Magnetic field effects due to the relaxation mechanism observed for the photo-induced electron transfer reaction of zinc(II) tetraphenylporphyrin and 2-methyl-1,4-naphthoquinone

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ABSTRACT

The magnetic field effects (MFEs) on the photo-induced electron transfer (PET) reaction of zinc(II) tetraphenylporphyrin (ZnTPP) with 2-methyl-1,4-naphthoquinone (2MNQ) in a mixed solvent of cyclo-hexanol and 2-propanol were investigated at 293 K by a nanosecond laser flash photolysis technique. Upon irradiation of ZnTPP, the electron transfer from ZnTPP to 2MNQ occurred and the corresponding cation and anion radicals were generated. The relative yield of the escaped 2MNQ anion radical, $R(B)$, showed appreciable MFEs. The $R(B)$ values increased between 0 and 0.1 T, then decreased again between 0.1 and 1.65 T. The observed MFEs can be explained in terms of the relaxation mechanism.

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1. Introduction

Magnetic field effects (MFEs) on photochemical reactions that occur via radical pairs and biradicals have been studied extensively during the last three decades [1,2]. Because a magnetic field can interact with electron spins of radical pairs, the spin conversions between singlet (S) and triplet (T_m; $m = 0, \pm 1$) states of radical pairs are influenced by the field. Consequently, the lifetimes of radical pairs and the yields of escaped radicals show appreciable MFEs. Such MFEs can be interpreted in terms of the radical pair mechanism and the triplet mechanism (RPM and TM, respectively). In the case of ordinary organic radicals, the MFEs can be interpreted in terms of the RPM, of which four variants are known [1,2]: (1) the hyperfine coupling mechanism (HFCM) due to the isotropic hyperfine interaction between electron and nuclear spins; (2) the Δg mechanism (ΔgM) due to the difference between the isotropic g-factors of two radicals in a pair; (3) the level-crossing mechanism (LCM) due to the crossing between the S and T_{+1} (or T_{-1}) levels; and (4) the relaxation mechanism (RM) due to the anisotropic g tensor (δg), HFC (δHFC), and spin–spin interactions of radical pairs.

MFEs on photo-induced electron transfer (PET) reactions have been studied extensively because radical ion pairs generated from PET reactions are influenced by magnetic fields in a manner similar to that of the neutral radical pairs mentioned above [1,2]. However, only a limited number of MFEs have been reported concerning porphyrin–electron acceptor PET reactions, which are artificial models of photosynthetic reactions. In 1982, Boxer et al. reported the MFEs on the PET reactions of quinone-depleted photosynthetic reaction centers (*R. spheroides*, R-26) in a hydrophobic protein complex [3]. More recently, Kuciauskas et al. reported the MFEs on the PET reactions of carotenoid–(free-base octaalkylporphyrin)–fullerene at 77 K in a 2-methyltetrahydrofuran glass matrix [4]. In fluid solutions, the MFEs on the PET reactions of porphyrin–acceptor linked compounds such as zinc(II) tetraphenylporphyrin (ZnTPP)–viologen [5–8], ZnTPP–fullerene [9], and ZnTPP–naphthalenediimide [10] have been studied previously. However, except for these linked compounds, the MFEs on the PET reactions between a porphyrin and an electron acceptor in fluid solutions surprisingly have not yet been reported. In this study, we examined the MFEs on the PET reaction between ZnTPP and 2-methyl-1,4-naphthoquinone (2MNQ) in a mixed solvent of cyclohexanol and 2-propanol. Appreciable MFEs on the yield of the escaped 2MNQ anion radical were observed.

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2. Experimental

2.1. Materials

Cyclohexanol (Cica, EP-grade) and 2-propanol (Cica, HPLC-grade) were used without further purification. 2-Methyl-1,4-naphthoquinone, 2MNQ, (Cica, EP-grade) was recrystallized twice from hexane and sublimated *in vacuo*. The purity of 2MNQ was assessed using a GC–MS (Shimadzu, QP-9000). Zinc(II) tetraphenylporphyrin (ZnTPP) was prepared by metalation of the corresponding free-base tetraphenylporphyrin and recrystallized twice from dichloromethane/methanol [11].

2.2. Nanosecond laser flash photolysis

Nanosecond laser flash photolysis experiments were carried out at 293 K with the second harmonic (532 nm) of a nanosecond Nd:YAG laser (Quanta-Ray, GCR-11; 7 ns fwhm) as an excitation light source. The excitation light was introduced perpendicularly to the monitoring light. To avoid sample damage, the sample solution was pumped through a quartz flow cell placed at the center of an electromagnet (TOKIN, SEE-10W). Applied magnetic field strength (B) was measured with a gauss meter (Lake-Shore, model 421) placed beside the quartz cell. Details of the apparatus are reported elsewhere [12]. Concentrations of ZnTPP and 2MNQ were 2.0×10^{-4} and 1.0×10^{-3} mol dm^{-3}, respectively. A mixed solvent of cyclohexanol and 2-propanol (3:1, v/v) was used for its high viscosity ($\eta = 16.1 \times 10^{-3}$ Pa s [13]), because no MFE was observed in 2-propanol ($\eta = 2.04 \times 10^{-3}$ Pa s [13]). Sample solutions were carefully deoxygenated by sonication and bubbling with argon gas.

