TIME-RESOLVED ESR STUDY OF QUASI-STABLE SPIN CORRELATED RADICAL PAIRS IN SDS MICELLAR SYSTEMS

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Abstract—Time-resolved ESR signals of quasi-stable spin correlated radical pairs were observed in the laser flash photolysis of xanthone and phenol derivatives in SDS micellar solutions. It was concluded that the fast population relaxation between two eigenstates of $S$ and $T_0$ occurs and the interaction of the spin correlated radical pair is preserved for a few $\mu$s in the micellar aggregate.

INTRODUCTION

The time-resolved ESR (TR ESR) technique is one of the most useful ways to study magnetic interactions of transient paramagnetic species and much information about the initial stage of their reactions can be directly obtained. This technique is especially adequate for the observation of spin polarization in the excited molecules and/or the radicals formed by chemical reaction. CIDEP (Chemically Induced Dynamic Electron Polarization) is the non-equilibrium spin polarization which is induced by the excited triplet molecule and the interactions of the radical pairs; it has been the subject of numerous theoretical and experimental studies to date [1].

In 1984, Sakaguchi et al. [2] have reported a TR ESR study on the hydrogen abstraction reactions in SDS micellar solutions, which showed the magnetic field effect on the reaction rate. They detected the TR ESR spectrum with hyperfine lines having alternating phases during the early period of the reaction, which changes into the CIDEP spectrum of the free radicals after a few $\mu$s. Later Closs et al. [3] and Buckley et al. [4] independently have shown that the spectrum could be explained by the spin exchange interaction between two paramagnetic species, namely the observation of a spin correlated radical pair (SCRPs). SCRP have been observed in such restrained environments as micelles [2,3], methylene-linked biradicals [5], and highly viscous liquids [4]. As for the methylene-linked system, Terazima et al. have succeeded in the simulation of a TR ESR spectrum assuming the fast population relaxation between the eigenstates formed by the mixing of the $S$ and $T_0$ of the SCRP, while the ordinary theory of SCRP could not reproduce the observed spectrum [5].
In the present paper, the SCRP s of the xanthone ketyl and the phenoxy radical produced in the micellar aggregates are reported. They last for a few µs without changing the spectral shape. The spectral simulations of these SCRP s lead to the conclusion that fast population relaxation between two mixed states (S and T₀) occurs in these micellar systems.

EXPERIMENTAL

Xanthone (Xn), 2,6-di-tert-butylphenol (DTBP), 2,6-di-tert-butyl-p-cresol (DTBC, 2,6-di-tert-butyl-4-methylphenol), and 3,5-di-tert-butylphenol supplied by Wako Pure Chemical Industries were purified by recrystallization. Biological grade sodium dodecyl sulfate (SDS) was used as the surfactant for the micellar solutions. Throughout these experiments, the concentration of SDS was kept at 1.0 x 10⁻¹ mol dm⁻³, and those of Xn and phenol derivatives were 2.0 x 10⁻³ mol dm⁻³, respectively. Since the CMC of the SDS micelle is 8.9 x 10⁻³ mol dm⁻³ and its aggregation number is 62 [6], each micelle contains one or two phenol and Xn molecules under this condition. Measurements were carried out using an X-band ESR spectrometer modified for the time-resolved experiments (time-resolution was about 60 ns) with no magnetic field modulation [7]. A boxcar integrator system was used to observe the spectra of the spin polarized transient paramagnetic species. The spectral simulations were performed by a microcomputer system (32 bit EPSON PC-386). An excimer laser (LAMBDA PHYSIK LPX 105, XeCl, λ=308 nm) of 100 mJ output per pulse was used as the excitation source. The sample solutions were deoxygenated by bubbling with pure nitrogen gas and flowed constantly (10 mL/min) through a flat cell of 0.3 mm light path installed in the TE₀₁₁ ESR cavity. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the TR ESR spectra observed in the laser flash photolysis of the system of Xn and DTBP included in the SDS micelle. According to the ordinary mechanism of photochemical reaction, this reaction in a micelle may be expressed as follows:

\[
Xn + hν \longrightarrow ^1Xn^* \quad (1)
\]

\[
^1Xn^* \longrightarrow ^3Xn^* \quad (2)
\]

\[
^3Xn^* + DTBP \longrightarrow ^*XnH + ^*DTBP \quad (3)
\]

where the asterisk denotes the respective excited state, and ^*XnH and ^*DTBP are the xanthone ketyl and di-tert-butylphenoxy radicals respectively. However, the ordinary TR ESR spectra of ^*XnH and ^*DTBP were not observed in the present system.

The anomalous spectra with alternating hyperfine lines shown in this figure can be explained, not by ordinary CIDEP polarization, but by the SCRP polarization [2-5]. The spectral shape did not change after a few µs in the present case, while the shape altered