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Dynamics of Flexible Triplet Biradicals

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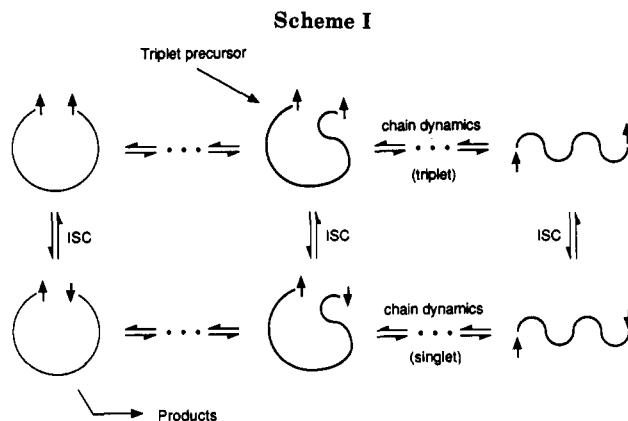
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Introduction. A large number of thermal and photochemical reactions proceed via biradical intermediates.¹ This is reason enough to study biradicals, but the interest in them goes deeper. The study of biradicals allows access to the details of a major category of chemical transformation, homolytic cleavage and recombination. The mutual interactions of the two unpaired electrons in a biradical have features in common with all weakly coupled systems—for example, the coupling responsible for electron transfer.² With two weakly interacting electrons, a radical can exist in either a singlet or triplet state. These states have totally different chemical properties^{1,3} yet coexist in the biradical at virtually the same energy. Typically, a biradical generated in the triplet state must first undergo intersystem crossing (ISC) to the singlet biradical before forming products. This presents one of the major challenges of photochemistry,⁴ to understand a reaction in which the molecule must hop from one potential energy surface to another. We shall see that the requirement to go from a triplet to a singlet biradical has a major effect on the kinetics and also affects the product ratio. More important, the results can be interpreted within a simple model.

Charles Doubleday was born in Corpus Christi, TX. He obtained his Ph.D. from the University of Chicago, did postdoctoral research at the University of Texas at Austin, moved to the State University of New York at Buffalo, and has been at Columbia University since 1983. His research interests are both experimental (kinetics of radicals, biradicals, and other transient intermediates) and theoretical (ab initio studies of radical and biradical reactions).

Nicholas J. Turro was born in Middletown, CT and received the A.B. degree from Wesleyan University in 1960. He did his graduate work as a NSF Predoctoral Fellow with George S. Hammond at Caltech and was awarded the Ph.D. in 1963. After a year's postdoc at Harvard with Paul D. Bartlett, he joined the Columbia University Chemistry Department, where he is now the Wm. P. Schweitzer Professor of Chemistry. Research interests have been in the areas of photochemistry, photoluminescent reactions, magnetic effects on reactions, and reactions in constrained environments.

Jin-Feng Wang was born in 1963 and received his B.Sc. in chemistry from Peking University in Beijing, China in 1982. At present, he is a graduate student under the instruction of Prof. N. J. Turro in the Chemistry Department of Columbia University.



The quickening pace of research into biradicals has been driven by modern spectroscopic methods that probe the optical and magnetic properties of these species. Scaiano⁵ pioneered nanosecond transient absorption for determining the lifetimes of flexible biradicals. His group and the Caldwell group⁶ have con-

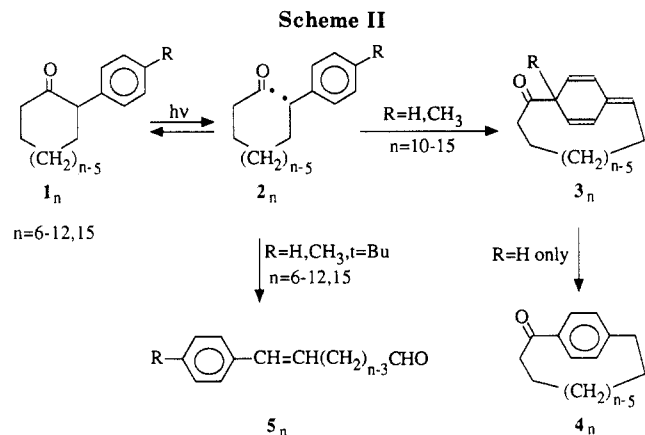
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tributed greatly to our knowledge of the kinetics of a variety of biradicals including types I^{5c,6e} and II, ^{5a,b,e,6a-c} Paterno-Büchi biradicals, ^{6d} hydrocarbon biradicals, ^{5d} and 1,3-biradicals. ^{6f} Closs and co-workers⁷ have shown that time-resolved magnetic polarization provides a unique perspective on biradical reactions and is a valuable complement to optical spectroscopy. Closs,⁸ Doubleday,⁹ Kaptein,¹⁰ and their co-workers explored magnetic field dependent CIDNP to obtain information on both the singlet-triplet splitting and chain dynamics of polymethylene biradicals. Weller's group¹¹ and Schulten's group¹² have demonstrated the power of analyzing the magnetic-field dependence of the intersystem-crossing yield of biradicals (measured by optical absorption) by means of computer simulations to extract information on the chain dynamics of polymethylene biradicals. Adam, Wilson, and co-workers¹³ have measured the lifetimes of small hydrocarbon biradicals by Stern-Volmer kinetics of oxygen quenching. Important EPR studies of matrix-isolated cycloalkane 1,3-diyls at cryogenic temperatures have been reported by Closs^{14a} and Dougherty.^{14b} Conjugated biradicals are