2.3. EPR measurements

Time-resolved EPR signals were measured at 293 K using an X-band EPR spectrometer (Bruker, ELEXSYS E580) without field modulation. The second harmonic of a Nd:YAG laser (Spectra Physics, INDI, 7 ns fwhm, 10 Hz) was used as an excitation light source. Concentrations of ZnTPP and 2MNQ in a mixed solvent of cyclohexanol and 2-propanol (3:1, v/v) were 4.0×10^{-4} and 6.0×10^{-3} mol dm^{-3}, respectively. The steady-state EPR spectrum was measured at 293 K with 100 kHz modulation using an X-band EPR spectrometer (Bruker, EMX 6/1). The microwave frequency was determined with a microwave frequency counter (HP, 5350B).

3. Results and discussion

3.1. Nanosecond laser flash photolysis on the PET reaction between ZnTPP and 2MNQ

In the absence and presence of 2-methyl-1,4-naphthoquinone (2MNQ) as an electron acceptor, laser flash photolysis was performed on ZnTPP in a mixed solvent of cyclohexanol and 2-propanol (3:1, v/v). Fig. 1(a) shows the typical transient absorption spectra observed for ZnTPP in the absence of 2MNQ. Strong triplet–triplet (T–T) absorption of ZnTPP [14] was observed around 450 nm. As shown in Fig. 1(a) (inset), the T–T absorption at 450 nm decayed very slowly with a lifetime of 33.8 µs. In addition of 2MNQ to the ZnTPP solution, the T–T absorption was effectively quenched, as evidenced by the typical transient absorption spectra shown in Fig. 1(b). From the spectral data reported previously [15,16], the 2MNQ anion radical has a transient absorption band around 450 nm. As shown in Fig. 1(b) (inset), the time profile of the transient absorption, $A(t)$, observed at 450 nm in the presence of 2MNQ had both a fast decay component (at times 0–10 µs) and an almost
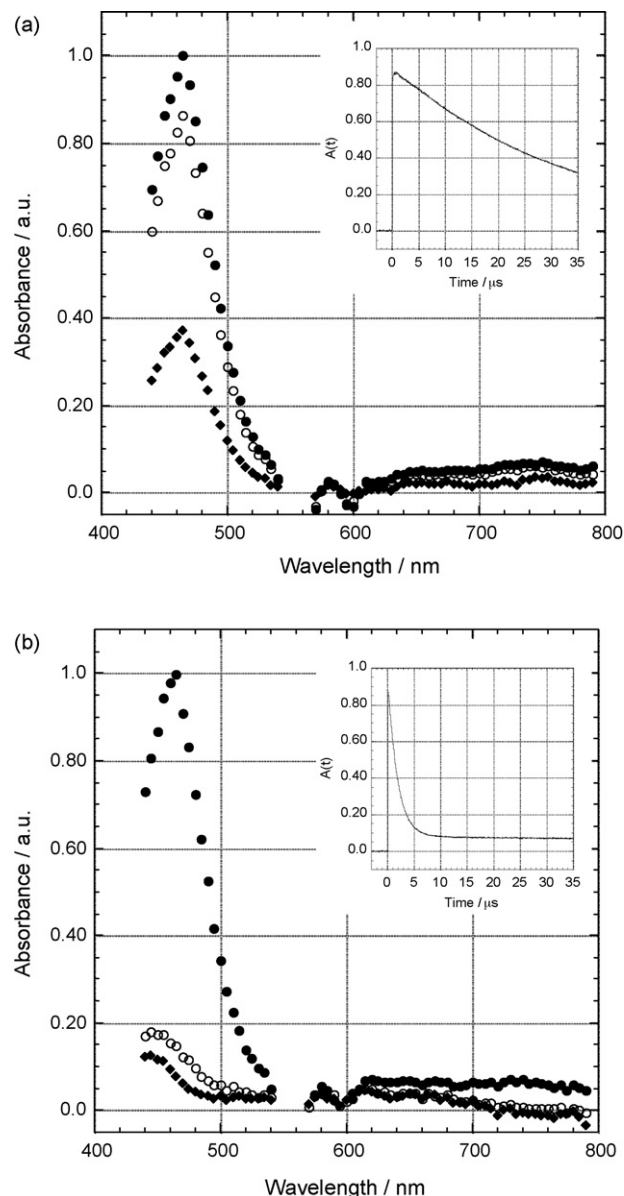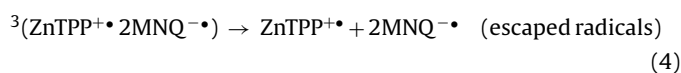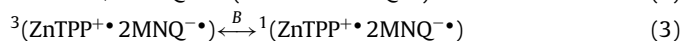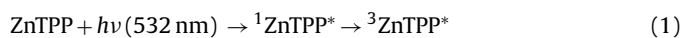

