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Singlet-Born SCRP Observed in the Photolysis of Tetraphenylhydrazine in an SDS Micelle: Time Dependence of the Population of the Spin States

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The spectrum of the singlet-born spin-correlated radical pair generated in the photolysis of tetraphenylhydrazine in a micelle is analyzed. The time evolution of the spectral pattern directly reflects the time dependence of the population of the individual spin states of the radical pair. The relaxation times between these states and the reaction rates of the geminate process are estimated, and the relaxation of the middle two states of the radical pairs is discussed.

Introduction

The peculiarly alternating structures observed in a time-resolved ESR (TRESR) spectra[1] have been interpreted in terms of the spin-correlated radical pair (SCRP)[2,3] and have been extensively studied.[4] However, most of the reported studies are concerned with the triplet-born SCRP. This is probably because the geminate radical pairs generated from the singlet state usually are short-lived due to their fast reactivity and, further, because most of organic photochemical reactions occur from the triplet state. If, however, singlet-born SCRP ever exists, the dynamic behavior of SCRP can be studied more unambiguously because of the following reason.

In the studies on polymethylene-linked biradicals, Terazima et al.[5] have found that their SCRP spectra can be simulated only by equating the population of the two middle spin states. They have therefore suggested that rapid relaxation takes place between these states. A similar suggestion has also been given by Ishiwata et al.[6] in the studies on a micelle system. In contrast to these suggestions, Avdievich et al.,[7] in the studies on a polymethylene-linked system, have suggested that the populations of the two middle states are nullified by rapid recombination reaction. The distinction between these two different mechanisms is difficult because both mechanisms give the same spectral shape.

This question can be easily solved if a singlet-born SCRP is ever observed, because in the case of the singlet-born SCRP nullification of the central two states by rapid recombination reaction means that SCRP does not exist at all. For this reason, we have endeavored to discover a singlet-born SCRP.

As an example of singlet-born SCRP, we, in the present paper, investigated the radical pair consisting of two diphenylamino radicals (DPA) generated by the photolysis of tetraphenylhydrazine (TPH)[8] in a micelle. We discuss the time evolution of all spin states of SCRP by the spectrum simulation with the kinetic calculation.

Experimental Section

TPH was synthesized according to a method described in the literature[9] and was purified repeatedly by recrystallization from a methanol−benzene mixture. Commercially available sodium *n*-dodecyl sulfate (SDS) (Wako Pure Chemical, first grade) was used as detergent for a micellar solution. The concentration of SDS was 0.1 mol dm^{-3}. Since TPH is not easily dissolved in the micellar solution, it was previously dissolved in a small amount of benzene, and this benzene solution was added to the SDS solution. The concentration of the benzene in the micellar solution was 0.2 mol dm^{-3} and the concentration of the TPH was 1 × 10^{-4} mol dm^{-3}. An X-band ESR spectrometer (BRUKER esp-380E) was used without magnetic field modulation. A pulsed excimer laser (XeCl 308 nm) was used to excite the sample inside the ESR resonator. The sample was deoxygenated by bubbling with nitrogen gas and flowed through a flat quartz cell. The flow rate of the solution was 7 mL min^{-1}. All the experiments were carried out at 24 °C.

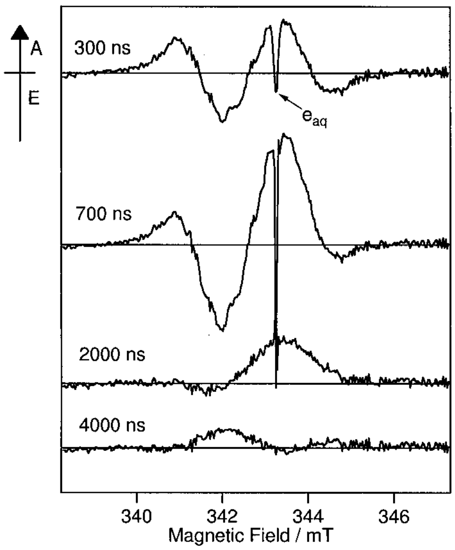

Figure 1. Time-resolved ESR spectra observed after laser excitation of tetraphenylhydrazine in an SDS micelle at room temperature.