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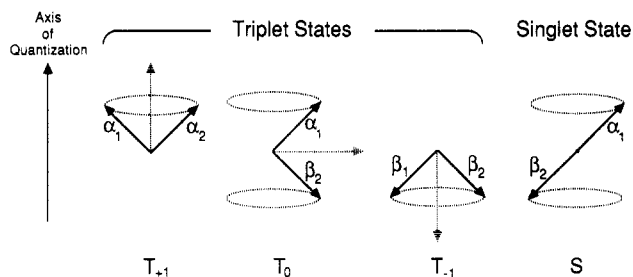
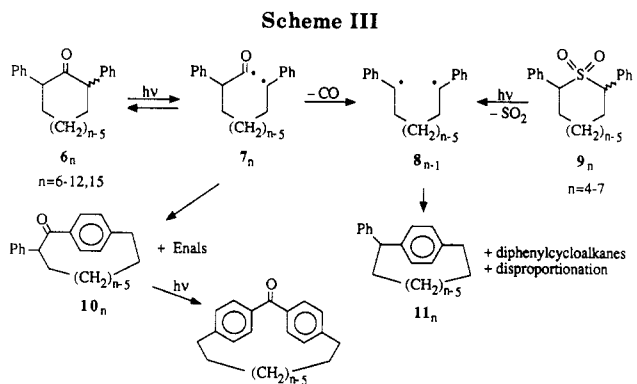


Figure 1. Vector model of singlet and triplet states, composed of combinations of individual eigenstates α and β for electrons 1 and 2. Dotted arrows are the resultant projections of total angular momentum along the axis of quantization. Circles indicate uncertainty in vector direction.



an important class of intermediates that will not be covered here. We refer the interested reader to excellent reviews in this area.^{1a}

In this Account we are concerned with triplet-derived flexible chain biradicals, and Scheme I shows the important processes. A triplet precursor (e.g., an $^3n, \pi^*$ ketone) cleaves with conservation of spin to produce a triplet biradical in a set of conformations where the radical centers are close together. Two processes ensue: ISC in a given conformation produces a singlet biradical in the same conformation, and internal rotation gives rise to chain dynamics, which changes the end-to-end distance. The ISC efficiency is different in each conformer, and we shall see how the connection between ISC, conformer population, and chain dynamics has important consequences for the reactivity and product distribution of the biradical. The final process in Scheme I is product formation (disproportionation or cyclization) from a small subset of singlet conformers having a short end-to-end distance, which we assume to occur very rapidly ($\ll 1$ ns).⁸⁻¹¹

Photolysis Products. Schemes II and III show the reactions studied, which generate the 1, n -biradicals 2_n and 8_{n-1} . (In Scheme II, only $R = H$ ketones are discussed in this Account.) Compounds 1 and 9 were synthesized by standard methods, and 6_n were synthesized (for $n = 10, 11, 12, 15$) from the unsubstituted ketones.¹⁵ For biradical chain lengths $n < 10$ carbons, we found the expected¹⁶ disproportionation products, but for $n \geq 10$, the paracyclophanes **4**, **10**, or **11** were the major products, in up to 95% yield.^{17,18} Although

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small yields of ortho and para coupling products have been observed in cumyl radical terminations,¹⁹ we have not yet identified orthocyclophanes in our product mixtures. Photolysis of **6** gives mainly decarbonylation at $\geq 10^\circ\text{C}$, but **10** predominates below -20°C . Quantum yields for disappearance of **1** or **6** range from 0.2 to 0.95.^{17,18}

Interactions Involving the Electron Spin. The unique character of triplet biradical chemistry is due to the ISC step. The laws that govern the singlet-triplet interaction give rise to some exotic results, such as negative activation energies, magnetic field dependent reaction rates and product distributions, and spectacularly large kinetic isotope effects. These results turn out to be related in a simple way to a few key concepts involving electron-spin interactions. The singlet (S) and triplet (T) states can be visualized in terms of the vectors in Figure 1.²⁰ Triplet sublevels are labeled T_{+1} , T_0 , T_{-1} , where the subscripts refer to projections of spin angular momentum along the axis of quantization. Each triplet sublevel has a nonzero projection of angular momentum along some spatial direction; the singlet has a projection of 0 in all directions. ISC occurs when an external torque produces a spin flip. The torques arise from interactions of the electron spins with additional angular momenta and are discussed below.

