Magnetic Field Effects Due to the Δ*g* Mechanism upon Chemical Reactions through Radical Pairs under Ultrahigh Fields of up to 30 T

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Abstract: Magnetic field effects (MFEs) due to the isotropic Δ*g* mechanism were studied for the hydrogen abstraction reactions of 4-methoxy-benzophenone with thiophenol in several solvents at 293 K by a laser flash photolysis technique under ultrahigh magnetic fields of up to 30 T. In 2-propanol, ethanol, and methanol, the yield of the escaped ketyl radical decreased with increasing magnetic field from 0 to 30 T. In 2-methyl-1-propanol, however, the decrease was almost saturated at 20 T and the yield above 20 T reduced to be $^2/_3$ of that at 0 T. Such saturation of the MFEs due to the isotropic Δ*g* mechanism in the reaction through radical pairs in solution was found for the first time.

Introduction

Magnetic field effects (MFEs) on chemical reactions through radical pairs have been studied extensively and constitute a rapidly developing field encompassing chemistry, physics, and biology.[1−3] This is a new branch which may be called "Spin Chemistry".[1] Almost all of MFEs, however, have hitherto been studied under magnetic fields (*B*) less than 17.5 T.[4−6] Under such fields, the MFEs on the reactions of radical pairs in solution have been interpreted by the radical pair and triplet mechanisms (RPM and TM). According to the RPM, the MFEs can be induced by the conversion between the singlet (S) and triplet (T_m) states of radical pairs through the following mechanisms:[1] (1) the Δ*g* mechanism (Δ*gM*) which is due to the difference between the *isotropic g*-factors of two radicals in a pair, (2) the hyperfine coupling mechanism (HFCM) due to the isotropic hyperfine interaction between electron and nuclear spins, (3) the level-crossing mechanism due to the crossing of the *S* and $T_{\pm 1}$ levels, and (4) the relaxation mechanism (RM) due to the *anisotropic* **g**-tensor (δg), HFC, and spin−spin dipolar interactions of radical pairs. Thus, the radical pair lifetime (τ_{RP}) and the escaped radical yield (*Y(B)*) are influenced by external magnetic fields.

On the other hand, the MFEs observed for the decay of a triplet exciplex has been interpreted by the TM.[3,6] In the TM,

the decay of the triplet exciplex to the singlet ground state is dependent on its sublevels through the spin−orbit interaction. When an external magnetic field is applied, the field mixes the zero-field triplet sublevels and thereby changes the overall decay kinetics and the yield into chemical reaction channels. The magnetically induced changes were, however, saturated at high fields ($B \leq 17.5$ T), because the Larmor frequency exceeds the sum of the largest sublevels-specific ISC rate constant and the relaxation rate among the zero-field sublevels.

Similar saturation (or reversion) of MFEs due to the RPM has been found for several reactions of organic radical pairs ($B \leq 10$ T),[1,2] biradicals ($B \leq 14$ T).[4] Such saturation (or reversion) has been interpreted in terms of the spin relaxation due to the *anisotropic δg*-, HFC-, and dipolar-interactions. In the case of the *isotropic* Δ*gM*, Boxer and co-worker reported the MFEs of the photosynthetic system which were slightly saturated at 5 T, but the magnetically induced change did not attain the limiting value of the *isotropic* Δ*gM*.[7] Thus, there had been no report on the saturation of the MFEs due to the *isotropic* Δ*gM* before our recent preliminary report.[8]

In 1997, we constructed a laser flash photolysis apparatus with a pulsed magnet to measure the MFEs on dynamic behavior of radical pairs under ultrahigh magnetic fields of up to 30 T. With this apparatus, the photoreduction of benzophenone in micellar SDS and Brij35 solutions was investigated under magnetic fields of 0−29.6 T.[9] In the SDS solution, the radical pair lifetime increased with increasing B from 0 to 3.36 T, but the lifetime attained a constant value with increasing B from 3.36 to 29.6 T. This saturation of the MFEs could be explained by the RM due to the *anisotropic δg*-, HFC-, and dipolar-interactions.

According to the *isotropic* Δ*gM*,[10] the τ_{RP} and *Y* values from a triplet precursor should decrease with increasing magnetic field (*B*), because the T_0−S spin conversion rate increases with

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(1) Nagakura, S.; Hayashi, H.; Azumi, T. *Dynamic Spin Chemistry*; Kodansha and Wiley: Tokyo and NY, 1998.

(2) Hayashi, H. *Photochemistry and Photophysics*; CRC Press: Boca Raton, FL, 1990; Vol. 1, Chapter 2. Hayashi, H.; Sakaguchi, Y. *Lasers in Polymer Science and Technology: Applications*; CRC Press: Boca Raton, FL, 1990; Vol. 2, Chapter 1. Hayashi, H.; Wakasa, M.; Sakaguchi, Y *J. Chin. Chem. Soc.* **1995**, *42*, 343.

(3) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51. Steiner, U. E.; Wolff, H.-J. *Photochemistry and Photophysics*; Rabek, J. F., Scott, G. W., Eds. CRC Press: Boca Raton, FL, 1991; Vol. IV, Chapter 1.

(4) Mukai, M.; Fujiwara, T.; Tanimoto, Y.; Okazaki, M. *J. Phys. Chem.* **1993**, *97*, 12660.

(5) Misra, A.; Dutta, R.; Nath, D.; Simha, S.; Chowdhury, M. *J. Photochem. Photobiol. A* **1996**, *96*, 155.

(6) Bürstner, D.; Wolff, H.-J.; Steiner, U. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *17*, 33.

(7) Boxer, S. G.; Christopher, E. D.; Chidsey, E. D.; Roelofs, M. G. *J. Am. Chem. Soc.* **1982**, *104*, 1452.

(8) Wakasa, M.; Nishizawa, K.; H.; Abe, H.; Kido, G.; Hayashi, H. *J. Am. Chem. Soc.* **1998**, *120*, 10565.

