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Microviscosity Dependence of Magnetic Isotope Effect on Radical Pair Decay Rates in SDS Micellar Solution

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The microviscosity dependences of the magnetic field and magnetic isotope effects on disappearance of radical pairs (RPs) comprising benzophenone ketyl and alkyl radicals were investigated in sodium dodecyl sulfate (SDS) micellar solutions. The increase in microviscosity of the SDS micelle by adding $MgCl_2$ caused not only a deceleration in the escape rate of the component radicals from the micelle but also a small magnetic isotope effect on the RP decay rate. The small magnetic isotope effect was explained by an increase in the correlation time of the radical motion, which is coupled with the anisotropic hyperfine interaction modulating the spin-lattice relaxation of RP.

Over the past two decades, magnetic field effects (MFEs) on photo-induced chemical reactions have been extensively studied,[1–10] and some mechanisms for MFEs have been already established.[1–7] Among them, the hyperfine interaction is well-known. In this mechanism, electron spins on photo-generated radical pairs (RPs) and biradicals are coupled with nuclear spins to induce MFEs on their lifetimes, followed by changes in yields of longer-lived intermediates and final products. Therefore, substitution of precursors of RPs and biradicals by magnetic isotopes, which have nuclear spins, results in magnetic isotope effects (MIEs) on their lifetimes.[3] In a recent study using high magnetic fields up to 14 T, we showed MFEs and their MIEs on lifetimes of biradicals generated by intramolecular hydrogen abstraction from isotope-substituted methylene-chain-linked benzophenone (BP) molecules (BP–O–$(CH_2)_n$–O–benzhydrol, n = 8, 10, and 12),[11] in which the formed biradicals consisted of two BP ketyl radicals ($BPH^\bullet$ s). In the biradical system, the large MIEs due to the anisotropic hyperfine interaction were measured even at 3 T, and the magnitude of the interaction was first evaluated and distinguished from the electron spin dipole-dipole interaction. On the other hand, to confirm MIEs at the high magnetic field in RPs generated in an intermolecular reaction system, we investigated the intermolecular hydrogen abstraction reaction of isotopic BPs in three kinds of micellar solutions.[12] The observed MFEs were strongly dependent on the kind of micelle, but attempts to detect MIEs failed in the previous experiment with a pulse magnet, though Hayashi and Nagakura had reported MIEs in the low concentration (0.08 mol dm^{-3}) of sodium dodecyl sulfate (SDS) at ≤ 1.34 T.[7,13] From comparing the two results between the above-mentioned biradicals and RPs, we concluded that the appearance of MIEs on their lifetimes was associated with physicochemical factors such as the inter-radical distance and microviscosity in their solvents. The effect of inter-radical distance was already suggested by Steiner's group to be important in RPs referring to the electron dipole-dipole interaction.[14] If the magnetic-isotope-independent dipole–dipole interaction is dominant, compared with that of the hyperfine interaction, it is easily imaginable that MIE becomes negligibly small. According to the theory,[5,11,13,15] the anisotropic hyperfine interaction is directly coupled with radical motions to modulate the spin-lattice relaxation (SLR) of RP, leading to a change in the RP lifetime. In other words, MIE due to the anisotropic hyperfine interaction is influenced by microviscosity of a solvent regulating a correlation time of the radical motion. Then, we here studied the effect of microviscosity of the SDS micelle on the lifetimes of RPs, which were formed by photo-induced hydrogen abstraction of BP from SDS, and elucidated the relation between MIE and microviscosity of the micelle. Microviscosity was changed by adding a divalent Mg^{2+}, which has already been known to enhance microviscosity of the SDS micelle.[16a] Exploring factors that optimize MIE is an important subject and will promote more efficient applications of MIE.

Experimental

Materials. Naturally-abundant benzophenone (^{12}C-BP) (Nacalai) was used after recrystallization by ethanol. [Carbonyl-^{13}C]benzophenone (^{13}C-BP) (ISOTEC, ^{13}C purity of 99%) was used as received. SDS (biological analysis grade, purity of > 99%), $MgCl_2$ (purity of > 98%), distilled water (HPLC grade), and 2-methylanthracene (purity of > 97%) were purchased from Nacalai and used without further purification. Concentrations of BPs and 2-methylanthracene in a 0.4 mol dm^{-3} aqueous SDS solution were 6.8×10^{-3} and 1×10^{-6} mol dm^{-3}, respectively. All SDS solutions were degassed by freeze-pump-thaw cycles to remove oxygen prior to laser-flash photolysis experiments.

Microviscosity. Values of microviscosity in 0.4 mol dm^{-3}

SDS solutions containing a variety of $MgCl_2$ concentrations (0, 0.05, and 0.1 mol dm^{-3}) were determined by fluorescence polarization measurements using 2-methylanthracene solubilized into the SDS solution as a fluorophore.[16a] The microviscosity relates directly to the degree of polarization by

$$(1/P-1/3)/(1/P_0-1/3)=1+kT\tau/(\eta v_0), \qquad (1)$$

where P is the degree of polarization at temperature T (293 K), k is the Boltzmann's constant, τ is a fluorescence lifetime of 2-methylanthracene, η is microviscosity, and v_0 is an effective volume (10^2 nm^3) of 2-methylanthracene.[16b] P_0 is the degree of polarization measured in an extremely viscous solvent and its value was taken from the literature ($P_0 = 0.2256$ measured in a rigid matrix of propylene glycol at 223 K).[16c] P was measured by a Hitachi 3010 fluorescence spectrophotometer. The fluorescence lifetime ($\tau = 3.5$ ns) remained constant regardless of the $MgCl_2$ concentration.

