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# Magnetic Field and Isotope Effects on Photochemistry of Chain-Linked Compounds Containing Benzophenone and Hydrogen-Donor Moieties

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The magnetic field effects on the decay kinetics for chain-linked triplet biradicals have been observed by the use of a laser photolysis apparatus with a conventional electromagnet and a pulsed magnet. Biradical lifetimes increase steeply to their maxima from the zero field to ca. 2 T. The biradical decay times tend to decrease gradually with further increase of the magnetic field intensity to 14 T. The decreased lifetimes for triplet biradicals can be explained in terms of spin−lattice relaxation due to hyperfine anisotropy and to **g** tensor anisotropy.

## 1. Introduction

Magnetic field effects (MFEs) on chemical reactions involving radical pairs and biradical intermediates have been extensively studied during the past two decades.[1−5] We have investigated magnetic field and magnetic isotope effects on dynamical behavior of biradicals produced on photolysis of methylene-linked chain molecules in the presence of magnetic fields less than 1 T with a conventional electromagnet.[6] This type of measurement has been extended to the high-field region up to 14 T with a pulse magnet.[7]

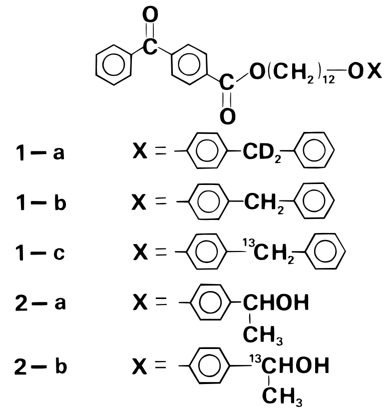
Magnetic field effects due to the difference between the longitudinal and transverse relaxation times ($T_1$ and $T_2$) have been first discussed by Brocklehurst.[8] The paramagnetic relaxation rate may be dependent upon the magnetic field intensity or changed by magnetic isotope substitutions.[9−13] This expectation was confirmed by the use of a high-magnetic-field laser photolysis apparatus.[14] It has been suggested that the decrease in biradical lifetimes observed in the high-field region can be attributed to the contribution of $g$ anisotropy to spin−lattice relaxation by analyzing the results observed for biradicals consisting of two equivalent benzophenone ketyl radicals.[14]

The major purpose of this paper is to show that the carbon-13 magnetic isotope effects observed on the decay rate of carbon-centered biradicals disappear in the very high-field region (>6 T) and to interpret the observed results in terms of the relaxation mechanism.[11,13] The photochemical reactions studied in this work are closely related to remote oxidation by benzophenone derivatives in the lowest excited triplet state.[15]

## 2. Experimental Section

**2.1. Material.** Chain-linked bichromophoric compounds used in the present work are shown in Scheme 1. All chain molecules were prepared according to methods described in the literature.[16] Hydrogen (or carbon) nuclei at the particular site of the hydrogen donor moiety is substituted with deuterium (isotope purity of ca. 98%) (or heavy carbon (C-13 purity of ca. 99%)). Satisfactory elemental and spectral analyses were obtained for all new compounds studied in this work. Structure and purity of these compounds were confirmed by means of NMR spectroscopy (270 MHz/500 MHz) and low-resolution mass spectrometry.

**SCHEME 1**



Benzene and acetonitrile of spectroscopy grade (Nacalai Tesque) were used as received. Concentrations of bichromphoric species were (3.0−3.8) × $10^{-4}$ M. The solutions were deaerated by several freeze−pump−thaw cycles.

