J. Am. Chem. Soc. **1998,** *120,* 10565−10566

Saturation of Magnetic Field Effects Due to the Δg Mechanism under Ultrahigh Fields of up to 28 T

Masanobu Wakasa,[†] Kiyoshi Nishizawa,[†] Haruo Abe,[‡]
Giyuu Kido,[‡] and Hisaharu Hayashi*[,†]

The Institute of Physical and Chemical Research (RIKEN)
Wako, Saitama 351-0198, Japan
National Research Institute for Metals
Tukuba, Ibaraki 305, Japan

Received February 16, 1998

Magnetic field effects (MFEs) on chemical reactions have been extensively studied during the last two decades.[1,2] The MFEs on reactions of radical pairs in solution can be interpreted by the radical pair mechanism. The conversion between the triplet (T_m) and singlet (S) radical pairs arises from the following mechanism:[1−4] (1) the Δg mechanism (ΔgM) which is due to the difference between the *isotropic g*-factors of two radicals in the 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. Thus, the radical pair lifetime (τ_{RP}) and the escape radical yield ($Y(B)$) are influenced by external magnetic fields. According to the ΔgM,[3] 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 increasing B. Such MFEs due to the ΔgM have been studied extensively under magnetic fields below 10 T,[1,2,5−12] where the changes in Y due to the ΔgM are theoretically predicted to be proportional to $B^{1/2}$.[1−3,13] Experimentally, good linear relationships between $R(B)$ ($= Y(B)/Y(0)$) and $B^{1/2}$ have been obtained.[1,5,6,11,12]

Recently, the saturation and reversion of MFEs under high fields ($10\ \mathrm{T} \le B \le B_{max}$) have been found for several reactions of organic radical pairs ($B_{max} = 10$ T)[2], biradicals ($B_{max} = 14$ T),[14] and Ru complexes ($B_{max} = 17.5$ T).[15] Such saturation and reversion have been interpreted in terms of the spin relaxation due to *anisotropic* δg-, HFC-, and dipolar-interactions. There has been, however, no report on the saturation of the MFEs due to the *isotropic* ΔgM. Theoretically, Schulten and Epstein predicted that such Δg-induced saturation of MFEs would occur at extremely large magnetic field values of the order of 10^3 T for Δg on the order of 0.01 in nonviscous solvent.[13] Because this prediction was obtained by the special selection of various unknown parameters, it is possible that the saturation field may be lowered if the parameters are chosen otherwise.

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.[16] We, therefore, have challenged the above-mentioned prediction and tried to find saturation behavior of the MFEs due to the *isotropic* ΔgM with this apparatus, measuring the hydrogen abstraction reaction of 4-methoxybenzophenone with thiophenol in 2-methyl-1-propanol. We observed that $Y(B)$ values of the ketyl radical decreased with increasing B from 0 to 10 T, but the decrease was almost saturated at 20 T. The saturated $Y(B)$ value was $^{2}/_{3}$ of the $Y(0\ \mathrm{T})$ one. To the best of our knowledge, this is the first observation of the saturation effect of the MFEs due to the *isotropic* Δg mechanism.

In the photochemical hydrogen abstraction reaction of 4-methoxybenzophenone (MBP) with thiophenol (PhSH), the following reactions are believed to occur:[6−9,11,17,18]

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

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

$${}^3(\mathrm{MBPH}^\bullet\ {}^\bullet\mathrm{SPh}) \rightarrow {}^1(\mathrm{MBPH}^\bullet\ {}^\bullet\mathrm{SPh}) \tag{3}$$

$${}^{3,1}(\mathrm{MBPH}^\bullet\ {}^\bullet\mathrm{SPh}) \rightarrow \text{escape radicals} \tag{4}$$

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

Here, ${}^1\mathrm{MBP}^*$ and ${}^3\mathrm{MBP}^*$ represent the singlet and triplet excited states of 4-methoxybenzophenone, respectively. ${}^1(\mathrm{MBPH}^\bullet\ {}^\bullet\mathrm{SPh})$ and ${}^3(\mathrm{MBPH}^\bullet\ {}^\bullet\mathrm{SPh})$ denote the singlet and triplet radical pairs composed of the 4-methoxybenzophenone ketyl ($\mathrm{MBPH}^\bullet$) and phenylthiyl ($\mathrm{PhS}^\bullet$) radicals, respectively. Using the third harmonic (355 nm) of an Nd:YAG laser, we carried out a laser flash photolysis study of 2-methyl-1-propanol solutions containing MBP (0.02 mol dm^{-3}) and PhSH (0.012−0.12 mol dm^{-3}) at 293 K. The T−T absorption of ${}^3\mathrm{MBP}^*$ and the transient absorption bands of $\mathrm{MBPH}^\bullet$ and $\mathrm{PhS}^\bullet$ were observed at 520,[19] 550,[19] and 450 nm,[20] respectively. The quenching rate constant of the T−T absorption with PhSH was obtained to be 5.8×10^8 s^{-1} mol^{-1} dm^3.