For a qualitative understanding of k_{ISC} , the observed ISC rate constant in the biradical, only two things matter: the S-T energy gap $E_{\text{ST}} \equiv E_{\text{S}} - E_{\text{T}}$, and the off-diagonal ISC matrix element which connects the S and T states and provides the torque to induce the spin flip. An increase in the ISC matrix element increases k_{ISC} ; an increase in E_{ST} decreases k_{ISC} . E_{ST} is a measure of the interaction between the electrons. It is like a force that maintains alignment of the spins in a triplet or singlet state. ISC can occur only if a magnetic torque (ISC matrix element) is strong enough to overcome E_{ST} and decouple the spins to produce the spin flip.

Electron-spin interactions can be divided into two types: those that affect only E_{ST} and those responsible for inducing ISC (off-diagonal matrix elements).

Interactions That Affect the S-T Gap. (1) *Interaction with an External Magnetic Field (Zeeman Interaction).*²¹ The Zeeman interaction splits the triplet states symmetrically about the T_0 level by an amount $g\beta H$, where H is the magnetic field strength and g and β are the average g value and the Bohr magneton, respectively. A field of 10 kG (1 tesla) produces a splitting of 1.07 cm^{-1} in a typical biradical ($350\text{ cm}^{-1} = 1\text{ kcal/mol}$). E_{ST} is independent of H . However, if $E_{\text{ST}} \neq 0$, one of the $T_{\pm 1}$ sublevels does intersect S for an appropriate value of H . This is discussed in a later section.

(2) *Interactions between the Two Electrons.* The most important effect in this category is E_{ST} , whose sign and magnitude depend on the biradical conformation.³

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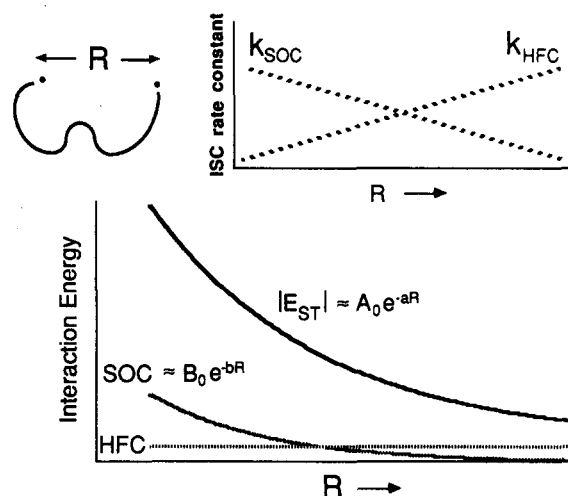


Figure 2. Dependence of energies and ISC rates on biradical end-to-end distance R . Top: qualitative R dependence of ISC rate constant for limiting cases of pure SOC and pure HFC mechanisms. Linearity is not implied. Bottom: qualitative R dependence of singlet-triplet energy gap E_{ST} and matrix elements for SOC and HFC.

Its dependence on the end-to-end distance R has been approximated¹⁰ as $|E_{\text{ST}}| = A_0 e^{-aR}$, where $A_0 = 8.83 \times 10^6\text{ cm}^{-1}$ and $a = 2.136\text{ \AA}^{-1}$. Another effect is the zero-field splitting,²¹ due mainly to the electronic dipolar interaction. It is generally neglected in large biradicals because it varies as R^{-6} and is expected to be less than 0.01 cm^{-1} .¹⁴

Interactions That Flip a Spin—ISC Mechanisms. (3) *Interaction with Nuclei—Hyperfine Coupling (HFC).* HFC is responsible for EPR splittings and CIDNP.⁸⁻¹¹ The electron and nuclear spins can be thought of as exerting mutual torques on each other. In alkyl radicals the α and β protons have HFC couplings of 22–30 G.²² ^{13}C HFC is larger than ^1H , especially in carbonyl carbons of acyl radicals (114–132 G).²² In contrast to the E_{ST} and spin-orbit coupling (SOC) interactions, HFC is purely local and is independent of R .

(4) *Interaction with Electronic Orbital Angular Momentum—Spin-Orbit Coupling.* With SOC, the torque is provided by electronic orbital angular momentum.^{20,23} We have suggested^{23b} that $\text{SOC} \propto e^{-bR} \sin \phi$, where $b = 3.07\text{ \AA}^{-1}$ and ϕ is the acute angle between the orbitals at the radical centers.

