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An ENDOR Study of the Relaxation Behavior of the Nuclei in Several Semiquinone Anion Radicals[1)]

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The ENDOR intensities of several semiquinone anion radicals were measured at various temperatures. The optimum temperature for the ENDOR intensity of protons in a radical was interpreted on the basis of their characteristic ways of relaxation. The electron nuclear dipolar (END) mechanism could be applied very well in most cases. However, in the case of protons whose END terms are very small this interaction might not explain the optimum temperature. Possible substitute mechanisms were discussed.

The ENDOR signal intensity depends on both the electron and nuclear relaxation times. As the temperature of a system changes, these relaxation times change in their characteristic ways, and this causes the temperature dependence of the intensity of the ENDOR signal. When the nuclei in a radical have their own relaxation paths of different temperature dependences, their ENDOR lines show a characteristic temperature dependence. Therefore, the ENDOR intensity is not an intrinsic parameter of the free radical. For this reason, ENDOR has a limitation as an analytical tool.

The investigation into the relaxation behavior which affects the ENDOR intensity is essential in providing fundamental knowledge for the assignment of the ENDOR spectra. Moreover, by the analysis of the temperature dependence, especially of the optimum temperature at which the strongest ENDOR line appears, we can find the relaxation mechanism of a nucleus relating to its position and its surroundings in a radical.

Freed[2,3)] has developed a theory of the ENDOR enhancement on the basis of the equation of motion for the density matrix of a system and has obtained qualitative agreement with Hyde's experimental results.[4)] He has explained the characteristic optimum temperature for each nucleus in terms of the electron nuclear dipolar (END) interaction being the dominant cause of the nuclear spin relaxation process in the liquid phase. In this process, a nucleus which has larger dipolar *hf* interaction with an electron spin must have a higher optimum temperature.

Allendoerfer and Maki[5)] have made a unique study of the optimum conditions for the ENDOR enhancement in the tri-*t*-butyl phenoxyl radical in the liquid phase. However, no other detailed study of the optimum temperature for the ENDOR enhancement has yet been done; thus, it is not clear whether or not the END interaction is a common process in the nuclear relaxation in solution ENDOR. Especially in the case of protons which have a small END term, like the *t*-butyl protons, the END interaction seems to be inefficient in explaining the optimum temperature.

In the present study, using some semiquinone anions as probes in an ENDOR study, the END interaction was proved to be the dominant cause of proton relaxation when the anisotropic *hf* interaction between a proton and an electron spin is of a considerable magnitude. Also, the temperature dependence of the ENDOR intensity for the protons with small anisotropic *hf* coupling was proved not to be explainable in terms of the END interaction, and other nuclear relaxation mechanisms which may explain the ENDOR intensity were discussed.

Experimental

Though the measurement of the temperature dependence of the ENDOR intensity is useful for the investigation of the relaxation phenomena in a radical, its quantitative measurement involves some experimental difficulties. These difficulties arise for the following reasons.

1. Change in the radical concentration by a chemical equilibrium.

This causes not only a change in the intensity itself, but also many incidental effects. Upon the change in the concentration, the rate of Heisenberg spin exchange varies according as this equation:[6)]

$$\omega_{\mathrm{HE}} = 4\pi Da[\mathrm{R}] \tag{1}$$

where D is the translational diffusion coefficient, a is the molecular radius, and [R] is the radical concentration. ω_{HE} lowers with the decrease in the temperature and affects the ENDOR enhancement factor.[2)]

2. Change in the spin-lattice relaxation time of the electron.

The viscosity of the solvent accordingly varies with the temperature. There are many electron-relaxation processes which are viscosity-dependent, *e.g.*, the relaxation *via* *g*- and *hf*-tensor anisotropy and that *via* spin-rotational interaction. Therefore, the saturation factor of an ESR line changes with the temperature and the degree of saturation changes when the microwave power level is kept fixed during the measurements.

Freed's theory shows[2)] that the Heisenberg exchange process diminishes the percentage of the enhancement of an ESR line by the ENDOR effect, but does not affect the optimum temperature, this has been confirmed by the experimental results of Hyde.[4)] Thus, the exchange process does not move the optimum temperature for the ENDOR intensity. These facts show that, by suitable arrangements, *e.g.*, the dilution and the calibration of the ENDOR intensity by its ESR intensity, the first experimental difficulty can be removed.