RP Lifetimes. RP lifetimes at 293 K in magnetic fields (0–13 T) were obtained by analysis of transient absorption decay profiles monitored at 548 nm, where the absorption was partly assigned to $BPH^{\bullet}$ composing RP.[17] A laser-flash photolysis apparatus equipped with magnets was described in detail elsewhere.[18] Briefly, the third harmonics ($\lambda = 355$ nm and fwhm = 4–6 ns) of a Nd : YAG laser (Spectra-Physics, GCR-11-1) was used for photoexcitation of BPs in the SDS solution. A conventional electric magnet (Tokin, SEE-10) was employed to determine the precise magnetic field intensity at < 1 T, whereas a homemade pulse magnet was employed at 0.1–13 T.

Results

Microviscosity. Because the anisotropic hyperfine interaction, one of the causes of MFEs on RP lifetimes, is directly coupled with radical motions, it is important to know and control the microviscosity of a site where RP is present in the micelle, for the purpose of optimizing MFEs and MIEs. $MgCl_2$ is known to increase microviscosity of SDS micellar solutions because of the positive divalent Mg^{2+} and the negative monovalent OSO_3^- of SDS.[16a] Table 1 lists values of microviscosity measured in 0.4 mol dm^{-3} SDS solutions with a variety of $MgCl_2$ concentrations (0, 0.05, and 0.1 mol dm^{-3}). From Table 1, it was found that (i) all of the values are > 10-times larger than those of typical organic solvents (normally less than 0.001 Ns m^{-2} (= 1 cP)), and (ii) $MgCl_2$ shows a trend to increase microviscosity of the micelle as the $MgCl_2$ concentration is increased. Although the concentration (0.4 mol dm^{-3}) of SDS in this work was larger than that in the literature,[16a,19] similar values of microviscosity were observed.

Table 1. Microviscosity of 0.4 mol dm^{-3} SDS Solutions with a Variety of $MgCl_2$ Concentrations

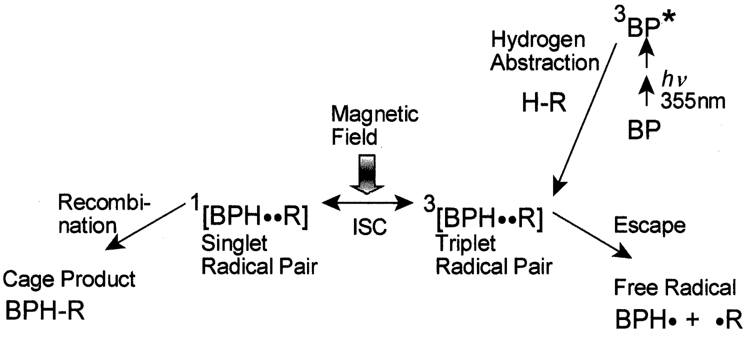
$MgCl_2$/mol dm^{-3}	Microviscosity$^{a)}$/Ns m^{-2}
0	0.0165
0.05	0.0256
0.1	0.0430

a) Experimental error was less than 8%.

MFE and MIE on the RP Lifetime. A reaction scheme for photoreduction and its succeeding processes of BP in an SDS solution is well-known, as shown in Scheme 1.[20] The excited triplet state ($^3BP^*$) of BP abstracts a hydrogen atom from a surfactant molecule (H-R) of SDS to form RP, comprising $BPH^{\bullet}$ and an alkyl radical ($^{\bullet}R$) generated on SDS in the micelle. The resulting triplet RP ($^3[BPH^{\bullet\bullet}R]$) in equilibrium with the singlet RP ($^1[BPH^{\bullet\bullet}R]$) deactivates to form free radicals ($BPH^{\bullet}$ and $^{\bullet}R$) from $^3[BPH^{\bullet\bullet}R]$ and cage products (BPH-R) from $^1[BPH^{\bullet\bullet}R]$, respectively. The magnetic field affects the processes among the triplet and singlet RPs to change both the RP lifetime and the yields of the free radicals and cage products.

As well as studies so far reported,[17,20] the laser-flash photolysis in this study also resulted in detection of a characteristic transient absorption band at 548 nm assigned to both $^3BP^*$ and $BPH^{\bullet}$, in which the latter is a component of both RP and the free radicals. Therefore, the RP lifetime and its MFE were obtained from the decay profiles observed at 548 nm, which obeyed a double exponential function.

