Magnetic field effects on the reaction of a triplet-born radical pair consisting of two equivalent sulphur-centre radicals under ultrahigh fields of up to 28 T

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A water-cooled pulsed magnet having a room temperature bore of diameter 20 mm was constructed. Magnetic field effects on a triplet sensitization reaction of \( p \)-aminophenyl disulfide (APDS) with xanthone (Xn) were studied in a sodium dodecylsulfate (SDS) micellar solution by a nanosecond laser flash photolysis technique under ultrahigh magnetic fields of up to 28 T. Upon irradiation of the SDS micellar solution containing APDS and Xn, triplet radical pairs of \( p \)-aminophenylthiyl radicals were generated. The yield of the escaped \( p \)-aminophenylthiyl radical was found to decrease by 6 ± 2% at 28 T compared with that at 0 T.

1. Introduction

Magnetic field effects (MFEs) on chemical reactions of radical pairs and biradicals in fluid solution have been studied extensively during the last three decades [1, 2]. Moreover, recent advances in superconducting technology enable us to study not only the MFEs on chemical reactions [2, 3] but also new type MFEs in various applications (crystalline orientation control, magnetic separation of materials, magnetic levitation, and materials processing) [4]. It is, therefore, obvious that strong magnetic fields will play an important role in future developments in chemistry and materials science. However, almost all studies to date have been made at magnetic fields below 10 T. There have been only a limited number of studies of MFEs at fields above 10 T. In 1993, Tanimoto et al. reported MFEs on the reactions of biradicals under magnetic fields below 14 T with a pulsed magnet, which had a room temperature bore of diameter 16 mm [5]. In 1994, Steiner et al. studied MFEs on the reactions of Ru complexes under magnetic fields below 14 T with a pulsed magnet, which had a room temperature bore of diameter 16 mm [5]. In 1997, in order to measure short-lived reaction intermediates under ultrahigh fields (\( B \leq 17.5 \) T) [6]. In 1997, in order to measure short-lived reaction intermediates under ultrahigh fields (\( B \leq 30 \) T), we constructed a nanosecond laser flash photolysis apparatus with a pulsed magnet at NIMS [7].

Using this apparatus, we have studied MFEs on the photo-induced hydrogen abstract reactions of benzophenone in sodium dodecylsulfate (SDS) and Brij35 micellar solutions [8] and those of 4-methoxybenzophenone with thiophenol in alcohols [9, 10]. This apparatus was useful for measuring MFEs under ultrahigh fields [11, 12], but was dismantled in 2002.

MFEs on the reaction of \( p \)-aminophenyl disulfide (APDS) with xanthone (Xn) in an SDS micellar solution have previously been studied under magnetic fields of up to 10 T [13]. In this study, we found that the disappearance process of the triplet radical pair consisting of two equivalent \( p \)-aminophenylthiyl radicals showed appreciable MFEs. The yield of the escaped \( p \)-aminophenylthiyl radical increased steeply with increasing magnetic field from 0 T to 1 T, but decreased gradually as the field was increased from 1 T to 10 T. At 10 T, the yield of the escaped radical became similar to that at 0 T. Since the generated radical pair was composed of two equivalent radical (\( \Delta g = 0 \)) and the MFEs observed at both low (\( B \leq 1 T \)) and high (1 T < \( B \leq 10T \)) fields were simultaneously quenched by the addition of a paramagnetic Gd\(^{3+}\) ion, the observed MFEs could be explained by the relaxation mechanism (RM) through anisotropic hyperfine and Zeeman interactions. However, the magnetic field dependence of the escaped radical yields observed in the high-field region shows no asymptotic dependence. This means that the escaped...
radical yields may continually decrease under higher fields ($10 \text{T} < B$). Such anomalous inversion of the MFEs cannot be explained by the ordinary RM.

In order to clarify the behaviour of MFEs due to the RM under magnetic fields above 10 T, we reconstructed the nanosecond laser flash photolysis apparatus with a newly designed magnet, a water-cooled Bitter-type pulsed magnet, at Saitama University. Using this apparatus, we studied MFEs on the triplet sensitization reaction of APDS with Xn in an SDS micellar solution under ultrahigh fields of up to 28 T. We found inversion of MFEs on the yield of the escaped radicals. In this paper, we present a full description of the work, some of which was reported in a preliminary paper [14].

