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ENDOR STUDIES OF THE STRUCTURE OF THE BANFIELD-KENYON RADICAL

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There have been several ESR investigations on the β-phenyl-hydroxylamine-β-methylpentane-δ-phenylimine oxide known as the Banfield and Kenyon radical (B.K. radical). Some ambiguities remain, however, in the assignment of the alkyl proton splitting, which has an unusually large value. Buchachenko has assumed that the eight closest protons of the aliphatic residue gave rise to the splitting.$^{1)}$ On the other hand, Griffiths proposed a possibility of the through-space interactions between the unpaired electron and the terminal methyl group, which may sterically approach closely the nitroxide residue as shown in Fig. 1.$^{2)}$

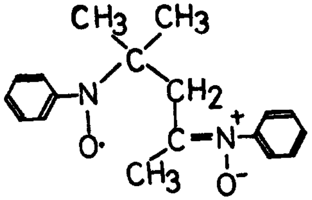

Fig. 1
The molecular structure of the B.K. radical.

In the present communication, we wish to present our ENDOR studies of the B.K. radical. The proton hyperfine coupling constants have been precisely determined and their values have been compared with those of t-butylphenyl nitroxide (BPNO).$^{3)}$ The number of aliphatic protons in the molecule was calculated by using the Maki and Allendoerfer equation.$^{4)}$ The temperature dependences of the ENDOR intensities and the mechanism of the anomalous alkyl splitting are investigated.

The radical was synthesized by oxidation of the condensation product between β-phenylhydroxylamine and acetone, according to the procedure of Banfield and Kenyon.$^{5)}$ The ENDOR spectra were recorded with a JEOL type ES-EDX-1 spectrometer, operating with 80 Hz magnetic field modulation. The continuous radio frequency of about 150 Watts, which is modulated by 6.5 KHz, is applied to the sample in the cavity for the NMR excitation.[6]

In Fig. 2, we show the ENDOR spectrum of the B.K. radical observed in toluene at -84°C. The hyperfine coupling constants of the B.K. radical and of the BPNO radical are summarised in Table I. The hyperfine coupling constants for the ring protons are indeed nearly the same in both radicals. The hyperfine coupling constant of the alkyl proton, a_R of the B.K. radical is exceptionally large compared with the value of the t-butyl proton splitting of the BPNO radical.

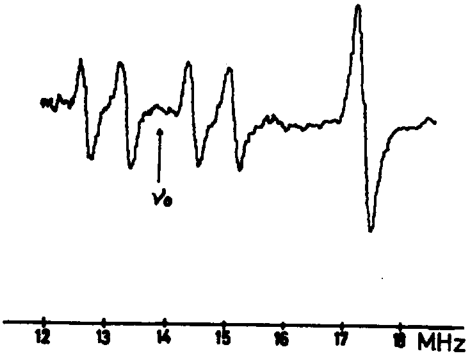

Fig. 2

The higher frequency half of the ENDOR spectrum observed at -84°C.

ν_0: free proton frequency

Table I

Hyperfine coupling constants of the B.K. and of the BPNO radicals.

		a_N	a_O, a_P	a_m	a_R
	ESR	12.56	2.48	0.90	0.41
B.K.	ENDOR		2.425	0.884	0.404
	ESR	12.08	2.09	0.89	
BPNO	ENDOR		1.993	0.906	0.092[a)]

It is of interest to compare the observed and calculated line intensity ratios. Since this gives us the number of the protons which actually give rise to the splitting. Using the same value of the electron spin-spin relaxation time, ($T_2 = 1.5 \times 10^{-7}$ sec.) assumed in the previous work,[3)] the line intensity ratios of each proton was calculated using the Maki and Allendoerfer equation:

$$I_{obs} = I_{max}\,(T_2\Delta\omega)^2 \,/\, \left[(T_2\Delta\omega)^2 + 2.5\right]$$

where I_{obs} is the observed ENDOR intensity, I_{max} the number of protons and $\Delta\omega$ the hyperfine coupling constant.[4)] The calculated line intensity ratios give satisfactory agreement with the observed ones measured in the optimum temperature region, when I_{max} of the alkyl protons is taken to be five as shown in Table II. When the parameters determined by the present ENDOR experiment are employed, the computer simulation of the ESR spectrum gives the excellent agreement with the observed spectrum. This is shown in Fig. 3.

