An Analysis of the CIDEP Mechanisms in the Hydrogen Abstraction Reactions of Excited Quinoxaline and Related Compounds

Keishi Ohara and Noboru Hirota*

Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606

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The Chemically Induced Dynamic Electron Polarization (CIDEP) mechanisms in the hydrogen abstraction reactions of excited azaaromatic compounds; quinoxaline, phenazine, and quinoline are investigated in detail. It is shown that several polarization mechanisms are involved and the observed CIDEP spectra vary strongly depending on various factors such as the concentration, the temperature, the delay time, and the excitation light intensity. The net emissive spin polarization is ascribed mainly to the radical–triplet pair mechanism (RTPM), which is strongly dependent on the concentrations of the radical and triplet molecules. It is shown that the triplet molecules are long-lived and the condition to produce the RTPM polarization is satisfied. The observed time evolutions of the transient EPR signals are qualitatively explained on the basis of the rate equations, which include the RTPM polarization and the relaxation.

In the last three decades, time resolved EPR (TREPR) studies have been carried out in numerous photochemical systems.[1—3] The phenomena of chemically induced dynamic electron polarization (CIDEP) have been investigated extensively from both experimental and theoretical points of view. Several CIDEP producing mechanisms have been proposed and they are now well-established. Historically, an ST_0 mixing radical pair mechanism (RPM)[4—6] was the first to be proposed, then followed by a triplet mechanism (TM)[7,8] and an $ST_\pm$ mixing RPM soon after.[9,10] It is rather recent that other mechanisms such as a spin-correlated radical pair (SCRP)[11,12] mechanism and a radical–triplet pair mechanism (RTPM)[13—15] were suggested. In most of early TREPR studies the observed CIDEP spectra were explained in terms of the combination of the TM and the ST_0 mixing RPM, without paying much attention to the contributions of other mechanisms. Therefore, some of the interpretations of the CIDEP spectra might have been erroneous. With better understanding of the CIDEP mechanisms, it seems worth while to reexamine some of the puzzling CIDEP phenomena in early studies.

CIDEP spectra of some azaaromatic compounds (azaaromatics) such as quinoxaline and phenazine are among such cases. These compounds were investigated in early TREPR studies.[16,17] In the photolysis of quinoxaline and phenazine in 2-propanol totally emissive CIDEP spectra were observed and assigned to the quinoxalinyl and phenazinyl radicals, respectively, which were produced by hydrogen abstraction reactions of the triplet states from 2-propanol. It is known that the excited triplet states of most of azaaromatics, including quinoxaline and phenazine undergo hydrogen abstraction reactions in the presence of appropriate hydrogen donors.[16—19] Since the intersystem crossing favorably populates the top spin sublevels of these $^3\pi\pi^*$ azaaromatics,[16,17,20,21] the net emissive (*E*) spin polarization was ascribed to TM. However, the reaction rate of triplet quinoxaline in 2-propanol was estimated to be 1.8×10^5 s^{-1} by the transient absorption method.[18,19] This rate is far too slow to produce an effective TM polarization, because the spin-lattice relaxation rate of an organic triplet state molecule is usually on the order of 10^8—10^9 s^{-1}. This situation is different from the case of pyrazine where the hydrogen abstraction rate of $^3n\pi^*$ pyrazine is very fast and the involvement of the TM is well established.[16—19,22] Thus the origin of the net emissive polarization of $^3\pi\pi^*$ azaaromatics is uncertain. Considering a relatively long lifetime of triplet quinoxaline in 2-propanol, the RTPM appears to be a possible cause of the emissive polarization.

The spin polarization due to the RTPM is produced through the interaction between doublet radicals and triplet state molecules. The generation mechanism of the RTPM polarization is explained on the basis of the doublet–quartet mixing in a radical–triplet pair. Recent studies suggested that the RTPM includes two mechanisms, one generating a net polarization and the other producing a hyperfine dependent polarization, which resemble the ST_- and ST_0 mixings in the RPM, respectively.[14,15] Detailed studies of the RTPM may provide useful information not only about the interactions in radical–triplet pairs but also the quenching processes of excited states by radicals that have not been studied in detail by other methods. Most of the published reports on the RTPM, however, have been concerned with the spin polarization generated by the interaction between stable radicals such as nitroxides and excited triplet state molecules. The importance of the RTPM polarization in the CIDEP spectra of reaction intermediate radicals has not been clearly recognized except in the cases of benzil,[13] 1-naphthol,[15] and C_{60}.[23] The main reason for this is the difficulty to satisfy the condition under which collisions between radicals and triplet molecules are sufficiently frequent with long correlation times required for effective RTPM interactions. This requires relatively long lifetimes of triplet molecules and sufficient concentrations of both radicals and triplet molecules.

In the present work, we have investigated the CIDEP spectra obtained by the photolysis of quinoxaline, phenazine, and quinoline in 2-propanol in detail. Both TREPR and transient absorption experiments have been made on these systems at various concentrations and temperatures. Time dependent changes of the CIDEP spectra show involvements of various CIDEP mechanisms. Relatively long-lived triplet states of these molecules satisfy the condition to observe the polarization due to the RTPM. We have tried to clarify the CIDEP mechanisms and dynamics of spin polarization from an analysis of the time evolution of the transient EPR signals. We show that the observed net *E* polarization is consistently explained by the RTPM.

Experimental

TREPR measurements were carried out with a modified JEOL EPR spectrometer as reported before.[17)] DC detected EPR signals taken without field modulation were amplified by a wide band preamplifier and fed to a boxcar integrator (Stanford Research System SR-250) for recording CIDEP spectra, or a digital oscilloscope (Tektronix TDS 520 or 2430A) for recording the time evolution of transient EPR signals. The output signals of a boxcar integrator were digitized by an A/D converter and stored in a personal computer. The time evolution data were also stored and processed by a personal computer. For taking these data the microwave power was kept low (usually 0.2 mW or less) to avoid the effect of transient nutation. Transient absorption experiments were carried out with a lab-built spectrometer of conventional design. A 150 W Xe lamp was used as a reference light source operating with a flash. A light transmitted through a sample was analyzed by a monochromator and detected by a photomultiplier tube (Hamamatsu Photonics). Time evolution signals were recorded with a digital oscilloscope and data were stored and processed by a personal computer. A XeCl excimer laser (Lumonics Hyper 400, 308 nm, 7.5 Hz) was used for photoexcitation of samples in both EPR and transient absorption experiments.

Sample solutions were deoxygenated by bubbling nitrogen gas before and during the experiments, and flowed in a quartz flat cell (optical path 1 mm) in an EPR cavity. The sample temperature was controlled with cold nitrogen gas flow.

Quinoxaline, phenazine, and quinoline were commercially available special grade reagents (Nacalai Tesque) used as received. Special grade solvents were used without further purification.

Results and Discussion

1. CIDEP Spectra under Different Conditions. First, we show the CIDEP results in the photolysis of quinoxaline, phenazine, and quinoline in 2-propanol under different conditions.

In the photolysis of quinoxaline (Qx) in 2-propanol the photochemical reaction is believed to proceed by the following scheme.[16—19)]

(I) $^3\mathrm{Qx}^* + (\mathrm{CH_3})_2\mathrm{CHOH} \longrightarrow \cdot\mathrm{QxH} + (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH}$

(II) $(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} + \mathrm{Qx} \longrightarrow \cdot\mathrm{QxH} + (\mathrm{CH_3})_2\mathrm{CO}$

Triplet state quinoxaline produced by photoexcitation abstracts a hydrogen atom from 2-propanol, and produces quinoxalinyl and 2-hydroxypropan-2-yl radicals. The 2-hydroxypropan-2-yl radical is quickly quenched by ground state quinoxaline and produces another quinoxalinyl radical as reported before.[16—19,22)] Other azaaromatics such as phenazine and quinoline, are known to react via similar reaction schemes (reaction I and II).