2. Experimental

2.1. Water-cooled pulsed magnet

In order to generate much higher fields than previously, a water-cooled pulsed magnet was constructed. The coil of the pulsed magnet is a Bitter-type made from an alloy of copper and silver. The pulsed magnet had a room temperature bore diameter 20 mm and a length of 160 mm. Pulsed magnetic fields were generated by supplying intense pulsed currents from a 10 mF condenser bank of 125 kJ (5 kV). The repetition rate of the discharge at an energy of 45 kJ (3 kV) was about 1 shot/3 min. This repetition rate was limited by water circulation for cooling the coils. Figure 1 shows the observed time profiles of the pulsed magnetic field and the spatial distribution of the magnetic field. Here, the magnetic field ($B$) was measured with a search coil. The maximum field was 32.2 T at 61.25 kJ (3.5 kV). Since the transient absorption is usually measured for 80 μs, we can use nearly constant fields (within ±0.1%) up to 32.2 T.

2.2. Laser flash photolysis apparatus

Figure 2 shows a schematic diagram of the laser flash photolysis apparatus with the pulsed magnet. Measurements of transient absorption were performed at 295 K by essentially the same method as described elsewhere [13, 15]. The sample solution was deoxygenated by bubbling with argon and pumping through a quartz cell (1 mL/min). The third harmonics (355 nm) of a Quanta-Ray GCR-130-10 Nd:YAG laser with a pulse width of 6 ns was used as an exciting light source. A double-beam probe system was used for measuring the transient absorption accurately. The probe light from a 500 W Xe arc lamp (Ushio UXL-500D) was divided into two beams. One of them was guided into the sample cell by a quartz optical fibre (3M FT1.0-UMT) and passed through a quartz cell. The other was detected directly. Each beam was guided into a photomultiplier (Hamamatsu R636-10) by the optical fibre.
2.3. Materials

*p*-aminophenyl disulfide (APDS, Tokyokasei Co.) was recrystallized twice from a 3:2 (v/v) mixture of toluene and pentane. Xanthone (Xn, Kanto Chemical) was recrystallized twice from ethanol. Sodium dodecylsulfate (SDS, Kanto Chemical) was recrystallized from a 1:1 (v/v) mixture of methanol and ethanol. Water was distilled and deionized. The concentrations of APDS, Xn, and SDS in the micellar solutions used were $5 \times 10^{-4}$, $1.0 \times 10^{-3}$, and $8.0 \times 10^{-2}$ mol dm$^{-3}$, respectively.

3. Results and discussion

3.1. Reaction scheme

The reaction scheme for the triplet sensitization reaction of *p*-aminophenyl disulfide (APDS) with xanthone (Xn) in a sodium dodecylsulfate (SDS) micellar can be represented as follows [13, 16]:

\[
\begin{align*}
Xn &\rightarrow^{	ext{hv}} 1Xn^* \rightarrow 3Xn^* \quad (1)
\\
3Xn^* + \text{APDS} &\rightarrow Xn + 3\text{APDS}^* \quad (2)
\\
3\text{APDS}^* &\rightarrow 3(\text{NH}_2\text{PhS}\cdots\text{PhNH}_2) \quad (3)
\\
3(\text{NH}_2\text{PhS}\cdots\text{PhNH}_2) &\rightarrow^B 1(\text{NH}_2\text{PhS}\cdots\text{PhNH}_2) \quad (4)
\\
3(\text{NH}_2\text{PhS}\cdots\text{PhNH}_2) &\rightarrow^c 2\text{NH}_2\text{PhS} \quad (\text{escaped radicals}) \quad (5)
\\
1(\text{NH}_2\text{PhS}\cdots\text{PhNH}_2) &\rightarrow^c \text{cage products} \quad (6)
\end{align*}
\]

