# Magnetic Field Effect on the Hydrogen Abstraction Reaction of Xanthone in Sodium **Dodecyl Sulfate Micellar Solution**

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The magnetic field effect on the hydrogen abstraction of xanthone from xanthene, 9,10-dihydroanthracene, and sodium dodecyl sulfate (SDS) surfactant has been studied in SDS micellar solution by steady-state (<260 mT) and laser flash photolysis (≤80 mT). In the steady-state photolysis, the relative quantum yield of the disappearance of xanthone decreases in the magnetic field. Transient absorption intensities of 9-xanthenyl and 9,10-dihydroanthracen-9-yl radicals in the laser flash photolysis show remarkable magnetic field dependence, when xanthene and 9,10-dihydroanthracene are used as the respective hydrogen donors. All the results are interpreted in terms of the radical-pair model.

The magnetic field effect on chemical reactions has been studied by many photochemists because of its wide applicability for controlling various reaction rates and yields.<sup>1-5,8</sup> As for the radical reaction in the condensed phase, the effect is usually interpreted in terms of the radical-pair model of CIDNP,<sup>6,7</sup> where the triplet-singlet intersystem crossing (isc) of the radical-pair intermediate occurs via electron-nuclear hyperfine interaction and is influenced by the external magnetic field. In homogeneous fluid solution such as ethanol, the magnetic field effect is rather small because of the fast escape rate of the component radicals from the solvent cage. On the other hand, it is quite significant in micellar solution, since a micelle cage increases the lifetime of the radical-pair intermediate.1b

In previous works, we studied the magnetic field effect on the hydrogen abstraction reaction of benzoquinones<sup>2,3</sup> and anthraquinones<sup>4,5</sup> from the sodium dodecyl sulfate (SDS) surfactant which composes the micelle, by steady-state and laser flash photolysis. Since a SDS surfactant molecule plays not only a role as a component of the micelle but also as a hydrogen donor in these cases, it is uncertain whether the magnetic field effect can generally appear in the hydrogen abstraction of carbonyls from various hydrogen donors or not. Furthermore, in the laser flash photolysis, the effect has been studied only for the radicals generated from the hydrogen acceptors (carbonyls) and no study has been reported for the counter radicals generated from the hydrogen donors. In the present paper, we report the photoinduced hydrogen abstraction of xanthone from xanthene and 9,10-dihydroanthracene in SDS micellar solution studied by steady-state and laser flash photolysis.<sup>8</sup> The relative quantum yield of the disappearance of xanthone by steady-state photolysis was observed to decrease in the presence of magnetic fields. In laser flash photolysis, radical intermediates generated from the hydrogen donors were observed to show a remarkable magnetic field effect. The results were interpreted in terms of the radical-pair model of CIDNP.

#### **Experimental Section**

Materials. Xanthone, xanthene, and 9,10-dihydroanthracene were recrystallized from ethanol. The purest grade of sodium dodecyl sulfate (SDS, Nakarai Chemicals) was used as received. Water was distilled and deionized.

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All the solutions were deaerated by passing through nitrogen gas

Steady-State Photolysis. (a) Relative Quantum Yield of the Disappearance of Xanthone. Typical procedures are as follows: 3 mL of SDS micellar solution in a 1-cm quartz cell at the center of an electromagnet was illuminated with a 500-W xenon arc lamp (Ushio, UXL-500-O) equipped with a Pyrex glass filter and a 10-cm water filter (>300 nm). The UV absorption spectra were measured with a Hitachi 124 spectrophotometer.

The relative quantum yield,  $\Phi$ , of the disappearance of xanthone was determined from the UV-spectral change:9

$$\ln A - \ln A_0 = -\Phi t \tag{1}$$

where  $A_0$  and A are the absorbances of xanthone at t = 0 and t, respectively. The absorption intensities at 340 nm were used for analysis.

