ENDOR Relaxation Study of the Effects of Intramolecular Cation Migration on the Ion-pair System*

Masaharu Okazaki and Keiji Kuwata

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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The ENDOR spectra of the ion-pair system of the 2,5-di-*t*-butyl-*p*-benzoquinone anion and the alkali metal cation in 1,2-dimethoxyethane were observed. The influence of the intramolecular cation migration on both the linewidth and the intensity of the ENDOR spectra was experimentally examined. The results obtained were discussed theoretically using the Kaplan-Alexander formula. The intramolecular exchange due to the cation migration was shown to be effective in ENDOR.

Many studies of the dynamic processes in the ion-pair system of a radical anion and an alkali cation in solution have been carried out.[1] As an example of these processes, the so-called linewidth alternation in the ESR spectrum due to the intramolecular cation migration among more than two sites is well known.[2] Kinetic study by measuring the changes in the linewidth of the ESR spectrum is difficult when the rate of the process is smaller than the apparent width of the inhomogeneously broadened line.

ENDOR is useful for the study of the dynamic processes with such small rates. The ENDOR intensity is sensitive to the combination and the competition among various relaxation processes including such a dynamic process.[3-5] Moreover, the ENDOR linewidth does not depend on the secular terms of the *g*-anisotropy of electron and the hf-anisotropy of the nucleus whose resonance frequencies are different from that of the pumping NMR transition.[4] The approach using the ENDOR linewidth has been applied to the kinetic study by a few groups.[6-10] Recently Möbius *et al.* have investigated the restricted rotation by analyzing the ENDOR linewidth quantitatively.[8-10] The study with the ENDOR linewidth, however, has the difficulty that the saturation broadening tends to hide the slight changes due to dynamic processes when the ESR and the NMR transitions are saturated to observe the ENDOR.

The investigation with the ENDOR intensity is more reliable in principle for the study of relaxation processes including such dynamic processes. The linewidth alternation of the ESR spectrum in the system of the 2,5-di-*t*-butyl-*p*-benzoquinone anion and the alkali cation in 1,2-dimethoxyethane was first studied by Chippendale *et al.*[11] In the present investigation the ENDOR study of this system was pursued and the observed results for both the ENDOR intensity and the linewidth were well reproduced by the introduction of the intramolecular exchange process into the theoretical calculation. It was confirmed that the intramolecular exchange due to such a dynamic process has large effects on the ENDOR intensity.

Experimental

The purification of 2,5-di-*t*-butyl-*p*-benzoquinone (DBQ) was done by recrystallization from ethanol. 1,2-Dimethoxyethane (DME) was dehydrated by refluxing over Na–K alloy for 10 h. The sample solution of the DBQ anion was prepared by the alkali metal reduction of DBQ in DME. The concentration of the DBQ anion in the sample solution was about 5×10^{-4} mol dm^{-3}.

In the observation of ENDOR the temperature at the sample position was monitored using a copper-constantan thermocouple, and was controlled by varying the flow rate of the chilled nitrogen in the temperature range from 185K to 243K. The ENDOR spectra were taken with a home-made spectrometer.[12] The microwave power was greater by 5 db than the power which gave the maximum amplitude of the ESR signal. The rf-power was kept constant at about 0.5 mT in the rotating frame. The rf-power was roughly estimated from the coherent splitting of the ENDOR spectrum of K^+DBQ^- in isopropyl alcohol according to the procedure of Freed *et al.*[5]

Method of Calculation

By the introduction of the effects of the intramolecular exchange, the equation of motion for the density operator of the spin system can be given as[13-15]

$$d\rho/dt = i[\rho, \mathscr{H}] - \Gamma(\rho-\rho^0) + (\boldsymbol{P}\rho\boldsymbol{P}-\rho)/\tau_{ex}, \qquad (1)$$

where $\boldsymbol{P}$ is an exchange operator[15] which represents the exchange between the two spin states shown in Fig. 1. These states are connected *via* the transition of k. τ_{ex} is the reciprocal of the exchange rate. $\Gamma(\rho-\rho^0)$ represents the relaxation of ρ to its thermal equilibrium state, ρ^0, due to the perturbational Hamiltonian modulated