The incident microwave power which gives the strongest ENDOR signal shifts as the temperature changes, but in the case of the semiquinone anion the shift is within the range of several db of microwave power. The measurement of the temperature dependency was done without changing the incident microwave power fed into the cavity. This may cause an error of the measurement of the optimum temperature.

The quinones used were of a guaranteed grade, and their anion radicals were produced by dissolving them into an alcohol which was in contact with the sodium metal. The solution was degassed thoroughly and then transferred into a glass sample tube 4 mm in o.d.

All the radicals formed were assigned to the primary radicals of the semiquinone anions on the basis of their ESR spectra. In the case of 2,5-dimethyl benzoquinone, the concentration of sodium ethylate was kept low in order to avoid further reaction.[7,8)]

The ENDOR spectra were observed at various temperatures by controlling the flow of the chilled nitrogen passing through the sample. The ENDOR spectrometer was based upon an ordinary ESR spectrometer with a 200 Hz field modulation. The RF power supply delivered a maximum output of peak 600 watts of sinusoidally amplitude-modulated power, and the modulation frequency was variable from 5 to 15 kHz. The field lock[4)] obtained by observing the ESR signal of DPPH was partly used.

Results

The features of the ENDOR signals of the 2,5-di-*t*-butyl-*p*-benzosemiquinone (DBQ) anion at various temperatures are shown in Fig. 1. This radical has two ring protons with a 6.13 MHz isotropic *hf* coupling and eighteen *t*-butyl protons with a 0.19 MHz isotropic *hf* coupling. The temperature dependences of the intensities of these lines in methanol, ethanol, and 2-propanol solution are shown in Figs. 2a and 3a, while the plots *versus* η/T, where η is the viscosity of the solvent, are shown in Figs. 2b and 3b. The intensity plotted on the ordinate was an integrated intensity because there was considerable variation in the ENDOR linewidths. In the case of the lines for the *t*-butyl group especially, two lines were very close to each other; these overlapping two lines were integrated together.

The η/T dependences of the intensity of the ENDOR line in the 2,5-dimethyl-*p*-benzosemiquinone (DMQ) anion and the 9,10-anthrasemiquinone (ANQ) anion in ethanol were also measured by the same procedure; they are shown in Figs. 4 and 5.

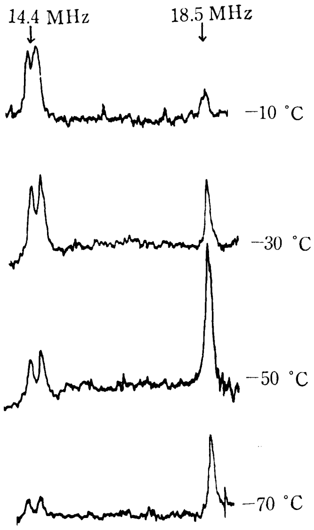

Fig. 1. The ENDOR spectra of 2,5-di-*t*-butyl-*p*-benzosemiquinone anion radical in ethanol at various temperatures.

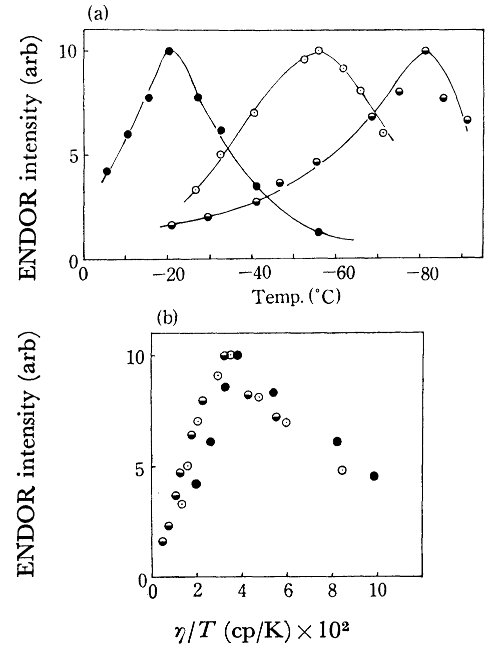

Fig. 2. The temperature (a) and η/T (b) dependences of ENDOR intensity of ring protons in 2,5-di-*t*-butyl-*p*-benzosemiquinone anion, ◒ in methanol, ⊙ in ethanol, ● in 2-propanol.

