Dynamics of Flexible Triplet Biradicals

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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 properties3 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 Wm. P. Schweitzer at the University of Chicago, did postdoctoral research at the University of California, 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 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-
troubled greatly to our knowledge of the kinetics of a variety of biradicals including types I,II, and \( \text{I}_{n}, \text{II}_{n}, \text{II}_{a,b,c} \) Paterno–Büchi biradicals, hydrocarbon biradicals, and 1,3-biradicals. Closs and co-workers have shown that time-resolved magnetic polarization provides a unique perspective on biradical reactions and is a valuable complement to optical spectroscopy. Closs, Doubleday, Kaptein, 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 group and Schulten's group have demonstrated the power of analyzing the magnetic-field dependence of the inter-system-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-workers 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 and Dougherty. Conjugated biradicals are an important class of intermediates that will not be covered here. We refer the interested reader to excellent reviews in this area.

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 \( ^{\text{n}}, \text{a}^{*} \text{ketone} \)) 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 conformation, and we shall see how the connection between ISC, conformation 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 (\( \ll 1 \text{ ns} \)).

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

\[ \text{Scheme II} \]

![Scheme II](image)

\[ \text{Scheme III} \]

![Scheme III](image)

**Figure 1.** Vector model of singlet and triplet states, composed of combinations of individual eigenstates \( \alpha \) and \( \beta \) 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.

small yields of ortho and para coupling products have been observed in cumyl radical terminations,\textsuperscript{19} we have not yet identified orthocyclopahanes in our product mixtures. Photolysis of 6 gives mainly decarboxylation at $\geq 10$ °C, but 10 predominates below $-20$ °C. Quantum yields for disappearance of 1 or 6 range from 0.2 to 0.95.\textsuperscript{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.\textsuperscript{20} Triplet sublevels are labeled T$_{\pm}$, T$_{0}$, T$_{-}$, 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 $k_{SOC}$, the observed ISC rate constant in the biradical, only two things matter: the S–T energy gap $E_{ST}$, where 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 $k_{SOC}$; an increase in $E_{ST}$ decreases $k_{SOC}$. $E_{ST}$ 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).

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 $\beta$ 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 cm$^{-1}$ = 1 kcal/mol). $E_{ST}$ is independent of $H$. However, if $E_{ST}$ $\neq$ 0, one of the T$_{\pm}$ 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.\textsuperscript{5}

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

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2}
\caption{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.}
\end{figure}
and the SOC and HFC matrix elements. The associated
dependence of $k_{ISC}$ is shown at the top. If ISC is due
equivalently to HFC ($k_{ISC} = k_{HFC}$), then $k_{ISC}$ must in-
crease as $R$ increases because the $S^+T$ gap gets smaller
with a constant HFC matrix element. For a pure SOC
mechanism ($k_{ISC} = k_{HFC}$), the matrix element is negli-
gible 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, $k_{ISC} = \sum f_i k_{ISC,i}$, 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 $\langle E_{ST} \rangle$ and $\langle R \rangle$, where angle brackets indicate an average over all con-
formers 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. Bi-
radicals were characterized by their transient UV
spectra ($\lambda_{max} = 320 \pm 2$ nm, fwhm \(\approx 10\) 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 $\tau$ on chain length $n$ for the 1,2-bi-
radicals 2$a$, $b$ and 8$n$. Under the conditions of these
experiments, $\tau^{-1}$ is a measure of the ISC rate, i.e., $\tau^{-1} = k_{ISC}$.
The dibenzyl biradicals 8$n$ exhibit three regions in Figure 3. For $n = 3, 4$, ISC appears to be
dominated by SOC. The dependence of $\tau$ on $n$ is con-
sistent 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 $\langle E_{ST} \rangle$. This situation—a
large energy separation and a small ISC matrix element—is unfavorable for ISC, and one sees the
largest values of $\tau$ for $n = 5, 6$. For $n \geq 9$, HFC is likely
the principal or exclusive ISC mechanism since (SOC)
is presumably very small. If $k_{ISC} = k_{HFC}$ 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-benzyl biradicals
2 is different from that of 8. $\tau$ is almost an order of
magnitude smaller for 2 than for 8, and the maximum value of $\tau$ occurs at $n = 9$ for 2 instead of around $n = 6$
or 7 for 8. We have suggested that the difference
in the lifetimes of 2 vs 8 is due to dominant SOC in 2. SOC
in atoms varies as the fourth power of the effective nuclear
charge, 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 biradicals spend most of its time in more extended
formers, a few formers with small $R$ can dominate
$k_{ISC}$ if they have SOC matrix elements much larger
than HFC ($\approx 0.003-0.004$ cm$^{-1}$). The reason why this
does not happen in 8 is presumably that it is a hydro-
carbon biradical, with lighter atoms and smaller SOC
than 2. The qualitative pattern of $\tau = k_{ISC}^{-1}$ for 2 in Figure 3 is what one expects if ISC requires a small
value of $R$. Evidence on the rates and equilibria of
cycle cyclization processes show that cycle is fa-
orable for $n = 6$, becomes most unfavorable for $n = 8-10$, and then becomes more favorable for larger chains.