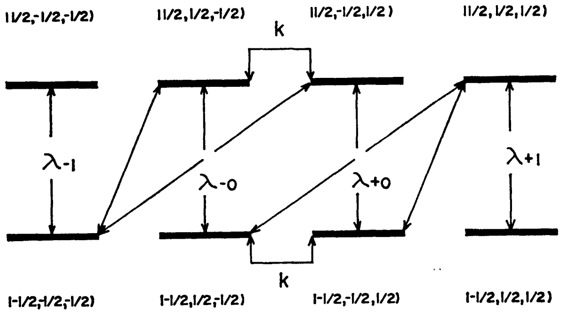

Fig. 1. Energy diagram of the system. Each level is expressed using wave function $|\sigma_e, \sigma_n^1, \sigma_n^2\rangle$. Oblique lines are flip-flip or flop-flop transitions arising from the modulation of the END interaction. Horizontal line with arrow shows the transition corresponding to the intramolecular exchange. $\lambda_{\pm1}$, $\lambda_{\pm0}$ designate the ESR transitions.

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by the random molecular motions. $\mathscr{H}$ is the spin Hamiltonian given by

$$\hbar\mathscr{H} = g_e\beta_e B_0 S_z + \sum_i(-\gamma_n\hbar B_0 I_z^i + a_i I_z^i S_z$$
$$-2B_2\gamma_n\hbar I_x^i \cos\omega_n t) + 2B_1 g_e\beta_e S_x \cos\omega_e t, \qquad (2)$$

where B_1 and B_2 are the strengths of the microwave and the rf-field at the frequencies of ω_e and ω_n respectively, and where g_e and γ_n are the g-factor of the electron and the magnetogyric ratio of the nuclei respectively. B_0 is the strength of the static field, I_z^i and S_z are the z components of the nuclear and electron spin angular momentum, β_e represents the Bohr magneton, and a_i is the isotropic hfsc for the nucleus numbered "i."

The energy levels of the system are shown in Fig. 1, where *t*-butyl protons are omitted from consideration. Each ESR transition is designated using the sum of the quantum numbers for the ring protons, such as λ_{-1}, λ_{-0}, λ_0, and λ_1. For example, λ_{-0} is the transition between $|1/2, 1/2, -1/2)$ and $|-1/2, 1/2, -1/2)$; here $|\sigma_e, \sigma_n{}^1, \sigma_n{}^2)$ represents the spinwave function of the system. The subscripts "e" and "n" indicate electron and nucleus respectively.

The ENDOR intensity observed at the λ_j ESR transition is expressed as E_j. The ENDOR spectra have three peaks, 17.7, 16.2, and 13.8 MHz in the frequency region higher than the free proton frequency of 13.75 MHz. The intensity of the highest frequency peak of 17.7 MHz is expressed as E_j^{high}; it is defined as follows

$$E_j^{\text{high}} = (Z''(\lambda_j\text{: rf on})$$
$$-Z''(\lambda_j\text{: rf off}))/Z''(\lambda_j\text{: rf off}), \qquad (3)$$

where Z'' corresponds to the absorption signal. E_j^{low} and $E_j^{t\text{-butyl}}$ are defined in the same manner as E_j^{high}. RE is defined as

$$RE = E_{-1}/E_{-0}. \qquad (4)$$

The ENDOR spectra were calculated according to the theory developed by Freed, using Eqs. 1 and 2 for an eight-level system as is shown in Fig. 1. The coherent effects were omitted for the sake of brevity in the calculation.[5] The matrix elements in Eq. 1 were calculated by the standard procedure.[16] The correlation time was approximated according to the model developed by Debye and Einstein.[17] These results are listed in Tables 1 and 2. The temperature dependence of the reciprocal of the correlation time $(\tau_{ex})^{-1}$ in Eq. 1 was described by means of the Arrhenius equation as

$$k = (\tau_{ex})^{-1} = A\exp(-E_a/RT), \qquad (5)$$

where A is the preexponential factor and E_a is the activation energy of the cation migration. The hfsc and the g-factor used in the calculation are listed in Table 3. The viscosity data for DME were taken from the literature.[18] The hydrodynamic radius was tentatively taken as 300 pm** on the basis of the molecular model.

