

Anomalous Magnetic Field Effects Interpreted by the Relaxation Mechanism under Ultrahigh Fields of up to 28 T

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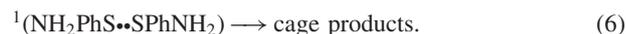
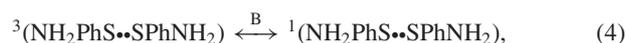
Magnetic field effects on the triplet sensitization reaction of *p*-aminophenyl disulfide were studied in a sodium dodecylsulfate micellar solution by a nanosecond laser flash photolysis technique under ultrahigh magnetic fields of up to 28 T. The yield of the escaped *p*-aminophenyl thiyl radical decreased by $6 \pm 2\%$ at 28 T compared with that at 0 T.

In the last three decades, much attention has been focused on magnetic field effects (MFEs) on chemical reactions of radical pairs and biradicals in solution.^{1,2} Moreover, recent advance in superconducting technology enables us to study new magnetic field effects in various applications, such as crystalline orientation control, magnetic separation of materials, magnetic levitation, and materials processing, under high magnetic fields (≤ 10 T).³ Extensive studies on the MFEs have hitherto been made below 10 T. On the other hand, there have been only a limited number of studies on the MFEs above 10 T.⁴⁻⁷ In 1997, we have constructed an ns-laser flash photolysis apparatus for measuring a transient absorption of short-lived reaction intermediates under magnetic fields above 10 T with a pulsed magnet at NIMS.⁵ Using this apparatus, we have studied the MFEs on photoinduced hydrogen abstract reactions of benzophenone in sodium dodecylsulfate and Brij35 micellar solutions⁶ and those of 4-methoxybenzophenone with thiophenol in alcohols.⁷ This apparatus had been sufficiently useful for measuring the MFEs under ultrahigh fields,^{8,9} but dismantled in 2002.

In 2004, we have reconstructed and improved the ns-laser flash photolysis apparatus with a pulsed magnet at Saitama University. In order to generate much higher field, a new water-cooled pulsed magnet which had a smaller room temperature bore with diameter of 20 mm and length of 160 mm was newly constructed. The maximum field was 32.2 T with 61.25 kJ. The repetition rate of the discharge at energy of 45 kJ was 1 shot/3 min. Measurements of transient absorption were performed at 295 K by essentially the same method as described elsewhere.^{6,7} The third harmonics (355 nm) of a Quanta-Ray GCR-130-10 Nd:YAG laser with a pulse width of 5 ns was used as an exciting light source. We used a double-beam probe system for measuring the transient absorption accurately. The probe light from a Xe arc lamp was divided into two beams. One of them was guided into the sample cell by a quartz optical fiber and passed through a quartz cell. The other was detected directly. Each beam was guided into a photomultiplier by the optical fiber.

Using this apparatus, we studied the MFEs on the triplet sensitization reaction of *p*-aminophenyl disulfide (APDS) with xanthone (Xn) in a sodium dodecylsulfate (SDS) micellar solution under ultrahigh magnetic fields of up to 28 T. The

concentrations of APDS, Xn, and SDS in the employed micellar solution were 5×10^{-4} , 1.0×10^{-3} , and 8.0×10^{-2} mol dm⁻³, respectively. The reaction scheme can be represented as follows:¹⁰⁻¹²



Here, ${}^1\text{Xn}^*$ and ${}^3\text{Xn}^*$ represent the singlet and triplet excited states of Xn, respectively. ${}^3\text{APDS}^*$ represents the triplet excited state of APDS. ${}^1(\text{NH}_2\text{PhS}\cdots\text{SPhNH}_2)$ and ${}^3(\text{NH}_2\text{PhS}\cdots\text{SPhNH}_2)$ denote the singlet and triplet radical pairs composed of two equivalent *p*-aminophenyl thiyl radicals, respectively. With laser excitation of Xn, ${}^3\text{Xn}^*$ is generated immediately. A triplet-triplet (T-T) energy transfer occurs from ${}^3\text{Xn}^*$ to APDS. The succeeding decomposition giving ${}^3(\text{NH}_2\text{PhS}\cdots\text{SPhNH}_2)$ occurs through ${}^3\text{APDS}^*$.

$\text{NH}_2\text{PhS}\cdot$ has a transient absorption band around 580 nm.¹⁰⁻¹³ The magnetic field dependence on the time profile of the transient absorption ($A(t)$) was carefully measured at 560 nm in the absence and presence of magnetic fields.¹⁴ Typically, the $A(t)$ curves observed at 0 and 28 T are shown in Figure 1. The decay of each $A(t)$ curve is composed of those of ${}^3\text{Xn}^*$,

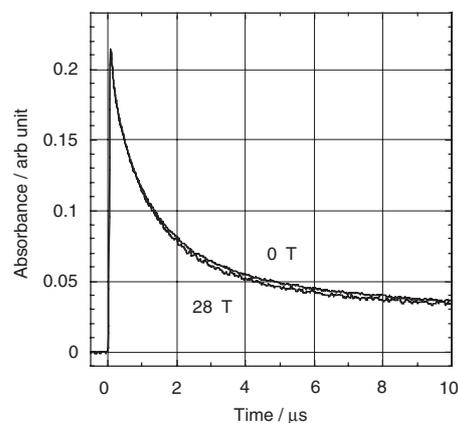


Figure 1. $A(t)$ curves observed at 560 nm in the absence and presence of a magnetic field of 28 T for a sodium dodecylsulfate (SDS) micellar solution containing *p*-aminophenyl disulfide and xanthone at 295 K.

