

Magnetic Field Effects on the Hydrogen Abstraction Reactions of Triplet Benzophenone with Thiophenol in Nonviscous Homogeneous Solutions

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The hydrogen abstraction reaction of triplet benzophenone with thiophenol at room temperature was investigated in several nonviscous homogeneous solutions ($\eta = 0.29\text{--}3.33$ cP) by means of a nanosecond laser flash photolysis technique under magnetic fields of 0–10 T. The escape yield of the benzophenone ketyl radical decreased with increasing magnetic field strength from 0 to 10 T. In 2-methyl-1-propanol ($\eta = 3.33$ cP), the yield at 10 T reduced to $80 \pm 2\%$ of that at 0 T. The observed magnetic field effects can be interpreted by the Δg mechanism when the geminate recombination process is faster than or comparable to the escape one.

Introduction

Magnetic field effects (MFEs) on the dynamic behavior of radical pairs have been widely investigated in confined systems such as micellar solutions, viscous solutions, and linked biradicals.^{1–3} Although there have been quite many reports of the MFEs on the dynamic behavior of radical ion pairs in nonviscous homogeneous solutions, it has been believed to be difficult to observe appreciable MFEs of neutral radical pairs in nonviscous homogeneous solutions for the following reasons: (1) For the appearance of appreciable MFEs, the radical pair lifetime should be comparable to the singlet–triplet spin evolution time of radical pairs. (2) In usual nonviscous homogeneous solutions at room temperature, the lifetime of neutral radical pairs ($10^{-9}\text{--}10^{-10}$ s) is much shorter than the spin evolution time ($10^{-8}\text{--}10^{-9}$ s).^{1–3}

To the best of our knowledge, however, there have been only two reports on the MFEs of the dynamic behavior of neutral radical pairs in nonviscous homogeneous solutions,^{4,5} although the MFEs on the product yields were reported in the early works of MFEs.^{6,7} Staerk and Razi Naqvi reported in the reaction of triplet benzophenone with *n*-hexane (solvent) that a slight decrease ($\sim 8\%$ at 0.6 T) in the free radical yield was observed with increasing magnetic fields (B) from 0 to 0.6 T.⁴ The mechanistic interpretation of this MFE was, however, unclear because the suggested Δg mechanism was not substantiated in a quantitative theoretical model calculation by Schulten and Epstein.⁸ More recently, Sakaguchi and Hayashi reported more reliable MFEs on the dynamic behavior of a neutral radical pair in nonviscous homogeneous solutions.⁵ In the reaction of triphenylphosphine, they reported that the yield of the escaped diphenylphosphinyl radical at 1.5 T reduced to 74% of that of at 0 T in 2-propanol. Although they concluded that the main feature of their MFEs was ascribed to the Δg mechanism, the interpretation of their MFEs has still been unclear. Thus, the study of MFEs of neutral radical pairs in nonviscous homogeneous solutions is now an underdeveloped research area.

Recently, we have found that the initial yields of biradicals formed by the hydrogen abstraction reactions of benzophenone–phenol⁹ or –thiophenol¹⁰ chain-linked compounds decrease with increasing B from 0 to 1.7 T. In these reactions, the recombination rate of biradical is so fast that the generation of the MFEs is completed within the time resolution of our apparatus (~ 10

ns). We, therefore, have noticed that if an MFE is finished within 10 ns, it is not necessary to use such confined systems as micellar solutions, viscous solutions, and linked biradicals. Then, we chose a reaction of benzophenone with thiophenol and studied the MFEs in nonviscous homogeneous solution. Since the expected radical pair has substantially a large Δg value^{11,12} and small hyperfine couplings,^{13–15} one can optimize the Δg mechanism. In this letter, we report on large MFEs observed for the hydrogen abstraction reaction of triplet benzophenone with thiophenol in several nonviscous homogeneous solutions.

