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CIDEP Studies in Low-Frequency Microwave Regions. Magnetic Field Dependence of the CIDEP of Spin-Correlated Radical Pairs

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The magnetic field dependence of the chemically induced dynamic electron polarization (CIDEP) spectra of spin-correlated radical pairs (SCRPs) was studied by time-resolved EPR at three different external magnetic fields, i.e., X band (9.2 GHz, 330 mT), S band (3.0 GHz, 100 mT), and L band (1.5 GHz, 50 mT). The CIDEP spectra were obtained by the photolysis of three systems, xanthone and 2,6-di-*tert*-butylphenol (2,6-DBP) in a sodium dodecyl sulfate (SDS) micelle solution, zinc tetrakis(4-sulfonatophenyl)porphyrin (ZnTPPS) and *p*-benzoquinone (*p*-BQ) in a cetyltrimethylammonium chloride (CTAC) micelle solution, and acetone in 2-propanol, at low temperatures. In the two micelle systems, the SCRP spectra scarcely depend on the external magnetic field, and the decay times do not change much on going from the X band to the L band. These observations are discussed in terms of the cage escape rate and the spin−lattice relaxation rate. The strong magnetic field dependence found for the net emissive polarization in the CIDEP spectra of the xanthone and 2,6-DBP system is ascribed to the magnetic field dependence of the triplet mechanism (TM). On the other hand, the intensity of the SCRP spectrum in the acetone system drastically decreases with decreasing the magnetic field. This observation is rationalized on the basis of the restricted motions of the SCRPs in the 2-propanol solution at low temperatures.

1. Introduction

The spin states of unpaired electrons and nuclei of chemical species play very important roles in chemical reactions, affecting rates, yields, and selectivities, especially in the existence of an external magnetic field. Over the last 2 decades, the spin and magnetic field effects (MFEs) on chemical reactions have been the subject of much interest, and numerous experimental and theroetical investigations have been made.[1−4]

The time-resolved electron paramagnetic resonance (TREPR) technique provides one of the powerful tools for investigating MFEs, not only because it can detect and identify short-lived intermediate radicals and radical pairs directly but also because it provides us with a method to observe the spin states of electrons and nuclei separately.[4−7] Specifically, the phenomenon of chemically induced dynamic electron polarization (CIDEP) observed in the TREPR spectra often gives unique information that is difficult to obtain by other means. A comparison between the CIDEP results and those obtained by other techniques in relation to MFEs is of considerable interest. However, CIDEP experiments so far have been performed mostly in the X band (9.5 GHz, 330 mT), though there have been some studies in other bands.[8−15] Experiments at different microwave (mw) frequencies are desirable for a complete understanding of the CIDEP phenomenon, because CIDEP due to several mechanisms (for example, the triplet mechanism (TM) and ST_- mixing of the radical pair mechanism (RPM)) depends strongly on the external magnetic field.[8−13,16,17] Furthermore, useful information may be obtained about the dynamics of intermediate radicals and radical pairs, because their relaxation times should be strongly dependent on the external magnetic field.[1−4] We therefore started to study CIDEP phenomena at low mw frequencies (low magnetic fields). In a recent paper, we discussed the MFEs on the TM in detail.[13] In this paper, we discuss the MFEs on the CIDEP of spin-correlated radical pairs (SCRPs).

SCRPs are short-lived intermediate species that play essential roles in the spin-state mixings in the course of reactions. CIDEP spectra of SCRPs provide detailed information about interactions in radical pairs and spin and reaction dynamics of intermediate radicals.[4−11,14,15] There have been many studies on the CIDEP of SCRPs, but they have been carried out mostly in the X band (9.5 GHz, 330 mT), except for some studies at higher mw frequencies.[8−10,14,15] However, in view of the MFEs on the CIDEP of SCRPs, studies at low magnetic fields are also interesting because more effective ST_- mixing and possible changes in relaxation times are expected. Moreover, in some cases, the CIDEP generation mechanisms in the SCRPs are of interest. For example, the SCRP spectra with excess net polarizations have been observed in some systems,[18−21] but it is difficult to determine unequivocally the generating mechanisms of the net polarization, whether it is the TM or ST_- mixing of RPMs or others. The MFEs on the CIDEP spectra would be useful for understanding the CIDEP mechanisms in such systems.

In this work, we have investigated the CIDEP spectra of SCRPs in three representative systems using the TREPR spectrometers in the L band (1.5 GHz, 50 mT) and S band (3.0 GHz, 100 mT) as well as the X band. We have succeeded in observing the CIDEP spectra of SCRPs at low mw frequencies for the first time. The systems studied are xanthone and 2,6-di-*tert*-butylphenol (2,6-DBP) in a sodium dodecyl sulfate (SDS) micelle solution, zinc tetrakis(4-sulfonatophenyl)porphyrin (ZnTPPS) and *p*-benzoquinone (*p*-BQ) in a cetyltrimethylammonium chloride (CTAC) micelle solution, and acetone in 2-propanol at low temperatures. The CIDEP spectra of the SCRPs in these systems have been investigated extensively in the X band, and their spectral features are well characterized.[20,22−26] Here we compare the spectra obtained at different magnetic fields and discuss the magnetic field dependence of the spectra and time developments of the CIDEP signals.

