

Mobility and ESR Spectra of Free Radicals Trapped in Irradiated Urea–Poly(ethylene oxide) Complex

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ABSTRACT: A detailed ESR study of free radicals trapped in irradiated urea-poly(ethylene oxide) complex was carried out. On annealing at room temperature, the triplet spectrum observed immediately after γ -irradiation at 77 K was converted to a quartet spectrum. Using the spectrum simulation method, the quartet spectrum was found to derive from the scission free radicals,

$$\text{C}_\gamma\text{H}_3\text{-O}-\overset{\text{H}_\beta}{\underset{\text{H}_\alpha \text{ H}_\beta'}{\text{C}_\alpha}}-\text{C}\sim$$
, in which the methylene group took on a *trans-gauche* type configuration.

Temperature dependences of hyperfine splitting widths due to β - and γ -protons were observed and analyzed in terms of the hindered oscillation of the β -methylene group and rotation around the C_α -O bond axis.

KEY WORDS Poly(ethylene oxide) / Urea-PEO Complex / Free Radicals / ESR / Mobility of Radical Site /

In previous papers,^{1,2} we concluded that the radical sites in urea-polyethylene complex (UPEC) were more mobile than those in polyethylene crystal by estimating the temperature dependences of ESR parameters of alkyl radicals and peroxy radicals. Our broad-line NMR study³ also clarified a much more mobile character of polyethylene molecules in the pores of urea molecules. These facts indicate that an intermolecular interaction between molecular chains is stronger in the polyethylene crystal than in UPEC due to the shorter interchain distance in the former. The mobility of the polymer chain and the intermolecular interaction are considered to influence the radiation effect in the polymer solids. Doublet and quartet ESR spectra arising from different radical species were observed in an irradiated solid of normal poly(ethylene oxide) and the urea-poly(ethylene oxide) complex (UPEOC), respectively, by Sugimoto *et al.*^{4,5} However, the precise structure of the radical and its mobility are still opened for further study.

The aim of the present paper is to analyze the ESR spectra of free radicals produced in irradiated UPEOC and their mobility with regard to the radiation chemistry of poly(ethylene oxide) chains.

EXPERIMENTAL

Preparation of the Urea–Poly(ethylene oxide) Complex (UPEOC)

Poly(ethylene oxide) (PEO) with a weight average molecular weight of 6000 was used for this study. It is well known that the urea–poly(ethylene oxide) complex can be prepared by mixing a solution of PEO with urea.^{6,7} UPEOC was made in the following way. Urea (22 g) was added to a solution of poly(ethylene oxide) (10 g) in benzene (1500 ml). This suspension was stirred in a round-bottomed flask for about one week. After filtering with suction, the powder was dried thoroughly *in vacuo* at 10^{-3} mmHg. UPEOC was identified by comparing its DSC curve with those of urea and poly(ethylene oxide). The melting temperature of UPEOC prepared in this study was found to be 146°C.

Irradiation Technique

The samples were subjected to ⁶⁰Co γ -irradiation at the liquid nitrogen temperature under a vacuum of 10^{-4} mmHg. The total dose was 2.8 Mr and the dose rate 0.17 Mr/h⁻¹.

ESR Measurements

ESR spectra were recorded with a JEOL ME-2 electron spin resonance (X band) spectrometer with 100 kHz field modulation at a microwave power of 0.1 mW. A JEOL temperature controller was used to control the temperature observation. An on line spectrum computer JEOL EC-6 was connected to the spectrometer and the data were punched out on paper tape by an A-D converter. The double integration of the first derivative curves was carried out by the electronic computer HITAC 8400. In this way, the relative concentration of free radicals was computed.

