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Effects of High Magnetic Field on the Lifetime of Chain-Linked Triplet Biradicals Composed of Xanthone Ketyl and Xanthenyl Radicals

Yoshifumi Tanimoto,* Hiroaki Tanaka, Yoshihisa Fujiwara, and Masao Fujiwara

Faculty of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan

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The magnetic field dependence (0−13.1T) of the lifetime of the chain-linked triplet biradicals, composed of xanthone ketyl and xanthenyl radicals, has been studied as a function of chain length. Upon increasing a magnetic field, its lifetime increases steeply to the respective maximum value at ca. 2 T. Upon further increasing the field, the lifetime of a long chain biradical decreases slightly, whereas those of all other biradicals are almost constant. Chain length dependence of the biradical lifetimes in a low magnetic field (0.1 to ca. 2 T) are discussed in terms of the spin−lattice relaxation (SLR) due to the dipole−dipole interaction between two radicals and the spin−orbit-induced intersystem crossing from triplet states of biradicals. A slight decrease in the lifetime, observed for a long chain-linked biradical in high magnetic field, is explained by the SLR due to the anisotropic Zeeman interaction.

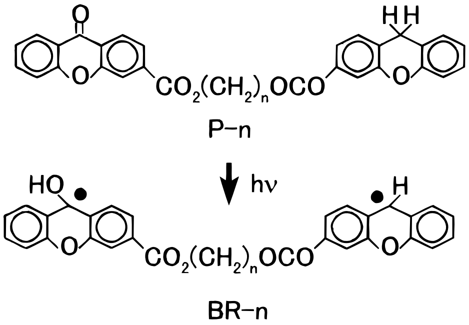
1. Introduction

Magnetic field effects (MFEs) on photochemical reactions have attracted much attention of photochemists after the pioneering works carried out in the 1970s.[1−6] The effects of a relatively low magnetic field (≤ ca. 1 T), generated by a conventional electromagnet, on photochemical processes have been studied very extensively over 20 years. Very recently the interest of a few chemists has shifted to the effects of a higher magnetic field (1 to ca. 30 T).[7−11]

Tanimoto and his collaborators have reported for the first time that the lifetime of a chain-linked triplet biradical shows reversal of MFE at ca. 2 T when intensities of the magnetic field are changed from 0 to ca. 14 T.[8b] Similar reversal of MFEs has been observed for many chain-linked biradicals in homogeneous solution and radical pairs in micellar solution.[8,9] These new findings are qualitatively interpreted in terms of the relaxation mechanism of a radical pair in which anisotropic Zeeman interaction enhances spin−lattice relaxation (SLR) among spin sublevels of a biradical or a radical pair in a high magnetic field.[12] To elucidate the contributions of various mechanisms of MFEs to the magnetic field dependence (MFD) of triplet biradical lifetimes, we have examined the MFEs and magnetic isotope effects on several biradicals.[11]

The MFEs on the chain-linked triplet biradicals, ^{3}BR-*n*, composed of xanthone ketyl and xanthenyl radicals, which are generated from chain-linked compounds, P-*n*, shown in Chart 1, have been well-studied by laser flash spectroscopy in magnetic fields below 1 T as well as by CIDNP and CIDEP.[13,14] These biradicals are, therefore, suitable for a study of effects of a high magnetic field. In this paper, we report the effects of a high magnetic field (≤13.1 T) on the lifetime of the chain-linked triplet biradicals, ^{3}BR-*n*, as a function of chain length *n*. The dependence of the lifetimes on *n* is attributable to both that of SLR, which is induced by the dipole−dipole interaction, and that of the spin−orbit (SO)-induced intersystem crossing (ISC) from a triplet biradical to ground-state products. Small reversal of the MFE observed for a long chain-linked biradical is attributable to the contribution of anisotropic Zeeman interaction to the SLR processes.

CHART 1



2. Experimental Section

All the precursors of biradicals (P-*n*, $n = 3, 5, 6, 8, 12, 16$) shown in Chart 1 were synthesized according to a literature procedure.[13b] Spectro-grade ethyl acetate (Nacalai) was used as supplied. All sample solutions were degassed by several freeze−pump−thaw cycles. Their concentration was about 1 $\times 10^{-4}$ mol dm^{-3}.