**2.2. Apparatus.** The transient absorption signals were obtained by means of laser flash photolysis with a pulsed magnet system which has been reported in a previous paper.[7] The pulsed magnetic field (<20 T, 20 ms duration, inhomogeneity of less than 2%) was generated by supplying an intense pulsed current from a capacitor bank (Nichikon, 5 kV, 5 kJ) to a homemade solenoid coil (9.7 mH, 0.7 Ω). The exciting light sources were the fourth harmonics (266 nm, fwhm 4−6 ns, 10 mJ/pulse) of an Nd:YAG laser (Spectra Physics, GCR-11-1) or an XeCl excimer laser (Lumonics EX-510, 308 nm, fwhm 8−10 ns, 10 mJ/pulse). The analyzing light source was an Xe arc lamp (Ushio, 150 W). The probe light was led to a detection system composed of a monochromator (Ritsu MC-20L), a photomultiplier tube (Hamamatsu R-636), a digital oscilloscope (Tektronix 2440), and a microcomputer (NEC, PC-9801) through a quartz optical fiber bundle (Fujikura, FBB-5-3M-A). A laser photolysis setup with a conventional electromagnet (Tokin SEE-9G) has been reported in previous papers.[6,16]

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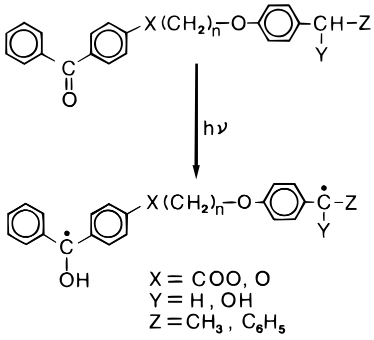
**SCHEME 2**



## 3. Results and Discussion

**3.1. Photochemical Primary Processes and Mass Isotope Effects.** In previous papers,[6,16] we have described the experimental results for photolysis of the chain-linked species in low-field region (<0.8 T). After the photoexcitation of benzophenone (BP) chromophore the starting species undergo the following processes: (1) Intersystem crossing from the lowest excited singlet state of the benzophenone moiety to its excited triplet state. (2) Intramolecular hydrogen abstraction by the BP excited triplet state from the benzylic CH bond of the hydrogen donor which results in the formation of the triplet biradical (see Scheme 2). (3) Intersystem crossing from the triplet biradical ($^3$BR) to the singlet biradical ($^1$BR). (4) Unimolecular and bimolecular reactions of BRs leading to the end product formation.

The transient species produced on photolysis of the bichromophoric species have been properly identified.[6,16] The early transient absorption signal is due to the lowest excited triplet state of the BP moiety. The transient signal whose decay profile is sensitive to the external magnetic field strength is ascribed to the BR intermediates. The decay times of short-lived excited triplet state and long-lived BRs were determined by means of least-squares fit to a double-exponential function. The decay time of the excited triplet is governed by two processes, i.e., intramolecular hydrogen abstraction ($k_{HA}$) and nonradiative transition ($k_{NR}$). The decay processes of BRs are intramolecular intersystem crossing ($k_{ST}$) and bimolecular quenching reaction of the parent molecule in the ground state ($k_e$[P]). On the basis of the above consideration, one can obtain the equation which describes the dynamic behavior of the excited triplet and $^3$BR:

$$\mathrm{d[T]/d}t = -(k_{HA} + k_{NR})[\mathrm{T}] = -k_a[\mathrm{T}] \qquad (1)$$

$$\mathrm{d[^3BR]/d}t = k_{HA}[\mathrm{T}] - \{k_{ST} + k_e[\mathrm{P}]\}[^3\mathrm{BR}] = k_{HA}[\mathrm{T}] - k_b[^3\mathrm{BR}] \qquad (2)$$

The time dependence of the transient absorption signal *A(t)* at the monitoring wavelength within ca. 20 μs after the laser pulse can be described by the following equation:

$$A(t)/l = \{[\mathrm{T}]_{t=0}k_{HA}/(k_a - k_b)\}\epsilon_T \exp(-k_a t) + \{[\mathrm{T}]_{t=0}k_{HA}/(k_a - k_b)\}\epsilon_{BR}\{\exp(-k_b t) - \exp(-k_a t)\} + C \qquad (3)$$

