

Laser Flash Photolysis Studies of the Reactions of Some 1,4-Biradicals¹

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In the last few years laser techniques have become increasingly available and attractive to the organic chemist. This is largely due to the commercial availability of reliable and powerful lasers, transient digitizers, and other electronic components necessary to carry out laser flash experiments. In this Account I discuss our studies in the area of biradical reactions; this is an area in which laser flash photolysis techniques have proven extremely useful. I will try to emphasize the possibilities, use, and limitations of the technique, which I believe should become increasingly common in the study of problems in organic chemistry.

The biradicals I will be discussing have been generated as intermediates in the Norrish type II reaction^{2,3} and the photoenolization of *o*-alkyl-substituted carbonyl compounds.⁴

A Glimpse at the Technique of Laser Flash Photolysis

Since the initial publication⁵ on the application of laser techniques to the measurement of transient optical absorptions, a number of technological improvements have made this type of experiment faster, easier, and more accurate.

The components necessary to carry out laser flash photolysis experiments can be divided into four groups: (A) the excitation source, (B) a monitoring system, (C) a detection system, and (D) signal processing facilities. Components B and C are effectively a spectrophotometer, which is required to have special characteristics of signal and time response.

The excitation source (A) is a pulsed laser. In almost all our studies we have used nitrogen lasers, which produce 337.1-nm pulses of 3–10 mJ and a duration of ~8 ns; the short duration of the pulse makes the time domain accessible by laser techniques about 3 orders of magnitude shorter than that accessible by conventional flash photolysis. Other possible excitation sources include excimer, ruby, neodymium, and dye lasers, which when combined with frequency multipliers provide an ample range of wavelengths from the far-UV well into the infrared region. As a general guideline, a laser must be able to generate 10⁻⁵ M transient in the monitored volume to be useful, and this requires energies in the 1–100 mJ/pulse range.

The monitoring system consists of a light source, quite frequently a xenon lamp, a series of lenses and filters to concentrate the appropriate spectral region on the sample, another series of lenses and filters to direct the light into the monochromator slit, and a mono-

chromator (See Figure 1). In order to achieve good signal-to-noise ratios in the short time scales used, it is frequently convenient to "pulse" the lamp. That is, the intensity of the monitoring beam is increased by a factor of 10–100 for a few milliseconds, while the experiment is carried out. This also increases the relative UV output of the lamp. Given the short duration of the experiments, the pulsed monitoring lamp can be regarded as a continuous wave source in this time frame. Excitation of the sample is usually carried out at 90° or at a small angle, as shown in Figure 1. The small angle approach leads to stronger signals,⁶ although at the expense of a reduction in the reaction volume and an increase in the (sometimes undesirable) sensitivity of the system to fluorescence and scattered light.

The detector system (C) consists of a photomultiplier (PMT, suitably wired to achieve fast and linear response at high light intensities), a unit capable of measuring the intensity of the monitoring beam (scope or A/D converter), and a unit capable of storing a signal vs. time profile, i.e., a fast scope and camera or a transient digitizer.

Signal processing (D) is where most variations can be found. Calculations based on photographs can be carried out manually or by feeding digitized data to a computer. If a transient digitizer is available, the data can be fed directly to the computer, making the instrument at least 1 order of magnitude more time efficient. The same computer can be used to control the experiment; in our laboratory we have been rather successful in developing this approach,⁷ in which a small computer serves to control the experiment, as well as to provide data gathering, processing, storage, and hardcopy facilities.

The basic output from the system is a profile of changes in optical density (ΔOD) vs. time at a given wavelength. It should be noted that the signal is not the optical density of the transient, but rather its difference from the absorption due to the precursor. Transient spectra are obtained by repeating the measurements at different wavelengths and reading the optical density at a given time after the laser pulse. From the time evolution of the signal it is frequently possible to determine the kinetic laws of the system. Most of the examples included herein follow first- or pseudo-first-order kinetics; for these, the "lifetime" refers to the reciprocal of the rate constant for transient

(1) Issued as NRCC-20360.

(2) Scaiano, J. C.; Lissi, E. A.; Encina, M. V. *Rev. Chem. Intermed.* 1978, 2, 139–196.

(3) Wagner, P. J. *Acc. Chem. Res.* 1971, 4, 168–177.

(4) Wagner, P. J. *Pure Appl. Chem.* 1977, 49, 259–270.