Transient absorption signals were measured using a pulse-magnetic-field laser photolysis apparatus described elsewhere.[8a,e] Exciting and probe light sources were an excimer laser (Lumonics, EX-510, 308 nm) and a xenon arc lamp (Ushio, UXL-150-O), respectively. The laser and probe lights were introduced coaxially to a sample cell that was installed at the center of a pulse magnet. The prove light was detected by a momochromator-photomultiplier-digital oscilloscope-personal computer system. Magnetic field (≤13.1 T) was generated by applying an electric current from a capacitor bank (5 kV, 50 kJ).

In the presence of a magnetic field above ca. 0.5 T, the lifetime of triplet biradicals ^{3}BR-*n* ($n = 12,16$) became as large as about 10 μs. To minimize the influence of bimolecular reaction on the biradical lifetime, the laser intensity was reduced as low as possible. The transient signals from ^{3}BR-*n* was detected at 340 nm where it had an intense absorption band.[13]

The transient signal of ^{3}BR-*n* decayed nonexponentially, and its intensity $I(t)$ at time t was expressed empirically by

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$$I(t) = I_{BR}\exp(-t/\tau_{BR}) + I_c \tag{1}$$

where I_{BR} and τ_{BR} were the initial intensity and lifetime of ^{3}BR-*n*, respectively, and I_c was the intensity due to a long-lived component that could be attributable to the absorption of photoproduct(s).

3. Results

3.1. Reaction Scheme and Biradical Lifetimes. The primary photochemical process of P-*n* has been discussed in detail in a previous paper:[13]

$$\text{P-}n + h\nu \rightarrow {}^1\text{P*-}n \rightarrow {}^3\text{P*-}n \tag{2}$$

$${}^3\text{P*-}n \rightarrow {}^3\text{BR-}n \tag{3}$$

$${}^3\text{BR-}n \rightarrow {}^1\text{BR-}n \tag{4}$$

$${}^1\text{BR-}n \rightarrow \text{recombination product(s)} \tag{5}$$

$${}^3\text{BR-}n \rightarrow \text{product(s)} \tag{6}$$

Upon photoexcitation of a xanthone moiety in P-*n*, the excited triplet P-*n* (^{3}P*-*n*) is generated via the excited singlet P-*n* (^{1}P*-*n*) (eq 2). ^{3}P*-*n* undergoes a fast intramolecular hydrogen abstraction reaction from a xanthene moiety at the other end of the chain, resulting in the formation of a triplet biradical, ^{3}BR-*n*, composed of a xanthone ketyl radical and a xanthenyl radical (eq 3). ^{3}BR-*n* is generated with a time constant of 10−20 ns. ^{3}BR-*n* disappears partly via intersystem crossing (ISC) to the singlet biradical, ^{1}BR-*n*, followed by a recombination reaction (eqs 4 and 5) and partly via a spin−orbit (SO)-induced direct ISC to ground-state product(s) (eq 6). Here bimolecular reaction and other process are neglected from the above reaction scheme, since the biradical concentration was reduced as low as possible in the present experimental condition. An external magnetic field affects the triplet−singlet spin conversion process in the biradicals as described below.

Figure 1 and Table 1 show the MFD of the lifetimes of ^{3}BR-*n*, analyzed using eq 1. There are two remarkable points: (1) The MFD of the lifetimes is composed of two regions. In a low magnetic field region (< ca. 2 T), the lifetime increases rapidly with increasing magnetic field strength. In a high field region (ca. 2−13 T), it decreases gradually with increasing magnetic field when $n = 12$, 16, whereas the lifetimes for short chain biradicals are almost constant. (2) Its maximum lifetime increases from 3.3 to 10.3 μs upon increasing *n* from 3 to 16.

