of four reduction waves (−1.51, −1.68, −1.99, and −2.11 V vs. SCE). A comparison of the electrochemistry of $\mathrm{Ru(bpy)_3}^{2+}$ with compound **7** suggests that the most positive wave is associated with both the $\mathrm{Ru(bpy)_3}^{2+/1+}$ couple and the formation of the porphyrin radical anion. The second wave correlates with the $\mathrm{Ru(bpy)_3}^{1+/0}$ redox couple and the third wave with the $\mathrm{Ru(bpy)_3}^{0/1-}$ system. The most negative wave is therefore assigned to the formation of the porphyrin dianion. Addition of Zn to the porphyrin ring **9** leads to the appearance of six quasi-reversible reduction waves, the differential-pulse polarogram of which is shown in Figure 2. The first two waves are similar to those found in **8** and are believed to be associated with the first two reductions of the Ru complex since addition of Zn is expected to cause a negative shift in the porphyrin reduction waves. Interestingly, the wave at −1.99 V vs. SCE observed for both $[\mathrm{Ru(bpy)_3}]^{0/1-}$ and complex **8** is not observed; rather two new waves at −2.27V and −2.39V vs. SCE are noted. Presumably one of these waves is associated with the third Ru reduction. The remaining two waves (−1.76 and −2.12 V vs. SCE) are associated with the Zn–porphyrin system. Spectroscopic experiments are currently being employed to unambiguously identify these waves. Yet, it is remarkable to note that the $\mathrm{Ru(bpy)_3}^0$ species is stabilized to an extent of 350 mV (~8 kcal/mol) with respect to the $\mathrm{Ru(bpy)_3}^{1-}$ species by the presence of the zinc porphyrin.

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Magnetic Field Effect on the Photosensitized Oxidation Reaction of 1,3-Diphenylisobenzofuran in SDS Micellar Solutions

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We wish to report a very significant magnetic field (MF) effect on the anthraquinone (AQ)-photoinduced oxidation reaction of 1,3-diphenylisobenzofuran (DPBF) in sodium dodecyl sulfate (SDS) micellar solution. Photoirradiation of the 330-nm absorption band of AQ and DPBF in aerated SDS micellar solution results in the formation of *o*-dibenzoylbenzene (DBB),[1] while DPBF itself is photostable in deaerated micellar solution. A typical UV spectral change during photolysis of the solution is shown in Figure 1a.[2] The bands at 330 and 410 nm are mainly due to AQ and DPBF, respectively. Since DPBF photoreacts very slowly in the aerated micellar solution without AQ, the oxidation of DPBF is mostly photosensitized by AQ. Further, a laser flash photolysis of this micellar solution[3] shows a remarkable quenching of anthrasemiquinone (AQH·) transients by oxygen in the micelle (apparent quenching rate, (1–2) × 10^6 $\mathrm{s^{-1}}$),[4] which implies a possible participation of hydroperoxy radical ($\mathrm{HO_2}\cdot$) in the present oxidation of DPBF, though DPBF is generally accepted as a singlet oxygen trap.[5]

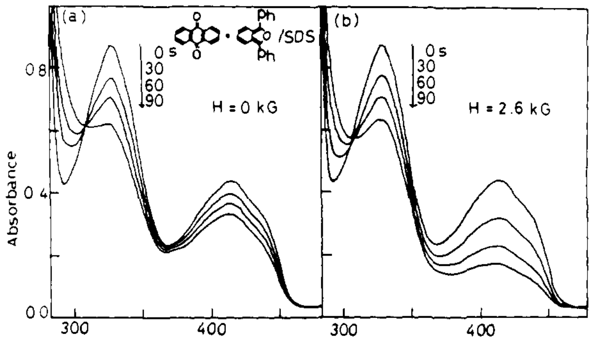

Figure 1. Magnetic field effect on the UV spectral change of the photolysis of the 0.4 M SDS micellar solution containing AQ (1 × 10^{-4} M) and DPBF (2 × 10^{-5} M) (see text): (a) 0 kG; (b) 2.6 kG.

