Magnetic field and magnetic isotope effects on the recombination kinetics of covalently-linked ketyl—phenoxyl triplet radical pairs

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The recombination kinetics of three photogenerated covalently-linked ketyl—phenoxyl triplet radical pairs, $^3[\mathrm{PhC^{\cdot}(OD)C_6H_4O(CH_2)_{\mathit{n}}OC_6H_4C_6H_4O^{\cdot}}]$ (n = 3, 6, and 10), and of the corresponding deuterated derivatives were examined by the laser flash technique under an external magnetic field (up to 0.2 T) in a $CDCl_3/CD_3OD$ (2:1) mixture. In zero magnetic field, radical pairs (RPs) with small exchange interactions (n = 6 and 10) are characterized by high values of the magnetic isotope effect (MIE), which reach 3 for pairs with n = 10. Under strong magnetic fields (up to 0.2 T), the values of MIE decrease to 1.2 to 1.1. The photochemical behavior of covalently-linked RPs is compared with that of similar unlinked RPs in micelles.

Key words: triplet radical pairs, magnetic effect, magnetic isotope effect, covalently-linked ketyl—phenoxyl radical pairs.

The dynamics of polymethylene-linked radical pairs (RPs) has attracted considerable attention because of the possibility of clarifying the mechanism of the effects of magnetic fields on radical reactions.[1—6] Detailed information about spin and molecular dynamics can be obtained from the analyzing the radical lifetimes as a function of the magnetic field strength (B) and the length of the polymethylene chain between radicals. The pronounced magnetic field effects on the recombination kinetics of covalently-linked RPs imply the existence of considerable magnetic isotope effects (MIE), which have been experimentally observed for several biradical systems.[1,7,8] However, no detailed studies of magnetic isotope effects in the recombination kinetics of biradicals have been performed at the present time.

In this work, in order to study the magnetic isotope effect, we used covalently-linked dyads in which benzophenone (Bp) and 4-phenylphenol (PpOH) moieties or their corresponding deuterated derivatives are linked by the polymethylene bridge $(CH_2)_n$, n = 3, 6, and 10 (Fig. 1). All experiments were carried out in a $CDCl_3/CD_3OD$ (2 : 1) mixture in order to exclude the normal kinetic isotope effect associated with the detachment or addition of a hydrogen atom. RPs were obtained as a result of the intramolecular detachment of deuterium from 4-phenylphenol by the triplet excited state of benzophenone (^{3}Bp). The same, but unlinked radical pairs have previously been studied in micellar solutions.[9,10] Relatively weak hyperfine coupling (HFC) manifesting itself in very small magnetic fields is a characteristic feature of these systems.[10] Therefore, it seemed that a comparison of magnetic and magnetic isotope effects in micellar and covalently-linked systems would be rather interesting from the viewpoint of probable variations in the spin and molecular dynamics related to the molecular organization of the system.

Experimental

The absorption spectra and decay kinetics of the short-lived intermediates were recorded by laser photolysis using a PRA LN-1000 nitrogen laser as the excitation source.[9] The kinetic spectrophotometer (10 ns resolution) included an averaging system consisting of a Biomation 6500 waveform re-

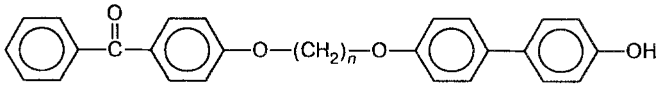

Fig. 1. Molecular structure of the covalently-linked dyad Bp—O—$(CH_2)_n$—O—PpOH (n = 3, 6, and 10).

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corder coupled to a computer. The kinetic curves were averaged over 128 laser pulses. In the magnetic field experiments, a quartz cell (8x8 mm) with a solution was placed between the two poles of a permanent magnet. The distance between the poles was varied, so that the maximum value of the magnetic field strength was 0.2 T. All solutions (10^{-4} M) were evacuated before the experiments. All experiments were carried out at 18 °C.

