Magnetic Field Effects on Hydrogen Abstraction of Thiobenzophenone as a Probe of Microviscosity

Miyuki Tanaka,[†] Tomoaki Yago,[†] Yoshio Sakaguchi,[‡] Tadashi Takamasu,[§] and Masanobu Wakasa^{*,†}

[†]Department of Chemistry, Graduate School of Science and Engineering, Saitama University, 255 Shimo-okubo, Sakura-ku, Saitama-shi, Saitama 338-8570, Japan

[‡]RIKEN (The Institute of Physical and Chemical Research), 2-1Wako, Wako-shi, Saitama 351-0198, Japan

[§]National Institute for Materials Science (NIMS), 3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan

ABSTRACT: Hydrogen abstraction reactions of thiobenzophenone with thiophenol in solutions of varying viscosities ($\eta = 0.29-42.0 \text{ cP}$) were studied by a nanosecond laser flash photolysis under magnetic fields of 0-15.5 T. In alcoholic solutions, the escaped radical yield (Y) of thiobenzophenone ketyl radical showed appreciable magnetic field effects (MFEs). The observed MFEs can be interpreted with the Δg mechanism through the triplet radical pair. The relative escaped radical yield (R(1.7T) = Y(1.7T)/Y(0T)) decreased



with increasing η at $0 < \eta \le 3.33$ cP, but then the yield increased with increasing η at 3.33 cP $< \eta \le 22.2$ cP. At much higher viscosity 22.2 cP $< \eta \le 42$ cP, R(1.7T) values become 1.0 within experimental errors. Such quenching of MFE was explained by the spin—orbit coupling recombination of close radical pairs associated with high viscosity. The MFEs on the present reaction is extremely sensitive to the solvent viscosity in the vicinity of the radical pairs. Using this probe reaction, microviscosities of sodium dodecyl sulfate (SDS) and Brij35 micellar solutions were estimated.

INTRODUCTION

Magnetic field effects (MFEs) on photochemical reactions through radical pairs (RPs) and biradicals have received considerable attention during the past 3 decades and the mechanism has been well-clarified experimentally and theoretically.¹⁻³ These research fields have been called spin chemistry. The most attractive subject of spin chemistry is the investigation of chemical reaction by the magnetic field effect probe (MFE probe).⁴⁻⁸ In RPs generated by photochemical reactions, the unpaired electron spins on each radical are coupled, giving two different spin states: singlet (S) and triplet (T). Magnetic fields interact with these spins and affect the reaction of the RPs without changing other parameters such as the reaction rate of singlet RPs, activation barrier, and diffusion motion of the radicals. Since the interaction between magnetic fields and spins can be described by quantum chemistry, MFE studies on RPs provide valuable information on their kinetics and dynamics and in particular on aspects of the reaction mechanism such as reaction precursor and intermediate. Thus, we call this technique MFE probe.

Using the MFE probe, we have reported on the microviscosity of alcoholic solutions⁵ and the nanoscale heterogeneous structure of ionic liquids.^{4,6,7} Also the estimation of microviscosity of micellar solution is a meaningful subject of the MFE probe. It has been studied by several techniques. From the fluorescence depolarization, the microviscosity of sodium dodecyl sulfate (SDS) micellar solution was reported to be 15-16 cP.⁹ Using

the intramolecular excimer formation, it was reported to be 10–19 cP.¹⁰ Recently, using electron spin resonance technique with spin probes of nitroxide labeled *n*-doxyl stearic acids (*n*-DSA), Bahri et al. reported the microviscosities were 12.3 (with 5-DSA) and 14.6 cP (with 16-DSA), respectively.¹¹ Moreover, fairly small and large values of 3.6 ¹² and 52 cP ¹³ were reported from the fluorescence quenching of 3,3-dimethyl-2-phenyl-3*H*-indole and diphenylhexatriene, respectively. Thus the reported values of microviscosity of SDS micellar solution were varied in the wide range of 3.6–52 cP,^{9–13} and it is worthwhile to study the microviscosity of SDS by the MFE probe.

