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Magnetic Field Effects on Hydrogen Abstraction of Triplet Benzophenone with Thiophenol in an SDS Micellar Solution

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The photoreduction of benzophenone with thiophenol was studied by a laser flash photolysis under the magnetic fields of 0-10 T. The escape yields of the benzophenone ketyl and phenylthiyl radicals decreased with increasing magnetic field strength. The observed magnetic field effect can be interpreted by the Δg mechanism in the case of a triplet radical pair.

Magnetic field effects (MFEs) on the chemical reactions of radical pairs and biradicals have received considerable attention.1-3) Especially, the reactions involving heavy-atom-centered radical, such as Si-, P-, S-, Ge-, and Sn-radicals, are attractive from the viewpoints of isotope separation by magnetic isotope effects (MIEs). The spin-orbit (SO) interaction of such heavy atoms, however, has widely been believed to enhance the spin conversion of radical pairs and to weaken their MFEs and MIEs.4) Bohne et al. reported that no MFE had been found for the photoreduction of benzophenone with thiophenol in a sodium dodecylsulfate (SDS) micellar solution under magnetic fields below 0.32 T.5) On the other hand, we found some MFEs on the reaction of S-centered radicals.6,7) Recently, we carried out a laser flash photolysis study on the same reaction that was studied by Bohne et al.5) and found MFEs on the dynamic behavior of ketyl and phenylthiyl radicals.

Laser flash photolysis (355 nm) was performed at room temperature on a degassed SDS (0.2 mol dm^{-3}) micellar solution containing thiophenol (PhSH, 31 x 10^{-3} mol dm^{-3}) and benzophenone (Ph_2CO, 2.9 x 10^{-3} mol dm^{-3}). In the present system, the following reaction has been believed to occur:5)

$$^3Ph_2CO^* + PhSH \longrightarrow Ph_2C^{\bullet}OH + PhS^{\bullet} \qquad (1)$$

Here, $^3Ph_2CO^*$, $Ph_2C^{\bullet}OH$, and $PhS^{\bullet}$ represent the triplet excited state of benzophenone, benzophenone ketyl and phenylthiyl radicals, respectively. The transient absorption bands of $Ph_2C^{\bullet}OH$, and $PhS^{\bullet}$ were observed at 530-540 and 450-470 nm, respectively.

Time profiles of the transient absorption (A(t)) were measured at 530 and 470 nm under magnetic fields (B) of 0-10 T. Typical curves obtained at 470 nm are shown in Fig. 1. Here, the decay parts of the A(t) curves were found to have fast and slow components. In comparison with the results reported for similar micellar solutions in a previous paper,8) the former is safely attributable to the radical pair decay and the latter is to the yield of the escaped radicals. We can see from this figure that the A(t) curves of $PhS^{\bullet}$ are appreciably changed by magnetic fields. The escaped yield of $PhS^{\bullet}$ decreased with increasing B and the yield observed at 10 T was ca 0.9 times as small as that at 0 T, although the fast componet of the A(t) curves is rounded through a slow responce time (~ 10 ns) of the present apparatus. Similar MFEs on the A(t) curves were also obtained at 530 nm. The magnitude of the MFE, however, was smaller than that obtained at 470 nm. At 540 nm, where Bohne et al. observed the kethyl radical, the condition was even worse, because of the triplet-triplet (T-T) absorption of Ph_2CO. This may be the reason why they could observe no MFE. Bohne et al. explained their absence of any MFE by the fast spin rotational relaxation due to the large anisotropy of the g-tensor for $PhS^•$.[5)]

The MFEs observed in the present study can be interpreted qualitatively in terms of the triplet-singlet (T-S) conversion of radical pair due to the Δg mechanism (ΔgM)[9)] together with the B-independent T-S conversion of the pair due to the spin-orbit coupling (SOC),[4)] because the present radical pair of $PhS^•$ (g= 2.0077)[5)] and $Ph_2C^•OH$ (g= 2.0030)[5)] has a large Δg and the reaction precursor is a triplet benzophenone. The T-S conversion rate increases with increasing B through the ΔgM and the escaped yield is reduced in the present system.

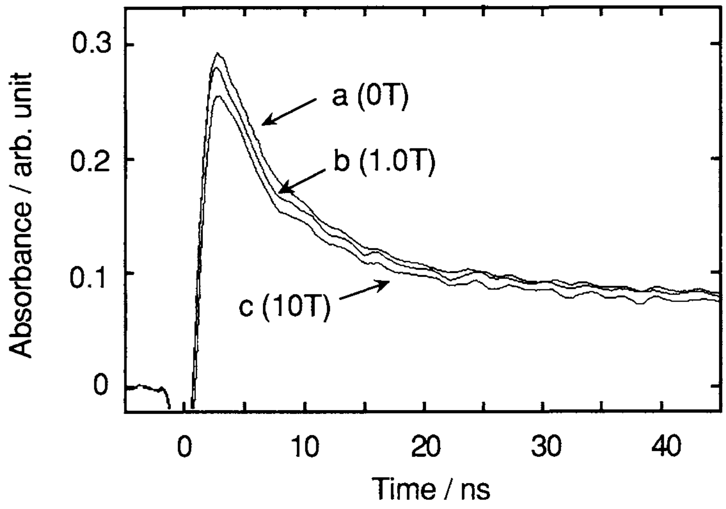

Fig. 1. A(t) curves observed at 470 nm at room temperature under the magnetic field of (a) 0 T, (b) 1.0 T, and (c) 10 T for the SDS micellar solution containing Ph_2CO and PhSH. At this wavelength, the contribution of the T-T absorption of Ph_2CO was estimated to be less than 20%. Because the T-T absorption should not be influenced by magnetic fields, the observed MFEs on the A(t) curves are ascribable to the reaction of $PhS^•$.

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References

1) U. E. Steiner and T. Ulrich, Chem. Rev., **89**, 51 (1989).
2) H. Hayashi and Y. Sakaguchi, "Lasers in polymer science and technology: applications," CRC Press, Baca Raton, FL (1990), Vol. 2.
3) H. Hayashi, "Photochemistry and photophysics," CRC Press, Baca Raton, FL (1990), Vol. 1.
4) I. V. Khudyakov, Y. A. Serebrennikov, and N. J. Turro, Chem. Rev., **93**, 537 (1993).
5) C. Bohne, M. S. Alnajjar, D. Griller, and J. C. Scaiano, J. Am. Chem. Soc., **113**, 1444 (1991).
6) H. Hayashi, Y. Sakaguchi, M. Tsunooka, M, H. Yanagi, and M. Tanaka, Chem. Phys. Lett., **136**, 436 (1987).
7) M. Wakasa, Y. Sakaguchi, and H. Hayashi, J. Phys. Chem., **97**, 1733 (1993).
8) M. Wakasa, Y. Sakaguchi, and H. Hayashi, J. Am. Chem. Soc., **21**, 8171 (1992).
9) H. Hayashi and S. Nagakura, Bull. Chem. Soc. Jpn., **51**, 2862 (1978).

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