Figure 1a shows the RP lifetimes in 0.4 mol dm^{-3} SDS solutions of ^{12}C- and ^{13}C-BPs and their magnetic field dependences in high magnetic fields up to 13 T in the absence of $MgCl_2$. The lifetimes in the respective BPs increased as the magnetic field increased, and remained almost constant at > 3 T. As for MIE, the lifetime in ^{13}C-BP was shorter than that in ^{12}C-BP in the magnetic field range from 0.04 to ca. 1.5 T, as shown in Fig. 1b and Table 2, while it was not experimentally distinguishable from that in ^{12}C-BP at > ca. 2 T. Table 2 compares the RP lifetimes and their MIEs in the low magnetic fields (≤ 2 T), which were measured using a conventional electric and a pulse magnets. In the case of a pulse magnet, it is not easy to generate an identical magnetic field repeatedly, if one considers the nature of the operating electric circuit of the apparatus. Therefore, it is hard to accumulate the transient absorption signal at the identi-



Scheme 1.

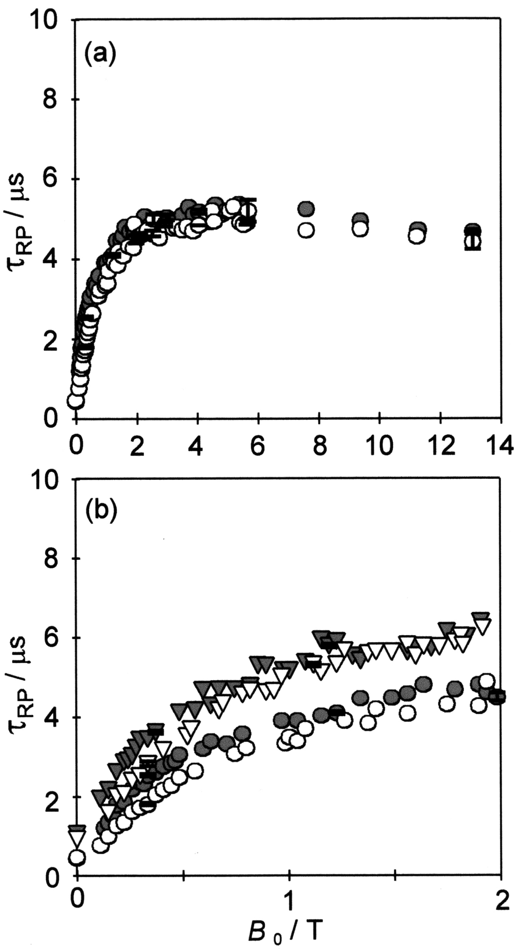


Fig. 1. Magnetic field dependences of RP lifetimes in 0.4 mol dm^{-3} SDS solutions of ^{12}C- and ^{13}C-BPs: ^{12}C-BP and [MgCl$_2$] = 0 mol dm^{-3} (●); ^{13}C-BP and [MgCl$_2$] = 0 mol dm^{-3} (○); ^{12}C-BP and [MgCl$_2$] = 0.1 mol dm^{-3} (▼); ^{13}C-BP and [MgCl$_2$] = 0.1 mol dm^{-3} (▽).

Table 2. RP Lifetimes (µs) in Low Magnetic Fields Obtained with a Conventional Electric and a Pulse Magnets

	Magnetic field/T												
Conventional Magnet	0[a]	0.04	0.07	0.1		0.2					0.5	0.93	
Pulse magnet					0.15		0.22	0.26	0.3	0.34			2
^{12}C-BP	0.36 ± 0.00	0.55 ± 0.01	0.79 ± 0.04	0.96 ± 0.02	1.4 ± 0.1	1.5 ± 0.0	1.9 ± 0.0	2.2 ± 0.1	2.4 ± 0.0	2.5 ± 0.1	2.6 ± 0.0	3.2 ± 0.1	4.5 ± 0.2
^{13}C-BP	0.37 ± 0.01	0.37 ± 0.02	0.49 ± 0.03	0.63 ± 0.02	1.0 ± 0.0	1.1 ± 0.0	1.4 ± 0.0	1.6 ± 0.1	1.7 ± 0.0	1.8 ± 0.1	2.1 ± 0.1	2.8 ± 0.1	4.6 ± 0.1

a) The values were measured at a residual magnetic field of 0.01 mT.

cal magnetic field. Especially, below 2 T where the RP lifetime varies sensitively according to the magnetic field (Fig. 1b), the repeated generation of the identical magnetic field is important in the signal accumulation in order to evaluate the accurate RP lifetime at the magnetic field. In our previous preliminary work,[12] we failed to detect MIE on the RP lifetime because we accumulated the signal within ± 5% fluctuation in the magnetic field intensity at the desired magnetic field (typically, 0.745–0.820 T at 0.782 T). In this work, therefore, we accumulated the signal at the definitely identical magnetic field and improved the accuracy in the RP lifetime. Furthermore, since the temperature of the sample solution is another important factor affecting the lifetime, the temperature was strictly controlled by removing the Joule's heat generated from the operating pulse magnet. Then, the accuracy in the lifetime improved so much that the standard deviation of the lifetime data became the same as that of the conventional magnet (Table 2), which produces an identical magnetic field constantly. Consequently, the standard deviation of the lifetime data decreased from 5% in the lifetime value in the previous study to 2% in this study on an average. As Hayashi and Nagakura observed in a lower SDS concentration (0.08 mol dm^{-3}),[13] our improved data with the pulse magnet showed clear MIE on the RP lifetime in the low magnetic field, suggesting the validity of using the data for evaluation of MIE in this study. On the contrary, above 3 T where the RP lifetimes were almost constant regardless of the magnetic field and thereby no hyperfine interaction responsible for MIE operated dominantly, the lifetimes obtained in both previous and present works are considered to be reliable enough for us to discuss MFE above 3 T.[12]