(a) Concentration Dependence of the CIDEP Spectra. Figure 1 shows the concentration dependence of the CIDEP spectra obtained in the photolysis of quinoxaline in 2-propanol at 0 °C. Broad spectra with partially resolved hyperfine structures were assigned to the quinoxalinyl radical as reported before.[16,17)] The spectrum of the 2-hydroxypropan-2-yl radical was not observed at higher concentrations (Figs. 1a and 1b), but observed weakly at a low concentration (Fig. 1c). This is because the 2-hydroxypropan-2-yl radical was quenched quickly ($k_q = 1.1 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$, $1\ \mathrm{M} = 1\ \mathrm{mol\,dm^{-3}}$) by ground state quinoxaline as represented by reaction (II).[22)] The CIDEP spectrum in Fig. 1a shows a total emission CIDEP. In a previous report,[17)] the net *E* polarization was ascribed to the TM. However, on the basis of the slow rate constant ($1.4 \times 10^4\ \mathrm{M^{-1}\,s^{-1}}$) determined by the transient absorption, it is difficult to justify this assignment. As shown in Fig. 1, the spectral pattern changed remarkably with the concentration of quinoxaline. At a high concentration of quinoxaline (0.022 M) the spectral pattern was total emission as reported before, whereas at a low concentration (0.0027 M) the pattern changed to *E*/*A*. The spectral change is explained by the change in the relative contributions of the total *E* and the *E*/*A* components. The *E*/*A* polarization is obviously due to the $\mathrm{ST_0}$ mixing of the RPM with triplet geminate

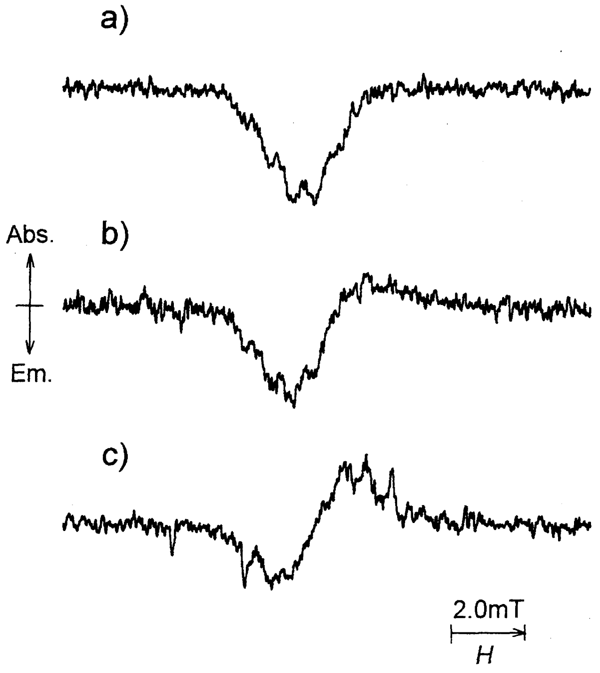


Fig. 1. Concentration dependence of the CIDEP spectrum observed in the photolysis of quinoxaline in 2-propanol at 0 °C. (a) 0.022 M, (b) 0.010 M, (c) 0.0027 M.

pair and/or F-pair. The net E polarization decreases drastically with decreasing the quinoxaline concentration. This observation cannot be compatible with the assignment that the emissive polarization is due to the TM.

Figure 2 shows the concentration dependence of the CIDEP spectrum obtained in the photolysis of phenazine in 2-propanol at 0 °C. The photoreaction of phenazine progresses by the scheme similar to that of quinoxaline. Observed spectra are assigned to the phenazinyl radical.[16,17] The 2-hydroxypropan-2-yl radical was not observed also because of the quenching by ground state phenazine. The concentration dependence is similar to that of quinoxaline, but the extent of the change is not so drastic. The net E polarization decreases with decreasing the phenazine concentration, but remains to be dominant even at a low concentration (0.0034 M).

(b) Excitation Power Dependence of the CIDEP Spectra. Figure 3 shows the excitation laser power dependence of the CIDEP spectrum in the photolysis of phenazine (0.010 M) in 2-propanol at 0 °C. The net E polarization decreases with decreasing the excitation power. However, the dependence was weaker compared with the concentration dependence. The result suggests that the concentrations of the excited state and/or radical affect the amount of the net polarization.

2. Mechanism Producing the Net Emission CIDEP. The relative contribution of the net E polarization is enhanced by increases of the concentrations of radicals and/or triplet molecules produced by increases of the initial concentrations of parent molecules and an increase of the excitation light intensity. The TM and ST_- mixing RPM cannot explain this result. On the other hand, the RTPM or the spin polarization transfer mechanism[24—27] may be able to explain it. The spin polarization transfer to radicals is known to occur in two situations; one is the case when a spin polarized radical reacts quickly and produces a secondary radical,[24—26] and the other is the case when a spin polarized triplet molecule interacts with a radical through spin exchange or chemical exchange.[27] For these mechanisms to be effective the primary species must have an effective net polarization and the transfer process must take place in a time comparable to the spin-lattice relaxation time. The net spin polarization of the primary species is usually generated by TM and/or ST_-M. In the present case, the secondary reaction represented by reaction (II) produces the quinoxalinyl (or phenazinyl) radical, but the primary reaction rate is far too slow. The spin polarization transfer from the triplet parent molecule is not likely to occur unless the radical concentration is very high and the spin polarization of the triplet state is conserved before the transfer. Therefore, the RTPM is considered to be the most probable mechanism.

The prerequisite for the RTPM to be effective is that both triplet molecules and radicals are sufficiently long-lived to interact together. We show here that the lifetimes of the triplet states and the produced radicals are indeed long enough to cause an effective RTPM interaction. Figure 4 shows the transient absorption spectrum obtained by the photolysis of quinoxaline (0.0012 M) in 2-propanol at room temperature. The absorption bands of the quinoxaline triplet and the quinoxalinyl radical are located around 420 nm. In an early time region within 1 μs, the spectrum is nearly given by the absorption of triplet quinoxaline, but in a later time region it shows the absorption of

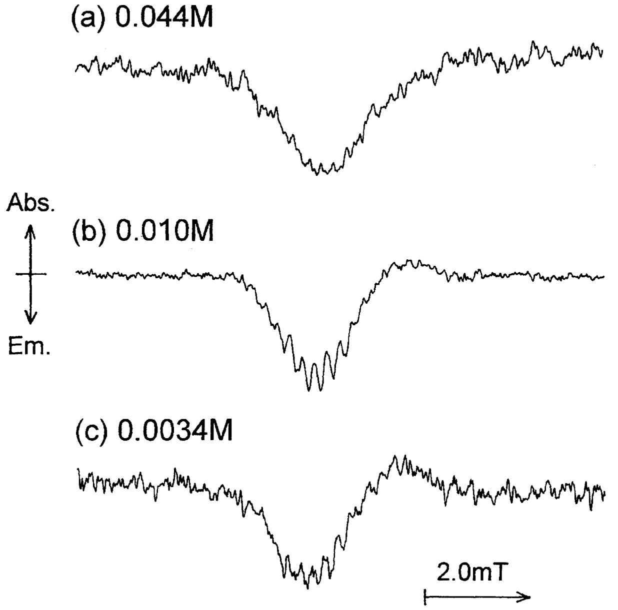


Fig. 2. Concentration dependence of the CIDEP spectrum observed in the photolysis of phenazine in 2-propanol at 0 °C. (a) 0.044 M, (b) 0.010 M, (c) 0.0034 M.

