SUBSTITUENT AND SOLVENT EFFECTS ON THE LIFETIMES
OF HYDROCARBON-BASED BIRADICALS

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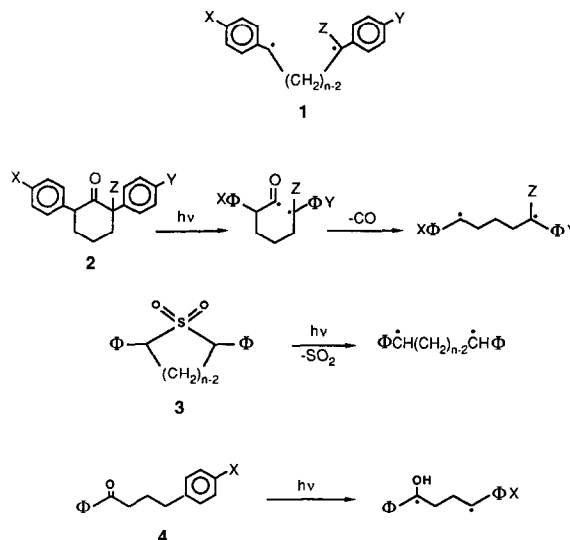
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Nanosecond transient absorption studies of the lifetimes (τ) of several substituted 1,n-diphenyl-1,n-diyls are reported in polar and non-polar solvents. A para-bromine substituent significantly shortens τ. Substitution of OH in the 1-position makes the lifetime highly solvent dependent. The substituent effect and the dependence of τ on biradical chain length is discussed in terms of spin–orbit coupling in the biradical.

The vast majority of published biradical lifetimes involve biradicals containing oxygen bonded to at least one of the carbon termini [1–5]. Since the presence of oxygen is expected to have a major effect on the biradical properties, we initiated a study of hydrocarbon based biradicals having two benzylic termini[†]. The focus of our study is the series of biradicals **1**, obtained by photolysis of ketones **2** to yield 1,5-biradicals, and by direct or acetone-sensitized photolysis of sulfones **3** to yield 1,n-biradicals ($n=4,5,6$). The substituents X, Y, Z corresponding to biradicals **1a–1j** are listed in table 1, which includes Caldwell's [2] results for the 1,4-biradicals **1h–1j** obtained from Norrish Type II photolysis of ketones **4**.

The data in table 1 bear on two issues. (1) Of the two 'important intersystem crossing (ISC) mechanisms in biradicals, electron–nuclear hyperfine coupling and spin–orbit coupling (SOC), SOC is dominant in biradicals containing an acyl radical terminus [3–5]. We have shown that SOC in purely hydrocarbon biradicals is much weaker than in acyl-containing biradicals [3]. The first issue is whether SOC is still a significant ISC mechanism in hydrocarbon biradicals. (2) Solvent polarity affects the

lifetimes of Norrish II 1,4-biradicals [1,2]. The second issue is whether solvent polarity also affects the lifetimes of hydrocarbon biradicals.

The syntheses of **2a** [3] and **3** ($n=3$ [7] and $n=5,6$ [3]) have been described. The novel compounds **2b**, **2c** and **2d** were prepared by base-promoted cyclization [8] of the substituted dibenzyl ketone [9] with 1,3-dibromopropane. **2e** was prepared by MoOPh oxidation of **2a** [10], and **3** ($n=4$) was prepared by the same route as **3** ($n=5,6$) [3]. The lifetimes τ of biradicals **1** were measured by monitoring their nanosecond transient UV absorption at 320 nm in

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[†] Tetrabenzylic hydrocarbon 1,4- and 1,5-biradicals have been reported. Their lifetimes are difficult to measure accurately because the decay is not a single exponential [6].

Table 1
Rate constants (τ^{-1}, $\pm 5\%$) for decay of biradicals 1 at 25°C

Entry	Precursor	n	X	Y	Z	τ^{-1} (10^6 s^{-1})			Ref.
						in CH$_3$OH	in CH$_3$CN	in alkane	
a	2	5	H	H	H	1.1	1.1	1.1[a]	[3]
b	2	5	Cl	H	H	1.1	–	–	this work
c	2	5	Br	H	H	3.6	–	3.6[a]	this work
d	2	5	Br	Br	H	5.3	–	–	this work
e	2	5	H	H	OH	2.8	3.1	16.7[a]	this work
f	3	4	H	H	H	–	5.3	–	this work
g	3	6	H	H	H	–	0.87	–	[3]
h	4	4	H	H	OH	7.8	–	18.5[b]	[2]
i	4	4	Cl	H	OH	6.8	–	14.5[b]	[2]
j	4	4	Br	H	OH	11.6	–	20.0[b]	[2]

[a] 2,2,4-trimethylpentane.   [b] Heptane.