Dependence of the $MgCl_2$ Concentration on MFE and MIE. Figure 2 depicts the dependence of the $MgCl_2$ concentration on MFE on the RP lifetime in a 0.4 mol dm^{-3} SDS solution of ^{12}C-BP. In comparison with the absence of $MgCl_2$, the RP lifetime increased in each magnetic field with increasing the $MgCl_2$ concentration. The RP lifetime of ^{13}C-BP also showed the same trend (Fig. 1b). However, MIE on the RP decay rate decreased with increasing the $MgCl_2$ concentration, as will be discussed later in detail.

Discussion

MFE on the RP Lifetime and the Microviscosity Dependence. Based on previous studies,[12,18,21] the obtained magnetic field dependence, that the RP lifetime increased and subsequently remained almost constant as the magnetic field increased, is interpreted by the following three mechanisms: (a) the isotropic hyperfine interaction at < ca. 0.1 T, (b) SLR modulated by the anisotropic hyperfine interaction and the electron spin dipole–dipole interaction at ca. 0.1–3 T, and (c) the escape process of the component radicals of RP from the SDS micelle at > 4 T. Strictly speaking, the magnetic field dependences in Figs. 1a and 2 show negligibly small decreases at > 4 T, which seem to be due to the extremely weak anisotropic Zeeman interaction of the component radicals. However, the anisotropic Zeeman interaction was tentatively ignored because of its extremely small contribution in comparison with that of the escape process. This interpretation is also supported by the study of Hayashi's group,[10] in which the RP lifetime remained almost constant even in the higher magnetic fields of 16–29.6 T, where the anisotropic Zeeman interaction should become more effective than that at 13 T. If the anisotropic Zeeman interaction operated dominantly at > 4 T, the RP lifetime should apparently decrease as the magnetic field increases.

As shown in Fig. 3, the sublevels (T_{+1}, T_0, and T_{-1}) of the initially generated triplet RP are degenerate with each other at 0 T, while the T_+ and T_- sublevels become apart energetically from the T_0 sublevel due to the Zeeman splitting in the presence of a magnetic field. In the mechanism (a), the intersystem crossing (ISC) rate, which is related to the isotropic hyperfine interaction of RP, from the triplet RP to the singlet RP is suppressed by the Zeeman splitting of the T_+ and T_- sublevels from the T_0 sublevel to induce an increase in the RP lifetime. At higher magnetic fields, since the Zeeman splitting is sufficient energetically, SLR in the mechanism (b) comes to play an important role in the RP lifetime. At ca. 0.1–3 T, in the case of RP without any heavy atoms, both the anisotropic hyperfine interaction due to each component radical and the dipole–dipole interaction due to RP modulate the SLR transitions ($T_+ \leftrightarrow T_0$, $T_+ \leftrightarrow S$, $T_- \leftrightarrow T_0$, and $T_- \leftrightarrow S$) to induce an increase in the RP lifetime along with the magnetic field. In the mechanism (c) at > 4 T, the escape rate of the component radical from the SDS micelle mostly limits the RP lifetime in place of the two mechanisms ((a) and (b)). This is because the presence of RP is essential for these two mechanisms.

The escape rate constants (k_{esc}s) in a variety of $MgCl_2$ concentrations were obtained by reciprocals of the mean RP lifetimes, which were averaged using all of the RP lifetimes from 4 through 13 T (Table 3). The value of k_{esc} ($(1.97 \pm 0.10) \times 10^5$ s^{-1}) at 0 mol dm^{-3} $MgCl_2$ was obtained to be very close to those ($(1.9–2.1) \times 10^5$ s^{-1}) obtained in other studies.[22] $BPH^\bullet$ composing RP dissolves inside the micelle in the heterogeneous micellar solution. Therefore, the behavior of $BPH^\bullet$ should be discussed by taking into account the influence not of macroscopic viscosity of the micellar solution but of microviscosity of the micelle. Hydrophobic 2-methylanthracene as a microviscosity probe is considered to give microviscosity of a hydrophobic site close to the micellar core rather than that of an outer site (a so-called Stern layer) of the micelle where $BPH^\bullet$ dissolves. Hence, the obtained values of microviscosity may not practically reflect absolute values for the dissolving site of $BPH^\bullet$.

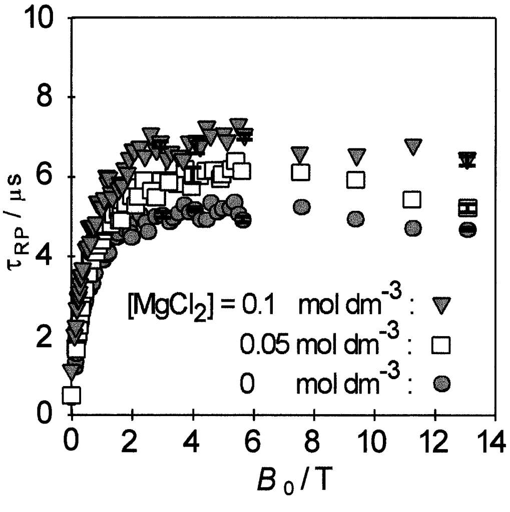


Fig. 2. Magnetic field dependences of RP lifetimes in 0.4 mol dm^{-3} SDS solutions of ^{12}C-BP with a variety of $MgCl_2$ concentrations.