RESULTS AND DISCUSSION

Conversion of Unstable Radicals into Stable Radicals

A triplet-like spectrum was observed at 77 K immediately following irradiation at the same temperature. Figure 1 shows a comparison of the spectra observed at 77 K before and after the heat treatment at 218 K. It is evident that the triplet spectrum is changed into a quartet-like spectrum by warming. Figure 2 shows the variation in the relative radical concentration and the relative intensity, I , of the specified peak shown in Figure 1 with the temperature of the heat treatment. This specified

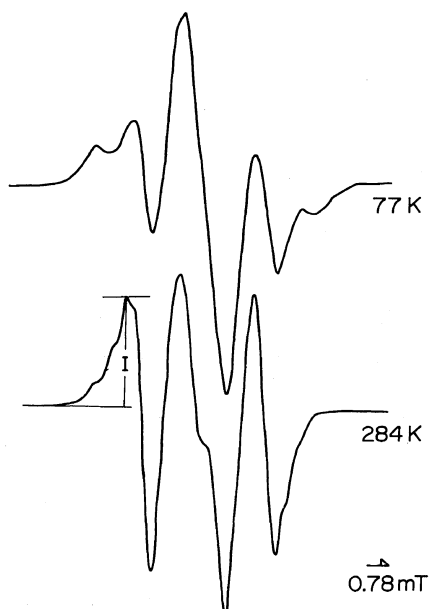


Figure 1. Change in ESR spectra at 77 K before and after heat treatment at 218 K.

peak is characteristic of the quartet spectrum corresponding to "stable radicals," still remaining after warming at 320 K. The spectra, which were the basic data for obtaining Figure 2, were observed at 77 K after heat treatment at respective temperatures. In spite of the increase in the specified peak intensity with temperature, the total concentration of free radicals shows no remarkable decrease with temperature. This fact indicates that the major parts of the free radical corresponding to triplet spectrum, which we call "unstable radicals," are converted into more stable radicals by warming. In other words, it may be concluded that the unstable radicals are the precursor of the stable radicals.

Assignment of the Stable Free Radicals

Figure 3 shows the ESR spectra of stable free

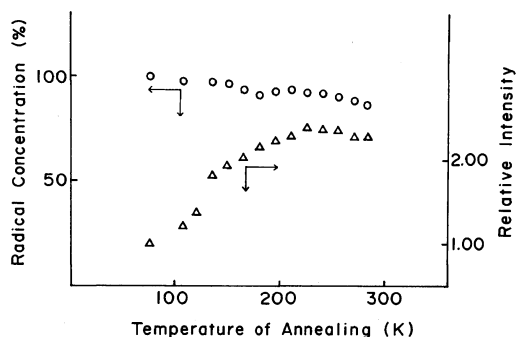


Figure 2. Change in the relative radical concentration (O) and the relative intensity (I) of the specified peak indicated by arrow in Fig. 1 (Δ).

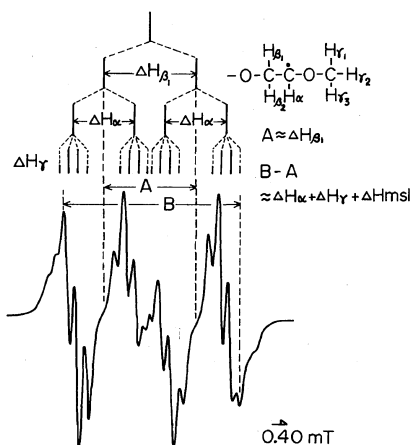
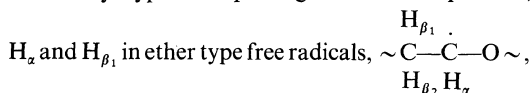
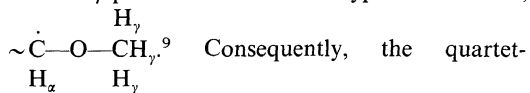


Figure 3. ESR spectra of stable radicals trapped in UPEOC observed at 293 K.

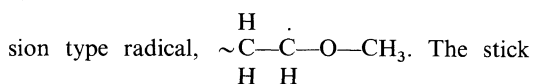
radicals observed at room temperature. This seems to be a quartet spectrum with the approximately equal intensities, each component of which is composed of quartet subsplitting with a binominal intensity. The main quartet is considered to be caused by hyperfine splittings due to two protons,



because the orders of magnitude of the values, 1.8 and 2.5 mT are similar to the values of splittings due to α and β protons of the similar radical reported in the other papers.^{8,9} As discussed in the next section, hyperfine splitting due to H_{β_2} proton should be canceled out. On the other hand, the value of quartet subsplitting is *ca.* 0.25 mT which is also in good agreement with the value of hyperfine splitting due to γ -proton of the ether type free radical,



Consequently, the quartet-quartet spectrum is considered to be that of the scission type radical,



The stick diagram in Figure 3 is a good representation of the assignment. The extralines observed outside the quartet-quartet spectrum is caused by an anisotropic hyperfine splitting due to α -proton;

it shows a so called amorphous pattern.