(9) Nishizawa, K.; Sakaguchi, Y.; Hayashi, H.; Abe, H.; Kido, G *Chem. Phys. Lett.* **1997**, *267*, 501.

increasing *B*. Under magnetic fields below 10 T, the changes in *Y* due to the ΔgM have been predicted to be proportional to $B^{1/2}$.[1−3,10] Experimentally, good linear relationships between $R(B)$ (= $Y(B)/Y(0)$) and $B^{1/2}$ have been obtained for many reactions.[1−2,11−14] Moreover, Schulten and Epstein theoretically predicted that the saturation of MFEs due to the ΔgM would occur at extremely large magnetic fields of the order of 10^3 T for the Δg values on the order of 0.01 in nonviscous solution.[15] We, therefore, have challenged their prediction and tried to find saturation behavior of the MFEs due to the ΔgM with our apparatus. In our preliminary report,[8] we found that the $R(B)$ values of the ketyl radical observed for the hydrogen abstraction reaction of 4-methoxybenzophenone with thiophenol in 2-methyl-1-propanol decreased with increasing *B* from 0 to 10 T, but that the decrease was almost saturated at 20 T. The saturated $R(B)$ value was $^2/_3$ of the $R(0$ T) one. To the best of our knowledge, this is the first observation of the saturation effect of the MFEs due to the *isotropic* ΔgM in the reaction through radical pairs in solution.

Here we present a full description of the work reported in the preliminary report.[8] The MFEs due to the ΔgM observed for the hydrogen abstraction reaction of 4-methoxybenzophenone with thiophenol in 2-methyl-1-propanol, 2-propanol, ethanol, and methanol are studied under ultrahigh magnetic fields of up to 30 T. To elucidate the detailed mechanism of the MFEs, we also carried out quantitative analyses by the diffusion model with *B*-dependence of the initial population of T_0 state.

Experimental Section

Materials. Benzophenone (BP, Kanto Chemical, Tokyo, Japan) and 4-Methoxy-benzophenone (MBP, Merck, Darmstadt, Germany) were recrystallized from methanol. Thiophenol (PhSH, Kanto Chemical, Tokyo, Japan) was purified by vacuum distillation. Solvents (2-methyl-1-propanol, 2-propanol, ethanol, methanol, and methylcyclohexane) were of guaranteed grade and were used without further purification. The concentrations of MBP and PhSH in the employed solutions were 0.02 and 0.012−0.12 mol dm^{-3}, respectively.

Laser Flash Photolysis. Laser flash photolysis experiments in the absence and presence of magnetic fields were performed on an apparatus which was similar to those described elsewhere.[9,16] Argon-bubbled solution was circulated through a quartz cell (20 mL/min). The third (355 nm) harmonic of a Quanta-Ray GCR-11 or GCR-103 Nd:YAG laser was used as an exciting light source. The transient absorption was recorded by a Hewlett-Packard HP54522A digitizing oscilloscope (2 GHz) with a photomultiplier. Magnetic fields (*B*) of up to 1.7 T were provided by a Tokin SEE-10W electromagnet and those of up to 10 T by an Oxford 37057 superconducting magnet. For measurements above 10 T, we used a long-pulsed magnet, which we have recently developed for the studies of chemical reactions in solution. This pulsed magnet has a room-temperature bore (23 mm), and its maximum field is 30 T.

Time-Resolved ESR at Room Temperature. Time-resolved ESR spectra were measured without field modulation with a JEOL JES-RE2X ESR spectrometer at 0.2−0.6 μs after laser excitation. The third harmonic of a Quanta-Ray GCR-3 Nd:YAG laser was used as an
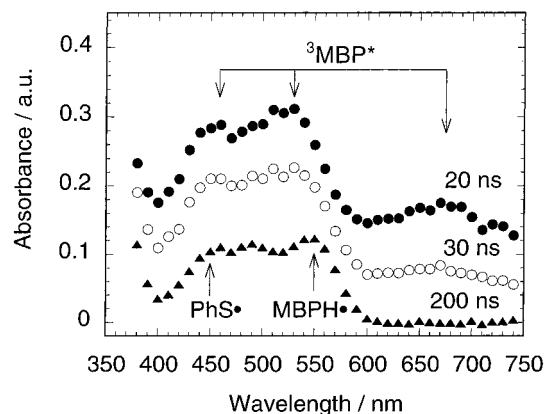

Figure 1. Transient absorption spectra observed at room temperature at delay times of 20 ns (●), 30 ns (○), and 200 ns (▲) after laser excitation of the 2-methyl-1-propanol solution containing 4-methoxybenzophenone and thiophenol.

exciting light source (30 Hz). The output signal was averaged by a Tektronix TDS 540 digitizing oscilloscope. Argon-bubbled solution of MBP (0.02 mol dm^{-3}) and PhSH (0.12 mol dm^{-3}) were circulated through a quartz cell (2 mL/min).

Time-Resolved ESR at 77 K. Triplet ESR signals were measured without field modulation with a JEOL JES-RE1X ESR spectrometer at 0.4−0.6 μs after laser excitation. A XeCl excimer laser (308 nm) of a Lumonics EX-742 excimer laser was used as an exciting light source (25 Hz). The output signal was averaged by an SRS SR250 boxcar integrator. The methylcyclohexane solution of BP or MBP (0.005 mol dm^{-3}) in a quartz tube of 4 mm was quickly immersed in liquid nitrogen contained in a quartz dewar. Magnetic field and microwave frequency were measured by an EFM-2000AX NMR field meter (ECHO Electronics) and an EMC-14 Microwave counter (ECHO Electronics), respectively.