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2. Experimental Section

TREPR measurements in the X, S, and L bands were carried out with a modified JEOL EPR spectrometer equipped with two microwave units, one for the X band and the other for the S and L bands, as reported before.[12,13] CIDEP spectra were obtained by accumulating dc-detected EPR signals without field modulation using a boxcar integrator (Stanford Research System SR-250 or PAR Model 160) whose gate width and delay time were usually 0.2 and 1 μs, respectively. A digital oscilloscope (Tektronix TDS 520 or 2430A) was used for recording the time evolutions of transient signals. In the measurements of the time evolutions, the mw power was kept as low as possible, 0.2 mW in the X band and 1 mW in the L band. Because of the low Q factor of the L-band resonator, the effective mw power is considered to be sufficiently low in the L band. The time evolution data were stored and processed in a personal computer. A Nd-YAG laser (Quanta-Ray GCR-170, SHG 532 nm, 5 Hz) was used for photoexcitation in the case of ZnTPPS and a XeCl excimer laser (Lumonics Hyper 400, 308 nm, 7.5 Hz) in other cases.

The sample solution was deoxygenated by bubbling nitrogen gas before and during the experiments and flowed in a quartz flat cell (optical path 1 mm for S and L bands, 0.3 mm for X band) or a quartz tube (1-mm o.d.). The sample temperature was controlled with cold nitrogen gas flow.

Xanthone, 2,6-DBP, and *p*-BQ were commercially available special-grade reagents (Nacalai tesque) used as received. ZnTPPS was synthesized from *meso*-tetrakis-4-sulfonatophenyl)-porphine dihydrochloride (Porphyrine Products, Inc.) in ethanol. SDS and CTAC were special-grade reagents (Nacalai Tesque) used as received. The micellar solutions were prepared with a concentration of 0.1 M in distilled water. The micelle concentrations were about 1−1.5 mM. (The critical micelle concentrations were 8 and 1.4 mM, and the aggregation numbers were 62 and 105 for SDS and CTAC, respectively.) Acetone, 2-propanol (Nacalai Tesque), acetone-d_6, and 2-propanol-d_8 (Aldrich) were used as received.

3. Basis of the Analysis

The CIDEP spectra of SCRP are now well understood.[6−10,18−20,24,27] The spectral simulation was carried out according to the reported method.[18,19] Radicals comprising the pair interact with each other by an exchange interaction (J) resulting in the mixing of the singlet state (S) with the triplet state (T) of the pair. Then, in the high-field approximation, the eigenfunction and eigenvalues of the radical pair are given as

$$|\psi_1\rangle = |\mathrm{T}_+\rangle \qquad \omega_1 = -J + \omega \tag{1}$$

$$|\psi_2\rangle = \cos\theta|\mathrm{S}\rangle + \sin\theta|\mathrm{T}_0\rangle \qquad \omega_2 = \Omega \tag{2}$$

$$|\psi_3\rangle = -\sin\theta|\mathrm{S}\rangle + \cos\theta|\mathrm{T}_0\rangle \qquad \omega_3 = -\Omega \tag{3}$$

$$|\psi_4\rangle = |\mathrm{T}_-\rangle \qquad \omega_4 = -J - \omega \tag{4}$$

with

$$\omega = \frac{1}{2}(\omega_a + \omega_b) \tag{5}$$

$$Q = \frac{1}{2}(\omega_a - \omega_b) \tag{6}$$

$$\Omega^2 = J^2 + Q^2 \tag{7}$$

and

$$\tan 2\theta = Q/J \tag{8}$$

Here, ω_a and ω_b are the frequencies of the EPR transitions of radical a and radical b, respectively. When radical pairs are produced by a reaction of the triplet state of the precursor molecule, the initial population of each triplet sublevel is usually assumed to be $^1/_3$.[24,27] Sublevels 2 and 3 have different populations by the state mixing between S and T_0. However, it has been suggested that in some systems, fast relaxation between sublevels 2 and 3 must be assumed to explain the observed spectra.[18,19] In this case, it is assumed that sublevels 2 and 3 have the same population. Moreover, the initial population of each triplet sublevel may be different because of the polarization due to the TM. This population difference is represented by a parameter α. When the population difference in the thermal equilibrium is neglected, the populations of the sublevels of SCRP are given by

