

Large Magnetic Field Effect on the Decay Rates of Triplet Hydrocarbon Diradicals

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Intersystem crossing rate constants, k_{ISC} , of triplet 1,*n*-diphenyl 1,*n*-diyl diradicals (n = number of carbons in diradical chain) generated by type I photolyses of α,α' -diphenylcycloalkanones were measured in an external magnetic field H variable up to 2 kG. No magnetic field effect was observed for $n = 4$ and 5, but for $n = 9, 11,$ and 14, k_{ISC} first increased then decreased as H was increased. For $n = 11$ and 14, the value of k_{ISC} decreased to an apparent asymptotic value at high field equal to 0.17 and 0.07, respectively, of the value of k_{ISC} at $H = 0$. For diradicals with $n \geq 9$, it is proposed that, at $H = 0$, electron-nuclear hyperfine coupling is the only important ISC mechanism, that at $H = 2$ kG electronic spin-lattice relaxation is the major ISC mechanism, that the three triplet magnetic sublevels do not equilibrate during the diradical lifetime, and that one of the outer two triplet magnetic sublevels is preferentially populated initially.

Introduction

The number of experiments in which an external magnetic field is used to probe reaction mechanism has grown rapidly in the last decade.^{1,2} For reactions that proceed via radical-pair or diradical intermediates, measurement of the magnetic field dependence (mfd) of various properties (reaction yields¹⁻⁴ or rates,⁵ isotopic enrichment,^{1,2,6} ODMR,¹ CIDNP⁷) generates information about spin interactions and about the diffusive motions of the radical pair or chain motions of the diradical. Not all the potential information in an mfd experiment is currently extractable because of an incomplete understanding of the phenomenon. In diradicals, spin interactions are coupled to the chain motions, and the full experimental implications of these interactions have not yet been explored.

Instead of measuring steady-state properties such as yields, our approach is to measure the effect of the external magnetic field H directly on the rate of diradical decay. In a previous study,⁵ we showed that mfd experiments can give a new piece of information: the mechanism of intersystem crossing (ISC) within the diradical. This important property is related to the product distribution⁸ as well as to the rate of product information,⁵ has a profound influence on the magnetic isotope effect,⁸ and affects the sign and magnitude of the temperature dependence of the diradical lifetime.⁹ In the present study, we examine diradicals whose lifetimes change by a factor of up to 19 when H is varied from 0 to 2 kG, a more than 1 order of magnitude greater change

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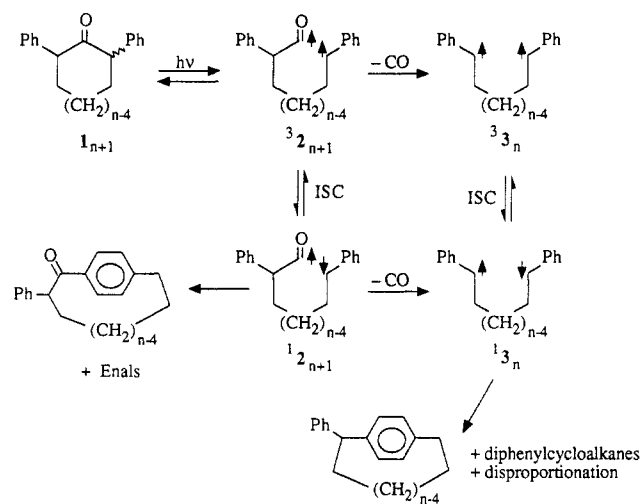


TABLE I: Data for 3_m , $n = 9, 11, 14$ (n = Number of Carbons in Chain), Parameters Extracted from Figure 1^a

n	H_{max}/G	$k_{ISC}/10^6 s^{-1}$			k_{ISC}^a/k_{ISC}^0
		$H = 0$	$H = H_{max}$	$H = 2$ kG	
9	300 ± 100	1.58 ± 0.06	1.8 ± 0.1	0.71 ± 0.05	b
11	120 ± 80	3.7 ± 0.1	4.4 ± 0.2	0.63 ± 0.05	0.17
14	30 ± 15	6.9 ± 0.9	9.2 ± 1.2	0.48 ± 0.05	0.07

