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Reversion of Magnetic Field Effects Observed in the Reaction of a Triplet-Born Radical Pair Consisting of Two Equivalent Sulfur-Centered Radicals

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Magnetic field effects (MFEs) on the triplet sensitization of *p*-aminophenyl disulfide were investigated in a sodium dodecylsulfate (SDS) micellar solution by means of a nanosecond laser flash photolysis technique at high magnetic fields up to 10 T. The yield of the escaped (*p*-aminophenyl)thiyl radical increased steeply with increasing magnetic field strength (*B*) from 0 to 1 T, but decreased gradually from 1 to 10 T. At 10 T, the yield of the escaped radical became similar to that at 0 T. The MFEs observed at both low ($B \leq 1$ T) and high ($1 \text{ T} < B \leq 10 \text{ T}$) fields were simultaneously quenched by the addition of a paramagnetic Gd^{3+} ion. Thus, these reverted MFEs were interpreted by the relaxation mechanism through anisotropic hyperfine and Zeeman interactions.

Introduction

Magnetic field effects (MFEs) on the chemical reactions of radical pairs and biradicals in solution have been of great interest during the last two decades.^{1–3} We have hitherto made extensive studies of the effects on the dynamic behavior of radical pairs in the presence of magnetic fields below 1.5 T with conventional electromagnets. Recently, Sakaguchi et al. extended the maximum magnetic field of our laser flash photolysis apparatus to 10 T with a superconducting magnet.^{4,5} Using this apparatus, we have found anomalous reversions of MFEs at high fields in several reactions.^{6–9} For the photoreduction of some aromatic-carbonyl compounds in micellar solutions, the lifetime of radical pairs and the yield of escaped radicals increased with increasing magnetic field (*B*) at low fields, but decreased again with increasing *B* at higher fields. The reverse fields of such MFEs were dependent upon reaction systems. It is possible to explain such reversions of MFEs by the following two mechanisms:^{6–9} mechanism 1,^{6,7} a combination of the MFEs due to the hyperfine coupling (HFC)^{1–3} and relaxation¹⁰ mechanisms at low fields and the MFEs due to the Δg mechanism^{1–3} at higher fields; mechanism 2,^{8,9} the MFEs due to the relaxation mechanism through anisotropic hyperfine and Zeeman interactions.¹⁰

From the viewpoint of experiments, however, there had been no method to discriminate between similar MFEs due to mechanisms 1 and 2 until we recently noticed^{11,12} that the effect of paramagnetic ions could distinguish the reversion due to mechanism 1 from that due to mechanism 2. A paramagnetic ion can quench the MFEs due to the HFC and relaxation mechanisms,¹³ but it cannot quench the MFEs due to the Δg mechanism.¹¹ Thus, we have first shown that the reverted MFEs due to mechanisms 1 and 2 can experimentally be separated by the addition of a paramagnetic ion.^{11,12}

To date, the reversions of MFEs have been reported in many reactions of radical pairs^{8,9,12} and biradicals,^{14,15} but the Δg values of generated radicals of such systems are not completely 0. Here, Δg is the difference between the isotropic *g* values of

two component radicals in a radical pair. Thus, the contribution of mechanism 1 cannot be removed from the reversions of MFEs observed for such systems. It is, therefore, important to study MFEs of reactions involving two equivalent radicals. More recently, Sakaguchi⁵ has studied MFEs on a biradical involving two equivalent ketyl radicals under magnetic fields of 0–10 T and found a small reversion in its MFEs above 2 T, which can be explained by only mechanism 2.

In the previous papers,^{16,17} we carried out laser flash photolysis of *p*-aminophenyl disulfide in a sodium dodecylsulfate (SDS) solution and found that the disappearance process of the triplet radical pair consisting of two (*p*-aminophenyl)thiyl radicals showed an appreciable MFE. This reaction system also seems to be favorable for the investigation of the reverted MFEs due to only mechanism 2, because the Δg value of two equivalent (*p*-aminophenyl)thiyl radicals in the radical pair should be 0.

In this paper, we report on the reversion of the MFEs observed at high magnetic fields up to 10 T in the reaction of the radical pair including equivalent sulfur-centered radicals generated with the triplet-sensitized photodecomposition of *p*-aminophenyl disulfide in an SDS micellar solution at room temperature. To confirm the mechanism of the reversion, we also carried out the paramagnetic quenching of MFEs and a measurement of the anisotropic *g* values of the (*p*-aminophenyl)thiyl radical.

Experimental Section

Materials. *p*-Aminophenyl disulfide (APDS) was obtained commercially (Tokyokase Co.) and recrystallized twice from a 3:1 (v/v) mixture of benzene and pentane. Xanthone (Xn) was repeatedly recrystallized from ethanol and sodium dodecylsulfate (SDS) from a 1:1 (v/v) mixture of methanol and ethanol. For the paramagnetic quenching, $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Soekawa Chemical Co.) was used without further purification. Water was distilled and deionized.