In order to certify the above assignment, the computer simulation was carried out under following conditions: (a) We assumed that the anisotropy of the coupling constant due to α -proton is axially symmetric and that of coupling constant due to β -proton is negligible. (b) The rough values of coupling constant due to α , β and γ -protons, ΔH_α , ΔH_β , and ΔH_γ and line width, ΔH_{msl} , are estimated from the values of A and B represented in Figure 3. The anisotropic hyperfine splitting due to α -proton, $A_{||}$ and A_{\perp} were also estimated to be 2.5 and 1.5 mT, respectively. The orders of magnitude of these values are similar to those obtained by another workers.⁹ By using the values of spectral parameters described previously, we could obtain theoretical spectra assuming that each of the components is gaussian line in shape. Several theoretical spectra were calculated by gradually changing the values of spectral parameters. These spectra were recorded on an X-Y plotter and compared with the observed spectra in order to get the best fit.

The experimental spectrum observed at 293 K and the calculated spectrum shown in Figure 4(C) seems the best fit with respect to the whole line shape and peak positions. Consequently, it can be concluded that stable radicals is the scission type radical,

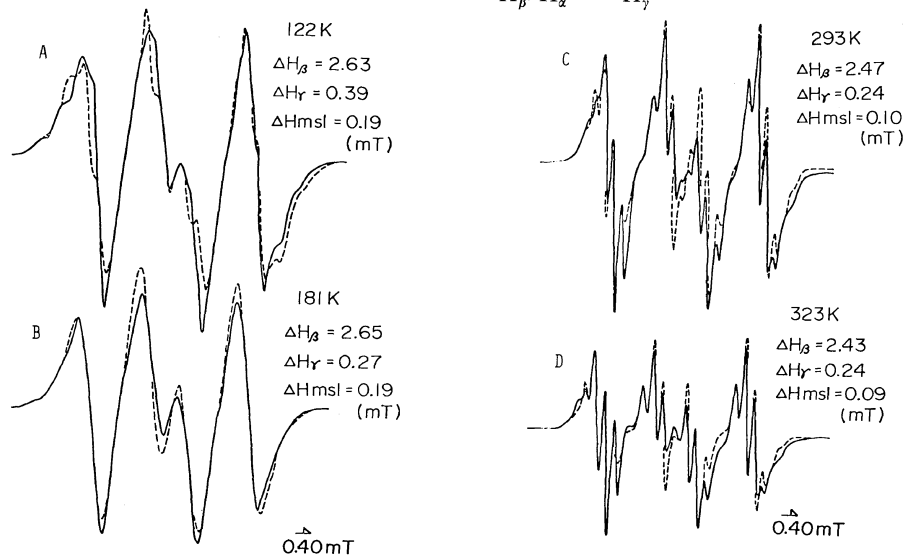
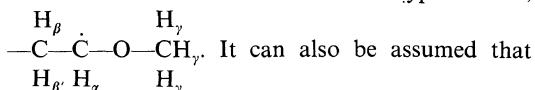
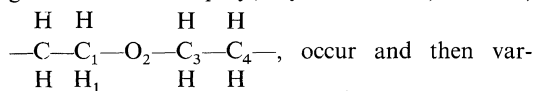


Figure 4. Change in ESR spectra of stable radicals trapped in UPEOC with observation temperature: —, experimental; ----, calculated.