^a See text for definitions. ^b Asymptotic region was not reached within 2 kG.

than the diradicals in our original study.⁵

Triplet diradicals^{3,3} are produced from type I cleavage of cycloalkanone **1** (Scheme I). Absorption of a photon produces **1** in the $1^1\pi\pi^*$ state; rapid ISC to the $3^1\pi\pi^*$ state ensues, followed by cleavage to form 3^2 . At 23 °C decarbonylation occurs in <10 ns to form 3^3 .¹⁰ Since all these processes occur within the duration of the laser pulse, 3^3 is the first species observed. Under our conditions, ISC is the rate-limiting step for diradical decay,^{5,11} so that $\tau^{-1} = k_{ISC}$, where τ is the lifetime of the diradical and k_{ISC} is the conformationally averaged ISC rate constant for decay of 3^3 . All decay rate constants therefore refer to decay of the triplet diradical.

Experimental Section

Lifetimes τ of 3_m , $n = 4, 5, 9, 11,$ and 14 (n = number of carbons in the chain) were measured in methanol solvent at 23 °C by nanosecond transient absorption spectroscopy in an apparatus previously described,¹¹ except that the sample holder was placed

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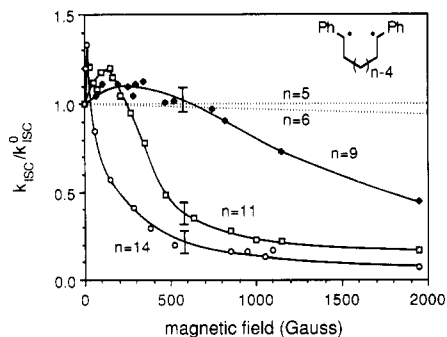


Figure 1. Plots of k_{ISC} for 3_n at magnetic field H relative to k_{ISC} at $H = 0$. Experimental points are included for $3_{9,11,14}$. For clarity, no points for $3_{4,5}$ are included since the field dependence (dotted lines) is negligible at ≤ 2 kG. Representative error bars are shown.

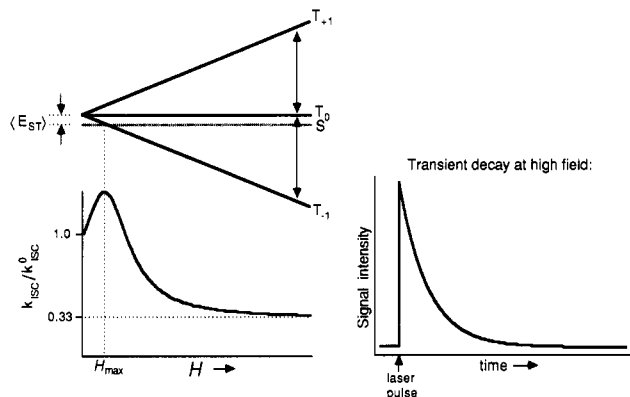


Figure 2. Magnetic and kinetic properties of a diradical with rapid transitions among the three triplet sublevels. For definitions of parameters, see text. Top: idealized dependence of spin energy levels on the magnetic field strength. The vertical double arrows indicate rapid transitions among triplet sublevels. Lower left: expected mfd curve corresponding to upper diagram. Lower right: transient decay at high field is expected to exhibit single-exponential decay as a result of the rapid transitions among triplet sublevels.

