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THE ENDOR SPECTRA OF t-BUTYLPHENYLNITROXIDE

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The ENDOR spectrum of t-butylphenylnitroxide were observed in either toluene or ethyl alcohol, and the solvent effects on the proton hyperfine coupling constants were investigated. Based on the Allendoerfer and Maki's correction, the observed ENDOR intensities were compared with those calculated from the electron spin-spin relaxation time, T_2.

A remarkable development of the ENDOR technique recently recalled the attentions on the studies of numerous organic free radicals in solutions. There have been extensive researches on the neutral radicals of the triphenylmethyl type, but the studies of nitrogen containing organic radicals such as nitroxide,1) imidazyl2) and verdazyl3) radicals are now under way.

In the present communication, we wish to report the ENDOR spectra of the t-butylphenylnitroxide observed in both toluene and ethyl alcohol. In both cases, perturbations of the proton hyperfine coupling constants due to the solvent effects are investigated, and the observed line intensities are referred to those predicted by the Allendoerfer and Maki's formula.4)

The t-butylphenylhydroxylamine (m.p. 115°C) was synthesized by the Grignard reaction between phenylmagnesiumbromide and nitrosobutane,5) and the nitroxide was generated by oxidation with silveroxide in vacuo. The ENDOR spectra were recorded by a JEOL type ES-EDX 1 spectrometer, operating with 80 Hz magnetic field modulation. About 150 watts of the continuous radio wave frequency - modulated by 6.5KHz are running inside of the cavity for NMR excitation.6)

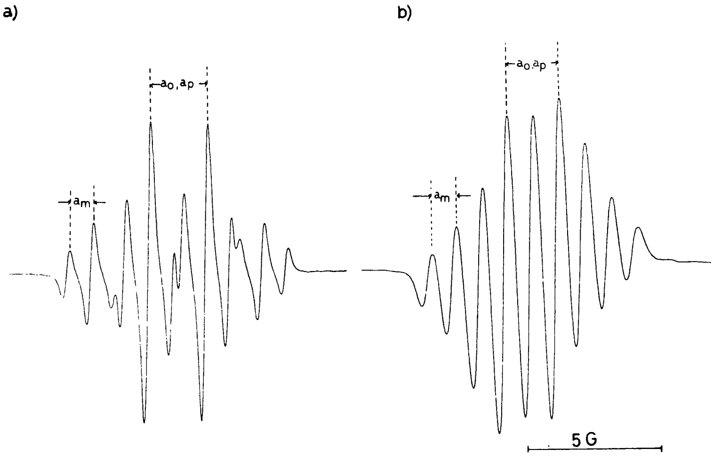

Fig. 1. One of the three nitrogen triplet pairs recorded at the low field side of the ESR spectra of t-butylphenylnitroxide.

Observed temperature: -40°C.

a) in toluene b) in ethyl alcohol

In Fig. 1, we show a part of the ESR spectra recorded both in toluene and ethyl alcohol. The ESR spectra are already interpreted in terms of three equivalent proton coupling constants of the ortho and the para position (a_o, a_p) and those of two meta position (a_m).[7] The hyperfine coupling constants determined by present ESR and ENDOR measurements are summarized in Table 1. Beside the small variations of the ring proton coupling constants due to so-called solvent effects,[8] one will note that the line width of the ESR absorption ΔH_{msl} is much broader in the case of ethyl alcohol (420 mG) rather than that measured in toluene (260 mG). An increase of the ESR line width is probably attributed to the enhancement in the unresolved splittings of the t-butyl protons. One may argue that the interaction between the radical and the solvent molecule such as hydrogen bond formation[9] will be expected in ethyl alcohol. We confirmed, however, that the ESR spectrum observed in CD_3OD did not show any important change in both line width and hyperfine structures.

Table I. Hyperfine Coupling Constants of t-Butylphenylnitroxide (gauss).