Thus from Figure 3 we form the qualitative hypo-
thesis that ISC in 2, is dominated by SOC for all values
of $n$ studied, and ISC in 8$n$ is dominated by HFC for
$n \geq 6$ and by SOC for $n = 3, 4$.

Substituent effects on $k_{ISC}$ were studied in the 1,5-
dibenzyl biradicals 8 by incorporating one or two p-Cl
or p-Br substituents. One p-Cl substituent has no ef-
cfect, but p-Br increases $k_{ISC}$ by a factor of 3.3 and di-
p-Br by a factor of 4.8 relative to un-
substituted 8$5$. The enhancements are the same in
isooctane and methanol. Since the Hammett $\alpha$ values
for Cl and Br are identical, the data suggest a sub-
stantial 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. 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 $1.7 \times 10^7$ s$^{-1}$ and $2.8 \times 10^7$ s$^{-1}$ in isooctane and
methanol, respectively. This factor of 6 solvent de-
pendence in OH-substituted 8$5$ is larger than the factor
of 2.4 for the corresponding Norrish II 1,4-biradicals.

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Dynamics of Flexible Triplet Biradicals

Effect of External Magnetic Field. The lifetimes of biradicals 2 and 8 are strongly perturbed by an external magnetic field. For 212, Figure 4 shows the magnetic-field dependence (mfd) of kISC relative to its value in the earth's field, kISC0. Mfd curves for dibenzyl biradicals 811,14 are similar. The mfd curves show a maximum in kISC followed by a decrease to an apparent asymptotic value at high field, kISC0. The field at which the maximum occurs, Hmax, increases as the chain length decreases. Table I lists Hmax and the other major features of the mfd curves in Figure 4. Mfd curves of this sort were first observed for biradical-derived CIDNP and, more recently, for triplet yields. A unique feature of our mfd studies of donor-acceptor biradicals and CIDNP of radical pairs in micelles. A unique feature of our mfd studies is the possibility of distinguishing among different ISC mechanisms. A small value (≤1/3) implies that most ISC occurs via the HFC mechanism or via spin–lattice relaxation. The values of kISC0/kISC0 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 212 and 88% for 211) 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. The agreement of these complete 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 rapid product formation). Rates of chain motions depend on both the temperature T and solvent viscosity η. To a first approximation ISC is expected to be independent of T and η. 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 = 6, 9, 12, 15, and for the dibenzyl biradicals 8, n = 5, 9, 11 in methanol and alkane solvent from +100 to -95 °C. For both 2 and 8, the Arrhenius plots of -log τ vs 1/T exhibit a change of slope and intercept from low to high temperature.