Results and Discussion

Figure 1 shows the time-resolved ESR spectra observed in the photolysis of TPH in an SDS micelle. At earlier time (<700 ns) the spectrum shows alternating A/E/A/E polarization patterns. (A and E mean the absorption and emission, respectively.) At later time (2000 ns) a net absorptive component is gradually developed, and finally (4000 ns) the spectrum is inverted to an E/A/E/A polarization pattern. This time dependence is not due to the Torrey's oscillation[10] because quite the same time dependence was observed by using a much weaker microwave power. The spectra showing alternating polarization patterns are assigned to SCRP. The signal of the SCRP is observed for a long time, as shown in Figure 1. This result indicates that

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the DPA radicals do not easily escape from the micelle because of their hydrophobic nature[11] and the recombination rate is slow. The emissive signal at 343.3 mT is assigned to the hydrated electron($g = 2.0003$).[12]

The time dependence of the SCRP spectra was analyzed in terms of a simple theoretical model described below.[2] The eigenstate, $|i\rangle$, and eigenvalues, ϵ_i, of the spin Hamiltonian of the SCRP are described as follows (in angular frequency units).

$$|1\rangle = |\mathrm{T}_{+1}\rangle \qquad \epsilon_1 = -J + \omega_l \tag{1a}$$

$$|2\rangle = \cos\theta|S\rangle + \sin\theta|T_0\rangle \qquad \epsilon_2 = \Omega \tag{1b}$$

$$|3\rangle = -\sin\theta|S\rangle + \cos\theta|T_0\rangle \qquad \epsilon_3 = -\Omega \tag{1c}$$

$$|4\rangle = |\mathrm{T}_{-1}\rangle \qquad \epsilon_4 = -J - \omega_l \tag{1d}$$

$$\Omega_l = (J^2 + Q_l^2)^{1/2} \tag{2a}$$

$$Q_l = \frac{1}{2}(\omega_n - \omega_m) \tag{2b}$$

$$\omega_l = \frac{1}{2}(\omega_n + \omega_m) \tag{2c}$$

and

$$\Omega_l \cos 2\theta = J \tag{3a}$$

$$\Omega_l \sin 2\theta = Q_l \tag{3b}$$

where J denotes the exchange interaction. The subscript l refers to the individual hyperfine states of the biradical. ω_n is the ESR resonance frequency of one DPA radical partner, and ω_m is that of the other DPA radical partner. If the initial population of the radical pair is exclusively in the singlet state, the populations of $|1\rangle$ and $|4\rangle$ are both zero, while those of $|2\rangle$ and $|3\rangle$ are in a ratio of $\cos^2\theta$ and $\sin^2\theta$, respectively. Since the intensity of the ESR line is expressed as the product of the transition probability and the population difference between the states connected by the transition, the relative intensity is described by

$$I_{12} = -I_{24} = I_{13} = -I_{14} = \frac{1}{2}\sin^2 2\theta \tag{4}$$

On the other hand, if the rapid population relaxation takes place between $|2\rangle$ and $|3\rangle$, the populations of $|2\rangle$ and $|3\rangle$ are equalized, and the intensities of the four transition lines are given by [5]

$$I_{12} = -I_{24} = \frac{1}{2}\sin^2\theta \tag{5a}$$

$$I_{13} = -I_{14} = \frac{1}{2}\cos^2\theta \tag{5b}$$

We calculated the ESR spectra according to the two models mentioned above: no relaxation and rapid relaxation models. The reported hyperfine coupling constants ($a_N = 0.880$ mT, a_p(2) = 0.428 mT, a_o(4) = 0.368 mT, a_m(4) = 0.152 mT) of the DPA radical were used for the simulation.[13] Further, each resonance line is assumed Lorentzian. In the no-relaxation model, the calculated spectrum is entirely different from the observed one whatever the parameters used (Figure 2a). In contrast to this, the calculated spectrum in the relaxation model almost reproduced the spectrum observed at 700 ns (Figure 2b). The shape of the calculated spectrum does not strongly depend on either the magnitude of J or the line width. We therefore conclude that the population relaxation between $|2\rangle$ and $|3\rangle$ takes place effectively.

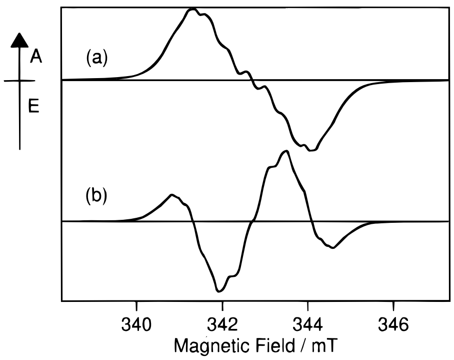
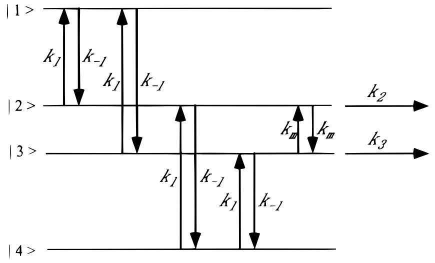


Figure 2. Simulated spectra of (a) no relaxation (b) rapid relaxation between $|2\rangle$ and $|3\rangle$. $J\hbar/g\mu_B = 0.004$ mT and the line width 0.4 mT are used.