3.2. Analysis of the MFD of Biradical Lifetime. Effects of a magnetic field on the lifetime of triplet biradicals have been studied in detail.[8,11,13] Figure 2 depicts schematically energy levels and spin conversion process of long chain biradicals composed of conventional organic radicals, which is the case of the biradicals discussed here. At zero field a singlet state (S) and three triplet sublevels (T_+, T_0, T_-) are degenerate and electron−nuclear hyperfine (hf)-induced ISC takes place between S and three triplet sublevels. In the presence of a magnetic field above ca. 0.1 T, the hf-induced $T_\pm \rightarrow$ S ISC is quenched, because of the Zeeman splitting of T_+ and T_-, though the hf-induced $T_0 \rightarrow$ S ISC remains the same. In addition, in the presence of a magnetic field, the T_0−S ISC is induced by the difference of isotropic *g* values of two component radicals (Δ*g* mechanism). In the case of ^{3}BR-*n*, the hf-induced ISC rate constant is estimated to be 10^7 s^{-1} or so. Since biradical lifetimes are a few microseconds in the presence of a magnetic field, the biradicals optically detected in the present experiment are considered to be those in T_+ and T_- sublevels. Under these circumstances, the spin lattice relaxation (SLR), which is induced by anisotropic hf (δhf) and Zeeman (δ*g*) interactions, governs the transitions among T_+, T_-, T_0, and S. Therefore, the decay rate constant k_{BR} of the triplet biradical in T_+ and T_- can be expressed by the following equation[8f,11b]

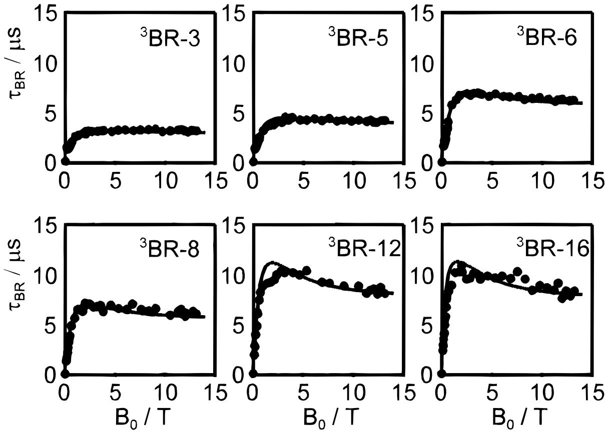

Figure 1. MFD of the lifetime of triplet biradicals, ^{3}BR-n. ●; observed. The curves in the figure are the simulated ones. See text.

TABLE l: Lifetimes (μs) of ^{3}BR-*n* in Magnetic Fields[a]

	B_0/T					
n	0	0.44	1.0	2.0	7.5	13.1
3	0.18	1.7	2.7	3.0	3.3	3.2
5	0.13	2.1	3.2	3.8	4.4	4.2
6	0.12	3.0	5.8	6.8	6.6	6.3
8	0.12	3.8	5.7	7.1	6.5	6.1
12	0.14	6.1	8.9	9.5	9.2	8.1
16	0.14	6.8	9.0	10.3	10.3	8.4

[a] Experimental error is about ±10%.

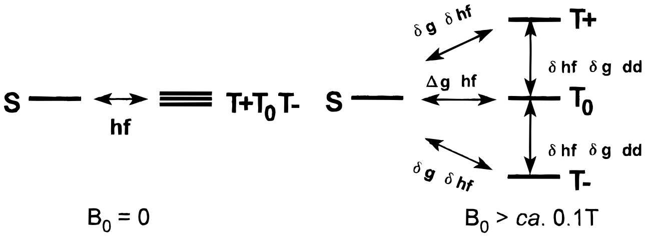

Figure 2. Energy levels and spin conversion process of a biradical.

