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MAGNETIC FIELD EFFECT ON THE HYDROGEN ABSTRACTION REACTIONS OF AROMATIC CARBONYLS IN SDS MICELLAR SOLUTION

Yoshifumi TANIMOTO,* Masanobu TAKASHIMA, and Michiya ITOH
Faculty of Pharmaceutical Sciences, Kanazawa University,
Takara-machi, Kanazawa 920

The magnetic field effect on the photoinduced hydrogen abstraction reactions of twelve aromatic carbonyls from xanthene and 9,10-dihydroanthracene has been studied in sodium dodecyl sulfate (SDS) micellar solution by laser flash photolysis.

The magnetic field effect on the hydrogen abstraction reactions of aromatic carbonyls have been extensively studied in micellar solutions by laser flash photolysis.[1-7] However few studies have been reported on the hydrogen abstraction reaction between two different molecules solubilized in micelles.[2,6,7] In the present paper, we studied the magnetic field effect on the hydrogen abstraction reactions of twelve carbonyls from two hydrogen donors(i.e., xanthene and 9,10-dihydroanthracene) solubilized in sodium dodecyl sulfate(SDS) micellar solutions by laser flash photolysis.

The laser flash photolysis measurements were made for deaerated SDS micellar solutions at room temperature using a Molectron UV-12 N_2 laser(337 nm) or a Lambda Physik EMG-50E excimer laser(308 nm) as an exciting light source.[3)]

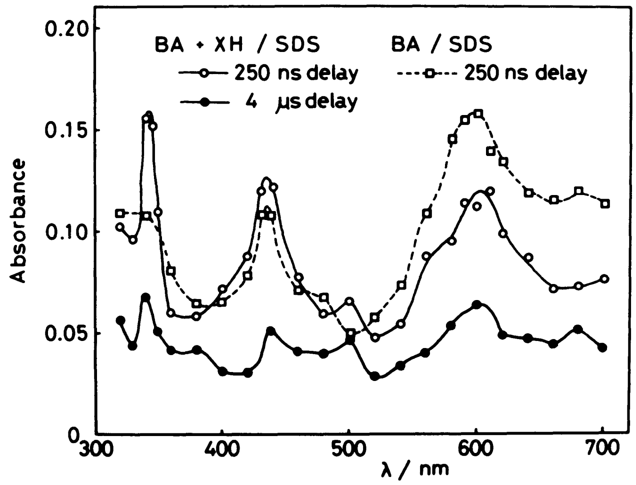
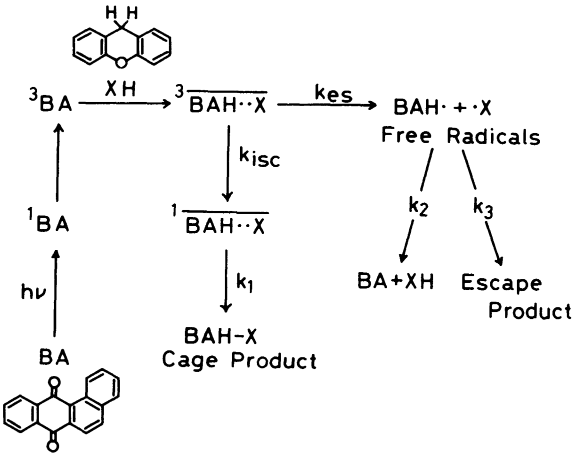


Fig. 1. Transient absorption spectra on the laser flash photolysis of the 0.4 mol dm^{-3} SDS micellar solution containing 3×10^{-4} mol dm^{-3} BA and 3×10^{-3} mol dm^{-3} XH.

Figure 1 shows transient absorption spectra of the laser flash photolysis of an SDS micellar solution containing 1,2-benzanthraquinone(BA) and xanthene(XH). In the absence of XH, a strong transient appears in the 320-700 nm region which is tentatively assigned to the T-T absorption of BA by analogy with that of xanthone[6,8)] and phenanthracenequinone.[9)] By the addition of XH to the solution, the T-T band shows a fast decay and a new band appears at 345 nm with a slight increase of the absorption intensity at 440 nm. The former and the latter are assigned to 9-xanthenyl

(X·) and 1,2-benzanthrasemiquinone(BAH·) radicals, respectively, from comparison with the literatures.[6,8-10]

Scheme 1 shows a reaction mechanism for the present photoinduced hydrogen abstraction reaction. Upon laser excitation, the excited triplet state of BA (^{3}BA) abstracts a hydrogen atom from xanthene to generate a triplet pair of BAH· and X· ($^3\overline{\text{BAH}\cdot\cdot\text{X}}$). The triplet-singlet intersystem crossing(ISC) of the radical pair and escape of the component radicals in the pair may take place competitively. A fast geminate recombination may occur in the singlet pair, while escaped radicals may undergo recombination or further reactions.



Scheme 1.