(5) Porter, G.; Topp, M. R. *Proc. R. Soc. London, Ser. A* 1970, 315, 173–184.

(6) Eg.: Goldschmidt, C. R.; Ottolenghi, M.; Stein, G. *Israel J. Chem.* 1970, 8, 29–36.

(7) Scaiano, J. C. *J. Am. Chem. Soc.* 1980, 102, 7747–7753.

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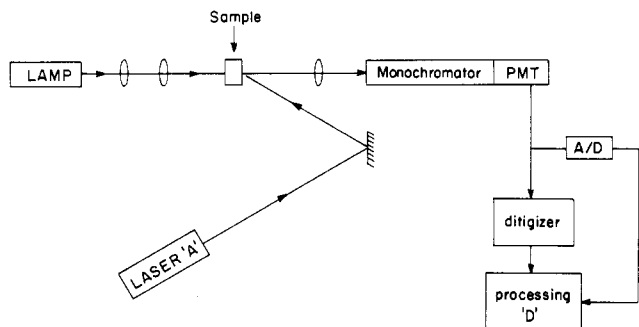


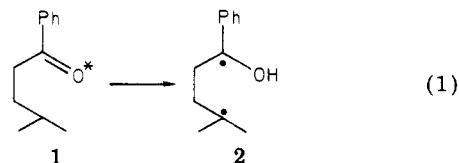
Figure 1. Laser flash photolysis system.

decay and corresponds to the time required for the concentration to decay to e^{-1} ($1/2.718$) of its initial value. Typical instruments can resolve lifetimes in the 10-ns to 100- μ s range.⁸

Biradical Generation, Characterization, and Lifetimes

All the reactions discussed in this Account occur from the triplet manifold. In the case of simple aromatic ketones, intersystem crossing occurs in the 10^{-10} – 10^{-11} s time scale and as a result is frequently the only process in which the singlet state participates.

In order for a transient species, in this case a biradical, to be amenable for time resolved laser flash photolysis study, its formation has to be substantially faster than its decay, so that significant concentrations build up during the experiment. In other words, the biradical lifetime should be longer than both the laser pulse and its triplet precursor lifetime. Reaction 1 is an example which meets these conditions.



The lifetime of 2, τ_B , is 97 ns in methanol (vide infra), which compares with a triplet lifetime (τ_T) of 4.7 ns and the pulse duration of ca. 8 ns.^{10,11} Naturally, it is necessary to establish that τ_T is short enough in experiments that do not require knowledge of the biradical lifetime.¹² Fortunately, triplet lifetimes can be determined by a variety of other techniques.^{3,10,14-17}

I will now use reaction 1 to illustrate how one can establish if a transient observed in a laser flash experiment is the Norrish type II biradical. Tests that involve intermolecular reactions are mentioned briefly and will be discussed in more detail in other sections.

(8) In some cases shorter lifetimes can be measured by integration of the Δ OD vs. time profile.⁹

(9) Scaiano, J. C. *J. Photochem.* 1981, 16, 71–74.

(10) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* 1977, 81, 2126–2131.

(11) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* 1977, 81, 828–832.

(12) Note that the actual value of the triplet lifetime is not used in any calculations; it is simply necessary to establish that it is sufficiently short that it will not interfere in biradical studies.¹³

(13) Bays, J. P.; Encinas, M. V.; Scaiano, J. C. *Macromolecules* 1980, 13, 815–820.

(14) Grotewold, J.; Soria, D.; Previtali, C. M.; Scaiano, J. C. *J. Photochem.* 1972/73, 1, 471–479.

(15) Scaiano, J. C.; Grotewold, J.; Previtali, C. M. *J. Chem. Soc., Chem. Commun.* 1972, 390–391.

(16) Wagner, P. J.; Thomas, M. J.; Harris, E. *J. Am. Chem. Soc.* 1976, 98, 7675–7679.

(17) E.g.: Wagner, P. J.; Kelso, P. A.; Kempainen, A. E.; Zepp, R. G. *J. Am. Chem. Soc.* 1972, 94, 7500–7505.

