Bull. Chem. Soc. Jpn., ***68***, *1315—1322(1995)*

Time-Resolved ESR Investigation of Several Ketyl–Phenoxyl Radical Pairs in a Sodium Dodecyl Sulfate Micelle

Natsuo Ishiwata, Hisao Murai,* and Keiji Kuwata

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

(Received November 10, 1994)

The CIDEP (chemically induced dynamic electron polarization) spectra of quasi-stable radical pairs formed in the laser flash photolysis of xanthone and several phenol derivatives in SDS (sodium dodecyl sulfate) micellar solutions were studied. In consideration of the spectral patterns of CIDEP and the results of the magnetic-field effects on the reaction, it is concluded that the steric bulkiness of phenol derivatives obstructs the free diffusion of the reactants and the intermediate radical pairs in the micelle. The dependence of the number and position of the *t*-butyl substituents upon the kinetic parameters and the interaction as the radical pairs in the micellar environment are presented.

Electron-spin resonance (ESR) is one of the most powerful spectroscopic methods used to study many paramagnetic species, such as radicals, triplet molecules, and important information (the spin-density distribution on the molecular frame, the g-tensor, the spin-relaxation time, dipole–dipole interaction, and so on) can be extracted. Energy separations of the spin sublevels are brought about by the magnetic interaction between the external magnetic field and the electron and/or the nuclear spins. These interactions between the spins and the magnetic field contribute not only to ESR, but to the magnetic-field effect upon chemical reactions.

CIDEP (chemically induced dynamic electron polarization), which is due to a non-equilibrium condition induced by chemical events, is observed by an ordinary ESR method and/or transiently by a time-resolved ESR (TRESR) method.[1)] The phase pattern of the CIDEP spectra always carries important information concerning the early period of a chemical reaction and later events. CIDEP studies have progressed, and the mechanisms proposed theoretically have been confirmed experimentally.[2,3)]

The most essential mechanisms of CIDEP are the RPM (radical-pair mechanism) and the TM (triplet mechanism).[1)] The former is explained by a singlet–triplet conversion of the radical pair, and a spin-selective interaction induces unbalanced spin states of each radical. The latter is explained by the spin polarization of the precursor triplet molecule, which is caused by intersystem crossing (ISC) from the excited singlet state due to the spin-orbit interaction.

Recently, two more new CIDEP phenomena, which are now known as SCRP (spin-correlated radical pair)[4,5)] and RTPM (radical triplet-pair mechanism),[6)] have been discovered. It is important to note that all CIDEP phenomena provide information about the interaction of the paramagnetic species, and/or the precursor excited states. Of course, CIDEP is based on the same theoretical background with other spin chemical observations, such as CIDNP (chemically induced dynamic nuclear polarization), external and internal MFE (magnetic-field effect), RYDMR (reaction yield-detected magnetic resonance), and so on.

In the present study, the time-resolved CIDEP spectra of the photochemical systems of seven different phenol derivatives (PhOH) and xanthone (Xn) were investigated in an SDS (sodium dodecyl sulfate) micelle.[7)] In these systems, hydrogen-abstraction reactions due to the excited Xn from PhOH take place in the photolysis. The spin-polarization pattern is altered by changing the phenols; this difference can be interpreted based on the general mechanisms of CIDEP (briefly introduced in a later section). In consideration of these substituent effects on the CIDEP results and the magnetic field effects previously studied on these systems,[8)] it could be shown that the polarization patterns were closely related to the motional and reactive properties of the radical pairs in a micelle.

Experimental

Seven phenol derivatives (2-*t*-butylphenol (OTBP), 3-*t*-butylphenol (MTBP), 4-*t*-butylphenol (PTBP), 2,6-di-*t*-butylphenol (DTBP(2,6)), 2,6-di-*t*-butylcresole (DTBC=2,6-di-*t*-butyl-4-methylphenol), 3,5-di-*t*-butylphenol (DTBP(3,5)), and 2,4,6-tri-*t*-butylphenol (TTBP)) were used as hydrogen donors. The photo-excited triplet state of xanthone is the hydrogen acceptor. All of the reagents were purified by recrystallization from alcohol solutions. A biological-grade SDS was used as the surfactant without further purification for the micellar solution. Throughout these experiments the concentration of SDS was kept at 1.0×10^{-1} mol dm^{-3}, and those of the Xn and phenol derivatives were 2.0×10^{-3} mol dm^{-3}, respectively. Under these conditions, one or two molecules of Xn and phenols were thought to be contained in each micellar aggregate.

CIDEP measurements were carried out using an X-band ESR spectrometer modified for the time-resolved observation (time resolution of about 60 ns) without any magnetic-field modulation.[9] The CIDEP spectra of the intermediate paramagnetic species were recorded using a boxcar integrator. A transient memory system (IWATSU DM901) was also used to observe the decay of CIDEP signals, and the data were analyzed by a microcomputer system (EPSON PC-386). The excitation light source was an excimer laser (Lambda Physik LPX 105, XeCl; $\lambda=308$ nm) with a 100 mJ/pulse output power. The solutions were deoxygenated by bubbling with pure nitrogen gas and flowed constantly (ca. 10 ml min^{-1}) through a flat quartz cell of 0.3 mm light-path installed in an ESR cavity in the TE_{011} mode. All of the experiments were carried out at room temperature.