Ar-saturated solvent, following photolysis of the precursor at 308 nm by a Lambda Physik excimer laser (fwhm 15 ns) on an apparatus previously described [11]. All biradicals were characterized by their transient UV absorption spectra ($\lambda_{max} = 320 \pm 2$ nm), and by the invariance of τ ($\pm 5\%$) to addition of up to 0.04 M isoprene, which, on our timescale, quenches the triplet precursor but not the biradical. Fig. 1 shows decay traces and transient absorption spectra for 1a and 1d.

The lifetime of 1f ($n=4$) could not be measured by direct photolysis of 3 ($n=4$), which led to massive fluorescence and apparent singlet state decomposition. However, the triplet biradical was successfully generated by triplet energy transfer from acetone to 3. The rate constant for triplet energy transfer from acetone to 3 ($n=3$) was found to be $(6.8 \pm 0.4) \times 10^7$ M^{-1} s^{-1} in CH$_3$CN. (This was obtained from the competitive quenching of acetone triplet by 10^{-4} M naphthalene and 0.01–0.04M 3, measured by monitoring the decay of naphthalene triplet–triplet absorption at 415 nm.) We presume that energy transfer from triplet acetone to the other sulfone rings ($n=4,5,6$) proceeds at about the same rate. A CH$_3$CN solution containing 0.05 M 3 ($n=4$), 0.35 M acetone, and 0.006 M isoprene was photolyzed with the excimer laser at 308 nm to produce the triplet sulfone, which decomposed to the triplet 1,4-biradical 1f. The risetime of the biradical signal is associated with triplet energy transfer to 3. Without added isoprene, the risetime was slow enough to

distort the biradical decay severely. Addition of 0.006 M isoprene shortened the triplet lifetime of acetone and decreased the risetime of the biradical signal so that its true decay rate could be measured.

It is reasonable to interpret τ^{-1} as k_{ISC}, the rate constant for ISC in the biradical. We have previously shown that the rate-determining step for biradical decay depends on temperature T, solvent viscosity η, and biradical chain length [11]. We found that, under the conditions employed here – short biradicals (1) and a small value of the ratio η/T – the rate-determining step is ISC [11].

Comparison of 1a – 1c in table 1 shows that Cl substitution (1b) produces no change in k_{ISC} relative to 1a but Br substitution (1c) enhances the rate by a factor of 3.3 (an increase of 2.5×10^6 s^{-1}). Double Br substitution (1d) enhances the rate over 1c by a factor of 1.5 (increase of 1.7×10^6 s^{-1}). Since the Hammett σ values for Cl and Br are identical, the data suggest a substantial heavy atom SOC effect for 1c and 1d. The Br/H enhancement in the 1,5-biradicals is roughly the same magnitude as the (solvent-dependent) Br/H enhancement in the Norrish II 1,4-biradicals (1h versus 1j) obtained by Caldwell [2].