Experimental Section

Benzophenone was recrystallize from methanol. Thiophenol was purified by vacuum distillation. Acetonitrile, methanol, ethanol, 1-propanol, 2-propanol, 2-methyl-1-propanol, *n*-hexane, and cyclohexane were used without further purification. Nonanenitrile ($\text{CH}_3(\text{CH}_2)_7\text{CN}$) was purified by vacuum distillation. The concentrations of benzophenone, thiophenol in the employed solutions were 20×10^{-3} and 120×10^{-3} mol dm⁻³, respectively.

Laser flash photolysis experiments in the absence and presence of a magnetic field were performed on an apparatus that was similar to that described elsewhere.¹⁶ Each nitrogen-bubbled solution was circulated through a quartz cell (20 mL/min). The third (355 nm) harmonic of a Quanta-Ray GCR-100 Nd:YAG laser 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 1.7 T were provided by a Tokin SEE-10W electromagnet and those up to 10 T by an Oxford 37057 superconducting magnet. The lowest magnetic field generated by a countercurrent 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.

Results and Discussion

Laser flash photolysis was performed at room temperature on each of the nonviscous homogeneous solution containing benzophenone (BP) and thiophenol (PhSH). The transient absorption bands of benzophenone ketyl (BPH[•], 550 nm)¹⁷ and

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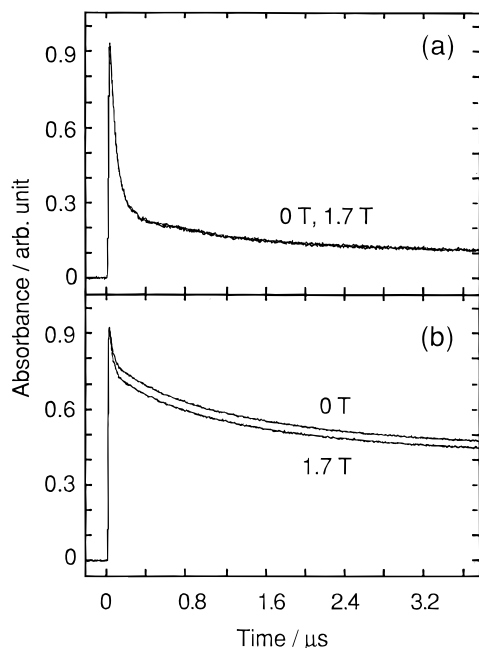
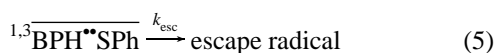
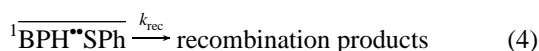
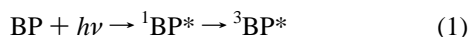


Figure 1. $A(t)$ curves observed for the hydrogen abstraction reaction of triplet benzophenone with thiophenol at 550 nm (a) in acetonitrile and (b) in nonanenitrile.

phenylthiyl (PhS^{\bullet} , 450 nm)¹⁸ radicals were observed with the T–T absorption of benzophenone ($^3\text{BP}^*$, 520 nm)¹⁹. The lifetime of the T–T absorption (τ_T) decreased with increasing concentration of thiophenol and its quenching rate constant in 2-methyl-1-propanol was typically obtained to be $7.2 \times 10^8 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$. From these results and well-established knowledge of the photochemistry of benzophenone,^{20,21} the following reactions have been believed to occur:



Here, ${}^1\text{BP}^*$, ${}^3\text{BP}^*$, ${}^1\text{BPH}^{\bullet}\text{SPh}$, and ${}^3\text{BPH}^{\bullet}\text{SPh}$ represent the singlet and triplet excited states of benzophenone, and the singlet and triplet radical pairs composed of the benzophenone ketyl (BPH^{\bullet}) and phenylthiyl (PhS^{\bullet}) radicals, respectively. The rate constants of triplet–singlet (T–S) conversion, recombination of the singlet radical pair, and escape from the radical pair are denoted by k_{TS} , k_{rec} , and k_{esc} .