SCHEME 1



The observed spectra in Figure 1 show the characteristic time dependence. For the discussion of the time dependence of the observed spectra, a simple kinetic model shown in Scheme 1 was used. The kinetic equations are

$$\frac{\mathrm{d}P_1}{\mathrm{d}t} = k_l(P_2 + P_3) - 2k_{-l}P_1 \tag{6a}$$

$$\frac{\mathrm{d}P_2}{\mathrm{d}t} = -(k_m + k_2 + k_l + k_{-l})P_2 + k_mP_3 + k_{-l}P_1 + k_lP_4 \tag{6b}$$

$$\frac{\mathrm{d}P_3}{\mathrm{d}t} = -(k_m + k_3 + k_l + k_{-l})P_3 + k_mP_2 + k_{-l}P_1 + k_lP_4 \tag{6c}$$

$$\frac{\mathrm{d}P_4}{\mathrm{d}t} = k_{-l}(P_2 + P_3) - 2k_lP_4 \tag{6d}$$

$$k_2 = k_r \cos^2\theta \tag{7a}$$

$$k_3 = k_r \sin^2\theta \tag{7b}$$

$$T_m = \frac{1}{2k_m} \tag{8a}$$

$$T_l = \frac{1}{k_l + k_{-l}} \tag{8b}$$

$$k_l = k_{-l}\exp\left(-\frac{\omega_l\hbar}{kT}\right) \tag{9}$$

where P_i is the population of the state $|i\rangle$, k_r is the rate constant for the radical recombination from $|S\rangle$ of the radical pairs, and T_m and T_l are the population relaxation time between middle two states, $|2\rangle$ and $|3\rangle$, and between other two states, respectively. The decay rates $|2\rangle$ and $|3\rangle$ by the recombination process are represented by the product of the singlet character and the recombination rate (eq 7) under the assumption that the off-

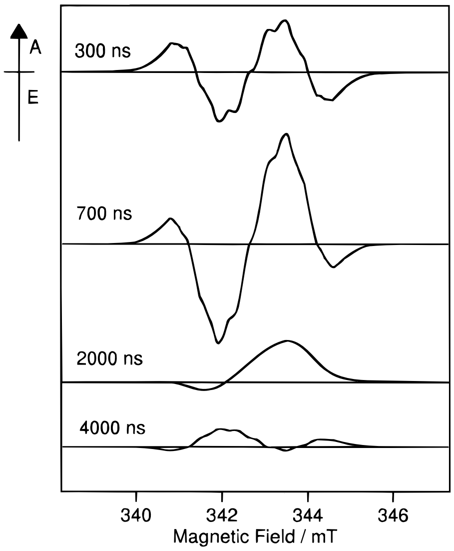


Figure 3. Simulated time-resolved ESR spectra of SCRP in consideration of the kinetic process (see the text) where $J\hbar/g\mu_B = 0.004$ mT, line width = 0.4 mT, $T_m = 0.2$ μs, $T_l = 4.5$ μs, and $k_r = 1.6 \times 10^6$ s^{-1} are used.

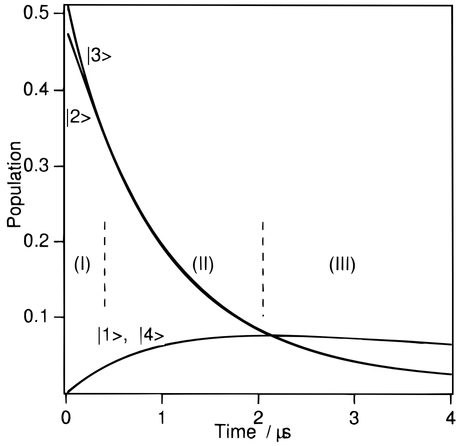


Figure 4. The calculated time dependence of the population of the states of the radical pairs by the kinetics discussed in the text where $Q\hbar/g\mu_B = 0.1$ mT, $J\hbar/g\mu_B = 0.004$ mT, $T_m = 0.2$ μs, $T_l = 4.5$ μs, and $k_r = 1.6 \times 10^6$ s^{-1} are used. At $t = 0$, the population of $|S\rangle$ is assigned to be unity.

diagonal elements of the density matrix of the states $|2\rangle$ and $|3\rangle$ are neglected. The Boltzmann distribution between $|1\rangle$ and $|2\rangle$, $|1\rangle$ and $|3\rangle$, $|2\rangle$ and $|4\rangle$, and $|3\rangle$ and $|4\rangle$ was taken into consideration (eq 9). On the other hand, the small population difference between $|2\rangle$ and $|3\rangle$ by the Boltzmann distribution is ignored. Further, the escape process of the radicals from the micelle was neglected because this process affects only the intensity of the whole SCRP spectrum and does not affect the spectral shape.