TABLE 1. TRANSITION PROBABILITIES[a]

$W_e^{g_2}$	$10^{-1}\hbar^{-2}(\beta B_0)^2(g':g')(\tau_r/1+\omega_e{}^2\tau_r{}^2)$
W_e^{sr}	$18^{-1}(\Delta g:\Delta g)\tau_r{}^{-1}$
W_n^i	$40^{-1}(A_i':A_i')\tau_r$
$W_{x_1}^i$	$60^{-1}(A_i':A_i')(\tau_r/1+\omega_e{}^2\tau_r{}^2)$
$W_{x_2}^i$	$10^{-1}(A_i':A_i')(\tau_r/1+\omega_e{}^2\tau_r{}^2)$
Intramolecular exchange	k

a) The contributions of the hf interaction term and its cross terms with g-anisotropy to the electronic transition were disregarded. $W_e^{g_2}$ and W_e^{sr} mean the electronic-transition probababilities arising from the modulation of the anisotropic g-tensor and the spin-rotation interaction respectively. W_n^i is the transition probability of the number i nucleus; *i.e.*, W_n^1 is of the nucleus at a low resonance frequency, while W_n^2 is of the nucleus at a high resonance frequency. $W_{x_1}^i$ and $W_{x_2}^i$ are the cross-relaxation probabilities arising from the END interaction of the "i" nucleus. 1 and 2 in the subscripts mean flip-flop and flop-flop or flip-flip transitions respectively. g' and Δg are the traceless part of the g-tensor and the deviation of g from the free-spin value respectively. (X: Y) denotes the inner product of the X and Y tensors.

TABLE 2. ESR AND NMR LINEWIDTHS[a]

ESR	$\lambda_{\pm1}$	$7/3(\sum_i W_n^i) + W_e^{g_2}(7/3+4/3\omega_e^2\tau_r^2) + W_e^{sr}$
	$\lambda_{\pm0}$	$7/3(\sum_i W_n^i) + W_e^{g_2}(7/3+4/3\omega_e^2\tau_r^2) + W_e^{sr} + k$
NMR	high freq.	$7/3W_n^2 + W_e^{g_2} + W_e^{sr} + W_n^1 + k$
	low freq.	$7/3W_n^1 + W_e^{g_2} + W_e^{sr}W_n^2 + k$

a) These expressions are given by disregarding the contributions from various cross terms, and also the cross relaxations.

TABLE 3. INPUT PARAMETERS[a]

Hyperfine tensors	proton 1	$A_{xx}=-0.21$G $A_{zz}=1.90$G	$A_{yy}=-1.69$G
	proton 2	$A_{xx}=-0.14$G $A_{zz}=1.24$G	$A_{yy}=-1.11$G
g-Tensor		$g_{xx}=2.0076$ $g_{zz}=2.0024$	$g_{yy}=2.0036$

a) The elements of the hf tensors of Na$^+$DBQ$^-$ in DME were calculated using McConnell-Strathdee's formula.[27] Here only the contribution of the electron at the adjacent carbon atom was assumed, and Q_{CH} was taken as 2.30 mT.

Results and Discussion

Figures 2 and 3 show the temperature dependencies of E_j^{high}, E_j^{low}, RE^{high}, and RE^{low} for Na$^+$DBQ$^-$ in DME. At temperatures higher than 220 K, E_{-1} is greater than E_{-0}. This tendency continued throughout the extrapolation of B_1 to infinity. The dependence on the rf-power was not examined for the lack of a reliable way to examine the incident rf-power on the sample, but the theoretical calculations show that RE^{high} and RE^{low} have small dependencies on the rf-power.