Fig. 1. The transient absorption spectra observed at delay times of 1.0 µs (●), 5.0 µs (○), and 30 µs (♦) after laser excitation of (a) ZnTPP and (b) ZnTPP with 2MNQ in cyclohexanol/2-propanol (3:1, v/v). (Insets) The time profiles observed at 450 nm for laser excitation of the samples in (a) and (b).

constant one (at times >10 µs). Since rate constants of the fast component showed clear concentration dependence only with 2MNQ [17], this component can safely be assigned to the T–T absorption of ZnTPP. The almost constant component, which was independent of the concentration of 2MNQ, can be assigned to the transient absorption of a 2MNQ anion radical. From these results, we can describe the PET reaction of ZnTPP with 2MNQ as follows:

$$ZnTPP + h\nu \,(532\,nm) \rightarrow {}^{1}ZnTPP^{*} \rightarrow {}^{3}ZnTPP^{*} \tag{1}$$

$$^{3}ZnTPP^{*} + 2MNQ \rightarrow {}^{3}(ZnTPP^{+\bullet}\,2MNQ^{-\bullet}) \tag{2}$$

$$^{3}(ZnTPP^{+\bullet}\,2MNQ^{-\bullet}) \xleftrightarrow{B} {}^{1}(ZnTPP^{+\bullet}\,2MNQ^{-\bullet}) \tag{3}$$

$$^{3}(ZnTPP^{+\bullet}\,2MNQ^{-\bullet}) \rightarrow ZnTPP^{+\bullet} + 2MNQ^{-\bullet} \quad (\text{escaped radicals}) \tag{4}$$
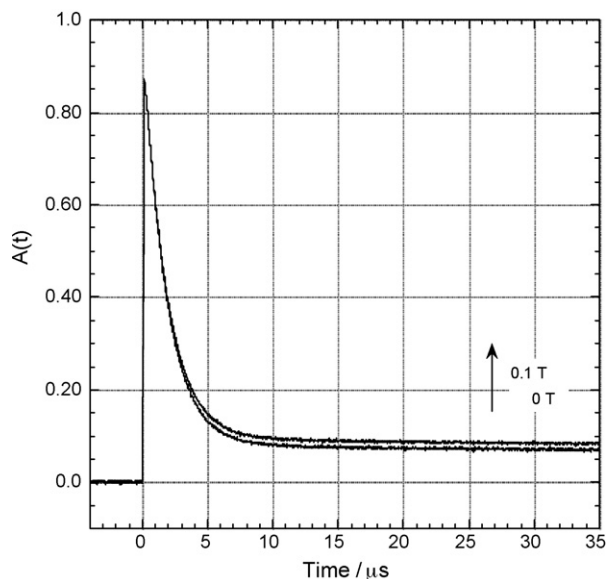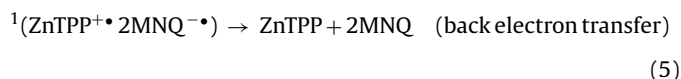
Fig. 2. The time profiles of the transient absorption observed at 450 nm for the PET reaction of ZnTPP and 2MNQ in cyclohexanol/2-propanol (3:1, v/v).

$$^{1}(ZnTPP^{+\bullet}\,2MNQ^{-\bullet}) \rightarrow ZnTPP + 2MNQ \quad \text{(back electron transfer)} \tag{5}$$

Here, $^{1}ZnTPP^{*}$, $^{3}ZnTPP^{*}$, $ZnTPP^{+\bullet}$ and $2MNQ^{-\bullet}$ represent the singlet and triplet excited states of ZnTPP, ZnTPP cation radical and 2MNQ anion radical, respectively. $^{1}(ZnTPP^{+\bullet}\,2MNQ^{-\bullet})$ and $^{3}(ZnTPP^{+\bullet}\,2MNQ^{-\bullet})$ denote the singlet and the triplet radical ion pairs composed of ZnTPP cation and 2MNQ anion radicals, respectively.