Results and Discussion

Reaction Scheme. Laser flash photolysis was performed at 293 K on the 2-methyl-1-propanol solution of MBP and PhSH (0.12 mol dm^{-3}). Time profiles of the transient absorption (A(t)) were measured in the absence of a magnetic field. The transient absorption spectra obtained at delay times of 20, 30, and 200 ns after laser excitation are shown in Figure 1. Here, the peaks due to the triplet−triplet (T−T) absorption of MBP was observed at 465, 520, 680 nm[17,18] and the decay of the triplet MBP was very fast ($\tau_T \sim$15ns). Figure 2 shows representative first-order plots for the decay of the T−T absorption at 520 nm in the presence of PhSH (0.012−0.12 mol dm^{-3}). The quenching rate constant of the triplet MBP with PhSH in 2-methyl-1-propanol was obtained to be 5.8×10^8 s^{-1} mol^{-1} dm^3. From the T−T absorption study, the generation of the 4-methoxybenzophenone ketyl radical (MBPH•) was observed at 550 nm.[18] The transient absorption of the phenylthiyl radical (PhS•) was also observed at 450 nm.[19,20] Similar transient absorption spectra were observed in 2-propanol, ethanol, and methanol. These results indicate that the fast hydrogen abstraction of triplet MBP with PhSH occurs in the present reactions, and that a triplet radical pair involving MBPH• and PhS• is generated very efficiently.

To elucidate the reaction intermediates, the time-resolved ESR measurements were carried out in 2-propanol at room temper-

(10) Freed, J. H. *Chemically Induced Magnetic Polarization*; Muus, L.; Atkins, P. W., McLauchlan, K. A., Pedersen, J. B., Eds.; D. Reidel: Dordrecht, The Netherlands, 1977; Chapter 19. Pedersen, J. B. *J. Chem. Phys.* **1977,** *67*, 4097.

(11) Tanimoto, Y.; Hayashi, Y.; Nagakura, S.; Sakuragi, H.; Tokumaru, K. *Chem. Phys. Lett.* **1976**, *41*, 267.

(12) Wakasa, M.; Nakamura, Y.; Sakaguchi, Y.; Hayashi, H. *Chem. Phys. Lett.* **1993**, *215*, 631.

(13) Wakasa, M.; Hayashi, H *J. Phys. Chem.* **1996**, *100*, 15640.

(14) Sakaguchi, Y.; Hayashi, H *J. Phys. Chem.* **1997**, *101*, 549.

(15) Schulten, K.; Epstein, I. R. *J. Chem. Phys.* **1979**, *71*, 309.

(16) Mochida, K.; Nagano, S.; Kawata, H.; Wakasa, M.; Hayashi, H. *J. Organomet. Chem.* **1997**, *542*, 75.

(17) Baral-Tosh, S.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.* **1984**, *88*. 1404.

(18) Shizuka, H.; Obuchi, H. *J. Phys. Chem.*, **1982**, *86*, 1297.

(19) Buckley, C. D.; Hunter, D. A.; Hore, P. J.; McLauchlan, K. A. *Chem. Phys. Lett.* **1987**, *135*, 307.

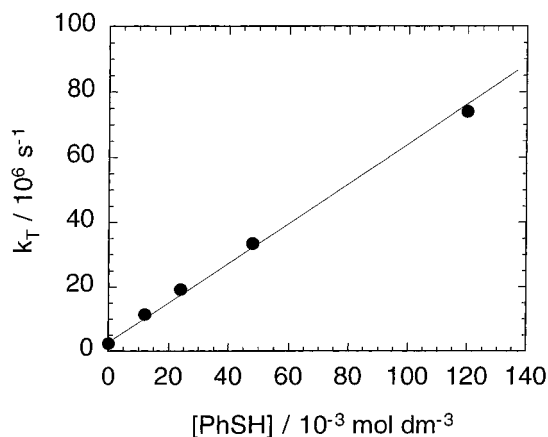(20) Jeschke, G.; Wakasa, M.; Sakaguchi, Y.; Hayashi, H. *J. Phys. Chem.* **1994**, *98*, 4069.

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Figure 2. First-order plots for the decay of the T−T absorption (k_T) in 2-methyl-1-propanol at 520 nm in the presence of thiophenol (0.012− 0.12 mol dm^{-3}).
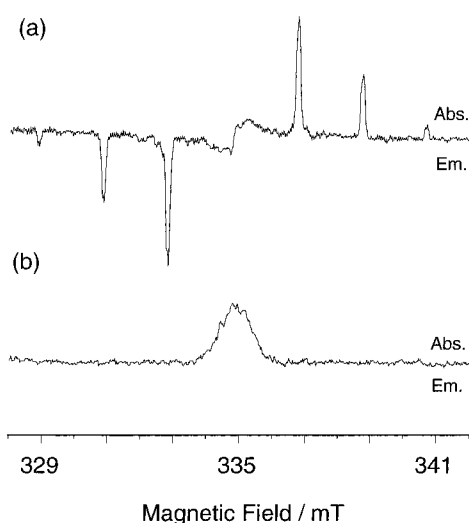

Figure 3. Time-resolved ESR spectra observed at delay time of 0.2− 0.6 μs after laser excitation of the 2-propanol solutions of 4-methoxybenzophenone (0.02 mol dm^{-3}) (a) without and (b) with thiophenol (0.12 mol dm^{-3}).

ature. The observed spectra at delay time of 0.2−0.6 μs after laser excitation are shown in Figure 3. These spectra show clear chemically induced dynamic electron polarization (CIDEP). In the absence of PhSH (Figure 3a), the spectrum is composed of two components. One of them can be assigned to the 2-hydroxy-2-propyl radical from its HFC ($6 \times A_H = 19.66$ G).[21] The other signal has a g value of 2.0027 and an E/A (A and E denote the absorptive and emissive phases, respectively) phase pattern which is attributed to the radical pair mechanism of a triplet pair with a negative exchange integral ($J < 0$).[1−3] Since this g value is very close to the value of the BP ketyl radical ($g = 2.0030$[22]), we assigned this signal to the MBP ketyl radical. In the presence of PhSH (Figure 3b), the spectrum is composed of only one component which has totally absorptive phase pattern. The signal due to the 2-hydroxy-2-propyl radical was not observed. This result indicates that the hydrogen abstraction from PhSH predominantly occurs instead of that from 2-propanol. From comparison with Figure 3a, the absorptive CIDEP signal can be assigned to the MBP ketyl radical.[23] On the other hand, the counter radical, phenylthiyl radical, could not be observed. This may be due to the fast spin relaxation of the thiyl radical.