$$P_1 = \frac{1}{3} + \alpha \tag{9}$$

$$P_2 = \frac{1}{6}\exp\left(-\frac{1}{2}k_\mathrm{r}t\right) \tag{10}$$

$$P_3 = \frac{1}{6}\exp\left(-\frac{1}{2}k_\mathrm{r}t\right) \tag{11}$$

$$P_4 = \frac{1}{3} - \alpha \tag{12}$$

Here, k_r is the rate constant of the radical recombination from the singlet state of the radical pair. When $Q \gg J$, transitions among spin sublevels produce hyperfine (hf) lines each of which is split by $2J$ into two lines with emission and absorption (E/A shape line). The relative transition intensities of the EPR lines are given by

$$I_{12} = -I_{24} = \sin^2\theta\left[\frac{1}{3} + \alpha - \frac{1}{6}\exp\left(-\frac{1}{2}k_\mathrm{r}t\right)\right] \tag{13}$$

$$I_{13} = -I_{34} = \cos^2\theta\left[\frac{1}{3} - \alpha - \frac{1}{6}\exp\left(-\frac{1}{2}k_\mathrm{r}t\right)\right] \tag{14}$$

Parameter α produces the net polarization by adding excess populations to the sublevels of the SCRPs. It should also be understood that the value of J used here represents a time average of the fluctuating J, because the radicals in the pair are not fixed and the value of J varies rapidly with time.

The decay of the CIDEP signal of the SCRP is usually determined by the cage escape rate of the radicals as well as the spin−lattice relaxation rate. The spin−lattice relaxation processes among spin states of the SCRPs have been discussed previously.[1−3,9,10,28,29] They are considered to be induced by the fluctuating local field (electron−nucleus dipole interaction, *g*-factor anisotropy, and spin rotation) and electron−electron dipole interaction. The main cause for the fluctuation of the local field is considered to be the rotational motion of the radicals. The spin−lattice relaxation time T_1 is given by the following equation:

$$\frac{1}{T_1} \approx \frac{{B_\mathrm{loc}}^2\tau_\mathrm{c}}{2(1 + {\omega_0}^2{\tau_\mathrm{c}}^2)} \tag{15}$$

Here, B_loc is the value of the local magnetic field that induces the relaxation transition and τ_c is the correlation time of the

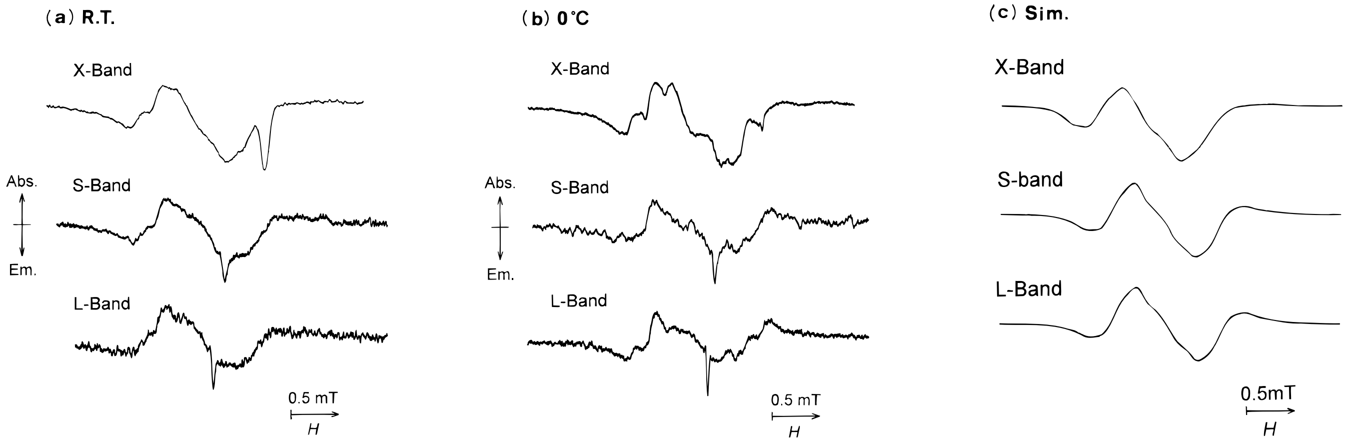
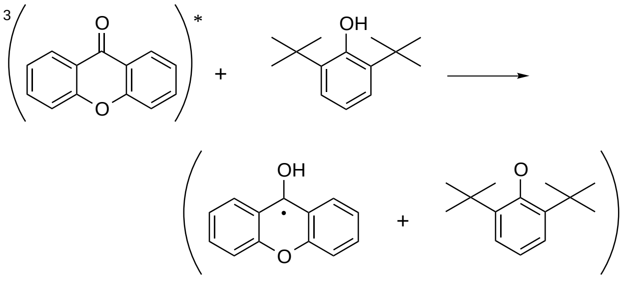