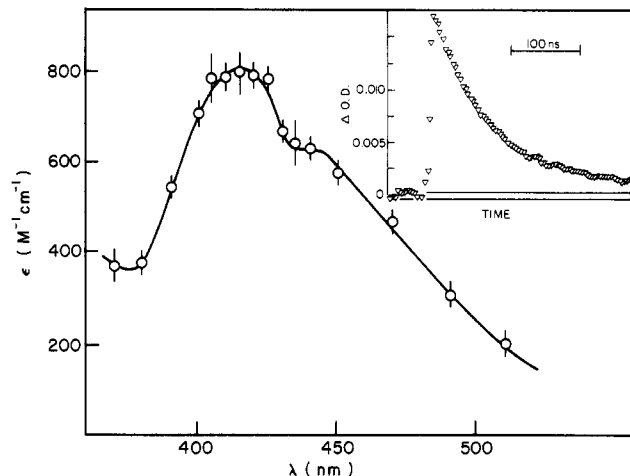


Figure 2. Transient spectra for biradical 2 in methanol and (insert) typical decay trace monitored at 415 nm. (Reproduced with permission from ref 18. Copyright 1977, North-Holland Publishing Co.)

(A) Laser excitation of γ -methylvalerophenone in methanol leads to the transient spectrum of Figure 2, which is virtually identical with that of the radical $\text{Ph}\dot{\text{C}}(\text{OH})\text{CH}_3$.^{18,19}

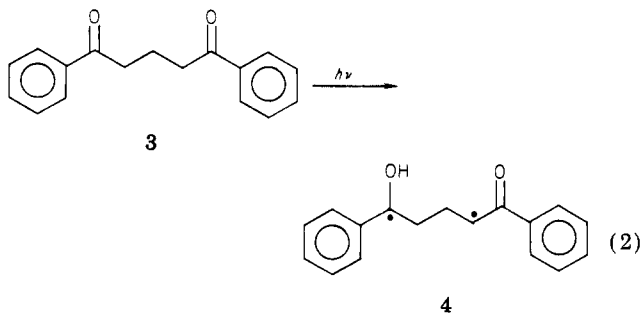
(B) The lifetime of this transient is 97 ns (see insert in Figure 2) and is not affected by addition of typical triplet quenchers; however, its yield of formation is reduced, thus showing that it has a triplet state precursor.

(C) Addition of electron acceptors leads to electron transfer processes characteristic of ketyl radical sites; experiments of this type also allow the evaluation of τ_B , and these values have been found to be in excellent agreement with those obtained by direct detection (see point B).^{10,11,20}

(D) Addition of typical radical scavengers, such as thiols, reduces the biradical lifetime and leads to ketyl radical formation.²¹⁻²³

(E) Substrates that are good scavengers in laser experiments also quench product formation to the extent predictable from the laser data.

A number of other ketones besides 1 also led to detectable biradicals. There are other examples where the triplet and biradical lifetimes are of comparable magnitude. For example, this is the case for 3 which leads to biradical 4.²⁴⁻²⁶



(18) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* 1977, 50, 431–434.

(19) Scaiano, J. C. *Tetrahedron*, 1982, 38, 819–824.

(20) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* 1978, 82, 2662–2664.

(21) Wagner, P. J.; Zepp, R. G. *J. Am. Chem. Soc.* 1972, 94, 287–289.

(22) Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* 1972, 94, 7480–7488.

(23) Encinas, M. V.; Wagner, P. J.; Scaiano, J. C. *J. Am. Chem. Soc.* 1980, 102, 1357–1360.

Table I
Selected Biradical Lifetimes at Room Temperature

biradical	solvent	τ_B /ns	ref
	methanol wet acetonitrile ^a benzene	97 76 30	11, 28 28 28
	wet acetonitrile	40	24
	wet acetonitrile	2000	29
	wet acetonitrile	1500	30
	wet acetonitrile methanol	580 300	30 31
	wet acetonitrile	24	30
	wet acetonitrile	930	30
	methanol	1600	27
	wet acetonitrile	2200	32
	wet acetonitrile	600	32
	water (pH 8.0) water (pH 11.0)	2000 1200	33 33

^a Wet acetonitrile refers to the solvent with 10–20% water. See original publications for detailed solvent composition.