(21) Livingston, R.; Zeldes, H. J. *Chem. Phys.* **1966**, *44*, 1245.
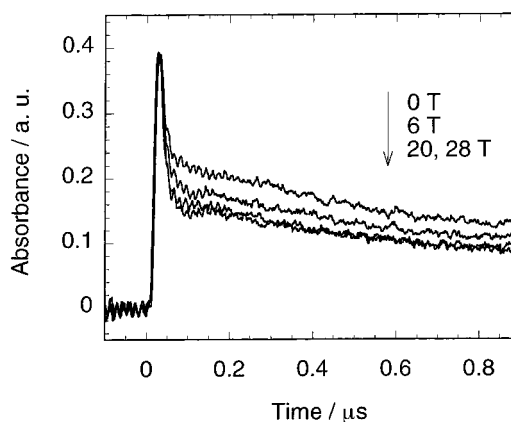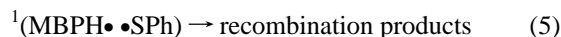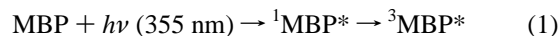(22) Wilson, R. *J. Chem. Soc. B* **1968**, 84

Figure 4. A(t) curves observed at 550 nm for the hydrogen abstraction reaction of triplet 4-methoxybenzophenone with thiophenol in 2-methyl-1-propanol at 0, 6, 20, and 28 T.

From these results, the reaction scheme can be represented as follows:

$$\text{MBP} + h\nu \ (355 \text{ nm}) \rightarrow {}^1\text{MBP*} \rightarrow {}^3\text{MBP*} \qquad (1)$$

$$^3\text{MBP*} + \text{PhSH} \rightarrow {}^3(\text{MBPH}\bullet \ \bullet\text{SPh}) \qquad (2)$$

$$^3(\text{MBPH}\bullet \ \bullet\text{SPh}) \rightarrow {}^1(\text{MBPH}\bullet \ \bullet\text{SPh}) \qquad (3)$$

$$^{3,1}(\text{MBPH}\bullet \ \bullet\text{SPh}) \rightarrow \text{escaped radicals} \qquad (4)$$

$$^1(\text{MBPH}\bullet \ \bullet\text{SPh}) \rightarrow \text{recombination products} \qquad (5)$$

Here, ^{1}MBP* and ^{3}MBP* represent the singlet and triplet excited states of 4-methoxybenzophenone, respectively. ^{1}(MBPH• •SPh) and ^{3}(MBPH• •SPh) denote the singlet and triplet radical pairs composed of the 4-methoxybenzophenone ketyl and phenylthiyl radicals, respectively.

Magnetic Field Effect on the Yield of the Escaped Radical in 2-Methyl-1-propanol. Time profiles of the transient absorption ($A(t)$) were measured in 2-methyl-1-propanol at 550 nm under magnetic fields of 0−30 T. Typical $A(t)$ curves observed at 0, 6, 20, and 28 T are shown in Figure 4. Each of the observed $A(t)$ curves has fast and slow decay components. The fast component is attributed to the decay of ^{3}MBP*, and the slow one to the dynamic behavior of escaped radicals. As clearly seen in this figure, the triplet lifetime is independent of B,[24] but the escaped radical yield ($Y(B)$) is appreciably affected by magnetic fields. Since the triplet lifetime was measured to be 15 ns, we can see that the A_B(300 ns) value is proportional to the escaped radical yield ($Y(B)$). Thus, $R(B) = Y(B)/Y(0 \text{ T}) = A_B \ (300 \text{ ns})/A_{0 \text{ T}} \ (300 \text{ ns})$ gives the MFE on the yield of the escaped MBP ketyl radical. The obtained $R(B)$ values from $A(t)$ curves are plotted against $B^{1/2}$ in Figure 5. We can see from this figure that the $R(B)$ value decreases with increasing B and that the decrease in $R(B)$ ($1 − R(B)$) is proportional to $B^{1/2}$ in the low field region ($0 \leq B \leq 4$ T). Similar linear relations between

(23) Since the triplet ESR signal of MBP at 77 K has a polarization pattern of E,EEE/AAA (to be discussed later) and the present radical pair has a lager Δg value (≥ 0.0055), the totally absorptive phase pattern is considered to be not due to the triplet mechanism but due to the radical pair mechanism of a triplet pair, where the corresponding radical has a smaller g value.[2]
(24) If the triplet state is spin polarized and relaxation time is field dependent, the triplet lifetime will be a function of B. However, we found that the triplet lifetime was independent of B. This may be due to the time resolution of our apparatus (~10 ns).
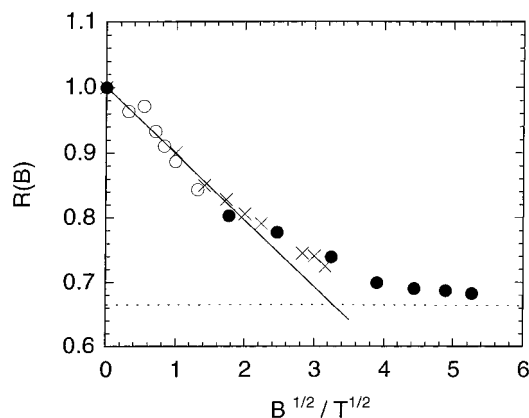
Figure 5. Magnetic field dependence of the yield of the escaped 4-methoxybenzophenone ketyl radical ($R(B) = A_B$ (300 ns)/$A_{0\,T}$ (300 ns)) observed at 550 nm in 2-methyl-1-propanol with an electromagnet (○), a superconducting magnet (×), and a pulsed magnet(●).