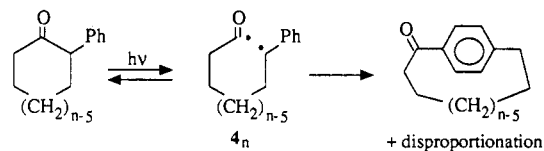
between the poles of a small electromagnet, variable up to 2 kG. Following excitation at 308 nm with a XeCl excimer laser (18-ns fwhm) or 266 nm with a Nd-YAG (6-ns fwhm), transient absorption of the benzylic moiety was monitored at 320 nm. Assignment of the transients was based on the transient absorption $\lambda_{\max} = 320 \pm 2$ nm and the invariance of τ to addition of diene quencher. In the Earth's field (≈ 0.5 G, hereafter approximated $H = 0$), the decay of 3_n appeared to be biphasic for $n \geq 9$. Our reported k_{ISC} values for 3_n were taken from the slower part of the decay, which accounted for 70–100% of the total decay amplitude, depending on n (larger amplitude for smaller n). In a magnetic field, the decays of 3_n fit well to single exponential over the entire decay.

Results and Discussion

Figure 1 shows the mfd results for 3_n , $n = 4, 5, 9, 11$, and 14 . The ordinate is k_{ISC}/k_{ISC}^0 , where k_{ISC} is the ISC rate constant at a given value of H and k_{ISC}^0 is the value at $H = 0$. The value of k_{ISC}/k_{ISC}^0 for $3_{4,5}$ is independent of H in the range $H = 0$ – 2 kG. However, the longer diradicals $3_{9,11,14}$ show a maximum in k_{ISC} at relatively low field ($H = H_{\max}$) and (for $3_{11,14}$) appear to level off to an asymptotic value k_{ISC}^{∞} at 2 kG. Table I lists the values of k_{ISC} at $H = 0$, $H = H_{\max}$, and $H = 2$ kG and $k_{ISC}^{\infty}/k_{ISC}^0$, the ratio of k_{ISC} in the asymptotic high-field region to k_{ISC} at $H = 0$.

The general features of the mfd curve are described in Figure 2. Because the ends of a diradical are constrained to stay within a maximum end-to-end distance, there is a measurable singlet-triplet energy gap $\langle E_{ST} \rangle \equiv \langle E_S - E_T \rangle$, where angle brackets indicate an average over an appropriate set of conformations adopted during the diradical's lifetime. Application of a magnetic field H leads to a T_{-1} -S crossing¹² at $H = H_{\max}$, and produces

SCHEME II



a local maximum in k_{ISC} . Thus, H_{\max} gives a measure of $\langle E_{ST} \rangle$.¹³ At high field, where the large Zeeman splitting removes the $T_{\pm 1}$ sublevels from the S level, k_{ISC} decreases to an asymptotic value k_{ISC}^{∞} because T_0 is the only level remaining close to S. E_{ST} decreases approximately exponentially with increasing end-to-end distance R .¹⁴ Since the root-mean-square value of R increases with increasing diradical chain links n , H_{\max} decreases with increasing n . This explains the progression of H_{\max} values in Table I and the absence of detectable magnetic field effect on $3_{4,5}$. The short diradicals have $\langle E_{ST} \rangle$ much larger than the available Zeeman splitting.

Compared to the H_{\max} values for 4_n (Scheme II) obtained in our previous mfd study⁵ ($H_{\max} = 600 \pm 100$, 120 ± 20 , and 20 ± 10 G, respectively, for $4_{10,11,12}$), H_{\max} for 3_n is expected to be smaller for a given value of n , because electron delocalization onto the extra phenyl ring of 3_n increases the effective value of R . A similar case was found, for example, in CIDNP mfd studies^{7c,15} of $4_{6,7,8}$ compared to the corresponding diradical without the phenyl group derived from the unsubstituted ketone.^{7a} Table I suggests that delocalization onto the phenyl groups is significant for 3_9 , which has a smaller H_{\max} than that of 4_{10} even though 3_9 has a shorter chain. Scatter in the data for $3_{11,14}$ precludes quantitative comparison with 4 .