In our previous studies of the MFE probe, hydrogen abstraction reactions of benzophenone (BP) were used as the probe reaction. BP is the most popular molecule for photochemistry, and its triplet excited state (³BP*) is very reactive.^{14–17} Since ³BP* easily reacts with alcohols and micellar solution, the reaction of BP cannot be used as the probe reaction in those solvents. Thus it is necessary to find a new probe reaction for the MFE probe. Recently, we found that thiobenzophneone (TBP), a sulfur analogue of benzophenone, is very inert to alcohols and micellar solution.¹⁸ Instead of BP, TBP may be used as a new MFE probe reaction. In this paper, we carried out the nanosecond laser flash photolysis of TBP with thiophenol in solutions of varying viscosities ($\eta = 0.29-42.0$ cP), SDS, and

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Figure 1. Transient absorption spectra observed for thiobenzophenone $(2.0 \times 10^{-3} \text{ mol dm}^{-3})$ in a 1/25 mixture of *i*-BuOH/*c*-HexOH at delay times of 0.1, 0.5, 1.0, and 2.0 μ s after laser excitation in the (a) absence and (b) presence of thiophenol $(1.0 \times 10^{-1} \text{ mol dm}^{-3})$.

polyoxyethylene dodecyl ether (Brij35) micellar solutions. Appreciable MFEs were observed in alcoholic solutions and Brij35 micellar solution, and then the MFEs were analyzed by the stochastic Liouville equation. Using the viscosity dependence of the MFEs, the microviscosities of SDS and Brij35 micellar solutions were estimated.

EXPERIMENTAL SECTION

Materials. Thiobenzophenone (TBP) was synthesized as described in the literature.^{19,20} The purity of synthesized TBP which was determined by gas chromatography (Shimadzu GC-18A) was >95%. Thiophenol (PhSH) was used as received. Hexane ($\eta = 0.29$ cP), benzene ($\eta = 0.6$ cP), methanol ($\eta = 0.55$ cP), ethanol ($\eta = 1.04$ cP), 1-propanol ($\eta = 1.94$ cP), 2-methyl-1-propanol (*i*-BuOH, $\eta = 3.33$ cP), cyclohexanol (*c*-HexOH, mp 296–298 K), sodium dodecyl sulfate (SDS), and polyoxyethylene dodecyl ether (Brij35) were used as received. All chemicals



Figure 2. Time profiles of transient absorption, A(t), observed for the reaction of thiobenzophenone in a 1/25 mixture of *i*-BuOH/*c*-HexOH at 400, 490, and 515 nm.

were purchased from Kanto Chemical Co., Inc. (Cica). Water was distilled and deionized (Millipore SIMP-9903). Mixtures of several ratios of *i*-BuOH and *c*-HexOH were used for highly viscous solvents. The viscosity listed for each chemicals and density of each solvent were measured by a viscometer (Yamauchi VM-10A-L) and a density meter (Anton Paar DMA 5000).

Nanosecond Laser Flash Photolysis. Laser flash photolysis was carried out with an apparatus that was essentially the same as the apparatus described elsewhere.^{21,22} The third harmonic (355 nm) of a Nd:YAG laser (Quanta-Ray GCR-130-10 or INDI) with a pulse width of 7 ns was used as an exciting light source. The probe light from a Xe short arc lamp (PerkinElmer Optoelectronics PE300BUV) connected with a custom-built pulsed current generator was divided into two beams, creating a double-beam probe system. One beam passed through a quartz sample cell placed in a magnet. The other was detected directly. Both beams were detected by photomultipliers (Hamamatu, R636-10) through monochromators (Oriel MS257 and Shimadzu SPG-120S, respectively). This double-beam probe system was constructed to accurately observe transient absorption by maintaining a flat baseline signal. Signal from the photomultiplier was terminated by a 50 Ω resistor and was recorded by a digitizing oscilloscope (LeCroy Wave Pro 960, 2 GHz). A personal computer was used to control the apparatus and record data. Magnetic fields of up to 1.7 T were provided by an electromagnet (Tokin SEE-10W)²¹ and up to 15.5 T by a homemade pulsed magnet.²² Argon-bubbled solutions were circulated through the quartz cell with a rate of 20 mL/min. All laser flash photolysis measurements were carried out at 296 K.