Theoretical Background of CIDEP

It is important and necessary to show how to understand the CIDEP spectra presented in this paper. A brief theoretical background is given here. At this stage, four different kinds of CIDEP mechanisms which induce spin-polarization on paramagnetic species are well known.

(I) TM. The triplet mechanism (abbreviated as TM) is one of the well-known causes of CIDEP. TM is induced by the ISC of the precursor excited molecule. The TM requires several conditions to appear,[10] and two of them are essentially important. The reaction must take place through the excited triplet state, and should be sufficiently fast to conserve the spin polarization of the excited precursor molecule. In this mechanism, the spectrum shows total emission or absorption of microwaves, which depends on the excited state of the precursor molecule. The intensities of the hyperfine (HF) lines are determined by the degeneracy of each spin state. This mechanism may be involved in the present discussion as emissive signals from the excited triplet states of Xn.

(II) RPM. The radical-pair mechanism, which is also important for most radical reactions, is abbreviated as RPM. In RPM, there are two important processes: S–T_0 mixing[1] and S–$T_{\pm1}$ mixing (or level crossing).[11,12] S–T_0 mixing is induced by the interaction of two radicals through diffusional motion in the solvent. Although this mixing induces a population deviation from thermal equilibrium on every HF level, the total electron-spin polarization of the whole system is not influenced. The mixing is controlled by the off-diagonal matrix element, as shown in Eq. 1. The spectrum shows emission at the low-field side and absorption at the high-field (E/A) side in the case of the triplet precursor (A/E in the case of the singlet precursor); here, the sign of the exchange interaction (J) is negative in most cases,

$$Q=\frac{1}{2}(g_1-g_2)\beta\hbar^{-1}B+\frac{1}{2}\left(\sum_i A_{1i}M_i-\sum_j A_{2j}M_j\right), \quad (1)$$

where the symbols have their usual significance. As is clear from this equation, the spectral pattern is dependent on both the differences in the g-factors and the HF coupling constants of both radical species which are involved in the reaction. The signal intensity is approximately proportional to the square root of Q. This mechanism also appears slightly in the present systems as the E/A pattern of the triplet precursor and $J<0$. Although the interaction of two free radicals which escaped from the geminate pair may induce S–T_0 mixing, only the geminate pair case is considered in the present report, because the present systems are restricted to those of the SDS micellar solution.

S–$T_{\pm1}$ mixing is not observable under ordinary solution conditions at room temperature. This mixing is induced by level crossing of the singlet state and one of the triplet states (T_{-1} or T_{+1}) of the radical pair. It is induced only under the conditions of a strong confinement of the radical pairs in the solution, such as polymethylene-linked biradicals,[13] radical pairs in a very viscous solution (and/or low-temperature conditions),[14] and a micellar solution,[15] like the present system. Furthermore, a large HF coupling constant is needed for efficient crossing.[11] This mechanism induces a total-emission (triplet precursor, $J<0$ and S–T_{-1} mixing) pattern or total-absorption (triplet precursor, $J>0$ and S–T_{+1} mixing) pattern. Although the signal intensity of each HF line of this mechanism is HF dependent, it is difficult to distinguish this mechanism from the TM when both radicals have complicated HF structures. In the present case, this mechanism may be one of the candidates of the total-emission pattern observed in the systems of Xn/PhOH/SDS; however, this mechanism may not be important, as shown in the latter discussion.

(III) RTPM. The radical triplet pair mechanism (RTPM),[6] which is known as being similar to RPM, is different in that the doublet radical and excited triplet state are involved. This mechanism involves the mixing of doublet and quartet states of the transiently interacting species. The dipole–dipole interaction is the main motive force of this mechanism. It may provide emissive polarization according to the previous report, so far.[16] In the present system, this mechanism must be negligible because the triplet state of Xn is quenched by a hydrogen-abstraction reaction in the micelle, and the existence of the extra triplet state of Xn in the micelle is unlikely according to the experimental conditions.

(IV) SCRP. The spin-correlated radical pair (SCRP)[4,5] is a direct observation of the transiently formed radical pair, itself. This polarization does not necessarily mean induction of the permanent polarization of the electron spins, contrary to the other CIDEP mechanisms, which involve observations of the carrying memory of the freed radicals. In most cases the S–T_0 interacting SCRP is known to appear, while the large exchange interacting SCRP (S–T_{-1} interaction) has been reported only in the case of short biradicals.[17] When two radicals interact as a radical pair with a certain exchange interaction (J), the magnitude of which is on the order of the HF interaction, the singlet and middle triplet (T_0) states can be mixed and new eigen states and eigenvalues can be expressed as follows:

