

# Observation and reaction control of a singlet-born radical pair formed photochemically in an SDS micelle

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A singlet-born radical pair formed in the photo-dissociation of tetraphenylhydrazine in SDS micellar solution is studied using an X-band time-resolved (tr-) EPR and a transient absorption detected magnetic resonance (ADMR) methods. The tr-EPR observation shows the fast spin relaxation between two middle states of the radical pair by the singlet-triplet dephasing. The ADMR method is more reliable for the determination of the kinetics data. The employment of short duration microwave-pulse clearly controlled the reaction of these radical pairs and the kinetic rate constants are determined. Furthermore, the changing of the microwave duration showed the quantum beats.

## Introduction

Radical pair dynamics in a supercage attracts the interest of many photo- and spin-chemists because of their spin selective reactivity and controllable nature by external magnetic field and electromagnetic field. Several reports of the triplet born cases exist, but those of the singlet born case are quite few except for the reports of the radical-ion pair systems.<sup>1-6)</sup>

In this review, a singlet-born radical pair formed photochemically in SDS micellar solution is studied using an X-band time-resolved (tr-) EPR and a transient absorption detected magnetic resonance (ADMR) methods. This system is the fast photo-dissociation<sup>7, 8)</sup> of tetraphenylhydrazine (TPH) *via* the singlet excited state. As for the TPH system, several observations of the photolysis and radiolysis using optical and EPR methods have been reported.<sup>9-12)</sup> The tr-EPR observation of this system showed a dramatic time evolution of the CIDEP (chemically induced dynamic electron polarization) spectral pattern.<sup>13, 14)</sup> The data proved the fast spin relaxation between two middle states composed of the singlet (S) and triplet ( $T_0$ ) states. This relaxation was rationalized by the singlet-triplet dephasing induced mainly by the modulation of the fluctuated exchange interaction. Although this observation of the CIDEP time-evolution also provided the estimate of the recombination reaction rate and spin-lattice relaxation time, the accuracy of these quantitative data obtained from the spin polarization seemed to be questionable. A reaction yield detected magnetic resonance (RYDMR) method is the observation technique of the chemical reaction yield which involves radical pairs and is one of the excellent ways to solve this problem. We employed a transient optical absorption detected magnetic resonance (ADMR) method, which provided the information of the concentration controlling of a radical pair as the intermediate species by microwave radiation under EPR conditions. In fact, the employment of a short duration microwave pulse ( $\pi$ -pulse) controlled the reaction of the RP, and the reaction rate constant from the singlet state and the spin-lattice relaxation time of this system were determined. Furthermore,

the changing of the microwave duration shows the quantum beat of this system induced by the electromagnetic field.

## Experimental

The concentration of SDS in aqueous media was 0.10 mol dm<sup>-3</sup>, and that of TPH was 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>. The sample was deoxygenated by bubbling with nitrogen gas and flowed through a quartz cell for tr-EPR and a quartz tube connected with optical fibers for the transient absorption measurement. All the experiments were carried out at room temperature. The response time of the microwave switching was 6 ns or better in case of ADMR observation and the microwave field,  $B_1$ , was controlled up to 3.25 mT using TWT amplifier. The tr-EPR and ADMR experiments were carried out using a pulsed excimer laser ( $\lambda = 308$  nm) for an excitation. The transient absorption band at around 700 nm was assigned to diphenylaminy radical (DPA) in an SDS micelle environment,<sup>15)</sup> and the wavelength of 690 nm was monitored using a monochromator.<sup>16-18)</sup>

## Time-resolved EPR observation

Figure 1 shows typical tr-EPR spectra observed in this system. From this figure, it is obvious that immediately after laser photolysis the spectrum of the spin correlated radical pair is A/E pattern that is reproduced by the calculation of a singlet precursor SCRIP using a theoretical model without spin relaxation between two middle states. At the stage of 300 ns after photolysis the spectral shape becomes A/E/A/E-like pattern that is explained by the spin relaxation of the two middle states. The singlet-triplet dephasing (STD) model tentatively explains the relaxation between two middle states where the distance fluctuation between two radicals in the pair induces the dephasing. This STD works as spin-lattice relaxation between the two states as the result. At later time ( $\sim 4$   $\mu$ s) the spectrum changed to the triplet precursor-like pattern of E/A/E/A with slight absorptive distortion (not shown here). This spectral pattern change is reasonably explained and reproduced by thermal relaxation of all