The effect of the Z substituent is twofold. The first effect is that Z=OH increases k_{ISC} relative to Z=H. The enhancement factor is 1.5 (increase of 2.5×10^6 s^{-1}) for $n=4$ (1f in CH$_3$CN versus 1h in CH$_3$OH) and 2.8 (increase of 2.0×10^6 s^{-1}) for $n=5$ in CH$_3$CN (1a versus 1e). A small increase in the SOC matrix element would account for the increase in k_{ISC}. This
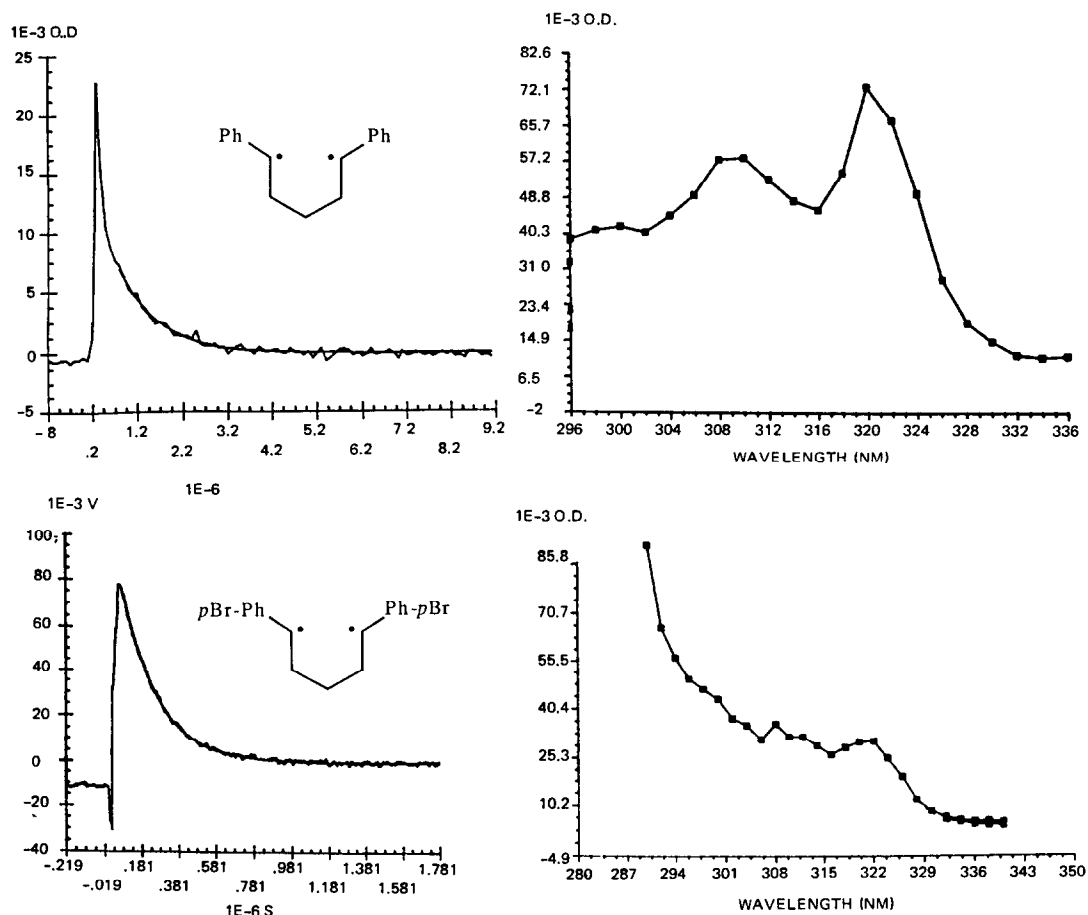
Fig. 1. Decay traces (left, abscissa in μs) and transient absorption spectra (right) for **1a** (top, from acetone-sensitized photolysis of **3**, $n=5$ in CH_3CN in the presence of isoprene) and **1d** (bottom, from **2d** in CH_3OH). The least-squares curve is superimposed upon each decay trace.

would be expected both by the heavy atom effect (in atoms, the SOC matrix element increases as the fourth power of the effective nuclear charge [12]) and by an increase in the ionic character of the biradical singlet state [13].

The second effect of Z is that replacement of H by OH makes the biradical lifetimes very sensitive to solvent polarity. Neither **1a** nor **1c** exhibits any solvent effect, but the lifetime of **1e** is highly solvent dependent. A solvent dependence of the lifetimes of Norrish II biradicals has been noted [1,2]. Explanations have been offered for this behavior [1,2], but no consensus has emerged. Table 1 shows that k_{ISC} increases by a factor of 2.4 for **1h** ($n=4$) and 6.0 for **1e** ($n=5$) on going from CH_3OH to alkane solvents.

It is interesting that the solvent effect is greater in the 1,5-biradical, which is expected to have a weaker average end-to-end interaction[tt] than the 1,4-biradical.

The 1,4-biradical **1f** allows the comparison of lifetimes of dibenzylic 1,n-biradicals, with $n=3,4,5,6$. The $n=3$ data come from Caldwell's [15] study of **5**.

He finds that in CH_3OH $k_{ISC}=6.7\times10^7$ s^{-1} for both **5a** and **5b**. This compares with $k_{ISC}/(10^6$ s$^{-1})=5.3$, 1.1, 0.87 for $n=4,5,6$ (table 1). The k_{ISC} values show a dramatic increase as the biradical chain

[tt] A reasonable measure of the interaction is the singlet–triplet energy gap (see ref. [14]).

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a   R=H, R'=Acetyl
b   R=R'=Acetyl
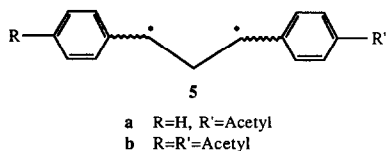
length n decreases from 5 to 4 to 3. Scaiano has reported a decrease in lifetime on going from an acyl-containing 1,6- to 1,5-biradical [16], and from a 1,5- to 1,4-biradical in the $1,1,n,n$-tetraphenyl-$1,n$-diyl series [6]. The effect of the oxygens on the lifetime of 5 is probably small, since 5a and 5b have the same lifetime and even parachlorine has no effect on 1b and 1i[‡].