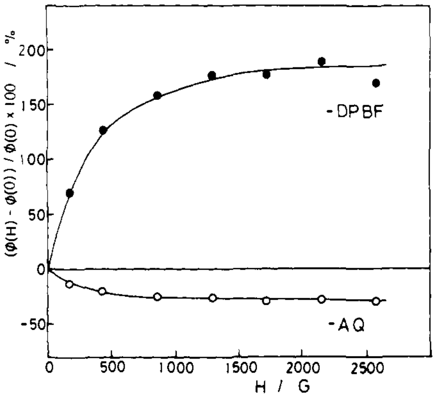

Figure 2. Magnetic field dependence of the relative quantum yield, ϕ, of disappearance of DPBF and AQ in the SDS micellar solution (see text).

Figure 1b shows the MF effect (2.6 kG) on the UV spectral change during the photolysis. The field significantly enhances the rate of disappearance of the 410-nm band (i.e., the quantum yield of disappearance of AQ), while it slightly decreases that of the 330-nm band (i.e., the disappearance of AQ). Figure 2 shows the MF dependence of the relative quantum yield, ϕ, of disappearance of DPBF and AQ determined from the spectral changes.[6] The change of the yield, $Q(H)$, at magnetic field H is defined as follows:

$$Q(H) = 100(\phi(H) - \phi(0))/\phi(0) \qquad (1)$$

The Q value of DPBF increases significantly up to ~1 kG and then slowly, while that of AQ decreases up to ~1 kG and is almost constant at higher field. At 2.6 kG, the Q values of DPBF and AQ are 180% and -30%, respectively.

AQ and DPBF are almost completely micellized. Taking into account the concentration of the solution,[7] coexistence of AQ and DPBF in the same micelle is infeasible. Therefore no direct reaction between AQ and DPBF in a micelle may occur. A proposed reaction mechanism is as follows:

$$\mathrm{AQ} \xrightarrow{h\nu} {}^1\mathrm{AQ} \rightarrow {}^3\mathrm{AQ} \rightarrow {}^3\overline{\mathrm{AQH}\cdot\cdot\mathrm{S}} \qquad (2)$$

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(1) The 0.8 M SDS micellar solutions containing AQ and DPBF were irradiated with a 500-W xenon-arc lamp equipped with a $\mathrm{NiSO_4}$–$\mathrm{CuSO_4}$ aqueous solution filter and a glass filter (Toshiba, UV-D33S) ($\lambda_{\max}$, 330 nm). Photoproducts in the solution were extracted with ethyl acetate and benzene, followed by the liquid chromatography. A main product was assigned to DBB by melting point, mass, and NMR measurements.

(2) Typically, 3 mL of aerated 0.4 M SDS micellar solution of AQ (1 × 10^{-4} M) and DPBF (2 × 10^{-5} M) in a 1-cm square quartz cell placed at the center of an electromagnet was irradiated with a 330-nm light.[1]

(3) For experimental setup, see ref 8a.

(4) Concentrations of oxygen are estimated to be 3 × 10^{-4} M in water and 1 × 10^{-3} M in the micelle: Matheson, I. B. C.; King, A. D., Jr. *J. Colloid Interface Sci.* **1978**, *66*, 464.

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(6) ϕ of DPBF was determined from the initial intensity change at 440 nm upon irradiation. ϕ of AQ was similarly determined from the change at 328 nm, after correcting the intensity due to DPBF.

(7) The concentration of the SDS micelle is estimated to be 6.5 × 10^{-3} M: Turro, N. J.; Yakta, A. *J. Am. Chem. Soc.* **1978**, *100*, 5951.

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$$ {}^3\overline{\mathrm{AQH}\cdot\cdot\mathrm{S}} \rightarrow {}^1\overline{\mathrm{AQH}\cdot\cdot\mathrm{S}} \rightarrow \mathrm{AQH{-}S} \quad (3) $$

$$ {}^3\overline{\mathrm{AQH}\cdot\cdot\mathrm{S}} \rightarrow \mathrm{AQH}\cdot + \cdot\mathrm{S} \quad (4) $$

$$ {}^3\overline{\mathrm{AQH}\cdot\cdot\mathrm{S}} + \mathrm{O_2} \rightarrow \mathrm{AQ} + \cdot\mathrm{S} + \mathrm{HO_2}\cdot \quad (5) $$

$$ \mathrm{AQH}\cdot + \mathrm{O_2} \rightarrow \mathrm{AQ} + \mathrm{HO_2}\cdot \quad (6) $$

$$ \mathrm{DPBF} + \mathrm{HO_2}\cdot \rightarrow\ \rightarrow \mathrm{DBB} \quad (7) $$