Our goal in the remainder of the paper is to interpret the large decrease in k_{ISC} at 2 kG. At high field, where the large Zeeman splitting removes the $T_{\pm 1}$ sublevels from the S level, k_{ISC} decreases to an asymptotic value k_{ISC}^{∞} because T_0 is the only level remaining close to S. The amount by which k_{ISC} decreases at high field relative to its value k_{ISC}^0 at $H = 0$ is related to the mechanism of ISC in the diradical.⁵ There are three major ISC mechanisms in diradicals: electron-nuclear hyperfine coupling (HFC), spin-orbit coupling (SOC), and electronic spin-lattice relaxation (T_1 process). T_1^{-1} is the lower limit for k_{ISC} . It corresponds to uncorrelated relaxation of each separate radical center and includes the effect of anisotropic g and hyperfine tensors, etc. For benzyl radicals at -62 °C, $T_1^{-1} = 1.2 \times 10^5$ s⁻¹,^{16a} and for alkyl and other π -radicals of moderate molecular weight at 10–20 °C, typical values of T_1^{-1} are $(3-5) \times 10^5$ s⁻¹.^{16b,c} The effect of spin interactions on radical recombination has been studied theoretically at various levels of sophistication.^{11,17} For the present purposes, we take a qualitative approach.

We can distinguish two limiting cases at high field, according to whether the triplet sublevels do or do not equilibrate rapidly prior to ISC:

Case 1. The T_{+1} , T_0 , T_{-1} sublevels are rapidly equilibrated prior to ISC (Figure 2), e.g., via dipolar electronic spin-lattice relaxation, which is not an ISC mechanism. Under these conditions, ISC for all three sublevels would be averaged into one decay constant.¹⁸ At high field, neglecting Boltzmann factors, we would

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(13) Figure 2 has $\langle E_{ST} \rangle < 0$, or S below T, the usual case in long polymethylene chains, deduced from CIDNP. See: Reference 7.

(14) The magnetic field affects ISC only in conformers where E_{ST} is within range of the Zeeman splitting. As we pointed out in ref 5, this implies that H_{\max} measures $\langle E_{ST} \rangle$ averaged over conformers with large R , rather than $\langle E_{ST} \rangle$ averaged over all conformers.

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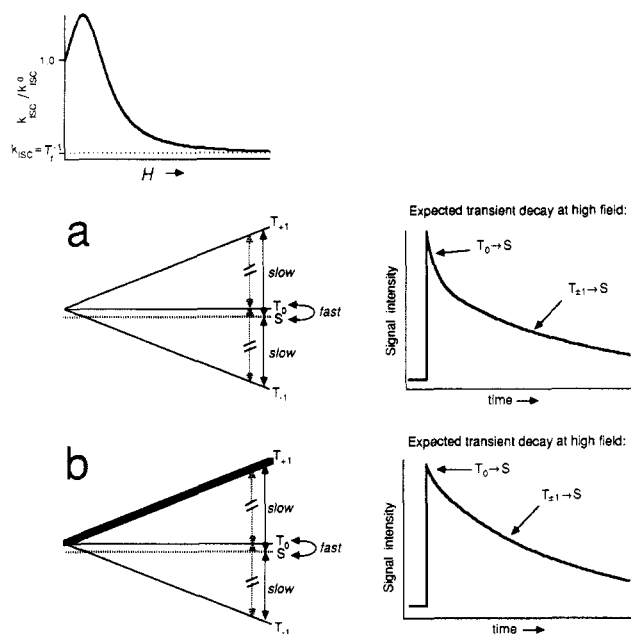


Figure 3. Magnetic and kinetic properties expected of a diradical in the absence of rapid transitions among triplet sublevels. Top: expected mfd curve. a, left: energy levels of spin states. The absence of rapid triplet-triplet transitions (broken double arrows) implies two decay rates, a fast $T_0 \rightarrow S$ rate and a slow $T_{\pm 1} \rightarrow S$ rate corresponding to T_1^{-1} . a, right: corresponding biexponential transient decay at high field. b, left: same as above left, except that the T_{+1} state is much more populated than the other sublevels (thick line). b, right: high-field transient decay is expected to look nearly single exponential because of small-amplitude fast decay (10% in this example).