In solution, a difference in ENDOR intensity has been found among hf lines with same degeneracy, and

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** The radius of the DBQ molecule was estimated using the Stewart model, and the cubic root value was 370 pm. Atherton and Day have employed 350 pm for the 2,6-di-*t*-butyl-4-methylphenoxy radical; *cf.* N. M. Atherton and B. Day, *Mol. Phys.*, **27**, 145 (1974).

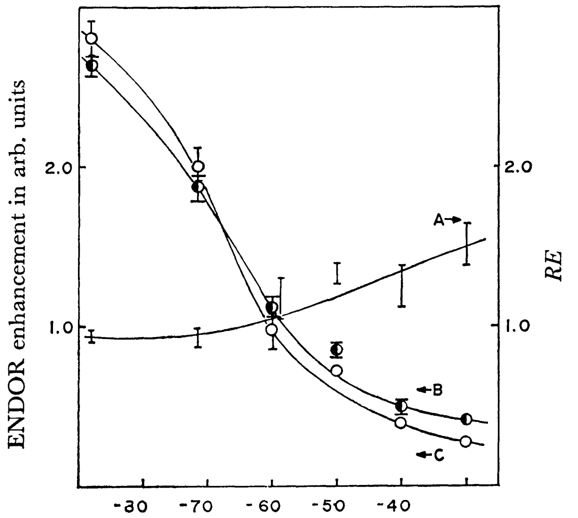

Fig. 2. ENDOR enhancements and the ratio as a function of temperature. B: E_{-1}^{high}; C: E_{-0}^{high}; A: RE^{high}.

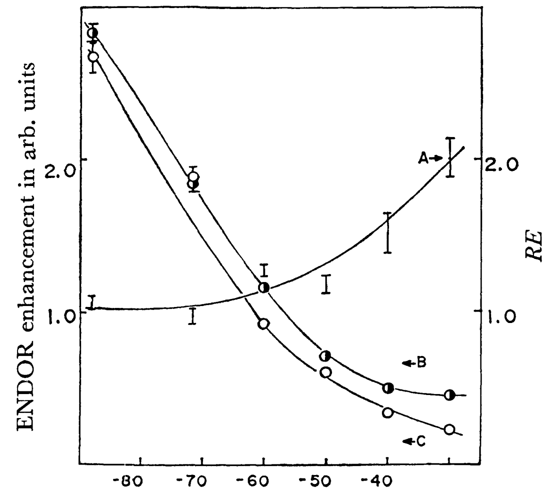

Fig. 3. ENDOR enhancements and the ratio as a function of temperature. B: E_{-1}^{low}; C: E_{-0}^{low}; A: RE^{low}.

this phenomenon has been explained on the basis of the cross relaxations due to the modulation of the isotropic hfc and electron nuclear dipole (END) interactions.[19–22] In the present system, however, the observed results could not be interpreted by the cross relaxations because E_{-1}^{high} and E_{-0}^{high} should be equal in the case of the cross relaxations. As is shown in the calculated results in Fig. 4, the temperature dependencies of RE's can be well interpreted by the introduction of the effect of the cation migration. The parameters used in the calculations in Figs. 4 and 5 were $3.0\times10^{10}\ \mathrm{s}^{-1}$ for A and 6.0 kcal mol^{-1} for E_a in Eq. 5. RE^{low} was larger than RE^{high} in the temperature range of the present experiment and also in the calculated results. Because this difference in the calculation comes from the cross relaxation, flip-flip, or flop-flop relaxation due to the modulation of the END interaction, this W_{x_2} may play an important role in the higher temperature region.