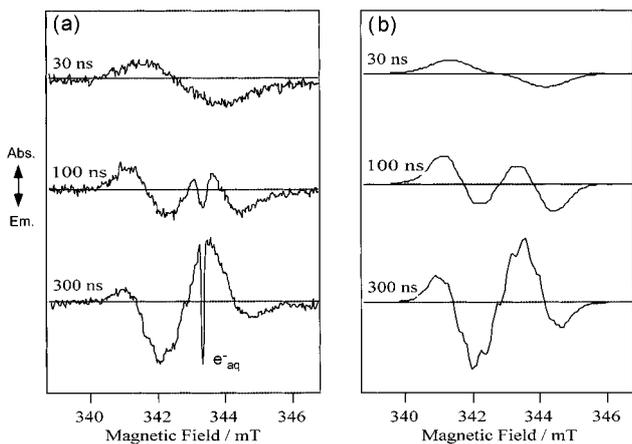


Fig. 1. (a) Tr-EPR spectra observed after laser excitation of TPH in an SDS micelle at room temperature. (b) Simulated tr-EPR spectra of the radical pair in consideration of the kinetic process (see text).

the spin states and the fast recombination reaction from the two middle states. According to these tr-EPR spectra and the calculation of the modified Liouville equation with exponential model provided the several parameters of the kinetics. The recombination rate ( $k_{\text{rec}}$ ), the spin-lattice relaxation time ( $T_1 = k_{\text{rlx}}^{-1}$ ), and the singlet-triplet dephasing time ( $T_m$ ) were estimated to be  $2 \times 10^{-6} \text{ s}^{-1}$ ,  $4.5 \mu\text{s}$ , and  $50 \text{ ns}$ , respectively. In this tr-EPR work, we investigated the spin polarization change by time, but there were many different causes of the spin polarization and the value of the exchange interaction used was rather arbitrary. To estimate more accurate kinetic parameters, measurement of the spin polarization ( $\alpha$  spin -  $\beta$  spin) is not always reliable and we need the observation of the concentration of the radical pair ( $\alpha$  spin +  $\beta$  spin) instead of the spin polarization.

#### ADMR observation

Figure 2(a) shows the timing chart of the present observation. Figure 2(b) shows the signal difference between MW-on and MW-off where  $t_1$  and  $\tau_{\text{mw}}$  were fixed to be  $100 \text{ ns}$  and  $12 \text{ ns}$ , respectively. The observation of the absorbance difference after delay of  $t_2$ ; namely, the subtraction of MW-on and MW-off absorbance is proportional to the population difference of the middle two states ( $S-T_0$  mixed states) and the outer two states ( $T_{+1}$  and  $T_{-1}$ ) at the stage of the MW irradiation.<sup>18)</sup> (1) For the observation of the ADMR spectrum, the observation window of  $500 \text{ ns}$  was opened for data acquisition where  $t_1$  and  $t_2$  were fixed to be  $100 \text{ ns}$  and  $500 \text{ ns}$ , respectively. The ADMR spectrum is well explained by the distribution of the hyperfine structure of the DPA radical as shown in Fig. 3. (2) The observation of the quantum beats by the microwave field was performed to determine the spin flip angle of the radical pair. The times of  $t_1$  and  $t_2$  were fixed and  $\tau_{\text{mw}}$  was incrementally changed. According to the observed beat signal (not shown here) we could estimate the approximate  $B_1$  value employing calculation of a modified Liouville equation<sup>14,18)</sup> with an exponential model that reproduced the beats. In these data, two kinds of beat signals appeared, a single frequency beat, which corresponded to the Rabi frequency, and a double frequency beat which was due to a simultaneous excitation of two spins in a radical pair.<sup>17,18)</sup> To determine the kinetic parameters of the recombination reaction rate from the middle two spin states