where $l$ is an optical path length, $C$ is a time-independent constant, and $\epsilon_T$ and $\epsilon_{BR}$ denote molar extinction coefficients for the triplet and BR at the monitoring wavelength, respectively. In the case of diphenylmethane derivatives, mass isotope effects on the excited triplet lifetime were observed. The lifetimes are listed in Table 1. Analyzing the preexponential factors in terms of $k_a$, $k_b$, $\epsilon_T$, and $\epsilon_{BR}$, we can estimate the H/D abstraction rate. The ratio $k_{HA}/k_a$ is evaluated to be 0.30 ± 0.03, on the assumption that $\epsilon_{BR}$ and $\epsilon_T$ are independent of, and $k_a$ and $k_b$ dependent on, the isotope substitution. The estimated hydrogen and deuterium transfer rates are also given in Table 1. It can be concluded that the H/D transfer is slower than the radiationless process which deactivates the excited triplet state. The isotope effect parameter $k_{HA}/k_{DA}$ (=1.5−1.6) is smaller than the corresponding value ($k_H/k_D$ = 2.7) reported for similar intermolecular hydrogen abstraction by the excited triplet benzophenone.[17] A deuterium isotope effect on the hydrogen abstraction rate has been reported to be 1.7 for the intramolecular photochemistry of γ-hydroxy-γ-butyrophenone derivatives.[18] These results suggest that the mass isotope effects on intramolecular H abstraction by aromatic carbonyls in the excited triplet are different from typical primary isotope effects in thermal reactions.[19]

**TABLE 1: Decay Processes for the Excited Triplet State of Benzophenone Derivatives Containing Diphenylmethyl Moiety**[a]

| | lifetime/ns | $k_a/10^6$ s$^{-1}$ | $k_{NR}/10^6$ s$^{-1}$ | $k_{H(D)A}/10^6$ s$^{-1}$ |
|---|---|---|---|---|
| NA | 186 | 5.4 | 3.8 | 1.6 |
| HC | 188 | 5.3 | 3.8 | 1.5 |
| D | 208 | 4.8 | 3.8 | 1.0 |

[a] NA = naturally abundant species, HC = heavy-carbon-labeled species, and D = deuterated species.

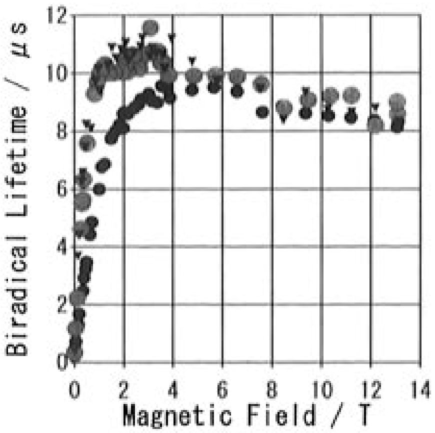


**Figure 1.** Magnetic field effects on lifetimes of the biradicals consisting of benzophenone ketyl and diphenylmethyl radicals (BR-1): circle, naturally abundant species; solid circle, heavy-carbon-labeled species; triangle, deuterated species.

**3.2. Magnetic Isotope and Magnetic Field Effects on the Biradical Decay Process.** The MFEs on the decay process of BRs were detected by analyzing the transient absorption intensity at 330 nm for BR-1 (X = COO, Y = H, Z = $C_6H_5$, and $n$ = 12 in Scheme 2) and 350 nm for BR-2 (X = COO, Y = OH, Z = $CH_3$, and $n$ = 12). The decay times of long-lived BRs are calculated from the observed decay profile by assuming the following modification of eq 3:

$$I(t) = A \exp[-t/\tau(\mathrm{S})] + B \exp[-t/\tau(\mathrm{L})] + C \qquad (4)$$

where *I(t)* is the transient absorption intensity, $A$, $B$, and $C$ are time-independent constants, and $\tau$(S) and $\tau$(L) are lifetimes corresponding to the short- and long-lived species, respectively.