$$|1> = |T_{+1}> \qquad E_1 = -J + E_0 \tag{2}$$

$$|2> = \cos\chi|S> + \sin\chi|T_0> \qquad E_2 = w \tag{3}$$

$$|3> = -\sin\chi|S> + \cos\chi|T_0> \qquad E_3 = -w \tag{4}$$

$$|4> = |T_{-1}> \qquad E_4 = -J - E_0 \tag{5}$$

Here, E_0, χ, and w can be represented as

$$\tan 2\chi = Q/J, \tag{6}$$

$$E_0 = (g_1 + g_2)\beta B/2\hbar, \tag{7}$$

and

$$w^2 = Q^2 + J^2. \tag{8}$$

The spectrum of SCRP is the transitions among the above four eigenstates, and the initial population of 1/3 of each triplet sublevel is assumed in the ordinary SCRP model of the triplet precursor. Consequently, every HF line of each radical splits to two phase alternating lines, showing an E/A-shaped HF line. The separation of the E/A peaks corresponds to approximately $2J$. The phase is also dependent on the multiplicity of the precursor state and the sign of the exchange interaction (J). In this paper, the determination of this contribution becomes very important and an assumption of fast relaxation between the | 2> and | 3> states (namely, S and T_0), which has been reported in the system of the polymethylene-linked biradical,[18] is introduced to reproduce the observed spectra by simulation.

Results

Xn is known to be excited by UV-light, and to be converted from the excited singlet state to the triplet state. The latter is chemically reactive. In an SDS micelle the excited triplet state of Xn does not react efficiently with the SDS molecule, but does react with third molecules, such as phenols, to form the ketyl and phenoxyl radicals, as follows:[7,8]

$$\mathrm{Xn} + h\nu \longrightarrow {}^1\mathrm{Xn}^*, \tag{9}$$

$${}^1\mathrm{Xn}^* \longrightarrow {}^3\mathrm{Xn}^*, \tag{10}$$

and

$${}^3\mathrm{Xn}^* + \mathrm{PhOH} \longrightarrow \cdot\mathrm{XnH} + \mathrm{PhO}\cdot, \tag{11}$$

where the asterisk denotes the respective excited state, and $\cdot$XnH and PhO$\cdot$ are the xanthone ketyl and the t-butyl-substituted phenoxyl radicals, respectively. After these reactions, the ketyl and phenoxyl radicals could be confined in a micellar aggregate, and might interact with each other. Once the radical pair (or one of the component radicals) exits from the micelle, they do not interact with each other any longer. No interaction between freed radicals is expected, due to the very low concentration conditions of whole radicals, which can

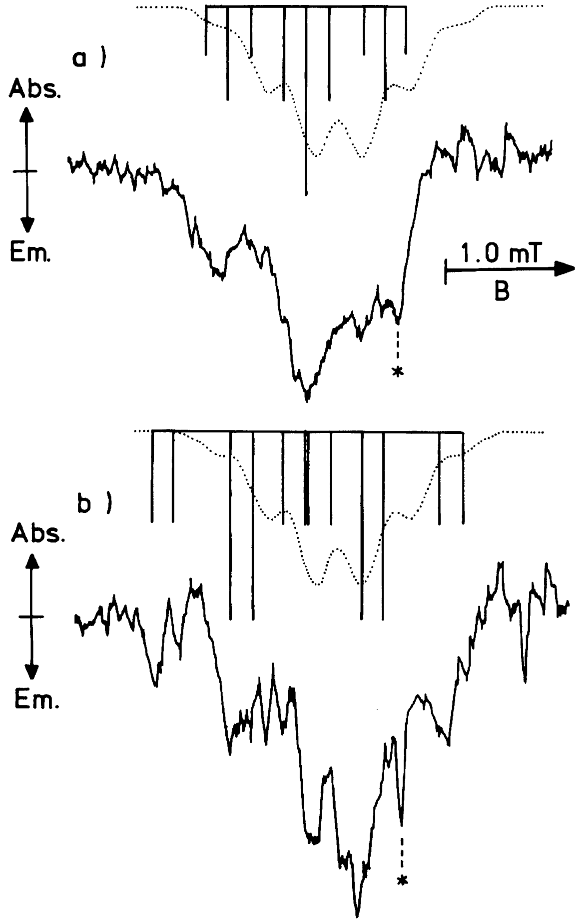


Fig. 1. CIDEP spectra observed in the photolysis of Xn and t-butylphenols a) PTBP and b) MTBP in the SDS micelle at delay time of 0.5 μs (gate width 0.2 μs). Stick spectra and dotted envelopes show the simulated phenoxyl type radicals and ketyl radical having emissive polarization, respectively. The asterisk indicates the field position of a hydrated electron. These definitions are used in the other figures. Parameters used for simulation are as follows: $\cdot$XnH: g=2.003, a(2,8)=0.41 mT, a(4,10)=0.38 mT, a(3,9)=0.10 mT, a(5,11)=0.06 mT, a(OH)= 0.27 mT; phenoxyl radical from PTBP: g=2.0045, a(2,6)=0.60 mT, a(3,5)=0.17 mT; phenoxyl radical from MTBP: g=2.0045, a(2,6)=0.60 mT, a(3)=0.17 mT, a(4)=1.0 mT. Here, the stick spectra do not include the HFS of methyl protons of t-butyl groups.