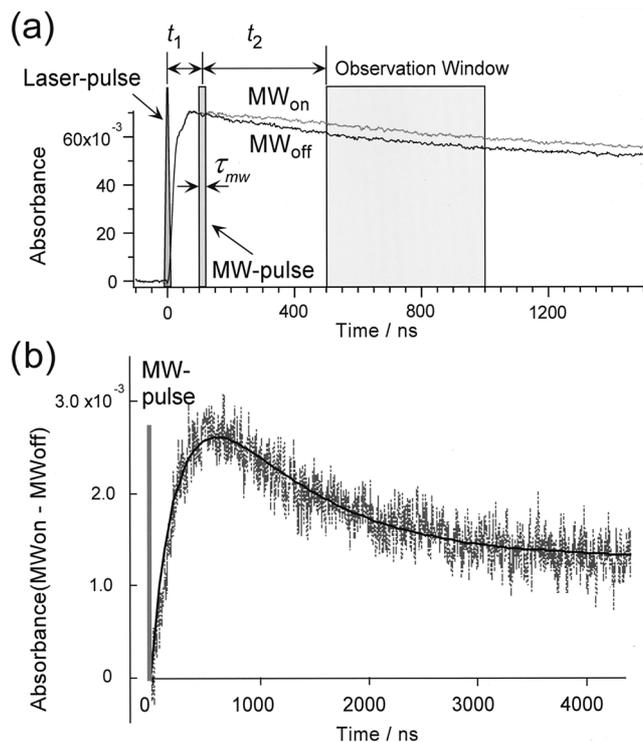


Fig. 2. (a) A timing chart of the ADMR observations (see text) where  $t_1$ ,  $t_2$ , and  $\tau_{\text{mw}}$  are initial delay of the MW-pulse after laser photolysis, second-order polarization developing period, and MW-pulse duration, respectively. The absorbance values during the observation window of MW-on and MW-off are time-integrated and subtracted as Absorbance ( $\text{MW}_{\text{on}} - \text{MW}_{\text{off}}$ ). (b) Time-evolution of the absorbance difference of MW-on and MW-off after  $\pi$ -pulse of  $12 \text{ ns}$  under  $B_1$  field of  $1.4 \text{ mT}$ . The solid line shows the best fitting of the simulated kinetic curve.

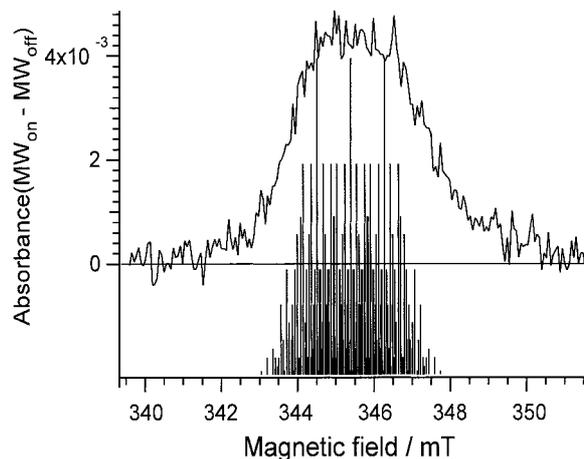


Fig. 3. ADMR spectrum observed using  $\tau_{\text{mw}}$  and  $B_1$  values given in Fig. 2(b). The stick spectrum is the simulated one using reported hyperfine coupling constants of the DPA radical.