In cases like this, we have shown that the triplet lifetime can be “tuned” to a conveniently short value by addition of a triplet quencher, selected so that it will not produce absorptions in the region of interest.²⁴ In general, dienes are a convenient choice. Naturally, the quenching of the triplet state lowers the yield of biradical formation, therefore leading to weak signals; in many cases signal averaging techniques can overcome these problems.²⁴

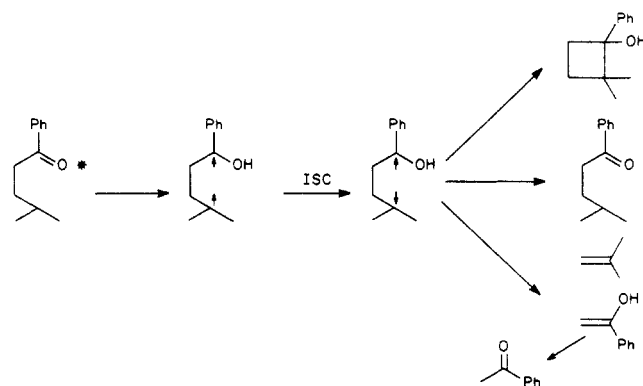
Table I summarizes some representative lifetimes for biradicals derived from the Norrish type II reaction and the related photoenolization of *o*-methylbenzoyl deriv-

(24) Bays, J. P.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 727–734.

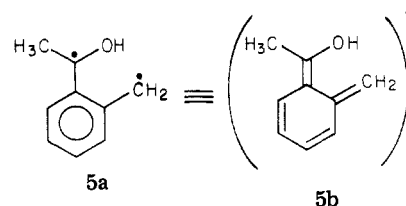
(25) Salvin, R.; Meybeck, J.; Faure, J. *J. Photochem.* **1976/77**, *6*, 9–16.

(26) Salvin, R.; Meybeck, J. *J. Photochem.* **1977**, *7*, 411–415.

Scheme I



atives. Many of these values were obtained from electron transfer studies (vide infra). All the biradicals in Table I have been derived from triplet-state reactions and are believed to be triplet states.^{10,19} This aspect will be developed in more detail in the section on paramagnetic quenchers. The biradicals generated as intermediates in photoenolization can also be regarded as the triplet states of the corresponding enols, e.g.,



Solvent effects on the lifetimes of Norrish type II biradicals show an enhancement of the lifetimes in polar solvents.²⁸ We have proposed¹⁹ that the results reflect an increase in the average distance between the radical sites in hydrogen bonding media, which in turn leads to a decrease in the rate of intersystem crossing. Consistent with this, polar solvents decrease the yield of cyclization products.³⁴

The behavior of biradicals in micelles can be regarded as a special case of solvent effects. The lifetime for **2** in sodium dodecyl sulfate micelles is 92 ns³⁵ and compares well with a value of 97 ns in methanol; this is indicative of a very polar environment and is in agreement with the high quantum yields of fragmentation observed in micellar solution.³⁶

Another example where the distance between the biradical ends seems to play a role in determining its lifetime is the case of **6**, where $\tau_B = 17$ ns in methanol.³⁷

(27) Scaiano, J. C.; Encinas, M. V.; George, M. V. *J. Chem. Soc., Perkin Trans. 2* **1980**, 724–730.

(28) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1978**, *59*, 246–248.

(29) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7108–7109.

(30) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970.

(31) Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 7713–7714.

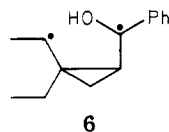
(32) Encinas, M. V.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* **1980**, 56–60.

(33) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 2146–2152.

(34) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506–7512.

(35) Scaiano, J. C.; Selwyn, J. *Photochem. Photobiol.*, **1981**, *34*, 29–32.

(36) Turro, N. J.; Liu, K.-C.; Chow, M. F. *Photochem. Photobiol.* **1977**, *26*, 413–415. Worsham, P. R.; Eaker, D. W.; Whitten, D. G. *Ibid.* **1978**, *100*, 7091–7093.



Up to this point I have not discussed the mechanism of the type II reaction, simply to emphasize that in principle laser studies do not require a detailed knowledge of the ultimate products of reaction. However, laser photolysis studies on systems where the products are not known or where a rough idea of the quantum yields involved is not available are of little value. Schemes I and II show the mechanisms of the Norrish type II and photoenolization reactions, illustrated for γ -methylvalerophenone and *o*-methylacetophenone, respectively. In the latter the syn and anti conformers lead to kinetically distinct triplets; this has been discussed in detail by Wagner, Wirz, and ourselves.^{4,30,31,38-40}

Biradical lifetimes show very small or no temperature dependence. For example, for 2 and 5 in methanol:

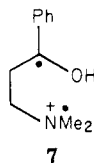
$$-\log(\tau_B/s) = 7.20 - 150/\theta \text{ for } 2^{19}$$

$$-\log(\tau_B/s) = 7.51 - 1630/\theta \text{ for } 5^{41}$$

where $\theta = 2.3RT$ with RT in cal/mol. The low pre-exponential factors and the insensitivity of the lifetimes to the enthalpy changes associated with decay have been taken to indicate that biradical lifetimes are determined by the rates of triplet-singlet intersystem crossing.^{10,19}

The lifetime of 2 has been shown to be insensitive to magnetic fields of up to 2000 G; this suggests that the interaction between the ends is large enough that it cannot be overcome by the Zeeman splittings produced in this field.¹⁹

The interaction between radical sites must, nevertheless, be small in comparison with enthalpy changes associated with chemical reactions, since the biradicals display in their reactions with diamagnetic scavengers typical monoradical properties. Further, the biradical spectrum of Figure 2 reflects simply the absorption of the ketyl chromophore.⁴² Acid-base properties also seem to be rather insensitive to the presence of a second radical site; thus, the pK_a of 7 is 10.0, very similar to that for the ketyl radical, $\text{Ph}\dot{\text{C}}(\text{OH})\text{CH}_3$.^{33,42}



Intermolecular Biradical Processes

Hydrogen Abstraction. Given the short lifetimes of type II biradicals (see Table I), hydrogen abstraction studies are only viable with molecules with very labile hydrogen atoms. Wagner reported in 1972 that type II biradicals abstract hydrogen from thiols, and the

(37) Bays, J. P.; Scaiano, J. C.; Sheppard, J. W., to be published.

(38) Wagner, P. J.; Chen, C.-P. *J. Am. Chem. Soc.* 1976, 98, 239-241.

(39) Das, P. K.; Scaiano, J. C. *J. Photochem.* 1980, 12, 85-90.

(40) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chem. Acta* 1977, 60, 2595-2607.

(41) Scaiano, J. C. *Chem. Phys. Lett.* 1980, 73, 319-322.

(42) Hayon, E.; Ibata, T.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* 1972, 76, 2072-2078. Lutz, H.; Breheret, E.; Lindqvist, L. *J. Phys. Chem.* 1973, 77, 1758.

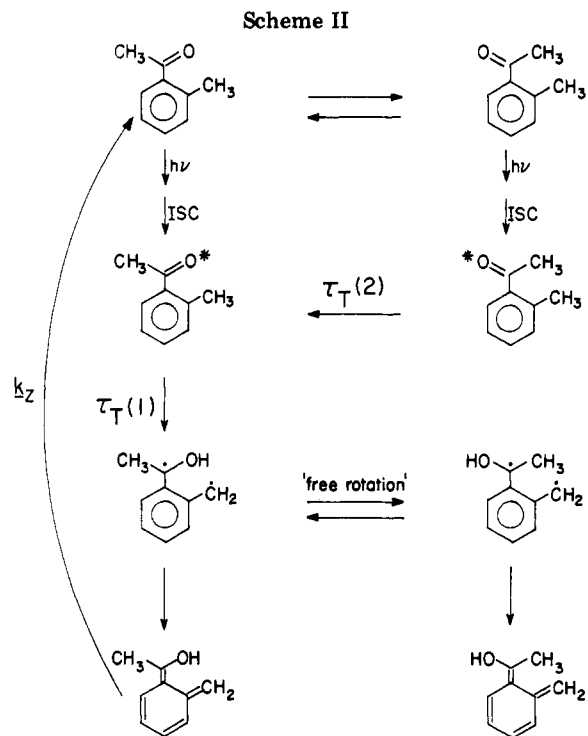
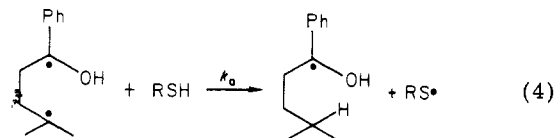
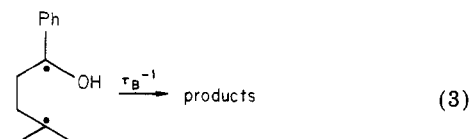


Table II
Absolute Rates of Hydrogen Abstraction by Biradicals²³

biradical source	substrate	$k/M^{-1} s^{-1}$ ^a
γ -methylvalerophenone	Bu_3SnH	1.1×10^6 ^b
γ -methylvalerophenone	$n\text{-C}_8\text{H}_{17}\text{SH}$	9×10^6
valerophenone	$n\text{-C}_8\text{H}_{17}\text{SH}$	1.13×10^7

^a At 22 °C in 1.2 M pyridine in benzene. ^b For comparison, abstraction by *tert*-butyl radicals at 27 °C occurs with $k = 1.9 \times 10^6 M^{-1} s^{-1}$.⁴⁴

results from competitive studies were used to estimate biradical lifetimes.^{21,22} We have recently reexamined this reaction using laser techniques.²³ Reactions 3 and 4 illustrate the mechanism in the case of 2.