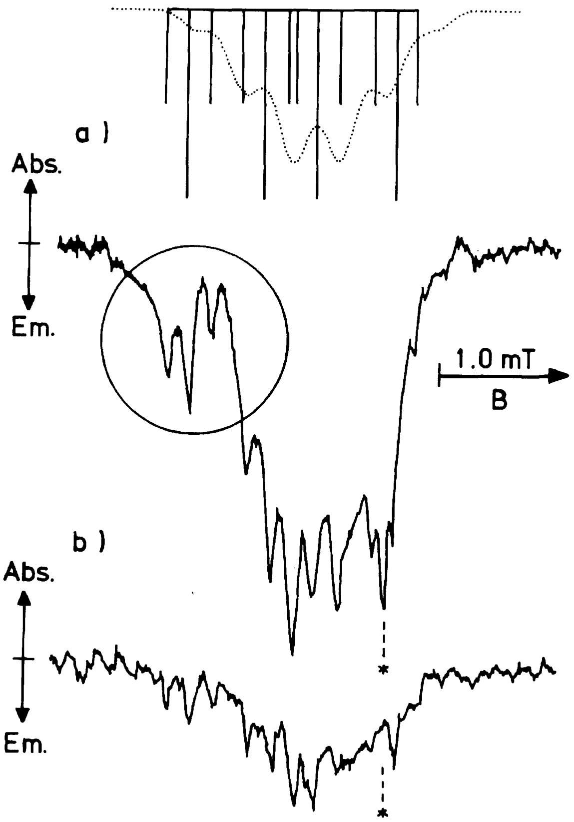


Fig. 2. CIDEP spectra observed in the photolysis of Xn and OTBP in the SDS micelle at delay time of a) 0.5 μs and b) 2.0 μs (gate width 0.2 μs). Parameters used for simulation are as follows: ·XnH: same as Fig. 1; phenoxyl radical from OTBP: g=2.0045, a(6)=0.60 mT, a(3,5)=0.17 mT, a(4)=1.0 mT.

be easily estimated based on the present experimental conditions mentioned above.

(I) *t*-Butylphenols. Figures 1a, 1b, and 2a show the TRESR spectra observed in the photolysis of Xn and three mono-*t*-butylphenols (PTBP, MTBP, and OTBP) dissolved in micellar solutions. The field position indicated by an asterisk in all of the spectra presented in this paper shows the resonance field of a hydrated electron, which is formed through the biphotonic ionization of Xn,[19] and is occasionally observable in the present systems. The main portion of these emission spectra was assigned to respective phenoxyl radicals because of their hyperfine structures (HFS). Most of the HF coupling constants of the protons of the phenoxyl radical derivatives are 0.6—0.7 mT at the ortho-position, 0.15—0.20 mT at the meta-position, and 0.9—1.0 mT at the para-position.[20] The spectrum of the Xn ketyl radical might be superimposed on the whole spectrum. The simulated ketyl radical and the stick spectra of the respective phenoxyl radical are presented in the figures. The emissive patterns and the spectral distortion are explained by the combination of the emissive TM and the slight E/A pattern of the RPM (S–T_0 mixing) of CIDEP theory. The appearance of the TM implies that the reaction of ^{3}Xn* with mono-*t*-butylphenols is sufficiently fast to transfer the residual spin polarization of ^{3}Xn* to the radicals.