Time profiles of the transient absorption ($A(t)$) were measured at 550 nm under magnetic fields of 0−28 T. The concentrations of MBP and PhSH in the employed 2-methyl-1-propanol solution were 0.02 and 0.12 mol dm^{-3}, respectively. Typical $A(t)$ curves observed at 0, 6, and 28 T are shown in Figure 1. Each of the observed $A(t)$ curves has fast and slow decay components. The fast component is attributed to the decay of ${}^3\mathrm{MBP}^*$, and the slow one to the dynamic behavior of escape radicals. As clearly seen in this figure, the triplet lifetime is independent of B ($0 \le B \le 28$ T),[21] but the Y value is appreciably affected. Since the triplet lifetime was measured to be 15 ns, we take the $A_B(300\ \mathrm{ns})$ value to be the escape radical yield ($Y(B)$). Thus, $R(B) = Y(B)/Y(0\ \mathrm{T})$

[†] The Institute of Physical and Chemical Research.

[‡] National Research Institute for Metals.

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

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

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

(4) Hayashi, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 322.

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

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

(7) Wakasa, M.; Sakaguchi, Y.; Hayashi, H. *Chem. Lett.* **1994**, 49.

(8) Wakasa, M.; Sakaguchi, Y.; Hayashi, H. *Mol. Phys.* **1994**, *83*, 613.

(9) Wakasa, M.; Hayashi, H. *J. Phys. Chem.* **1995**, *99*, 17074.

(10) Sakaguchi, Y.; Hayashi, H. *Chem. Phys. Lett.* **1995**, *245*, 591.

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

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

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

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

(15) Bürbner, D.; Wolff, H.-J.; Steiner, U. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1772.

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

(17) Scaiano, J. C. *J. Photochem.* **1973/74**, *2*, 81.

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

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

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

(21) As suggested by a reviewer, 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).

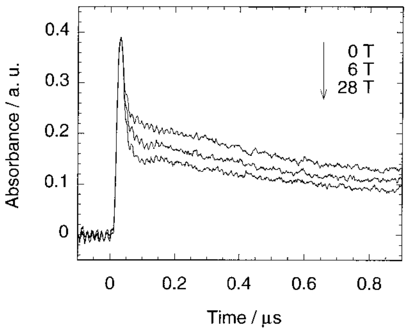

Figure 1. $A(t)$ curves observed at 550 nm for the hydrogen abstraction reaction of triplet 4-methoxybenzophenone with thiophenol in 2-methyl-1-propanol at 0, 6, and 28 T.

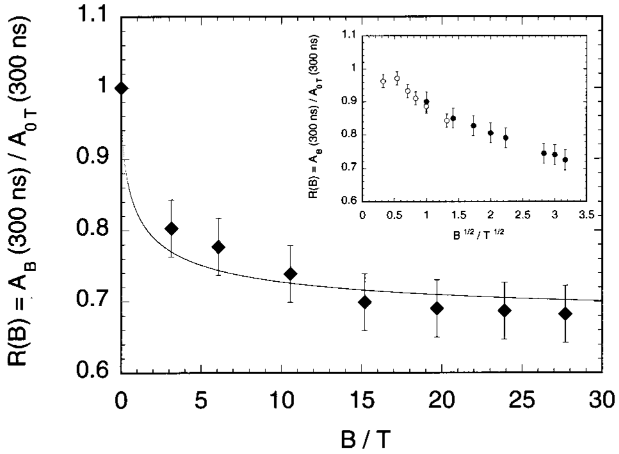

Figure 2. Magnetic field dependence of the yield of the escape 4-methoxybenzophenone ketyl radical ($R(B) = A_B$ (300 ns)/$A_{0\ \mathrm{T}}$ (300 ns)) observed at 550 nm in 2-methyl-1-propanol ($\eta = 3.33$ cP) with a pulsed magnet. Insert: the $R(B)$ values observed at lower fields (≤10 T) by an electromagnet (○) and a superconducting magnet (●).

$= A_B$ (300 ns)/$A_{0\ \mathrm{T}}$ (300 ns) gives the MFE on the yield of the escape MBPH$^\bullet$. The obtained $R(B)$ values from $A(t)$ curves are plotted against B in Figure 2. In addition, the plots of $R(B)$ values versus $B^{1/2}$ observed at lower fields (≤10 T) by an electromagnet and a superconducting magnet were inserted in Figure 2.