Time-Resolved EPR. Time-resolved EPR spectra were measured without field modulation with a JEOL JES-RE2X ESR spectrometer at 1-2 and $2-3 \ \mu s$ after laser excitation. The third harmonic (355 nm) of a Nd:YAG laser (Quanta-Ray GCR-3, 30 Hz) was used as an exciting light source. The output signal was averaged by a digitizing oscilloscope (Tektronix TDS 540). Argon-bubbled *i*-BuOH solution containing TBP (2.0×10^{-3} mol dm⁻³) and PhSH (2.0×10^{-1} mol dm⁻³) was circulated through a quartz cell with a rate of 20 mL/min.

RESULTS AND DISCUSSION

Transient Absorption Spectra and Lifetime of Triplet Excited State of TBP in Alcohols and Micellar Solution. Laser flash photolysis of TBP was performed in benzene ($\eta = 0.6 \text{ cP}$), various mixtures of *i*-BuOH and *c*-HexOH [3/1 to 1/50 (v/v), 7.4–62 cP] and a SDS (1.60 \times 10⁻¹ mol dm⁻³) micellar solution. The transient absorption spectra observed for TBP $(2.0 \times 10^{-3} \text{ mol dm}^{-3})$ in a 1/25 mixture of *i*-BuOH/*c*-HexOH $(\eta = 50 \text{ cP})$ at delay times of 0.1, 0.5, 1.0, and 2.0 μ s after laser excitation are typically shown in Figure 1a. The spectrum had three peaks at 400, 490, and 515 nm, and essentially the same spectra were observed in all solvents used in the absence of PhSH. Transient peaks observed at 400 and 515 nm have been similarly reported in benzene and assigned to the triplet-triplet (T-T) absorption of TBP by Das et al.²³ Time profiles of the transient absorption, A(t), observed at 400, 490, and 515 nm are shown in Figure 2. All A(t) curves observed at these wavelengths gave good agreements with an exponential fit ($k = (1.5-1.6) \times$ 10^6 s^{-1}). Thus those peaks are concluded to be the same origin and can be safely assigned to the T-T absorption of TBP.

With the analyses of A(t) curves observed in each solution, the lifetimes (τ) of triplet excited state of TBP (³TBP^{*}) were listed in Table 1 together with those of BP for comparison. The lifetimes of ³TBP* are found to be extremely longer than those of ³BP*. This difference can be explained by the less reactivity with a lower triplet energy of ³TBP* (166 kJ mol⁻¹) than that of ³BP* (³n π *, 290 kJ mol⁻¹). As shown in Table 1, τ of ³BP* observed in various mixtures of i-BuOH/c-HexOH shows little change with solvent viscosity, but τ of ³TBP* becomes longer with increasing solvent viscosity within experimental errors. Moreover, rate constant k (=1/ τ) for the decay of ³TBP* increases with increasing concentration of TBP as shown in Figure 3. These results indicate that the disappearance process of ³TBP* is not caused by the reaction with solvent molecules but is caused by self-quenching with its ground state. The self-quenching rate constant (k_{SQ}) in a 1/50 mixture of *i*-BuOH/*c*-HexOH ($\eta = 62$ cP) was estimated to be $3.2 \times 10^8 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$ form Figure 3. In the case of BP, ³BP* is considered to disappear by the reaction with solvent molecules. Although the A(t) curves observed in the SDS micellar solution show more complicated dependence with the concentration of TBP, ³TBP* is similarly quenched with its ground state and does not react with SDS micellar molecules. This lower reactivity of ³TBP* enables us to use the present system as a new MFE probe reaction in alcohols and micellar solution.

Reaction of ³TBP* with Thiophenol in Alcohols. To clarify the reactivity of ³TBP*, in the presence of thiophenol (PhSH, 1.0 \times 10⁻¹ mol dm⁻³), the laser flash photolysis was carried out in the 1/25 mixture of *i*-BuOH/*c*-HexOH. The spectra observed at delay times of 0.1, 0.5, 1.0, and 2.0 μ s after laser excitation are shown in Figure 1b. A strong T-T absorption of ³TBP* was observed at 515 nm. The decay of the T-T absorption accelerated with increasing concentration of PhSH. From the PhSH concentration dependence of the ³TBP* decay rate constant, the rate constants (\hat{k}) for the reaction between ³TBP* and PhSH have been determined to be $1.1 \times 10^7 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^{3.18}$ As shown in Figure 1b, transient absorption observed around 380 and 450 nm decayed much slower than those observed in the absence of PhSH. From our previous reports,²⁴ the transient absorption observed around 450 nm can safely be assigned to phenylthiyl radical (•SPh). On the other hand, we assigned the