3.2. MFEs on the PET reaction between ZnTPP and 2MNQ

Since the reaction 3 can be affected by the magnetic fields (B), $A(t)$ curves were carefully measured at 450 nm for the almost constant component of the 2MNQ anion radical in the absence and presence of magnetic fields up to 1.65 T. As clearly seen in the $A(t)$ curves observed at 0 and 0.1 T (Fig. 2), the almost constant component due to the 2MNQ anion radical showed appreciable MFEs. Since the lifetime of the T–T absorption ($^{3}ZnTPP^{*}$) determined from the fast component was 0.67 μs, we can deduce that the $A(12\,μs,\,B\,T)$ value is proportional to the escaped radical ion yield ($Y(B)$). Thus, a relative radical ion yield $R(B) = Y(B)/Y(0\,T) = A(12\,μs, B\,T)/A(12\,μs, 0\,T)$ gives the MFE on the yield of the escaped 2MNQ anion radical. The obtained $R(B)$ values are plotted against B in Fig. 3. As shown in the figure, the $R(B)$ values steeply increased between 0 and 0.1 T, with the yield of the escaped 2MNQ anion radical increasing by 20% at 0.1 T compared with that at 0 T. The $R(B)$ values then gradually decreased between 0.1 and 1.65 T.

3.3. Mechanism of the MFEs observed for the PET reaction of ZnTPP and 2MNQ

In the case of ordinary organic radical pairs, the reversion of MFEs can be interpreted in terms of following mechanisms [1,2]: (1) the hyperfine coupling mechanism (HFCM) together with the Δg mechanism (ΔgM); (2) the level-crossing mechanism (LCM); and (3) the relaxation mechanism (RM) due to the anisotropic hyperfine coupling and the anisotropic Zeeman interaction. Let us consider each of these mechanisms in turn.
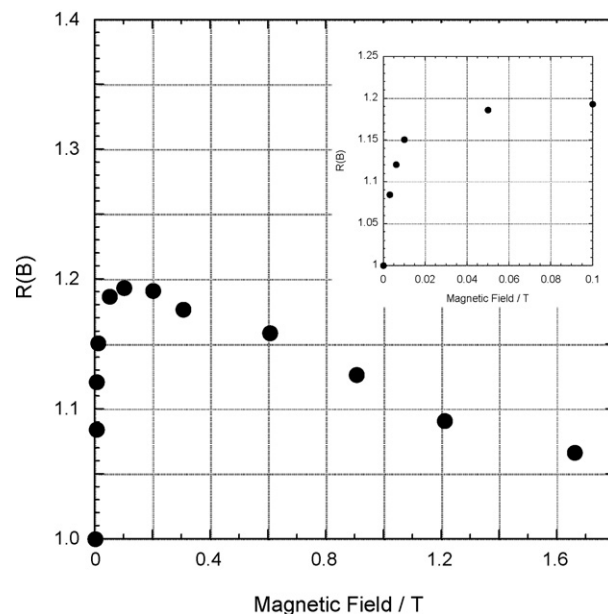

Fig. 3. MFEs of the relative radical ion yield observed for the PET reaction of ZnTPP and 2MNQ in cyclohexanol/2-propanol (3:1, v/v). Inset: The magnetic field dependence at $B \leq 0.1$ T.

(1) The hyperfine coupling mechanism (HFCM) together with the Δg mechanism (ΔgM): According to the HFCM, the yields of the triplet-born escaped radical increase with increasing B [1,2]. However, the magnetically induced increase of the escaped radical yield is saturated under relatively low fields. The magnetic field required to achieve half-saturation of the yield, $B_{1/2}$, is experimentally derived as follows [1,2]:

$$B_{1/2} = \frac{2(B_1^2 + B_2^2)}{B_1 + B_2} \tag{6}$$

The individual B_i value characterizing the radical ($i = 1$ or 2) is given by

$$B_i = \left(\sum_j I_{ij}(I_{ij} + 1)A_{ij}^2 \right)^{1/2} \tag{7}$$

where I_{ij} and A_{ij} are the quantum number and the isotropic HFC constant of the jth nuclear in radical i, respectively. Using reported HFC constants [18,19], the $B_{1/2}$ value of the radical pair of 2MNQ anion and ZnTPP cation radicals was calculated to be 1.24 mT [20]. This means that the MFEs should be saturated under magnetic fields of 3–5 mT, if the MFEs occur by the HFCM. As seen in Fig. 3 (inset), the MFEs were saturated at 50 mT. Thus, the MFEs observed at $0\,T < B \leq 0.1$ T cannot be explained by the HFCM.