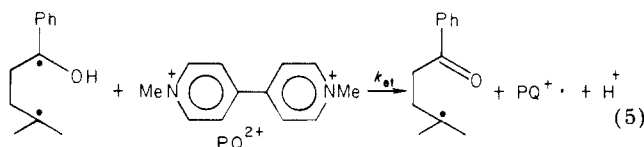
A characteristic of these reactions is that when the biradical is trapped (reaction 4), the lifetime of the detectable chromophore (i.e., ketyl) is actually increased. The reason is that biradicals are much shorter lived than free radicals; the latter can be regarded as stable species in the time scale of these experiments. We have demonstrated that the kinetic analysis is straightforward in this case, because the kinetics of biradical decay coincide with the kinetics for ketyl radical formation.²³

Table II shows values of rate constants for hydrogen abstraction by biradicals. It is noteworthy that the rate of abstraction from tri-*n*-butylstannane for the biradicals is in excellent agreement with the value measured for *tert*-butyl radicals,^{43,44} thus supporting Wagner's

proposal that these biradical processes reflect mono-radical behavior.^{21,22}

The quenching of the photofragmentation of valerophenone by phenols is believed to result from a combination of triplet quenching and biradical scavenging,⁴⁵ the latter involving abstraction by the alkyl site.

Electron Transfer. Ketyl radicals are known to be excellent electron donors;⁴⁶ thus, it is not surprising that biradicals with ketyl sites will behave similarly.⁴⁷ Biradical reactions of this type were the first ones studied with laser techniques,¹¹ and many of the known lifetimes were derived from experiments of this type (see Table I). Paraquat dications (methyl viologen), PQ^{2+} , have been the most commonly used acceptors, e.g., reaction 5.



The radical cation, PQ^+ , has strong absorption bands at 398 and 603 nm and is easily detectable.^{46,48} The formation of PQ^+ follows pseudo-first-order kinetics, leading to an experimental rate constant associated with its buildup that we will call k_{exptl} . The values of k_{exptl} are related to the biradical lifetime (τ_B) and k_{et} according to eq 6.

$$k_{\text{exptl}} = \tau_B^{-1} + k_{\text{et}}[PQ^{2+}] \quad (6)$$

Thus, k_{et} and τ_B can both be obtained from a study of the buildup of PQ^+ for different concentrations of the electron acceptor PQ^{2+} . The main advantage of a technique of this type is that it does not depend upon the detection of a different transient in each system; rather, the same species (PQ^+) can be monitored in all cases. This is particularly important in systems where the corresponding biradical shows only very weak absorptions, as is the case for nonaromatic ketones.^{29,32,49} PQ^+ is unusually easy to monitor; in our early experiments¹¹ we have shown that the monitoring system in the laser photolysis apparatus (light source, pulser, filters, lenses, and monochromator) can be replaced by an He/Ne alignment laser ($\lambda = 632.8$ nm) of a type which is available in many laboratories.

In these systems it is important to establish that the species trapped by PQ^{2+} is indeed the biradical and not some other transient such as the triplet state;⁵⁰ therefore, these experiments are limited to systems where the triplet lifetime is substantially shorter than the biradical

(43) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 1055-1056; **1968**, *90*, 7047-7055.

(44) Chatgililoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739-7742.

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(47) Small, R. D.; Scaiano, J. C. *J. Photochem.* **1976/77**, *6*, 453-456.

(48) Farrington, J. A.; Ledwith, A.; Stam, M. F. *J. Chem. Soc., Chem. Commun.* **1969**, 259-260. Farrington, J. A.; Ebert, M.; Land, E. J.; Fletcher, K. *Biochim. Biophys. Acta* **1973**, *314*, 372-381.

(49) Encinas, M. V.; Lissi, E. A.; Scaiano, J. C. *J. Phys. Chem.* **1980**, *84*, 948-951.