$$k_{BR} = 1/\tau_{BR} = {}^1\!/_2\{k(1{:}\delta\text{hf}, \delta g) + k(2{:}\delta\text{hf}, \delta g)\} + k(\text{dd}) + k_T \tag{7}$$

where $k(1{:}\delta\text{hf}, \delta g)$ and $k(2{:}\delta\text{hf}, \delta g)$ are the SLR rate constants of radicals 1 and 2, which are governed by the δhf and δ*g* interactions, respectively, and *k*(dd) is the SLR rate constant induced by the dipole−dipole (dd) interaction between two electrons at two radical centers. The term k_T is the rate constant for the intersystem recombination directly from triplet sublevels of a biradical to ground-state product(s), which is caused by the SO interaction and assumed to be magnetic-field-independent.[15−19] $k(i{:}\delta\text{hf}, \delta g)$ and *k*(dd) are further expressed as

$$k(i{:}\delta\text{hf}, \delta g) = \gamma^2 H_{loc}{}^2\tau_{ci}/(1 + \gamma^2 B_0{}^2\tau_{ci}{}^2) + (1/5)(\beta/h)^2(g{:}g)B_0{}^2\tau_{ci}/(1 + \gamma^2 B_0{}^2\tau_{ci}{}^2) \tag{8}$$

and

$$k(\mathrm{dd}) = \gamma^2 H_{\mathrm{dd}}{}^2 \tau_c{}'/(1 + \gamma^2 B_0{}^2 \tau_c{}'^2) \qquad (9)$$

where β is the Bohr magneton and γ is the magnetogyric ratio of the electron on the radical, which is assumed to be equal to that of a free electron. The parameters τ_{ci} and $\tau_c{}'$ are rotational correlation times of tumbling Brownian motion for the anisotropic δhf and δg interactions of component radicals and for the dd interaction between two electrons at two radical centers, respectively. The parameters H_{loc} and $(g{:}g)$ are the locally fluctuating field due to the δhf interaction and the inner product of the anisotroic g tensor, respectively. With increasing a magnetic field, both the SLR rate constant due to the δhf interaction, i.e., the first term of the right-hand side of eq 8, and that due to the dd interaction, i.e., eq 9, decrease asymptotically to zero, whereas the SLR rate constant due to the δg interaction, i.e., the second term of the right-hand side of eq 8, increases.

Generally speaking, the MFD of the triplet biradical lifetime shown in Figure 1 should be expressed by eq 7. From experimental points of view, however, it is extremely difficult to distinguish between the contribution from a radical 1 and that from a radical 2. In addition, it is practically impossible to differentiate the contribution of the δhf interaction from that of the dd interaction without the use of magnetic isotope-substituted biradicals,[11] since both mechanisms affect similarly the triplet biradical lifetime in a magnetic field. Furthermore, in a previous paper,[8f] we have studied the effect of high magnetic fields on the lifetime of a triplet biradical generated from the photoreaction of α-cyclodextrin inclusion complex of phenothiazine−viologen chain-linked compound, which exhibits a most drastic reversal of the effect in the magnetic field above ca. 2 T. From the detailed analysis of its MFD, it is proposed that a short correlation time, which cannot be assigned to the radical motion as a whole, is indispensable to reproduce the observed lifetime change above ca. 2 T. On the basis of the above-mentioned reasons, the MFD of the biradical lifetime shown in Figure 1 is analyzed using the following *empirical* expression:[8f,11b]

$$\begin{aligned} k_{\mathrm{BR}} &= 1/\tau_{\mathrm{BR}} \\ &= k(\delta\mathrm{hf}, \mathrm{dd}) + k(\delta g) + k_{\mathrm{T}} \end{aligned} \qquad (10)$$

where

$$k(\delta\mathrm{hf}, \mathrm{dd}) = \gamma^2 H_{\mathrm{eff}}{}^2 \tau_c{}''/(1 + \gamma^2 B_0{}^2 \tau_c{}''^2) \qquad (11)$$

and

$$k(\delta g) = (1/5)(\beta/h)^2 (g{:}g)_{\mathrm{eff}} B_0{}^2 \tau_c{}'''/(1 + \gamma^2 B_0{}^2 \tau_c{}'''^2) \qquad (12)$$

The term $k(\delta\mathrm{hf}, \mathrm{dd})$ is the sum of the contribution from the δhf interactions at radicals 1 and 2 and the dd interaction between two electrons, whereas the term $k(\delta\mathrm{g})$ is the sum of the contribution from the δg interactions at radicals 1 and 2. Here H_{eff}, $\tau_c{}''$, $(g{:}g)_{\mathrm{eff}}$, and $\tau_c{}'''$ are the effective local magnetic field, its correlation time, the effective $(g{:}g)$ value, and its correlation time, respectively.