According to the ΔgM, the spin conversion between T_0 and S states of a radical pair is accelerated by the magnetic fields if the two radicals have different isotropic g-values. Thus, the triplet radical pairs show decreased escaped radical yields as a result of MFEs. The decrease in $R(B)$ observed above 0.1 T may be explained qualitatively by this model. We tried to estimate the rate constant of the triplet–singlet (T–S) spin conversion due to the ΔgM. Isotropic g-values of $ZnTPP^{+\bullet}$ and $2MNQ^{-\bullet}$ were reported previously [18,19], though these values vary between reports. Thus, we measured the g-values of $ZnTPP^{+\bullet}$ and $2MNQ^{-\bullet}$. A time-resolved EPR measurement of $ZnTPP^{+\bullet}$ and $2MNQ^{-\bullet}$ was carried out in a mixed solvent of cyclohexanol and 2-propanol (3:1, v/v) at 293 K. The spectrum observed at 1.0 μs after laser excitation (Fig. 4) clearly shows a chemically induced dynamic electron polarization (CIDEP). The CIDEP gave a totally absorptive signal due to the triplet mechanism,
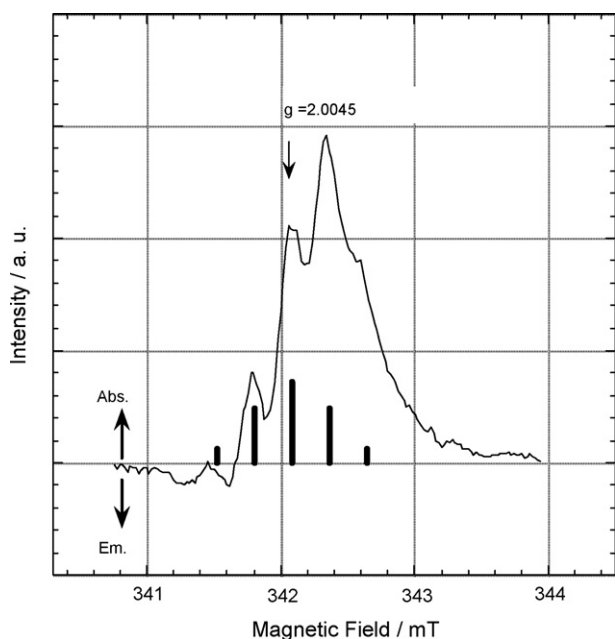
Fig. 4. Time-resolved EPR spectrum observed for the PET reaction of ZnTPP and 2MNQ in a mixed solvent of cyclohexanol and 2-propanol (3:1, v/v). Stick diagram shows the calculated EPR signal patterns for 2MNQ anion radical.

and distorted one due to the S–T$_0$ mixing radical pair mechanism. From the observed spectrum, the g-value of 2MNQ$^{-\bullet}$ was determined to be 2.0045 ± 0.0001 [20]. Recently, Kitahama and Sakaguchi reported the optically detected ESR (ODESR) study of the same PET reaction in the same mixed solvent [16]. However, the g-value of 2MNQ$^{-\bullet}$ could not be observed from the broad and noisy ODESR spectrum. As regards ZnTPP$^{+\bullet}$, the g-value was not clearly obtained from the time-resolved EPR measurement. Instead, by measuring the steady-state EPR spectrum of ZnTPP$^{+\bullet}$ generated by chemical oxidation of ZnTPP with bromine as described in literature [18a], we obtained a g-value of 2.0027 ± 0.0002 for ZnTPP$^{+\bullet}$. The difference in g-values (Δg) between ZnTPP$^{+\bullet}$ and 2MNQ$^{-\bullet}$ was estimated to be 0.0018. The rate constant of the T–S spin conversion due to the ΔgM is given by

$$k_{\Delta gM} = \frac{1}{2} \Delta g \mu_B B \hbar^{-1} \tag{8}$$

At 0.1 T, $k_{\Delta gM}$ was $7.9 \times 10^6 \, \text{s}^{-1}$. For comparison, the rate constant of the T–S spin conversion due to the HFCM is given by

$$k_{HFCM} = \frac{1}{2} g \mu_B B_{1/2} \hbar^{-1} \tag{9}$$

Here, g is the g-value of a free electron (=2.0023). In the present radical pair, k_{HFCM} was estimated to be $4.4 \times 10^8 \, \text{s}^{-1}$ using the $B_{1/2}$ value of 5 mT. This k_{HFCM} value is 56 times as large as the rate of the T–S spin conversion due to the ΔgM ($k_{\Delta gM}$). This means that the T–S spin conversion due to the ΔgM has no way to overcome that of due to HFCM at the reversion field. If reversion of the MFEs occur at $0.1 \, \text{T} < B \le 1.65 \, \text{T}$, $k_{\Delta gM}$ should become comparable with or larger than k_{HFCM}. Thus, the MFEs observed at $0.1 \, \text{T} < B \le 1.65 \, \text{T}$ cannot be explained by the ΔgM.

From the reasons above mentioned, the increase of escaped radical yield cannot be explained only by the HFCM, furthermore, the decrease of that cannot be rationalized by the ΔgM. To explain the experimental result, it is necessary both of the HFCM and the ΔgM ensured at the same time, but neither is well achieved. From these discussions, we conclude that the observed MFEs cannot be interpreted using the HFCM together with the ΔgM.