Table 1.	Lifetime (τ) of T-T Absorption of TBP and BP in
Benzene,	Mixtures of <i>i</i> -BuOH/ <i>c</i> -HexOH, and an SDS Micellar
Solution	

		τ_{i}^{a} ns	
solvent	η , cP	³ TBP*	³ BP*
benzene	0.6	81	
3/1	7.4	230	56
2/3	17	330	37
1/3	26	480	37
1/25	50	660	29
1/50	62	620	32
SDS		820	450
^a The experimer	tal arrors of τ are w	ithin $\pm 4\%$	



Figure 3. Thiobenzophenone concentration dependence of the decay rate constant (k) of T-T absorption observed in a 1/50 mixture of *i*-BuOH/*c*-HexOH at 380 nm.

transient absorption observed around 380 nm to thiobenzophenone ketyl radical (TBPH•) for the following reasons: (1) The yields of the slower component observed at 380 nm increased with increasing concentration of PhSH,¹⁸ indicating that this band is ascribable to the species formed by the reaction of ³TBP* and PhSH; (2) a weak time-resolved EPR signal²⁵ with a relatively high g value (2.005) was measured; (3) a similar ketyl radical of benzophenone has a transient absorption band around 360 nm;²⁶ (4) the product analysis of the photochemical reaction of TBP in THF suggests the formation of thiobenzophenone ketyl radical.²⁷

From these results, we can safely describe the present photochemical reaction of TBP as follows:

 $TBP + h\nu(355nm) \rightarrow {}^{1}TBP^{*} \rightarrow {}^{3}TBP^{*}$ (1)

- ${}^{3}\text{TBP}^{*} + \text{TBP} \rightarrow \text{TBP} + \text{TBP}(\text{self-quenching})$ (2)
- ${}^{3}\text{TBP}^{*} + \text{PhSH} \rightarrow {}^{3}(\text{TBPH} \cdot \cdot \text{SPh})$ (3)

³(TBPH··SPh)
$$\xrightarrow{B}$$
 ¹(TBPH··SPh) (4)

- 1,3 (TBPH··SPh) \rightarrow TBPH· + ·SPh(escaped radicals) (5)
 - $^{1}(\text{TBPH} \cdot \cdot \text{SPh}) \rightarrow \text{recombination products}$ (6)



Figure 4. Time profiles of transient absorption observed at 380 nm in the absence and presence of a magnetic field of 15.5 T.



Figure 5. Magnetic field dependence on the relative radical yield (R(B)) of thiobenzophenone ketyl radical observed in *i*-BuOH at 380 nm. The red line shows a simulated curve obtained from the SLE analysis.

Here, ¹TBP*, ³TBP*, TBPH·, and ·SPh represent the singlet and triplet excited states of TBP, thiobenzophenone ketyl, and phenylthiyl radicals, respectively. ¹(TBPH··SPh) and ³(TBPH··SPh) denote the singlet and triplet RPs of TBPH· and ·SPh, respectively. Since the spin conversion process between triplet and singlet RPs (eq 4) can be affected by the magnetic field (*B*), MFEs on the yield of the escaped radical should be observed for the present reaction.

Magnetic Field Effects on the Reaction of ³TBP* with Thiophenol. In the presence of PhSH ($2.0 \times 10^{-1} \text{ mol dm}^{-3}$), A(t) curves were measured at 380 nm in solutions of varying viscosities ($\eta = 0.29-42.0 \text{ cP}$) under the magnetic fields of 0-15.5 T. The A(t) curves observed in *i*-BuOH ($\eta = 3.33 \text{ cP}$) in the absence and presence of a magnetic field of 15.5 T are typically



Figure 6. Solvent viscosity dependence of R(1.7T). The red line shows a simulated curve obtained from the SLE analysis.

shown in Figure 4. In all solutions, similar A(t) curves were observed. The A(t) curves observed in *i*-BuOH showed an exponential decay component ($\tau = 170 \text{ ns}$) for ³TBP* and almost constant component for TBPH·. We can see from this figure that the yield of escaped TBPH· decreased at 15.5 T. Similar MFE of the yield of escaped ·SPh at 1.7 T decreased by 4% was also observed in *i*-BuOH, although the intensity of the transient absorption of ·SPh at 450 nm was weak.