Upon photoirradiation of AQ in a micelle, the excited triplet state of AQ (^{3}AQ) abstracts a hydrogen atom from a dodecyl sulfate anion (HS) to give the triplet pair (${}^3\overline{\mathrm{AQH}\cdot\cdot\mathrm{S}}$) of AQH· and dodecyl sulfate radical (·S). The intersystem crossing (isc) to the singlet pair (${}^1\overline{\mathrm{AQH}\cdot\cdot\mathrm{S}}$) and dissociation of the triplet pair to free radicals occur competitively. The singlet pair may react to give covalent product (AQH–S).[8] The AQH· radical in the triplet pair and the AQH· free radical in water may react with oxygen to form the HO$_2$· radical. The HO$_2$· radicals generated in the micelle may escape into the water phase. Finally, these HO$_2$· radicals may attack DPBF solubilized in another micelle,[9] resulting in the formation of DBB as a stable photoproduct.[10,11] The MF effect shown in Figure 2 is mostly interpreted in terms of the radical pair model of CIDNP,[12,13] where the AQH· radical (an initiator of oxidation) concentration is affected by the magnetic field. At zero field, all triplet sublevels (T_+, T_0, and T_-) in the triplet radical pair undergo electron–nuclear hyperfine-induced isc to the singlet state (S). In a weak magnetic field, the isc of only T_0–S and T_-–S may occur because of the Zeeman splitting of triplet sublevels as described in the previous paper.[8a] This change of the isc rate results in the enhancement of the AQH· radical yield and the reduction of ϕ of AQ. Actually, the MF-induced increase of the triplet radical pair lifetime and of the AQH· free radical concentration was already reported in laser flash photolysis.[8a] The decrease of the Q value of AQ is in parallel with the previous observation.[8b]

The triplet excited state of AQ does not seem to be involved in the present oxidation because of its short lifetime ($\leq$30–40 ns). Although the excited triplet state of pyrene sensitizes the oxidation of DPBF in SDS micellar solution,[5] no MF effect was observed. The addition of a singlet oxygen scavenger, NaN$_3$ (9×10^{-3} M) into the AQ–DPBF micellar solution does not cause a reduction of ϕ of DPBF but actually a slight increase. No heavy water effect on ϕ was observed, though the lifetime of the singlet oxygen was reported to be very sensitive to heavy water substitution.[14] No superoxide generation was detected in the photolysis of the aerated SDS micellar solution of AQ (1×10^{-4} M) containing nitro blue tetrazolium (3×10^{-5} M).[15] These facts suggest that neither the singlet oxygen nor the superoxide enters the present oxidation mechanism. Furthermore, benzophenone was also used as the initiator of the DPBF oxidation, since the photochemistry and its MF dependence are similar to those of AQ:[16,17] Benzophenone-photosensitized oxidation of DPBF in SDS micellar solution does show a MF effect as expected (the Q value of DPBF is 60% at 2.6 kG). This fact also supports the present mechanism. Since the oxidation of DPBF by radical initiators was already reported,[10,11] the present observation is attributable to a remarkable magnetic field effect on the radical initiation reaction.

An exceptionally large MF-induced change was reported on the dibenzyl ketone photosensitized emulsion polymerization of styrene:[18] The average polymer molecular weight increases about 400% at magnetic field of 1–10 kG due to the MF-induced concentration change of benzyl radical, a polymerization initiator. The present MF effect is comparable with that of the styrene polymerization. The present result clearly demonstrates the importance of the magnetic field for controlling photochemical processes.

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Registry No. DPBF, 5471-63-6; AQ, 84-65-1; SDS, 151-21-3.

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Low-Spin Five-Coordinate Ferric Porphyrin Complex: [5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrinato](hydrosulfido)iron(III)

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Recent studies have indicated that the heme center in cytochrome P-450 has an axial thiolate ligand in the resting state,[1] and this ligand appears to remain coordinated during at least part of the reaction cycle.[2] Correspondence of various spectroscopic properties of chloroperoxidase (CPO) with those of cytochrome P-450 has led to the proposal that the heme environment in these enzymes is similar.[1,3] These proposals have been strengthened by the finding that only model systems that contain thiolate axial ligation are able to mimic[3,4] the unique spectral properties of cytochrome P-450 and CPO. To date, synthetic ferric porphyrins with a single axial thiolate ligand are all high spin;[5-7] addition of a Lewis base is necessary to convert the iron atom to the

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