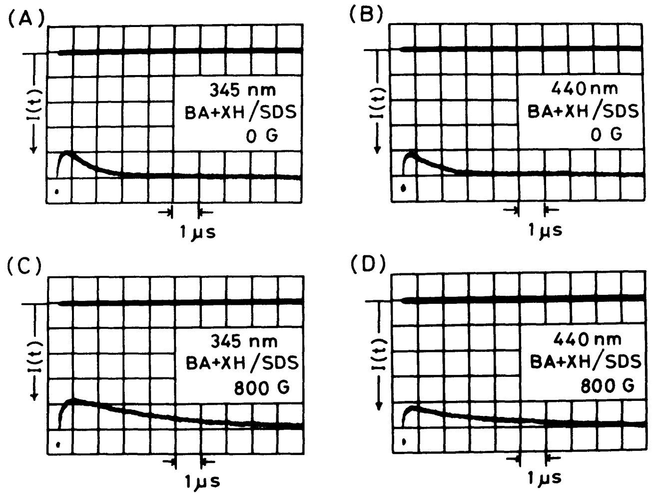


Fig. 2. Typical oscillograms on the laser flash photolysis of the SDS micellar solution containing BA and XH.

Figure 2 shows the magnetic field effect on the decays of X· and BAH·. At zero field, the time evolution of both radicals can be expressed as a sum of two pseudo-first-order decays;[11] the fast and slow decays correspond to those of the triplet radical pair and the free radicals, respectively, by analogy with the hydrogen abstraction of xanthone from xanthene in the SDS micellar solution.[6] At 800 G(1 G = 10^{-4} T), pre-exponential factors of the fast decay components of X· and BAH· are reduced and the decays are almost single exponential. Some kinetic parameters are shown in Table 1. According to a radical pair model of CIDNP,[12,13] the triplet-singlet ISC of the radical pair occurs via electron-nuclear hyperfine interaction and is expected to be reduced in a magnetic field because of Zeeman splitting of triplet sublevels. Present observation completely agrees with the prediction mentioned above. Further, as shown in Fig. 2 and Table 1, the fast decay rates of both radicals are in good agreement with each other at zero field and show similar magnetic field dependence. This is the first unequivocal optical spectroscopic evidence that the radical pair is intervened as a re-

Table 1. Magnetic field effect on the decay rate constants of 9-xanthenyl radical in SDS micellar solutions

Hydrogen acceptor	0 G	800 G
1,2-Benzanthraquinone	1.8×10^{6} s^{-1}	--- s^{-1}
	3.6×10^{5}	3.6×10^{5}
	1.6×10^{6} a)	---
	3.5×10^{5} a)	3.5×10^{5} a)
Duroquinone	2.3×10^{6}	---
	2.9×10^{5}	3.4×10^{5}
Flavone	1.7×10^{6}	1.2×10^{6}
	3.1×10^{5}	3.0×10^{5}
Xanthone[b]	1.7×10^{6}	---
	2.9×10^{5}	2.9×10^{5}

a) Decay rate constants of 1,2-benzanthrasemiquinone radical. b) Ref. 6.

Table 2. Hydrogen abstraction reactions for which the magnetic field effect was observed by the following techniques; laser flash photolysis(LP), steady-state photolysis(SP), product yield analysis(PY), and two-step laser excitation fluorescence(TL)

	Hydrogen donor		
Hydrogen acceptor	SDS	Xanthene	9,10-Dihydroanthracene
2,5-Dimethyl-p-benzoquinone	LP,[a] SP[a]	---	---
2,6-Dimethyl-p-benzoquinone	LP,[a] SP[a]	---	---
2-(2,4-Dioxapentyl)-p-benzoquinone	LP,[a] SP[a]	---	---
Anthraquinone	LP,[b] SP,[b] TL[b]	LP	LP
Anthraquinone-2-carboxylic acid	LP,[b] SP,[b] TL[c]	LP	LP
Anthraquinone-2-sulfonic acid, sodium salt	LP,[b] SP[b]	---	---
1,2-Benzanthraquinone	---	LP	---
Naphthoquinone	LP[d]	LP	---
Phenanthracenequinone	---	LP	---
Duroquinone	---	LP	---
Ubiquinone 50	---	LP	---
Xanthone	SP[e]	LP,[e] SP,[e] PY[e]	LP,[e] SP[e]
Flavone	---	LP	LP
Chromone	---	LP	LP
Acetophenone	---	LP	LP
Anthrone	LP,[c] TL[c]	LP	LP
Benzophenone	LP,[f] SP[g]	LP	---

a) Ref. 3. b) Ref. 4. c) Unpublished work. d) Ref. 5. e) Ref. 6. f) Ref. 1.
g) Ref. 2.

action intermediate, though in previous studies it was assumed for interpretation.

Furthermore, the magnetic field effect was studied for the hydrogen abstraction reactions of several carbonyls in the SDS micellar solution. In the absence of hydrogen donors(xanthene or 9,10-dihydroanthracene), no remarkable hydrogen abstraction reaction from the SDS surfactant was observed for most carbonyls by laser flash photolysis. On the other hand, when xanthene or 9,10-dihydroanthracene was added to the solution, the significant magnetic field effect was observed on the transient decays of X· or 9,10-dihydroanthracen-9-yl radical. No detectable magnetic field effect was observed on the transients generated from carbonyls(i.e., ketyl or semiquinone radical). This is mostly due to the small molecular extinction coefficients of them and to the spectral overlap of other transient species such as the T-T absorption of carbonyls. All the results are summarized in Tables 1 and 2, together with reported ones. These are mostly interpreted in the reaction mechanism similar to the one shown in Scheme 1. We can see from the tables that the magnetic field effect is commonly observed in the hydrogen abstraction reactions of aromatic carbonyls in the micellar solution. Detailed analysis of the data is in progress and will be reported in near future.

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