Laser Flash Photolysis. Laser flash photolysis experiments in the absence and presence of a magnetic field were performed on an apparatus which was similar to that described elsewhere.^{4,5} Each nitrogen-bubbled SDS solution was circulated through a

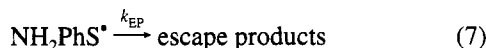
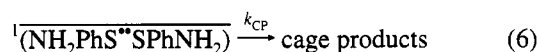
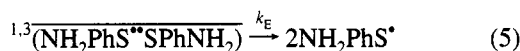
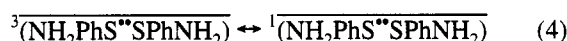
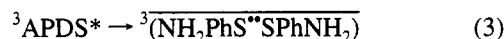
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quartz cell (1 mL/min). The third (355 nm) harmonic of a Quanta-Ray GCR-100 Nd:YAG laser with a pulse width of 5 ns was used as an exciting light source. The transient absorption was recorded by a Hewlett-Packard HP54522A digitizing oscilloscope with a time resolution of 0.5 ns. Magnetic fields (B) up to 10 T were provided by an Oxford 37057 superconducting magnet. To avoid the influence of its magnetic field, we set our photomultiplier far from the magnet and guided our probing light by a quartz optical fiber. We used a double-beam system for measuring the transient absorption accurately. Magnetic fields were measured by an F. W. Bell 9200 Gaussmeter with an FAR92-1815 probe. The lowest magnetic field generated by a counter current for canceling the residual field was less than 0.2 mT. Hereafter, the experiments under the lowest magnetic field are denoted as those in the absence of a magnetic field. The concentrations of APDS, Xn, and SDS in the employed micellar solution were 5.0×10^{-4} , 1.0×10^{-3} , and 8.0×10^{-2} mol dm $^{-3}$, respectively.

ESR Spectra. ESR spectra were taken on a JEOL-RE3X ESR spectrometer at -160 °C. Microcrystalline APDS was sealed in a quartz tube (ϕ 4 mm) under argon atmosphere. The irradiation of the sample was carried out using a Xe lamp (USHIO Electric Co., Type UXL-500D). The g values were determined with the Mn $^{2+}$ /MgO signals observed simultaneously.

Results and Discussion

In the triplet sensitization reaction of *p*-aminophenyl disulfide (APDS) with xanthone (Xn) in an SDS micellar solution, the following reactions are believed to occur:^{16,17}



Here, ${}^1\text{Xn}^*$ and ${}^3\text{Xn}^*$ represent the singlet and triplet excited states of xanthone, respectively. ${}^1(\text{NH}_2\text{PhS}^*\text{SPhNH}_2)$ and ${}^3(\text{NH}_2\text{PhS}^*\text{SPhNH}_2)$ denote the singlet and triplet radical pairs composed of two equivalent (*p*-aminophenyl)thiyl radicals (NH_2PhS^*), respectively. k_E , k_{CP} , and k_{EP} denote the rate constants for the escape of radicals from the radical pair, for the reaction from the singlet radical pair, and for the reaction from escaped radicals, respectively. Since the exciting light was mainly absorbed by Xn, ${}^3\text{Xn}^*$ should immediately be generated after laser excitation. The triplet-triplet (T-T) energy transfer occurs from ${}^3\text{Xn}^*$ to APDS. Since the concentration of micelles was 1.2×10^{-3} M, nearly half of the micelles which were occupied by Xn did not contain APDS. Therefore, both intramicellar and intermicellar T-T energy transfers should occur in the present case. The succeeding decomposition giving the triplet radical pair of the (*p*-aminophenyl)thiyl radicals occurs through ${}^3\text{APDS}^*$. This decomposition process was reported to be completed in less than 1 ps.¹⁸