Furthermore, the analysis of MFD of the biradical lifetime shown in Figure 1 is carried out in two magnetic field regions. This is because the term $k(\delta\mathrm{hf}, \mathrm{dd})$ affects the biradical lifetime predominantly at the relatively low magnetic field (<2 T), whereas the $k(\delta g)$ term does in the high magnetic field (>2 T).[11]

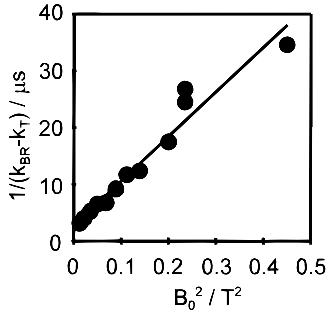

Figure 3. Plot of $1/(k_{\mathrm{BR}} - k_{\mathrm{T}})$ vs B_0 for ^{3}BR-16.

TABLE 2: k_{T}, $H_{\mathrm{eff}}{}^2$, τ_c, and r for ^{3}BR-n

n	$k_{\mathrm{T}}/10^5\ \mathrm{s}^{-1}$	$H_{\mathrm{eff}}{}^2/\mathrm{mT}^2$	τ_c/ps	r^a/nm
3	2.9	1.54	10	1.28
5	2.0	1.10	14	1.43
6	1.3	0.98	20	1.48
8	1.3	0.85	29	1.61
12	0.8	0.48	29	
16	0.8	0.39	30	

[a] The mean distance between two radicals. Taken from ref 13b.

3.3. Analysis of the Biradical Lifetime in the Low Magnetic Field Region (<2 T). In the low magnetic field region, the contribution of the SLR due to the δg interaction to the biradical lifetime is considered to be small. Thus, $k(\delta\mathrm{g})$ can be neglected from eq 10 for the analysis in the low magnetic field region. Since there is a linear relationship between $1/(k_{\mathrm{BR}} - k_{\mathrm{T}})$ and $B_0{}^2$, as given in the following equation

$$1/(k_{\mathrm{BR}} - k_{\mathrm{T}}) = 1/k(\delta\mathrm{hf}, \mathrm{dd}) = 1/(\gamma^2 H_{\mathrm{eff}}{}^2 \tau_c{}'') + (\tau_c{}''/H_{\mathrm{eff}}{}^2) B_0{}^2 \qquad (13)$$

The $1/(k_{\mathrm{BR}} - k_{\mathrm{T}})$ values are plotted against $B_0{}^2$ for a tentatively assumed k_{T} value. The k_{T} value is then determined from the one obtained when the plot of $1/(k_{\mathrm{BR}} - k_{\mathrm{T}})$ vs $B_0{}^2$ becomes linear. The parameters $H_{\mathrm{eff}}{}^2$ and $\tau_c{}''$ are obtained from the slope and intersection of the straight line calculated by the least-squares method. Figure 3 shows an example of the plot of eq 13 for the lifetime of ^{3}BR-16. From this plot, k_{T}, $H_{\mathrm{eff}}{}^2$, and $\tau_c{}''$ are obtained to be $0.8 \times 10^5\ \mathrm{s}^{-1}$, 0.39 mT^2, and 30 ps, respectively. k_{T}, $H_{\mathrm{eff}}{}^2$, and $\tau_c{}''$ are calculated analogously for all other biradicals as summarized in Table 2. Upon increasing n from 3 to 16, the k_{T} value decreases from 2.9×10^5 to $0.8 \times 10^5\ \mathrm{s}^{-1}$. Similarly, the $H_{\mathrm{eff}}{}^2$ value decreases from 1.54 to 0.39 mT^2, whereas $\tau_c{}''$ increases from 10 to 30 ps.