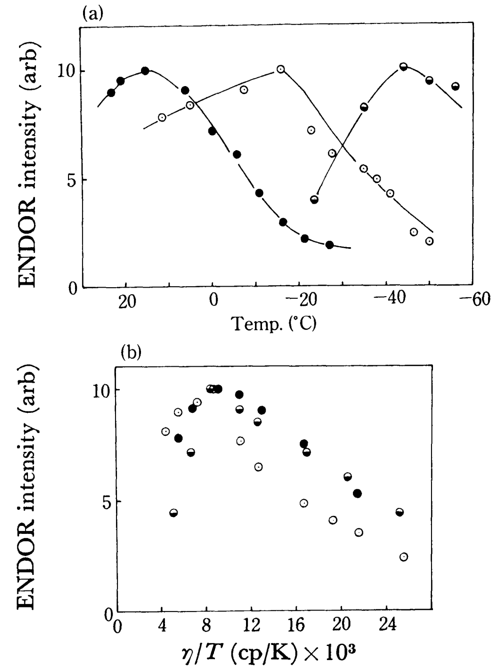

Fig. 3. The temperature (a) and η/T (b) dependence of ENDOR intensity of *t*-butyl protons in 2,5-di-*t*-butyl-*p*-benzosemiquinone anion, ◒ in methanol, ⊙ in ethanol, ● in 2-propanol.

Discussion

In an organic radical, *g*- and *hf*-anisotropy play dominant roles in the electron-spin relaxation. In this situation the assumption of a simple exponential correlation function with a correlation time of τ_R leads to the transition probability of the electron spin

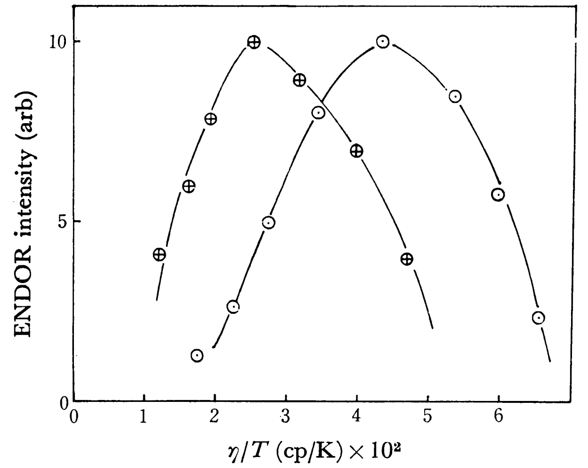

Fig. 4. The η/T dependence of ENDOR intensity of 2,5-dimethyl-*p*-benzosemiquinone anion radical in ethanol, ⊕ ring proton, ⊙ methyl proton.

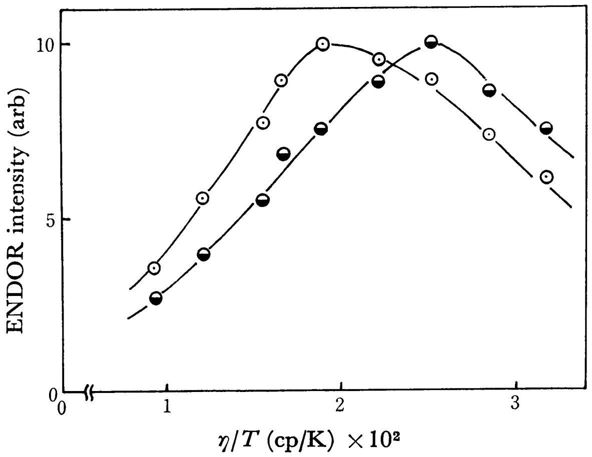

Fig. 5. The η/T dependence of ENDOR intensity of 9,10-anthrasemiquinone anion radical in ethanol, ◒ 1-proton, ⊙ 2-proton.