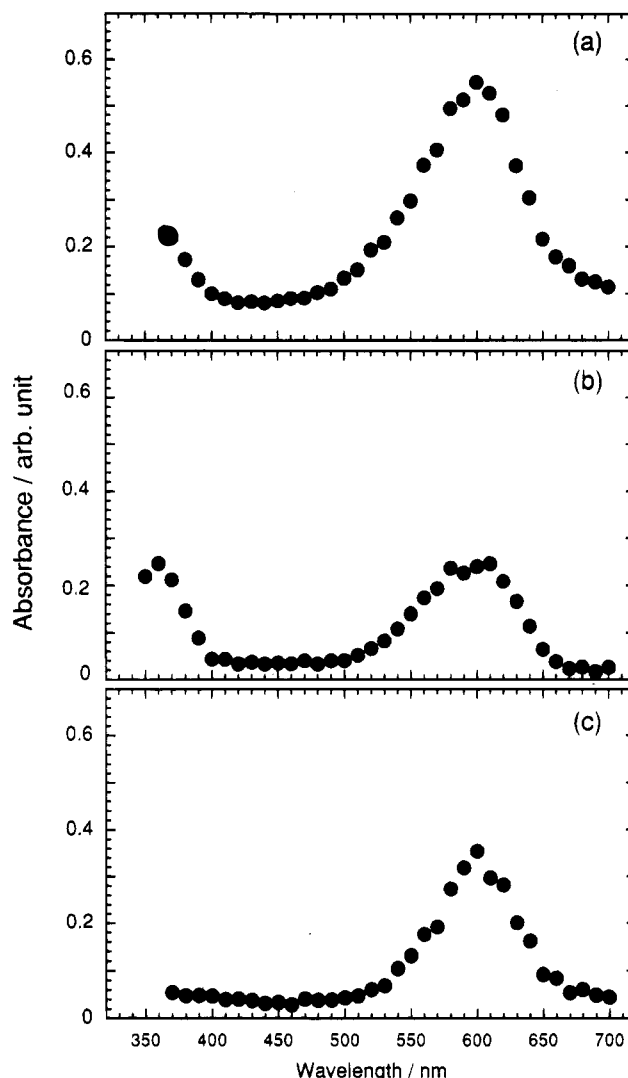


Figure 1. Transient absorption spectra observed at room temperature at a delay time of 100 ns after laser excitation of the SDS micellar solutions containing (a) *p*-aminophenyl disulfide and xanthone, (b) only *p*-aminophenyl disulfide, and (c) only xanthone.

Laser flash photolysis was performed at room temperature on the SDS micellar solution containing APDS and Xn. Time profiles of the transient absorption ($A(t)$) were measured in the wavelength range 370–700 nm upon irradiation with the third harmonic (355 nm) of the Nd:YAG laser. The transient absorption spectrum obtained at a delay time of 100 ns after laser excitation is shown in Figure 1a. For comparison with this spectrum, the spectra observed for the SDS solutions containing only (b) APDS and (c) Xn, respectively, are also shown in Figure 1. We can see from Figure 1b,c that NH_2PhS^* and ${}^3\text{Xn}^*$ have transient absorption bands around 360 and 580 nm (for NH_2PhS^*)¹⁶ and 600 nm (for ${}^3\text{Xn}^*$)¹⁹ respectively. Because ${}^3\text{Xn}^*$ has no clear absorption band around 360 nm and because the transient absorption band observed around 600 nm in Figure 1a is too strong to assign as only NH_2PhS^* , NH_2PhS^* and ${}^3\text{Xn}^*$ should be observed in Figure 1a.

NH_2PhS^* has two transient absorption bands around 360 and 580 nm, but the magnetic field dependence on $A(t)$ curves was measured at 380 nm in the magnetic field range $0 \text{ T} \leq B \leq 10 \text{ T}$, because the $A(t)$ curves observed at the longer wavelength region contain a large contribution from ${}^3\text{Xn}^*$. Some typical results obtained for the solution containing APDS and Xn at 380 nm are shown by curves a–c in Figure 2. The contribution of ${}^3\text{Xn}^*$ at 380 nm is also shown by curve d in Figure 2, which

was calculated from the following methods: (1) The decay profile of $^3\text{Xn}^*$ at 380 nm was taken to be the same as that observed for the SDS micellar solution containing APDS and Xn at 660 nm, where the signal intensity of $^3\text{Xn}^*$ is much larger than that of $p\text{-NH}_2\text{PhS}^*$. (2) The initial intensity of $^3\text{Xn}^*$ at 380 nm was estimated to be 0.56 times as small as that observed at 660 nm from the observed spectrum of $^3\text{Xn}^*$ (Figure 1c).

As shown in Figure 2, the $A(t)$ curves of NH_2PhS^* were appreciably changed by magnetic fields. The decay of NH_2PhS^* was decelerated with increasing B from 0 to 1.0 T, but was accelerated with increasing B from 1.0 to 10 T. At 10 T, the decay became similar to that at 0 T. Although we also measured $A(t)$ curves of the SDS micellar solution containing only Xn, no MEF was observed at 380 and 600 nm under magnetic fields of 0–10 T. The disappearance process of NH_2PhS^* generated with direct excitation gave no MFE,¹⁶ and the decay of $^3\text{Xn}^*$ did not show any changes by the fields. Therefore, MFEs observed in the reaction of NH_2PhS^* are attributable to the triplet radical pair involving two NH_2PhS^* .