Table II

The observed and the calculated ENDOR intensity of the B.K. radical.

	o, p	m	alkyl
Observed	1.00	0.49	0.57
Calculated	1.00	0.48	0.33$^{a)}$
			0.55$^{b)}$
			0.66$^{c)}$

a) $I_{max} = 3$ b) $I_{max} = 5$ c) $I_{max} = 6$

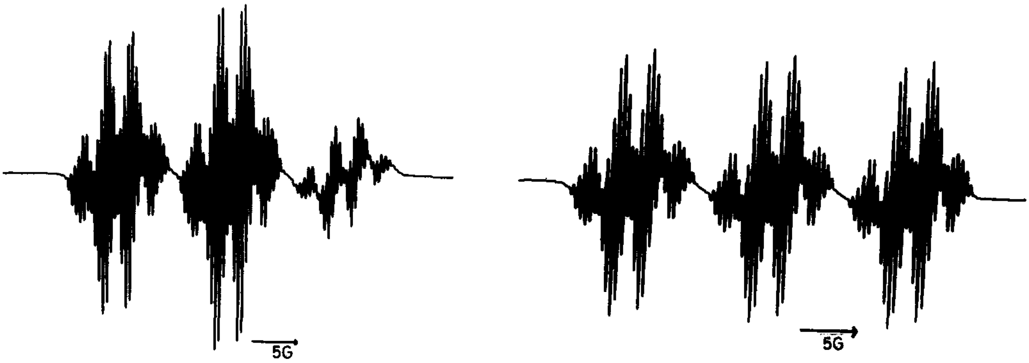

Fig. 3 ESR Spectrum of the B.K. radical observed at -50°C ESR Simulation of the B.K. radical

In order to know the relaxation behavior of the alkyl protons, the temperature dependence of the ENDOR intensities is observed in the range from -60°C to -100°C. In Fig. 4, sharp maxima can be seen for the ring protons at -90°C ~ -95°C. At the same time, a broad maximum is noted for the alkyl protons at -85°C. The fact that the alkyl protons show the maximum ENDOR intensity in the vicinity of the optimum temperature range of the ring protons, is quite interesting, since a free rotation of the alkyl group reduces effectively the anisotropic hyperfine interaction and this effect causes usually a considerable deviation of the optimum temperature from those of the ring protons.[4), 6)] This suggests that segment movement of the long alkyl chain will be strongly restricted due to the steric effect. Based on the present investigations, one may assume the possibility of the two different mechanisms to explain the alkyl proton splitting; that is, the hyperconjugation of the methyl and the methylene groups in the 1,1'-dimethylethylene residue, or the through-space interaction due to the terminal methyl and the methylene group in the aliphatic chain.

In both cases, hindered movement of the long alkyl chain plays an important role in increaseing the probability of an interaction between the unpaired electron and the aliphatic protons.

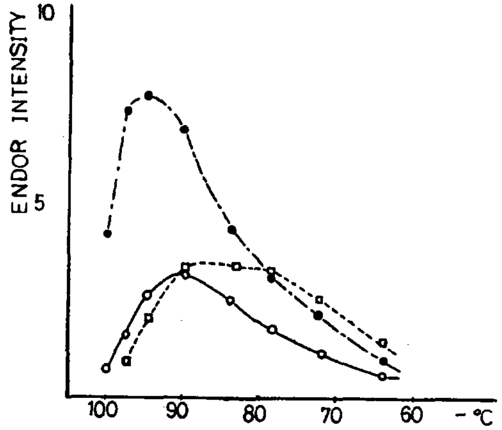

Fig. 4 Temperature dependence of ENDOR intensity.

●—·—● ortho and para ring protons

○——○ meta ring protons

□- - - -□ alkyl protons

Reference:

1) A.L. Buchachenko, Optika Spectroskopia, 13, 795 (1962)

2) V.S. Griffiths and G.R. Parlett, Nature, 204, 69 (1964)

3) K. Ishizu, H. Nagai, K. Mukai, M. Kohno, and T. Yamamoto, Chem. Letters, No.12 (1973) in press.

4) R.D. Allendoerfer and A.H. Maki, J. Mag. Resonance, 3, 396 (1970)

5) F.H. Banfield and J. Kenyon, J. Chem. Soc., (1926)

6) T. Yamamoto, K. Sato and T. Miyamae, Japan. J. Appl. Phys., 11, 1508 (1972)