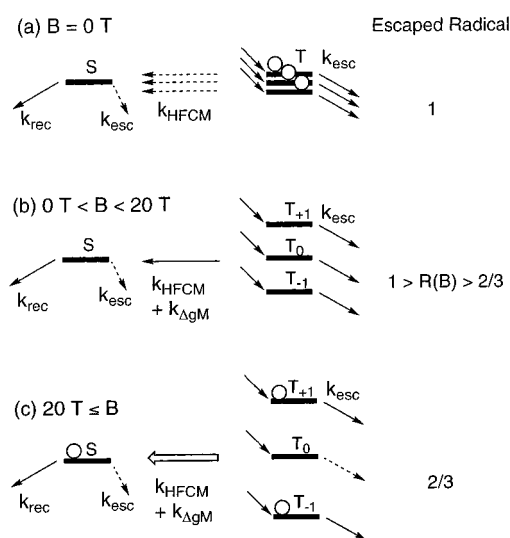**Figure 6.** T−S spin conversion of the present radical pair generated from a triplet precursor at (a) $B = 0$ T, (b) 0 T $< B <$ 20 T, and (c) 20 T $\leq B$.

$R(B)$ and $B^{1/2}$ have been found for many reaction systems.[1−3,11−14] Such MFEs can qualitatively be explained by Figure 6, which schematically shows the energy diagram of singlet and triplet radical pairs. In this figure, the rate constants of T_m−S conversion due to the HFCM and ΔgM are represented by k_{HFCM} and $k_{\Delta gM}$, respectively, and the constants of the recombination from the singlet radical pair, and the escape rate from the pair are k_{rec}, and k_{esc}, respectively. At zero field, if the escape process (k_{esc}) is much faster than the T−S conversion (k_{HFCM}), almost all of triplet radical pairs are escaped from the pairs as shown in Figure 6a. At low fields (0 $\leq B \leq$ 4 T), the T_0−S conversion is accelerated by a weak magnetic perturbation ($\Delta g\beta B$), and the escaped radical yield decreases with increasing B as shown in Figure 6b. It is noteworthy from Figure 5 that the observed $R(B)$ values starts to deviate from the $R(B) - B^{1/2}$ relationship with increasing B from 4 T. Furthermore, we found that the decrease in $R(B)$ was almost saturated above 20 T as clearly seen in Figure 5. The $R(B)$ values observed above 20 T were almost $2/3$ of the $R(0$ T$)$ one. This is the limiting value of the ΔgM, where $1/3$ of the triplet radical pairs disappear by the recombination process as shown in Figure 6c.[1−3,10] To the best of our knowledge, this is the first observation of the saturation of the MFEs due to the *isotropic* Δg mechanism in the reaction through radical pairs in solution.[25]

The g value of the MBP ketyl radical was observed to be 2.0027 by the time-resolved ESR measurements. Even though PhS• signal was not observable in our study, but Mörle et al. reported a g value of 2.0082 based on the broad and unsymmetrical signal observed at 77 K.[26] Thus, the Δg value of the present radical pair is tentatively considered to be 0.0055, but it is possible to be much larger.[27] Since the present reaction system has such a large Δg value, the saturation of the MFEs can qualitatively be interpreted by a complete T_0−S spin conversion by the ΔgM when the recombination reaction from singlet radical pairs occurs extremely fast. As mentioned above, if k_{esc} is much larger than k_{HFCM} at zero field, almost all of the radicals in the prepared triplet radical pair escaped from the pairs as shown in Figure 6a. At high fields ($B \geq$ 20 T), the radicals in the $T_{\pm 1}$ pairs escaped from the pairs as shown in Figure 6c, but the T_0 pairs can be converted to the S ones. If the T_0−S conversion ($k_{HFCM} + k_{\Delta gM}$) process and the recombination from the S pairs are much faster than the escape process ($k_{HFCM} + k_{\Delta gM}, k_{rec} \gg k_{esc}$), the pairs initially produced at T_0 should predominantly recombine from the S pairs. This means that $1/3$ of the triplet radical pairs can disappear by the recombination process instead of the escape one, as shown in Figure 6c. Thus, the saturation of the MFEs observed for the reaction of MBP and PhSH in 2-methyl-1-propanol can qualitatively be explained by the complete T_0−S spin conversion due to the ΔgM.

Quantitative Analysis by the Diffusion Model. We shall analyze our experimental results by the following theory presented by Freed and Pedersen which are applicable for large ΔgB values:[10]

$$R(B) = 1 - p\Lambda \frac{\dfrac{\sqrt{qB}}{2}\left\{1 + \dfrac{1}{2}\ln(1 + \sqrt{qB})\right\}}{1 + \dfrac{\sqrt{qB}}{2}\left\{1 + \dfrac{1}{2}\ln(1 + \sqrt{qB})\right\}} \quad (6)$$

$$q = \Delta g\beta d^2/2\hbar D \quad (7)$$

Here, Λ ($= 1$) is a constant for the degree of diffusion controlled reaction, p ($=$ constant) is a initial population of T_0 state, d is the distance of closest approach, and D is a diffusion constant. The observed $R(B)$ values were analyzed by the least-squares method to satisfy eq 6. The p and $\sqrt{q}$ values were obtained to be 0.43 and 0.64 $T^{-1/2}$, respectively and the simulated $R(B)$ curve is plotted by a full curve in Figure 7 together with the observed data. The saturation of the MFEs due to the ΔgM can be reproduced fairly well by this model. However, the obtained p value ($= 0.43$) means that the initial population of T_0 state is 0.43. It is well-known that the top sublevel (T_Z) of the triplet state of benzophenone is predominantly populated upon photoexcitation. One may assume the triplet of MBP has the similar population scheme, therefore the population of the present radical pair in the T_0 state should be smaller than $1/3$. Moreover, the T_0 state should be polarized at low fields, but the population of the triplet sublevels should become equal at high fields ($p = 1/3$). If the p value is fixed to $1/3$, which is a high field limit, the simulated $R(B)$ curve is somewhat deviated from the observed data at low fields as shown by a dotted curve in Figure 7. We

(25) Boxer and co-worker reported that the MFE due to the Δg mechanism observed for the photosynthetic system was slightly saturated at 5 T.[7] The radical pair in this study, however, is not located in a solvent cage, but is confined in an organized system.