Figure 1. CIDEP spectra in the X, S, and L bands observed in the photolysis of xanthone and 2,6-DBP in a SDS micelle solution at (a) room temperature (delay time: 0.5 μs) and (b) 0 °C (1.0 μs). In some spectra, particularly at 0 °C, peaks due to the separate radicals are superimposed. The concentrations of xanthone, 2,6-DBP, and SDS are 2.1×10^{-3}, 2.1×10^{-3}, and 0.10 M, respectively. (c) The simulated spectra in the X, S, and L bands. Parameters used in the simulation are given in the text.

fluctuation. The relaxation time determined by the fluctuation of the electron dipole interaction is also given by a similar equation. The magnetic field dependence of T_1 may be classified in two cases, fast ($\omega_0\tau_c \ll 1$) and slow ($\omega_0\tau_c \gg 1$) fluctuation regions. In the fast fluctuation region, T_1 is independent of the external magnetic field, whereas in the slow region, T_1 decreases rapidly with decreasing the external magnetic field. Though the absolute value of T_1 depends on B_{loc}, the ratio of T_1 at different magnetic fields is determined only by τ_c.

4. Results and Discussion

(a) Xanthone/2,6-DBP in a SDS Micelle. Figure 1 shows the CIDEP spectra in the X, S, and L bands observed in the photolysis of xanthone and 2,6-DBP in a SDS micelle solution at room temperature and 0 °C. The hydrogen-abstraction reaction of triplet xanthone from 2,6-DBP in the SDS micelle produces xanthone ketyl and phenoxyl radicals to form the SCRP:



The spectra show a characteristic E/A/E/A pattern assigned to the SCRP composed of the xanthone ketyl and the 2,6-DBP phenoxyl radical. The sharp signals observed at slightly different positions with different mw frequencies are assigned to the solvated electron ($g = 2.0003$).[21] There are also peaks of the separated radical superimposed on the spectra. The X-band spectrum at room temperature agrees well with that reported by Ishiwata *et al.* previously.[20] The spectra were slightly better resolved at 0 °C. The observed spectra show clear magnetic field dependence. In the X band, the spectra have a considerable net emission (E) in addition to the E/A/E/A pattern of the SCRP as reported before,[20] but in the S band, the net E contribution becomes much smaller, and in the L band, it is hardly detectable. To see these features more quantitatively, we have simulated the spectra by the method described above.

The simulated spectra shown in Figure 1c are in reasonable agreement with the observed ones. The parameters used in the simulation are the following: the g factor and the hyperfine coupling (hfc's) constants of xanthone ketyl are 2.0030, 0.410 mT (number of equivalent protons: 2), 0.380 mT (2), 0.100 mT (2), 0.060 mT (2), and 0.270 mT (1) and those of 2,6-DBP phenoxyl radical are 2.0045, 0.200 mT (2), 0.960 mT (1), and $J = -0.2$ mT.[20] These parameters are common in the X, S, and L bands. On the other hand, parameter α varies with the magnetic field, $\alpha = 0.025$, 0.008, and 0.002 in the X, S, and L bands, respectively. The results of the simulation clearly show that the main spectral feature with the E/A/E/A pattern of the SCRP spectrum, which is mainly determined by J and the hfc's, is scarcely affected by the magnetic field. The interaction between the radicals in the pair represented by exchange integral J in the spectra is independent of the external magnetic field. On the other hand, the net E polarization, which is given by parameter α in the simulation, decreases with decreasing the magnetic field. This observation excludes the possibility that the net polarization is due to ST_- mixing (ST-M) of RPM, because the polarization due to ST-M is expected to increase at lower magnetic fields.[11,12]

Magnetic field dependence of the net polarization was observed in the pyrazine/2-propanol and maleic anhydride/2-propanol systems reported previously.[13] There we discussed the magnetic field dependence of the contribution of the TM using the Atkins−Evans theory.[16] The observed magnetic field dependence of the net E polarization in these SCRP spectra can also be rationalized on the basis of the TM. It is considered that the reaction of triplet xanthone with 2,6-DBP is rapid enough to transfer the TM polarization to the produced SCRP in the SDS micelle. This result suggests that both precursor triplet xanthone and 2,6-DBP are together within the micelle sphere. Furthermore, the magnetic field dependence of parameter α is quite similar to that found for pyrazine and maleic anhydride systems. Figure 2 shows the results calculated by using the Atkins−Evans theory for the spin−lattice relaxation time ($^3T_1$) of triplet xanthone ($|D| = 2.0$ GHz and $|E| = 0.52$ GHz)[30] and the spin polarization of the produced radicals due to the TM (P_{TM}) vs the rotational correlation time (τ_R) of triplet xanthone. From the comparison of the observed magnetic field

