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Magnetic Field Effects on the Primary Photoprocess of Anthrone in Micellar Solution by Laser Flash Photolysis and Two-Step Laser Excitation Fluorescence

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The magnetic field effects on hydrogen abstraction reaction of anthrone have been studied in micellar solution by laser flash photolysis and two-step laser excitation (TSLE) fluorescence. The decaytime of the anthrone ketyl radical determined by laser flash photolysis increases from 370 ns at zero field to 890 ns at 80 mT. The results are in accordance with the magnetic field effects on the risetime of the cage product by the TSLE fluorescence. All of the results are discussed in terms of the radical pair model.

Particular interest has recently been taken in the effects of magnetic field on chemical reactions.[1] This is caused by versatile applicability such as the enrichment of nuclear magnetic isotopes. Mangetic field effects on photochemical reactions in condensed phase are interpreted mainly in terms of the radical pair model, where the lifetime of radical pair determines significance of the effects. In homogeneous solution, diffusion of radicals is so fast that the lifetime of the pair is as short as 10^{-8}—10^{-9} s, and usually no significant effects are expected for the chemical reaction. In this context, aqueous micellar solution will provide an excellent environment for enhancement of chemical reaction by magnetic field. Since organic compounds are solubilized in the micellar phase of normal micelle system due to hydrophobic interaction, the radical pair generated is confined in micellar cages; this results in long lifetime of 10^{-6} s or so. Based on this reason, we have studied the effects of magnetic field on photochemical reactions in micellar solution.[2—5]

In the present paper, we report results of the effect of magnetic field on the hydrogen abstraction reaction of anthrone in micellar solution by laser flash photolysis and two-step laser excitation (TSLE) fluorescence technique. Transient absorption of the anthrone ketyl radical and the TSLE fluorescence of cage product are strongly influenced by the magnetic field ($\leqslant$ 80 mT). All of the results are discussed in terms of the radical pair model.

Experimental

Anthrone (Tokyo Kasei Co.) and sodium dodecyl sulfate (Nakarai Co., for biological use, denoted as SDS hereafter) were used as received. Distilled water was further deionized. All solutions were deaerated by flowing nitrogen for 10 min.

In the laser flash photolysis, an N_2 laser (Molectron UV-12, 337 nm) and a xenon arc lamp were used as excitation and probe light sources, respectively. Two-step laser excitation (TSLE) fluorescence was measured by means of an excimer laser (Lambda Physik EMG-50E, 308 nm) and an N_2 laser pumped dye laser (Molectron UV-12 and DL-14, 406 nm), as the first and the second laser, respectively. Timing of each laser was adjusted with a home-made delay circuit. Magnetic field was applied with a home-made Helmholtz coil ($\leqslant$ 80 mT). Details of the systems were similar to those described elsewhere.[3,6] All measurements were carried out at room temperature.

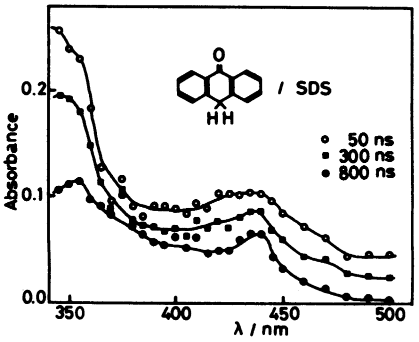
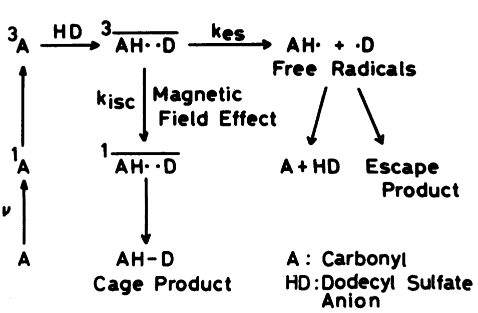


Fig. 1. Transient absorption spectra of anthrone (2×10^{-3} mol dm^{-3}) in SDS (0.4 mol dm^{-3}) micellar solution.

Results and Discussion

Transient Absorption and Mechanism. Figure 1 shows transient absorption spectra of anthrone in SDS micellar solution. The absorption band around 350 nm is assigned to the anthrone ketyl radical with reference to the literature,[7] though the spectrum at 50 ns delay is slightly shifted to shorter wavelength, because of the overlap with the short-lived triplet-triplet absorption band of anthrone. The risetime of the ketyl radical was estimated to be 40 ns. We have reported several hydrogen abstraction reactions of aromatic carbonyls in the triplet states,[2—4] whose reaction mechanism is shown in Scheme 1. By analogy with



Scheme 1. Photoreaction pathways of aromatic carbonyls in SDS micellar solution.