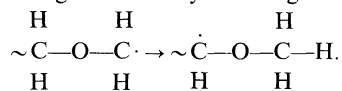
Table I. Possible free radicals produced in irradiated poly(ethylene oxide),
$$\begin{array}{c} \text{H H} \quad \text{H H} \\ \sim\text{C}-\text{C}_1-\text{O}_2-\text{C}_3-\text{C}_4-\text{O}\sim \\ \text{H H} \quad \text{H H} \end{array}$$

| Destructed chemical bond | Primarily produced free radicals | Secondarily produced radicals |
|--------------------------------|--|--|
| C ₁ -H ₁ | $\begin{array}{c} \text{H} \quad \text{H} \\ \sim\text{C}-\dot{\text{C}}-\text{O}-\text{C}\sim \\ \text{H H} \quad \text{H} \end{array}$ (a) | |
| C ₁ -O ₂ | $\begin{array}{c} \text{H H} \\ \sim\text{C}-\text{C}-\text{O}\cdot \\ \text{H H} \end{array}$ (b) → | $\begin{array}{c} \text{H} \\ \sim\text{C}-\dot{\text{C}}-\text{OH} \\ \text{H H} \end{array}$ (d) |
| | $\begin{array}{c} \text{H H} \\ \sim\text{O}-\dot{\text{C}}-\text{C}\cdot \\ \text{H H} \end{array}$ (c) → | $\begin{array}{c} \text{H} \\ \sim\text{O}-\dot{\text{C}}-\text{CH} \\ \text{H H} \end{array}$ (e) |
| C ₃ -C ₄ | $\begin{array}{c} \text{H H} \quad \text{H} \\ -\text{C}-\text{C}-\text{O}-\text{C}\cdot \\ \text{H H} \quad \text{H} \end{array}$ (f) → | $\begin{array}{c} \text{H} \quad \text{H} \\ -\text{C}-\dot{\text{C}}-\text{O}-\text{CH} \\ \text{H H} \quad \text{H} \end{array}$ (g) |

during γ -irradiation three types of chemical degradations of poly(ethylene oxide) chain,



occur and then various free radicals are produced. We can also assume that less stable radicals are converted into more stable radicals as shown in Table I. Since the stable radicals observed in the present study are attributed to the scission type radical, (g), destruction of the chemical bond C₃-C₄ during γ -irradiation is very likely. Unstable radical species which convert to the stable radicals, (g), is not identified completely. However, the unstable radical species possibly is scission type radical, (f), because of the triplet spectrum. Consequently, it is reasonable to consider that the radical conversion mentioned in the previous section is brought about by the migration of the proton,

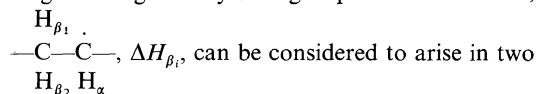


Structure of Scission Type Free Radicals in UPEOC

It is well known that the configuration of a free radical site can be clarified by estimating the values

of hyperfine splitting due to β -protons. In the present section, we discuss again the assignment of the stable radical in view of the values of hyperfine splitting due to β -protons of free radicals trapped in UPEOC and demonstrate its structure with relation to the conformation of poly(ethylene oxide) chains.

The hyperfine splitting due to β -protons of the neighbouring methylene group in the radical,



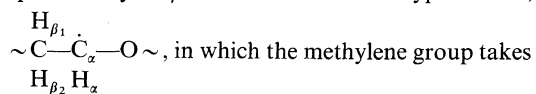
may be considered to arise in two ways; i) by π - δ polarization involving the spin polarization of sp^2 -orbital on the β -carbon and ii) by hyperconjugative interaction with the p -orbital on the α -carbon. These mechanisms are represented as the first and second terms, respectively, in the following equation by Heller and McConnell,¹⁰

$$\begin{aligned} \Delta H_{\beta_i} &= A + K\rho \cos^2\theta_i \\ &= A + B \cos^2\theta_i \end{aligned} \quad (1)$$

where K is a constant, ρ is the spin density, and θ_i is the projected angle between the C _{β_i} -H _{β_i} bond and the π -electron axis on the plane perpendicular to the direction of the C _{α} -C _{β} bond.

