists of overlapped lines of two radicals except weak side lines, while the ENDOR spectrum shows three peaks above free proton frequency quite clearly. The hfsc's can be determined accurately. From the change in relative intensity, it is easy to tell that from which radical the line comes. In Table 1 accurate hfsc's are shown which were determined by the analysis of ENDOR spectra.

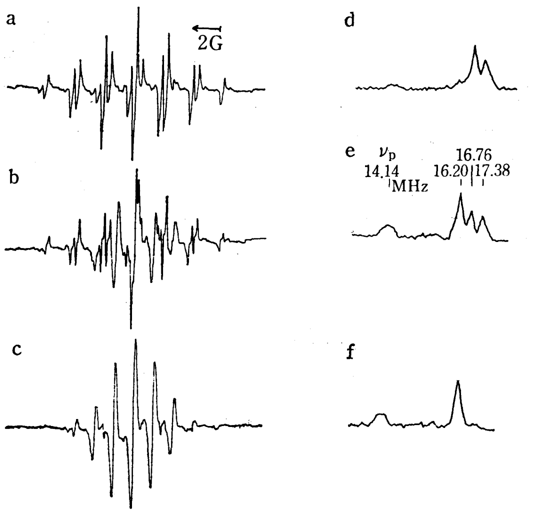

Fig. 1. ESR (a, b, c) and ENDOR (d, e, f) spectra of *p*-xyloquinone–C_2H_5ONa–C_2H_5OH system (quinone and C_2H_5ONa were in 1 : 2 molar ratio). a and d: just after mixing, b and e: after 5 hr at room temperature, c and f: after 3 days at room temperature.

Table 1.

Radical	hfsc (gauss)	Assignment
1	$a_1=1.87$	*p*-xylosemiquinone anion
	$a_2=2.31$	a_1: ring protons
		a_2: methyl protons
2	$a_1=1.47$	diethoxy-*p*-xylosemiquinone anion
	$a_2<0.2$	a_1: methyl protons
		a_2: ethoxy protons

Radical 1 in Table 1 can be ascribed to *p*-xylosemiquinone anion radical.1) Radical 2 has protons which have a large hf coupling and very small one. The large coupling considering about the binomial distribution of the ESR spectrum is assigned to two methyl groups. And remaining coupling is ascribed to ethoxy protons by considering the further reaction in alkali–alcohol media.3) The fact that ENDOR lines of these groups are rather broad may show that there are two residual small hf coupling which come from the methylene and methyl protons of ethoxy group.

In this reaction system, the two radicals could be identified by their ESR spectra. But by use of ENDOR technique two radicals were identified without the isolation of ESR spectra and the hfsc's were determined accurately even in a radical mixture. This seems to be one of the useful applications of ENDOR.

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1) B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, **30**, 1006 (1959).

2) J. S. Hyde, *ibid.*, **43**, 1806 (1965).

3) K. Kuwata and Y. Shimizu, This Bulletin, **42**, 864 (1969).

4) **Note Added in Proof:** Similar kind of work by N. M. Atherson and A. J. Blackhurst appears in *J. Chem. Soc. (Faraday Trans. II)*, **1972**, 470.