1-(4-Benzoylphenoxy)-10-[4-(4'-hydroxyphenyl)phenoxy]decane (Bp—O—$(CH_2)_{10}$—O—PpOH). A DMF solution (10 mL) of 0.2 g of 1-(4-benzoylphenoxy)-10-bromodecane (prepared from 4-hydroxybenzophenone and 1,10-bromodecane according to the described procedure[4]) and 0.8 g of 4,4'-biphenol were stirred at 18 °C for 12 h with 1 g of K_2CO_3 in a flask with a magnetic bar. The solvent was removed *in vacuo*, and the residue was dissolved in the $CHCl_3/CH_3OH$ (10 : 1) mixture and chromatographed on a column with silica gel (25x2 cm, SiO_2 5/40). After removal of the solvent, a white powder of 1-(4-benzoylphenoxy)-10-[4-(4'-hydroxyphenyl)phenoxy]decane was obtained (TLC in $CHCl_3/CH_3OH$ (10 : 1) showed one spot with R_f = 0.58). The dyads with n = 6 and 3 were prepared in a similar way (R_f = 0.60 and 0.62 for n = 6 and 3, respectively). The corresponding deuterated dyads were prepared similarly from deuterated 4-hydroxybenzophenone and 4,4'-biphenol, which were synthesized by an isotope-exchange reaction (the degree of deuteration ≥95 %) according to the method described previously.[10]

Results and Discussion

Fig. 2 shows transient absorption spectra recorded at different time intervals after the laser excitation (337 nm) of a solution of $BpO(CH_2)_{10}OPpOD$ in a $CDCl_3/CD_3OD$ (2 : 1) mixture. Short-lived intermediates (their lifetimes are estimated as smaller or equal to the resolution time of the registration system) are observed immediately after the laser flash. These intermediates have characteristic absorption bands (520 and 650 nm), which coincide with the bands of the triplet-triplet absorption of benzophenone.[11] The decay of benzophenone triplets is accompanied by the appearance of relatively long-lived intermediates, whose absorption spectra coincide with the superposition of the absorption spectra of $BpD^{\cdot}$ ketyl radicals (a band at 550 nm)[4,11] and $PO^{\cdot}$ radicals (an intense band at 620 nm).[12] The same transient absorption spectra are observed for the dyads with n = 6 and 3. Thus, the photoexcitation of Bp—O—$(CH_2)_{10}$—O—PpOD initiates processes that are well known for similar unlinked systems,[9,10] namely, the decay of the triplet-excited state of benzophenone (^{3}Bp) occurs due to the efficient transfer of hydrogen from phenylphenol to ^{3}Bp to form the corresponding ketyl—phenoxyl RP.

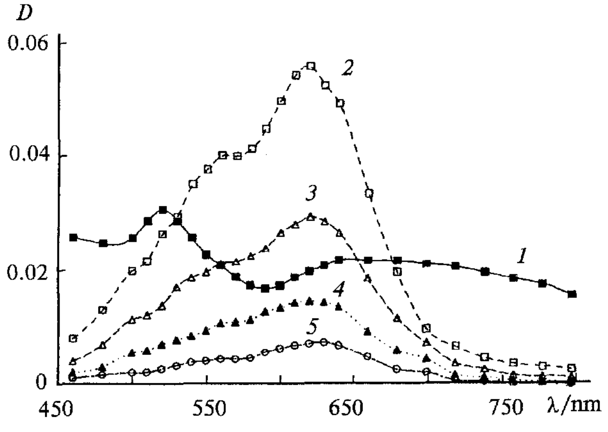

Fig. 2. Absorption spectra of the intermediates observed in the laser excitation of solutions of Bp—O—$(CH_2)_{10}$—O—PpOD in a $CDCl_3/CD_3OD$ (2 : 1) mixture in an external magnetic field (0.2 T) recorded 10 ns (*1*), 100 ns (*2*), 1 ms (*3*), 2 ms (*4*), and 4 ms (*5*) after the laser flash.

Recombination rate constants of RPs (k_H) and their deuterated derivatives (k_D) measured in a zero magnetic field and external magnetic fields are presented in Table 1. For the dyads with n = 10 and 6, the application of the magnetic field results in a decrease in the values of k_H and k_D and a decrease in MIE, which is characterized by the k_H/k_D ratio. For systems with n = 3, the magnetic effect (the ratio of the recombination constants in a zero magnetic field and in external magnetic fields) and MIE are close to 1.

The dependences of $k_{H/D}$ *vs.* B for RP and their deuterated analogs are presented in Fig. 3. For RP with n = 10 the value of $k_{H/D}$ decreases monotonically as B increases; it decreases sharply from 0 to 10 mT and then at $B \geq 20$ mT decreases more smoothly. It should be noted that in the case of the deuterated system with n = 10 the value B = 0.1 mT is enough for a noticeable decrease in the value of the recombination rate constant. For the deuterated system with n = 10, $B_{1/2}$ (the value of the magnetic field strength at which the magnetic effect is equal to half its maximum value) is four times lower than that for the protonated system (see Table 1). Unlike the dependences for RPs with n = 10, the magnetic field dependences for RPs with n = 6 have maxima at 1 mT (Fig. 3, *b*).