Figure 4. Dependence of ISC rate constants kISC for 2 on external magnetic field H at 23 °C. The ordinate is the ratio of kISC at a given value of H to kISC at H = 0 (kISC0). Errors bars are ±2σ.

Table I: Magnetic-Field Dependence of kISC for Acyl–Benzyl Biradicals 2 and Dibenzyl Biradicals 8

| biradical | Hmax (G) | kISC0/kISC | kISC0/10^6 s^-1 at H=
<table>
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<tr>
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<tbody>
<tr>
<td>212</td>
<td>600 ± 100</td>
<td>10.6 ± 0.3</td>
<td>12.0 ± 0.4</td>
</tr>
<tr>
<td>211</td>
<td>120 ± 50</td>
<td>12.3 ± 0.4</td>
<td>14.0 ± 0.4</td>
</tr>
<tr>
<td>814</td>
<td>30 ± 10</td>
<td>14.9 ± 0.5</td>
<td>16.9 ± 0.6</td>
</tr>
<tr>
<td>811</td>
<td>300 ± 100</td>
<td>1.68 ± 0.06</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>812</td>
<td>130 ± 50</td>
<td>3.7 ± 0.1</td>
<td>4.4 ± 0.2</td>
</tr>
<tr>
<td>813</td>
<td>30 ± 15</td>
<td>6.9 ± 0.9</td>
<td>9.2 ± 1.2</td>
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*See text for definitions. †Asymptotic high-field value was not reached.

H increases beyond Hmax, the T1 sublevel gets further from the S level, and kISC decreases to an asymptotic value kISC0 where the T1 sublevels are far from S.

A detailed analysis of the ratio of kISC at high field vs 0 field, kISC0/kISC0, reveals the competition among the various ISC mechanisms. kISC0/kISC0 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 (≤1/3) implies that most ISC occurs via the HFC mechanism or via spin–lattice relaxation. The values of kISC0/kISC0 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 212 and 88% for 211) 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. The agreement of these completely different methods is noteworthy.

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 kISC0/kISC0.

temperature, 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. 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$_{11}$ 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.

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 $\tau$ for 2$_n$ on solvent viscosity $\eta$, in the high- and low-temperature limits. If ISC is really rate limiting at high temperature, then $\tau$ should be independent of $\eta$, but at low temperature, $\tau$ should depend strongly on $\eta$ if chain motions are rate limiting. We measured $\tau$ for 2$_n$ (n = 6 - 12, 15) at -81 °C in pentane (n = 0.79 cP) and heptane (2.6 cP) and at +15 °C in nnonane (0.77 cP) and tetradeacne (2.6 cP). The results 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$_{11}$ is unique in the biradical literature. It occurs at high temperature where ISC is rate limiting ($\tau = k_{ISC}$). 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. A similar 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$_{11}$ 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 $(R)$. Chain-rule differentiation of $k_{ISC}(T, (R))$ gives

$$\frac{d}{dT}k_{ISC} = \left(\frac{\partial k_{ISC}}{\partial T}\right)_{(R)} + \left(\frac{\partial k_{ISC}}{\partial (R)}\right)_{T} \frac{d(R)}{dT}$$

(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 $\partial k_{ISC}/\partial (R)$ term is qualitatively given in the upper plot in Figure 2. For 8$_{11}$, $k_{ISC}$ ≈ $k_{HFC}$, and for 2$_n$, $k_{ISC}$ ≈ $k_{SOC}$. The sign of this term is therefore positive for 8$_{11}$ and negative for 2$_n$. For $d(R)/dT$, 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). Excepting experimentally, Flory showed that larger $(R)$ is favored by lower temperature in polyethylene. Thus $d(R)/dT$ is negative.

Now we have the information we need. For dibenzyl biradicals 8$_{11}$, one gets $(+)(-) = (-)$, and for acyl-benzyl biradicals 2$_n$, $(+)(-) = (+)$. A negative temperature dependence for 8$_{11}$ 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$_9$ we measured $E_a = +0.5$, 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 $\tau$ 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. 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, and small effects in biradicals had been reported, these were the first really large effects in biradicals.