(5) *Spin-Lattice Relaxation.*²¹ Coupling with magnetic torques generated by random solvent motions produces relaxation via independent spin flips at each separate radical center. This ISC mechanism typically provides the *lower limit* for the ISC rate constant of the biradical, which should be about the same as the relaxation rate T_1^{-1} for the corresponding monoradical. For a variety of conjugated and unconjugated π -radicals, $T_1^{-1} \approx 3\text{--}5 \times 10^5\text{ s}^{-1}$ at room temperature.²⁴

Dependence of Spin Interactions and ISC Rate Constant on End-to-End Distance R . Figure 2 (bottom) shows the qualitative R dependence of E_{ST}

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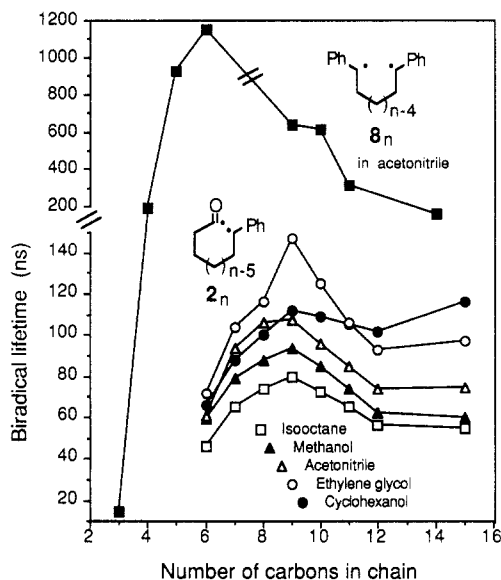


Figure 3. Biradical lifetime vs chain length n for $1,n$ -biradicals 8_n and 2_n in different solvents at room temperature. The value for 8_3 is taken from ref 6f.

and the SOC and HFC matrix elements. The associated R dependence of k_{ISC} is shown at the top. If ISC is due exclusively to HFC ($k_{\text{ISC}} = k_{\text{HFC}}$), then k_{ISC} must increase as R increases because the S-T gap gets smaller with a constant HFC matrix element. For a pure SOC mechanism ($k_{\text{ISC}} = k_{\text{HFC}}$), the matrix element is negligible at large R but can be very large at small R . Thus k_{ISC} due to SOC decreases as R gets larger. With such a strong dependence of k_{ISC} on biradical geometry, each biradical conformation has a different value of k_{ISC} . The situation greatly simplifies when conformational interconversion is much faster than ISC. In this high-temperature limit, the observed ISC rate constant is the mean of all the individual ISC rate constants of each conformer. That is, $k_{\text{ISC}} = \sum_i f^i k_{\text{ISC}}^i$, where f^i is the equilibrium mole fraction of triplet conformer i and k_{ISC}^i is the ISC rate constant for conformer i . We shall also refer to other average quantities such as $\langle E_{\text{ST}} \rangle$ and $\langle R \rangle$, where angle brackets indicate an average over all conformers adopted during the biradical lifetime.

Results and Discussion of Nanosecond Laser Experiments. The lifetimes of the biradicals **2** and **8** were measured by a standard nanosecond transient absorption apparatus. Ketones **1** and **6** were typically photolyzed at 308 nm with a XeCl excimer laser (18 ns fwhm, <20 mJ/pulse) and monitored at 320 nm. Biradicals were characterized by their transient UV spectra ($\lambda_{\text{max}} = 320 \pm 2$ nm, fwhm ≈ 10 nm) and by the invariance of the lifetime to diene quenching.

Effect of Biradical Geometry. Chain Length and Substituent. Figure 3 shows the dependence of the biradical lifetime τ on chain length n for the $1,n$ -biradicals 2_n ^{25a} and 8_n ^{25b}. Under the conditions of these experiments, τ^{-1} is a measure of the ISC rate, i.e., $\tau^{-1} = k_{\text{ISC}}$. The dibenzylic biradicals 8_n exhibit three regions in Figure 3. For $n = 3, 4$, ISC appears to be dominated by SOC. The dependence of τ on n is consistent with the R dependence of SOC in Figure 2, since $\langle R \rangle$ decreases as n decreases. For $n = 5, 6$, the increase

in $\langle R \rangle$ is apparently sufficient to decrease SOC while still leaving a sizable value of $\langle E_{\text{ST}} \rangle$. This situation—a large energy separation and a small ISC matrix element—is unfavorable for ISC, and one sees the largest values of τ for $n = 5, 6$. For $n \geq 9$, HFC is likely the principal or exclusive ISC mechanism since $\langle \text{SOC} \rangle$ is presumably very small. If $k_{\text{ISC}} \approx k_{\text{HFC}}$ for 8_n , $n \geq 9$, Figure 2 predicts that k_{ISC} should increase as R increases. This is in fact observed. $\langle R \rangle$ increases as n increases; therefore, k_{ISC} increases for $n \geq 9$.

In Figure 3 the pattern for the acyl-benzylic biradicals **2** is different from that of **8**. τ is almost an order of magnitude smaller for **2** than for **8**, and the maximum value of τ occurs at $n = 9$ for **2** instead of around $n = 6$ or 7 for **8**. We have suggested^{25a} that the difference in the lifetimes of **2** vs **8** is due to dominant SOC in **2**.²⁶ SOC in atoms varies as the fourth power of the effective nuclear charge,²⁷ and delocalization of the odd electron onto the acyl oxygen suggests a larger SOC in **2** than in **8**. When the ends of **2** come close together, SOC becomes large enough to cause rapid ISC. Even though the biradical spends most of its time in more extended conformers, a few conformers with small R can dominate k_{ISC} if they have SOC matrix elements much larger than HFC (≈ 0.003 – 0.004 cm⁻¹). The reason why this does not happen in **8** is presumably that it is a hydrocarbon biradical, with lighter atoms and smaller SOC than **2**. The qualitative pattern of τ ($=k_{\text{ISC}}^{-1}$) for **2** in Figure 3 is what one expects if ISC requires a small value of R . Evidence on the rates and equilibria of chain cyclization processes show that cyclization is favorable for $n = 6$, becomes most unfavorable for $n = 8$ – 10 , and then becomes more favorable for larger chains.²⁸

Thus from Figure 3 we form the qualitative hypothesis that ISC in 2_n is dominated by SOC for all values of n studied, and ISC in 8_n is dominated by HFC for $n > 6$ and by SOC for $n = 3, 4$.