The magnetic field dependences of MIE are presented in Fig. 4. For n = 10, MIE increases as B increases and attains its maximum value at B = 1 mT. A

Table 1. Magnetic and kinetic parameters ($k_{H/D}$, k_{HFC}, and $B_{1/2}$) for the recombination of triplet RPs and their deuterated derivatives

System	$(k_H/k_D) \cdot 10^{-6}/s^{-1}$		$k_{CTB} \cdot 10^{-6}$ [a] $/s^{-1}$	$B_{1/2}$/mT[b]
	$B = 0$	$B = 0.2$ T		
3, h	0.38	0.37	—	—
3, d	0.33	0.34	—	—
6, h	2.4	0.48	1.9	5
6, d	0.77	0.38	0.39	5
10, h	3.6	0.80	2.8	2
10, d	2.0	0.71	1.3	0.5

[a] The error in the determination of k_H/k_D does not exceed 5%. [b] The error in the determination of $B_{1/2}$ does not exceed 20%.

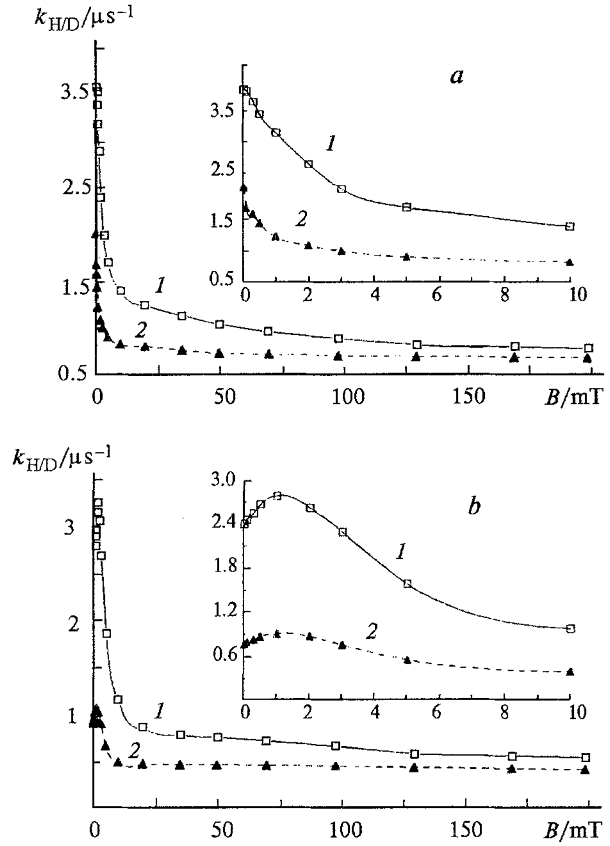

Fig. 3. Dependence of the rate constant ($k_{H/D}$) of the decay of triplet RPs (*1*) and their deuterated derivatives (*2*) on the magnetic field strength, n = 10 (*a*) and n = 6 (*b*).

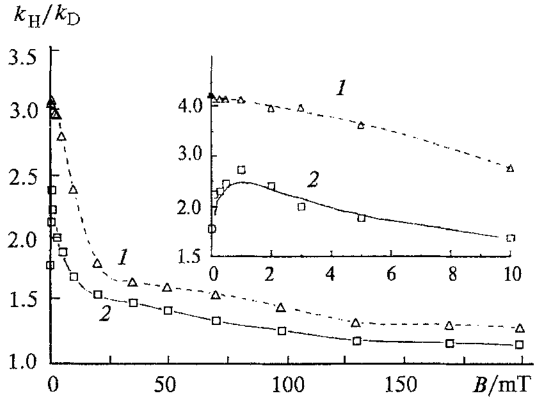

Fig. 4. Effect of an external magnetic field on the MIE value (k_H/k_D) for triplet RPs and their deuterated derivatives, n = 6 (*1*) and n = 10 (*2*).

further increase in B results in a decrease in MIE. Like the magnetic field dependences of $k_{H/D}$, these dependences have "sharp" (2 mT $\leq B \leq$ 20 mT) and "smooth" ($B \geq$ 20 mT) regions (see Figs. 3 and 4). MIE for n = 6 is greater than for n = 10.