*3.2.1. High-Field Region (0.1−0.8 T).* Figures 1 and 2 illustrate the dependence of the decay times of BR-1 and BR-2 on the magnetic field intensity, respectively. There are appreciable magnetic isotope effects on the decay rates. The isotope effects on the decay process can be described by the following parameter:

$$k_d(\mathrm{L})/k_d(\mathrm{N}) = \tau_{BR}(\mathrm{N})/\tau_{BR}(\mathrm{L}) \qquad (5)$$

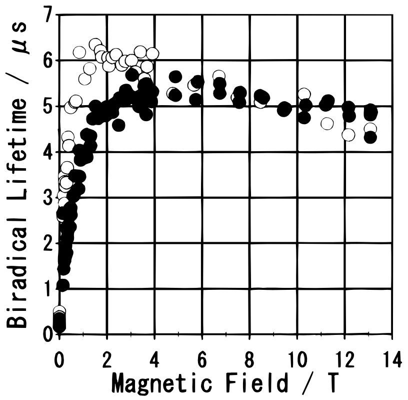


**Figure 2.** Magnetic field effects on lifetimes of the biradicals consisting of benzophenone and acetophenone ketyl radicals (BR-2): circle, naturally abundant species; solid circle, heavy-carbon-labeled species.

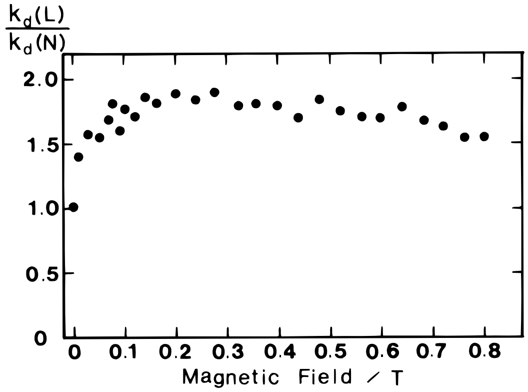


**Figure 3.** Magnetic field effects on the rate ratio of the decay rates for the naturally abundant and C-13 labeled BR-1.

where $k_d$ is the disappearance rate for the biradical, $\tau_{BR}$ is the biradical lifetime, and N and L refer to the naturally abundant and the isotope-labeled species, respectively. This ratio approaches to unity in the presence of a very weak field (<0.08 mT) or very strong fields (>4 T, see Figure 3 and vide infra). In the case of heavy carbon substitution the decay time ratio as a function of the magnetic field strength can be regarded as asymmetric convex. The curve of rate ratio is an approximate concave for the deuterated species. The asymptotic behavior in the very high-field region will be described in terms of spin−lattice relaxation due to anisotropic Zeeman interaction (vide infra).

In order to interpret the observed MFEs, it is reasonable to exclude the intersystem recombination and spin−rotational relaxation, because these two processes are independent of magnetic field strength. This assumption is rationalized, because the BRs studied in this work contain no heavy atoms. It is also reasonably concluded that no mass isotope effects are involved in the decay process of the isotope labeled BRs, since the ratio of $k_d(L)/k_d(N)$ shows an apparent dependence on the external magnetic field strength. If the mass isotope effects are of dominant importance, the rate ratio is expected to be less than unity because the zero-point energy decreases on the heavy carbon substitution. Consequently, the observed results should be accounted for by the magnetic isotope effects.

If the biradical decay rate in the high-field region (>0.1 T) is approximated by the following equation for the spin−lattice relaxation