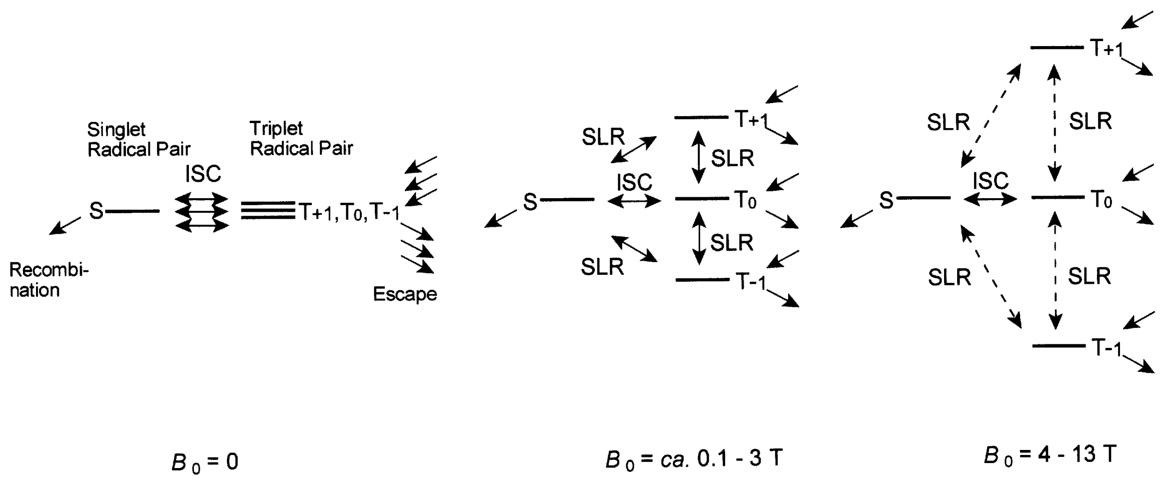


Fig. 3. A schematic energy diagram of singlet level (S) and triplet sublevels (T_{+1}, T_0, and T_{-1}) of RP in the absence and presence of the magnetic field (B_0). Solid and broken arrows show SLRs that are influential and uninfluential to RP lifetimes, respectively.

Table 3. Mean RP Lifetimes Averaged at > 4 T in SDS Solutions of ^{12}C-BP with a Variety of $MgCl_2$ Concentrations and Calculated k_{esc}

$MgCl_2$/mol dm^{-3}	Mean RP lifetime/μs	$k_{esc}/10^5$ s^{-1}
0	5.07 ± 0.25	1.97 ± 0.10
0.05	5.96 ± 0.34	1.68 ± 0.10
0.1	6.82 ± 0.34	1.47 ± 0.07

Table 4. Magnetic Field Dependences of $1/(k_{RP} - k_{esc})$ (μs) in SDS Solutions of ^{12}C-BP with a Variety of $MgCl_2$ Concentrations

$MgCl_2$/mol dm^{-3}	Magnetic field/T		
	0.63	0.97	1.2
0	10	17	21
0.05	12	21	35
0.1	12	22	44

However, judging from the fact that the observed increase in microviscosity results from the interaction of Mg^{2+} with the micellar surface, we can conclude that the Stern layer adjacent to the micellar surface will show the same trend in microviscosity toward the $MgCl_2$ concentration. In fact, the value of k_{esc} reasonably showed a decrease along with the increase in the $MgCl_2$ concentration, that is, the increase in microviscosity (Tables 1 and 3). This phenomenon may be understood by the enhanced hardness of the micelle and the enlarged micellar volume owing to the newly-generated ionic linkage between one Mg^{2+} cation and two OSO_3^- anions of two SDS molecules.[23] Thus, the values of microviscosity in this study were employed only for comparison among $MgCl_2$ concentrations in order to avoid influences arising from the differences between the dissolving sites of 2-methylanthracene and BPH$^•$ in the micelle.

On the other hand, the anisotropic hyperfine and dipole–dipole interactions inducing an increase in the RP lifetime are surely operative at ca. 0.1–3 T, as described above. In distinction from the effect of microviscosity on the escape process, the net effect on both the anisotropic hyperfine and dipole–dipole interactions can be obtained by subtracting k_{esc} from the observed RP decay rate constant (k_{RP}), which is a reciprocal of the observed RP lifetime (τ_{RP}). Table 4 shows that a relaxation time ($1/(k_{RP} - k_{esc})$) due to the anisotropic hyperfine and dipole–dipole interactions increases along with the $MgCl_2$ concentration, indicating that SLR modulated by the two interactions is also under influence of microviscosity. As a result of the above-mentioned decrease in k_{esc} in addition to the decrease in ($k_{RP} - k_{esc}$) on increasing the $MgCl_2$ concentration, there appears to be no detectable change among the magnetic fields showing the points of inflection in the three plots of the magnetic field dependence (Fig. 2). Since Mg^{2+} is diamagnetic, the ion never seems to affect the RP lifetime significantly.[24] Since Cl^- is repulsive to OSO_3^- of SDS owing to the same negative charge, it is unlikely to exist close to RPs inside the micelle. Therefore, we concluded that the increase in microviscosity is responsible for the increase in $1/(k_{RP} - k_{esc})$. The net effect of microviscosity on the anisotropic hyperfine interaction will be estimated as the effect on MIE in the next section, whereas the net effect on the dipole-dipole interaction could not be estimated, as will be described later.