A reasonable explanation for the dependence of k_{ISC} on chain length is that SOC is responsible for the change. From one-electron theory [13], SOC in biradicals is expected to increase approximately exponentially with decreasing end-to-end distance R, and this has been confirmed very recently by ab initio calculations including all terms in the Breit–Pauli spin–orbit Hamiltonian [17]. The relation of k_{ISC} to R cannot be determined from table 1 because, except for 5, the biradicals adopt several values of R during their lifetimes. However the relation certainly appears to be strongly non-linear.

In summary, evidence has been presented that SOC is a significant ISC mechanism in hydrocarbon 1,4- and 1,5-biradicals. This conclusion is supported by the heavy-atom substituent effect and by the distance dependence of k_{ISC}. The solvent polarity effect on biradical lifetimes previously noted for Norrish II

[‡] Preliminary experiments in this laboratory suggest that the unsubstituted dibenzylic 1,3-biradical 5, $R=R'=H$ (same as 1, $n=3$, $X=Y=Z=H$) may have about the same lifetime as Caldwell's biradicals 5. Acetone-sensitized photolysis of 3, $n=3$ in CH_3CN in the presence of isoprene, using as the exciting light the frequency-doubled output (312 nm) of a DCM dye laser pumped by the second harmonic (532 nm) of a Nd–YAG laser (fwhm, 6 ns), yielded a transient with a lifetime of 20 ± 4 ns ($\tau^{-1} = (5\pm1)\times10^7$ s^{-1}). The lifetime is not shortened by additional isoprene. The transient spectrum showed $\lambda_{max}=320\pm3$ nm, determined by acetone-sensitized photolysis of 3, $n=3$ in CH_3CN both with and without added isoprene, using an excimer laser at 308 nm. Assignment of the transient to 1 is possible but not secure, since the spectrum and lifetime were measured under different conditions.

1,4-biradicals [1,2] has been shown to be even greater for 1,5-biradicals with a hydroxy-substituted terminus. Without the hydroxy substituent the lifetimes are insensitive to solvent polarity.

References

[1] J.C. Scaiano, Accounts Chem. Res. 15 (1982) 252.
[2] R.A. Caldwell, Pure Appl. Chem. 56 (1984) 1167.
[3] M. Zimmt, C. Doubleday Jr., I.R. Gould and N.J. Turro, J. Am. Chem. Soc. 107 (1985) 6724.
[4] M. Zimmt, C. Doubleday Jr. and N.J. Turro, J. Am. Chem. Soc. 107 (1985) 6726.
[5] G.L. Closs and O.D. Redwine, J. Am. Chem. Soc. 107 (1985) 4543, 6131.
[6] D.H.R. Barton, B. Charpiot, K.U. Ingold, L.J. Johnston, W.B. Motherwell, J.C. Scaiano and S. Stanforth, J. Am. Chem. Soc. 107 (1985) 3607.
[7] R.M. Dodson, E.H. Jancis and G. Klose, J. Org. Chem. 35 (1970) 2520.
[8] R.F.C. Brown, G.J. Hardham and R.A. Leppik, Australian J. Chem. 25 (1972) 2049.
[9] N.J. Turro and G.C. Weed, J. Am. Chem. Soc. 105 (1983) 1861.
[10] E. Vedejs, D.A. Engler and J.E. Telschow, J. Org. Chem. 43 (1978) 188.
[11] M. Zimmt, C. Doubleday Jr. and N.J. Turro, J. Am. Chem. Soc. 108 (1986) 3618.
[12] W.G. Richards, H.P. Trivedi and D.L. Cooper, Spin–orbit coupling in molecules (Clarendon Press, Oxford, 1981).
[13] L. Salem and C. Rowland, Angew. Chem. Intern. Ed. Engl. 11 (1972) 92.
[14] G.L. Closs and C. Doubleday Jr., J. Am. Chem. Soc. 95 (1973) 2735.
[15] K. Mizuno, N. Ichinose, Y. Otsuji and R.A. Caldwell, J. Am. Chem. Soc. 107 (1985) 5797.
[16] D. Weir and J.C. Scaiano, Chem. Phys. Letters 118 (1985) 526.
[17] L. Carlacci, C. Doubleday Jr., T. Furlani, H. King and J.W. McIver Jr., J. Am. Chem. Soc., submitted for publication.