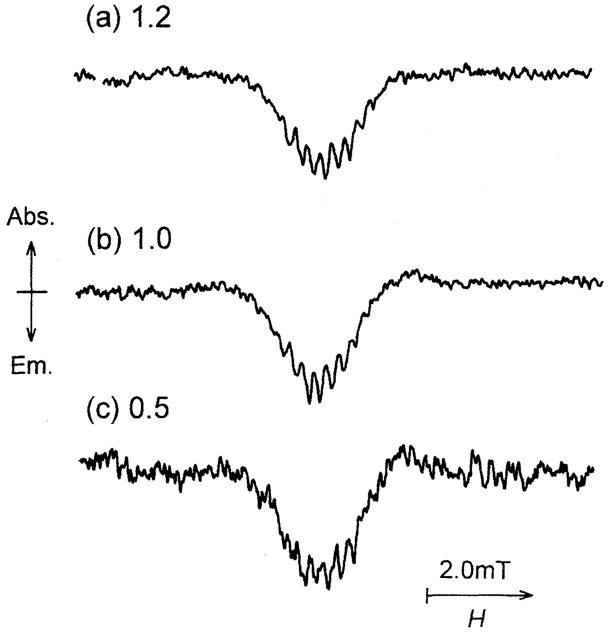


Fig. 3. Excitation laser power dependence of the CIDEP spectrum of phenazine (0.0010 M) in 2-propanol at 0 °C. Relative power: (a) 1.2, (b) 1.0, (c) 0.5. Signal intensities are normalized to similar sizes. (The absolute signal intensity at 0.5 is much weaker than those at 1.0 and 1.2.)

the quinoxalinyl radical which perfectly agrees with that reported in literature.[18,19] The absorption of 2-hydroxypropan-2-yl is located around 350 nm, but it is too weak to be observed. The decay of the transient absorption at 430 nm is also shown in Fig. 4. The decay curve consists of a fast decay of quinoxaline triplet and a slow one of the quinoxalinyl radical, and could be analyzed by two exponential decays at low concentrations. The lifetimes of the quinoxaline triplet determined by the least squares fits of the data are 3.0 μs at R.T. and 4.7 μs at −30 °C. The lifetime at R.T. is in reasonable agreement with the lifetime estimated from the reported quenching rate constant of triplet quinoxaline.[18] The lifetime of the quinoxalinyl radical was more than 20 μs at both R.T. and −30 °C. It should be noted, however, that the triplet decay is strongly dependent on the concentration of quinoxaline and the excitation power. As the inset in Fig. 4 shows the triplet decays at higher concentrations are remarkably faster and cannot be expressed by a single exponential curve. They seem to be better described by combinations of first and second order decays. Presumably triplet–triplet (T–T) annihilation becomes significant at higher concentrations.

Similarly, the transient absorption spectrum obtained by the photolysis of phenazine (0.0011 M) in 2-propanol at room temperature shows absorption bands of the phenazine triplet and the phenazinyl radical around 420 nm, which agree with the literature.[14] The lifetime of the phenazine triplet determined by a least squares fit of the time evolution data are 3.6 μs at R.T. The phenazinyl radical is also quite long-lived.

The results of the transient absorption experiments thus indicate that the condition for the RTPM to be important is satisfied.

3. Qualitative Features of the Time Dependence of the CIDEP Spectra. In this section, we first discuss time dependent changes of the CIDEP spectra qualitatively. Figure 5 shows the time dependent changes of the CIDEP spectra observed in the photolysis of quinoxaline (0.0036 M)/2-propanol at 0, −30, and −60 °C. The CIDEP spectra show different time dependence depending on the temperature. At 0 °C the spectral pattern is *E*/*A* in all the time regions of observation. The net component is very weak. On the other hand, at −30 °C the spectrum initially shows an *A*/*E** pattern within 0.5 μs, then changes quickly to an opposite phase, i.e., *E*/*A* (1.0 to 2.0 μs), and then decays slowly, changing the phase to *E**/*A* character (≥4.0 μs) at last. The contribution of the net *E* polarization is increased in a later time region. The spectral change at −60 °C is similar to that at −30 °C, but the contribution of the net *E* polarization is considerably larger compared with that at higher temperatures. These results are qualitatively explained in the following way.

The *A*/*E* polarization observed in the early time region is explained in terms of the ST_0 mixing RPM of the singlet precursor provided that the exchange integral *J* is negative. The *E*/*A* polarization observed in the following time region is gen-

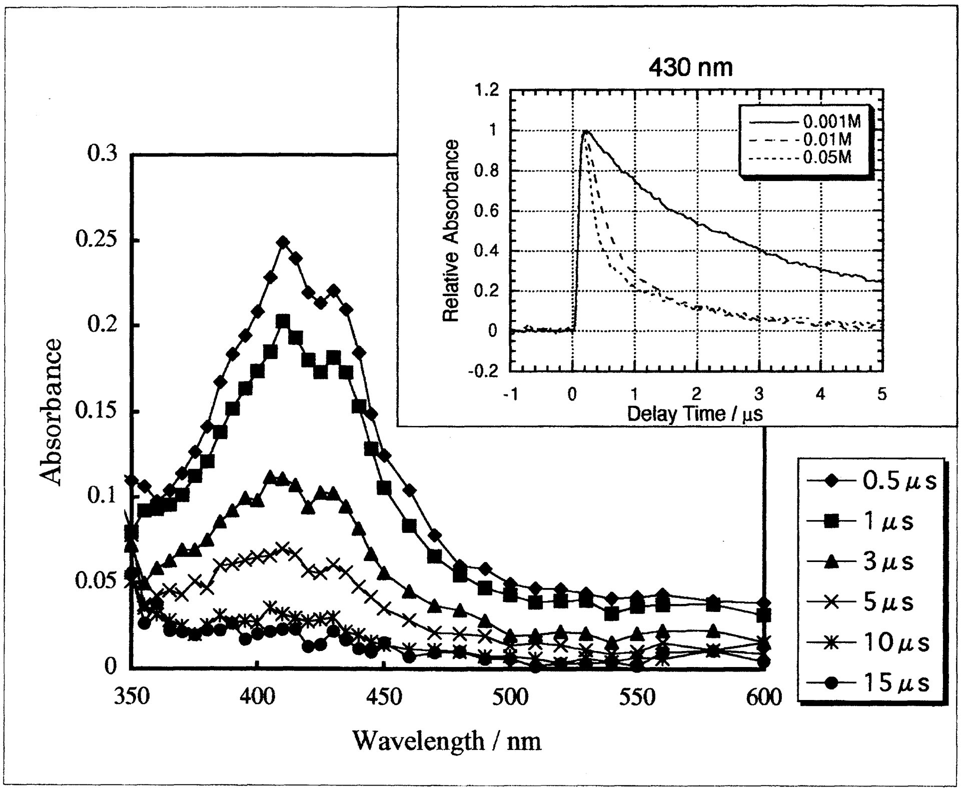


Fig. 4. Transient absorption spectra observed in the photolysis of quionoxaline (0.0010 M) in 2-propanol at room temperature. The time developments of the transient absorption signals at 430 nm at different quinoxaline concentrations are given in the inset.