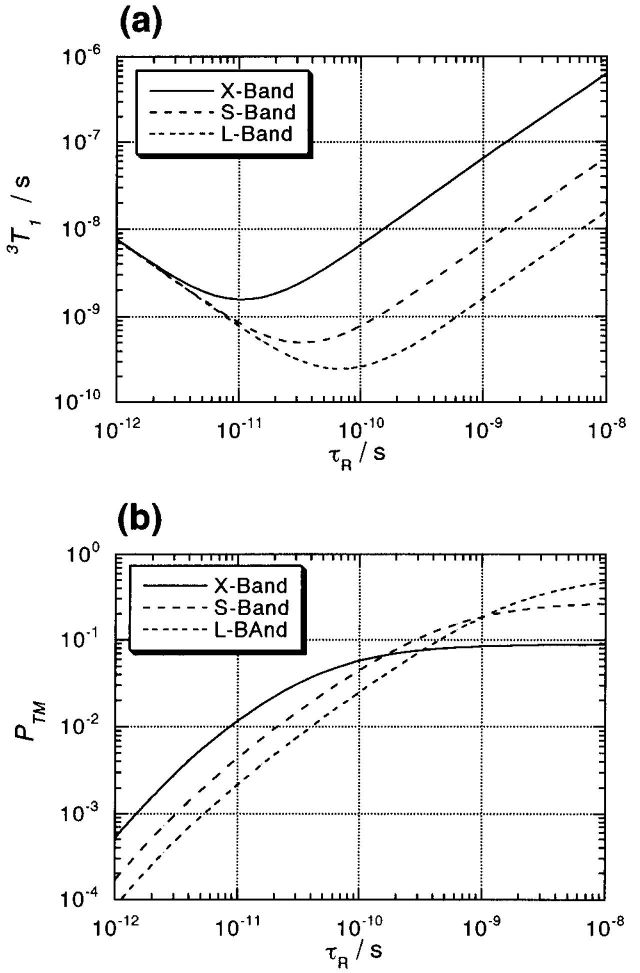


Figure 2. Calculated values of (a) $^3T_1$ and (b) P_{TM} vs τ_R in the X, S, and L bands for xanthone and 2,6-DBP in a SDS micelle. It is assumed that $|D| = 2.0$ GHz, $|E| = 0.52$ GHz, and $k_T = 3 \times 10^8$ s^{-1}.

dependence of the TM polarization with the results given in Figure 2, it is suggested that triplet xanthone in the micelle is rotating fast and its correlation time τ_R is $\leq 10^{-10}$ s around room temperature. Taking into account the molecular size of xanthone, this result indicates that the viscosity of the inside of the micelle is low as in hydrocarbons.

Figure 3a shows the time evolutions of the SCRP CIDEP signals in the X and L bands observed in xanthone and 2,6-DBP in the SDS micelle at 0 °C. The decays are expressed approximately by single-exponential curves, and the decay rates determined by least-squares fits of the data are 3.3×10^5 and 5.0×10^5 s^{-1} in the X and L bands, respectively. The former value is somewhat smaller than the value obtained by Murai *et al.*[20,31] at room temperature. From an analysis of the magnetic field effect on the transient absorption, Murai *et al.*[31] estimated the escape rate constant to be 3.2×10^5 s^{-1} at room temperature. At 0 °C, the escape rate would be slower and be comparable to or smaller than the spin−lattice relaxation rate. The increase of the decay rate on going from the X band to the L band is considered to be due to the increase of the spin−lattice relaxation rate. Assuming that the spin−lattice relaxation rate is comparable to the escape rate in the X band, T_1(X band)/T_1(L band) becomes about 2. Then τ_c is estimated to be $\sim 2 \times 10^{-11}$ s from eq 15.

The rotational correlation times of small radicals in micelles have been investigated before. For example, the rotational correlation times of small stable nitroxide radicals in the SDS micelle were estimated to be 3×10^{-11} s from a line-width analysis.[32] In the simulation of the TREPR and stimulated nuclear polarization spectra, rotational correlation times of (3−5) $\times 10^{-11}$ s were successfully used to calculate the relaxation rates of the benzoyl radical in alkyl sulfate micelles induced by anisotropy of hyperfine interaction.[33,34] If we take τ_c to be 3×10^{-11} s, eq 15 with $T_1 \approx 2 \times 10^{-6}$ s in the L band predicts T_1 in the X band to be $\sim 7 \times 10^{-6}$ s. Considering the uncertainties in the estimation of T_1 and the approximate nature of eq 15, the agreement between our value and the reported values may be considered reasonable. Relaxation induced by the electron−electron dipolar interaction is not important here, because the relaxation time should be much longer for this process.[29]