3.4. Analysis of the Biradical Lifetime in the High Magnetic Field Region (2−13 T). The lifetime of ^{3}BR-16 is affected remarkably by the magnetic field. Especially in the high magnetic field region, its lifetime decreases gradually. Thus, the MFD of the lifetime for ^{3}BR-16 is analyzed by a numerical simulation method using eq 10. In this simulation parameters for the δg interaction, i.e., $(g{:}g)_{\mathrm{eff}}$ and $\tau_c{}'''$, are only varied, whereas all other parameters obtained from the analysis in the low magnetic field are fixed. Figure 4a shows the influence of $(g{:}g)_{\mathrm{eff}}$ on the MFD of the lifetime for BR-16 when $\tau_c{}'''$ is fixed at 1 ps. At $(g{:}g)_{\mathrm{eff}} = 10^{-5}$ the lifetime decreases very rapidly, whereas at $(g{:}g)_{\mathrm{eff}} = 10^{-7}$ the lifetime is almost constant. At $(g{:}g)_{\mathrm{eff}} = 10^{-6}$ the simulated curve reproduces quite well the observed data. Figure 4b demonstrates the influence of $\tau_c{}'''$ when $(g{:}g)_{\mathrm{eff}}$ is fixed at 10^{-6}. The most reasonable agreement of the simulated curve and the observed data is achieved when $\tau_c{}''' = 1$ ps. From the analysis, $(g{:}g)_{\mathrm{eff}}$ and $\tau_c{}'''$ are determined to be 10^{-6} and 1 ps, respectively.

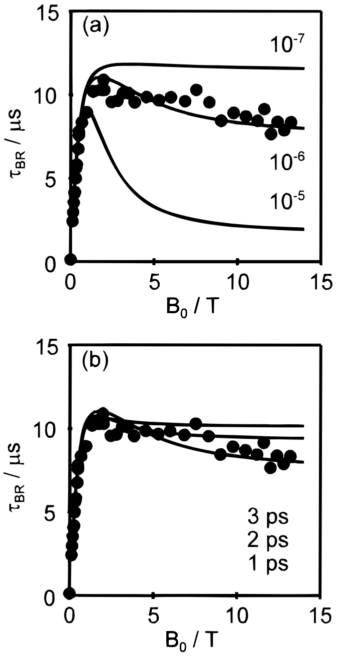

Figure 4. Influence of $(g{:}g)_{\text{eff}}$ and τ_c''' on the MFD of the lifetime of 3BR-16. (a) Influence of $(g{:}g)_{\text{eff}}$. τ_c''' is fixed at 1 ps. (b) Influence of τ_c'''. $(g{:}g)_{\text{eff}}$ is fixed at 10^{-6}. See text.

The lifetimes of biradicals with $n = 3-12$ are not analyzed in the high magnetic field region, since their change in the high magnetic field is insignificant. Alternatively, to check the quality of the above analysis, the magnetic field dependences (ca. 0.1−13.1 T) of the lifetimes of ^{3}BR-*n* with $n = 3-12$ are calculated using the respective parameters shown in Table 1 and those for the δg interaction mentioned above. These calculated curves are also shown in Figure 1. Agreement between the calculated curves and the observed data is satisfactory, indicating that the analytical procedure applied here seems reasonable. In the case of BR-3, the lifetime is almost constant in the higher magnetic field, since it is mainly governed by the SO-induced intersystem recombination process.

4. Discussion

In a previous paper,[13e] we obtained the effective anisotropic hf interaction, $H_{\text{eff}}'^2$, for ^{3}BR-*n* from the temperature dependence of the lifetime of ^{3}BR-*n* ($n = 8-16$) at 0.6 T. In this analysis, the biradical lifetime ($1/k_{\text{BR}}$) was assumed to be controlled solely by the anisotropic hf interaction, and the SLR due to the dd interaction, as well as the intersystem recombination from triplet sublevels, was neglected. The rotational correlation time of the radicals at two ends of the chain, τ_{ci}, was fixed for all the biradicals with $n = 6-16$. Under these assumptions, k_{BR} was given by eq 14:

$$k_{\text{BR}} = \gamma^2 H_{\text{eff}}'^2 \tau_{ci}/(1 + \gamma^2 B_0^{\,2} \tau_{ci}^{\,2}) \qquad (14)$$

The $H_{\text{eff}}'^2$ values were obtained to be 2.19 ($n = 6$), 1.82 ($n = 8$), 1.77 ($n = 12$), and 1.44 mT^2 ($n = 16$). The H_{eff}^2 values obtained from the present work (Table 2) are much smaller than those obtained previously. As shown in Table 2, the contribution of k_T to k_{BR} cannot be neglected, as it increases about three times by decreasing *n* from 16 to 3. The present analysis seems more reliable, since the contribution of k_T to k_{BR} is subtracted and the correlation time, τ_c'', is not fixed but remained as a parameter to be determined.