W_e, which is identical with $1/T_{el}$ as:

$$W_e \propto \tau_R/(1+\omega_e^2\tau_R^2) \tag{2}$$

where ω_e is the Larmor frequency of the electron spin.

At high temperatures spin-rotational relaxation occurs by the fluctuating field caused by a molecular tumbling motion, but the deviation of the *g* values of semiquinone anions from the free electron *g* value is too small to cause spin-rotational relaxation.[9]

On the other hand, the nuclei in a radical are in the special situation because of the large magnetic dipole moment of an electron spin very close to them. Thus, the magnetic relaxation behavior of the nuclei may be very different from that in a diamagnetic molecule.

The nuclear transition probability for a radical is decided mainly by the electron-nuclear dipolar (END) interaction fluctuating by the Brownian motion of the molecule, because other nuclear relaxation processes, *e.g.*, nuclear dipole-dipole interaction, chemical shift anisotropy, and nuclear spin-rotational interaction, are comparatively small and may be neglected when the anisotropic *hf* interaction is of a considerable magnitude.

In a fluctuating END interaction, the nuclear transition probability can be written as:

$$W_n^{\mathrm{END}} \propto \tau_R/(1+\omega_n^2\tau_R^2) \tag{3}$$

where ω_n is the Larmor frequency of the nucleus. When we adopt the Stokes-Einstein model, the isotropic rotational correlation time is given by:

$$\tau_R = 4\pi\eta a^3/3kT \tag{4}$$

where η is the viscosity of the solvent and a is the molecular radius. A schematic figure of the η/T dependence of W_e and W_n is shown in Fig. 6. Under ordinary experimental conditions in the liquid phase,

$$\omega_e^2\tau_R^2 \gg 1 \tag{5}$$

and

$$\omega_n^2\tau_R^2 \ll 1 \tag{6}$$

Under these conditions, W_e slows down when the sample is cooled, while, on the contrary, W_n becomes larger.

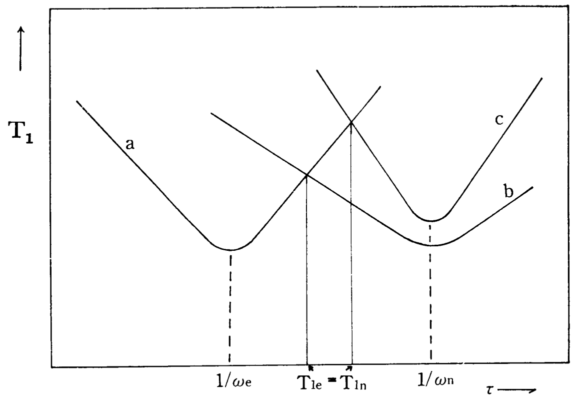

Fig. 6. The schematic figure of the τ dependence of T_{1e} and T_{1n}.
a: T_{1e}, b: T_{1n} with smaller END term, c: T_{1n} with larger END term.

In the temperature range where Eqs. (5) and (6) hold, W_e can be written as:[2]

$$W_e = A(1/\tau_R) \tag{7}$$

where A is the constant relating to the magnitude of the *g* and *hf* anisotropy. Moreover, W_n^{END} can be written as:[1]

$$W_n^{\mathrm{END}} = B\tau_R \tag{8}$$

where B is the constant which is related to the magnitude of the anisotropic *hf* interaction.

Thus, the ratio of the two transition probabilities becomes:

$$b = \frac{W_n^{\mathrm{END}}}{W_e} = (B/A)\tau_R^2 \tag{9}$$

The optimum conditions for the observation of the ENDOR signal are realized when the two transition probabilities become almost comparable,[2,3] that is, when:

$$b \sim 1 \tag{10}$$

The optimum η/T of an ENDOR line is decided by B/A and when a radical has two groups of protons, the ratio of the optimum η/T's becomes:

$$\frac{(\eta/T)_1}{(\eta/T)_2} = \left(\frac{B_2}{B_1}\right)^{1/2} \tag{11}$$

Thus, the ENDOR line of protons in a radical which have larger END terms has a smaller optimum η/T, *i.e.*, a higher temperature. This situation is shown schematically in Fig. 6.