( $k_{\text{rec}}$ ) and the spin-lattice relaxation time ( $T_1 = k_{\text{rlx}}^{-1}$ ), two kinds of the observation methods were carried out as follows: (3) The observation of the pulse shift dependence where  $t_2$  and  $\tau_{\text{mw}}$  were fixed and  $t_1$  was changed incrementally (not shown here). Here the  $\pi$ -MW pulse works as a flash lamp

to take a snapshot of the population difference. The population difference gradually decreases and its sign is inverted at about 600 ns after photolysis. In the calculation of the modified Liouville equation the reaction rate of  $k_{\text{rec}} = 5 \times 10^6 \text{ s}^{-1}$  and the relaxation time of  $T_1 = 1.0 \mu\text{s}$  were determined.<sup>15)</sup> These values are different from those estimated by the CIDEP data mentioned above.<sup>13, 14)</sup> The parameters obtained by the present RYDMR time-evolution experiment is more reliable, because this gives the information of a direct concentration change by time and not the spin polarization. (4) To confirm and to get more information about this RP in a micelle, the observation of the time evolution of the absorbance difference after a single MW-pulse was done as mentioned above (Fig. 2 (b)). The solid line drawn in Fig. 2 (b) is the best fitting of the above mentioned model and the rate constants estimated by this way are  $k_{\text{rec}} = 5.1 \times 10^6 \text{ s}^{-1}$ ,  $k_{\text{rlx}} = 6.7 \times 10^5 \text{ s}^{-1}$  ( $T_1 = 1.5 \mu\text{s}$ ) and the escape rate of  $k_{\text{esc}} = 3.5 \times 10^5 \text{ s}^{-1}$ . The values of  $k_{\text{rec}}$  and  $T_1$  are nearly identical to those estimated by the pulse shift method. The slow recombination rate of this singlet-born radical pair system make the present ADMR observation possible and the slow rate may be due to rather linear structure of DPA radical after dissociation of TPH where DPA group is bent.<sup>11)</sup>

#### References

- 1) S. N. Batchelor, K. A. McLauchlan, and I. A. Shkrob: *Chem. Phys. Lett.* **181**, 327 (1990).
- 2) S. N. Batchelor, K. A. McLauchlan, and I. A. Shkrob: *Mol. Phys.* **75**, 501 (1992).
- 3) K. Enjo, K. Maeda, H. Murai, and T. Azumi: *Appl. Magn. Reson.* **12**, 423 (1997).
- 4) K. Enjo, K. Maeda, H. Murai, and T. Azumi: *J. Phys. Chem. B* **101**, 10661 (1997).
- 5) Y. Iwasaki, H. Murai, K. Maeda, and T. Azumi: *Chem. Phys.* **230**, 201 (1998).
- 6) T. Itoh, A. Matsuyama, K. Maeda, and H. Murai: *Chem. Phys. Lett.* **333**, 242 (2001).
- 7) R. W. Anderson and R. M. Hochstrasser Jr.: *J. Phys. Chem.* **80**, 2155 (1976).
- 8) M. G. Hyde and G. S. Baddard: *Chem. Phys.* **151**, 239 (1991).
- 9) G. N. Lewis and D. Lipkin: *J. Am. Chem. Soc.* **64**, 2801 (1942).
- 10) T. Shida and A. Kira: *J. Phys. Chem.* **73**, 4315 (1969).
- 11) D. A. Wiersma, J. H. Lichtenbelt, and J. Kommandeur: *J. Chem. Phys.* **50**, 2794 (1969).
- 12) K. Matsuda, H. Murai, and Y. J. I'Haya: *Chem. Phys. Lett.* **125**, 577 (1986).
- 13) T. Fukuju, H. Yashiro, K. Maeda, H. Murai, and T. Azumi: *J. Phys. Chem. A* **101**, 7783 (1997).
- 14) T. Fukuju, H. Yashiro, K. Maeda, and H. Murai: *Chem. Phys. Lett.* **304**, 173 (1999).
- 15) A. Kageyama, H. Yashiro, and H. Murai: *Mol. Phys.* in press.
- 16) K. Maeda, Y. Araki, Y. Kamata, K. Enjo, H. Murai, and T. Azumi: *Chem. Phys. Lett.* **262**, 110 (1996).
- 17) Y. Araki, K. Maeda, and H. Murai: *Chem. Phys. Lett.* **332**, 515 (2000).
- 18) V. R. Gorelik, K. Maeda, H. Yashiro, and H. Murai: *J. Phys. Chem. A* **105**, 8011 (2001).