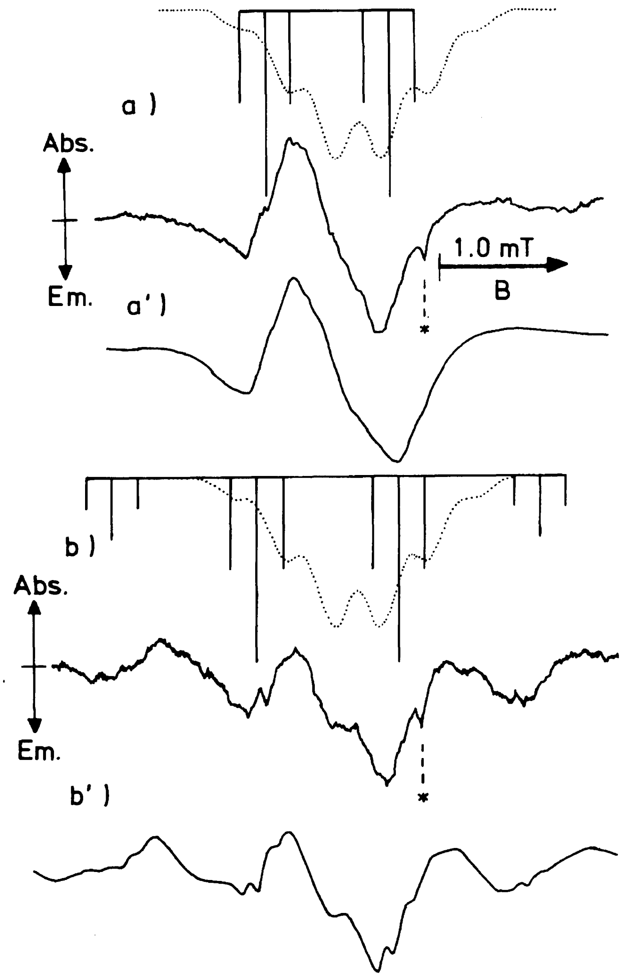


Fig. 3. CIDEP spectra of SCRP in the SDS micelle. a) observed spectrum from Xn/DTBP(2,6), delay time of 1.0 μs (gate width 0.2 μs), a′) the fast-relaxation model (J=−0.2 mT) + TM polarization, b) observed spectrum from Xn/DTBC, delay time of 1.0 μs (gate width 0.2 μs). b′) the fast-relaxation model (J=−0.4 mT) + TM polarization. Parameters used for simulation are as follows; ·XnH: same as Fig. 1; DTBP(2,6): g=2.0045, a(3,5)=0.20 mT, a(4)=0.96 mT; DTBC: g=2.0045, a(3,5)=0.20 mT, a(CH_3)=1.1 mT.

Although the main polarization patterns are explained by the TM and RPM, there is an additional slight distortion of the hyperfine (HF) lines in the systems of MTBP and OTBP. This distortion might be due to the SCRP, since a much clearer spectra of SCRP was observed in the other systems (presented in the latter part of this paper). Figures 2a and 2b show the time-resolved spectra observed in the system of Xn/OTBP. As shown in this figure, the encircled portion of this spectrum, the lines of which should be the 1 : 2 : 1 triplet, due to two meta-protons of phenoxyl radical, shows an anomalous distortion, probably due to the SCRP.

This distortion could not be reproduced by the ordinary TM and RPM simulations. This distortion disappears rapidly, and the spectrum of Fig. 2 observed at a later time may not contain the contribution of the SCRP. This indicates that the interaction based on SCRP does not last for a long period in these systems containing *t*-butylphenols. In other words, separation of the two radical centers by free diffusion takes place even in the micellar system. Soon after the birth of radicals, although two radicals become located at a close distance and interact tightly, free diffusion causes a separation of the two radicals, which makes the J value zero; also, the penetration of one radical through the micellar barrier also erases the SCRP signals. This is similar to the case previously observed in the system of benzophenone in an SDS micelle.[21]

(II) Di-*t*-butylphenols. Figures 3a and 3b show the TRESR spectra observed in the photolysis of Xn and two di-*t*-butylphenols (DTBP(2,6) and DTBC) dissolved in micellar solutions, respectively.[7] These spectra could not be explained simply by ordinary TM or RPM. Having anomalous phase-alternating HF lines, they were explained by a modified SCRP theory. The resonance points and intensity were calculated by assuming identical populations of the middle two states (| 2> and | 3> of Eqs. 3 and 4) (fast relaxation model) instead of the simple SCRP model. The spectra were well simulated (Fig. 3a′,3b′) by a superposition of the modified SCRP spectra of both ·XnH and phenoxyl radicals, where a slight emissive TM component was added in order to adjust the whole spectral shape. According to this simulation, it is concluded that the fast-relaxation model is plausible, and that the best fitting values of the exchange interaction of the DTBP and DTBC systems were determined to be −0.2 mT, and −0.4 mT, respectively. Though these trials brought successful results, it should be noted that there exists a problem concerning this single J model. The actual system might have a certain distribution of J values, which were caused by the dynamic behavior of the radical pair in the micelle. Therefore, the single J values estimated here should be understood to be representative in these systems. Although the origin of fast relaxation is not yet clear, the small energy separation, the dephasing of the two states and the repetitive interaction of S–T_0 mixing near to the $J=0$ region in a micelle might be the causes of this relaxation. To obtain a more detailed picture of CIDEP mechanism, a theoretical calculation of the radical pairs' dynamics, such as an analysis using the stochastic Liouville equation, should be carried out concerning the micelle.

The spectral shape of the SCRP did not change for a few micro seconds in the cases of Xn/DTBP(2,6) and Xn/DTBC, while the spectra of radical pairs disappeared in the system of OTBP and the previously reported ordinary micellar systems.[21,22] In these particular systems, the average exchange interaction among the radical pairs seemed to be preserved until the signal vanished. It may be explained that the bulky substituents of the phenoxyl radicals prevent a free diffusion of the radicals in the micellar aggregate.