Here, $1Xn^*$ and $3Xn^*$ represent the singlet and triplet excited states of Xn, respectively. $3\text{APDS}^*$ represents the triplet excited state of APDS. $1(\text{NH}_2\text{PhS}\cdots\text{PhNH}_2)$ and $3(\text{NH}_2\text{PhS}\cdots\text{PhNH}_2)$ denote the singlet and triplet radical pairs composed of two equivalent *p*-aminophenylthiyl radicals, respectively. With laser excitation of Xn, $3Xn^*$ is generated immediately (reaction (1)). A triplet–triplet (T–T) energy transfer occurs from $3Xn^*$ to APDS (reaction (2)). The succeeding decomposition giving $3(\text{NH}_2\text{PhS}\cdots\text{PhNH}_2)$ occurs through $3\text{APDS}^*$ (reaction (3)). This decomposition process was reported to be completed in less than 1 ps [17]. The triplet radical pairs can convert to the singlet pairs, and this process is affected by magnetic fields (reaction (4)). The triplet pairs can partially escape from the pair to form escaped radicals (reaction (5)). The singlet radical pairs react to form cage products (reaction (6)). Here, $k_E$ and $k_{CP}$ denote the rate constants for the escape of radicals from the pair and for the reaction from the singlet radical pair, respectively.

3.2. Transient absorption spectra

Laser flash photolysis was performed at 295 K on the SDS micellar solution containing APDS and Xn. Time profiles of the transient absorption ($A(t)$) were measured in the wavelength range 350–700 nm upon irradiation of the third harmonic (355 nm) of the Nd:YAG laser. The transient absorption spectra observed at delay times of 0.1, 2.0, and 5.0 μs after laser excitation are shown in figure 3. Here, the transient absorption peak due to the triplet–triplet (T–T) absorption of $3Xn^*$ was observed at
600 nm [18] and decayed very fast. Its decay rate was obtained to be $0.91 \times 10^6 \text{s}^{-1}$ ($\tau_T = 1.1 \mu\text{s}$). This result indicates that the T–T energy transfer from $^3\text{Xn}$ to APDS occurs effectively (reaction (2)). The transient absorption bands observed at delay time of 5 $\mu\text{s}$ after laser excitation can safely be assigned to $p$-aminophenylthiyl radical, by comparison with a previous report ($\lambda_{\text{max}} = 360$ and 580 nm) [19].

### 3.3. Magnetic field effects

Since Xn has an absorption band at around 350 nm, the monitoring light intensity at 360 nm was not enough to measure the $A(t)$ curves with a good S/N ratio. Therefore we measured the $A(t)$ curves of $p$-aminophenylthiyl radical at 560 nm, although the transient absorption at 560 nm overlapped the T–T absorption of $^3\text{Xn}$ ($\lambda_{\text{max}} = 600 \text{ nm}$). Typical $A(t)$ curves observed in the absence and presence of a magnetic field of 28 T are shown in figure 4. Although the magnitude of the MFEs observed at 28 T is not large, at most 6%, the effect is undoubted and very important for the study of MFEs on the chemical reactions under ultrahigh fields.

In the present reaction, the observed $A(t)$ curves should have three decay components. The first component corresponds to the decay of T–T absorption ($T(t)$), the second one to the radical pair decay ($RP(t)$) in the micellar cage, and the third one to the disappearance process of the escaped radical ($E(t)$). Thus, the decay of $A(t)$ curves can be represented as follows:

$$A(t) = T(t) + RP(t) + E(t)$$

(7)

According to the relaxation mechanism (RM) [2, 20], the time profiles of the radical pair decay $RP(t)$ in the absence and presence of a magnetic field are as follows.