MIE on the RP Decay Rate and the Microviscosity Dependence. According to the theory,[5,11,13,15] the SLR transitions modulated by the anisotropic hyperfine interaction (the mechanism (b)) is directly associated with radical motions. Therefore, it is easily conceivable that changing microviscosity of the SDS micelle affects not only MFE but also MIE. Through the experiment of changing microviscosity, the microviscosity necessary for large MIE will become clear. In other word, the experiment would demonstrate that microviscosity is one of the important physicochemical parameters for MIE. Although the isotropic hyperfine interaction at < ca. 0.1 T (the mechanism (a)) is also associated with MIE, the magnetic field region below 0.1 T was excluded from an object for study because of the different origin of MFE from the mechanism (b) depending on the radical motions. Moreover, the mechanism (c) is relating to neither magnetic nor mass isotope effects. Therefore, the microviscosity effect on MIE was referred only to the SLR mechanism at 0.1–3 T (the mechanism (b)) in this study.

Theoretically, k_{RP} at the high magnetic field is expressed as[5,8,11]

$$k_{\mathrm{RP}} = 1/\tau_{\mathrm{RP}} = (1/2)\{k(\mathrm{BPH}^\bullet) + k(^\bullet\mathrm{R})\} + k(\mathrm{dd}) + k_{\mathrm{T}}, \quad (2)$$

where $k(\mathrm{BPH}^\bullet)$ and $k(^\bullet\mathrm{R})$ are the SLR rate constants governed by the anisotropic hyperfine interaction in each component radical, and $k(\mathrm{dd})$ is the SLR rate constant determined by the dipole-dipole interaction in RP. k_{T} is the rate constant for direct disappearance from the triplet RP sublevels, and consists mostly of the escape rates of the component radicals from the SDS micelle. Since the three terms of $k(^\bullet\mathrm{R})$, $k(\mathrm{dd})$, and k_{T} in the right-hand term of Eq. 2 are independent of the magnetic isotope of BP, the difference ($\Delta k_{\mathrm{RP}(13-12)}$) in the RP decay rate constants ($k_{\mathrm{RP}(13)}$ and $k_{\mathrm{RP}(12)}$) between $^{13}\mathrm{C}$-BPH$^\bullet$ and $^{12}\mathrm{C}$-BPH$^\bullet$ is explicitly denoted as

$$\begin{aligned}\Delta k_{\mathrm{RP}(13-12)} &= k_{\mathrm{RP}(13)} - k_{\mathrm{RP}(12)}\\ &= (1/2)\{k(^{13}\mathrm{C\text{-}BPH}^\bullet) - k(^{12}\mathrm{C\text{-}BPH}^\bullet)\}\\ &= (1/2)\gamma^2\{H_{\mathrm{loc}(13)}{}^2 - H_{\mathrm{loc}(12)}{}^2\}\tau_c/\\ &\quad (1+\gamma^2 B_0{}^2\tau_c{}^2)\\ &= (1/2)\gamma^2\Delta H_{\mathrm{loc}(13-12)}{}^2\tau_c/(1+\gamma^2 B_0{}^2\tau_c{}^2), \quad (3)\end{aligned}$$

where γ is the magnetogyric ratio of the electron on BPH$^\bullet$ and is assumed to be equal to that of a free electron, τ_c is a correlation time of tumbling Brownian motion of BPH$^\bullet$ for the anisotropic hyperfine interaction, B_0 is the external magnetic field intensity, and H_{loc} is a locally fluctuating magnetic field corresponding to the magnitude of the anisotropic hyperfine interaction. It is noteworthy that Eq. 3 expresses the contribution of only the anisotropic hyperfine interaction due to BPH$^\bullet$ and no contribution due to $^\bullet$R. The reciprocal of Eq. 3 is

$$\begin{aligned}1/\Delta k_{\mathrm{RP}(13-12)} &= 2\{1/(\gamma^2\Delta H_{\mathrm{loc}(13-12)}{}^2\tau_c)\\ &\quad + B_0{}^2\tau_c/\Delta H_{\mathrm{loc}(13-12)}{}^2\}. \quad (4)\end{aligned}$$

Therefore, τ_c and $\Delta H_{\mathrm{loc}(13-12)}$ for BPH$^\bullet$ are obtained from both the intercept $(1/(\gamma^2\Delta H_{\mathrm{loc}(13-12)}{}^2\tau_c))$ and the slope $(\tau_c/\Delta H_{\mathrm{loc}(13-12)}{}^2)$, when the data of $1/\Delta\, k_{\mathrm{RP}(13-12)}$ are drawn versus $B_0{}^2$.