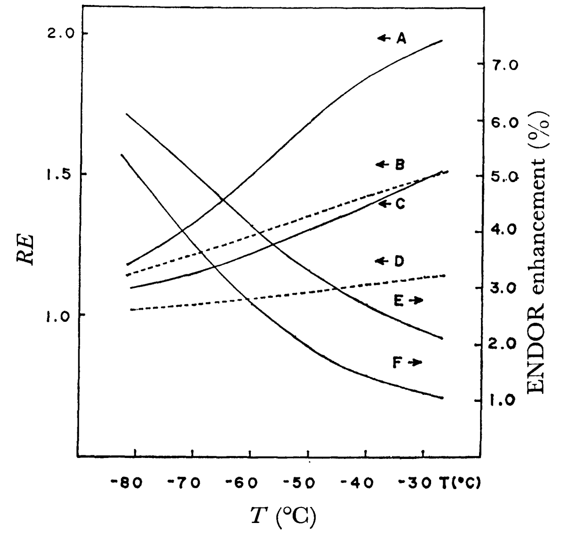

Fig. 4. ENDOR enhancement (calculated) as a function of temperature. A: RE^{low}; B: RE^{low} (without intramolecular exchange); C: RE^{high}; D: RE^{high} (without intramolecular exchange); E: E_{-1}^{low}; F: E_{-0}^{low}. The parameter B_1 was set as, $B_1=\sqrt{1.5}\,(T_1T_2)^{-1/2}(g_e\beta_e)^{-1}\hbar$ for each temperature. The parameter B_2 was set to be 0.5 mT throughout the calculation.

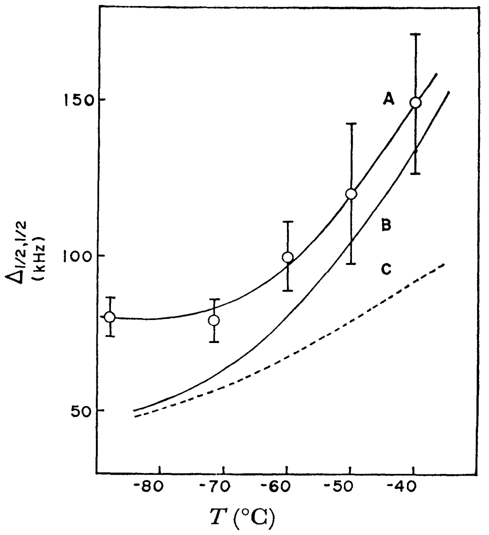

Fig. 5. ENDOR linewidth *vs.* temperature for Na$^+$-DBQ$^-$ in DME. A: experimental; B: calculated with intramolecular exchange; C: calculated without intramolecular exchange. The parameters were the same as those taken in the calculation demonstrated in Fig. 4. The experimental conditions were shown in the text.

In the present system, all the levels are nondegenerate; thus, Heisenberg spin exchange contributes to all the nuclear transitions to the same extent. Therefore, it can not be the origin of the difference between E_{-1} and E_{-0}.

The ENDOR linewidth is a parameter which reflects the cation migration. The experimental and calculated results for the linewidth are shown together in Fig. 5. No difference was found between linewidths in the ENDOR spectra at the λ_{-1} and λ_{-0} ESR transitions.

The solid line shows the result of the calculation including intramolecular exchange, while the dotted line shows those of the calculation without exchange. The ENDOR linewidth rises steeply with the temperature. It increases by about 70 kHz as the temperature increases from −71.5 to −40 °C. There is no distinct change in the ESR spectra in this temperature range.

The Heisenberg spin exchange is a mechanism, the temperature dependence of whose rate is similar to that of the observed ENDOR linewidth. Leniart *et al.* have obtained the ESR linewidth of semiquinones in DME and have reported the rates of spin exchange at various temperatures.[23] Their results give an increase in the ENDOR linewidth of about 30 kHz in the concentration of about 5×10^{-4} mol dm^{-3} in the temperature range from −71.5 to −40 °C.[24] Thus, the contribution of this mechanism was ignored throughout the present calculation.[24]

Both the experiment and the calculation were carried out under the conditions of partial saturation; the saturation broadening is probably one of the main causes of the linewidth. Though the results obtained under partial saturation are less reliable than the ENDOR linewidth extrapolated to zero microwave and rf-power, it is useful only practically in the study of the systems which give merely a weak ENDOR signal.