have $k_{ISC}^{\infty} = (k_{ISC}^0 + 2T_1^{-1})/3$, where T_1 refers to uncorrelated spin-lattice relaxation of each end. The k_{ISC}^0 term corresponds to $T_0 \rightarrow S$ ISC and T_1^{-1} to $T_{\pm 1} \rightarrow S$. The lower limit for the ratio $k_{ISC}^{\infty}/k_{ISC}^0$ is $1/3$, obtained when $k_{ISC}^0 \gg T_1^{-1}$.

Case 2. Interconversion among triplet sublevels is much slower than ISC (Figure 3). In this case, one expects that a decay characterized as a single exponential at $H = 0$ would become a double exponential at high field. The initial fractional populations of the triplet sublevels are $F(T_{-1})$, $F(T_0)$, and $F(T_{+1})$, which sum to 1. At high field, one would expect a fast $T_0 \rightarrow S$ decay with rate constant k_{ISC}^0 and relative amplitude $F(T_0)$, followed by a slow $T_{\pm 1} \rightarrow S$ decay with rate constant T_1^{-1} and relative amplitude $F(T_{+1}) + F(T_{-1})$. If the initial triplet populations are all $1/3$, then the first one-third of the decay would be fast and the final two-thirds slow (Figure 3a, right side). A plot of the slow decay vs H would be expected to resemble the left side of Figure 3a, and at high field, the slow decay would correspond to $k_{ISC}^{\infty} = T_1^{-1}$. The expected value of $k_{ISC}^{\infty}/k_{ISC}^0$ is T_1^{-1}/k_{ISC}^0 , which can be $< 1/3$.

At high field, we observe both single-exponential decay and a large magnetic field effect, $k_{ISC}^{\infty}/k_{ISC}^0 < 1/3$. These two observations are inconsistent with expectations based on Figure 2 (case 1 above) or on Figure 3a (case 2). Figure 2 implies that single-exponential decay should be coupled with $k_{ISC}^{\infty}/k_{ISC}^0 > 1/3$, and Figure 3a implies that if $k_{ISC}^{\infty}/k_{ISC}^0 < 1/3$, then one observes a double exponential. Certainly, a value of $k_{ISC}^{\infty}/k_{ISC}^0$ much less than $1/3$ appears to eliminate any mechanism in which the three triplet sublevels equilibrate prior to ISC. A possibility is suggested in Figure 3b. The triplet sublevels do not interconvert, but in this case the initial triplet population is strongly biased in favor of one of the $T_{\pm 1}$ sublevels as a result of triplet sublevel

selective ISC from the excited singlet ketone **1** to the lowest triplet state of **1**. This is the well-known triplet mechanism of CIDEP.^{19,20} If 80% of the triplets were generated in the T_{+1} state and 10% in each of the other two, the 10% fast $T_0 \rightarrow S$ decay may well go unnoticed. Consistent with this interpretation is our preliminary observation of exclusively emissive CIDEP, possibly via the triplet mechanism,²¹ in time-resolved EPR spectra of **3**, at room temperature.²² We therefore adopt Figure 3 as a working hypothesis for the large magnetic field effect. The essential features are the nonequilibrating triplet sublevels combined with triplet mechanism electron spin polarization.