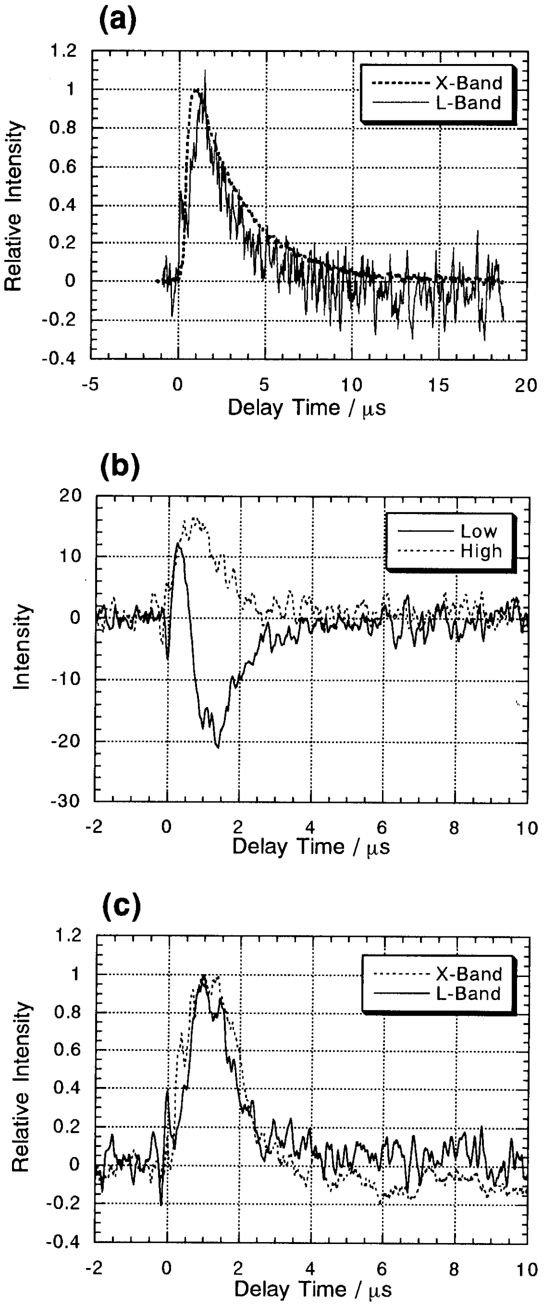


Figure 3. (a) Time evolutions of the CIDEP signals of the SCRPs observed in the photolysis of xanthone and 2,6-DBP in a SDS micelle at 0 °C in the X and L bands. (b and c) Time evolutions of the EPR signals observed in the photolysis of ZnTPPS and *p*-BQ in a CTAC micelle at 0 °C. (b) At the low-field side (E) and high-field side (A) in the E/A peak shape in the L band. (c) SCRP signals in the X and L bands.

(b) ZnTPPS/*p*-BQ in a CTAC Micelle. Figure 4 shows the CIDEP spectra of ZnTPPS and *p*-BQ in a CTAC micelle

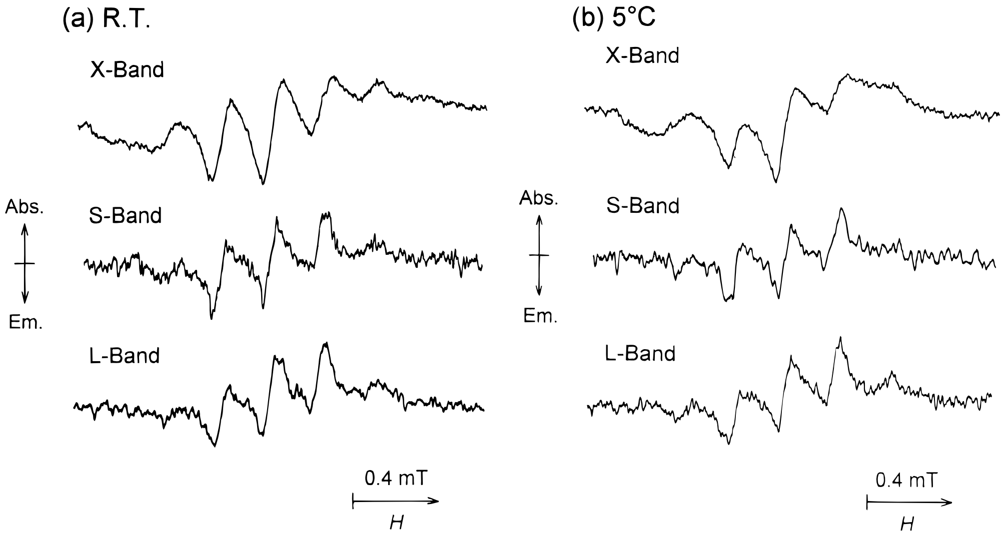


Figure 4. SCRP CIDEP spectra in the X, S, and L bands observed in the photolysis of ZnTPPS and *p*-BQ in a CTAC micelle at (a) room temperature and (b) 5 °C. The concentrations of ZnTPPS and *p*-BQ are 0.5 × 10^{-3} and 1.9 × 10^{-3} M, respectively.

solution at room temperature and 5 °C. The reaction is considered to proceed according to the following scheme:

$$^3\text{ZnTPPS}^{4-} + \text{BQ} \xrightarrow{\text{ET}} \text{ZnTPPS}^{\bullet 3-} + \text{BQ}^{\bullet -}$$