ANQ Anion. In order to confirm the results described above, the ANQ anion radical in ethanol was studied. The ENDOR spectrum of this radical shows simple features because there are only two groups of equivalent protons; their isotropic *hf* coupling constants are $a_1=1.50$ MHz and $a_2=2.73$ MHz.

The magnitude of the B constant is proportional to the square of the END terms. The contribution of the END terms to the magnitude of B may be assumed to be proportional to $\langle 1/r^3\rangle_{\text{av.}}^2$, where r is the distance between the proton and the unpaired electron and where $\langle\ \rangle_{\text{av.}}$ denotes the averaged value over the unpaired electron distribution. The END terms of the ring protons are approximately proportional to the spin density of adjacent carbon atoms if the cross contribution from the spin density on other carbon atoms is neglected. According to the McConnell relationship between the spin density on a carbon atom and the Fermi contact term of a proton,[10)]

$$\rho_i = \frac{a_i}{Q} \tag{12}$$

where ρ_i is the spin density on the i-th carbon atom, a_i is the isotropic *hf* coupling constant of the proton bonded to the i-th carbon atom, and where Q is a constant peculiar to the radical.

The results of the above discussion lead to this equation:

$$B_i \propto \langle 1/r^3\rangle_{\text{av}}^2 \propto \rho_i^2 \propto a_i^2 \tag{13}$$

Thus,

$$\frac{(\eta/T)_1}{(\eta/T)_2} = \frac{a_2}{a_1} \tag{14}$$

In the ANQ radical, the ratio of the optimum η/T's between the protons of Positions 1 and 2 is estimated to be:

$$\left[\frac{(\eta/T)_1}{(\eta/T)_2}\right]_{\text{ANQ}} = 1.8 \tag{15}$$

The ratio of the η/T's which give the maxima in Fig. 5 is *ca.* 1.3. The coincidence between the theory and the experiment is fairly good and shows that the dominant mechanism of the relaxation of nuclear spins at Positions 1 and 2 in the ANQ anion is the END mechanism.

DMQ Anion. Figure 4 shows the η/T dependence of the ENDOR intensity for the ring ($a_1=5.24$ MHz) and the methyl protons ($a_2=6.47$ MHz) in the DMQ anion. Even though the isotropic *hf* coupling constant is larger than the ring protons, the optimum η/T of the methyl protons is larger than that of the ring protons.

According to Eq. (14), this result seems to conflict with the theoretical prediction of the optimum η/T. In the ANQ anion both protons are ring protons, and the electronic structures around them are very similar, whereas in the DMQ anion the comparison is made between the ring and methyl protons.

Generally, the *hf* anisotropy of the methyl proton is small compared to that of the ring proton, as has been shown by single crystal studies. The results for the DMQ anion can be interpreted in terms of the small END interaction of the methyl protons in spite of the large isotropic *hf* interaction.

The assumption of the END mechanism enables us to estimate the amount of the END term of the methyl protons. From Fig. 4, the ratio of the optimum η/T's for the methyl and ring protons is 1.8: 1. By a simple calculation, the $g_e\beta_e g_N\beta_N \langle 1/r^3\rangle_{\text{av}}$. of the methyl protons was estimated to be 2 MHz.

There is another plausible interpretation which has been proposed by Atherton and Day for the β-proton in the 2,6-di-*t*-butyl-4-cyclohexyl phenoxyl radical.[11)] They proposed the fluctuation of the isotropic *hf* coupling of the β-proton as a cause of the nuclear relaxation. They made use of the difference in selection rules for the relaxation *via* the END interaction and isotropic *hf* modulation in explaining the dependence of the ENDOR intensity on the sitting ESR line of the magnetic field during the ENDOR measurement. However, there is still a quantitative uncertainty concerning the rotational correlation time of a substituent and the amount of the END interaction which has the same selection rule (S^+I^- and S^-I^+) as the isotropic *hf* modulation.