Next, we measured the magnetic field dependence of the MFEs under magnetic fields of 0-15.5 T. In the presence of PhSH in *i*-BuOH, the lifetimes of T-T absorption of TBP (³TBP^{*}) was obtained to be 170 ns. Thus the $A(3\mu s)/A(0\mu s)$ value is safely proportional to the escaped radical yield Y(B). The ratio $R(B) = Y(B)/Y(0T) = A(3\mu s, BT)/A(0\mu s, 0T)$ gives the relative radical yield of the escaped TBPH \cdot . The obtained R(B)values in *i*-BuOH are plotted against B in Figure 5. The R(B)value decreased with increasing B. Since the present reaction occurs through the triplet excited state ³TBP* (eq 3), the observed MFEs on the escaped TBPH· can safely be explained by the Δg mechanism (Δg M), which originates from the difference between the isotropic g factors of 2.005 for TBPH. and 2.0082^5 for \cdot SPh, together with the spin-orbital coupling (SOC) induced direct recombination.^{1-3,5} Details of the SOC induced direct recombination will be discussed later.

To clarify the viscosity dependence of the MFEs, the R(B) values were obtained in solutions of varying viscosities ($\eta = 0.29-42.0 \text{ cP}$) under a magnetic field of 1.7 T. In Figure 6, R(1.7 T) values are plotted against viscosities. The viscosity dependence on the R(1.7 T) values shows an inversion. R(1.7 T) decreased with increasing solvent viscosity in the range of $\eta \leq 3.33$ cP and then increased with increasing solvent viscosities of $22.2 \text{ cP} < \eta \leq 42.0$ cP, R(1.7 T) became 1.0 within experimental errors and the MFEs were completely quenched. This figure clearly shows that the MFEs observed in the present reaction were highly dependent on η . Since the simple diffusion model predicts the decrease of R(1.7 T) with increasing η and the saturation in highly viscous solvents, the observed MFEs cannot be explained by the simple diffusion model.^{21,28,29} Such dependence of MFEs on η can be

Scheme 1. Diffusion Model Associated with the SOC Recombination



explained by the strong SOC.⁵ In the present reaction of TBPH· and ·SPh, two heavy sulfur atoms should induce the strong SOC. In addition to the change in the isotropic *g*-values of TBPH· and ·SPh, this strong SOC causes the following spin dynamics in the RPs: (1) acceleration of spin relaxation by increasing anisotropy of the *g*-tensor, (2) acceleration of spin relaxation by enhancing spin rotational coupling, and (3) mediation of the recombination of triplet RPs.^{30–32} These three effects have been known to quench the MFEs on RPs containing heavy atoms.³⁰

As shown in Scheme 1, in the present reaction, the close RPs are produced with triplet spin multiplicity through the hydrogen abstraction reaction (eq 3). In those close RPs, the S and T states cannot mix because of their large exchange interaction. Radicals diffuse from the close RPs with a rate constant of k_{diff} , producing separated RPs. In the separated RPs, the S and T states are nearly degenerated and the S-T mixing is promoted by the ΔgM , the hyperfine coupling mechanism (HFCM), and spin relaxations. By diffusional motion of radicals, the separated RPs either escape to form escaped radicals or reform close RPs. In the absence of the SOC, the recombination occurs from only singlet close RPs with a rate constant of k_{rec} (eq 6). Therefore the MFEs on the yield of the escaped radicals can be observed.