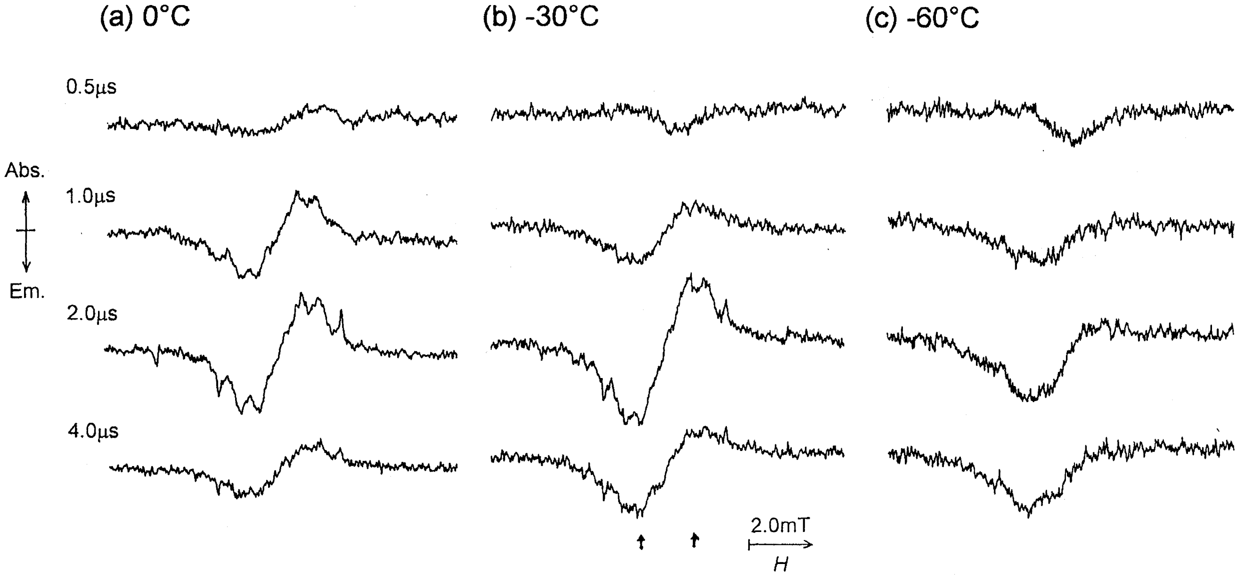


Fig. 5. Time evolution of the CIDEP spectra observed in the photolysis of quinoxaline (0.0036 M) in 2-propanol at (a) 0 °C, (b) −30 °C, and (c) −60 °C. Arrows in (b) indicate the positions at which time evolution of the signal was measured. (see Fig. 7).

erated by the ST_0 mixing RPM of the triplet precursor. The results suggest that both the excited singlet and triplet states react competitively. This situation is similar to that found previously in the CIDEP of acetone in triethylamine.[28,29] The minor singlet reaction is hidden by the major triplet reaction at higher temperatures, but at lower temperatures (≤ -30 °C), involvement of the singlet reaction apparently becomes clear in an early time region, because the triplet reaction becomes slower. The triplet reaction increases with time and becomes dominant in a later time region, changing the *A/E* polarization of the singlet geminate pair RPM to the *E/A* polarization of the triplet RPM. The *E/A* polarization persists for a long time. The *E/A* polarization observed in a later time region (>10 μs) is considered to be due to the F-pair RPM, which should rise with the spin-lattice relaxation rate and decay with a time constant determined by the second order decay of the radical.[29] The net *E* polarization increases with decreasing the temperature. The lifetime of the triplet state of quinoxaline increases with decreasing the temperature as confirmed by the transient absorption experiments. Then the RTPM polarization is enhanced, because the chance of the encounter between the triplet and radical is increased. Furthermore, the increased viscosity at lower temperatures prolongs the correlation time of the RTPM interaction, enhancing the polarization. The results support the suggestion that the net polarization is caused by the RTPM.

Figure 6a shows the time evolution of the CIDEP spectrum observed in the photolysis of quinoline (0.013 M) in 2-propanol at -15 °C. The spectrum is assigned to the quinolinyl radical. The CIDEP spectrum changes with time from *A/E** to net *E*. Here the contribution of the *E/A* polarization appears to be very weak. The result is explained mainly by the *A/E* polarization due to the singlet precursor ST_0 mixing RPM and the net *E* polarization due to the RTPM. Long-lived characters of triplet quinoline and the quinolinyl radical were also confirmed by the transient absorption experiment. The reaction scheme and the CIDEP generation mechanism are believed to be similar to the case of quinoxaline, though the signals were much weaker in quinoline.

The photoreaction and the CIDEP development mechanisms of the phenazine/2-propanol system are considered to be similar to the quinoxaline system except that the singlet reaction was not observed. Figure 6b shows the time evolution of the CIDEP spectrum observed in the photolysis of phenazine (0.0034 M) in 2-propanol at 0 °C. The spectrum shows *E**/*A* character at all times, in contrast to quinoxaline which shows almost symmetric *E/A* character at the same concentration. Stronger emissive components are also ascribed to the RTPM.

The CIDEP producing mechanisms in this series of azaaromatics are considered to be common, but the relative contributions of different mechanisms vary depending on the individual system. For example, whether the singlet precursor RPM is significant or not depends on the competition between the singlet reaction and the intersystem crossing process. Thus absence of the CIDEP due to the singlet RPM in the case of phenazine is presumably due to the more efficient intersystem crossing compared to the singlet reaction.

4. Time Evolution of the Polarization. In this section, we try to analyze the time evolution of the CIDEP signals more quantitatively. As the discussion of the previous section indicates, several different polarization mechanisms are involved. Complete quantitative treatments are quite difficult and accurate analytical expressions cannot be obtained. Therefore several simplifications are made. Furthermore, in discussing the RTPM we mainly focus our attention to the net polarization, because it is very difficult to separate the hyperfine dependent RTPM from the RPM polarization. We first consider various processes involved in the present systems and give approximate expressions for various concentrations and polarizations.

(1) Triplet Concentration. The processes involved in

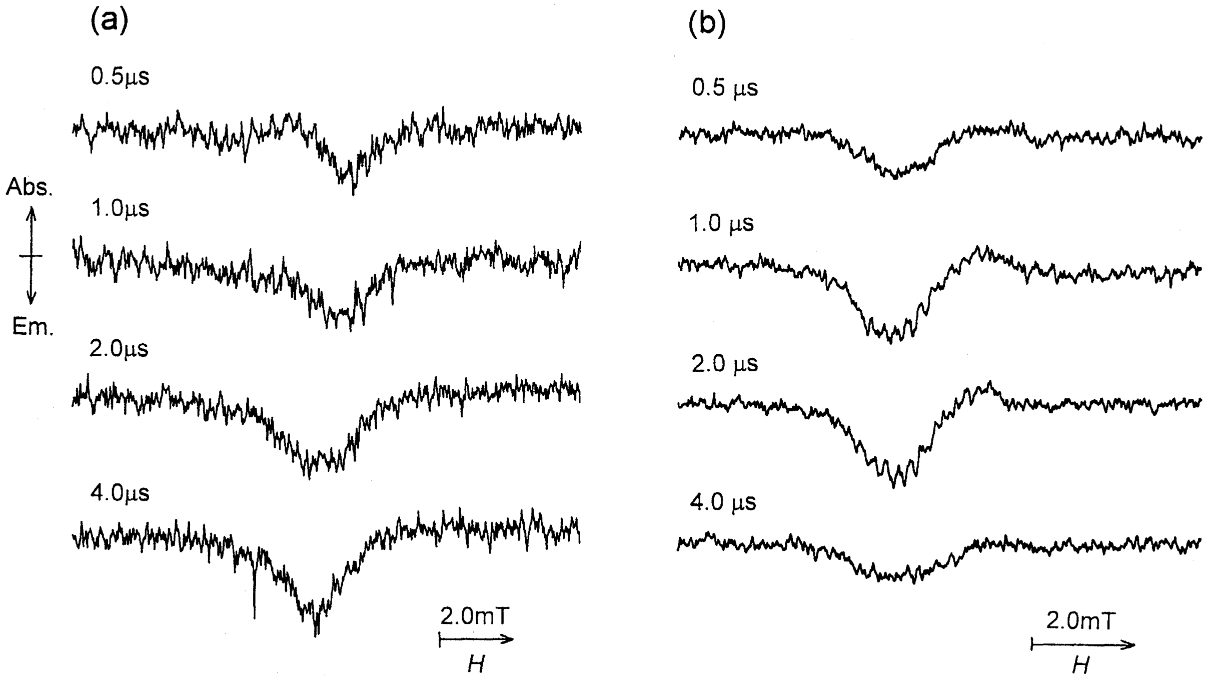


Fig. 6. Time evolution of the CIDEP spectra observed in the photolysis of (a) quinoxaline (0.013 M) in 2-propanol at −15 °C and (b) phenazine (0.0034 M) in 2-propanol at 0 °C.