Substituent effects on k_{ISC} were studied²⁹ in the 1,5-dibenzylic biradical 8_5 by incorporating one or two *p*-Cl or *p*-Br substituents. One *p*-Cl substituent has no effect, but *p*-Br increases k_{ISC} by a factor of 3.3 and di-*p*-Br₂ increases k_{ISC} by a factor of 4.8 relative to unsubstituted 8_5 . The enhancements are the same in isooctane and methanol. Since the Hammett σ values for Cl and Br are identical, the data suggest a substantial heavy-atom SOC effect for the Br-substituted biradicals. The Br/H enhancement in 8_5 is about the same as the solvent-dependent Br/H enhancement in Norrish II 1,4-biradicals.^{6a} Replacement of a benzylic hydrogen in 8_5 by OH increases k_{ISC} by a factor of 2.6 in methanol and makes k_{ISC} solvent dependent: k_{ISC} is 1.7×10^7 s⁻¹ and 2.8×10^6 s⁻¹ in isooctane and methanol, respectively.²⁹ This factor of 6 solvent dependence in OH-substituted 8_5 is larger than the factor of 2.4 for the corresponding Norrish II 1,4-biradical.^{6a,29}

(26) One might ask whether T_1^{-1} makes a major contribution to k_{ISC} in **2**, since T_1 in acyl radicals is well under 1 μ s at -90 °C (Paul, H.; Fischer, H. *Helv. Chim. Acta* 1973, 56, 1575). Figure 3 suggests only a minor contribution at most, since the solvent viscosity varies over more than 2 orders of magnitude, but k_{ISC} for **2** changes by less than a factor of 2.

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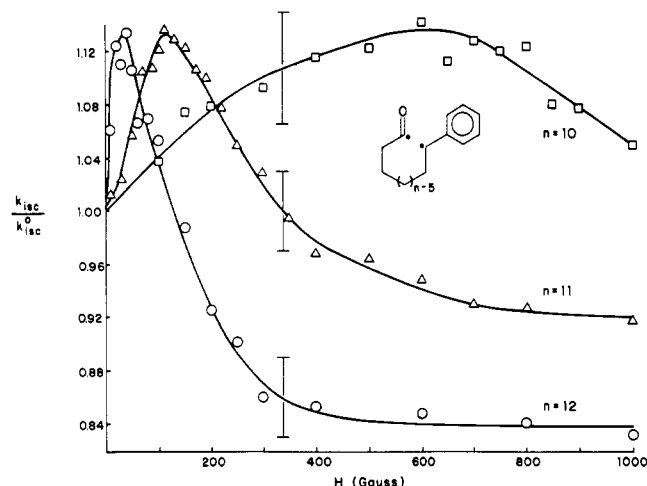


Figure 4. Dependence of ISC rate constants k_{ISC} for 2_n on external magnetic field H at 23 °C. The ordinate is the ratio of k_{ISC} at a given value of H to k_{ISC} at $H = 0$ (k_{ISC}^0). Errors bars are $\pm 2\sigma$.

Table I
Magnetic-Field Dependence of k_{ISC} for Acyl-Benzyl Biradicals 2_n and Dibenzyl Biradicals 8_n ^a

biradical	H_{max} , G	$k_{\text{ISC}}^{\infty}/k_{\text{ISC}}^0$	$k_{\text{ISC}}/10^6 \text{ s}^{-1}$ at values of H		
			$H = 0$	$H = H_{\text{max}}$	$H = 2 \text{ kG}$
2_{10}	600 ± 100	b	10.6 ± 0.3	12.0 ± 0.4	10.6 ± 0.4
2_{11}	120 ± 20	0.91	12.3 ± 0.4	14.0 ± 0.4	11.2 ± 0.4
2_{12}	30 ± 10	0.84	14.9 ± 0.5	16.9 ± 0.6	12.5 ± 0.4
8_9	300 ± 100	b	1.58 ± 0.06	1.8 ± 0.1	0.71 ± 0.05
8_{11}	130 ± 80	0.17	3.7 ± 0.1	4.4 ± 0.2	0.63 ± 0.05
8_{14}	30 ± 15	0.07	6.9 ± 0.9	9.2 ± 1.2	0.48 ± 0.05

^aSee text for definitions. ^bAsymptotic high-field value was not reached.