The recombination reaction competes with the diffusional motion to form separated RPs. As η increased, the lifetime of the singlet close RPs increased, providing enough time to allow recombination. Thus the magnitude of MFEs increased with increasing η in the range of $\eta \leq 3.33$ cP. In the presence of the SOC, the triplet close RPs can also recombine with a rate constant of k_{SOC} .

$$^{3}(BPH \cdot SPh) \rightarrow recombination products$$
 (7)

If $k_{\text{SOC}} < k_{\text{rec}}$, in solvents of lower viscosity ($\eta \le 3.33 \text{ cP}$), the singlet RPs were the main species that proceeded to recombine, because close RPs had a short lifetime. As η increased, the lifetime of the close RPs increased, providing enough time to allow recombination from triplet RPs. Therefore, both singlet and triplet RPs recombined in highly viscous solutions (3.33 cP < η), leading to quenching of the MFEs.

Analysis of MFEs with the Stochastic Liouville Equation. MFEs observed in solutions of varying viscosities ($\eta = 0.29-42.0$ cP) can be qualitatively explained by the Δg M associated with the SOC recombination. To clarify the details of the mechanism, we performed the quantitative analysis on the observed MFEs by using the stochastic Liouville equation (SLE).^{33,34} The details of the SLE analysis are described in our previous paper.⁶ The SLE analysis includes the effects of spin-spin interactions, molecular

Table 2.	Parameters	Used for	the	SLE	Anal	ysis
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parameter		parameter	
J_0 , rad s ⁻¹	$-1 imes 10^{12}$ a	$k_{\rm SOC}$, s ⁻¹	$9 imes 10^9$ b
β , nm ⁻¹	20 ^a	$k_{\rm SR}$, s ⁻¹	$6\times 10^{6\ b}$
d _a , nm	0.4 ^{<i>a</i>}	g _a	2.005 ^c
d _b , nm	0.2 ^{<i>a</i>}	δg_{a}	0.006 ^b
<i>A</i> , mT	-0.4 ^{<i>a</i>}	g _b	2.0082 ^a
δA , mT	0.2 ^{<i>a</i>}	$\delta g_{ m b}$	0.02 ^a
$k_{\rm rec}$, s ⁻¹	5×10^{10} ^a		
Defense of ^b Ee	time to J for an the ST T		J I

"Reference 5. " Estimated from the SLE analysis. " Observed by the timeresolved EPR.

diffusion, recombination reactions, and spin relaxations. The spin Hamiltonian consists of the exchange interaction (J), the hyperfine interaction (A), and the Zeeman interactions caused by the magnetic field. The *J* gives the energy gap between the S and T states and is exponentially decayed with radical—radical distance (r) as follows:

$$J = J_0 \exp[\beta(r-d)] \tag{8}$$

where J_0 is a magnitude of the exchange interaction (J) at the closest distance d and β is an exponential falloff parameter. The radical diffusion, which is assumed to be simple Brownian motion, is treated with the finite difference technique and the mutual diffusion constant (D). D is represented as a sum of the diffusion coefficients D_a (for TBPH·) and D_b (for ·SPh). The diffusion coefficient for each radical is represented with the Stokes–Einstein equation as follows:

$$D_{\rm i}(\eta) = \frac{k_{\rm B}T}{6\pi\eta d_{\rm i}} \quad ({\rm i}={\rm a},{\rm b}) \tag{9}$$

where d_i is the radius of a radical and η is the solvent viscosity, respectively. As was reported previously,⁵ we need to introduce the correlation factor (γ) for the radical radius to account the slow molecular motion in RPs originating from the hydrodynamic and the solvent structure effects.

$$d_{i} = \gamma a_{i} \quad (i = a, b) \tag{10}$$

Here a_a and a_b are the radical radii expected from the transient grating technique. In this study, we used $a_a = 0.4$ nm and $a_b = 0.2$ nm for TBPH \cdot and \cdot SPh, respectively. d_a and d_b are radical radii that produce diffusion coefficients effective for the generation of the MFEs with the assumption of the simple Brownian motion. As was used in the previous study, we used the value of $\gamma = 3$ for the simulation of the MFEs observed in alcoholic solutions. The singlet RPs are recombined with the rate constant $k_{\rm rec}$ at the closest distance d, whereas the triplet RPs are recombined with the rate constant $k_{\rm SOC}$ at the closest distance d. The SLE analysis also includes the spin relaxations by anisotropy (δA) of the hyperfine interaction, anisotropies (δg) of the g-factors, and the spin rotational interactions. We assumed the rate ($k_{\rm SR}$) of the spin rotational relaxation is independent of the magnetic field, and the constant value of $k_{\rm SR}$ was used.