Figure 3 shows the ESR spectra calculated in this way. The calculated and the observed spectra agree with each other. Estimated values of T_m, T_l, and k_r in this simulation are 0.2 μs, 4.5 μs, and 1.6 × 10^6 s^{-1}, respectively. The magnitude of J must be very small ($J\hbar/g\mu_B = 0.004$ mT) to reproduce the absorptive component by thermal equilibrium at very late time (4 μs).

With these kinetic parameters, the behavior of the population between spin states of radical pairs can be expressed by three characteristic time regions (Figure 4). In the initial time region (I), P_2 and P_3 are different. In the second time region (II), P_2 and P_3 are almost the same due to the relaxation (T_m) between $|2\rangle$ and $|3\rangle$. In the third time region (III) P_2 and P_3 become smaller than P_1 and P_4; this leads to a spectrum like a triplet-born SCRP.

The relaxation between the middle two states of the radical pair is caused by the modulation of J, which is considered as ST dephasing (STD). It is expressed by the following super-operator in the Liouville space.[14]

$$\hat{W} = -\sum_{j=0,\pm} w(|ST_j\rangle\langle ST_j| + |T_jS\rangle\langle T_jS|) \tag{10}$$

In the micellar system w is expressed as[14]

$$w = 4\pi Dl/V \tag{11}$$

where D is the relative diffusion coefficient, V is the volume of a micelle, and l is expressed by the following equation in the strong exchange interaction case ($J_0 > D\alpha^2$).[14]

$$l = d + \alpha^{-1}\{\ln(2|J_0|/D\alpha^2) + 1.15\} \tag{12}$$

where J_0 is the maximum exchange interaction at the distance of closest approach d, and α^{-1} is the characteristic length factor in the exponential dependent exchange interaction. The population change of the states $|2\rangle$ and $|3\rangle$ by the modulation of J is formulated by the representation of $\hat{W}$ by the eigenstate of the spin Hamiltonian.

$$\begin{aligned}\frac{\partial\rho_{22}}{\partial t} &= \sum_{i,j=1-4}\langle 22|\hat{W}|ij\rangle\langle ij|\rho\rangle \\ &= -\frac{w}{2}\sin^2 2\theta\rho_{22} - \frac{w}{4}\sin 4\theta(\rho_{23} + \rho_{32}) + \\ &\qquad \frac{w}{2}\sin^2 2\theta\rho_{33} \qquad (13a)\end{aligned}$$

$$\frac{\partial\rho_{33}}{\partial t} = \frac{w}{2}\sin^2 2\theta\rho_{22} + \frac{w}{4}\sin 4\theta(\rho_{23} + \rho_{32}) - \frac{w}{2}\sin^2 2\theta\rho_{33} \tag{13b}$$

These equations indicate that the STD causes the population relaxation between $|2\rangle$ and $|3\rangle$. In eq 13a,b the second term has the far smaller influence than the other term, because the density matrix elements ρ_{23} and ρ_{32} oscillate with the angular frequency Ω. Therefore, in eq 6b,c the k_m value is represented by

$$k_m \approx \frac{w}{2}\sin^2 2\theta \tag{14}$$

For the reasonable values $d = 5 \times 10^{-10}$ m, $J_0 = 1 \times 10^{11}$ s^{-1}, $D = 5 \times 10^{-11}$ m^2 s^{-1}, $\alpha = 2 \times 10^{10}$ m^{-1}, $V = 2 \times 10^{-26}$ m^3, we obtain $k_m = 1 \times 10^7$ s^{-1}. This magnitude is comparable to the experimental result ($k_m = 2.5 \times 10^6$ s^{-1}). Therefore, we concluded that the modulation of the exchange interaction is the main cause of the population relaxation between $|2\rangle$ and $|3\rangle$.

Conclusion

In this study we demonstrate the singlet-born SCRP. The observed spectrum is reproduced by the simple kinetic model giving consideration to the recombination process, the relaxation between all states of the radical pairs. The time dependence of the spin states of the radical pairs can be clearly discussed by the singlet-born SCRP. We conclude that the driving force causing the relaxation between the middle two states of the radical pairs is the modulation of the exchange interaction.

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