the production and decay of the triplet state is considered to be the following.

$$\begin{aligned}
&\mathrm{S_1} \xrightarrow{\mathrm{ISC}} \mathrm{T}\\
&\mathrm{T} \xrightarrow{k_\mathrm{p}} \mathrm{S_0}\\
&\mathrm{T}+\mathrm{ROH} \xrightarrow{k_\mathrm{T}} \cdot\mathrm{R}+\cdot\mathrm{ROH}\\
&\mathrm{T}+\mathrm{Q} \xrightarrow{k_\mathrm{q}^\mathrm{TS}} \text{quench}\\
&\mathrm{T}+\cdot\mathrm{R} \xrightarrow{k_\mathrm{q}^\mathrm{TR}} \text{quench}\\
&\mathrm{T}+\mathrm{T} \xrightarrow{k_\mathrm{q}^{TT}} \text{quench}
\end{aligned}$$

Here, k_p is the intrinsic decay rate constant, k_T is the triplet reaction rate constant, k_q^TS, k_q^TR, and k_q^TT are the quenching reaction rate constants by the ground state parent molecule, the radical, and the triplet state itself, respectively. The production process is considered to be much faster than our observation time. When the triplet concentration is low, the second order term may be neglected. Then the triplet concentration is given by a simple form:

$$[\mathrm{T}] = [\mathrm{T}]_0 \exp(-k'_\mathrm{T}t) \tag{1}$$

with

$$k'_\mathrm{T} = k_\mathrm{p} + k_\mathrm{T} + k_\mathrm{q}^\mathrm{TS}[\mathrm{Q}] + k_\mathrm{q}^\mathrm{TR}[\mathrm{R}]$$

Here, $[\mathrm{T}]_0$ represents initial triplet concentration. When the quenching by the triplet itself cannot be neglected a larger apparent decay rate constant k'_T is observed.

(2) Radical Concentration. The radical is considered to be produced mainly by the reaction of the triplet state, but it is suggested that the reaction of the singlet excited state also produces the radical as described in the previous section. There are several possible processes of radical quenching which include the second order chemical decay and the RTPM interaction itself. Then the radical production and decay are represented by;

$$\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}t} = k_\mathrm{T}[\mathrm{T}] - k_\mathrm{q}^\mathrm{TR}[\mathrm{T}][\mathrm{R}] - k_{2\mathrm{r}}[\mathrm{R}]^2 \tag{2}$$

Here, k_T is the apparent rate constant of the radical producing reaction from the excited triplet state. $k_{2\mathrm{r}}$ is the second order decay rate constant. Since the lifetime of the singlet state is very short, probably less than 20 ns, the concentration of the radical produced from the singlet precursor is treated as an initial radical concentration. When the second and third terms are neglected in Eq. 2, the solution is given by;

$$[\mathrm{R}] = [\mathrm{R}]_0 + \frac{k_\mathrm{T}}{k'_\mathrm{T}}[\mathrm{T}]_0\{1-\exp(-k'_\mathrm{T}t)\} \tag{3}$$

where $[\mathrm{R}]_0$ is the initial radical concentration which is given by the singlet reaction and the steady state concentration.

(3) Polarizations Due to Geminate Pair and F-Pair RPM. Spin polarization due to the geminate and F-pair RPM have been discussed in detail in a previous report.[29)]

(a) Geminate Pair RPM Polarization. Spin polarization due to the geminate pair RPM is given by;

$$\begin{aligned}P_\mathrm{RPM} &= P_\mathrm{RPM}^0\{\exp(-t/T_1^\mathrm{R}) - \exp(-k_\mathrm{f}t)\}\\ &\quad + P_\mathrm{RPM}^\infty\{1-\exp(-t/T_1^\mathrm{R})\}\end{aligned} \tag{4}$$

Here, P_RPM^0 and P_RPM^∞ are the initial polarization and the polarization at thermal equilibrium of the geminate-pair RPM, respectively. T_1^R is the spin-lattice relaxation time of the radical. k_f is the growth rate constant of the polarization due to the geminate-pair RPM.

(b) F-Pair RPM Polarization. When the initial radical concentration is high and its decay is determined by the second order radical decay, the magnitude of the F-pair polarization is approximately given by,[29)]

$$P_{\mathrm{FRPM}} = ak_{\mathrm{F}}[\mathrm{R}]_0^2 \cdot T_1^{\mathrm{R}} \left\{ \frac{1}{(k_{2\mathrm{r}}[\mathrm{R}]_0 t + 1)^2} - \exp(-t/T_1^{\mathrm{R}}) \right\} \quad (5)$$

(4) RTPM Polarization. The RTPM polarization is generated when a triplet state and a radical make a collision and interacts each other. The polarization decays with the spin-lattice relaxation time. Then, when we can neglect the second order radical decay, the RTPM polarization (P_{RTPM}) is obtained by solving the following differential equation.[30—32]

$$\frac{\mathrm{d}P_{\mathrm{RTPM}}}{\mathrm{d}t} = k_{\mathrm{RTPM}}[\mathrm{T}][\mathrm{R}] - \frac{P_{\mathrm{RTPM}} - P^{\infty}}{T_1^{\mathrm{R}}} \quad (6)$$

Here, k_{RTPM} is the rate constant of the RTPM and T_1^{R} is the spin-lattice relaxation time of the radical. P^{∞} is the polarization at the thermal equilibrium. Assuming that [T] and [R] are given by Eqs. 1 and 3, respectively, the solution of Eq. 6 is given by the following equation;

$$P_{\mathrm{RTPM}} = \alpha \exp(-2k'_{\mathrm{T}}t) - \beta \exp(-k'_{\mathrm{T}}t) + \gamma \exp(-t/T_1^{\mathrm{R}}) + P^{\infty} \quad (7)$$

$$\alpha = \frac{k_{\mathrm{RTPM}} \frac{k_{\mathrm{T}}}{k'_{\mathrm{T}}} [\mathrm{T}]_0^2}{2k'_{\mathrm{T}} - 1/T_1^{\mathrm{R}}},$$

$$\beta = \frac{k_{\mathrm{RTPM}}[\mathrm{T}]_0 \left([\mathrm{R}]_0 + \frac{k_{\mathrm{T}}}{k'_{\mathrm{T}}} [\mathrm{T}]_0 \right)}{k'_{\mathrm{T}} - 1/T_1^{\mathrm{R}}},$$

$$\gamma = \beta - \alpha - P^{\infty}$$

The solution represented by Eq. 7 is meaningful under the condition of $1/T_1^{\mathrm{R}} \neq k'_{\mathrm{T}}$ and $1/T_1^{\mathrm{R}} \neq 2k'_{\mathrm{T}}$ which is usually valid. Then, the time evolution of the RTPM polarization is represented by three exponential components. The time development always consists of one rise and two decay components. In this case, the rate of one decay component is much larger than the rate of the rise component, and another decay component is much smaller. Here, we consider two cases. One is $k'_{\mathrm{T}} > 1/T_1^{\mathrm{R}}$, and another is $2k'_{\mathrm{T}} > 1/T_1^{\mathrm{R}} > k'_{\mathrm{T}}$. In the former case the rise constant is determined mainly by k'_{T} and the decay constant is by $1/T_1^{\mathrm{R}}$. In the latter case the rise constant is determined by $1/T_1^{\mathrm{R}}$ and the decay constant is by k'_{T}. In both cases α is positive, and the $2k'_{\mathrm{T}}$ term represents a quick decay component which may not appear clearly in the time evolution of the signal. Therefore, the time development of the RTPM polarization should look like one rise and one decay.