The kinetics of the recombination of covalently-linked triplet RPs involve several processes and interactions, which can be dependent or independent of the magnetic field. For the radical pairs considered, the frequency of intramolecular encounters of covalently-linked radicals is likely to be significantly greater than the rate constant of their recombination.[1–3] The lower limit for the frequency of intramolecular encounters can be estimated from the observed rate constants ($\geq 10^8$ s^{-1}) of the intramolecular quenching of ^{3}Bp with phenylphenol. Thus, the decay of RP occurs in a regime of "fast encounters" and the time scale of RP recombination is determined by the spin dynamics.[1–3]

As a first approximation, the average value of the exchange interaction between unpaired electrons or the singlet-singlet splitting in RP (2J) can be determined by the distance between radical centers, *i.e.*, it depends on the polymethylene chain length.[1–3] The value of 2J can be greater than the values of Zeeman splitting and HFC for RP with a short spacer of three carbon and two oxygen atoms (n = 3).[2,5,13] As a result, RP with n = 3 decays mostly due to the intersystem transition to the ground state induced by spin-orbit coupling (SOC), which is independent of the magnetic field and nuclei spin.[1,2,6,9,10] It is likely that this mechanism is also responsible for the recombination of RPs with long spacers and of similar unlinked RPs in micelles in a strong magnetic field.[1,2,6,9,10] The value of the corresponding rate constant k_{SOC} can be estimated from the limiting value of $k_{H/D}$ at high B. One would expect that k_{SOC} would be independent of the chain length as has already been observed for the recombination of other triplet RPs with similar spacers in strong magnetic fields.[6,13] However, for the RPs considered at B = 0.2 T, an increase in n results in a noticeable increase in $k_{H/D}$ (see Table 1), which can be related both to the contribution of paramagnetic relaxation (see discussion below and in Refs. 4, 9, and 10) and to the change in SOC caused by the change in the mutual orientation of the radicals as the chain lengthens.

The average value of the exchange interaction in RP can be estimated from the value of the maximum in the magnetic field dependence ($2J \approx B_{max}$).[2] It can be seen from Fig. 3 that when the chain lengthens 2J decreases from 1.0 mT for RP with n = 6 and becomes close to zero for RP with n = 10. In a zero magnetic field, the relative contribution of the intersystem recombination induced by SOC decreases as the chain lengthens and the magnetic-field-sensitive recombination induced by HFC becomes an important route of RP decay. The corresponding magnetic and magnetic isotope effects become pronounced for RPs with n = 6 and 10 (Figs. 3 and 4 and Table 1).

In terms of the simplest exponential approach, in the limit of fast encounters, $k_{H/D} = k_{HFC} + k_{SOC}$, where k_{HFC} is the rate constant of triplet-singlet transitions induced by the isotropic HFC.[9,10] In general, the use of the exponential approximation for HFC-induced transitions is restricted for biradicals with appreciable values of J.[2] However, it has been shown experimentally that in many cases the recombination kinetics of covalently-linked RPs are well described by a monoexponential law,[1,2,4,6,13] which confirms the validity of this exponential approximation, at least for RPs with low values of J.

The corresponding values of k_{HFC} calculated as the difference between the values of $k_{\mathrm{H/D}}$ at $B = 0$ and 0.2 T (see Table 1) is an order of magnitude lower than the values of effective HFC constants. For RP and its deuterated derivative, the values of A_{HFC} are 1.1 and 0.29 mT or $1.9 \cdot 10^8$ and $5.2 \cdot 10^7$ rad s^{-1}, respectively.[10] These values were calculated[14] using the following expression