Figure 4 shows the three plots of $1/\Delta k_{\mathrm{RP}(13-12)}$ versus $B_0{}^2$ in a variety of $\mathrm{MgCl_2}$ concentrations. It is found from Fig. 4 that a slope of the plot becomes steeper as the $\mathrm{MgCl_2}$ concentration increases. Taking into account the microviscosity in Table 1, this trend in the slope means the smaller $\Delta k_{\mathrm{RP}(13-12)}$ is in the more viscous SDS micelle, which leads to the important results that MIE on the RP decay rate depends on microviscosity and becomes larger in the less viscous SDS micelle. Although MIEs in biradicals so far studied were relatively large,[9,11] the relation between MIE and microviscosity obtained above might explain the large MIEs in biradicals in the non-viscous organic solvents used.

The important point to note here is that the increase in microviscosity increases the RP lifetime (τ_{RP} in Fig. 2), but nevertheless decreases MIE in the RP decay rate ($\Delta k_{\mathrm{RP}(13-12)}$), as described above. The former increase means the effect of microviscosity on τ_{RP} itself, which is regulated by the anisotropic hyperfine and dipole–dipole interactions, whereas the latter decrease means the effect on the difference between the anisotropic hyperfine interactions of $^{13}\mathrm{C}$-BPH$^\bullet$ and $^{12}\mathrm{C}$-BPH$^\bullet$.

When Eq. 4 was applied to all the data in Fig. 4, all the variables (three τ_cs for the three $\mathrm{MgCl_2}$ concentrations and $\Delta H_{\mathrm{loc}(13-12)}$) were evaluated through the global analysis with the least-square fitting method. $\Delta H_{\mathrm{loc}(13-12)}$ and each τ_c were varied during the fitting routine so as to reproduce the three plots in Fig. 4 simultaneously. $\Delta H_{\mathrm{loc}(13-12)}$ was determined as a value commonly used for the three plots since it was considered independent of microviscosity. As for $\Delta H_{\mathrm{loc}(13-12)}$, the obtained

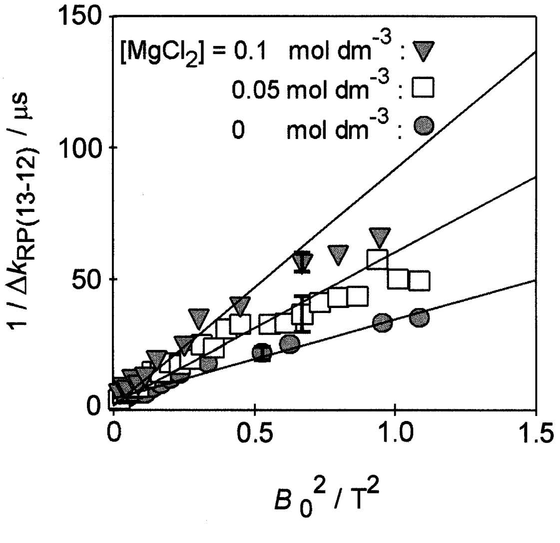


Fig. 4. Plots of $1/\Delta k_{\mathrm{RP}(13-12)}$ versus $B_0{}^2$ in a variety of $\mathrm{MgCl_2}$ concentrations.

value of $(10 \pm 0) \times 10^{-4}$ T was very close to that in methylene-chain-linked biradicals of BPH$^\bullet$–O–$(CH_2)_n$–O–BPH$^\bullet$ both experimentally $((6.3–8.3) \times 10^{-4}$ T) and theoretically $(9.3 \times 10^{-4}$ T).[11] The obtained τ_c values were tabulated in Table 5. The τ_c value at 0 mol dm^{-3} $MgCl_2$ was identical with that in the previous study.[18] At each magnetic field, Eq. 4 mathematically gives another answer for τ_c, which affords the identical relaxation time $(1/\Delta k_{RP(13-12)})$. Concretely, they are calculated to be 2.2, 1.1, and 0.72 ps in 0, 0.05, and 0.1 mol dm^{-3} $MgCl_2$ concentrations, respectively, when $\Delta H_{loc(13-12)} = 10 \times 10^{-4}$ T and $B_0 = 1$ T. However, those values showed a decrease against the increase in microviscosity. Based on a proportional relation between τ_c and microviscosity, as will be described next, the combination of those values was excluded in this study.

If the radical motion in the micelle obeys the hydrodynamics theory of Stokes–Einstein–Debye, the rotational correlation time (τ_c') is expressed as

$$\tau_c' = \eta V/(kT), \qquad (5)$$

where η is microviscosity of the SDS micelle, and V is a radical volume of BPH$^\bullet$. Equation 5 denotes that τ_c' is proportional to η. In fact, the result in Table 5 demonstrates the relation of the increase from 15 to 45 ps in the correlation time in proportion to the increase from 0.0165 to 0.0430 Ns m^{-2} in microviscosity. Therefore, the obtained values of microviscosity were suitable to compare τ_c throughout a series of $MgCl_2$ concentrations, although the dissolving site of 2-methylanthracene as a microviscosity probe might be practically different from that of BPH$^\bullet$, as already described.