In a recent paper,[11b] we reported the magnetic field and magnetic isotope effects on the chain-linked triplet biradicals consisting of two equivalent benzophenone ketyl (BPH) radicals (BPH−O−(CH$_2$)$_n$−O−BPH, $n = 8$, 10, 12). The following conclusions are derived from these analyses: (1) The H_{dd}^2 for BPH−O−(CH$_2$)$_{12}$−O−BPH, which is connected by 14 chain units including two ether oxygen atoms, is estimated to 0.19 mT^2 with a correlation time of ca. 26 ps. (2) From the comparison of the observed H_{loc} and theoretical one for natural and ^{13}C-substituted BPH, the H_{loc} values obtained theoretically are suggested to be reliable as an estimation of H_{loc} of biradicals.

Now let us examine the H_{eff}^2 and τ_c'' values for ^{3}BR-*n* shown in Table 2 in detail, taking into account the consideration mentioned above. Upon increasing *n* from 3 to 16, the H_{eff}^2 value decreases from 1.54 to 0.39 mT^2 in concomitant increase with the τ_c'' value from 10 to 30 ps. These dependences of H_{eff}^2 and τ_c'' on *n* seem to be parallel with the changes expected for those for the dd interaction, as the interradical distance increases from 1.28 ($n = 3$) to 1.61 nm ($n = 8$).[13b] However, in the case of ^{3}BR-16, whose total number of chain units is 20, the H_{eff}^2 value (0.39 mT^2) is much larger than the H_{dd}^2 value (0.19 mT^2) obtained for BPH−O−(CH$_2$)$_{12}$−O−BPH.[11b] Since H_{eff}^2 for ^{3}BR-16 is comparable with the theoretical H_{loc}^2 value for ^{3}BR-*n* (0.37 mT^2),[13e] the MFD of the ^{3}BR-16 lifetime can be mainly explained by the δhf mechanism. In other cases, it is considered that the MFD in the low field is attributable to the mixed mechanism of the dd and δhf interactions. Most probably the dd interaction is dominant in the case of the short chain biradical, ^{3}BR-3.

In a previous paper,[8f] the MFD of the lifetime of a triplet biradical generated from a cyclodextrin inclusion complex of phenothiazine and viologen chain-linked compound (Phe-V) has been discussed in detail. In Phe-V, the drastic lifetime change is observed (i.e., 0.14 (0 T), 6.6 (1 T), and 2.2 μs (13 T)). The lifetime at 13 T is about 30% of that at 1 T. This significant reversal of MFE on the lifetime could be only explained by a large ($g{:}g$) value (10^{-5}) and a very short correlation time (1 ps) for the δg interaction. In other biradicals, i.e., BPH−O−(CH$_2$)$_{12}$−O−BPH and its analogues, the lifetime decrease in the high magnetic field above ca. 2 T is quite small and, therefore, parameters for the δg interaction are not obtained. From the analysis of the lifetime of ^{3}BR-16, $(g{:}g)_{\text{eff}}$ and τ_c''' are obtained to be 10^{-6} and 1 ps, respectively. Since, in the present case, the lifetime decrease in the high magnetic field is not very significant, a small ($g{:}g$) value is reasonable to explain the results shown in Figure 1. The correlation time τ_c''' for ^{3}BR-*n* is the same as that for Phe-V. This indicates that a very short correlation time is certainly necessary to explain the observed MFD in the high magnetic field. The origin and meaning of this short correlation time are still unclear. As discussed in detail in a previous paper,[8f] we propose tentatively that τ_c''' is associated with a local motion at component radicals such as torsional motion at a >C−O− bond connecting a radical group and a chain. The relevance of a short correlation time has been suggested in literature reports.[20,21] A biradical undergoes conformational changes "locally" and "as a whole" with a wide spectrum of frequencies. It seems that of the wide spectrum of frequencies available to molecular motions, only a frequency energetically matched to a specific transition is sorted out.