Buley *et al.*¹¹ found the small splitting (0.14 mT) to be due to the aldehydic proton, H _{β_1} , in the radical, CH₂·(OH)·C _{α} H _{α} -C _{β_1} H _{β_1} O, in which the aldehydic group takes a plane perpendicular to the p -orbitals; *i.e.*, $\theta_{\beta_1} = 90^\circ$. Hence, these authors concluded that the spin polarization mechanism should lead to a splitting only of the order of 0.1 mT with consideration of the splitting due to methyl protons in the acetyl radical, ·CH₂-C(=O)-CH₃, and thus the

hyperconjugation interaction was neglected. The spin density at β -carbon of the ether type radical,



on a tetrahedral conformation, is less than that in the case of the radical, CH₂(OH)C _{α} H _{α} -C _{β_1} H _{β_1} O. Consequently, the spin polarization mechanism in the hyperfine splitting due to the β -proton of the ether type radical can not be neglected completely. Thus eq 1 may be simplified as follows:

$$\Delta H_{\beta_i} = K\rho \cos^2\theta_i = B \cos^2\theta_i \quad (2)$$

The hyperfine splitting widths due to the two β -

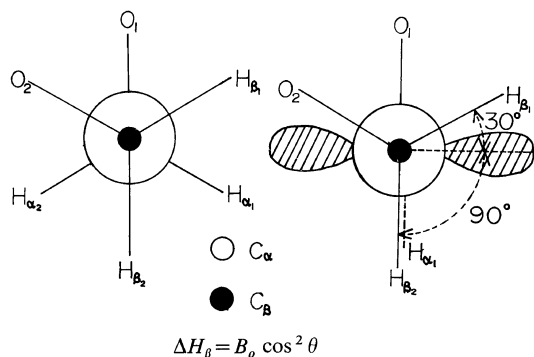


Figure 5. Schematic illustration of steric configuration of the atoms at the site of the stable radical.

protons of the radical, $\sim \text{C} \begin{smallmatrix} \text{H}_{\beta_1} \\ \text{H}_{\beta_2} \end{smallmatrix} \text{C} \begin{smallmatrix} \cdot \\ \text{H}_{\alpha} \end{smallmatrix} \text{O}-\text{CH}_3$, were estimated to be 2.62 and 0.0 mT in the previous section. However, if the stable free radicals are assumed to be a chain radical, $\sim \text{C} \begin{smallmatrix} \text{H}_{\beta_1} \\ \text{H}_{\beta_2} \end{smallmatrix} \text{C} \begin{smallmatrix} \cdot \\ \text{H}_{\alpha} \end{smallmatrix} \text{O}-\text{C} \begin{smallmatrix} \text{H}_{\gamma} \\ \text{H} \end{smallmatrix} \text{C} \sim$,

the value of one of the hyperfine splittings due to β -protons should be of the order of magnitude of the coupling constant due to the γ -proton, 0.24 mT. That is, subsplitting quartet of experimental spectra can be considered as arising from splittings due to two γ -protons and one β -proton is the chain radical. These assumed values of ΔH_{β_1} and ΔH_{β_2} , when substituted into eq 2, give the following relations,

$$\Delta H_{\beta_1} = 2.62 = B \cos^2 \theta_1 \quad (3)$$

$$\Delta H_{\beta_2} = 0.24 = B \cos^2 \theta_2 \quad (4)$$

Since the β -methylene group is in the regular tetrahedral arrangement, eq 5 is satisfied as shown in Figure 5,

$$\theta_2 - \theta_1 = 60^\circ \quad (5)$$

Equations 3, 4 and 5 lead to eq 6,

$$\frac{\cos^2 \theta_1}{\cos^2 (60^\circ + \theta_1)} = 10.9 \quad (6)$$

and the following values were also obtained,

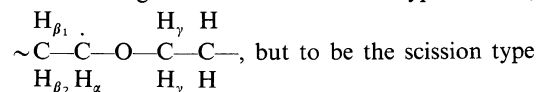
$$\theta_1 = 13.0^\circ \quad (7)$$

$$\theta_2 = 73.0^\circ \quad (8)$$

$$B = 2.76 \text{ mT} \quad (9)$$

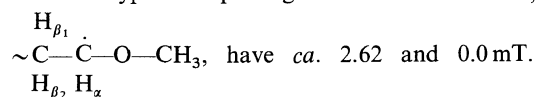
The value of B obtained in eq 9 should be less