5. Time Evolution of CIDEP Signals. The exact time evolution of the CIDEP signal observed in a CW time-resolved EPR experiment is in general complicated because of the constant interaction of the spin system with the microwave. It should be described by the solution of a modified Bloch equation, but such a solution cannot be obtained easily without making simplifications in the present case. In a CW time-resolved EPR experiment, we observe time dependence of the transverse magnetization M_y, but for simplicity here we assume that M_y is approximately proportional to M_z whose time evolution is described by the time evolution of various polarizations discussed in the previous section. This approximation is adequate when the microwave power is sufficiently low. We have confirmed that the measured decay curves are not dependent on the microwave power in our measuring region (≤ 0.2 mW).

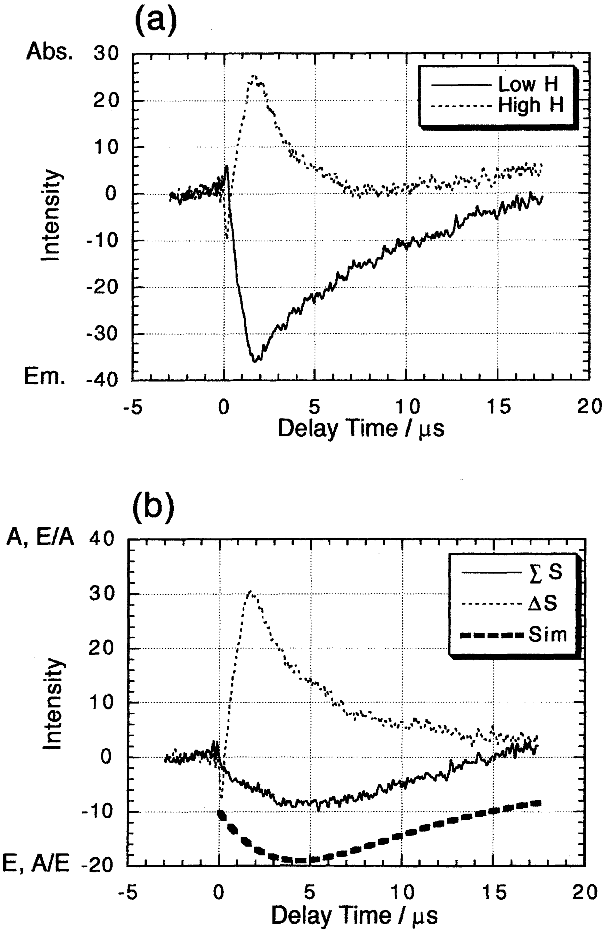


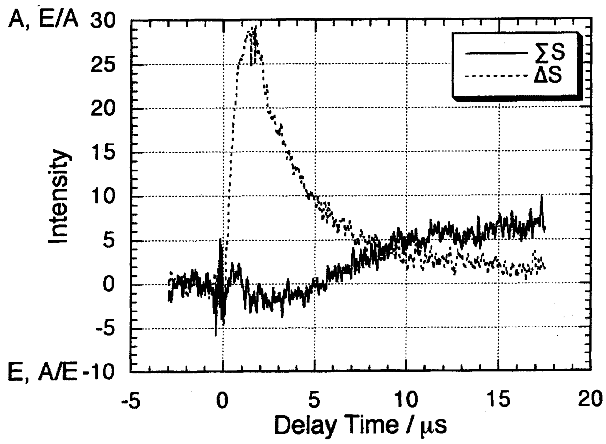
Fig. 7. Time evolution of the transient EPR signals obtained in the photolysis of quinoxaline (0.0036 M) in 2-propanol at −30 °C. (a) Intensities of signals at a low field position (——) and the corresponding high field position (····), (b) Intensities of the net component (ΣS) and the antiphase component (ΔS). Simulated time evolution curve based on Eq. 7 ($1/k'_{\mathrm{T}}$=5 μs, T_1^{R}=3.4 μs, β/α=−2.0) is also shown by a broken line whose initial value is displaced by −10.

Figure 7a shows the time evolution of the CIDEP signals at a low field position from the center of the spectrum and the corresponding high field position (indicated by arrows in Fig. 5b observed in the quinoxaline (0.0036 M)/2-propanol system at −30 °C. The signals show a strange change with time. This is because the time developments of the net component and the antiphase (*E*/*A* or *A*/*E*) component are quite different. A quantitative analysis requires the separation of the each component. The time evolutions of the *E*/*A* (or *A*/*E*) component and the net component of the polarization can be separated by taking the difference (ΔS) and the sum (ΣS) of the signal intensities at the low field and the corresponding high field positions shown by arrows in Fig. 5b. The ΔS component is considered to include three $\mathrm{ST_0}$ mixing RPM components, singlet geminate pair, triplet geminate pair and F-pair. The ΔS component due to the geminate pair RPM rises quickly to *A*/*E* (singlet precursor) followed by *E*/*A* (triplet precursor) with the apparent reaction rate of the triplet and decays with the spin-lattice relaxation rate. The *E*/*A* component which remains at longer times (over 10 μs) is presumably due to the F-pair RPM. This is possible because of a large initial concentration of the radical produced by the singlet reaction. The F-pair RPM polarization should decay with the second order decay rate constant of the radical as represented by Eq. 5. The spin-lattice relaxation time of the radical is determined to be 3.4 μs by the fits of the decay curve of the *E*/*A* component. On the other hand, the ΣS component rises to net *E* much more slowly than the ΔS component, and decays more slowly to a small absorption which is presumably due to the thermal equilibrium signal. The rise time of the ΣS is close to the spin-lattice relaxation time of about 3.4 μs. The rise and decay curve is simulated reasonably well with the triplet lifetime of 5 μs determined by the transient absorption experiment (Fig. 7b). Exact agreement between the triplet decay time determined by the transient absorption and the decay time of the EPR signal is not expected because of the difference in the experimental conditions and the approximate nature of Eq. 7. However, the time evolution of the net polarization is believed to be determined mainly by the RTPM dynamics.

There is one puzzling observation about the time evolution of the ΔS component. The time evolution of ΔS is interpreted on the basis of the contributions of the singlet and triplet geminate pair RPM. The *E*/*A* component due to the triplet geminate pair rises rapidly within 1 μs. However, the triplet lifetime is too long to explain this rise. Therefore, there may be another process to give rise to a fast rising *E*/*A* polarization.