Effect of External Magnetic Field. The lifetimes of biradicals 2 and 8 are strongly perturbed by an external magnetic field. For 2_{10-12} , Figure 4³⁰ shows the magnetic-field dependence (mfd) of k_{ISC} relative to its value in the earth's field, k_{ISC}^0 . Mfd curves for dibenzyl biradicals $8_{9,11,14}$ are similar.³¹ The mfd curves show a maximum in k_{ISC} followed by a decrease to an apparent asymptotic value at high field, k_{ISC}^{∞} . The field at which the maximum occurs, H_{max} , increases as the chain length decreases. Table I lists H_{max} and the other major features of the mfd curves in Figure 4. Mfd curves of this sort were first observed for biradical-derived CIDNP⁸⁻¹⁰ and, more recently, for triplet yields¹¹ of donor-acceptor biradicals and CIDNP³² of radical pairs in micelles. A unique feature of our mfd studies that distinguishes them from previous mfd work on biradicals is that ours are based on measured rates.

Figure 5 shows how the mfd curve arises. The magnetic field changes the Zeeman splitting between the triplet sublevels T_{+1} , T_0 , T_{-1} , but leaves $\langle E_{\text{ST}} \rangle$, the average T_0 -S spacing, unchanged. If $\langle E_{\text{ST}} \rangle \neq 0$, application of a magnetic field leads to a crossing between T_{-1} and S, since the singlet usually lies below the triplet.⁸ At $H = H_{\text{max}}$, the ISC efficiency reaches a local maximum because of the T_{-1} -S degeneracy. Thus H_{max} gives a measure of $\langle E_{\text{ST}} \rangle$. Recall from Figure 2 that $E_{\text{ST}} \propto e^{-aR}$. Since $\langle R \rangle$ increases with increasing biradical chain length n , H_{max} decreases with increasing n . As

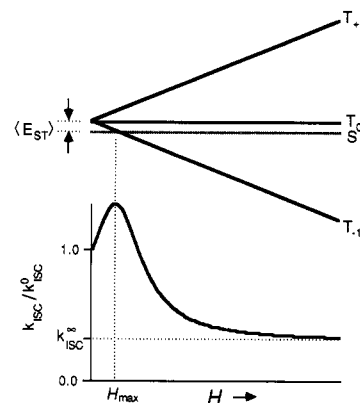


Figure 5. Energy-level diagram for a biradical in a magnetic field H , with corresponding mfd plot analogous to Figure 4. At high field the asymptotic value of the ordinate is $k_{\text{ISC}}^{\infty}/k_{\text{ISC}}^0$.

H increases beyond H_{max} , the T_{-1} sublevel gets further from the S level, and k_{ISC} decreases to an asymptotic value k_{ISC}^{∞} where the $T_{\pm 1}$ sublevels are far from S.

A detailed analysis of the ratio of k_{ISC} at high field vs 0 field, $k_{\text{ISC}}^{\infty}/k_{\text{ISC}}^0$, reveals the competition among the various ISC mechanisms.^{30,31} $k_{\text{ISC}}^{\infty}/k_{\text{ISC}}^0$ is found to be less than 1. A value close to 1 implies that most of the ISC occurs via the SOC mechanism. A small value ($\leq 1/3$) implies that most ISC occurs via the HFC mechanism or via spin-lattice relaxation. The values of $k_{\text{ISC}}^{\infty}/k_{\text{ISC}}^0$ in Table I show a clear difference between the biradicals 2 and 8 . ISC in the acyl-benzyl biradicals 2 is dominated by SOC (we estimate 76% for 2_{12} and 88% for 2_{11})³⁰ while ISC in the benzyl-benzyl biradicals 8 is dominated by HFC. Our numerical estimates for percent SOC in 2 are close to estimates in similar acyl-containing biradicals made from time-resolved CIDNP by the Closs group.⁷ The agreement of these completely different methods is noteworthy.

Effect of Temperature and Viscosity. In Scheme I, the possible rate-determining steps for decay of a triplet biradical are ISC or chain dynamics (excluding very rapid⁸⁻¹¹ product formation). Rates of chain motions depend on both the temperature T and solvent viscosity η .^{28,33} To a first approximation ISC is expected to be independent of T and η .³⁴ Within these constraints one can envision two kinetic extremes. In the high-temperature limit, chain motions are very fast, conformational equilibrium is reached prior to ISC, and ISC is the rate-limiting step for biradical decay. In the low-temperature limit, chain motions are slow enough to permit S-T equilibration, and chain motions (the approach of the two ends) are the rate-limiting step. These two extremes were in fact identified experimentally, but the system produced some surprises.