(26) Mörle, W.; Jezierski, A.; Singer, H. *Z. Chem.* **1979**, *19*, 147.

(27) The isotropic g value of PhS• is possible to be much larger than 2.0082, because Zandstra et al. reported its anisotropic g values to be 2.10 and 2.00.[28]
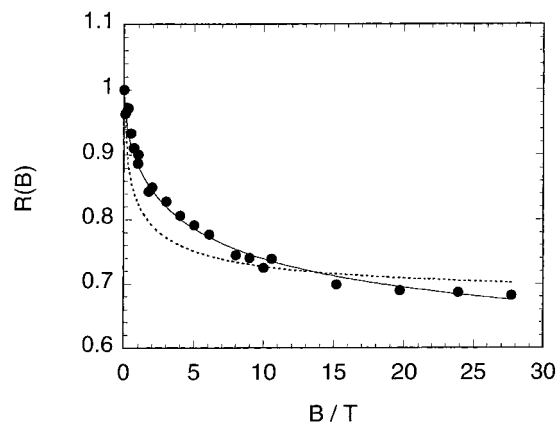
Figure 7. The simulated $R(B)$ curves obtained by the diffusion model with eq 6: $(-)$ $p = 0.43$ and $(\cdots)$ $p = 1/3$.

Table 1. Zero-Field Splitting Parameters and Populating Rates of Benzophenone and 4-Methoxybenzophenone

	X/GHz	Y/GHz	Z/GHz	D_{ZFS}/GHz[a]	$Px:Py:Pz$	ref
MBP	∓ 1.3	∓ 0.5	± 1.8	2.7	0:0:1	this work
BP	∓ 2.0	∓ 1.0	± 3.0	4.5	0:0:1	this work
BP	-2.1	-1.0	3.1	4.7		29

[a] $D_{ZFS} = (3/2)$ Z.

can see, therefore, that eq 6 cannot fully explain the observed MFEs in the present study, if a single proper value is used for p. Thus, we should take the B-dependence of the initial population ($p(B)$) of the T_0 state of the radical pair into consideration. To obtain the $p(B)$ values of the radical pair, we should measured the zero-field splitting (ZFS) constants (X, Y, and Z) of triplet MBP. Its spin Hamiltonian ($\mathcal{H}$) is represented as follows:[29]

$$\mathcal{H} = g\beta \mathbf{H}\cdot\mathbf{S} + XSx^2 + YSy^2 + ZSz^2 \qquad (8)$$
$$X + Y + Z = 0$$

To the best our knowledge, the ZFS constants of triplet MBP have not yet been reported. Then, we carried out time-resolved ESR measurements at 77 K. Figure 8 shows the time-resolved ESR spectra of triplet MBP in methylcyclohexane together with that of BP for comparison. The spectra of both MBP and BP have the polarization pattern of E,EEE/AAA from the low field side to the high field side. This spectral pattern indicates that the excited triplet sates of MBP is polarized on the top sublevel (T_Z) as shown in the case of triplet BP.[29] Next, to determine the zfs constants of triplet MBP, we made simulation with the procedure reported by Kottis and Lefebvre,[30] taking into account of the populations of the triplet sublevels. The simulated spectra are shown in Figure 8. The values of ZFS (X, Y, Z, and D_{ZFS}) and the populating rate ($Px:Py:Pz$) obtained from the simulation are summarized in Table 1. Although the signs of the ZFS constants of triplet MBP could not be obtained only by the present time-resolved ESR measurements, it is considered that their signs are same as those of triplet BP reported by Mucha et al.[29]

According to the triplet mechanism of CIDEP,[10] the B-dependence of the initial population ($p(B)$) of the radical pair at $B > |D_{ZFS}|$ may be represented with the Z value of its triplet precursor as follows:

(28) Zandstra, P. J.; Michaelsen, J. D. *J. Chem. Phys.* **1963**, *39*, 933.
(29) Mucha, H. A.; Pratt, D. W. *J. Chem. Phys.* **1977**, *66*, 5339.
(30) Kottis, P.; Lefebvre, R. *J. Chem. Phys.* **1963**, *39*, 393.

$$p(B) = \frac{1}{3} - p_B\frac{D_{ZFS}}{B} \qquad (9)$$

$$D_{ZFS} = (3/2)Z \qquad (10)$$

where, p_B is a polarization factor. Thus, eq 6 can approximately be represented as follows:

$$R(B) = 1 - \left(\frac{1}{3} - p_B\frac{D_{ZFS}}{B}\right)\Lambda\frac{\frac{\sqrt{qB}}{2}\left\{1 + \frac{1}{2}\ln(1 + \sqrt{qB})\right\}}{1 + \frac{\sqrt{qB}}{2}\left\{1 + \frac{1}{2}\ln(1 + \sqrt{qB})\right\}} \qquad (11)$$

Using the obtained D_{ZFS} value of triplet MBP, we analyzed the observed $R(B)$ values with eq 11. The simulated $R(B)$ curve is plotted in Figure 9a. This figure shows that the MFEs observed at both low and high fields can be reproduced fairly well by this model. Moreover, the p_B value was obtained to be 0.38. From this value, the initial population of the T_0 state at 0.15 T is estimated to be 0.19 and that at 30 T, 0.33. They are in reasonably agreed with the observed polarization of triplet MBP.