$$k_{rlx} = 2\tau_R(2\pi[V]/h)^2/(1 + \omega^2\tau_R^2) \qquad (6)$$

the ratio $k_d(L)/k_d(N)$ may be regarded as $[V(L)]^2/[V(N)]^2$ on the

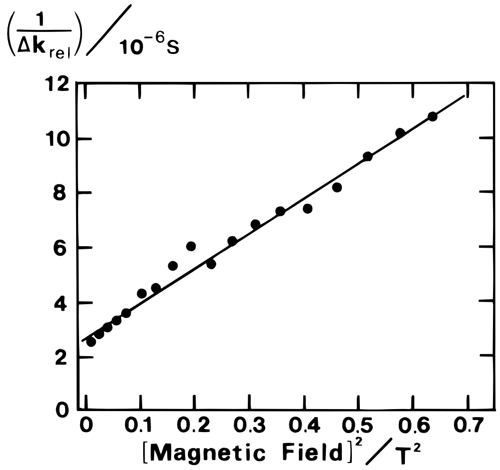
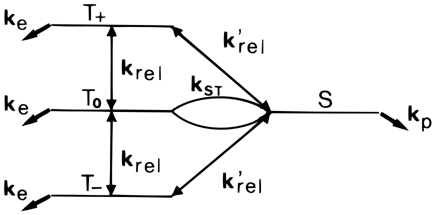


**Figure 4.** Plot of $(\Delta k_{rel})^{-1}$ against $H^2$ for BR-1.

**SCHEME 3**



assumption that the rotational correlation time is independent of the isotope substitution. Here $V(X)$ (X = N or L) denotes the anisotropic interaction which causes spin−lattice relaxation, $\tau_R$ is the rotational correlation time, and $\omega = \gamma H_{ex}$ where $H_{ex}$ is the external field strength. The magnetic isotope effects observed in the field region below 2 T can be attributed to the spin−lattice relaxation (SLR) by the anisotropic hyperfine interactions of an electron and nuclear spins. The SLR time increases with the increasing external field strength and decreases on the introduction of the heavy carbon. These results are reasonably explained by the following equation for SLR:[7]

$$1/T_1(\delta\text{hf}) = \gamma^2(H_{loc})^2\tau_R/(1 + \omega^2\tau_R^2) \qquad (7)$$

where $\gamma$ is the gyromagnetic ratio of the electron and $H_{loc}$ is the locally fluctuating field for the electron. The heavy carbon substitution increases the magnitude of the local field, and the SLR time is appreciably shortened for the $^{13}$C-labeled species. On the other hand, deuteration of the benzyl CH bond increases the BR lifetime due to the decrease in $H_{loc}$.

Scheme 3 illustrates a kinetic scheme involving the singlet and triplet biradicals. Two different spin−lattice relaxation rates are to be considered, i.e., that among the triplet sublevels $k_{rel}$ and that between the triplet and singlet levels $k_{rel}'$. Although SLR of the two component radicals individually contribute to these two processes, we use a single value for $[V]$ and $\tau_R$ as the effective value for the sake of simplicity. These values are estimated in the following way. The difference in the decay rate is determined as $\Delta k_{rel} = k_d(L) - k_d(N)$, and the inverse $(\Delta k_{rel})^{-1}$ is plotted against $H^2$ (see Figure 4).[7] From the intercept $(=h^2/4\pi^2\tau_R[V(\Delta)]^2)$ and slope $(=h^2\gamma^2\tau_R/4\pi^2[V(\Delta)]^2)$ in the linear relationship, $[V(\Delta)]/g\beta = 0.75$ mT and $\tau_R = 10$ ps are evaluated for BR-1 and $[V(\Delta)]/g\beta = 0.98$ mT and $\tau_R = 12$ ps for BR-2. (The intercept and slope obtained from the plot including the data in the high-field regions up to 2 T are essentially the same as those mentioned above.) Here $[V(\Delta)]$ corresponds to the increase in the anisotropic hyperfine interaction which enhances the spin−lattice relaxation rate. The difference $\Delta k_{rel}$ contains

**TABLE 2: Magnitude of Relaxation Parameters ([$V$(X)]/$g\beta$) in mT**[a]

| | [$V$(X)] | [$V$(dd)] | [$V$($\delta$ hf)] |
|---|---|---|---|
| | Diphenylmethane Derivatives | | |
| NA | 0.84 | 0.64 | 0.55 |
| HC | 1.13 | 0.64 | 0.93 |
| D | 0.80 | 0.64 | 0.48 |
| | Phenylethanol Derivatives | | |
| NA | 1.03 | 1.01 | 0.21 |
| HC | 1.42 | 1.01 | 1.00 |