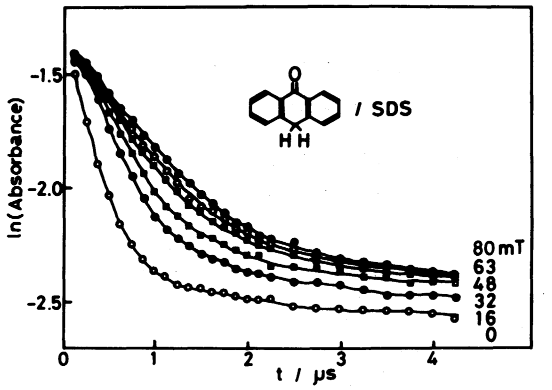


Fig. 2. Magnetic field effects on the decay of the anthrone ketyl radical at 355 nm.

the photoreactions of these carbonyls reported, the excited triplet anthrone may abstract a hydrogen atom from an SDS surfactant to yield a triplet pair between anthrone ketyl radical and dodecyl sulfate anion radical. The triplet pair disappears via two competing processes, i.e., the intersystem crossing to singlet pair followed by geminate cage reaction, and the dissociation of triplet pair into the component free radicals (escape products). The adduct of the ketyl radical with the surfactant seems responsible to the geminate cage reaction,[10] while 9-anthrol to the escape product. In a radical pair, the triplet-singlet intersystem crossing as well as relaxation within the triplet manifold occurs via electron-nuclear hyperfine interaction and these rates are decreased by applying a magnetic field because of the Zeeman splitting of the triplet sublevels.[1] Therefore, in a magnetic field, the decay rate of the triplet radical pair and also the formation rate of the cage product are expected to be reduced.

Figure 2 shows the effects of magnetic fields on the decay of ketyl radical observed at 355 nm. Without applying field, the decay of the radical appears to consist of fast and slow processes, though the decay does not proceed exponentially. In the presence of magnetic field, the decay rate of the fast process becomes slow and the apparent intensity at 4 μs delay increases. When the generation of the triplet pair and the geminate cage reaction are very fast and the decay of the ketyl radical escaped from the pair is slow enough within the time scale of microsecond, as shown in the Scheme, the absorption intensity of the ketyl radical, $I(t)$, can be expressed as follows:[2]

$$I(t) \propto I_f \exp(-k_f t) + I_s, \qquad (1)$$

where $k_f = k_{isc} + k_{es}$, $I_f = k_{isc}/(k_{isc} + k_{es})$, and $I_s = k_{es}/(k_{isc} + k_{es})$. The first and the second terms in the right side of Eq. 1 represent the concentrations of the ketyl radical in the triplet pair and in the escaped free radical, respectively. Thus, Fig. 2 indicates that the external magnetic field reduces the decay rate of the triplet pair and enhances the yield of the escaped free radical. Decay curves in Fig. 2 were analysed by Eq. 1 in order to estimate k_f (Table 1).[11] In the presence of a magnetic field (80 mT), the decay rate of triplet pair is reduced by ≈60%, as expected from the Scheme.

Table 1. Magnetic Field Effects on k_f and k_r ($10^6\,s^{-1}$)

	H/mT					
	0	16	32	48	63	80
k_f	2.7	1.8	1.6	1.3	1.2	1.1
k_r	2.6					1.4

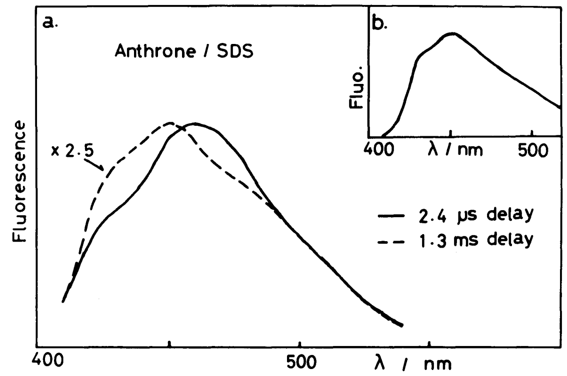


Fig. 3. (a) The TSLE fluorescence spectra of anthrone (3×10^{-4} mol dm^{-3}) in SDS (0.4 mol dm^{-3}) micellar solution. (b) Fluorescence spectrum of 9-anthrol in SDS micellar solution.