In the case of a triplet radical pair, its $A(t)$ curves observed in a micellar solution usually have two decay components. The first component corresponds to the radical pair decay (RP(t)) in the micellar cage; the second one to the disappearance process of the escaped radical from the micelle. Therefore, the decay of $A(t)$ curves can be described by the following equation:^{1–3}

$$A(t) = \text{RP}(t) + I_E \exp(-k_{EP}t) \quad (8)$$

According to the relaxation mechanism,¹⁰ RP(t) of eq 8 can be represented as follows:

at $B = 0$ T

$$\text{RP}(t) = I_0 \exp(-k_0 t) \quad (9)$$

at $B \gg 0$ T

$$\text{RP}(t) = I_f \exp(-k_f t) + I_s \exp(-k_s t) \quad (10)$$

where k_0 , k_f , and k_s are given as follows:

$$k_0 = (1/4)k_{CP} + k_E \quad (11)$$

$$k_f = (1/2)k_{CP} + k_s \quad (12)$$

$$k_s = k_R + k_{R'} + k_E \quad (13)$$

Here, k_0 is the decay rate constant of the radical pair in the absence of a magnetic field, and k_f and k_s are the fast and slow ones in the presence of magnetic fields, respectively. I_0 , I_f , and I_s 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} are the rate constants of reactions 5 and 6, respectively. k_E and k_{CP} should be independent of B . For the present reaction, the k_E and k_{CP} values have previously been observed for the direct excitation of APDS and reported to be 5.2×10^6 and $4.8 \times 10^6 \text{ s}^{-1}$, respectively.¹⁷ Since the relaxation rates k_R and $k_{R'}$ are influenced by B , the MFEs should appear on both k_f and k_s . However, the measurement of the MFEs on k_f seems to be difficult, because the radical pair decay of this component is very fast. On the other hand, the MFEs on k_s have been observed and reported in many cases.

In eq 8, I_E and k_{EP} represent the yield of the escaped radical and its decay rate constant, respectively. In the present study, the $A(t)$ curves observed at 380 nm are too complicated to analyze simply using eq 8. The complicated decay profiles are

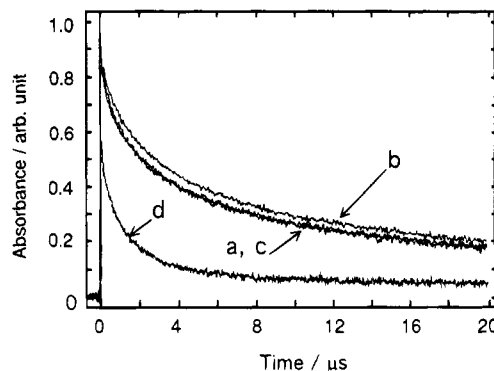


Figure 2. $A(t)$ curves observed at room temperature at 380 nm by triplet sensitization of the SDS micellar solution containing p -aminophenyl disulfide (a) in the absence and in the presence of a magnetic field: (b) 1.0 T and (c) 10 T. (d) $A(t)$ curve calculated for the T–T absorption of xanthone in this solution at 380 nm.

attributable to the contributions of (1) the T–T absorption of xanthone, (2) the transient absorption of NH_2PhS^* generated with direct excitation of APDS, and (3) the slow formation of NH_2PhS^* by the intermicellar T–T energy transfer. In the present reaction, therefore, we could not obtain exact k_0 , k_f , and k_s values. On the other hand, the MFEs on the yield of the escaped radical (I_E) can be obtained without complicated analysis.

The lifetime of the T–T absorption of Xn observed at 600 nm was about 1.5 μs (reaction 2), and the S–S bond was decomposed within 1 ps¹⁸ (reaction 3). Therefore, the formation of the (p -aminophenyl)thiyl radical seems to be certainly completed at 10 μs after laser excitation, but as seen from curve d in Figure 2, a small amount of the contribution of $^3\text{Xn}^*$ still remains in $A(10 \mu\text{s})$. Then, the contribution of $^3\text{Xn}^*$ at 380 nm was subtracted from the $A(t)$ curves as follows:

$$A'(t, 380 \text{ nm}) = A(t, 380 \text{ nm}) - 0.56A(t, 660 \text{ nm}) \quad (14)$$

Here, $A(t, 380 \text{ nm})$ and $A(t, 660 \text{ nm})$ represent the transient absorption observed at 380 and 660 nm, respectively, for the SDS micellar solution containing APDS and Xn at a delay time of $t \mu\text{s}$ after laser excitation. As mentioned above, the factor obtained was 0.56 from the initial intensities of $^3\text{Xn}^*$ at 380 and 660 nm.