We examined the temperature dependence of τ for the acyl-benzyl biradicals 2_n , $n = 6, 9, 12, 15$, and for the dibenzyl biradicals 8_n , $n = 5, 9, 11$ in methanol and alkane solvent from +100 to -95 °C.^{25b,35} For both 2 and 8 , the Arrhenius plots of $-\log \tau$ vs $1/T$ exhibit a change of slope and intercept from low to high tem-

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perature, and in each case the break is centered around -10 to 0 °C. Below -40 °C, typical Arrhenius parameters are $\log A = 10-11$ and $E_a = 3-4$ kcal/mol for **2**.³⁵ Low-temperature parameters for **8** appear to be similar, but could not be accurately determined because slow decarbonylation makes **7** predominate below ca. -40 °C. At high temperature (>0 °C), the Arrhenius parameters for **2** are typically $\log A = 8$ and $E_a = 1$ kcal/mol. However, at $0-100$ °C, **8**_{9,11} exhibit *negative activation energies; they decay more slowly as the temperature is raised!* We measured $E_a = -1.9$ for **8**₉ and -0.9 for **8**₁₁, ± 0.3 kcal in each case.^{25b}

Whatever the sign of E_a , the change in Arrhenius parameters from low to high temperature is consistent with a change in rate-determining step for biradical decay from ISC at high temperature to chain dynamics at low temperature. To corroborate this interpretation, we measured the dependence of τ for **2**_n on solvent viscosity η , in the high- and low-temperature limits.³⁵ If ISC is really rate limiting at high temperature, then τ should be independent of η , but at low temperature, τ should depend strongly on η if chain motions are rate limiting. We measured τ for **2**_n ($n = 6-12, 15$) at -81 °C in pentane ($\eta = 0.79$ cP) and heptane (2.6 cP) and at $+15$ °C in nonane (0.77 cP) and tetradecane (2.6 cP). The results³⁵ show a pronounced viscosity dependence at -81 °C but no dependence at $+15$ °C. This provides strong support for the proposed interpretation.

The negative E_a for **8**_{9,11} is unique in the biradical literature. It occurs at high temperature where ISC is rate limiting ($\tau = k_{\text{ISC}}$). This renders unlikely a mechanism in which an intermediate of lower energy than **8** (e.g., a π -complex of the two phenyl rings) precedes product formation.³⁶ Such an intermediate would presumably be formed in the singlet state since the triplet is repulsive, but the kinetics are due to the prior ISC step. It is interesting that, of all the biradicals whose Arrhenius parameters have been measured, **8**_{9,11} are the only ones with negative E_a and the only ones in which ISC is dominated by the HFC mechanism. In our opinion this is not a coincidence.

For a qualitative understanding of the T dependence of k_{ISC} at high temperature, it is convenient to consider k_{ISC} as a function of T and $\langle R \rangle$. Chain-rule differentiation of $k_{\text{ISC}}(T, \langle R \rangle)$ gives

$$\frac{d}{dT}k_{\text{ISC}} = \left(\frac{\partial k_{\text{ISC}}}{\partial T} \right)_{\langle R \rangle} + \left(\frac{\partial k_{\text{ISC}}}{\partial \langle R \rangle} \right)_T \frac{d\langle R \rangle}{dT} \quad (1)$$

ISC is usually not regarded as T dependent, and the first term is expected to be small. To a first approximation we ignore it and concentrate on the chain-rule product. To understand the sign of the high-temperature Arrhenius slope, we need to know the sign of each of the two derivatives.

The $\partial k_{\text{ISC}}/\partial \langle R \rangle$ term is qualitatively given in the upper plot in Figure 2. For **8**_{9,11}, $k_{\text{ISC}} \approx k_{\text{HFC}}$, and for **2**_n, $k_{\text{ISC}} \approx k_{\text{SOC}}$. The sign of this term is therefore positive for **8**_{9,11} and negative for **2**_n. For $d\langle R \rangle/dT$, we note that a close approach of the two ends of the biradical requires an enthalpically unfavorable situation of several gauche interactions within the chain. On average, a smaller value of R is associated with a greater number of gauche interactions (higher enthalpy). Ex-

perimentally, Flory showed that larger $\langle R \rangle$ is favored by lower temperature in polyethylene.³⁷ Thus $d\langle R \rangle/dT$ is negative.

Now we have the information we need. For dibenzylic biradicals **8**_{9,11}, one gets (+)(-) = (-), and for acyl-benzyl biradicals **2**_n, (-)(-) = (+): a negative temperature dependence for **8**_{9,11} and a positive one for **2**_n. This analysis suggests that *the high-temperature Arrhenius slope is diagnostic for the dominant ISC mechanism*. A positive activation energy implies that ISC is favored in conformers with small R , which implies that SOC is the dominant ISC mechanism. A negative activation energy implies that ISC is faster in conformers with large R , and HFC is the dominant mechanism. The hypothesis can be tested in the **8**_n series, because the smaller members are dominated by SOC (see discussion of Figure 3) and the sign of E_a should be positive. *This is in fact observed*. For **8**₅ we measured $E_a = +0.5$,^{25b} consistent with dominant SOC.

In summary, the Arrhenius plot provides information on the nature of the rate-limiting step for biradical decay (ISC vs chain dynamics) and the dominant mechanism of ISC (SOC or HFC). The temperature dependence of τ is not simply a routine experiment for determining "barriers", but is rich in information about chain motions, chain equilibria, and spin dynamics.