**$B = 0 \text{T}$**

Case a ($k_{\text{CP}} \gg k_0$): $RP(t) = I_0 \exp[-(k_0 + k_E)t]$  \hspace{1em} (8)

Case b ($k_0 \gg k_{\text{CP}}$): $RP(t) = I_0 \exp[-(1/4)k_{\text{CP}} + k_E)t]$  \hspace{1em} (9)

**$B > 0 \text{T}$**

Case a ($k_{\text{CP}} \gg k_B$): $RP(t) = I_f \exp[-k_f t] + I_s \exp[-k_s t]$  \hspace{1em} (10)

Case b ($k_B \gg k_{\text{CP}}$): $RP(t) = I_f \exp[-k_f' t] + I_s \exp[-k_s t]$  \hspace{1em} (11)

where $k_f$, $k_f'$, and $k_s$ are given as follows:

$$k_f = k_R + 2k_R + k_E$$ \hspace{1em} (12)

$$k_f' = (1/2)k_{\text{CP}} + k_R + k_R' + k_E$$ \hspace{1em} (13)

$$k_s = k_R + k_R' + k_E$$ \hspace{1em} (14)
Here, $k_0$ and $k_R$ are the spin conversion rate constants in the absence and presence of magnetic fields, respectively. $I_0$, $I_f$ and $I_t$ are the initial populations of triplet sublevels, $[T_0]+[T_{+1}]+[T_{-1}]$, $[T_0]$, and $[T_{+1}]+[T_{-1}]$, respectively. $k_E$ and $k_{CP}$ should be independent of $B$ and those values in the present reaction have previously been observed for the direct excitation of APDS to be $5.2 \times 10^6$ and $4.8 \times 10^6 \text{s}^{-1}$, respectively [16]. On the other hand, the spin relaxation rates $k_R$ and $k'_R$ are influenced by $B$. Here, $k_R$ is the spin relaxation rate between $T_{+1}$ and $T_0$, $k'_R$ is that between $T_{+1}$ and $S$. Therefore, the MFEs should appear on $k_f$, $k'_f$ and $k_r$.

Usually, one can investigate the MFEs on the spin relaxation rates $k_R$ and $k'_R$ from the analysis of $A(t)$ curves. In the present study, however, the $A(t)$ curves observed at 560 nm are too complicated to analyse simply using equations (7)–(11). The complicated decay profiles are attributable to the contributions of (1) the T–T absorption of $^3\text{Xn}^*$, (2) the coincident generation of $p$-aminophenylthiyl radical with the decay of $^3\text{Xn}^*$, and (3) the unknown disappearance process of the escaped radical.

The MFEs on the yield of escaped $p$-aminophenylthiyl radical can be obtained without any complicated analysis of the $A(t)$ curves. The lifetime of the T–T absorption of $^3\text{Xn}^*$ is 1.1 $\mu$s, and the decomposition of $^3\text{APDS}^*$ is completed in less than 1 ps. Therefore, the formation of $p$-aminophenylthiyl radical is certainly completed at 4 $\mu$s after laser excitation. We can see that the $A(8 \mu$s, 560 nm) value is proportional to the yield of the escaped radical ($Y$). Thus the relative MFEs on the yield of the escaped radical are given by

$$R(B) = \frac{Y(B \text{T})}{Y(0 \text{T})} = \frac{A(B \text{T}, 8 \mu\text{s}, 560 \text{nm})}{A(0 \text{T}, 8 \mu\text{s}, 560 \text{nm})}$$

The observed $R(B)$ values are plotted in figure 5 together with those observed previously at fields below 10 T [13]. This figure shows that the $R(B)$ values increased steeply when increasing magnetic field from 0 T to 1 T, but decreased gradually as the field was increased from 1 T to 28 T. The $R(10 \text{T})$ value almost recovered to the value at 0 T. Finally, the $R(28 \text{T})$ value became $0.94 \pm 0.02$. It is noteworthy that such anomalous inversion of the MFEs has not yet been found in the reaction of a triplet-born radical pair composed of two equivalent radicals.

### 3.4. Mechanism of the magnetic field effects

MFEs on chemical reactions can be interpreted as radical pair and triplet mechanisms (RPM and TM) [1, 2]. According to the RPM, the MFEs are induced by the spin conversion between singlet and triplet radical pairs through the following mechanisms: (1) the $\Delta g$ mechanism ($\Delta g\text{M}$) which is due to the difference between the isotropic $g$-factors of the two radicals in a pair, (2) the hyperfine coupling mechanism (HFCM) due to the isotopic hyperfine interaction between electron and nuclear spins, (3) the relaxation mechanism (RM) due to the spin-spin dipolar interaction of radical pairs and the anisotropies in $g$-tensors ($\delta g$) and in hyperfine couplings ($\delta\text{HFC}$). In the present reaction, the triplet radical pair composed of two equivalent $p$-aminophenylthiyl radicals is generated and the $\Delta g$ value is zero. Therefore, the $\Delta g\text{M}$ can safely be excluded from the consideration. Moreover, since the MFEs due to the HFCM usually complete under a much lower field ($B < 0.1 \text{ T}$), the observed MFEs cannot be explained by the HFCM.