Thus, we can safely consider that the $A'(10 \mu\text{s})/A'(0 \mu\text{s}) (=Y)$ ratio represents the relative yield of the escaped (p -aminophenyl)thiyl radical at $t = 10 \mu\text{s}$. This means that the $Y(B)/Y(0) (=R(B))$ ratio can give the MFE on the yield of the escaped (p -aminophenyl)thiyl radical. The plots of $R(B)$ against B are shown in Figure 3. The experimental error of $R(B)$ is within ± 0.02 . As clearly seen from these plots, the $R(B)$ value increases steeply with increasing B from 0 to 1 T, and the $R(1 \text{ T})$ value obtained was 1.11 ± 0.02 . On the other hand, the $R(B)$ value decreases more gradually with increasing B from 1 to 10 T. Finally, the $R(10 \text{ T})$ value almost recovered to the value at 0 T. Although the MFEs observed in the present reaction are not so large, the degree of reversion of the MFEs is the largest ever reported among the reactions of radical pairs^{8,9,12} and biradicals^{5,14,15} due to mechanism 2. In these reactions, their $A(t)$ curves observed above 10 T have not returned to the ones observed at 0 T.

To confirm the mechanism of the reverted MFEs of the present reaction, we carried out a quenching experiment using a paramagnetic ion. Since the quenching ability of the MFEs due to the relaxation mechanism had been found to be the largest for Gd^{3+} among the lanthanoid ions (La^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} ,

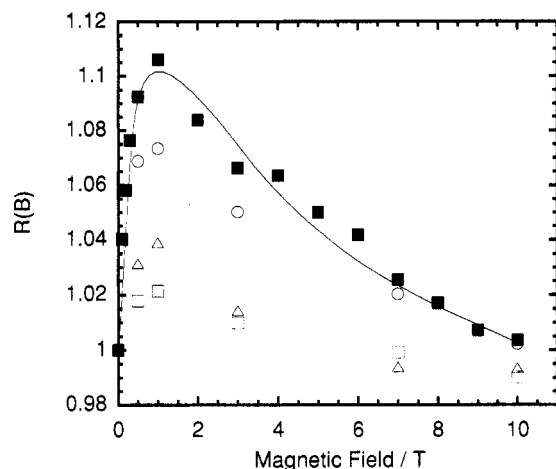


Figure 3. Magnetic field dependence of the ratio $R(B) = Y(B)/Y(0)$ observed at 380 nm by triplet sensitization of the SDS micellar solution containing *p*-aminophenyl disulfide (■) in the absence of Gd^{3+} and in the presence of Gd^{3+} : (○) 0.5×10^{-3} , (△) 1.0×10^{-3} , and (□) 2.0×10^{-3} M. The experimental error of $R(B)$ is within ± 0.02 .

Dy^{3+} , Ho^{3+} , Er^{3+} , and Lu^{3+} ,¹³ Gd^{3+} was used for a paramagnetic quencher in the present reaction. $A(t)$ curves were measured at 380 nm in the presence of Gd^{3+} under magnetic fields of 0–10 T, and the obtained $R(B)$ values were also plotted in Figure 3. We can clearly see from this figure that the MFEs observed in both low and high fields were simultaneously quenched by the addition of Gd^{3+} . In the previous papers,^{11,12} we have reported that a paramagnetic ion can quench the MFEs due to the relaxation mechanism but that it cannot quench the MFEs due to the Δg mechanism. Therefore, if the reverted MFEs observed in this reaction were ascribable to the relaxation and Δg mechanisms (mechanism 1), the MFEs in both low and high fields would not be simultaneously quenched.

The magnetic field effects of $R(B)$ observed for the triplet sensitization of APDS can be explained by the relaxation mechanism through the anisotropic hyperfine and Zeeman interactions (mechanism 2) by the following reasons: (1) the radical pair generated in the present study consists of two equivalent (*p*-aminophenyl)thiyl radicals and the Δg value is completely 0; (2) the MFEs observed in both low and high fields are simultaneously quenched by the addition of Gd^{3+} . In the present reaction, therefore, the contribution of the Δg mechanism was certainly removed from its reverted MFEs.

The magnetically induced increase of the escaped radical yield decreased in the high-field region. Although this decrease can be interpreted by the anisotropic Zeeman interaction, the doubtless principal values of the g tensor have not yet been reported for the unsubstituted and substituted phenylthiyl radicals. For the unsubstituted phenylthiyl radical (PhS^{\bullet}), the anisotropic g values were independently reported by Schmidt²⁰ and Zandstra.²¹ Schmidt et al. gave the values of $g_x = g_y (=g_{\perp}) = 2.003$ and $g_z (=g_{\parallel}) = 2.017$ in solid diphenyl disulfide at 77 K,²⁰ while Zandstra et al. reported the values of $g_{\perp} = 1.9982$ and $g_{\parallel} = 2.1246$, which agreed with a quantum chemical calculation.²¹ Although the isotropic g value of the (*p*-aminophenyl)thiyl radical was published with an inconsistency ($g_{iso} = 2.0078$ by Mörke et al.²² and $g_{iso} = 2.0055$ by McLauchlan²³), the anisotropic g values have not yet been reported. Thus, with irradiation of microcrystalline APDS at $-160^{\circ}C$, we carried out ESR measurements of its g anisotropy. Figure 4 shows the anisotropic ESR spectrum of the (*p*-aminophenyl)thiyl radical. As seen from this figure, the high-field feature is very simple and the $g_{\perp} (=g_x = g_y)$ value obtained is 2.002. On the other hand, the low-field part is so distorted