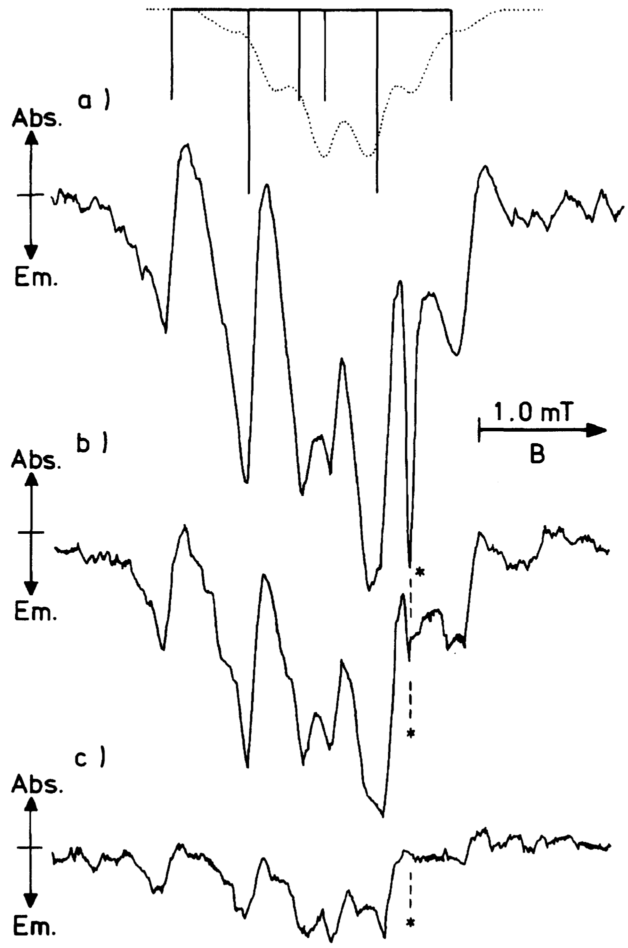


Fig. 4. CIDEP spectra observed in the photolysis of Xn and DTBP(3,5) in the SDS micelle at delay time of a) 0.5 μs, b) 2.0 μs and c) 4.0 μs (gate width 0.2 μs). Parameters used for simulation are as follows: ·XnH: same as Fig. 1; DTBP(3,5): $g=2.0045$, $a(2,6)=0.60$ mT, $a(4)=1.0$ mT.

Figure 4 shows the TRESR spectra observed in the photolysis of Xn and DTBP(3,5) dissolved in a micellar solution. The spectral pattern was emissive, and the distortion of each HF line was also clearly observed. Although this behavior is similar to that of mono-type systems, the distortion does not disappear quickly. Since the 3,5-disubstituted phenol derivative has less steric hindrance than does the 2,6-ones at the hydroxy group, the reaction of the hydroxy group with $^3Xn^*$ becomes faster, and these spectra show a stronger emissive polarization than do those of 2,6-disubstituted ones by the TM. The interaction between radicals in the pair is prolonged, as in the DTBP(2,6) case, and the distortion due to the SCRP lasts for a few micro seconds in this case.

(III) Tri-*t*-butylphenols. The TRESR spectra observed in the photolysis of the Xn and TTBP system in a micellar solution showed phase-alternating HF lines (Fig. 5) similar to those of the DTBP(2,6) system, though no TM contribution was recognized. The signal intensity was weak and the spin-polarization was exclusively due to SCRP. It might be explained that the reaction rate of hydrogen abstraction is very slow, because of the three bulky substituents which prevent free diffusion of the TTBP molecule, and reduce the chance of a reactive collision with ^{3}Xn* in the micelle. The substituents may also prolong the interaction time of the radical pair in the micelle.

(IV) Resume of TRESR Data and a Comparison with the Magnetic-Field Effect (MFE) upon the Transient Optical Absorption. All of the data of the CIDEP results are presented in Table 1. According to the TM contribution of these data, it can be guessed that the intensity of the TM component apparently provides a measure of reactivity of the excited Xn with each phenol derivative. The stability of the SCRP spectra of all of these data implies that the species ejected from the micellar aggregate is mainly the phenoxyl-type radicals.

An investigation of a transient optical absorption of the system of Xn and four types of phenols (PTBP, DTBP(2,6), DTBC, and TTBP) under a magnetic field has already been reported by our group.[8] In this previous report, it was concluded that the reaction rate from the singlet state (k_P), the escape rate from the micelle (k_E), and the spin-relaxation rate of radical pairs ($k_\mathrm{R}+k'_\mathrm{R}$) were influenced by the substituent of phenol. By increasing the bulkiness of the phenols, these rates of all the systems decrease; in other words, the mobility of the radical pair in the micelle is affected by the size of the substituent and all the physical and chemical behaviors of these systems are influenced. The kinetic data are given in Table 2, along with definitions of the kinetic parameters. They are also schematically drawn in Fig. 6. As can be seen in this table, the k_P values of all the systems presented here are quite large compared to the other rates. Although a combination of the fast-relaxation model and the fast k_P may wipe out both populations of the $\mid 2>$ and $\mid 3>$ levels, an identical spectral shape of SCRP is reproducible by a simulation in this situation. This means that the relaxation among $\mid 2>$ and $\mid 3>$ is much faster than the k_P values.

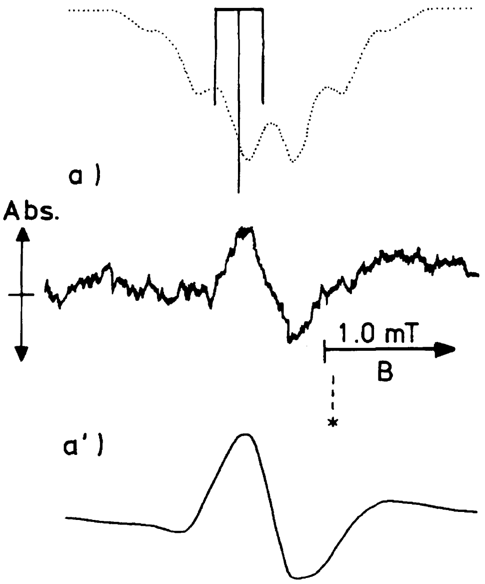
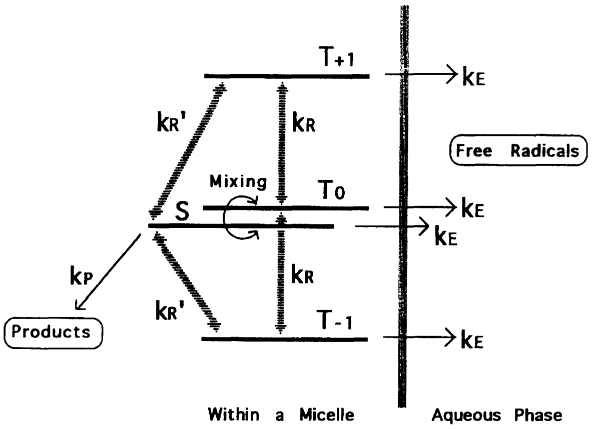