According to the RM [1, 20], the yield of the escaped radicals generated from the triplet-born radical pairs usually increases with increasing magnetic field in the low-field region ($0 < B \leq 2 \text{ T}$) by the deceleration of the spin conversion due to $\delta\text{HFC}$, and decreases again with increasing magnetic field to the high-field region ($B > 2 \text{ T}$) by the acceleration of the spin conversion due to $\delta g$. However, as shown in previous reports [5, 7, 8], the yield of the escaped radicals in the high-field region ($2 \text{ T} < B < 30 \text{ T}$) should not become smaller than that at 0 T. In the case of the ordinary RM (Case b in the previous section), the spin conversion at 0 T ($k_{\text{HFC}} = 10^9\text{–}10^9 \text{s}^{-1}$) is much faster than the reaction of a singlet radical pair ($k_{\text{CP}} = 10^3\text{–}10^5 \text{s}^{-1}$) and the
singlet and triplet states are degenerated [20]. Under such condition, the spin conversion in the high-field region cannot be affected by the acceleration \((k_B, k'_R = 10^{10} - 10^{11}\text{s}^{-1})\) due to \(\delta g\). Thus, the MFEs observed in the present study cannot be explained by the ordinary RM.

One possible explanation of the present MFEs is the RM together with slow spin conversion at 0 T \((k_{HFC} = 10^5 - 10^7\text{s}^{-1})\) (Case a in the previous section). The spin conversion at 0 T is caused by the isotopic tumbling motion of one radical around the other in micelle at a separation where two component radicals have dipole–dipole interaction. \(\tau_{AB}\) is the correlation time of the radical pair and concerned with tumbling motion of one radical around the other in micelle at a separation where two component radicals have dipole–dipole interaction. \(\tau_j\) is the correlation time of each component radical. In \(|V_{jj}|^2\), \(|V_{jHFC}|^2\), and \(|V_{3j}|^2\) of equations (19) and (20), only \(|V_{3j}|^2\) is strongly dependent on \(B\).

Since the many parameters in equations (19)–(20) have not yet been measured, the \(k_R + k'_R\) values were calculated using the following parameters: \(g^A = g^B = 2.01\) [13], \(\delta d^A/\mu_B B = \delta d^B/\mu_B B = 0.002\text{T}\) [13], \(\delta g^A = \delta g^B = 0.02\) [13], \(\tau_{AB} = 1.0 \times 10^{-10}\text{s}\) [8], \(\tau_A = \tau_B = 1.0 \times 10^{-12}\text{s}\) [8], and \(r_{AB} = 1.0\text{nm}\) [8]. In figure 6, \(\log (k_R + k'_R)\),

\[
\begin{align*}
V_{dd} & = \frac{2\tau_{AB}}{\omega^2 + 2\tau_{AB}} \quad (19) \\
V_{j} & = k^g_j + k^HFC_j \\
& = \frac{2\tau_j}{\omega^2 + 2\tau_j} + \frac{2\tau_j}{\omega^2 + 2\tau_j} \quad (20) \\
\omega & = \hbar \mu_B B
\end{align*}
\]

Here, \(|V_{dd}|^2\) is the average of the square of the matrix elements of the electron dipole–dipole interaction between radicals A and B. \(|V_{jHFC}|^2\) is that of \(\delta HFC\) on radical \(j\). \(|V_{3j}|^2\) is that of \(\delta g\) on radical \(j\). \(\tau_{AB}\) is the correlation time of the radical pair and concerned with tumbling motion of one radical around the other in micelle at a separation where two component radicals have dipole–dipole interaction. \(\tau_j\) is the correlation time of each component radical. In \(|V_{jj}|^2\), \(|V_{jHFC}|^2\), and \(|V_{3j}|^2\) of equations (19) and (20), only \(|V_{3j}|^2\) is strongly dependent on \(B\).