Solvent Viscosity Dependence. To elucidate the detailed mechanism of the MFEs observed for the present reaction, we also measured the solvent viscosity (η) dependence of $R(B)$. The magnetic field dependence of $R(B)$ observed in 2-propanol ($\eta = 2.04$ cP),[31] ethanol ($\eta = 1.08$ cP),[31] and methanol ($\eta = 0.55$ cP)[31] are plotted in parts b−d of Figure 9. As clearly seen in these plots, the magnetically induced change of the yield of the escaped ketyl radical was found to decrease with decreasing solvent viscosity from 2-methyl-1-propanol ($\eta = 3.33$ cP)[31] to methanol and that the complete saturation of the MFEs could not be observed in 2-propanol, ethanol, and methanol. Such viscosity dependence can qualitatively be explained by the competition between escape (k_{esc}) and spin conversion ($k_{HFCM} + k_{\Delta gM}$) process. In each of the solvents with lower viscosity than 2-methyl-1-propanol, the k_{esc} value may be much larger than the $k_{HFCM} + k_{\Delta gM}$. In such less viscous solvents, the escape process becomes dominant and the MFEs due to $k_{\Delta gM}$ is depressed. Thus, the saturation of the MFEs could not occur efficiently.

Next, the magnetic field dependence of $R(B)$ observed in 2-propanol, ethanol, and methanol were analyzed by eq 11 with the same parameters ($p_B = 0.38$, $D_{ZFS} = 2.7$ GHz). The simulated $R(B)$ curves are plotted in Figure 9b−d. These plots show that the $R(B)$ values observed in all solvents could be reproduced fairly well by this model with the same parameters. In addition, eq 7 suggests that $\sqrt{q}$ is inversely proportional to the square root of diffusion constant (D), which can be given by the Stokes−Einstein relation:

$$D_i = kT/6\pi\eta\rho \qquad (12)$$

$$D = D_1 + D_2 \qquad (13)$$

Thus, $\sqrt{q}$ is given as follows:

$$\sqrt{q} = \sqrt{\frac{\Delta g\beta d^2\, 6\pi\eta\rho}{4\hbar kT}} \qquad (14)$$

Equation 14 indicates that there should be a linear relationship between $\sqrt{q}$ and $\sqrt{\eta}$. In Figure 10, the $\sqrt{q}$ values obtained by

(31) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley: New York, 1986.
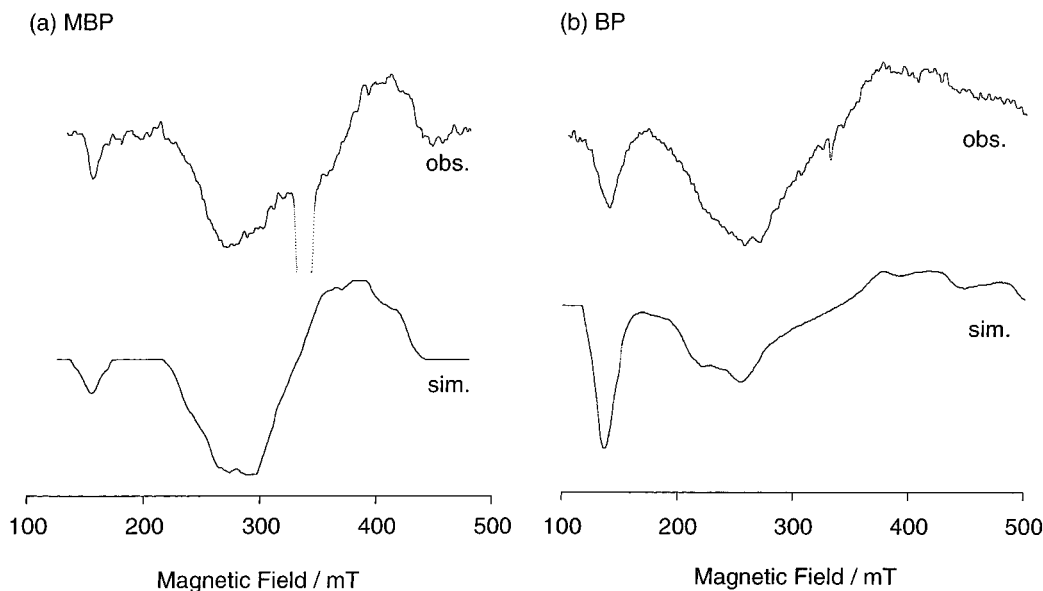
Figure 8. Time-resolved ESR spectra of the excited triplet states of (a) 4-methoxbenzophenone and (b) benzophenone in methylcyclohexane at 77 K.
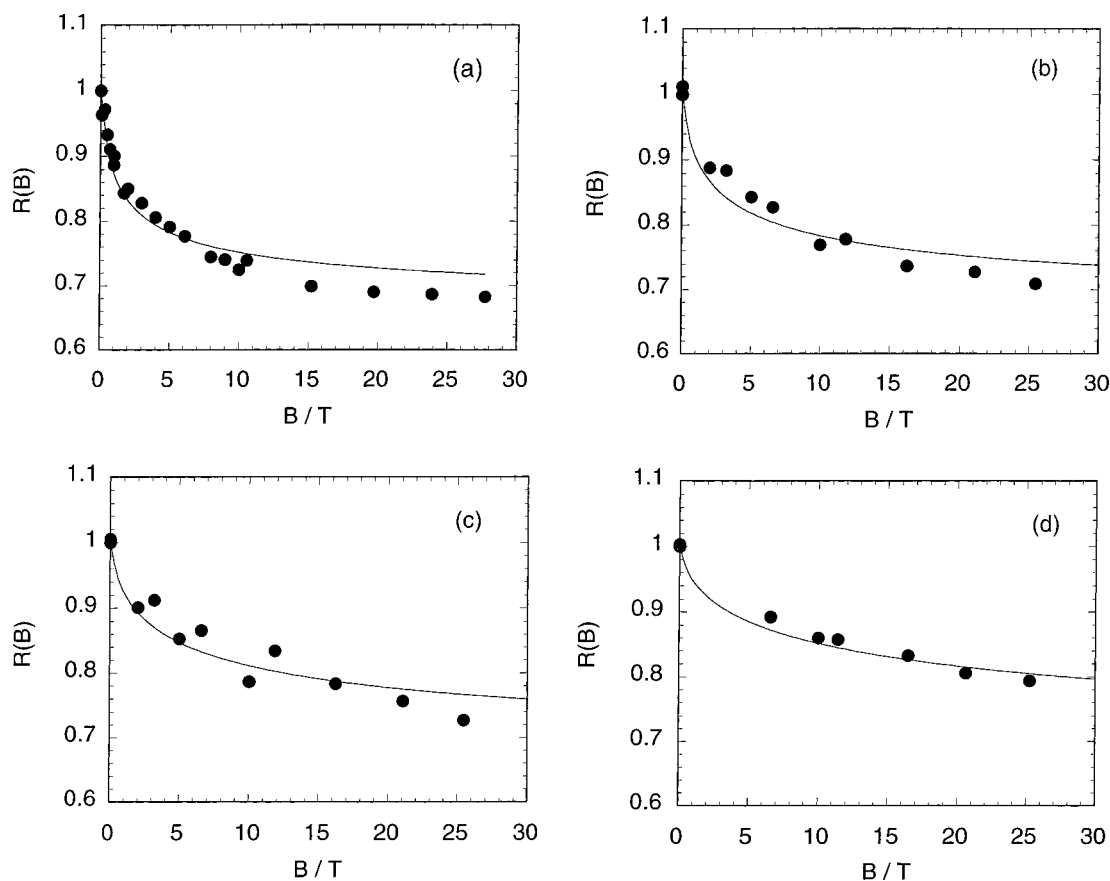