$^{1,3}(\text{NH}_2\text{PhS}\cdot\cdot\text{SPhNH}_2)$, and escaped $\text{NH}_2\text{PhS}\cdot$.¹² As shown in Figure 1, the fastest decay component due to $^3\text{Xn}^*$ is unaffected by the magnetic field. On the other hand, middle decay component due to $^{1,3}(\text{NH}_2\text{PhS}\cdot\cdot\text{SPhNH}_2)$ is clearly affected by the field (eq 4). Thus, the yield of the escaped $\text{NH}_2\text{PhS}\cdot$ is also affected (eq 5). In the present study, the yields of the escaped $\text{NH}_2\text{PhS}\cdot$ decreased by $6 \pm 2\%$ at 28 T compared with that at 0 T. Although the magnitude of the MFEs observed is not so large at most 6%, the effects are undoubted and very important for the MFEs on the chemical reactions under ultrahigh fields.

From the present and previous¹² results, the magnetic field dependence can be summarized as follows: The yields of the escaped *p*-aminophenyl thiyl radical increased steeply with increasing magnetic field from 0 to 1 T, but decreased gradually from 1 to 28 T. At 10 T, the yield became similar to that at 0 T. Under much higher fields, the yields decreased with increasing magnetic field, producing a about 6% decrease at 28 T. Such anomalous MFEs have not yet been found in the reaction of triplet-born radical pair composed of two equivalent radicals.

MFEs on chemical reactions have generally been interpreted by the radical pair and triplet mechanisms (RPM and TM).^{1,2,15} According to the RPM, the MFEs are induced by the spin conversion between singlet and triplet radical pairs through the Δg , the hyperfine coupling, and the relaxation mechanisms ($\Delta g\text{M}$, HFCM, and RM). In the present reaction, a triplet radical pair composed of two equivalent *p*-aminophenyl thiyl radicals is generated and the Δg 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 much lower field ($B < 0.1$ T), the observed MFEs cannot be explained by the HFCM.

Next, consider the RM.^{1,16} The yield of the escaped radicals generated from the triplet radical pairs usually increases with increasing magnetic field under low field region ($0 < B \leq 2$ T) by the deceleration of the spin conversion due to anisotropic hyperfine couplings (δHFC), and decreases again with increasing magnetic field under high field region ($2\text{ T} < B$) by the acceleration of the spin conversion due to anisotropic *g*-tensors (δg). Moreover, as shown in the previous reports,^{4-6,17} the escaped radical yields at the high field region ($2\text{ T} < B < 30$ T) should not become smaller than those at 0 T. Therefore, the MFEs observed for the present study cannot be explained by the ordinary RM, in which the spin conversion at 0 T ($k_0 = 10^8\text{--}10^9\text{ s}^{-1}$) is much faster than the reaction of singlet radical pair ($k_p = 10^5\text{--}10^7\text{ s}^{-1}$). Under such condition, the spin conversion cannot be affected by its acceleration ($k_R, k_{R'} = 10^5\text{--}10^7\text{ s}^{-1}$) due to δg under high field region.

One possible explanation of the present MFEs is the RM together with slow spin conversion at 0 T ($k_0 = 10^5\text{--}10^7\text{ s}^{-1}$) as shown in Figure 2. The spin conversion at 0 T is caused by the isotopic hyperfine coupling (HFC). In the present radical pair, the HFC may be very small¹⁸ because the unpaired electron is usually localized on sulfur atom and the magnetic isotope of sulfur is only ^{33}S whose abundance is as small as 0.75%. On the other hand, the k_p and k_{esc} values have been observed and reported to be 4.8×10^6 and $5.2 \times 10^6\text{ s}^{-1}$, respectively.¹¹ The $k_R + k_{R'}$ value at 28 T can be estimated to be $1 \times 10^7\text{ s}^{-1}$ using adequate parameters.^{6,16} Thus, the triplet-singlet spin conversion under ultrahigh fields can be accelerated by δg if the spin conversion at 0 T is as slow as $10^5\text{--}10^7\text{ s}^{-1}$.

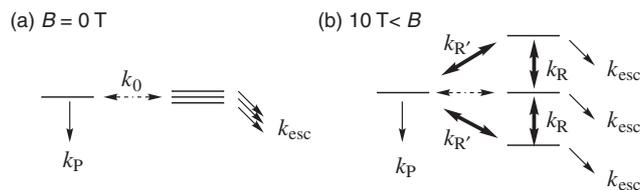


Figure 2. Triplet-singlet spin conversion of a radical pair by the RM with slow spin conversion at 0 T.

In conclusion, we have found anomalous MFEs on the reaction of triplet-born radical pair composed of two equivalent sulfur-centered radicals under ultrahigh fields of up to 28 T. The observed MFEs can be explained by the RM together with slow spin conversion at 0 T. More theoretical examination is currently in progress.

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