(2) The level-crossing mechanism (LCM): The LCM can safely be excluded from our consideration. In this mechanism, the spin conversion between S and T$_{+1}$ (or T$_{-1}$) occurs only at the level-crossing magnetic field, and the yield of the escaped radicals decreases at first and then increases again if the radical pair is triplet. As shown in Fig. 3, opposite field dependence was observed for our system.

(3) The relaxation mechanism (RM): According to the RM proposed by Hayashi and Nagakura [21], the spin relaxation rates of k_R and $k_{R'}$ for a radical pair consisting of radical A and radical B are given by

$$k_R = k_{dd} + k_A + k_B \tag{10}$$

$$k_{R'} = k_A + k_B \tag{11}$$

Here, k_R is the spin relaxation rate between T$_{\pm 1}$ and T$_0$, and $k_{R'}$ is that between T$_{\pm 1}$ and S. k_{dd} is the rate constant for inter-radical relaxation induced by the electron spin–spin interaction.

The rate constant for intra-radical relaxation of a radical j ($j = $ A, B), k_j, is given by

$$k_j = k_j^{\delta HFC} + k_j^{\delta g} \tag{12}$$

Here, $k_j^{\delta HFC}$ and $k_j^{\delta g}$ are the rate constants of spin relaxation by the anisotropic hyperfine coupling and the anisotropic Zeeman interaction, respectively. The magnetic field dependence of k_R and $k_{R'}$ can be calculated from the analytical forms of k_{dd}, $k_j^{\delta HFC}$ and $k_j^{\delta g}$ as follows [2,21]:

$$k_{dd} = \frac{\mu_B^4 g_A^2 g_B^2}{10 \hbar^2 R^6} \frac{3 \tau_{AB}}{1 + \omega^2 \tau_{AB}^2} \tag{13}$$

$$k_j^{\delta HFC} = \frac{1}{30 \hbar^2} (A_{\parallel}^j - A_{\perp}^j)^2 \frac{2 \tau_j}{1 + \omega^2 \tau_j^2} \tag{14}$$

$$k_j^{\delta g} = \frac{1}{30 \hbar^2} \mu_B^2 B^2 (g_{\parallel}^j - g_{\perp}^j)^2 \frac{2 \tau_j}{1 + \omega^2 \tau_j^2} \tag{15}$$

$$\omega = \hbar^{-1} g \mu_B B \tag{16}$$

Here, g_A and g_B represent the isotropic g-values of radical A and B, respectively. τ_{AB} is the correlation time of radical pair. $A_{\parallel}$ and $A_{\perp}$ denote the anisotropic hyperfine coupling constants; $g_{\parallel}$ and $g_{\perp}$ denote the anisotropic g-values. τ_j is the correlation time of each component radical. We can see from Eqs. (13)–(16) that k_{dd} and $k_i^{\delta HFC}$ decrease with increasing B, but $k_i^{\delta g}$ increases with increasing B. If the anisotropy of the g-value ($g_{\parallel} - g_{\perp}$) is not zero, the spin relaxation rate ($k_R + k_{R'}$) gradually decreases with increasing magnetic fields and then reverses to increase again in the high-field region. The deceleration of spin relaxation increases the yield of the escaped radical generated from the triplet radical pair but the acceleration decreases the yield. Thus, the MFEs observed for the PET reaction of ZnTPP with 2MNQ can be explained qualitatively by this mechanism.