The parameters used for the SLE analysis are listed in Table 2. Compared with the previously studied BP and PhSH system,⁵ k_{SOC} , k_{SR} , and δg_{b} values were increased because of the increase of the heavy atom effects in the present photochemical system. The MFEs observed up to 15.5 T in *i*-BuOH and the viscosity



Figure 7. Time profiles of transient absorption observed at 380 nm in an SDS ($1.6 \times 10^{-1} \text{ mol dm}^{-3}$) micellar solution containing TBP ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) and PhSH ($2.5 \times 10^{-2} \text{ mol dm}^{-3}$) in the absence and presence of a magnetic field of 1.7 T.

dependence observed at 1.7 T are well-reproduced by the SLE analysis as shown in Figures 5 and 6. From the SLE analysis, we concluded that the observed MFEs are interpreted by the ΔgM and the quenching of the MFEs observed in the high-viscosity region is explained by the SOC mediated recombination from the triplet RPs. Moreover, large heavy atom effects by sulfur atoms are considered to give the relatively small magnitude of the MFEs in the present photochemical reactions systems.

Microviscosity of SDS Micellar Solution. $^3\mathrm{TBP}^*$ is rather inert to alcohols and SDS micellar solution, and MFEs on the hydrogen abstraction reactions of TBP with PhSH are extremely sensitive to the solvent viscosity. Thus the present reaction may be used as a new MFE probe reaction. Using this probe reaction, the microviscosity of SDS micellar solution was investigated. The A(t) curves were measured in SDS (1.6×10^{-1}) mol dm⁻³) micellar solution containing TBP (2.0×10^{-3} mol dm⁻³) and PhSH (2.5×10^{-2} mol dm⁻³) under magnetic fields of 0-1.7 T. A(t) curves observed at 380 nm in the absence and presence of a magnetic field of 1.7 T are typically shown in Figure 7. The observed A(t) curves have three decay components. The first component ($\tau = 12 \text{ ns}$) is ascribable to the decay of ³TBP* through the self-quenching of ³TBP* with the ground state of another TBP in an SDS micelle (eq 2). The second one ($\tau = 256$ ns) is ascribable to the hydrogen abstraction reaction of ³TBP* with PhSH in an SDS micelle (eq 3). The last component shows the dynamics of the escaped TBPH. As shown in Figure 7, no MFE was observed at 1.7 T. Moreover, any changes on R(B) were not observed under magnetic fields of 0-1.7 T. We, therefore, concluded that the MFEs on the present reaction of TBP with PhSH are quenched in the SDS micellar solution. The quenching of MFEs is explained by the SOC mediated recombination from the triplet RPs in high-viscosity solution. From the results of the viscosity dependence on the MFEs as shown in Figure 6, a microviscosity of SDS micellar solution is estimated to be larger than 22.2 cP, because no MFEs was observed in the SDS micellar solution. This result agrees with our recent report in which the microviscosity of SDS micellar



Figure 8. Magnetic field dependence on the relative radical yield (R(B)) of thiobenzophenone ketyl radical observed in Brij35 at 380 nm. The red line shows a simulated curve obtained from the SLE analysis.

Table 3. Cage Parameters Used for the SLE Analysis

parameters		parameters	
$D, m^2 s^{-1}$	3.4×10^{-9}	P _{esc}	3×10^{-3}
η , cP	3	R, nm	4 ^{<i>a</i>}
^a References 37	and 38.		

solution was estimated to be 25 cP by using another MFE probe reaction of BP. 35

In the case of SDS micellar solution, no MFE was observed for the present probe reaction of TBP and PhSH. Although it is difficult to determine the theoretical measurement limits for the MFE probe, the strong SOC induced by the two heavy sulfur atoms may cause the limitation of the probe and it is related with the parameters (g, δg , and k_{SOC}) of SLE analysis.