Figure 8 shows the time evolution of the *E*/*A* polarization and the net polarization of the quinoxaline (0.0036 M)/2-propanol system at 0 and −60 °C. From the temperature dependence, it is seen that the relative intensity of the net *E* polarization increases drastically with decreasing the temperature. The *E*/*A* polarization at −60 °C also shows a very slow decay due to the F-pair polarization dynamics represented by Eq. 5. The spin-lattice relaxation times estimated by the fits of the decay of the *E*/*A* polarization as described before are 2.5 μs at 0 °C and 7.5 μs at −60 °C. At 0 °C, the rise and the decay times of the net polarization are about 2.5 and 3.5 μs, respectively, which are in good agreement with the spin-lattice relaxation time and the triplet lifetime, respectively. The results can be explained by the RTPM dynamics model represented by Eq. 7. On the other hand, at −60 °C the rise time was around 2 μs which is shorter than the spin-lattice relaxation time. The decay time at −60 °C is around 20 μs, which is considered to be determined primarily by the triplet lifetime at this temperature. The time development at −60 °C is considered to be mainly due to the RTPM dynamics, but a quantitative agreement with the prediction of Eq. 7 is not good in the early time region.

(a) 0°C



(b) -60°C

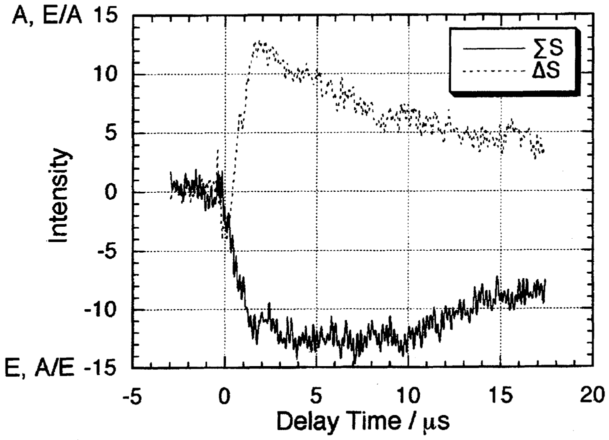


Fig. 8. Time evolution of the net component (ΣS) and the antiphase component (ΔS) of the transient EPR signal of the quinoxaline (0.0036 M)/2-propanol system at (a) 0 °C and (b) −60 °C.

Figure 9 shows the time evolution of the EPR signal at the center position of the spectrum observed in more concentrated quinoxaline (0.010 and 0.051 M) solutions at different temperatures. At these concentrations, the CIDEP spectra show almost total emission with a slight *E*/*A* distortion. Therefore, we can consider the center signal to represent the net polarization. The rise times of the signals are much shorter compared with those at a low concentration (0.0036 M). The decay times at 0.010 M are 3.3, 5, and ca. 15 μs at 0, −30, and −60 °C, which agree with those at 0.0036 M, and indicate the triplet lifetimes. At 0.01 M, the rises are faster and the decays at lower temperatures are somewhat faster. The time developments in later time regions can be explained by the RTPM dynamics, but the cause for the fast rise must be found. A most likely explanation is the involvement of the T–T annihilation at higher concentrations of the triplet state. The T–T annihilation process reduces the triplet lifetime drastically in an early time region, increases the apparent decay rate constant k_T', and increases the rise of the net polarization. As the decay curves in Fig. 4 show, shortenings of the triplet apparent lifetimes at higher con-

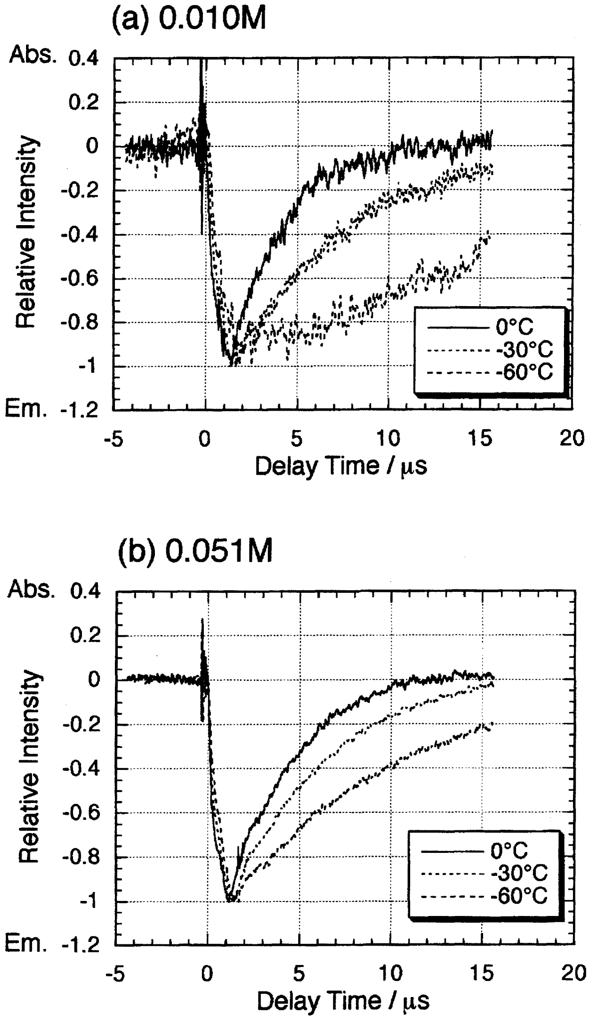


Fig. 9. Time evolution of the transient EPR signals at the center of the spectra obtained in the photolysis of quinoxaline in 2-propanol at (a) 0.010 M and (b) 0.051 M.

centrations of quinoxaline are clearly seen in the transient absorption signals. Another possibility is the polarization transfer from the triplet state to the radical. This mechanism was recently shown to be important in systems consisting of metalloporphyrins and nitroxide radicals.[27] The relaxation times of triplet porphyrins are exceptionally long because of their small zero field splitting constants and large molecular volumes. In the cases of ordinary organic molecules, the triplet relaxation times are less than 10 ns and this process is unlikely to be important in the present systems.

Figure 10 shows the time evolutions of the net and the *E*/*A* components of the EPR signals observed in phenazine (0.0036 M) in 2-propanol at 0, −30, and −60 °C. The net polarization rises quickly with almost the same rate as the *E*/*A* component, which is close to the response time of our apparatus. The decay rate of the net component is slower than that of the *E*/*A* component. The rise rates of both components are almost the same at all temperatures, whereas the decay rates decrease with decreasing the temperature. The slow decay of the net component is considered to be determined by the