Using these equations, we analyzed the experimental data for the PET reaction of ZnTPP with 2MNQ. Since the many parameters have not yet been determined experimentally, the $k_R + k_{R'}$ values were calculated with the following parameters reported previously [21–25] (superscripts denote individual radicals; radical A for ZnTPP$^{+\bullet}$ and radical B for 2MNQ$^{-\bullet}$): $g_A = 2.0027$ (this work), $g_B = 2.0045$ (this work), $\left| A_{\parallel}^A - A_{\perp}^A \right| / g \mu_B = \left| A_{\parallel}^B - A_{\perp}^B \right| / g \mu_B = 1 - 2 \, \text{mT}$ [21,22], $\left| g_{\parallel}^A - g_{\perp}^A \right| = 0.0005$ [23], $\left| g_{\parallel}^B - g_{\perp}^B \right| = 0.00323 - 0.01$, $\tau_A = 1.0 \times 10^{-9} \, \text{s}$ [24], $\tau_B = 1.0 - 0.5 \times 10^{-11} \, \text{s}$ [24], $\tau_{AB} = 1.0 - 100 \times 10^{-10} \, \text{s}$ [24] and $R = 1.0 \, \text{nm}$ [19]. In Fig. 5, typically obtained log $(k_R + k_{R'})$ values are plotted against B using the specific parameters denoted
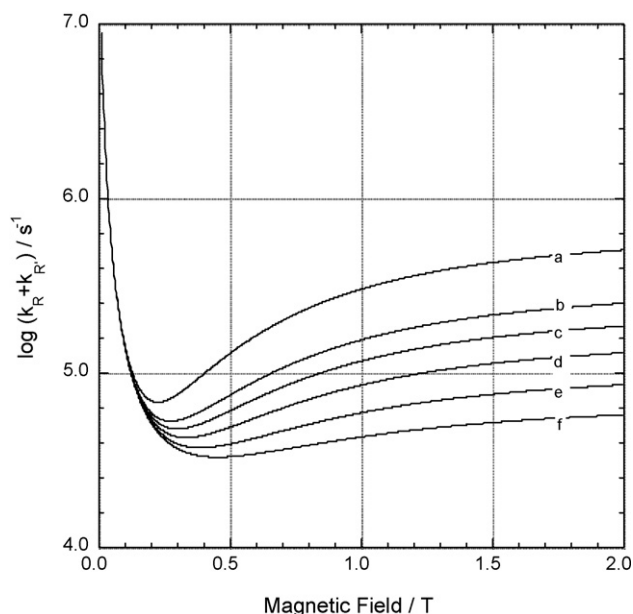
Fig. 5. Calculated magnetic field dependence of the spin relaxation rates of $k_R + k_{R'}$ for a model radical pair having the following parameters: $g_A = 2.0027$, $g_B = 2.0045$, $\left|A_\parallel^A - A_\perp^A\right|/g\mu_B = \left|A_\parallel^B - A_\perp^B\right|/g\mu_B = 0.001\,\mathrm{T}$, $\left|g_\parallel^A - g_\perp^A\right| = 0.0005$, $\tau_A = 1.0 \times 10^{-9}\,\mathrm{s}$, $\tau_B = 0.5 \times 10^{-11}\,\mathrm{s}$, $\tau_{AB} = 1.0 \times 10^{-9}\,\mathrm{s}$, and $R = 1.0\,\mathrm{nm}$, (a) $\left|g_\parallel^B - g_\perp^B\right| = 0.01$, (b) $\left|g_\parallel^B - g_\perp^B\right| = 0.007$, (c) $\left|g_\parallel^B - g_\perp^B\right| = 0.006$, (d) $\left|g_\parallel^B - g_\perp^B\right| = 0.005$, (e) $\left|g_\parallel^B - g_\perp^B\right| = 0.004$, and (f) $\left|g_\parallel^B - g_\perp^B\right| = 0.00323$.

in the figure caption. All calculated $k_R + k_{R'}$ values show clear field dependence, decreasing with increasing B at lower fields but gradually increasing at higher fields. Moreover, reversion of the $k_R + k_{R'}$ value is observed at 0.2 T with $\left|g_\parallel^B - g_\perp^B\right| = 0.01$. Thus, the MFEs observed in the present study can be rationalized in terms of this model. However, $\left|g_\parallel^B - g_\perp^B\right|$ of 0.00323–0.007 [25], were used, the reversion occurred at somewhat larger fields of 0.3–0.4 T. This may be due to simple analysis of the MFEs by the RM proposed by Hayashi and Nagakura [21]. More theoretical studies using stochastic Liouville equation are now in progress.

Finally, we try to calculate the magnetic field dependence of the escaped radical ion yield ($R(B)$) using the calculated rate constants (k_{HFCM} and $k_R + k_{R'}$) and the reported kinetic parameters (k_{esc} and k_{rec}) [16]. The escape and recombination rates (k_{esc} and k_{rec}) of the present reaction in the same mixed solvent were reported to be 0.9×10^6 and $16 \times 10^6\,\mathrm{s}^{-1}$, respectively [16] and k_{HFCM} was estimated to be $4.4 \times 10^8\,\mathrm{s}^{-1}$ by Eq. (9). Since k_{HFCM} is much larger than k_{rec}, the escaped radical ion yields at 0 T ($Y_{esc}(0\,\mathrm{T})$) can be estimated to be 0.053 using the simple kinetic model as shown in Fig. 6(a). This means that ca. 95% of radical pairs are converted to the singlet pairs and disappeared through the recombination process, but 5% of radical pairs are escaped from the pairs. This calculated yield is best rationalized to the observed $A(t)$ curve as shown in Fig. 2, where the escaped radical yield is about 5–10% though the $A(t)$ curve included small amount of contribution of the T–T absorption. At $B > 0$ T, in the case of the triplet radical pairs in the T_0 state (33%), both T–S spin conversion and escaping processes similarly occur. The pairs in $T_{\pm 1}$ states (66%) cannot be converted to the single pair by the HFCM, but can by the RM as shown in Fig. 6(b). Thus, $Y_{esc}(B\,\mathrm{T})$ is given by

$$Y_{esc}(B\,\mathrm{T}) = p\left(\frac{1}{3}\frac{k_{esc}}{(k_{rec} + k_{esc})} + \frac{2}{3}\frac{k_{esc}}{(k_R + k_{R'} + k_{esc})}\right) \quad (17)$$