[a] Abbreviations are the same as those for Table 1. $\beta$ = Bohr magneton.

no contribution from the spin−lattice relaxation due to the dipole−dipole or the anisotropic Zeeman interaction. The magnitude of the anisotropic magnetic interaction can be estimated from the observed rate ratio $k_d(L)/k_d(N)$ and the following relation:

$$[V(\mathrm{L})]^2 = [V(\mathrm{N})]^2 + [V(\Delta)]^2 \tag{8}$$

The results are shown in Table 2. The relative importance of the dipole−dipole and the anisotropic, hyperfine interactions is estimated according to the analysis similar to that described by Levin and co-workers,[11]

$$[V(\mathrm{X})]^2 = [V(\mathrm{dd})]^2 + [V(\delta\mathrm{hf})]^2 \quad (\mathrm{X} = \mathrm{N\ or\ L}) \tag{9}$$

Here we have neglected the contribution from the anistropic Zeeman mechanism, because the $g$ value for diphenylmethyl radical has been reported to be rather isotropic[20] and the data obtained in the low-field region are analyzed. The magnitude of [$V$(dd)] and [$V$($\delta$hf)] are also given in Table 2. The [$V$($\delta$hf)] value for the biradical contains the contribution from each component radical:[20]

$$[V(\delta\mathrm{hf})]^2 = [V(\mathrm{R}_1)]^2 + [V(\mathrm{R}_2)]^2 \tag{10}$$

where [$V(\mathrm{R}_i)$] refers to the local field in the component radicals.[21] When [$V$(R)]/$g\beta$ = 0.15 mT is employed for benzophenone ketyl radical,[21] the corresponding local field for the diphenylmethyl radical is estimated to be 0.53 mT. This value is comparable to that reported for xanthenyl radical (0.55 mT),[21] which can be closely associated with the diphenylmethyl radical.

Because the present analysis is simplified in that the single rotational correlation time is taken into consideration, the values listed in Table 2 should be interpreted in a semiquantitative way. However, it can be reasonably concluded that the spin−lattice relaxation rate due to dipole−dipole interaction is comparable to that due to the anisotropic hyperfine interaction. The magnitude of anisotropic hyperfine interaction must be similar for the radical pairs in micellar media reported by Levin et al.[11,22] and the biradicals studied in the present work. Since the rotational correlation time increases by a factor of about 10 on going from the biradicals in homogeneous solutions to the radical pairs in micellar media, the relatively small role of anisotropic hyperfine coupling suggests that the major source of the spin−lattice relaxation in micellar solutions is attributable to the dipole−dipole interaction. From the relation [$V$(dd)] = $(3/20)^{1/2}g^2\beta^2/R^3$ in ref 22, the effective interradical distances were estimated to be 1.04 nm for the BR-1 and 0.89 nm for BR-2. These values are consistent with those commonly expected for biradicals containing 12 methylene groups.[23]

Levin and collaborators have argued that the anisotropic hyperfine interaction plays a negligible role in paramagnetic relaxation under magnetic fields higher than 0.2 T.[11] This holds only for deuteration effects in micellar media. In general, large magnetic isotope effects can be observed for carbon-centered biradicals derived from bichromophoric chain species containing the heavy carbon at a particular site in the presence of magnetic fields up to 4 T. The substitution with $^{13}$C may considerably enhance the anisotropic hyperfine interaction.