We can see from this figure that $R(B)$ decreases with increasing B. As clearly seen from the inserted figure, the decrease in $R(B)$ ($1 - R(B)$) is proportional to $B^{1/2}$ in the low field region ($0 \leq B \leq 10$ T). We previously found similar MFEs in the low field region ($B \leq 10$ T).[1,5,6,11,12] Such $B^{1/2}$ dependence observed in the low field region can be explained by the diffusion model of radical pairs.[3] As shown in Figure 3b, the T_0-S conversion is accelerated by a weak magnetic perturbation ($\Delta g\beta$B), and the escape radical yield decreases with increasing B. In this figure, the rate constants of T_m-S conversion due to the HFCM and ΔgM are represented by k_{HFCM} and $k_{\Delta g\mathrm{M}}$, respectively, and the constants of the recombination from the singlet radical pair, and the radical escape from the pair are k_{rec}, and k_{esc}, respectively.

We found, however, that the decrease in $R(B)$ was almost saturated at 20 T as clearly seen in Figure 2. The $R(B)$ value becomes $^2/_3$ of the $R(0\ \mathrm{T})$ one for $B \geq 20$ T. This is the limiting value of the ΔgM.[1−3] 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 present reaction, the Δg value is tentatively considered to be 0.0052, but it is possible to be much larger.[22]

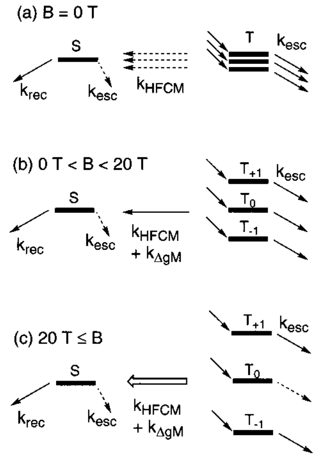

Figure 3. T−S spin conversion of a radical pair generated from a triplet precursor (T_0 and $\mathrm{T}_{\pm1}$) at (a) $B = 0$ T, (b) $0\ \mathrm{T} < B < 20$ T, and (c) $B \geq 20$ T.

Such saturation can qualitatively be interpreted by a complete T_0-S spin conversion when the recombination reaction from singlet radical pairs occurs extremely fast. If k_{esc} is much larger than k_{HFCM} at zero field, almost all of radicals in the prepared triplet radical pair escape from the pairs as shown in Figure 3a. At high fields ($B \geq 20$ T), the radicals in the $\mathrm{T}_{\pm1}$ pairs escape from the pairs as shown in Figure 3c, but the T_0 pairs can be converted to the S ones. If the T_0-S conversion ($k_{\mathrm{HFCM}} + k_{\Delta g\mathrm{M}}$) process and the recombination from the S pairs are much faster than the escape process ($k_{\mathrm{HFCM}} + k_{\Delta g\mathrm{M}}$, $k_{\mathrm{rec}} \gg k_{\mathrm{esc}}$), the pairs initially produced at T_0 predominantly recombined 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 3c. Thus, the saturation of the MFEs observed in the present photochemical reaction can qualitatively be explained by the complete T_0-S spin conversion due to the ΔgM.

Let us analyze the present experimental results by the ordinary theories which are applicable for large ΔgB. Schulten and Epstein obtained saturation behavior at very high fields of the total singlet geminate recombination yield from a triplet precursor.[13] We, however, could not use their theory because their maximum yield was as small as $^1/_6$. On the other hand, we can apply the following theory presented by Freed and Pedersen to our results:[3]

$$R(B) = 1 - {}^1/_3\,\Lambda\,\frac{\dfrac{\sqrt{q}}{2}\left\{1 + \dfrac{1}{2}\ln(1 + \sqrt{q})\right\}}{1 + \dfrac{\sqrt{q}}{2}\left\{1 + \dfrac{1}{2}\ln(1 + \sqrt{q})\right\}} \qquad (6)$$

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

where, Λ is a constant for the degree of diffusion controlled reaction. D is a diffusion constant. We simulated the B dependence of $R(B)$ by this model with a set of adequate parameters ($\Delta g = 0.0052$, $d = 10$ Å, $D = 1.0 \times 10^{-6}$ cm^2 s^{-1}, $\Lambda = 1$) and plotted our simulation in Figure 2. We can see from this figure that the saturation of the MFEs due to the ΔgM can be reproduced fairly well by this model. Thus, we conclude that the extremely large magnetic fields ($>10^3$ T) for the Δg-induced saturation predicted by Schulten and Epstein[13] are not necessary, if suitable reaction systems are chosen. However, the observed $R(B)$ values shown in Figure 2 are somewhat deviated from the simulation. The present experimental results, therefore, suggest that more theoretical investigations are necessary for explaining our results on the Δg-induced saturation.

JA980503T

---

(22) The g value of PhS$^\bullet$ was reported to be 2.0082,[23] but it is possible to be much larger.[24] Because the g value of MBPH$^\bullet$ has not yet been reported, we assumed it to be the same as that of the benzophenone ketyl radical ($g = 2.0030$).[25]

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

(24) Zandstra, P. J.; Michaelsen, J. D. *J. Chem. Phys.* **1963**, *39*, 933.

(25) Wilson, R. *J. Chem. Soc. B* **1968**, 84.