Time profiles of the transient absorption ($A(t)$) were measured at 550 nm under magnetic fields of 0–1.7 T. At first, we chose acetonitrile ($\eta = 0.34 \text{ cP}^{22}$) as a solvent, because it was used for the previous reactions of benzophenone–phenol⁹ or –thiophenol¹⁰ chain-linked compounds. The $A(t)$ curves observed in the absence and presence of magnetic fields are shown in Figure 1a. The observed $A(t)$ curves have fast and slow decay components. The fast component is ascribable to the T–T absorption of ${}^3\text{BP}^*$ and the slow one to the BPH^{\bullet} . Although the MFEs on $A(t)$ curves were clearly observed previously for the chain-linked biradicals generated in acetonitrile,¹⁰ the magnetically induced change on $A(t)$ curves observed at 550

TABLE 1: Relative Magnetic Field Effect ($R(B)$) on the Yield of the Escaped Benzophenone Ketyl Radical and Solvent Viscosity (η) at 298 K

solvent	η/cP	$R(1.7 \text{ T})^a$	$R(10 \text{ T})^a$
hexane	0.29 ^b	1.00	
acetonitrile	0.34 ^b	1.00	
methanol	0.55 ^b	0.97	0.87
cyclohexane	0.89 ^b	0.95	
ethanol	1.08 ^b	0.94	
nonanenitrile	> 1.4 ^c	0.94	
1-propanol	1.94 ^b	0.94	
2-propanol	2.04 ^b	0.94	
2-methyl-1-propanol	3.33 ^b	0.90	0.80

^a Experimental errors of $R(B)$ are within ± 0.02 . ^b Reference 23.

^c Reference 24.

nm in acetonitrile was unclear. This may be due to the fact that the viscosity of acetonitrile is too low for the T–S conversion rate (k_{TS}) to compete with the escape rate (k_{esc}). Then a more viscous solvent, nonanenitrile ($\eta > 1.4 \text{ cP}^{23}$), was used at room temperature. The $A(t)$ curves observed for this solution at 550 nm in the absence and presence of magnetic fields are shown in Figure 1b. The contribution of the T–T absorption is scarcely small. However, the $A(t)$ curves of BPH^{\bullet} are similarly observed in nonanenitrile. The discrepancy of the contribution of the T–T absorption may be due to the difference of the efficiency on the hydrogen abstraction reaction in each solvent. As seen in this figure, the $A(t)$ curves of the ketyl radical observed in nonanenitrile were appreciably changed by magnetic fields.

These results suggest that the MFEs on the present reaction are highly dependent on solvent viscosity. We, therefore, measured $A(t)$ curves in several nonviscous solutions (*n*-hexane, cyclohexane, acetonitrile, nonanenitrile, methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-1-propanol). Since the $A(3 \mu\text{s})$ value can safely be used for the MFEs on the escape yield of the ketyl radical, we can see that the $A(3 \mu\text{s}, B \text{ T})/A(3 \mu\text{s}, 0 \text{ T})$ ratio ($=R(B)$) gives the MFE on the yield of the escaped ketyl radical. The obtained $R(1.7 \text{ T})$ values and solvent viscosity (η)²² at 298 K are listed in Table 1. Experimental errors of $R(B)$ are within ± 0.02 .

As clearly seen in Table 1, the magnetically induced decrease in the yield of the escaped ketyl radical was observed at 1.7 T in more viscous solvents than methanol ($\eta = 0.55 \text{ cP}^{22}$). As shown in Table 1, the $R(1.7 \text{ T})$ value was found to decrease with increasing η , attaining 0.90 ± 0.02 at $\eta = 3.33 \text{ cP}$ (in 2-methyl-1-propanol). This means that the T–S conversion rate (k_{TS}) becomes comparable to the escape rate (k_{esc}) from the geminate radical pair as the solvent viscosity increases. In low viscous solutions such as *n*-hexane and acetonitrile, the k_{esc} value may be much larger than the k_{TS} one. Staerk and Razi Naqvi reported, however, that a small decrease (–8% at 0.6 T) of the free radical yield generated in the reaction of triplet benzophenone with solvent (*n*-hexane).⁴ In our study, no such MFE reported by Staerk et al. could be reproduced at 0.6 T in *n*-hexane.