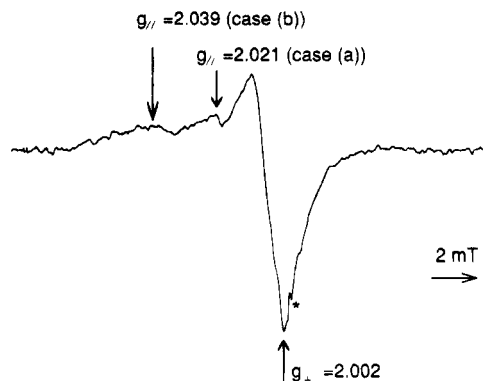


Figure 4. Anisotropic ESR spectrum of the (*p*-aminophenyl)thiyl radical observed with UV irradiation of microcrystalline *p*-aminophenyl disulfide at $-160^{\circ}C$. The g values were determined by the Mn^{2+}/MgO signals observed simultaneously. The signal denoted by * ($g = 2.001$) is due to the color center of an employed dewar.

by the signals due to the decomposition products that two ESR signals attributable to $g_{\parallel} (=g_z)$ are observed at $g_{\parallel} = 2.021$ and 2.039. From the viewpoint of experiments, we have no method to decide the correct g_{\parallel} value.

Using these g_{\parallel} values (case (a) $g_{\parallel} = 2.021$ and case (b) $g_{\parallel} = 2.039$), we estimated the relaxation rate constants (k_R and $k_{R'}$). Here, k_R and $k_{R'}$ correspond to the relaxation between $T_{\pm 1}$ and T_0 states and that between $T_{\pm 1}$ and S states, respectively. The k_R and $k_{R'}$ values can be calculated with a well-known transition probability ($P\langle T_{\pm 1}|\Gamma\rangle$).¹⁰

$$k_R = P\langle T_{\pm 1}|T_0\rangle \quad (15)$$

$$k_{R'} = P\langle T_{\pm 1}|S\rangle \quad (16)$$

Here, $P\langle T_{\pm 1}|\Gamma\rangle$ is represented as

$$P\langle T_{\pm 1}|\Gamma\rangle = \sum_i 2|V^i|^2 \tau_i / [(h/2\pi)^2 (1 + \omega^2 \tau_i^2)] + 2|V^{ab}|^2 \tau_{ab} \delta_{\Gamma T_0} / [(h/2\pi)^2 (1 + \omega^2 \tau_{ab}^2)] \quad (17)$$

where $\delta_{T_0 T_0} = 1$ and $\delta_{S T_0} = 0$. V^i and V^{ab} are the off-diagonal matrix elements between the $T_{\pm 1}$ and Γ states. V^i consists of the anisotropic parts of the Zeeman (δg^i) and the hyperfine (δa^i) tensors. V^{ab} is due to the electron spin–spin dipolar interaction between radicals a and b . τ_{ab} and τ_i are the rotational correlation times of the radical pair and each component radical. In this calculation, we consider the case where

$$\omega(h/2\pi) = |E_{T_{\pm 1}} - E_{T_0}| = |E_{T_{\pm 1}} - E_S| = (g^a + g^b)\beta B/2 \quad (18)$$

g^a and g^b are the isotropic g values of the component radicals, and β is the electric Bohr magneton. Now let us calculate $k_R + k_{R'}$ numerically with the aid of eqs 17 and 18. Since many parameters in these equations have not yet been measured, they are assumed adequately. The following parameters are fixed: $g^a = g^b = 2.01$,^{22–24} $\delta a^a/\beta B = \delta a^b/\beta B = 0.002$ T,⁸ $\tau_{ab} = 1.0 \times 10^{-9}$ s,¹⁰ $\tau_a = \tau_b = 1.0 \times 10^{-11}$ s,²⁵ and $r_{ab} = 0.6$ nm.⁸ Log($k_R + k_{R'}$) values obtained for case (a), $g_{\parallel} = 2.021$ ($\delta g^a = \delta g^b = g_{\parallel} - g_{\perp} = 0.019$), and case (b), $g_{\parallel} = 2.039$ ($\delta g^a = \delta g^b = g_{\parallel} - g_{\perp} = 0.037$), were plotted against B in Figure 5. Then, the k_s values were calculated by using $k_R + k_{R'}$, k_{CP} , and k_E and are also plotted in Figure 5.