Here, p represents a factor of the generated triplet radical pairs ($0 < p \leq 1$). Since the SOC-induced recombination of the triplet close
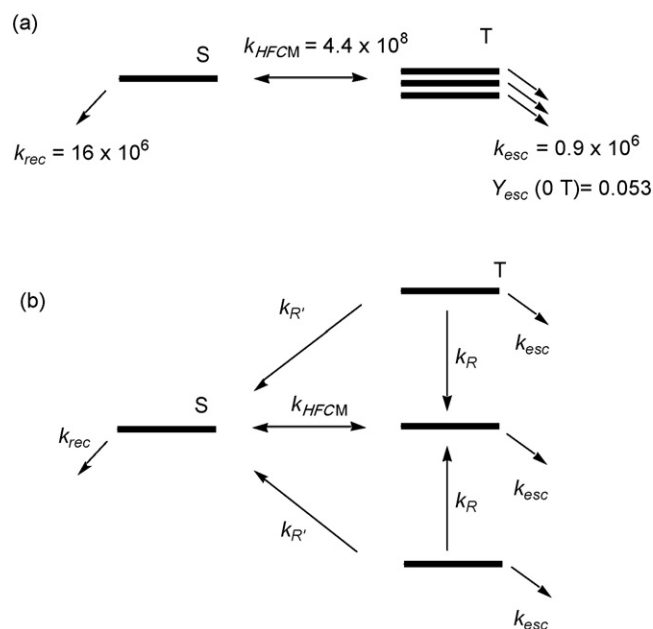

Fig. 6. Reaction scheme, T–S spin conversion and spin relaxation of the present radical pairs generated from a triplet precursor at (a) $B = 0$ T, and (b) $B > 0$ T.
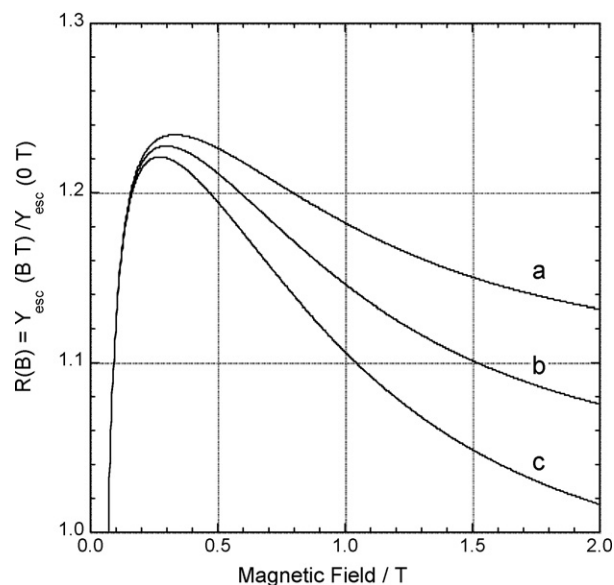

Fig. 7. $R(B)$ ($=Y_{esc}(B\,\mathrm{T})/Y_{esc}(0\,\mathrm{T})$) values calculated by Eq. (17) using $k_R + k_{R'}$ values obtained with (a) $\left|g_\parallel^B - g_\perp^B\right| = 0.005$, (b) $\left|g_\parallel^B - g_\perp^B\right| = 0.006$, (c) $\left|g_\parallel^B - g_\perp^B\right| = 0.007$.

pairs should occur in the radical pairs included heavy atom such as zinc, p may become very small. At $B = 0.1$–0.2 T, the spin relaxation rates ($k_R + k_{R'}$) were much smaller than k_{esc} and the $R(B)$ values were observed to be 1.2. Thus the p value was roughly estimated to be 0.1. Using the p value of 0.1, $R(B)$ ($=Y_{esc}(B)/Y_{esc}(0\,\mathrm{T})$) were calculated by Eq. (17) (Fig. 7). The observed MFEs can be reproduced fairly well by the calculated $R(B)$ curve.

4. Conclusions

In the present work, the MFEs on the photo-induced electron transfer (PET) reaction between zinc(II) tetraphenylporphyrin (ZnTPP) and 2-methyl-1,4-naphthoquinone (2MNQ) in a mixed sol-

vent of cyclohexanol and 2-propanol were investigated. The yield of the escaped 2MNQ anion radical showed appreciable MFEs upon the application of magnetic fields. The MFEs observed for PET reactions can be explained in terms of the relaxation mechanism of the triplet radical pair.

Acknowledgements

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