The ratio $k_{ISC}^{\infty}/k_{ISC}^0$ contains information on the ISC mechanism.⁵ HFC is independent of the diradical end-to-end distance R , and the SOC matrix element varies roughly as e^{-cR} ($c = \text{constant}$). In conformers with small R , SOC is the dominant ISC mechanism, while at large R SOC is negligible and HFC becomes dominant.²³ If SOC were the exclusive ISC mechanism, one would expect $k_{ISC}^{\infty}/k_{ISC}^0$ to be 1.0 (no magnetic field effect).⁵ If all ISC took place at small R where SOC is appreciable, then $|E_{ST}|$ would be much larger than the Zeeman splitting of 2 kG and H would have no effect on k_{ISC} . k_{ISC}^{∞} can be less than k_{ISC}^0 only when at least some ISC occurs in conformers with large R (via HFC). In the diradicals **4**, for example, SOC is the dominant ISC mechanism²⁴ and $k_{ISC}^{\infty}/k_{ISC}^0$ is nearly 1 (0.91 for **4**₁₁ and 0.84 for **4**₁₂).⁵ If the deviation of $k_{ISC}^{\infty}/k_{ISC}^0$ from 1.0 is associated with the HFC mechanism, one can calculate the HFC/SOC ratio from a knowledge of $k_{ISC}^{\infty}/k_{ISC}^0$. In the case of **4**, the HFC/SOC ratio was estimated to be 0.14 for **4**₁₁ and 0.32 for **4**₁₂.⁵

In the present experiments, the $k_{ISC}^{\infty}/k_{ISC}^0$ values for **3**_{11,14} are well below $1/3$ (Table I). Such large magnetic field effects indicate HFC as the dominant ISC mechanism at $H = 0$. At 2 kG, our highest field, **3**_{9,11,14} have $k_{ISC} = 7.1 \times 10^5$, 6.3×10^5 , and 4.8×10^5 s⁻¹, respectively. These are close to the expected T_1^{-1} value of $3\text{--}5 \times 10^5$ s⁻¹.¹⁶ Thus, spin-lattice relaxation is a major, and probably the dominant, ISC mechanism for these diradicals at high field.

Conclusion

Our results demonstrate that biradicals that undergo ISC via the HFC mechanism can exhibit extremely large magnetic field effects. The magnitude of the effect requires that the three triplet sublevels do not equilibrate during the diradical lifetime, and the single-exponential transient decay suggests that the sublevels are initially formed with a strongly nonequilibrium population distribution. In addition, the application of a magnetic field completely changes the dominant mechanism of ISC for **3**_{9,11,14}, from HFC at $H = 0$ to spin-lattice relaxation at $H = 2$ kG. This is in complete contrast to the magnetic properties of **4**_{11,12}, for which SOC is the major mechanism of ISC at all fields studied and whose decay is only slightly perturbed by a magnetic field.

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Registry No. **3**₄, 108708-21-0; **3**₅, 98737-11-2; **3**₉, 115988-72-2; **3**₁₁, 120361-05-9; **3**₁₄, 120385-13-9.

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(21) In principle, the emission could be due to depletion of the T_{-1} level by $T_{-1} \rightarrow S$ ISC in the diradical. This is unlikely, since for **3**₉ (E_{ST}) is less than one-tenth of the Zeeman splitting (X-band EPR; 3.3 kG). Emissive CIDEP due to $T_{-1} \rightarrow S$ ISC in aliphatic hydrocarbon biradicals is described in: Closs, G. L.; Forbes, M. *J. Am. Chem. Soc.* **1987**, *109*, 6185.

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(24) In atoms, SOC increases as the fourth power of the effective nuclear charge. Delocalization of the odd electron in the acyl radical center of **4** onto oxygen is expected to give rise to significantly larger SOC in **4** than on **3**.

(18) No polyexponential transient decay is introduced by the existence of three sublevels as long as they interconvert rapidly. However, HFC inherently gives rise to a distribution of lifetimes because each combination of nuclear spin states has a different HFC matrix element. (Measurements of these rates are reported in: Closs, G. L.; Miller, R.; Redwine, O. D. *Acc. Chem. Res.* **1985**, *18*, 196.) We presume that the distribution of HFC matrix elements represents the major contribution to the slight biphasic appearance of the decay of **3**_{9,11,14} at zero field.