(b) Product Yield. Relative yields of photoproducts of the SDS micellar solution containing xanthone and xanthene were determined with a Jasco Tri Rotor III high-pressure liquid chromatograph (HPLC) equipped with a UV detector. Products were identified by comparing their retention times with those of authentic samples synthesized.<sup>10</sup>

Laser Flash Photolysis. A Molectron UV-12 N<sub>2</sub> laser (337) nm, pulse width  $\sim 10$  ns) a USSI 3CP-3 xenon flash lamp (pulse width  $\sim 40 \ \mu s$ ) were used as an exciting light source and as an analyzing light source, respectively. The transient signals were detected by a monochromator-photomultiplier-oscilloscope system. The details were published elsewhere.<sup>3</sup>

#### **Results and Discussion**

Based on the analogy of the reaction scheme in the hydrogen abstraction reaction of benzoquinones<sup>2,3</sup> and anthraquinones<sup>4,5</sup> in SDS micellar solution, a reaction mechanism for the photolysis of xanthone in SDS micellar solution is shown in Scheme I. The

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Figure 1. The magnetic field effect on the UV-spectral change of the photolysis of  $1 \times 10^{-4}$  M xanthone and  $1 \times 10^{-3}$  M xanthene in 0.4 M SDS micellar solution: (A) in the absence of a magnetic field (broken line is a background); (B) in the presence of a magnetic field (180 mT); (C) plots of eq 1 for the absorbances at 340 nm of (A) and (B).

excited triplet state of xanthone ( ${}^{3}XO$ ) abstracts a hydrogen atom from a hydrogen donor (HD) to form a triplet pair ( ${}^{3}XOH \cdot D$ ) composed of a xanthone ketyl radical (XOH·) and a radical ( $\cdot D$ ) generated from the hydrogen donor. From the triplet pair, the isc to the singlet pair ( ${}^{1}XOH \cdot D$ ) and the escape of component radicals from the micellar cage take place competitively. The cage recombination reaction occurs via the singlet pair, while escape radicals may undergo recombination or further reactions.

According to the radical-pair model of CIDNP,<sup>6,7</sup> the triplet-singlet isc of a radical pair occurs by electron-nuclear hyperfine interaction. At zero field, all triplet sublevels are degenerate with the singlet state, and hence the isc from all triplet sublevels to the singlet state occurs. In a relatively weak magnetic field, the isc is reduced because of the Zeeman splitting of triplet sublevels, as reported in previous papers.<sup>2–5</sup>

Steady-State Photolysis. (a) Relative Quantum Yield of the Disappearance of Xanthone. Figure 1A shows a typical UVspectral change during the photolysis of the SDS micellar solution of xanthone and xanthene. Upon irradiation, the intensity of a 340-nm band due to xanthone gradually decreases. A similar spectral change was observed in the photolysis of the SDS micellar solution of xanthone and 9,10-dihydroanthracene. Although the fading of the 340-nm band was observed in the micellar solution of xanthone alone, its rate is 1 order of magnitude slower than those of formers. These spectral changes suggest that the hydrogen abstraction reaction of xanthone from hydrogen-donating additives or SDS surfactant takes place in the solution. Actually, on the photolysis of the micellar solution of xanthone and xanthene, the adduct of xanthene to xanthone, xanthone dimer, and xanthene dimer were obtained as photoproducts (see below). Figure 1B shows the magnetic field effect on the spectral change of the SDS micellar solution of xanthone and xanthene on the photolysis. The fading rate of the 340-nm band is reduced significantly. From the plots of eq 1 shown in Figure 1C, it is shown that the relative quantum yield,  $\Phi$ , of the disappearance of xanthone is reduced by about 25% in the presence of a magnetic field (180 mT). The magnetic field effect on  $\Phi$  of xanthone for 9,10-dihydroanthracene and SDS surfactant was similarly analyzed. Figure 2 shows the magnetic field dependence of  $\Phi$  of xanthone for three hydrogen donors mentioned above. Here, we define the change of the yield, Q(H), at the magnetic field, H, as follows:

$$Q(H) = \left[ (\Phi(H) - \Phi(0)) / \Phi(0) \right] \times 100$$
 (2)

where  $\Phi(0)$  and  $\Phi(H)$  are the yields in the absence and presence of a magnetic field, respectively. The Q values for xanthene, 9,10-dihydroanthracene, and SDS surfactant are 25%, 25%, and 40%, respectively, at 260 mT.