**TABLE 3: $g$ Values for Ketyl and Related Radicals**

| | $g$ value | references |
|---|---|---|
| diphenylmethyl | 2.0024 | 20 |
| benzophenone ketyl | 2.00298 | 24 |
| acetophenone ketyl | 2.0030 | 25 |

**TABLE 4: Intersystem Crossing Rates {$k$(T$_0$−S)} Due to the Zeeman Mechanism, Observed Decay Rates, and Calculated Spin−Lattice Relaxation Rates for Naturally Abundant Species**

| | {$k$(T$_0$−S)}$_{\mathrm{calc}}$ | | {$k_d$}$_{\mathrm{obs}}$ | |
|---|---|---|---|---|
| BR | $k$(4 T)/$10^7$ s$^{-1}$ | $k$(10 T)/$10^7$ s$^{-1}$ | $k$(4 T)/$10^5$ s$^{-1}$ | $k$(10 T)/$10^5$ s$^{-1}$ |
| BR-1 | 20 | 51 | 1.0 | 1.1 |
| BR-2 | 0.7 | 1.8 | 1.8 | 2.0 |

| BR | {$k$($\delta$hf) + $k$(dd)}$_{\mathrm{calc}}$ $k$(10 T)/$10^2$ s$^{-1}$ | {$k$($\delta g$)}$_{\mathrm{calc}}$ $k$(10 T)/$10^5$ s$^{-1}$ | $\langle\delta g^2\rangle/10^{-6}$ |
|---|---|---|---|
| BR-1 | 7.1 | 1.1 | 4.4 |
| BR-2 | 8.8 | 2.0 | 9.6 |

*3.2.2. Very High-Field Region (>1 T).* The observed MFEs on the decay rate in the high-field region (>4 T) cannot be explained on the basis of the anisotropic hyperfine interaction, since no magnetic isotope effects were observed above 4 T. The observed results should be interpreted in terms of the Zeeman (or $\Delta g$) mechanism and/or paramagnetic relaxations which are independent of nuclear magnetic moments. There are two possibilities as to the relaxation mechanism, i.e., SLR due to dipole−dipole interaction and anisotropy of the **g** tensor.

The intersystem crossing (ISC) induced by the Zeeman mechanism can be estimated by the following equation:

$$k_{\mathrm{isc}}(\Delta g) = 2\pi\Delta g\beta H_{\mathrm{ex}}/h \tag{11}$$

where $\beta$ is the Bohr magneton, $H_{\mathrm{ex}}$ is the external magnetic field intensity, and $h$ is the Planck constant. The $k_{\mathrm{isc}}(\Delta g)$ values are estimated according to the above equation and on the assumption that the $g$ values for benzophenone and acetophenone ketyls and diphenylmethyl radical in BR-1 and BR-2 are the same as those for the corresponding radicals with no substituent at the para position, the $g$ values of which are listed in Table 3. The estimated ISC rates are given in Table 4, which also lists the decay rate constants for the BRs measured by means of laser photolysis. It is concluded that the T$_0$−S ISC is not the rate-determining step of the BR decay in the high-field region. Since the Zeeman mechanism cannot increase the ISC rate between T$_+$−S or T$_-$−S, the $\Delta g$ mechanism is of minor importance in the decay process of biradicals. This conclusion is supported by the fact that the symmetric BR consisting of two benzophenone ketyls (X = O, Y = OH, Z = C$_6$H$_5$, and $n$ = 3−12 in Scheme 2) show the decrease in lifetimes in the very high-field region.[14,26]

The spin−lattice relaxation time induced by $g$ anisotropy is expressed as the following equation:[27]

$$1/T_1(\delta g) = \{4\pi^2\langle\delta g^2\rangle\beta^2 H_{\mathrm{ex}}^{\ 2}/5h^2\}\{\tau_{\mathrm{R}}/(1 + \omega^2\tau_{\mathrm{R}}^{\ 2})\} \tag{12}$$

where $\langle\delta g^2\rangle = g_1^{\ 2} + g_2^{\ 2} + g_3^{\ 2} - 3[(g_1 + g_2 + g_3)/3]^2$ ($g_1$, $g_2$, and $g_3$ are $g$ values for the principal axis of the **g** tensor of a radical) and $\tau_{\mathrm{R}}$ is the correlation time. It is useful to examine the magnetic field dependence of two different spin−lattice