Microviscosity of Brij35 Micellar Solution. Since no MFE was observed in the SDS micellar solution, a similar experiment of the present reaction in Brij35 was also carried out. The A(t) curves were measured in Brij35 $(5.0 \times 10^{-2} \text{ mol dm}^{-3})$ micellar solution containing TBP $(1.0 \times 10^{-3} \text{ mol dm}^{-3})$ and PhSH $(1.0 \times 10^{-2} \text{ mol dm}^{-3})$ under magnetic fields of 0-1.7 T. The obtained R(B) values are plotted against *B* in Figure 8. The observed R(B) values increased steeply in the range of $0 < B \leq 0.06$ T and then gradually decreased with increasing *B* in the range of 0.06 T $< B \leq 1.7$ T.

The RP dynamics in micellar solution differs from that in homogeneous alcoholic solutions. Therefore using the cage model,³⁵ the SLE analysis was performed for the observed magnetic field dependence of R(B). The calculated results are plotted (red line) in Figure 8. The cage parameters used for the SLE analysis are listed in Table 3. In the present cage model, RPs are confined in a spherical cage with radius R.³⁶ At the boundary, RP escaped from the cage with the probability $P_{\rm esc}$. The $P_{\rm esc}$ value is defined as $k_{\rm out}/k_{\rm in}$, where $k_{\rm out}$ and $k_{\rm in}$ are the escape rate and reflection rate at the boundary of the cage, respectively. The parameters of D and η represent the diffusion coefficient and microviscosity in the vicinity of the RP. As shown in the figure,

the magnetic field dependence of R(B) is well-reproduced by the SLE analysis even in the lower field of 0–0.2 T. From these analyses, a microviscosity of Brij35 micellar solution is estimated to be 3 cP. Although the microviscosity of the SDS micellar solution is extensively reported, ^{9–13} there is little reported on the microviscosity of Brij35. Thus the present study demonstrated that the microviscosity of Brij35 micellar solution might be estimated using the MFE probe. From the results, complete quenching of the MFE in the SDS micellar solution may be explained by (1) larger microviscosity (>22 (this work) and 25 cP³⁵), (2) small micelle size (1.8 nm³⁵), and (3) small $P_{\rm esc}$ (1.2 × 10^{-4 35}). Such strong cage effects of SDS cause the frequent reencounters which occurred on the time scale of SOC relaxation, so this may explain why the MFE is so effectively quenched inside SDS micelles.

Finally, there is a problem clarifying the location of the probe molecule inside the micelle. Other probes for the microviscosity such as the fluorescence depolarization technique also have the same problem. In the present study, a simple cage model was used. Thus the observed microviscosity may be an averaged value in the diffusive regions of the two partners. Using the more refined cage model such as the solvent separated radical pair (SSRP) model, one can obtain the detail of microviscosities for the different regions. However such specialized study is beyond the scope of the present study for a demonstration of the MFE probe. Otherwise the present bimolecular reaction is considered to be a meaningful system, because the actual microviscosity which the molecule feels during the reaction may be observed. The MFEs are caused by the interaction between magnetic field and unpaired electron spins. Thus only microenvironments in the vicinity of the RP (in the range of several nanometers) can selectively be monitored by the present MFE probe.

CONCLUSION

Photochemical reactions of TBP with PhSH in alcoholic solutions and SDS and Brij35 micellar solutions were studied by a nanosecond laser flash photolysis. In alcoholic solutions, appreciable MFEs were observed and analyzed by the SLE. The MFEs observed up to 15.5 T and the viscosity dependence are well-reproduced by the SLE analysis. The MFEs can be explained by the Δg M together with the spin—orbital coupling induced direct recombination. These results indicate that the hydrogen abstraction reaction of TBP with PhSH is useful as a new MFE probe reaction. Using this probe reaction, it was demonstrated that microviscosities of SDS and Brij35 micellar solutions were estimated to be >22 and 3 cP, respectively.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mwakasa@chem.saitama-u.ac.jp.

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(25) The absorptive broad spectrum could be reproduced in every measurement and is not background drift. From the fact that the similar MFE was observed at 450 nm for \cdot SPh, the hydrogen abstraction reaction of TBP with PhSH is concluded to occur efficiently, forming thiobenzophenone ketyl radical (TBPH \cdot). The absorptive phase pattern on the observed time-resolved EPR spectrum may be ascribable to the thermal populating signal of TBPH \cdot , because the signal intensity did not change in the time range of $1-5 \,\mu s$.

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