Solvent		a_o, a_p	a_m	a_{t-BU}	a_N
Toluene	ESR	2.09	0.89	----	12.08
	ENDOR	2.290	0.940	----	-----
Ethyl Alcohol	ESR	1.88	0.90	----	13.30
	ENDOR	1.993	0.906	0.092	-----

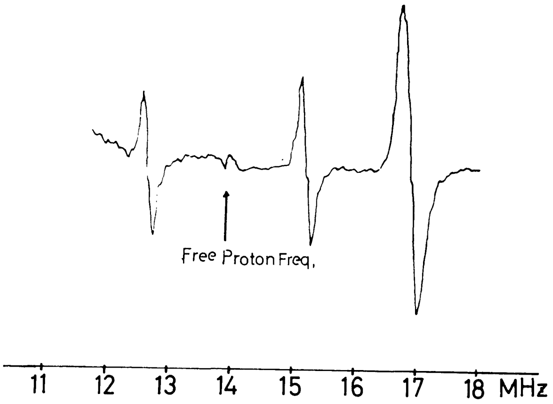

Fig. 2 The higher-frequency half of the ENDOR of t-butylphenylnitroxide observed in ethyl alcohol at -95°C.

The ENDOR experiment was primarily carried out in toluene at the temperature range from -100°C and -115°C. The ENDOR lines corresponding to the ring protons were easily observed, but the ENDOR lines for the t-butyl protons were not easily recorded, and sometimes they appeared as a weaker single line around the free proton frequency. In ethyl alcohol, however, the ENDOR lines for the t-butyl protons can be clearly recorded as well as those of the ring protons at -90°C - -100°C as shown in Fig. 2. As is seen in Table 1, the a_o and a_m values decrease and the a_N value increases in ethyl alcohol affected due to the interaction between the radical and the solvent molecule. The present ENDOR investigation demonstrates that the coupling constant of the t-butyl protons also increases in the polar solvent. This finding is considered to be quite reasonable, since the spin density on the neighboring nitrogen atom is enhanced by the solvent effect at the same time.

According to Allendoerfer and Maki, ENDOR enhancement factor, F, has been calculated as the function of the electron spin-spin relaxation time, T_2, and of the hyperfine coupling constant, ΔW: that is,

$$F = I_{obs}/I_{max} = (T_2\ \Delta W)^2/[(T_2\ \Delta W)^2 + 2.5]$$

where I_{max} is the number of protons and I_{obs} the observed intensity. In the present case, $I_{max} = 3$ is taken for the ortho- and the para-equivalent protons $I_{max} = 2$ for the meta-protons respectively. It is difficult to estimate the T_2 value directly from the ESR spectrum, because the ESR hyperfine lines are composed of the unresolved splitting of t-butyl protons. The observed intensity ratio $(I_{obs})_{o,\ p}/(I_{obs})_m = 1.83$, however, shows a good agreement with the calculated value $(I_{exp})_{o,\ p}/(I_{exp})_m = 1.96$ taking $T_2 = 1.5 \times 10^{-7}$ sec.

In terms of the Allendoerfer and Maki's expression, the fact of a difficult observation of t-butyl ENDOR in toluene probably means that of the t-butyl is too small to give observable ENDOR enhancement.

References

1) R. D. Allendoerfer and J. H. Engelmann, Mol. Phys., 20, 569 (1971).
2) R. D. Allendoerfer and A. S. Pollock, Mol, Phys., 22, 661 (1971).
3) K. Mukai, T. Yamamoto, M. Kohno, N. Azuma and K. Ishizu, to be published.
4) R. D. Allendoerfer and A. H. Maki, J. Mag. Resonance., 3, 396 (1970).
5) A. Galder, A. R. Forrester, P. G. James and G. R. Luckhurst, J. AM. Chem. Soc., 91, 3727 (1969).
6) T. Yamamoto, K. Sato and T. Miyamae, Japan., J. Appl. Phys., 11, 1508 (1972).
7) H. Lemaire, Y. Marechal, R. Ramasseul and A. Rassat, Bull. Soc. Chem. France, 372 (1965).
8) Y. Deguchi, Bull. Chem. Soc. Japan, 35, 260 (1962).
9) K. Mukai, H. Nishiguchi, K. Ishizu, Y. Deguchi and H. Takaki, Bull. Chem. Soc. Japan, 40. 3731 (1967).

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