Taking into account the small MIE in high microviscosity, we see that the deceleration in the radical motion due to the high microviscosity is clearly responsible for the small MIE. Applying an overall volume of BPH$^\bullet$ into Eq. 5, we evaluated the correlation time (τ_c') for an overall rotational motion was > 1000 ps as a spheric radical. However, the value was too large to assign the obtained small τ_c (15 ps) to the overall rotational motion. In our previous studies,[8] we proposed two kinds of radical rotations as an origin of the small τ_c: ① anisotropic overall rotations around radical long and short axes of an ellipsoidal radical; ② local motions such as a phenyl rotation inside a radical framework. These rotations can theoretically afford a smaller correlation time, compared with that for an overall rotation of a spheric radical. In this study, however, the conception of the former anisotropic overall rotations could not actually account for the obtained small τ_c. Therefore, the latter local motion was here discussed for the small τ_c. In our previous study on an electron transfer reaction in an inclusion complex of a phenothiazine-viologen linked compound into cylclodextrin,[8a] we could point out that *one* of actual local motions, a butterfly motion in a phenothiazine ring, was responsible for such a small τ_c. Although the origin of the small τ_c obtained in this work can not exactly be denoted at present, an experimental result of the dielectric relaxation allows us to imagine the existence of a local motion with a rather small correlation time even in BPH$^\bullet$: the correlation time of diphenylamine in Nujol® at 313 K was reported to be 33.1 ps at 0.0653 Ns m^{-2}, which was explained by a local motion of an intramolecular rotation of phenyl rings around their C–N bonds.[25] The experiment presents an important result that the relaxation in a partially rotatable molecule can be controlled by the intramolecular rotation with a rather small correlation time even in the high viscosity. Also in the case of BPH$^\bullet$, therefore, such an internal rotation of phenyl rings, *one of some local motions actually existing in the radical*, seems to play an important role in the magnetic relaxation, since BPH$^\bullet$ is similar to diphenylamine in the structure, size, and conjugation. Although the viscosity of Nujol® reported in the literature was macroscopic and was not obtained by the same technique of the fluorescence polarization measurement using 2-methylanthracene as this study, the conversion of the correlation time in the dielectric relaxation to that in the magnetic relaxation is helpful to understand the smallness of the correlation time for the local motion even in the high viscosity: the correlation time (33.1 ps) in the dielectric relaxation corresponds to 11 ps (one third of 33.1 ps) in the magnetic relaxation in a rough approximation where the phenyl ring is regarded spheric.

Table 5. Microviscosity Dependence of τ_c

$MgCl_2$/mol dm^{-3}	Microviscosity/Ns m^{-2} a)	τ_c/ps
0	0.0165	15 ± 2
0.05	0.0256	29 ± 2
0.1	0.0430	45 ± 4

a) Cited from Table 1.

Strictly speaking, the observed data at higher B_0^2 in Fig. 4 appear to deviate from the calculated solid lines. Besides the experimental error of approximate 10%, the following might be a possible explanation of it. As discussed above, it is feasible to guess the presence of plural τ_cs, which are assignable to local motions in the partially rotatable radical and associated with the magnetic relaxation. In such a case, assuming that in one narrow range of B_0 one of the plural τ_cs participates in the actual SLR, it would be imaginable that the operating τ_c is replaced in other ranges of B_0. It is because the actual SLR is regulated by *such* τ_c *as satisfies the relation of* $\gamma^2 B_0{}^2 \tau_c{}^2 = 1$ *in Eq. 3 as much as possible, among several* τ_c*s attributable to the actual local motions and related to the magnetic relaxation.* As B_0 increases, it seems that the different τ_c comes into operation in turn and its value reduces according to the relation. If this is the case, it is understandable that the slope in Fig. 4 becomes more gentle with increasing B_0 (or B_0^2), as the slope is more gentle in the case of the smaller τ_c (the lower $MgCl_2$ concentration). Our previous results, that much smaller τ_cs (ca. 1 ps) assigned to local motions were obtained at much higher B_0 (~13 T) by analysis of the anisotropic Zeeman interaction modulating SLR,[8] may support this hypothesis of magnetic-field-dependent exchange of τ_c participating in SLR.

Finally, although we tried to estimate the net effect of microviscosity on the dipole-dipole interaction of RP by subtracting the effects on both the anisotropic hyperfine interaction and the escape rate, no valid effect was obtained in this work. This may originate from mutually opposite effects in the dipole-dipole interaction that a shortened inter-radical distance and a lengthened correlation time make the RP lifetime short and long, respectively, when microviscosity increases.

Summary

The microviscosity dependences of MFE and MIE on disappearance of RPs comprising $BPH^{\bullet}$ and $^{\bullet}R$ in SDS micellar solutions were investigated by the laser-flash photolysis equipped with a conventional electric and a pulse magnets. The increase in microviscosity gave rise to the small MIE on the RP decay rate, in addition to deceleration in the escape rate of the component radicals from the micelle. The small MIE was explained by the increase in the correlation time of the radical local motion in the viscous SDS solution. From such observations, it is concluded that lower microviscosity is necessary to get the larger MIE on the RP decay rate in 0.4 mol dm^{-3} SDS solution.

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