According to Scheme I, there are two competing processes from the triplet radical pair. One of them is the isc to the singlet radical pair followed by the cage reaction. Another is the escape of component radicals from the pair, followed by the free-radical reactions. The former is responsible for the irreversible loss of



Figure 2. Magnetic field dependence of the change, Q(H), of the relative quantum yield of the disappearance of xanthone.



Figure 3. High-pressure liquid chromatograms of the photolyzed 0.4 M SDS micellar solution of  $1.2 \times 10^{-3}$  M xanthone and  $3.0 \times 10^{-3}$  M xanthone (A) in the absence of a magnetic field and (B) in the presence of a magnetic field (180 mT).

xanthone, while the latter partly regenerates xanthone. Since the triplet-singlet isc rate is reduced in the presence of a magnetic field, the free-radical yield (therefore, the yield of regeneration of xanthone) mostly increases. In other words, the relative quantum yield of the disappearance of xanthone decreases in the magnetic field. Actually, according to the scheme, Q(H) is shown to be proportional to the difference of the quantum yield of triplet-singlet isc rate,  $\phi_{\rm isc}(H) - \phi_{\rm isc}(0)$ , where  $\phi_{\rm isc} = k_{\rm isc}/(k_{\rm isc} + k_{\rm es})$ . Thus, the magnetic field dependence shown in Figure 2 is the reflection of that of  $\phi_{\rm isc}$ . Since the escape rate constant,  $k_{\rm es}$ , is mostly magnetic field independent, the field dependence of Q is attributable to that of  $k_{\rm isc}$ , as expected from the radical-pair model.

(b) Product Yield. The magnetic field effect on the photoproduct yields as well as the loss of xanthone was examined for the SDS micellar solution of xanthone and xanthene. Figure 3A shows a typical HPLC chart of the photolyzed solution. The products were identified to the adduct of xanthene to xanthone, xanthone dimer, and xanthene dimer as described in the Experimental Section. Figure 3B shows the effect of the magnetic field (180 mT) on these product yields. In the presence of a magnetic field (180 mT), the recovery of xanthone and xanthene slightly increases (10%), while the yield of the photoadduct decreases (-10%). Further, it is noteworthy that the yields of xanthone and



Figure 4. Transient absorption spectra following laser excitation of the 0.4 M SDS micellar solution of  $5 \times 10^{-5}$  M xanthone and  $1 \times 10^{-3}$  M xanthone: ( $\Box$ ) in the absence of xanthene, at 125-ns delay; ( $\odot$ ) in the presence of xanthene, at 125-ns delay; ( $\odot$ ) in the presence of xanthene, at 2-µs delay.

TABLE I: The Decay Rates (s<sup>-1</sup>) of the T-T Absorption of  $5 \times 10^{-5}$  M Xanthone at 610 nm with  $3 \times 10^{-3}$  M Hydrogen Donors in 0.4 M SDS Micellar Solution

none	xanthene	9,10-dihydroanthracene
	$2.5 \times 10^{7}$	$4.6 \times 10^{6}$
$1.7 \times 10^{5}$	$6.7 \times 10^{5 a}$	$6.2 \times 10^{5 a}$

<sup>a</sup>This decay may be attributed to xanthone in the hydrogen donor free micelle, which may be quenched by the intermicellar processes.

xanthene dimers significantly increase (400%). The photoadduct is mostly generated via cage reaction, while the dimers are generated as free-radical products. According to Scheme I, the external magnetic field causes (1) the decrease of the reactants recovery, (2) the decrease of the yield of the cage product (the photoadduct), and (3) the increase of the yields of the free-radical products (dimers). As for (1) and (2), the changes shown in Figure 3 seem to be in parallel with the above prediction, though they are almost within experimental error. However, the increase of the yields of dimers is very significant and entirely consistent with the scheme. Furthermore, this magnetic field induced increase of the dimers is also consistent with the transient absorption measurements as will be mentioned later, where the magnetic field induces the increase of the escape free radicals leading to the formation of the dimers. Thus, the magnetic field induced increase of the dimers is good evidence that the triplet-singlet isc rate is reduced in the magnetic field.