As clearly seen from Figure 5, in each of cases (a) ($g_{\parallel} = 2.021$) and (b) ($g_{\parallel} = 2.039$), the $k_R + k_{R'}$ value showed a steep B dependence and a reversion of its MFEs was obtained. On the other hand, the $k_s (=k_R + k_{R'} + k_E)$ value showed a

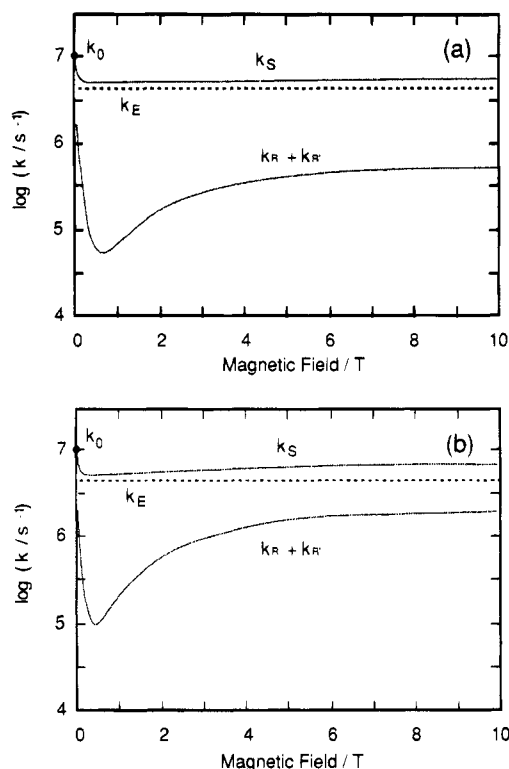


Figure 5. Magnetic field dependence of the rate constant of the spin relaxation ($k_R + k_{R'}$) and the radical pair decay ($k_s (=k_R + k_{R'} + k_E)$): (a) $g_{\parallel} = 2.021$, $g_{\perp} = 2.002$ and (b) $g_{\parallel} = 2.039$, $g_{\perp} = 2.002$. The other parameters are described in the text.

gradual B dependence, and the reversion of its MFEs was dependent upon g_{\parallel} values. In case (a), k_s is mainly determined by k_E , and the reversion of the MFEs at the high-field region is not clear, as shown in Figure 5a. In case (b), k_s is determined by the sum of k_R , $k_{R'}$, and k_E , and the reversion of the MFEs on k_s was obtained, as shown in Figure 5b. Similar results were obtained in the following parameter sets: (i) $\tau_{ab} = 1.0 \times 10^{-9}$ s, 1.0×10^{-12} s $\leq \tau_a (= \tau_b) \leq 5.0 \times 10^{-11}$ s; (ii) $\tau_a = 1.5 \times 10^{-11}$ s, 1.0×10^{-10} s $\leq \tau_{ab} \leq 1.0 \times 10^{-8}$ s; (iii) $\tau_{ab} = 1.0 \times 10^{-9}$ s, $\tau_a = \tau_b = 1.5 \times 10^{-11}$ s, 0.4 nm $\leq r_{ab} \leq 0.8$ nm. The other parameters are the same as written above. Since the reverted MFEs could not be reproduced using the g_{\parallel} value of case (a), we consider that case (b) might be better than case (a) for the g_{\parallel} value of the (*p*-aminophenyl)thiyl radical.

Finally, we simulated the MFEs on the yield (I_E) of the escaped radical using the parameter sets obtained above. From eqs 8–13, I_E can be represented as follows:

at $B = 0$ T

$$I_E(0 \text{ T}) = I_0 \frac{k_E}{k_0 - k_{EP}} \quad (19)$$

at $B \gg 0$ T

$$I_E(B \text{ T}) = I_f \frac{k_E}{k_f - k_{EP}} + I_s \frac{k_E}{k_s - k_{EP}} \quad (20)$$

If three sublevels of the triplet radical pair are equally populated, I_f and I_s are described as $I_f = (1/3)I_0$ and $I_s = (2/3)I_0$. In eq 20, k_f is much larger than k_{EP} and k_E . $k_E/(k_f - k_{EP})$ is much smaller than $k_E/(k_s - k_{EP})$. Thus, $I_E(B \text{ T})$ can approximately be represented as follows:

$$I_E(B \text{ T}) \approx \frac{2}{3} I_0 \frac{k_E}{k_s - k_{EP}} \quad (21)$$

Since k_{EP} is obtained as $< 10^4$ s $^{-1}$, the contribution of k_{EP} is negligible and the relative yield of the escaped radical ($R'(B)$) can be approximated as follows:

$$R'(B) = \frac{I_E(B \text{ T})}{I_E(0 \text{ T})} \approx \left(\frac{2}{3} I_0 \frac{k_E}{k_s} \right) / \left(I_0 \frac{k_E}{k_0} \right) = \frac{2k_0}{3k_s} \quad (22)$$