Fig. 5. CIDEP spectra from Xn and TTBP in the SDS micelle. a) observed at delay time of 2.0 μs (gate width 0.2 μs), a′) simulated SCRP ($J=-0.2$ mT). Parameters used for simulation are as follows: ·XnH: same as Fig. 1; TTBP(2,5): $g=2.0045$, $a(3,5)=0.17$ mT.

Discussion

We can now compare the present CIDEP results with those of the MFE of the same systems.

(I) *t*-Butylphenols. As for monosubstituted *t*-butylphenols, the diminished appearance of the SCRP component in the CIDEP spectra may be due to the short interaction time as the radical pair in the micelle. This situation is apparently evidenced by the MFE data of the PTBP system tabulated in Table 2. The spin-relaxation rate ($k_\mathrm{R}+k'_\mathrm{R}$) is also fast compared to the other systems. The fast disappearance of the SCRP component can also be explained by the fast k_P and k_E, especially the escape of radicals from the micelle. The separation of two radicals diminishes the contribution of the SCRP, as explained previously. According to the above-mentioned behavior of these molecules in a micelle, the contribution of the TM to the emissive component of CIDEP signal can be understood to be important because the less bulky molecular structure



$[\cdot\mathrm{XnH}\text{ --- }\mathrm{PhO}\cdot]_\mathrm{SDS}$

Fig. 6. Schematic diagram of radical pair dynamics in the SDS micellar solution. Here, the definition of the rate constants is the same as that in Table 2 (see text).

Table 1. Contribution of Different CIDEP

Phenols	No. of *t*-butyl	TM(E)	RPM(E/A)	SCRP(E/A)	Signal intensity
PTBP$^{a)}$	1	XX	X	—	Good
MTBP	1	XX	X	X$^{b)}$	Good
OTBP	1	XX	X	X$^{b)}$	Good
DTBP(3,5)	2	XX	—	XX$^{c)}$	Strong
DTBP(2,6)$^{a)}$	2	X	—	XX$^{c)}$	Strong
DTBC$^{a)}$	2+methyl	X	—	XX$^{c)}$	Strong
TTBP$^{a)}$	3	—	—	XX$^{c)}$	Weak

a) Kinetic data are given in Table 2. b) Diminished quickly. c) Lasted long time. XX: relatively strong. X: recognized. — very weak or unclear.

Table 2. MFE in SDS Micelles by Transient Optical Absorption$^{a)}$

Phenols	No. of *t*-butyl	k_P (10^6 s^{-1})$^{b)}$	k_E (10^6 s^{-1})$^{c)}$	$k_R+k_{R'}$ (10^6 s^{-1})$^{d)}$
PTBP	1	14	1.2	0.53
DTBP(2,6)	2	8.6	0.32	0.24
DTBC	2+methyl	6.6	0.24	0.35
TTBP	3	1.8	0.13	0.17

a) From Ref. 8. b) Reaction rate from the singlet state to products. c) Escape rate from the micelle. d) Spin relaxation rates of $T_{\pm1}-T_0$ and $T_{\pm1}-S$ under the magnetic field of 1.34 T.

of the phenols may accelerate the reaction of the reactants.

(II) Di-*t*-butylphenols. Concerning disubstituted *t*-butylphenols, the clear appearance of the SCRP spectra is safely rationalized by the long interaction time and relatively strong magnitude of the exchange interaction in these systems, probably because of an increase in the bulkiness of phenols. This is evidenced by the kinetic data shown in Table 2, which give a much slower escape rate and slower spin-relaxation rate of the di-*t*-butyl substituted ones. The slight emissive component of the CIDEP spectra of these systems may be attributable to the TM. However, plots of the MFE of these compounds (DTBP(2,6) and DTBC) show an unexplainable bump near to 0.2—0.5 T[8] which may suggest the possibility of level crossing, such as $S-T_{-1}$ mixing. Such level crossing may provide emissive TM-like polarization, though no more evidence of this phenomenon is available at this stage.

(III) Tri-*t*-butylphenols. As for trisubstituted *t*-butylphenol (TTBP), all of the kinetic data shown in Table 2 are extremely small compared to that of other systems. This is, of course, due to the bulkiness of the phenoxyl radical formed from TTBP. The weak CIDEP signal is rationalized by the slow reaction of the phenol with the excited triplet state of Xn, because of the slow diffusion and steric hindrance of the bulky structure, both of which make the appearance of TM polarization difficult (as mentioned before).