Laser Flash Photolysis. Transient absorption measurements can provide the unequivocal answer for the mechanism of the magnetic field effect on the present reaction. Figure 4 shows the transient absorption spectra of xanthone and xanthene in SDS micellar solution. In the absence of xanthene, the xanthone T-T absorption band appears in the 610-nm region,<sup>11</sup> whose decay exhibits a single exponential. By the addition of xanthene into the solution, a new transient band exhibiting a rise appears at 345 nm, which is assigned to the 9-xanthenyl radical.<sup>12</sup> Further, the decay of T-T absorption of xanthone becomes nonexponential, including a fast decay component. Since the rise rate  $(2.8 \times 10^7)$ s<sup>-1</sup>) of the transient absorption of 9-xanthenyl radical agrees with the decay rate  $(2.5 \times 10^7 \text{ s}^{-1})$  of the fast decay component of xanthone T-T absorption, the 9-xanthenyl radical seems to be generated by the hydrogen abstraction of the excited triplet state of xanthone from xanthene. In the present reaction mechanism, the transient absorption due to xanthone ketyl radical is expected in the 480-nm region.<sup>11</sup> However, it was not observed at the

TABLE II: Magnetic Field Effect on the Decay of Transients (s<sup>-1</sup>)

	9-xanthenyl		9,10-dihydro- anthracen-9-yl	
	0 mT	80 mT	0 mT	80 mT
$k_{rise}$	$2.8 \times 10^{7}$	$2.8 \times 10^{7}$	5.9 × 10 <sup>6</sup>	$6.2 \times 10^{6}$
$k_{\rm f}$	$1.7 \times 10^{6}$	a 2.8 × 10 <sup>5</sup>	$3.3 \times 10^{6}$	a 5.0 × 10 <sup>5</sup>

 $^{a}$  Too weak for the analysis.  $^{b}$  These values were assumed. See text for discussion.



Figure 5. Oscillograms of the transients at 345 nm in the photolysis of the SDS micellar solution of xanthone and xanthene (A) in the absence of a magnetic field and (B) in the presence of a magnetic field (80 mT).



Figure 6. Oscillograms of the transients at 332 nm in the photolysis of the SDS micellar solution of xanthone and 9,10-dihydroanthracene (A) in the absence of a magnetic field and (B) in the presence of a magnetic field (80 mT).

present stage. Probably the molar extinction coefficient of the radical might be too small.

Furthermore, the laser flash photolysis of the SDS micellar solution of xanthone and 9,10-dihydroanthracene shows a weak transient absorption band at 330 nm, which is probably attributable to the 9,10-dihydroanthracen-9-yl radical generated from the hydrogen abstraction of the excited triplet state of xanthone from 9,10-dihydroanthracene.<sup>12</sup> These kinetic parameters are shown in Tables I and II. The T-T absorption of xanthone is magnetic field independent as expected. Figures 5 and 6 show

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Figure 7. Magnetic field dependence of  $k_{\rm f}$  and  $I_{\rm f}/I_{\rm s}$ .



Figure 8. Magnetic field dependence of  $k_{isc}$  and  $k_{cs}$ .

the magnetic field effect on the transients of 9-xanthenyl and 9,10-dihydroanthracen-9-yl radical, respectively. The decay profiles were analyzed as a sum of two exponential decays:

$$I(t) = I_f \exp(-k_f t) + I_s \exp(-k_s t)$$
(3)

I(t) is the absorption intensity of the respective radical at t = t,  $k_f$  and  $k_s$  are the decay rate constants of a "fast" and "slow" component, respectively, and  $I_f$  and  $I_s$  are the respective coeffi-

cients. These parameters are also shown in Table II.

Further analysis at several magnetic fields was done for the transients due to 9-xanthenyl radical, since the transient intensity of 9,10-dihydroanthracen-9-yl radical was too weak for accurate analysis. Figure 7 shows the magnetic field dependence of  $k_f$  and  $I_f/I_s$  for 9-xanthenyl radical, calculated by assuming that  $k_s$  is magnetic field independent. With increasing magnetic field,  $k_f$  gradually decreases and  $I_f/I_s$  increases.