The spectra are characterized by E/A-type hyperfine peaks that are assigned to the SCRP signals of the *p*-BQ anion radical (a_H = 0.236 mT). This result is similar to that found for the X-band spectrum of ZnTPPS and duroquinone in a CTAC micelle solution reported previously.[22,23] The ZnTPPS^{3-} and *p*-BQ$^-$ anion radicals are trapped by the CTAC cationic micelle and interact with each other. In the X band, a broad background signal presumably due to ZnTPPS^{3-} radical is observed, but this signal is much reduced in the S- and L-band spectra. Such a reduction of a broad signal at low magnetic field was also observed in the case of ZnTPP cation radical in alcohols studied previously.[13] This is probably due to short spin−lattice relaxation times of ZnTPPS^{3-} at low magnetic fields. The mw frequency dependence of T_1 indicates that T_1 becomes much shorter at low mw frequencies when τ_c is larger than ~10^{-10} s. Such a value is reasonable for τ_c of a large molecule like ZnTPPS. A slight distortion of the E/A type over the entire spectrum observed in the X band, which is ascribed to the ST$_0$M RPM due to the difference in the *g* factors (Δg) between ZnTPPS^{3-} (g = 2.0025) and *p*-BQ anion (g = 2.0040) radicals, also decreases at low magnetic fields. Consequently, the spectra in the S and L bands are more symmetric. The E/A-type SCRP spectra are almost the same in X, S, and L bands, but the line widths of the SCRP spectra appear to be slightly different depending on the magnetic field.

In Figure 3b and 3c, the time evolutions of the E/A line shape in the L band and the SCRP CIDEP signals in the X and L bands observed for ZnTPPS and *p*-BQ in the CTAC micelle at 0 °C are shown. A quick rise and decay of the net A polarization was observed in the L band as shown in Figure 3b, but this was not observed in the X band. This component is considered to arise from the radicals that have the polarization of the TM. The net A polarization due to the TM would increase with decreasing the magnetic field because of the large rotational correlation time of ^{3}ZnTPPS^{4-}, as found for ^{3}ZnTPP in our previous work.[13] Because of poor *S*/*N* ratios, it is difficult to make an accurate comparison of the decays in the X- and L-band signals. However, Figure 3c shows that the decay rates are similar in both X and L bands, being about 1.0 × 10^6 s^{-1}. In previous works on ZnTPPS and duroquinone (DQ) in a CTAC micelle,[22,23] the escape rate was estimated to be 4 × 10^5 s^{-1}. In the present system, a similar or larger escape rate is expected (because *p*-BQ is more soluble to water compared with DQ), and the SCRP CIDEP signal decay may be determined by it. However, the fact that the decay rate is not enhanced much on going from the X band to the L band indicates that the spin−lattice relaxation time is still relatively long even in the L band.

(c) Acetone/2-Propanol. The CIDEP spectra obtained in the photolysis of acetone in 2-propanol have been investigated extensively.[24−26,35,36] The hydrogen-abstraction reaction of triplet acetone from 2-propanol produces a pair of 2-hydroxypropan-2-yl radicals. The CIDEP spectra are strongly dependent on temperature, indicating that various polarization mechanisms are involved. It is now well-established that the SCRP spectrum of the 2-hydroxypropan-2-yl radical pair can be observed at very low temperatures. Here we focus our attention on the SCRP spectrum. Figure 5a shows the low-temperature CIDEP spectra in the X, S, and L bands observed in the photolysis of acetone in 2-propanol. As reported previously, the X-band spectrum shows an E/A central peak at −45 °C and a strong distortion of the central portion of the spectrum at further lower temperatures that were ascribed to the superposition of the SCRP spectrum. In the S and L bands, however, the SCRP spectrum is not clearly observed even at very low temperatures. This is partly because of the enhancement of the emissive polarization due to the ST-M and the presence of the second-order splittings as reported before.[12] However, the relative contribution of the SCRP spectrum also appears to be diminished. To examine this point further, we have studied the photolysis of acetone-d_6 in 2-propanol-d_8. The relative intensity of the SCRP signal should be greatly enhanced, since the polarization due to the ST$_0$ and ST$_-$ mixing RPM in the deuterated system is greatly reduced because of much smaller hfc's of the deuterated radical.