Magnetic Isotope Effects. Photolysis of the ketones **6** at natural isotopic abundance gives rise to ¹³C enrichments in the carbonyl-containing products that are among the largest ever observed.³⁸ The kinetic isotope effects are roughly 2 orders of magnitude larger than typical mass isotope effects and are clearly attributable to magnetic isotope effects. Although magnetic isotope effects had been observed many times before in radical pairs,³⁹ and small effects in biradicals had been reported,^{39c} these were the first really large effects in biradicals.

Starting with natural-abundance *cis*-**6**_n ($n = 6, 10-12, 15$) or *trans*-**6**₁₂, we measured³⁸ the ¹³C distribution in the recovered starting material, its *cis-trans* isomer, and the cyclophane **10**, all produced by decay of acyl-containing biradical **7**. Isotopic enrichment was evaluated by GCMS as the % increase (β) in ¹³C content over natural abundance for a given photolytic conversion. β values were measured as large as 179% (2.9% ¹³C content) in **10**₁₂ obtained from photolysis of *cis*-**6**₁₂ in hexane. Major findings were as follows: (1) β values for the isomeric products (cyclophane and *cis-trans* isomeric starting ketone) were *much higher* than β for the recovered starting material, which was usually negligible; (2) β increases with increasing temperature. The second feature has been observed in radical-pair systems,³⁹ but the first feature is unique to biradicals.

The magnetic isotope effect arises from a competition between two decay routes for the triplet biradical **7**: ISC to form **17** followed by rapid formation of carbonyl-containing products, and decarbonylation to form **38**

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and eventual formation of hydrocarbon products. Only the HFC mechanism is responsible for isotopic fractionation, since SOC does not depend on nuclear spin. Biradicals 37 that contain ^{13}C nuclei with large HFC undergo ISC faster and compete better with decarbonylation than biradicals that lack ^{13}C . The phenylacetyl radical has a ^{13}C HFC of 124 G at the carbonyl position,²² much larger than the typical proton HFC of ≤ 30 G.

The mechanism above is consistent with experiment except for one flaw: it incorrectly predicts identical ^{13}C enrichments in all CO-containing products, including the starting material. To address this problem we consider the details of the SOC and HFC mechanisms. SOC in the biradical **7** is only effective in conformers with small R , while the HFC mechanism takes over at large R (Figure 2, bottom). Since only HFC is nucleus-selective, CO-containing products formed via ISC at large R are expected to have a higher β than products formed via ISC at small R . 37 is initially produced in conformations with relatively small R . SOC-dominated ISC at small R yields mainly recyclization to generate unenriched starting material. Formation of cyclophane **10**, however, requires the benzylic positions to be very far apart, and one expects and finds **10** to be highly enriched. Formation of the cis-trans isomer of **6** also requires a value of R large enough to accommodate internal rotation in the biradical.

This interpretation requires that whether one starts with *cis*-**6** or *trans*-**6**, the starting material must be

unenriched while the *cis*-*trans* isomer and **10** must be enriched. This was confirmed for **6**₁₂. Photolysis at 10 °C of *cis*-**6**₁₂ gives $\beta = 0, 90, 128\%$ ($\pm 30\%$) for *cis*-**6**₁₂, *trans*-**6**₁₂, and **10**₁₂, respectively, whereas photolysis of *trans*-**6**₁₂ gives $\beta = 68, 2, 131\%$ for the same three compounds.³⁸ This confirmation strongly supports the above model.

In summary, the physical basis for the difference in ^{13}C enrichment among the products of biradical decay is the inherent tendency of HFC and SOC to produce different products, and this in turn comes from the R dependences of the different ISC mechanisms shown in Figure 2.

Conclusion. Through a combination of product studies, isotope effects, and transient absorption kinetics including the effect of biradical chain length and substituent, solvent, temperature, and magnetic field, we have made progress in elucidating the relation of the rates and product distributions to the spin interactions in the biradicals. Probably the most surprising result is the profound effect exerted by extremely small interactions such as the S-T gap, SOC, and HFC upon the dynamics and product distribution of triplet biradicals.

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Dioxiranes: A New Class of Powerful Oxidants

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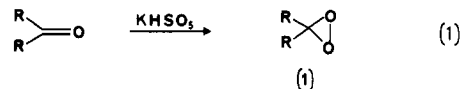
An oxidant that is efficient in transferring oxygen, selective in its reactivity, mild toward the oxidized product, and conveniently prepared from commercially available materials, possesses catalytic activity, and is recyclable and environmentally agreeable would un-

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questionably be the synthetic chemist's delight. Such an oxygen transfer reagent does not exist to this day, but an oxidant coming closest to these imposing characteristics is the dioxirane **1**.¹ The recent feat² of preparing dimethyldioxirane (**1a**) from the corresponding ketone and caroate (KHSO_5), as illustrated in eq 1, has provided convenient access to a powerful oxidant of unusual utility for synthetic purposes.¹⁻⁴



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