probable, being much smaller than 3.92–5.0 mT obtained in the studies of the aliphatic radicals carried out so far.^{12–16} Griffith⁹ also estimated the value of B to be 4.17 mT in the case of the ether type radical, $\sim \text{CH}_2-\text{O}-\dot{\text{C}}_{\alpha}\text{H}_{\alpha}-\text{CH}_3$, by analysing the hyperfine splitting width of β -methylene protons. Hence, it is reasonable that the stable radical should not be assigned to be the chain type radical,



radical, $\sim \text{C} \begin{smallmatrix} \text{H}_{\beta_1} \\ \text{H}_{\beta_2} \end{smallmatrix} \text{C} \begin{smallmatrix} \cdot \\ \text{H}_{\alpha} \end{smallmatrix} \text{O}-\text{CH}_{\gamma}$, as concluded in the

previous section. In addition, it was concluded that the hyperfine splitting widths of the radical,



These values were substituted into eq 2 and the angles, θ_1 and θ_2 , were found to be 30° and 90° , respectively. As a result, the structure of the stable radical (g) can be picturized as shown in Figure 5. It is well known that the conformation of poly(ethyleneoxide) chains in normal crystalline phase are of *trans-trans-gauche* type¹⁷; i.e., a 7_2 -helical structure as represented in Figure 5. Since this conformation is in good agreement with that of the free radical (g), it can be said that the 7_2 -helical structure of poly(ethylene oxide) chain still exists in irradiated UPEOC.

Variation of ESR Spectra of Scission Type Radicals Trapped in UPEOC

Figure 4 shows the change of ESR spectra of stable radicals produced in irradiated UPEOC with the temperature of observation. The ESR spectra of stable radicals changed remarkably and sharper spectra were observed when the observation temperature was about 200 K. Because of this motional narrowing of line widths, subsplittings due to γ -proton were well resolved at temperatures higher than 200 K.

We can see that subsplittings are also observed at lower temperature, 122 K, as shown in Figure 4(A). However, at an intermediate temperature, 181 K, the subsplitting disappears as shown in Figure 4(B). This seems to result from some very complicated temperature dependences of the ESR parameters, ΔH_{α} , ΔH_{β} , ΔH_{γ} and ΔH_{msl} . For example, it may be

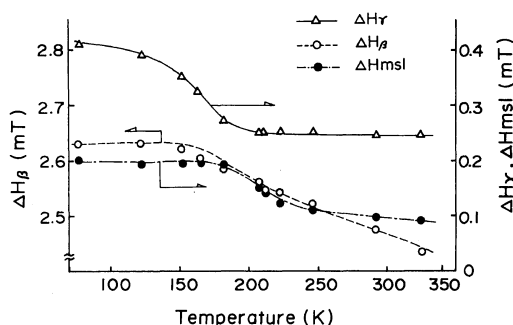


Figure 6. Hyperfine splitting widths due to β - and γ -protons and line width of the stable radicals vs. temperature of observation: Δ (---), ΔH_γ ; \circ (---), ΔH_β ; \bullet (---), ΔH_{msl} .

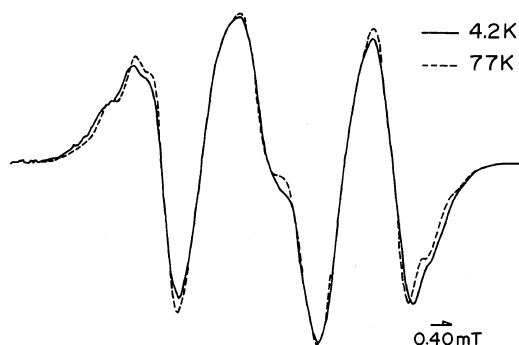


Figure 7. Comparison of the ESR spectra of the stable radical observed at 77 K (---) and at 4.2 K (—).

considered that the ratio of ΔH_γ to ΔH_{msl} determines the resolution of subsplitting due to γ -protons. By the computer simulation method described in the previous section, the ESR parameters at various temperatures were determined.