The calculated $R'(B)$ values are plotted against B in Figure 6. Applied parameters are $g^a = g^b = 2.01$, $\delta a^a/\beta B = \delta a^b/\beta B = 0.002$ T, and $r_{ab} = 0.6$ nm. $g_{\parallel} = 2.039$, $g_{\perp} = 2.002$, (a) $\tau_a = \tau_b = 2.0 \times 10^{-11}$ s, $\tau_{ab} = 1 \times 10^{-9}$ s, (b) $\tau_a = \tau_b = 2.0 \times 10^{-11}$ s, $\tau_{ab} = 5 \times 10^{-10}$ s, (c) $\tau_a = \tau_b = 2.0 \times 10^{-11}$ s, $\tau_{ab} = 2 \times 10^{-10}$ s, (d) $\tau_a = \tau_b = 2.0 \times 10^{-11}$ s, $\tau_{ab} = 1 \times 10^{-10}$ s, (e) $\tau_a = \tau_b = 1.5 \times 10^{-11}$ s, $\tau_{ab} = 1 \times 10^{-9}$ s, and (f) $\tau_a = \tau_b = 5.0 \times 10^{-11}$ s, $\tau_{ab} = 1 \times 10^{-9}$ s. In Figure 6, these $R'(B)$ curves are compared with the $R(B)$ curve obtained experimentally.

Figure 6 shows that the reversion of the MFEs on $R(B)$ can be reproduced fairly well by curves a–e and the parameter sets (a)–(e) are suitable for the description of the radical pair dynamics. Thus, we conclude that the present reversion of the MFEs on $R(B)$ is ascribable to the relaxation mechanism through the anisotropic hyperfine and Zeeman interactions. However, the observed $R(B)$ plots shown in Figure 6 cannot fully be explained by curves a–e. This may be mainly due to a too simple analysis of the radical pair decay by the model shown in eqs 8–13. For a more quantitative analysis of the present MFEs, one should use the stochastic Liouville equation^{26,27} including all necessary interactions, but this is beyond the scope of the present paper.

Conclusion

In the present study, MFEs on the triplet sensitization of *p*-aminophenyl disulfide are investigated in the SDS micellar solution at high magnetic fields up to 10 T, and the reversion of the MFEs on $R(B)$ is observed. To the best of our knowledge, this is the largest reversion of the MFEs due to the relaxation mechanism among the reactions of radical pairs and biradicals reported so far. Since the generated radical pair consists of two equivalent (*p*-aminophenyl)thiyl radicals, the contribution of the Δg mechanism is completely removed. Moreover, the MFEs observed at both low and high fields are simultaneously quenched by the addition of a paramagnetic ion. Thus, the reverted MFEs are interpreted by the relaxation mechanism through the anisotropic hyperfine and Zeeman interactions.

Two principal g values of the (*p*-aminophenyl)thiyl radical are measured, and the g_{\perp} value (2.002) and two possible g_{\parallel} values (2.021 and 2.039) are obtained. From the calculation of the relaxation rate (k_R and $k_{R'}$), the g values of the (*p*-aminophenyl)thiyl radical are considered to be $g_{\perp} = 2.002$ and $g_{\parallel} = 2.039$. Using these anisotropic g values and other parameters, the reverted MFEs on $R(B)$ can be reproduced fairly well. This result indicates that the mechanism of the reverted MFEs observed in the present study is ascribable to the relaxation mechanism through the anisotropic hyperfine and Zeeman interactions. Further studies of MFEs on the triplet sensitization of other substituted diphenyl disulfides in SDS micellar solutions under magnetic fields of 0–10 T are now in progress.

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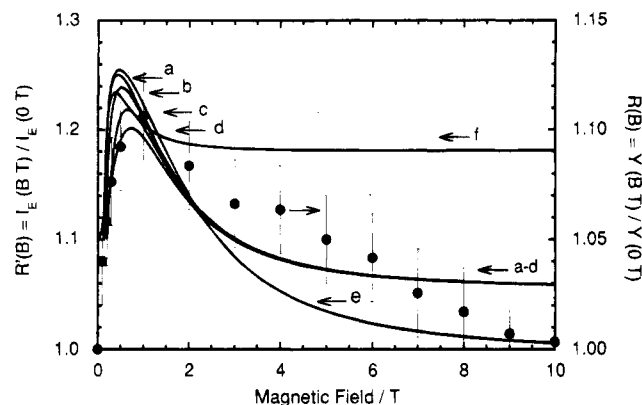


Figure 6. Magnetic field dependence of the calculated $R'(B)$ values. The simulation parameters are described in the text. The $R(B)$ values observed experimentally are also shown by filled circles (●). The experimental error of $R(B)$ is within ± 0.02 .

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