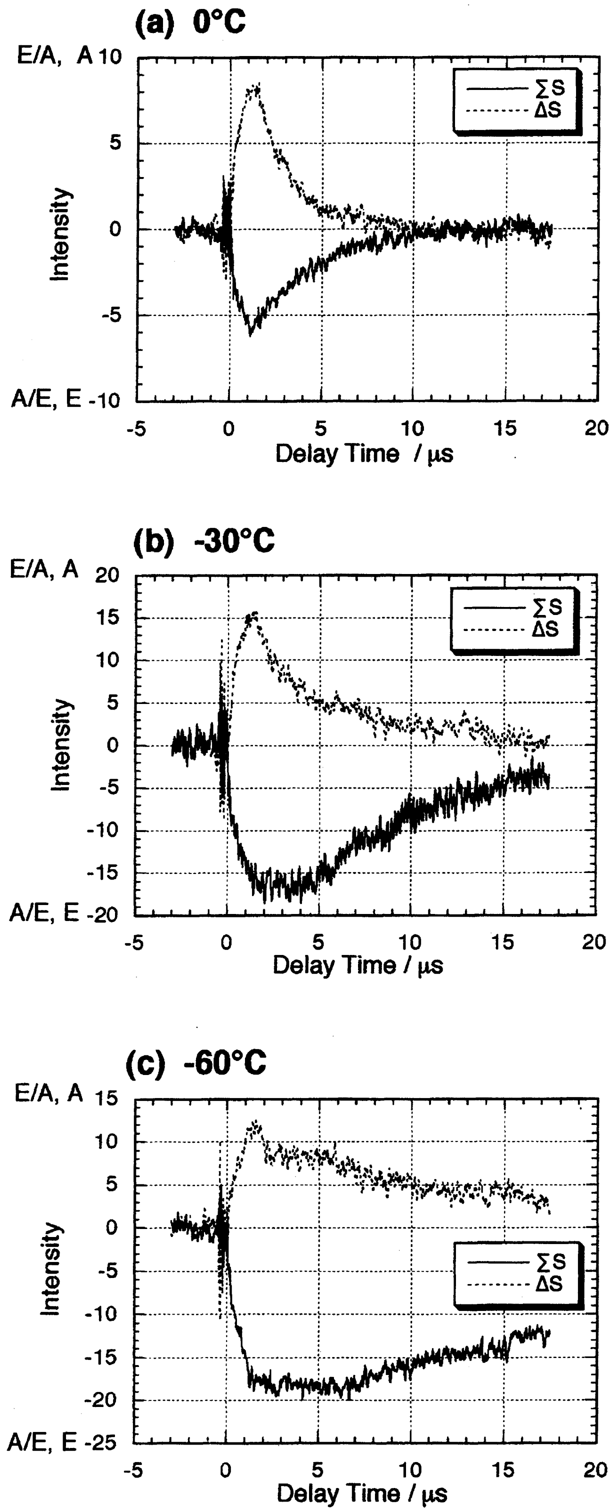


Fig. 10. Time evolution of the net component (ΣS) and the antiphase component (ΔS) of the transient EPR signal of the phenazine (0.0034 M)/2-propanol system at (a) 0 °C, (b) −30 °C, and (c) −60 °C.

triplet lifetime, which drastically increases with a decrease of the temperature. The time evolution of the net component in a later time region (>3 μs) can also be explained by the RTPM dynamics represented by Eq. 7. The rise of the net polarization at low temperatures consists of a fast and a slow component. The slow rise component is explained by the RTPM dynamics as the rise constant is determined by the spin-lattice relaxation time, but the fast rising net component in the early time region cannot be explained clearly. A fast decrease of the triplet concentration by the T–T annihilation can also give rise to the fast rise of the RTPM polarization as in the case of quinoxaline, if the triplet production is very efficient and T–T annihilation takes place with a diffusion controlled rate. Another possibility is that a reaction from a higher excited triplet state takes place via a two photon process and the produced radical has a net E polarization of the TM. Such a case was found in benzil.[13,33] However, further detailed investigations are needed to clarify the exact cause of the fast rise in phenazine. On the other hand, the decay of the E/A component is determined mainly by the spin-lattice relaxation of the radical. At lower temperatures, the contribution of the F-pair polarization increases. The decay is not single exponential because it is determined by a combination of the decays of the geminate pair and the F-pair RPM.

Conclusion

The CIDEP development mechanisms of azaaromatic compounds, quinoxaline, phenazine and quinoline are investigated in detail. It is shown that several polarization mechanism are involved and the dominant mechanism is strongly dependent on the concentration and temperature. The net emissive polarization is explained mainly by the RTPM between the produced radical and the precursor triplet. At a low concentration, the time evolution of the net component agrees reasonably with the prediction of the RTPM model, which indicates that the rise is mainly determined by the spin-lattice relaxation rate and the decay by the triplet lifetime. The RTPM usually gives a net E polarization of a slow rise and a slower decay compared with those of the TM and the geminate pair RPM, but at high concentrations the emissive polarizations are found to show fast rises. This may be due to T–T annihilation. However, for a more complete understanding of the polarization mechanisms, more precise analysis of the time developments of the polarizations is needed. The RTPM polarization is expected to play an important role generally, when the concentrations of triplet states and radicals are high and triplet states are relatively long-lived.

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References

1) "Spin Polarization and Magnetic Field Effects in Radical Reactions," ed by Y. N. Molin, Elsevier, Amsterdam (1984).

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

3) H. van Willigen, P. R. Levstein, and M. H. Ebersole, *Chem. Rev.*, **93**, 173 (1993).

4) F. J. Adrian, *J. Chem. Phys.*, **54**, 3918 (1971); **57**, 5107 (1972).

5) J. B. Pedersen and J. H. Freed, *J. Chem. Phys.*, **58**, 2746 (1973); **59**, 2869 (1973).

6) S. K. Wong, D. A. Huchinson, and J. K. S. Wan, *J. Am. Chem. Soc.*, **95**, 622 (1973).

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

8) J. B. Pedersen and J. H. Freed, *J. Chem. Phys.*, **62**, 1706 (1975).

9) F. J. Adrian and L. Monchick, *J. Chem. Phys.*, **71**, 2600 (1979).

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

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

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

13) C. Blätler, F. Jent, and H. Paul, *Chem. Phys. Lett.*, **166**, 375 (1990); *Res. Chem. Intermed.*, **16**, 201 (1991).

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

15) A. Kawai and K. Obi, *J. Phys. Chem.*, **96**, 5701 (1992); *Res. Chem. Intermed.*, **19**, 866 (1993).

16) S. Basu, K. A. McLauchlan, and G. R. Sealy, *Chem. Phys. Lett.*, **88**, 84 (1982).

17) S. Yamauchi and N. Hirota, *J. Phys. Chem.*, **88**, 4631 (1984).

18) D. V. Bent, E. Hayon, and P. N. Moorthy, *Chem. Phys. Lett.*, **27**, 544 (1974); *J. Am. Chem. Soc.*, **97**, 5065 (1975).

19) P. N. Moorthy and E. Hayon, *J. Phys. Chem.*, **78**, 2615 (1974).

20) M. S. de Groot, I. A. M. Hesselmann, J. Schmidt, and J. H. van der Waals, *Mol. Phys.*, **15**, 19 (1968).

21) J. Schmidt, D. A. Artheunis, and J. H. van der Waals, *Mol. Phys.*, **22**, 1 (1971).

22) K. Ohara, N. Hirota, C. A. Steren, and H. van Willigen, *J. Phys. Chem.*, **100**, 3070 (1996).

23) S. Michaeli, V. Meiklyar, M. Schulz, K. Möbius, and H. Levanon, *J. Phys. Chem.*, **98**, 7444 (1994).

24) K. Ohara, H. Murai, and K. Kuwata, *Bull. Chem. Soc. Jpn.*, **65**, 1672 (1992).

25) K. A. McLauchlan and N. J. K. Simpson, *Chem. Phys. Lett.*, **154**, 550 (1989).

26) K. Akiyama, M. C. Depew, and J. K. S. Wan, *Res. Chem. Intermed.*, **11**, 25 (1989).

27) J. Fujisawa, K. Ishii, Y. Ohba, M. Iwaizumi, and S. Yamauchi, *J. Phys. Chem.*, **99**, 17082 (1995).

28) K. Tominaga, S. Yamauchi, and N. Hirota, *J. Phys. Chem.*, **92**, 5160 (1988).

29) K. Ohara, N. Hirota, C. A. Steren, and H. van Willigen, *Chem. Phys. Lett.*, **232**, 169 (1995).

30) G.-H. Goudsmit and H. Paul, *Chem. Phys. Lett.*, **208**, 73 (1993).

31) A. I. Shushin, *Chem. Phys. Lett.*, **208**, 173 (1993).

32) G.-H. Goudsmit, H. Paul, and A. I. Shushin, *J. Phys. Chem.*, **97**, 13243 (1993).

33) M. Mukai, S. Yamauchi, and N. Hirota, *J. Phys. Chem.*, **93**, 4411 (1992); **96**, 2179 (1992).