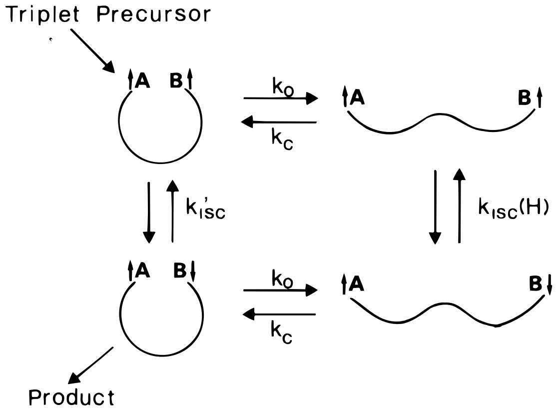


**Figure 5.** Two-site model for long-chain biradical: $k_o$ (rate for the conformational change from the closed form to the open one), $k_c$ (rate for conformational change from the open form to the closed one), $k_{isc}$ (intersystem crossing rate for the open form), and $k_{isc}'$ (intersystem crossing rate for the closed form).

relaxation rates. The SLR due to hyperfine anisotropy vanishes when $\omega$ approaches infinity, whereas the SLR rate due to **g** tensor anisotropy converges to a certain value $(4\pi^2\langle\delta g^2\rangle\beta^2/5h^2\gamma^2\tau_R)$ when the field strength approaches infinity. This indicates that the magnetic isotope effect on the biradical decay process disappears at a sufficiently high magnetic field. The observed results are in agreement with the theoretical prediction of asymptotic behavior. On going from the low field to the very high field, the dominant contributor to $[V(X)]$ is switched from the hyperfine anisotropy to the **g** tensor anisotropy.

The SLR rate is evaluated from the correlation time, and anisotropic magnetic interaction obtained from analysis of the low-field region and the calculated rates are given in Table 4. These are negligibly small in comparison with the observed biradical decay rates at 10 T. Therefore, the anisotropic hyperfine and dipole−dipole interactions play no important role in the very high-field region. The anisotropic parameter $\langle\delta g^2\rangle$ is estimated from the observed lifetime at 10 T and the correlation time by the use of eq 12. The order of magnitude for the anisotropic parameter is in agreement with **g** tensor anisotropy for related carbon-centered radicals reported in the literature.[20,28]

*3.2.3. Two-Site Model in the Zero Field.*[29] In the absence of magnetic fields, the biradical disappearance rate is independent of the isotopic substitution. The observed results can be explained by the use of a two-site model of a polymethylene biradical. The two conformers with short and long interradical distances have been proposed for acyl−alkyl biradicals which are formed on photolysis of cyclic ketones.[30,31] The present observation of no apparent magnetic isotope effects may be explained in terms of magnitude of the rate constants shown in Figure 5. The biradical formed immediately after intramolecular hydrogen abstraction is characterized as a triplet with folded conformation. If the intersystem recombination or intersystem crossing rate for the folded biradical ($k_{isc}'$) and the rate for conformational change from the extended form to the folded one ($k_c$) are smaller than any other rates for the processes shown in Figure 5, there should be no magnetic isotope effects on the biradical disappearance rate at zero magnetic field. On application of an external magnetic field, the strength of which is higher than or comparable to the isotropic hyperfine interaction, the singlet−triplet mixing becomes retarded, and the magnetic isotope effects are observed on the biradical decay kinetics.

## 4. Concluding Remarks

The present analysis of experimental data for the naturally abundant and C-13 labeled biradicals indicates that the major contributor to the spin−lattice relaxation is switched from the anisotropic hyperfine interaction to the anisotropic Zeeman interaction. Since the models employed here may be crude in some respects, the following points should be taken into account explicitly for an elaborate model: (1) The chain dynamics has to be included in the kinetic scheme. (2) The importance of the intersystem recombination should be quantitatively evaluated.

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