In the case of DMQ anion there was no apparent change in the relative signal intensity upon a change in the sitting point of the ESR spectra during the ENDOR measurements. No other experimental result which can be the evidence for the isotropic modulation mechanism was found in the present study.

DBQ Anion. The ring protons of the DBQ anion showed the most intense ENDOR signal at $\eta/T=3.5\times10^{-2}$ cp/K (Fig. 2). The optimum temperatures are very different for the three solvents, *i.e.*, methanol, ethanol, and 2-propanol, but the curves almost coincide with each other in the η/T plot. This shows all the relaxation processes relating to the ENDOR intensity are η/T-dependent in the present system.

The optimum η/T for the *t*-butyl protons is much smaller than that of the ring protons. This result could not be interpreted by the nuclear relaxation mechanism caused by END interaction, because the *t*-butyl protons which have the isotropic *hf* coupling of 0.19 MHz are not thought to have a larger END interaction than the ring protons, which have a 6.13 MHz isotropic *hf* coupling. In fact, in the liquid crystal phase the shift of the *t*-butyl *hf* coupling in the 2,4,6-tri-*t*-butylphenoxyl radical is negligibly small.[12)]

On the basis of the difference in the magnitudes of the END interactions of two types of protons in the DBQ anion, we can predict a larger optimum η/T for the *t*-butyl protons than that of the ring protons by applying the END mechanism. The experimental results show, however, that the *t*-butyl protons have a much smaller optimum η/T than the ring protons. The same tendency was found in the experimental results of the ENDOR of the 2,4,6-tri-*t*-butylphenoxyl radical.[5)]

The transition probability of electron spin[13)] may show the η/T dependence, which is characteristic of the relaxation by the g and *hf* anisotropy even at room temperature, because the difference in the components of the g-tensor from the free electron g-value is small enough for us to neglect the contribution of the electron spin-rotation to W_e. The normal situation of the electron-spin relaxation as discussed above suggests that the nuclear relaxation is effective in determining the optimum η/T for the *t*-butyl protons.

The fact that the optimum η/T for the *t*-butyl protons is much smaller than that of the ring protons shows the existence of a nuclear relaxation mechanism which is effective when η/T becomes small. Some of the mechanisms described below may become effective in determining the optimum conditions:

1. Nuclear Spin-rotational Relaxation: When the nuclear spin-rotational interaction is effective, W_n increases with an increase in the temperature (decreasing η/T).[14] As a result, the η/T where W_e and W_n become comparable shifts to a lower value. However, in order to get a W_n as high as W_e the spin-rotational constant should be as large as 1 MHz, which is exceptionally large.

2. Isotropic Modulation: When this mechanism is dominant for the ENDOR enhancement, the enhancement factor is expressed by W_{x2}/W_e,[2,3] where W_{x2} is the nonsecular ($+-\longleftrightarrow-+$) transition probability. The effective correlation time for the *t*-butyl substituent is smaller than that of the electron spin and W_{x2} has a maximum at a slightly larger η/T value than the point where $\omega_e\tau_R\sim 1$. The enhancement factor reaches its maximum at the η/T where W_{x2} is at its maximum; this η/T possibly has a smaller value than that of the optimum η/T for the ring proton. The modulation amplitude of *hfs* for the *t*-butyl protons may be small because the absolute value of its *hf* coupling constant is very small.

3. The Violation of the $\omega_e\tau_R\gg 1$ Condition: At high temperatures $\omega_e\tau_R\gg 1$ condition is not always valid. When $\omega_e\tau_R<1$, there is a temperature where $W_e\sim W_n$. The measurement of T_1 and T_2 showed, however, that even at 25 °C T_1 was longer than T_2. By the rough estimation of τ_R at the optimum η/T for the *t*-butyl protons, it becomes 2×10^{-9} s, much larger than $1/\omega_e$ (2×10^{-11} s).

In the present stage of this study, the lack of quantitative data prevents a detailed determination of the ENDOR mechanism of the *t*-butyl protons. The first and the second mechanism may, however, explain the optimum temperature to some extent. We also cannot discard such intermolecular mechanism as the intermolecular dipolar mechanism or the modulation of the intermolecular contact interaction by molecular motion.

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