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MAGNETIC FIELD EFFECT ON THE INTRAMOLECULAR HYDROGEN ABSTRACTION REACTION OF n-TETRADECYL ANTHRAQUINONE-2-CARBOXYLATE

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The magnetic field effect on the intramolecular hydrogen abstraction of n-tetradecyl anthraquinone-2-carboxylate was studied in aerated 1,1,2-trichlorotrifluoroethane, using steady-state photolysis, two-step laser excitation fluorescence, and laser flash photolysis.

The magnetic field effect on intermolecualr hydrogen abstraction reactions has been extensively studied in micellar micro-heterogeneous solutions,[1-5] since a "micelle cage" increases lifetimes of radical pair intermediates. In homogeneous solution, studies of the magnetic field effect are rather scanty.[2,6] Since, in liquid homogeneous solution, diffusive separation of radicals in the pair is usually much faster than the triplet-singlet intersystem crossing(ISC) of the pair, its lifetime is very short and the magnitude of the effect is rather small. However, if one can restrict the separative diffusive motion of radical pairs connecting them by a methylene chain, one can see a remarkable effect on the reaction even in homogeneous solution. In previous papers,[4] we studied the magnetic field effect on the hydrogen abstraction reaction of anthraquinones from sodium dodecyl sulfate (SDS) micelles. As an extension of these works, we have undertaken a study of the intramolecular hydrogen abstraction of n-tetradecyl anthraquinone-2-carboxylate in aerated 1,1,2-trichlorotrifluoroethane using steady-state photolysis, two-step laser excitation fluorescence, and laser flash photolysis.

n-Tetradecyl anthraquinone-2-carboxylate(AQC14) was synthesized with condensation of sodium anthraquinone-2-carboxylate and n-tetradecyl bromide. 1,1,2-Trichlorotrifluoroethane(TCTFE) was purified with a column of activated alumina. A xenon arc lamp equipped with $NiSO_4$-$CoSO_4$ aqueous solution and Toshiba UV-D33S glass filters(λ_{max}, 330 nm) was used as a steady-state excitation light source.[3] Two-step laser excitation(TSLE) fluorescence measurements were made using an excimer laser(Lambda Physik EMG-50E, 308 nm) and an N_2 laser-pumped dye laser(Molectron UV-

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12 and DL-14, 440 nm) as an actinic and a probe light source, respectively.[7] Timing of two lasers was adjusted with a delay circuit. In laser flash photolysis, the excimer laser was used as an exciting light source.[3]

The UV absorption of AQC14 shows a band in the 330 nm region. Upon steady-state irradiation, the intensity of this band rapidly decreases. Since anthraquinone is photo-inactive in this solvent(TCTFE) having no hydrogen atom, this fast photo-induced disappearance of AQC14 may be attributable to the intramolecular hydrogen abstraction reaction of AQC14. Figure 1 shows the magnetic field dependence of the relative quantum yield ϕ of disappearance of AQC14 in aerated TCTFE. The yield ϕ decreases by about 12% in the magnetic field(100-260 mT).

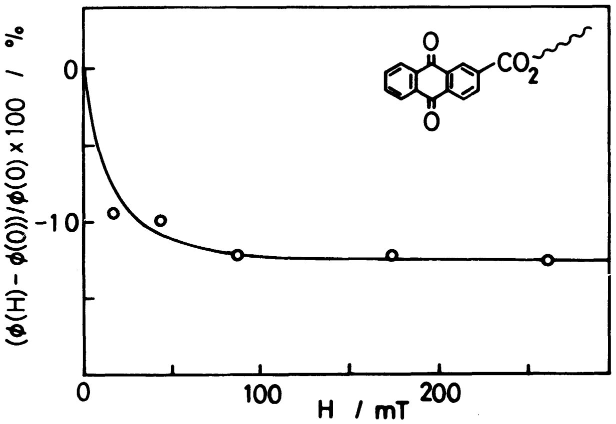
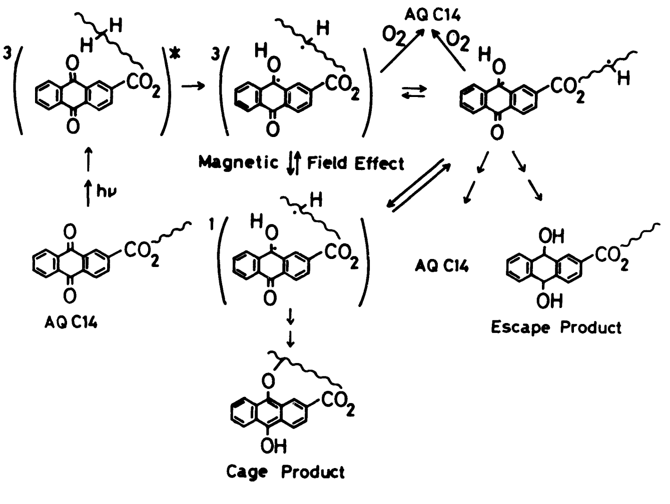


Fig. 1. Magnetic field dependence of relative quantum yield ϕ of disappearance of AQC14 in aerated TCTFE. Here, $\phi(0)$ and $\phi(H)$ are the yields in the absence and presence of a magnetic field H, determined from the UV-spectral changes of the 330 nm band during the course of irradiation.



Scheme 1.