Using 2-methyl-1-propanol as a solvent, we measured the magnetic field dependence of the yield of the escaped ketyl radical at 550 nm. The obtained $R(B)$ values are plotted against $B^{1/2}$ in Figure 2a. This figure shows that the $R(B)$ values simply decreases with increasing B from 0 to 1.7 T. At 1.7 T, the magnetically induced decrease was not yet saturated. To obtain $R(B)$ values under higher fields up to 10 T, we carried out laser flash photolysis of this reaction using a superconducting magnet. The $R(B)$ values thus observed are also plotted in Figure 2a. In the high-field region ($1.7 \text{ T} < B \leq 10 \text{ T}$), the $R(B)$ values was found to be continuously decreased with increasing B . Finally,

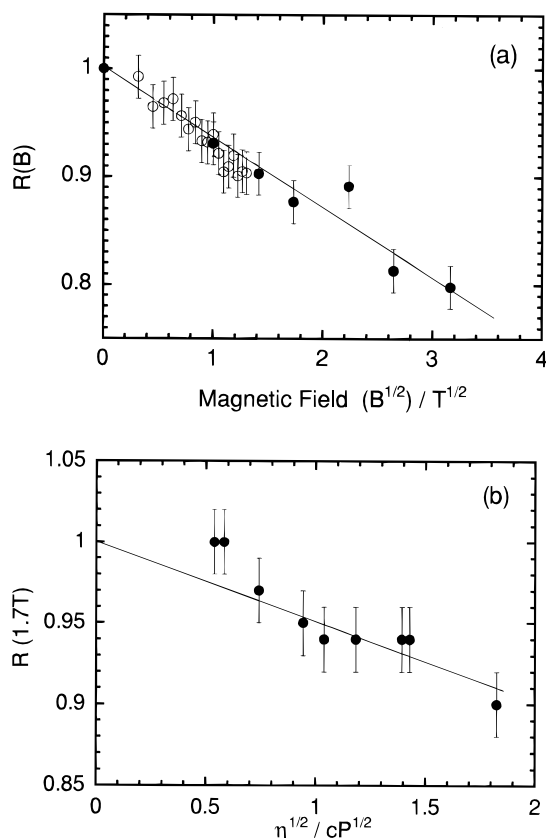


Figure 2. (a) Magnetic field dependence of the yield of the escaped benzophenone ketyl radical ($R(B) = A(3 \mu\text{s}, B \text{ T})/A(3 \mu\text{s}, 0 \text{ T})$) observed at 550 nm in 2-methyl-1-propanol ($\eta = 3.33 \text{ cP}$) using an electromagnet (open circles) and a superconducting magnet (filled circles). (b) Solvent viscosity ($\eta^{1/2}$) dependence of the $R(1.7 \text{ T})$ value of the escaped benzophenone ketyl radical observed at 1.7 T.

the $R(10 \text{ T})$ value in 2-methyl-1-propanol became as small as 0.80 ± 0.02 . Similarly, the $R(10 \text{ T})$ one in methanol was obtained to be 0.87 ± 0.02 . It is noteworthy that the plot of $R(B)$ vs $B^{1/2}$ in Figure 2a have a good linear relationship, which is generally expected from the Δg mechanism.^{2,3,7}

According to the T_0 -S conversion, its rate constant (k_{T_0-S}) can be given as follows:¹⁻³

$$k_{T_0-S} = k_{\Delta g M} + k_{\text{HFCM}} \quad (6)$$

$$k_{\Delta g M} = \frac{1}{2} \Delta g \beta B / \hbar \quad (7)$$

$$k_{\text{HFCM}} = \frac{1}{2} g \beta B_{1/2} / \hbar \quad (8)$$

Here $B_{1/2}$ is the half-field of the saturation of hyperfine coupling mechanism (HFCM).²⁴ In the present radical pair of the benzophenone ketyl and phenylthiyl radicals, the k_{HFCM} , $k_{\Delta g M}$ (at 1.7 T), and $k_{\Delta g M}$ (at 10 T) values can be estimated to be 1.8×10^8 , 3.9×10^8 , and $2.3 \times 10^9 \text{ s}^{-1}$, respectively.¹¹⁻¹⁵ Although, the calculated k_{HFCM} value is fairly smaller than the $k_{\Delta g M}$ ones, it is not too small to be neglected at the magnetic fields below 1.7 T. In the experimental results below 1.7 T, however, the MFEs due to the HFCM could not be observed as shown in Figure 2a. Although this is a mysterious phenomenon, we will consider only the contribution of $k_{\Delta g M}$ in the discussion below.