Starting with natural-abundance cis-6, (n = 6, 10-12, 15) or trans-6, we measured 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 isomerizing 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, 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 7 followed by rapid formation of carbon-13-containing products, and decarbonylation to form 8.


(40) For an example of such a mechanism in radical recombination, see: Olson, J.; Koch, T. J. Am. Chem. Soc. 1986, 108, 756.
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 undeniably 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. The recent feat of preparing dimethyldioxirane (1a) from the corresponding ketone and caroate (KHSO₄), as illustrated in eq 1, has provided convenient access to a powerful oxidant of unusual utility for synthetic purposes.1−4

$\text{R} \quad \text{O} \quad \text{KHSO}_4 \quad \text{R} \quad \text{O}$

(1)

Waldemar Adam received his B.Sc. in 1958 from the University of Illinois and his Ph.D. from MIT (F. D. Greene) in 1961. He was appointed Assistant Professor at the University of Puerto Rico in 1961, Associate Professor in 1966, and Professor in 1970. Since 1980 he has occupied the Chair of Organic Chemistry at the University of Würzburg. Mechanistic organic chemistry, with emphasis on peroxides, photochemistry, and synthetic and biomedical applications, counts as his major research effort.

Ruggero Curci received a Doctorate Degree in Chemistry from the University of Bari in 1961. In 1964 he was appointed Assistant Professor, and in 1968 he moved to the University of Padova, where he earned the "Libera Docenza" (Associate Professorship, with tenure) in 1970. In 1975 he was appointed to the Chair of Organic Chemistry at the University of Palermo, and three years later he returned to the University of Bari as Professor. His major research interests include synthesis and reaction mechanisms of organic and inorganic peroxides.

John O. Edwards conducted his studies (interrupted by a stint in the U.S. Marine Corps) at Colgate University (A.B. in 1947) and the University of Wisconsin. He held a postdoctoral position at Cornell University and was Research Chemist at the Du Pont Co., prior to coming to Brown University in 1952. As Professor Emeritus, he continues to carry out research on peroxide reactions and on the application of NMR to the study of transition-metal chemistry in solution.

Abstract

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 undeniably 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. The recent feat of preparing dimethyldioxirane (1a) from the corresponding ketone and caroate (KHSO₄), as illustrated in eq 1, has provided convenient access to a powerful oxidant of unusual utility for synthetic purposes.1−4

$\text{R} \quad \text{O} \quad \text{KHSO}_4 \quad \text{R} \quad \text{O}$

(1)

Waldemar Adam received his B.Sc. in 1958 from the University of Illinois and his Ph.D. from MIT (F. D. Greene) in 1961. He was appointed Assistant Professor at the University of Puerto Rico in 1961, Associate Professor in 1966, and Professor in 1970. Since 1980 he has occupied the Chair of Organic Chemistry at the University of Würzburg. Mechanistic organic chemistry, with emphasis on peroxides, photochemistry, and synthetic and biomedical applications, counts as his major research effort.

Ruggero Curci received a Doctorate Degree in Chemistry from the University of Bari in 1961. In 1964 he was appointed Assistant Professor, and in 1968 he moved to the University of Padova, where he earned the "Libera Docenza" (Associate Professorship, with tenure) in 1970. In 1975 he was appointed to the Chair of Organic Chemistry at the University of Palermo, and three years later he returned to the University of Bari as Professor. His major research interests include synthesis and reaction mechanisms of organic and inorganic peroxides.

John O. Edwards conducted his studies (interrupted by a stint in the U.S. Marine Corps) at Colgate University (A.B. in 1947) and the University of Wisconsin. He held a postdoctoral position at Cornell University and was Research Chemist at the Du Pont Co., prior to coming to Brown University in 1952. As Professor Emeritus, he continues to carry out research on peroxide reactions and on the application of NMR to the study of transition-metal chemistry in solution.