In the case of K^+DBQ^-, *RE* departs from 1.0 at a lower temperature than in the case of Na^+DBQ^-. This fact corresponds to the results obtained for the ESR linewidth by Chippendale *et al.*, who have reported that the potassium ion starts its migration between two oxygen atoms at a lower temperature than does the sodium ion.[11]

Figure 6 shows the E_{-1} and E_{-0} of *t*-butyl protons at various temperatures, where superscripts denote the counter ions. A large difference between E_{-1} and E_{-0} was found; it may be considered to be another piece of evidence for the effect of the intramolecular exchange on the ENDOR intensity. The optimum temperatures for E_{-1} and E_{-0} were also different, as was to be expected from the fact that the temperature dependence of the intramolecular exchange is different from that of the other relaxation mechanisms.

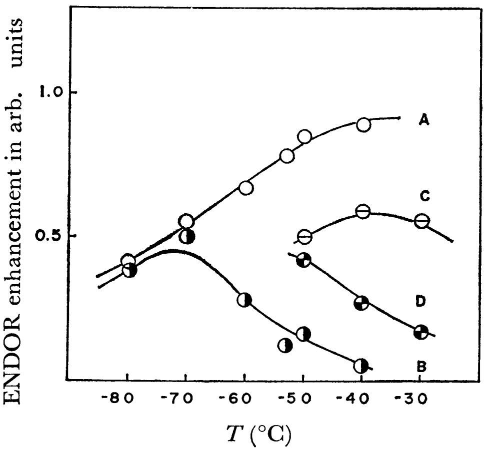

Fig. 6. ENDOR enhancement *vs.* temperature for the *t*-butyl protons of DBQ anion in DME. A: $E_{-1}(K^+)$; B: $E_{-0}(K^+)$; C: $E_{-1}(Na^+)$; D: $E_{-0}(Na^+)$. Counter ions are given in the parentheses.

As the hfsc of the *t*-butyl protons is of the same order as the ESR linewidth of the spin packet, the effect which has been pointed out by Allendoerfer and Maki becomes important.[25] This relationship gives the relative ENDOR intensities as a function of T_2 and hfsc:

$$E = E^0(T_2\Delta\omega)^2/[2.5+(T_2\Delta\omega)^2], \tag{6}$$

where E^0 is the ENDOR enhancement in the case of $T_2\Delta\omega\gg1$ and where $\Delta\omega$ is hfsc expressed in s^{-1}. The observed results, however, can not be described in terms of this effect because: 1) the spin packets of the ESR transitions, λ_{-1} and λ_{-0}, are equally broadened by the intramolecular exchange when the rate is much smaller than the hfsc of the *t*-butyl protons; 2) a tentative calculation using Eq. 6 shows that $RE^{t\text{-butyl}}$ is much smaller than 1.2 at 230 K, even if the value of k is simply added to the linewidth of the λ_{-0} ESR transition. Here 1.0×10^6 s^{-1} and 1.1×10^6 s^{-1} were used for the reciprocals of the spin-spin relaxation time of the λ_{-1} and λ_{-0} ESR transitions respectively.

The effect of the intramolecular cation migration on the ENDOR intensity is also apparent in the case of *t*-butyl protons.

Conclusion

The intramolecular cation migration in the system of the DBQ anion and the Na cation in DME was investigated by means of ENDOR at the smaller exchange rate. The ENDOR intensities of the DBQ anion at λ_{-1} and λ_{-0} ESR transitions were different from each other. The ratio (*RE*) of the ENDOR intensities, E_{-1} and E_{-0}, increased when the temperature was raised, becoming greater than 1.5 at temperatures higher than 240 K. This feature was successfully explained using the Kaplan-Alexander theory.

Besides the various mechanisms which determine the ENDOR intensity,[12,26] a new mechanism, the intramolecular exchange, was shown also to be important in ENDOR.

The fact that RE^{low} is greater than RE^{high} for the ring protons suggests a contribution of the flop-flop or flip-flip relaxation due to the END interaction with the ENDOR intensity[19] at high temperatures. The study of the dynamic process with both the linewidth and the intensity of ENDOR was shown to be more reliable than the study with only the linewidth.

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