Figure 5b shows the CIDEP spectra in the X, S, and L bands observed at about 1 μs after the photolysis of acetone-d_6 in 2-propanol-d_8 at low temperatures. The X-band spectrum shows an E/A peak in the center of the SCRP spectrum at −45 °C, and the SCRP spectrum dominates over the entire spectrum at very low temperatures. In the S- and L-band spectra, the emissive polarizations due to the ST-M are much weaker, but the SCRP spectra are still very weak. Therefore, it is concluded

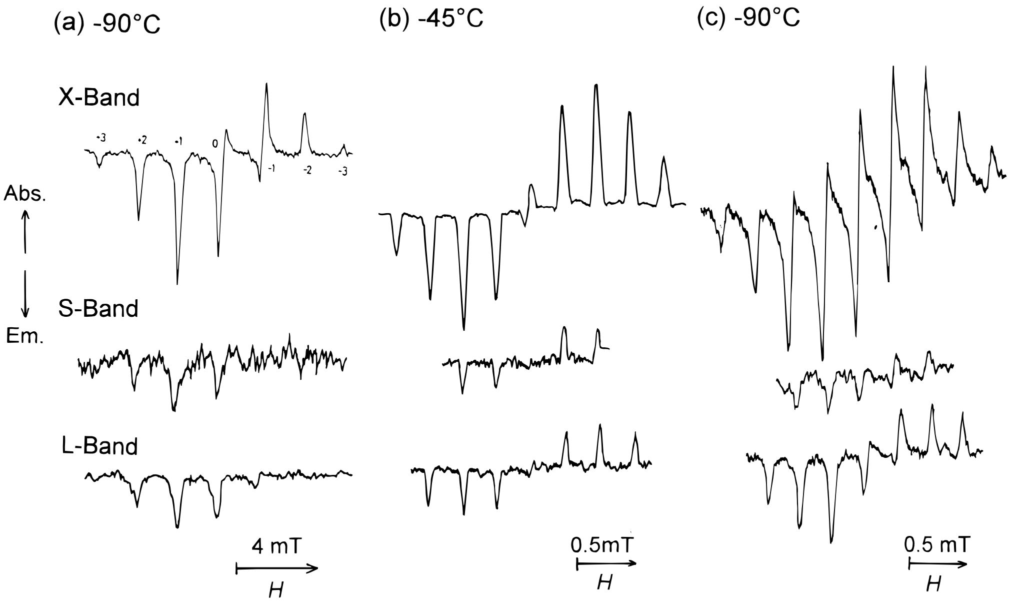


Figure 5. (a) SCRP CIDEP spectra in the X, S, and L bands observed in the photolysis of acetone (0.1 M) in 2-propanol. (b and c) SCRP CIDEP spectra observed in the X, S, and L bands on the photolysis of acetone-d_6 (0.1 M) in 2-propanol-d_8. Observed temperatures are shown in the figure.

that the intensities of the SCRP signals are actually reduced at lower magnetic fields.

The magnetic interaction relevant in producing the SCRP polarization is considered to be independent of the magnetic field. Other factors affecting the SCRP polarization, such as the correlation time and the reaction rate in the singlet manifold, are mainly determined by the diffusion processes in the solution and are also independent of the magnetic field. Then the change of the spin−lattice relaxation time is the most likely cause of the weak SCRP signal at low magnetic fields. Unfortunately, the decay of the SCRP signal could not be measured because of the weak signal intensity and the poor *S*/*N* ratio in the L band. However, the relative intensity of the SCRP signal with respect to that of the separate radical is increased with shorter delay times, indicating that the decay time of the SCRP signal is short.

In a previous work, $1/T_1$ of the SCRP signal of the deuterated system in the X band was estimated to be 5.5×10^5 s^{-1} at -80 °C.[25,26] When the system deviates from the fast fluctuation region, T_1 in the L band becomes much shorter. If the correlation time effective for the relaxation is on the order of 10^{-10} s, eq 15 predicts that T_1 in the L band becomes 1 order of magnitude shorter than that in the X band. There is some evidence that the rotational correlation time of the radical in the pair is actually relatively long. It was found that the hf line widths of the SCRP spectrum of the 2-hydroxypropan-2-yl radical depend on the magnetic quantum number of the nuclei (M_I), and the rotational correlation time of the radical in the pair was estimated to be an order of magnitude longer than that of the separated radical. This observation was explained in terms of the restricted motion of the radical pair in the solvent structure at low temperatures. Thus, the observed weak intensities of the SCRP spectrum at low magnetic fields appears to be explained in terms of faster signal decays due to shorter relaxation times.

5. Conclusions

We have studied the magnetic field dependence of the CIDEP spectra of the SCRP obtained by the photolysis of three systems, xanthone and 2,6-DBP in an SDS micelle solution, ZnTPPS and *p*-BQ in a CTAC micelle solution, and acetone in 2-propanol, at low temperatures. In the two micelle systems, the SCRP spectra scarcely depend on the external magnetic field, and the decay times also do not change much on going from the X band to the L band. These observations are explained in terms of the cage escape rate and the spin−lattice relaxation rate. The strong magnetic field dependence found for the net emissive polarization in the CIDEP spectra of the xanthone and 2,6-DBP system is ascribed to the magnetic field dependence of the TM. On the other hand, the intensity of the SCRP spectrum in the acetone system decreases with decreasing the magnetic field. This observation is rationalized on the basis of the restricted motions of the SCRP in the 2-propanol solution at low temperatures.

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