According to the Δg mechanism of the radical pair mechanism in homogeneous solution, the escape yield (Y) from a triplet precursor can be given as follows:³

$$Y = 1 - \frac{1}{3} \Lambda \sqrt{q} / (2 + \sqrt{q}) \quad (9)$$

$$q = \Delta g \beta B d^2 / (2 \hbar (D_1 + D_2)) \quad (10)$$

where Λ is a constant for the degree of diffusion-controlled reaction. D_i is a diffusion constant, and it can be given by the Stokes-Einstein relation:

$$D_i = kT / 6 \pi \eta \rho_i \quad (11)$$

At $B = 1.7 \text{ T}$, \sqrt{q} is much smaller than 2. Thus, $R(B)$ can approximately be represented as follows:

$$R(B) = Y(B)/Y(0) = 1 - \frac{1}{6} \Lambda \sqrt{\Delta g \beta B d^2 / 2 \hbar (D_1 + D_2)} \quad (12)$$

Equations 11 and 12 indicate that the plots of $R(B)$ vs $B^{1/2}$ and $R(B)$ vs $\eta^{1/2}$ should have linear relationships. As shown in Figure 2a, the plot of $R(B)$ vs $B^{1/2}$ has a good linear relationship. Consequently, we can conclude that the MFEs observed for the present reaction in 2-methyl-1-propanol are ascribable to the Δg mechanism.

To elucidate the mechanism of MFEs observed in the other solvents, the $R(1.7 \text{ T})$ values are plotted against $\eta^{1/2}$ in Figure 2b. This figure shows that there is a fairly good linear relationship between $R(B)$ and $\eta^{1/2}$. Thus, the observed MFEs in these solvents are also considered to be due to the Δg mechanism. In the cases of acetonitrile and *n*-hexane, however, the observed $R(1.7 \text{ T})$ values slightly deviate from this linear relationship. This discrepancy may be due to the following reasons: (1) In this discussion, the Λ value is assumed to be independent of solvent. For a more quantitative interpretation, the solvent dependence of the Λ value should be considered. (2) In acetonitrile and *n*-hexane, the difference between $A(3 \mu\text{s}, 1.7 \text{ T})$ and $A(3 \mu\text{s}, 0 \text{ T})$ may be too small to be detected experimentally. At 10 T, the difference may probably be observed. To elucidate these problems, we are making further studies, which are beyond the scope of this letter.

Another possible mechanism for explaining the present MFEs is the triplet mechanism,²⁵ where a decrease in the yield of escaped radicals by magnetic fields is also expected. However, a characteristic feature of the triplet mechanism is that the MFEs are saturated when the Larmor frequency exceeds the sum of the largest substate-specific ISC rate constant and the relaxation rate one among the zero-field substate. Actually, we calculated B dependence of $R(B)$ by the USF method with usual parameter sets ($k_{\text{esc}} = 2.5 \times 10^9 \text{ s}^{-1}$, $k_{\text{TS}} = 10^9 - 10^{11} \text{ s}^{-1}$, and D_r (rotational diffusion coefficient) $= 10^9 - 10^{10} \text{ s}^{-1}$)^{25,26} and always obtained the saturation field to be less than 2 T. Since the MFEs observed for the present reaction were not saturated even at 10 T as shown in Figure 2a, the triplet mechanism does not seem to explain the present MFEs.

In the present study, we found appreciable MFEs on the reaction of a neutral radical pair in nonviscous homogeneous solutions. It is noteworthy that confined systems are not necessary for appearance of MFEs if the recombination rate of the pair is faster than or comparable to the escape one.

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