Here, it is concluded that the most probable escaping component from the micelle is the *t*-butylphenoxyl radicals, and not the ketyl radical, according to a comparison between two independent results of the CIDEP and MFE. A more detailed analysis of these CIDEP and the MFE results, including the theoretical calculation, is now underway and will appear elsewhere.

Conclusion

The CIDEP spectra of transient species formed from seven different systems of Xn and *t*-butyl phenols in laser photolysis were studied in an SDS micelle. Bulky substituents (*t*-butyl group) on phenol affect both the reaction rate of the excited triplet state of Xn with phenols and the dynamic behavior of the transient radical pairs in the micelle. The systems having phenols with more than two *t*-butyl groups provide clear quasi-stable SCRP in the SDS micelle. This phenomenon is rationalized by the more confined motion of the transient radical pair in the micelle compared to the monosubstituted one. The position of substituents also affects the polarization pattern. In the case of mono- and 3,5-disubstituted phenol systems a strong emissive TM polarization is provided. The TM polarization is a good measure of the radical-formation rate, which is controlled by the steric hindrance and the diffusion in the micelle. The present report shows that a reaction system which is controllable by an external magnetic field and the ESR conditions must be constituted by designing the appropriate reactants in a micelle.

This work was supported by Grants-in-Aid for Scientific Research on Priority Area "Molecular Magnetism" (Area No. 228/05226224/06218219) and "Photoreaction Dynamics" (Area No. 249/06239242) from the Ministry of Education, Science and Culture.

References

1) L. T. Muus, P. W. Atkins, K. A. McLauchlan, and J. B. Pedersen, "Chemically Induced Magnetic Polarization," Reidel, Dordrecht (1977).

2) K. A. McLauchlan, "Advanced EPR," ed by A. J. Hoff, Elsevier, Amsterdam (1989), Chap. 10.

3) H. Murai and H. Hayashi, "Radiation Curing in Polymer Science and Technology," ed by J. P. Fouassier and J. F. Rabek, Elsevier Applied Science, London (1993), Vol. 2, Chap. 2.

4) G. L. Closs, M. D. E. Forbes, and J. R. Norris, Jr., *J. Phys. Chem.*, **91**, 3592 (1987).

5) C. D. Buckley, D. A. Hunter, P. J. Hore, and K. A. McLauchlan, *Chem. Phys. Lett.*, **135**, 307 (1987).

6) C. Blöttler, F. Jento, and H. Paul, *Chem. Phys. Lett.*, **166**, 375 (1990).

7) Preliminary report: N. Ishiwata, H. Murai, and K. Kuwata, *Res. Chem. Intermed.*, **19**, 59 (1993).

8) H. Murai, N. Ishiwata, K. Kuwata, Y. Sakaguchi, and H. Hayashi, *Chem. Phys. Lett.*, **203**, 482 (1993).

9) K. Ohara, H. Murai, and K. Kuwata, *Bull. Chem. Soc. Jpn.*, **62**, 2435 (1989).

10) P. W. Atkins and G. T. Evans, *Mol. Phys.*, **27**, 1633 (1974).

11) T. J. Burkey, J. Lusztyk, K. U. Ingold, J. K. S. Wan, and F. J. Adrian, *J. Phys. Chem.*, **89**, 4288 (1985).

12) C. D. Buckley and K. A. McLauchlan, *Chem. Phys. Lett.*, **137**, 86 (1987).

13) G. L. Closs and M. D. E. Forbes, *J. Phys. Chem.*, **95**, 1924 (1991).

14) K. Tominaga, S. Yamauchi, and N. Hirota, *J. Chem. Phys.*, **88**, 553 (1988).

15) A. D. Trifunac, *Chem. Phys. Lett.*, **49**, 457 (1977).

16) A. Kawai, T. Okutsu, and K. Obi, *J. Phys. Chem.*, **95**, 9130 (1991).

17) M. D. E. Forbes, and S. R. Ruberu, *J. Phys. Chem.*, **97**, 13223 (1993).

18) M. Terazima, K. Maeda, T. Azumi, Y. Tanimoto, N. Okada, and M. Itoh, *Chem. Phys. Lett.*, **164**, 562 (1989).

19) N. Ishiwata, H. Murai, and K. Kuwata, *J. Phys. Chem.*, **97**, 7129 (1993).

20) Landolt-Börnstein, "Numerical Data and Functional Relationships in Science and Technology, Group II: Atomic and Molecular," Vol. 9c2, ed by K.-H. Hellwege, 1979, and Vol. 17e, ed by O. Madelung, 1988, Spinger-Verlag, Berlin and Heidelberg, references are therein.

21) Y. Sakaguchi, H. Hayashi, H. Murai, and Y. J. I'Haya, *Chem. Phys. Lett.*, **110**, 275 (1984).

22) Y. Sakaguchi, H. Hayashi, H. Murai, and Y. J. I'Haya, *Chem. Phys. Lett.*, **120**, 401 (1985).