Here, \(k_{dd}\) is the rate constant for the inter-radical relaxation induced by the electron spin–spin interaction. \(k_j\) is the rate constant for intra-radical relaxation of radical \(j\). \(k_j\) is given by

\[
k_j = k^g_j + k^HFC_j
\]

Here, \(k^g_j\) and \(k^HFC_j\) are the rate constants of spin relaxation by the anisotropic Zeeman interaction and the anisotropic hyperfine coupling, respectively. Thus, the magnetic field dependence of \(k_R + k'_R\) can be calculated from the analytical forms of \(k_{dd}\) and \(k_j\) as follows [20]:

\[
\begin{align*}
& k_{dd} = \frac{|V_{dd}|^2}{\omega^2 + 2\tau_{AB}} \\
& k_j = k^g_j + k^HFC_j \\
& = \frac{|V_{jHFC}|^2}{\omega^2 + 2\tau_j} + \frac{|V_{j}|^2}{\omega^2 + 2\tau_j} \\
& \omega = \hbar \mu_B B
\end{align*}
\]

Figure 6. Calculated magnetic field dependence of the spin relaxation rates of \(k_R + k'_R\) and \(k_{dd} + k^HFC + k^HFC\) for a model radical pair having the following parameters: \(g^A = g^B = 2.01\), \(\delta d^A/\mu_B B = \delta d^B/\mu_B B = 0.002\text{T}\), \(\delta g^A = \delta g^B = 0.02\), \(\tau_{AB} = 1.0 \times 10^{-10}\text{s}\), \(\tau_A = \tau_B = 1.0 \times 10^{-12}\text{s}\), and \(r_{AB} = 1.0\text{nm}\).
dependence of the calculated $k_{dd} + k_{HFC}^{B} + k_{R}^{B}$, and $log (k_{A}^{d} + k_{HFC}^{d} + k_{R}^{d})$ values are plotted against $B$. The calculated $k_{R} + k_{R}'$ values showed clear $B$ dependence. In the present parameter set, the $k_{R} + k_{R}'$ value steeply decreased with increasing magnetic field in the low-field region ($B < 1$ T), but increased gradually in the high-field region ($1 \text{ T} < B \leq 30$ T).

Since the escaped radical yield at 0 T was found to be similar to that at 10 T, the spin conversion rate at 0 T ($k_{HFC}$) is considered to be same as the spin relaxation rate ($k_{R} + k_{R}'$) at 10 T. From figure 6, the $k_{HFC}$ value was estimated to be $1 \times 10^{7}$ s$^{-1}$. Using this value, we calculated the averaged isotropic HFC constant of the present radical to be 0.22 mT, which may be reasonable for $p$-aminophenylthiyl radical. This result indicates that the spin relaxation at fields above 10 T is faster than the spin conversion at 0 T if the spin conversion rates at 0 T is $1 \times 10^{7}$ s$^{-1}$ and the escaped radical yield observed at fields above 10 T should become smaller than that at 0 T. Thus, the observed MFEs on the escaped radical yield can be qualitatively reproduced by the magnetic field dependence of the calculated $k_{R} + k_{R}'$ value.

4. Conclusions

Using a newly constructed pulsed magnet and a nanosecond laser flash photolysis apparatus, we have studied the magnetic field effects (MFEs) on the triplet sensitization reaction of $p$-aminophenyl disulfide with xanthone in a sodium dodecylsulfate micellar solution under ultrahigh magnetic fields of up to 28 T. Anomalous MFEs on the escaped $p$-aminophenylthiyl radical generated from the triplet radical pair were observed. The observed MFEs can be qualitatively explained by the RM together with slow spin conversion at 0 T. The spin relaxation rates were calculated using a defined parameter set. The magnetic field dependence of the calculated relaxation rate can reproduce the observed MFEs on the yield of escaped $p$-aminophenylthiyl radical.

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