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Magnetic field effect on photosensitized oxidation of 1,3-diphenylisobenzofuran in SDS micellar solution

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ABSTRACT

Magnetic field effect ($\leq$0.2 T) on photosensitized oxidation of 1,3-diphenylisobenzofuran (DPBF) in aerated SDS micellar solution was studied using high-performance liquid chromatography. When anthraquinone and 4-methylbenzophenone were used as sensitizers, the formation yield of o-dibenzoylbenzene increased remarkably along with the oxidation yield of DPBF by application of a magnetic field. The results were interpreted in terms of the radical pair mechanism in which concentration of free radicals, generated from the photoreaction of sensitizers, increases by application of the magnetic field.

1. Introduction

Magnetic fields are simple and useful tools to influence various chemical, physical and biological phenomena [1]. Therefore, numerous studies have examined magnetic field effect (MFE) on chemical reactions and other phenomena. However, some experimentally obtained results are not reproducible by re-examination. For example, MFE related to the thermal reaction of benzyl and pentafluorobenzyl halides with *n*-butyllithium in hexane [2] was not reproducible through re-examination [3]. MFE on adenosylcobalamin-dependent ethanolamine ammonia lyase on an ethanolamine substrate [4,5] could not be reproduced [6]. It is therefore of great importance to re-examine the reported results because MFE is sometimes unclear.

Remarkable MFE ($\leq$0.25 T) on anthraquinone (AQ)-photosensitized oxidation of 1,3-diphenylisobenzofuran (DPBF) in aerated sodium dodecyl sulfate (SDS) micellar solution have been reported by one author [7]. Upon photoirradiation of AQ, DPBF was decomposed to o-dibenzoylbenzene (DBB). The effect on degradation of AQ and DPBF was examined from the UV-spectral changes of AQ and DPBF during photoirradiation, but not on the product DBB because no DBB absorption band suitable for analysis was available in the wavelength region that was studied.

To examine the MFE ($\leq$0.2 T) of the reaction described above from upstream to downstream, we studied MFE on chemical yields of the AQ- and 4-methylbenzophenone-photosensitized reaction of DPBF using high-performance liquid chromatography (HPLC). It is confirmed that MFE on formation yield of DBB is in agreement with that on degradation yield of DPBF. The results are explainable by the radical pair mechanism. The MFE on the oxidation yield of DPBF is a reflection of that on the photoreaction of the sensitizer because the concentration of free radicals derived from sensitizers, which is the initiator of the oxidation reaction, increases as a result of the magnetic field application.

2. Experimental

1,3-Diphenylisobenzofuran (DPBF), anthraquinone (AQ), 4-methylbenzophenone (mBP), 2,2′-azobis(isobutyronitrile) (AIBN), o-dibenzoylbenzene (DBB), sodium dodecyl sulfate (SDS), acetonitrile, and methanol were purchased from Wako Pure Chemical Industries Ltd. (Scheme 1). They were used as received. Deionized and distilled water was used. The respective concentrations of DPBF, AQ, mBP, AIBN, and SDS were 0.25×10^{-4}, 1×10^{-4}, 0.5×10^{-4}, 1.0×10^{-2} and 0.4 mol dm^{-3}.

Typically, an aerated 0.4 mol dm^{-3} SDS solution (2 mL) containing AQ and DPBF was irradiated using 313 nm light from an Xe arc (UXL-300SX; Ushio Optical Modulex) filtered using glass filters of UTVAF-50S-34U and UTVAF-50S-33U (Sigma Koki Co., Ltd.) and a solution filter K_2CrO_4 (7.15 mg/100 mL; path length, 2 cm)

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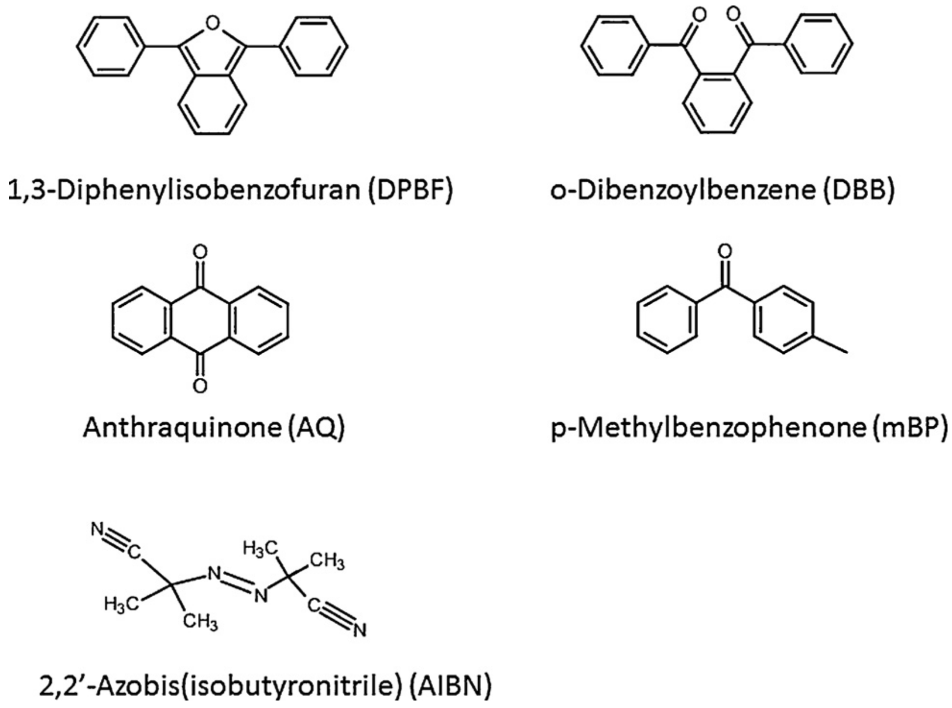