According to Scheme I, the time evolution of the absorption intensity, I(t), of 9-xanthenyl radical can be expressed as follows:

$$I(t) = c\{(1 + a - b) \exp(-k_{\rm f}t) + b \exp(-k_{\rm s}t)\}$$
(4)

Here, c is a constant,  $k_f = k_{isc} + k_{es}$ ,  $k_s = k_2 + k_3$ ,  $a = k_{isc}/(k_1 - k_f)$ , and  $b = k_{es}/(k_f - k_s)$ . From the intensity ratio of two decay components and the decay rate constants,  $k_f$  and  $k_s$ , we can estimate  $k_{isc}$  and  $k_{es}$ , by assuming  $k_1 \gg k_f$ . Figure 8 shows the magnetic field dependence of  $k_{isc}$  and  $k_{es}$  for the 9-xanthenyl radical. With increasing magnetic field,  $k_{isc}$  decreases from 1.4  $\times 10^6 \text{ s}^{-1}$  (0 mT) to 0.4  $\times 10^6 \text{ s}^{-1}$  (80 mT), while  $k_{es}$  is almost constant within experimental error. This is in good agreement with the expectation from the scheme.

The magnetic field effect on the reactant (steady-state photolysis), short-lived intermediate (laser flash photolysis), and photoproducts (steady-state photolysis) has been studied for the photochemical reaction of xanthone in SDS micellar solution. All the results are clearly explained by the radical-pair model, where the triplet-singlet isc of the radical-pair intermediate is reduced in a magnetic field. Furthermore, the magnetic field effect has been observed for two hydrogen donors besides SDS surfactant. The fact strongly suggests that the magnetic field effect should generally appear in the hydrogen abstraction reaction in the micellar solution.

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**Registry No.** Xanthone, 90-47-1; xanthene, 92-83-1; 9,10-dihydroanthracene, 613-31-0; SDS, 151-21-3.

# Nuclear Magnetic Resonance Study of Alkane Mixtures. <sup>2</sup>H Spin–Lattice Relaxation Times for Cyclopentane Mixed with Cyclic and Branched Alkanes of Different Molecular Shape

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Deuteron  $T_1$  relaxation times have been measured between -20 and 40 °C for cyclopentane- $d_{10}$  in the cis and trans isomers of Decalin and 1,2- and 1,4-dimethylcyclohexane and in two nonane isomers, 3,3-diethylpentane and 2,2,5-trimethylhexane. Published thermodynamic data indicate anomalously negative excess enthalpies and positive excess heat capacities on mixing cyclopentane with the trans isomers, which are of flat molecular shape, and also with 3,3-diethylpentane, whose molecules are highly sterically hindered. This was interpreted as indicating a "condensation" of the cyclopentane molecule onto the surfaces of these solvent molecules leading to a restriction of cyclopentane motion. The experimental reorientational correlation times  $\tau_c$  are different for each solvent at a given  $\eta/T$  value. The existing theories for  $\tau_c$  cannot explain the details of this behavior. Nevertheless, correlation times of cyclohexane- $d_{12}$  in several of the solvents, where  $C_p^E$  is negative and of the same magnitude for both isomers, showed that the solvent effects on  $\tau_c$  are qualitatively similar to those in the cyclopentane- $d_{10}$ case. We conclude that the NMR evidence does not support the interpretation that a perturbation of cyclopentane motion by equatorial–equatorial solvent molecules is responsible for the anomalous thermodynamic behavior of these systems.

#### Introduction

The enthalpy and heat capacity change on mixing, i.e., the excess quantities  $H^{E}$  and  $C_{p}^{E}$ , have been reported earlier for a series of cycloalkanes, from cyclopentane to cyclooctane mixed at 25 °C with the cis and trans isomers of various dimethylcyclohexanes and of Decalin,<sup>1a</sup> and with two nonane isomers, 3,3-diethylpentane

and 2,2,5-trimethylhexane.<sup>1b</sup> For cyclohexane, -heptane, and -octane,  $H^{E}$  is positive as expected for nonpolar systems. However,

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