By analogy with the hydrogen abstraction of anthraquinones in SDS micellar solutions,[4] and the intramolecular hydrogen abstraction of alkyl esters of benzophenone-4-carboxylic acid,[8] we propose a reaction mechanism of the present photoreaction as shown in Scheme 1. The excited triplet state of anthraquinone chromophore in folded conformations of AQC14 may abstracts a hydrogen atom from its methylene chain to generate a triplet biradical of anthrasemiquinone and alkyl radical. The triplet-singlet ISC and separation of component radicals into stretched conformations occur competitively. A cage product(ring-closure product) may be generated via the singlet biradical. Biradicals of stretched conformations may undergo conformational changes to folded structures and scavenging reactions such as bimolecular recombination and quenching by oxygen, leading to the regeneration of AQC14. However, since the bimolecular recombination is much slower than the conformational change of the biradical, oxygen quenching of the biradical may be a main reaction process in the aerated solution, which competes with the triplet-singlet ISC of the biradical.$^{9)}$ As discussed in the radical pair generated in the hydrogen abstraction of anthraquinones,$^{4)}$ the triplet-singlet ISC of a biradical may occur via electron-nuclear hyperfine interaction. At zero field, all triplet sublevels are mostly degenerate with the singlet state. In a magnetic field, the degeneracy between two triplet sublevels and the singlet state is lifted because of electronic Zeeman effect. The triplet-singlet ISC rate may be reduced in the presence of a magnetic field. Therefore, the observed magnetic field effect in Fig. 1 may be attributable to the reduction of triplet-singlet ISC rate, which leads to the increase in the yield of the AQC14 recovery at the expense of the reduction of the cage product yield. This is the first observation of the magnetic field effect on the intramolecular hydrogen abstraction reaction.

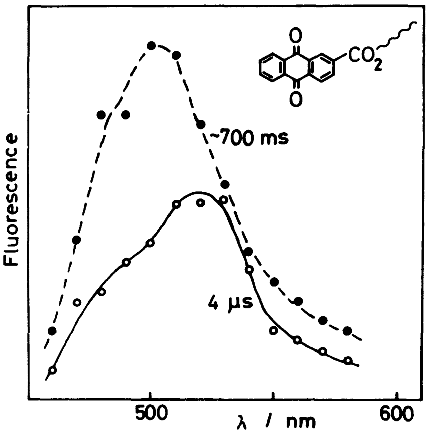


Fig. 2. Time-resolved TSLE fluorescence spectra of AQC14 in aerated TCTFE.

This interpretation is also supported by the TSLE fluorescence study of AQC14. Photolysed solution of AQC14 shows a UV absorption band in the 400 nm region due to photoproducts. Thus, when this band is excited by the second pulse laser just after the first laser excitation of AQC14, the TSLE fluorescence of photoproducts should be observed. Figure 2 shows time-resolved TSLE fluorescence spectra of AQC14 in aerated TCTFE. At 4 μs delay after the first laser excitation, the fluorescence band maximum appears at 520 nm, while at 500 nm at 700 ms delay. The 520 and 500 nm bands may be attributable to the cage product(ring-closure product) and hydroquinone of AQC14, respectively, since, in the photolysis of anthraquinone in SDS micellar solution, the fluorescence band maxima of surfactant-anthrahydroquinone ether and anthrahydroquinone were observed at 495 and 482 nm, respectively.$^{4,10)}$ Figure 3 shows time evolution of the TSLE fluorescence intensity of the cage product, which was obtained by plotting the fluorescence intensity at 520 nm vs. delay time of the second laser to the first. The risetime of the cage product was obtained to be 2.4 μs. From the separate measurements at fixed delay time, the TSLE fluorescence intensity of the cage product at 6 μs delay was shown to decrease by about 10% in a magnetic field(80 mT). However, its rise-

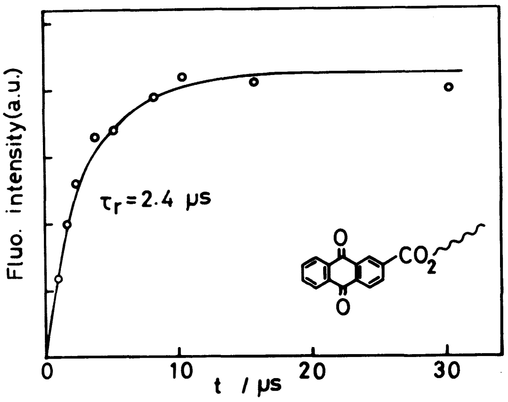


Fig. 3. Time evolution of the TSLE fluorescence intensity of AQC14 at 520 nm.

time is magnetic field independent within experimental error. The magnetic-field-induced decrease of the cage product yield is in good agreement with the mechanism shown in Scheme 1.

The magnetic field effect on transient absorption of this solution was attempted by laser flash photolysis. However, no detectable magnetic field effect was observed on the transients in the 360-600 nm region, though a strong absorption band appears at 380 nm. This is mostly due to the overlap of the T-T absorption band of the quinone and that of its semiquinone radical, since the rate of the intramolecular hydrogen abstraction seems to be rather slow(mostly, 10^6-10^7 s^{-1}), judging from the intermolecular hydrogen abstraction of anthraquinones from the SDS micelles.4)

The magnetic field effect on triplet-singlet ISC of biradicals may be influenced by inter-radical distances and their conformations. Further study for a series of alkyl esters of anthraquinone-2-carboxylic acid is now in progress and will be reported soon.

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