Scheme 1.

for the AQ-photosensitized reaction. The absorption spectra were measured using a spectrophotometer (USB4000 and DT-MINI-2-GS; Ocean Optics Inc.). After photoirradiation, reaction mixtures were analyzed using high-performance liquid chromatography (HPLC, LC-20 series; Shimadzu Corp.), where a Wakopack Handy ODS column (4.6 mm × 150 mm) and an elution solvent of acetonitrile and water (3:1) were used. In the case of mBP- and AIBN-photosensitized reaction, a Hiber LiChrosorb RP-18 ODS column (4.6 mm × 250 mm) and an elution solvent of methanol and water (9:1) were used. The solute concentrations were obtained by comparing the integrated signal intensities of authentic samples.

Magnetic fields were applied by attaching a pair of rare-earth permanent magnets on the side surface of a cell holder.

3. Results and discussion

Fig. 1a portrays the absorption spectral changes of an aerated SDS micellar solution of AQ and DPBF during photolysis at 0 T. The absorption bands at 320 nm and 410 nm are assigned, respectively, to AQ and DPBF. Upon photoirradiation at 313 nm, the absorbance of both AQ and DPBF decreases gradually. In the presence of a 0.1 T magnetic field, the degradation of DPBF occurs remarkably more rapidly than that at 0 T, whereas that of AQ becomes slightly slower (Fig. 1b), as described in an earlier report [7].

UV spectral analysis is a convenient method to ascertain how a magnetic field affects photochemical reactions. However, the values obtained from the UV spectra presented in Fig. 1 are apparently inaccurate because at least two absorption bands are overlapped

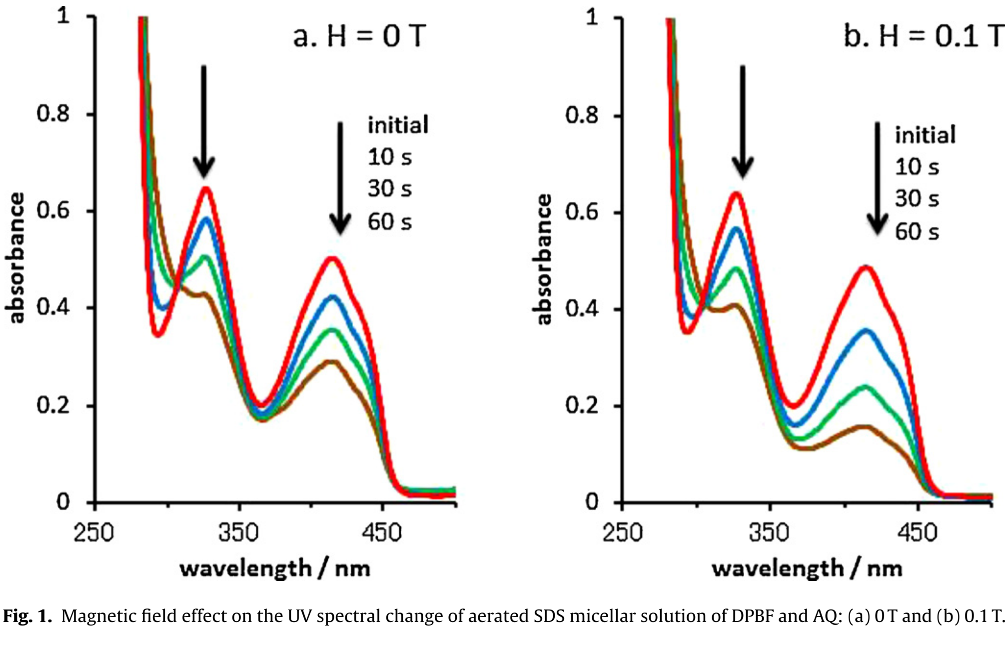

Fig. 1. Magnetic field effect on the UV spectral change of aerated SDS micellar solution of DPBF and AQ: (a) 0 T and (b) 0.1 T.