The direct ISC from triplet state of biradicals and radical pairs to ground-state product(s) has been reported to be caused by the SO interaction.[15−19] In the present analysis, this process is assumed to be magnetic-field-independent, since the present biradicals have no heavy atom. If this process could be magnetic-field-dependent as in the cases of radical pairs

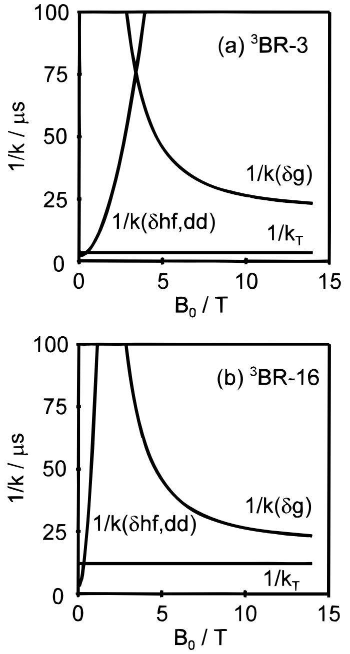

Figure 5. MFD of $1/k_T$, $1/k(\delta\mathrm{hf, dd})$, and $1/k(\delta g)$ for (a) ^{3}BR-3 and (b) ^{3}BR-16.

containing a heavy atom such as iodine and ruthenium atoms,[10,17,18] a biradical with a short chain, i.e., BR-3, should show the most significant reversal of the MFE. Contradictory to this prediction, its lifetime is almost constant in the magnetic field above ca. 2 T as shown in Figure 1. Therefore, the direct SO-induced ISC in BR-*n* is considered to be magnetic-field-independent.

As shown in Table 2, the k_T value decreases from 2.9×10^5 to 0.8×10^5 s^{-1} by increasing *n* from 3 to 16. The rate constant for the SO-induced ISC from a triplet biradical, which is a function of an interradical distance, is expected to decrease with increasing *n*, since the distance is calculated to increase from 1.28 ($n = 3$) to 1.61 nm ($n = 8$).[13b] Thus, the observed dependence of k_T on *n* is understandable only when k_T is mainly controlled by the SO-induced ISC process. In the case of the triplet biradicals composed of acyl and alkyl radicals, the rate constant for the SO-induced ISC is reported to be about 10^7 s^{-1}.[17,18] Since an acyl radical has an oxgen atom at its radical center, the SO interaction should be significant compared with the interaction in the present biradicals. The present k_T values are comparable with those obtained in the radical pairs in micellar solution, generated from the photoreaction of aromatic ketones.[19]

Finally, the magnetic field dependences of $k(\delta\mathrm{hf, dd})$, $k(\delta g)$, and k_T for ^{3}BR-3 and ^{3}BR-16 are depicted in Figure 5. In the case of ^{3}BR-3, it is clear that τ_{BR} in the magnetic field above ca. 0.5 T is predominantly controlled by k_T, whereas, in the case of ^{3}BR-16, τ_{BR} in the high magnetic field (>ca. 7 T) is slightly affected by the SLR due to the δg mechanism.

5. Conclusion

The MFD (0−13 T) of the lifetime of the triplet biradicals, ^{3}BR-*n*, composed of xanthone ketyl and xanthenyl radicals has been studied as a function of chain length *n*. Upon increasing the magnetic field, the lifetime increases steeply to the respective maximum values at ca. 2 T. The maximum lifetime increases from ca. 3 μs ($n = 3$) to 10 μs ($n = 16$). Upon further increasing the field, the lifetime for ^{3}BR-*n* ($n = 16$, 12) decreases slightly, whereas the lifetime of all other biradicals are almost constant in the magnetic field above ca. 2 T. Chain length dependence of the biradical lifetime is attributable to those of the SLR due to the dd interaction and the SO-induced ISC from triplet states of biradicals to ground-state product(s).

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