$$A_{\mathrm{HFC}} = (\Sigma a_i^2 I_i(I_i + 1))^{1/2},$$

where a_i and I_i are HFC constants and spin quantum numbers of nuclei, respectively. Thus, the values of k_{HFC} for covalently-linked RPs are several times lower than those for similar unlinked systems in micelles, which are estimated as close to $A_{\mathrm{HFC}}/2$. [10] On the other hand, in a zero magnetic field there is definite quantitative agreement between the values of k_{H} for $n = 6$ and 10 (Table 1) and analogous rate constants for other aromatic RPs and radical ion pairs with the same spacers.[4,6,13] Therefore, retardation of the HFC-induced recombination of covalently-linked RPs seems to be a general phenomenon even for very small J. This may be caused by the fact that the probability of the recombination of singlet radical pairs formed as the result of triplet-singlet transitions is less than unity due to the anisotropic character of the motion of radicals fixed by the polymethylene chain. On the other hand, the quantitative explanation that takes into account the coherent nature of the HFC-induced spin evolution seems to be general for biradicals characterized by a high frequency of intramolecular encounters. Since the frequency of encounters between radical centers linked by a flexible polymethylene chain is greater than the HFC frequency, the experimental rate constant of RP recombination can be lower than A_{HFC} due to dephasing in the spin evolution.[15] In other words, the term $\sin^2(A_{\mathrm{HFC}}\tau)$, which describes the spin evolution in the dynamic regime after short times,[2] should be restricted by the time scale of the encounters rather than by the time of the overall reaction.

The $B_{1/2}$ values for RPs with $n = 10$ are close to the sum of the root-mean-squares of the effective HFC for both radicals ($= 2A_{\mathrm{HFC}}$, see Table 1), as is expected for RPs with small J. [16] The high sensitivity of deuterated RPs with $n = 10$ to weak magnetic fields (≤ 0.1 mT) (Fig. 3, *a*) has previously been observed in micellar solutions, and has been explained by the interplay of small HFC with small exchange interactions, which is realized in this system.[10] These distinctions between the magnetic field dependences for k_{H} and k_{D} at $n = 10$ result in the appearance of a maximum on the corresponding MIE dependence (Fig. 4, curves *1*).

The increase in J as the chain length decreases from $n = 10$ to $n = 6$ results in a decrease in k_{HFC} and enhancement of the MIE (Table 1, Fig. 4). The effects observed in a zero magnetic field can be satisfactorily described by the simple, well-known parameter[2,15] $A_{\mathrm{HFC}}{}^2/(A_{\mathrm{HFC}}{}^2 + J^2)$ in which the value of $2J$ is equal to B_{max}.

Increasing the magnetic field strength in the range from 1 to 20 mT results in a considerable decrease in $k_{\mathrm{H/D}}$ and in the MIE due to a decrease in the probability of HFC-induced triplet-singlet transitions (Figs. 3 and 4). However, both the magnetic effect and the MIE are still observed in strong magnetic fields (from 0.1 to 0.2 T) for RPs with $n = 6$ and 10. These effects are caused by spin relaxation transitions due to uncorrelated interactions of each electron with the medium and to fluctuations of the dipole interactions between two unpaired electrons.[2,4,6,9,10,17] The first mechanism is based on the anisotropy of HFC and should result in some MIE, but the second mechanism is HFC-independent. Both mechanisms predict a decrease in the relaxation rate as B^2 increases. A comparison of the values of $k_{\mathrm{H/D}}$ and MIE in the range from 20 to 200 mT for RPs with $n = 6$ and 10 results in the following conclusions. 1. The contribution of the dipole-dipole relaxation is small for both RPs. This follows from the fact that k_{D} does not depend on B at $B \geq 20$ mT (Fig. 3). 2. The rate of HFC-induced relaxation increases slightly as the chain length increases from $n = 6$ to $n = 10$. That is why the difference $k_{\mathrm{H}} - k_{\mathrm{D}}$ at $B \geq 20$ mT is slightly larger for $n = 10$ than for $n = 6$ (Fig. 3). 3. The MIE at $B \geq 20$ mT is greater for $n = 6$ than for $n = 10$ (Fig. 4) due to the corresponding increase in rate of the recombination of RP with $n = 10$ *via* the mechanism insensitive to the magnetic field. As mentioned above, this mechanism can be caused by SOC-induced intersystem transitions or paramagnetic relaxation, which are insensitive to the magnetic field, *e.g.*, due to spin-rotational coupling.[10]

Thus, the study of the kinetics of the recombination of covalently-linked triplet RPs with different exchange and hyperfine interactions, which depend on the length of the flexible methylene chain and the isotope substitution, allows one to see the roles of the different types of interactions. The high kinetic MIE for RPs with small exchange interactions indicate that HFC-induced spin evolution is the factor that determines the recombination rate in small external magnetic fields. A further increase in the magnetic field strength is accompanied by a decrease in the MIE due to SOC-induced intersystem transitions insensitive to the external magnetic fields. The interplay of the different types of factors results in the following regularity: the MIE is higher for RPs with similar values of hyperfine and exchange interactions.

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