Figure 9. The observed $R(B)$ values and the simulated $R(B)$ curves by the diffusion model involving B-dependent initial polarization of T_0 state with eq 11 in (a) 2-methyl-1-propanol, (b) 2-propanol, (c) ethanol, and (d) methanol.

the least-squares method with eq 11 are plotted against $\sqrt{\eta}$. This figure shows that there is a good linear relationship between $\sqrt{q}$ and $\sqrt{\eta}$ as expected by eq 14. From these results, we can conclude that the present MFEs observed in 2-methyl-1-propanol, 2-propanol, ethanol, and methanol can be explained by this diffusion model involving the B-dependent initial polarization. Furthermore, it is noteworthy that the most important factor for the saturation of the MFEs due to the ΔgM is the solvent viscosity. Finally, the diffusion constants of the

present reactions are considered. It is difficult to determine experimentally the diffusion constants for the present radicals in solution. Then, we calculated the D value in 2-methyl-1-propanol by eq 7 with a set of adequate parameters ($\sqrt{q} = 1.05$, $\Delta g = 0.01$, $d = 5$ Å) and obtained to be 1×10^{-6} s^{-1} cm^2. This value is somewhat smaller than that estimated from the Stokes$-$Einstein relation ($D_i = 1.86 \times 10^6$ s^{-1} cm^2). For a more quantitative analysis of the present MFEs, one should use the stochastic Liouville equation including all necessary interac-
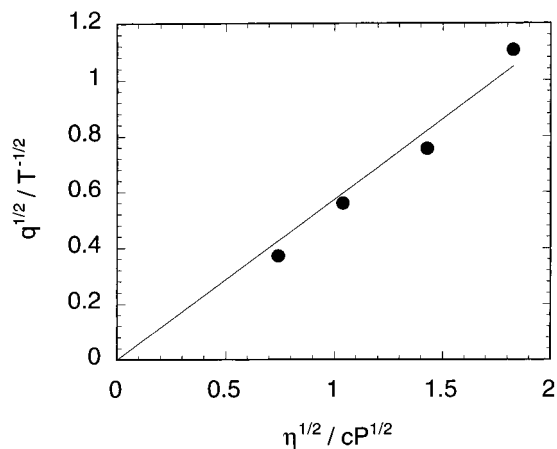
Figure 10. Solvent viscosity (η) dependence on the $\sqrt{q}$ values which are obtained from the simulated curves in Figure 9a−d.

tions,[32,33] but this is beyond the scope of the present experimental paper.

Schulten and Epstein theoretically predicted that the saturation of MFEs due to the Δg mechanism would occur at extremely large magnetic fields of the order of 10^3 T for Δg on the order of 0.01 in nonviscous solution.[15] Although we could not understand the reason their maximum yield of the total singlet recombination from a triplet precursor is as small as $^1/_6$, the prediction of the extremely large magnetic field may be ascribable to the selection of the large diffusion constant. In the present study, the diffusion constant observed is 1 order of

(32) Pedersen, J. B.; Lolle, L. I. *Appl. Magn. Reson.* **1993**, *5*, 89.

(33) Pedersen, J. B.; Shushin, A. I.; Jørgensen, J. S. *Chem. Phys.* **1994**, *189*, 479.

magnitude smaller than that used by Schulten et al. This may be the reason they predicted such extremely large magnetic fields to be necessary for the saturation of the MFEs due to the Δg mechanism.

Conclusions

In the present study of the MFEs on the reaction of triplet MBP with PhSH under ultrahigh magnetic fields of up to 30 T, we found the saturation of the MFEs due to the *isotropic* Δg mechanism in the reaction through radical pairs in solution. Such saturation of the MFEs can be qualitatively interpreted by a complete T_0−S spin conversion due to the Δg mechanism with an extremely fast recombination reaction from singlet radical pair. The viscosity dependence on the MFEs observed in 2-methyl-1-propanol, 2-propanol, ethanol, and methanol conclude that the preset MFEs can be explained by the diffusion model involving the *B*-dependent initial polarization of the T_0 sublevel and that the most important factor for the saturation of MFEs is the solvent viscosity. The extremely large magnetic fields ($>10^3$ T) for the Δg-induced saturation predicted by a previous theory are not necessary, if suitable reaction systems are chosen.