ΔH_α does not show any detectable decrease throughout the temperature range studied. Figure 6 shows the variation in the values of ΔH_β , ΔH_γ , and ΔH_{msl} . ΔH_β does not change until 150 K and then it abruptly decreases above this temperature. On the other hand, ΔH_γ begins to decrease at a very low temperature compared with the curve for ΔH_β , indicating that γ -protons are quite mobile even at the temperature of liquid nitrogen.

As will be discussed in detail in the next subsection, hyperfine splitting decreases with rising temperature and ΔH_γ seems to increase at a temperature lower than 77 K. In connection with this matter, the spectrum of a stable radical was ob-

served also at liquid helium temperature. A comparison of the spectra observed at 4 K and 77 K is shown in Figure 7. According to the discussion on the stick diagram of the spectrum (Figure 3), the outer shoulders of the main quartet correspond to the values of ΔH_γ . The spectrum observed at 4 K appears to have a slightly broader ΔH_γ . Thus, it may be said that the difference in the spectra observed at 4 K and 77 K reflects the difference in the mobility of the radical sites at these temperatures. A detailed discussion on the spectral change at the temperatures below 77 K will be presented in a future study.

Molecular Motion of the Scission Type Radical in UPEOC

Recently, the effect of hindered rotation of the molecular site on the localization of the unpaired electron was discussed by Bullock and Howard^{18,19} in the case of the cation of 1,2,4,5-tetrahydroxybenzene and other related compounds. These authors discussed the temperature dependence of hyperfine splitting and suggested that the value of the hyperfine coupling constant due to the proton of hydroxyl group depends on the spin density of the carbon atom bonded to the oxygen and the spin polarization. The latter is related either to the twisted angle of the plane of the benzene ring or the value of the overlap integral of p -orbitals on the oxygen and carbon atoms. We also made similar considerations in this regards.

Rotation about the axis of the C_α -O bond in the scission radical, $\begin{matrix} H_\gamma & & H_\beta \\ | & & | \\ H_\gamma C-O-C_\alpha-C_\beta \\ | & & | \\ H_\gamma & & H_{\beta'} \end{matrix}$, was considered. This rotation results in the delocalization of the unpaired electron at the oxygen atom, and leads to smaller hyperfine splitting due to γ -protons. These interpretations fit well with experimental results on the temperature dependence of the hyperfine splittings due to γ -protons. The temperature dependence of the coupling constant due to β -proton shown in Figure 6 is interpreted in terms of the exchange of two β -protons due to the hindered oscillation about the C_α - C_β bond.

When θ_0 and $\Delta\theta$ are defined as the equilibrium angle and the displacement due to torsion, the average value of the coupling constant, $\langle\Delta H_\beta\rangle$ due to β -proton is expressed by the following equation.¹

$$\begin{aligned}\langle \Delta H_\beta \rangle &= B\rho \langle \cos^2 \theta \rangle = B\rho \langle \cos^2 (\theta_0 + \Delta\theta) \rangle \\ &= B\rho [\cos^2 \theta_0 \langle \cos^2 \Delta\theta \rangle \\ &\quad + \sin^2 \theta_0 (1 - \langle \cos^2 \Delta\theta \rangle)]\end{aligned}\quad (10)$$

As stated in the previous section, θ_0 was found to be 30° . Substituting this value, $\theta_0 = 30^\circ$, into eq 10, we obtained,

$$\langle \Delta H_\beta \rangle = B\rho(1/4 + (1/2) \cos^2 \Delta\theta) \quad (11)$$

$\langle \Delta H_\beta \rangle$ in eq 10 or eq 11 decreases with increasing temperature since the amplitude of torsional oscillation, $\Delta\theta$, increases with increasing temperature. This character is well shown by experimental facts. Based on this discussion with regard to the motions of β - and γ -protons, it may be concluded that γ -protons are more mobile than β -protons in the

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scission type radical, $\text{CH}_3\text{—O—C—C}\sim$. It should
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be said that the temperature dependence of ΔH_β and ΔH_γ was observed separately in our study, meaning that, in this paper, it has been possible to make a separate discussion of the local mobilities of methylene and methyl groups.

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