Two-Step Laser Excitation (TSLE) Fluorescence. In order to analyse the magnetic field effects on photoadduct formation, we examined the TSLE fluorescence of anthrone in SDS micellar solution; two steps consist of the initial laser excitation as the reaction light source and the following probe laser excitation. Figure 3a shows the TSLE fluorescence spectra of anthrone in the solution. The spectrum at 2.4 μs delay after the first laser excitation has a peak around 460 nm, and the peak shifts to the shorter wavelength by ≈10 nm at 1.3 ms delay. The lifetime of TSLE fluorescence seems to be composed of two decay components (3—4 and 12 ns). On the other hand, 9-anthrol, synthesized by reduction of anthrone, has a fluorescence band maximum around 450 nm (lifetime 12 ns) (Fig. 3b). Thus the TSLE fluorescence band around 450 nm, which appears at 1.3 ms delay after the first laser excitation, is attributable mainly to 9-anthrol. The TSLE fluorescence around 460 nm at 2.4 μs delay is likely to be due to the photoadduct of the anthrone ketyl radical with the SDS surfactant (a product of the geminate cage reaction). Figure 4 demonstrates the magnetic field effects on the time evolution of the TSLE fluorescence at 460 nm. The risetime $1/k_r$ was estimated to be 380 ns at zero field and 710 ns at 80 mT, k_r being the formation rate of the photoadduct. The TSLE fluorescence intensity at 6.4 μs delay decreases by ≈10% in the magnetic field (80 mT). These results imply that the rate of formation and the yield of cage product, the photoadduct, is reduced

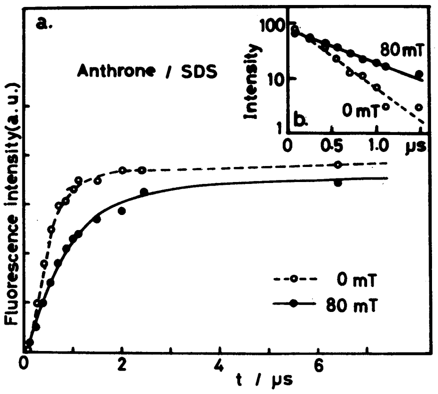


Fig. 4. (a) Magnetic field effects on the time evolution of the TSLE fluorescence at 460 nm. (b) Semilogarithmic plots of the intensities of (a), $I_\infty - I(t)$, the intensity at 5 μs delay, where it reaches plateau, being used as I_∞.

in the magnetic field.

Furthermore, the risetimes $1/k_r$ of the adduct with and without magnetic field (80 mT) determined by the TSLE fluorescence agree with the corresponding decaytimes $1/k_f$ of the anthrone ketyl radical by laser flash photolysis within experimental error (Table 1). This coincidence implies that the fast deactivation process of the triplet radical pair, composed of anthrone ketyl radical and dodecyl sulfate anion radical, is attributable to the intersystem crossing to the singlet pair followed by the fast geminate cage reaction as shown in Scheme 1. The decrease in the yield of cage product, determined by TSLE fluorescence, with concomitant increase in the escaped radical yield, determined by laser flash photolysis, in a magnetic field also supports the mechanism proposed (Scheme 1), in which both processes compete to each other.

In the previous papers,[3] we studied the transient absorption and the TSLE fluorescence of anthraquinone in SDS micellar solution in magnetic field. The decays and yields of anthrasemiquinone radical as well as those of photoadduct of semiquinone with surfactant are influenced by the external magnetic field. Present results agree well with those in the studies mentioned above.

In conclusion, by combining results by laser flash photolysis with those by TSLE fluorescence, it is unequivocally demonstrated that radical pair intervenes as a short-lived intermediate in the reaction and that intersystem crossing as well as relaxation of the radical pair is reduced by external magnetic field.

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References

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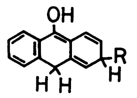
10) The photoadduct may have the following structure by analogy with the photoproduct of benzophenone in SDS micellar solution,[8,9] though we failed in its chemical identification because of instability to air.



, R = Dodecyl Sulfate Anion

11) The absorption due to the photoadduct may also appear at 355 nm. However, we can estimate the k_f values, since the risetime of the adduct is the same as the decaytime of the triplet pair.