(50) Das has recently measured absolute rate constants for several carbonyl triplets and shown that they frequently exceed $10^9 \text{ M}^{-1} \text{ s}^{-1}$. (Das, P. K. *Tetrahedron Lett.* **1981**, 1307-1310.)

Table III
Rate Constants for the Reaction of Various Electron Acceptors with the Biradical from γ -Methylvalerophenone at Room Temperature^a

acceptor	$k_{\text{et}}/\text{M}^{-1} \text{ s}^{-1}$
	3.9×10^9
	1.4×10^9
	4.0×10^9
	2.6×10^9
	$\leq 1 \times 10^8$
	7.6×10^8
	1.7×10^8
	$\leq 2 \times 10^7$
$\text{C}_6\text{H}_5\text{N}_2^+$	3.3×10^9 ^b
$p\text{-CH}_3\text{OC}_6\text{H}_4\text{N}_2^+$	5.5×10^9 ^b

^a In 20% water-acetonitrile unless otherwise indicated.

^b In methanol.

lifetime. It should be noted that the triplet lifetime tuning technique (using dienes) mentioned above can lead to complications if used when electron acceptors are present because triplet dienes can behave as electron donors;⁵¹ thus, a plot of k_{exptl} vs. $[PQ^{2+}]$ could reflect properties of the diene triplet rather than those of the biradical. Occasionally, triplet quenchers can be safely added if the biradical lifetime is long enough that only very small concentrations of PQ^{2+} are required.³⁰

Typical k_{et} values are in the $1\text{--}7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ range. Interestingly, the lowest value measured ($7.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) corresponds to the biradical for *o*-phthalaldehyde, the only species examined which has a σ -radical site.

The temperature dependence of the reaction of **2** with PQ^{2+} was measured in methanol; $\log(k_{\text{et}}/\text{M}^{-1} \text{ s}^{-1}) = 11.4 - 2500/\theta$,¹⁰ leading to $k_{\text{et}} = 3.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C.

Table III summarizes kinetic data for the reaction of **2** with several electron acceptors;²⁰ it includes data from some recent experiments which demonstrate that type II biradicals are very reactive toward diazonium salts.⁵²

Addition to Unsaturated Systems. As in the case of hydrogen abstraction, the short biradical lifetimes require very reactive substrates for addition to be efficient. Di-*tert*-butyl selenoketone has been shown to be an excellent biradical trap.⁵³ No laser experiments were carried out on this system, but the combination of lifetimes obtained in laser experiments (see Table I)

(51) A few other examples of electron transfer from triplet olefins to PQ^{2+} have been reported: Caldwell, R. A.; Pac, C. *Chem. Phys. Lett.* **1979**, *64*, 303-306. George, M. V.; Vijaya Kumar, Ch.; Scaiano, J. C. *J. Phys. Chem.* **1979**, *83*, 2452-2455.

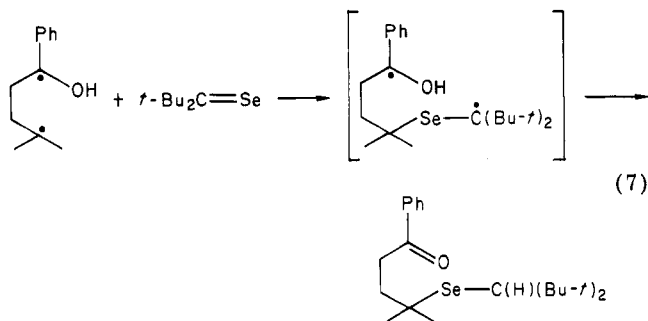
(52) Scaiano, J. C.; Nguyen, Kim-Thuan *J. Photochem.* submitted for publication.

(53) Scaiano, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 1494-1498.

Table IV
Rate Constants for the Interaction of the Biradical from γ -Methylvalerophenone with Paramagnetic Quenchers at Room Temperature

scavenger	solvent	$k_q/M^{-1} s^{-1}$	ref
oxygen	methanol	6.5×10^9	57
		6.7×10^9	18
<i>t</i> -Bu ₂ NO·	methanol	2.5×10^9	58
		benzene	1.2×10^9
Cu(acac) ₂	methanol	2×10^9	60

with the results from steady irradiation studies lead to a rate constant of $7 \times 10^8 M^{-1} s^{-1}$ for reaction 7 in benzene at 32 °C.



Addition to carbon-carbon double bonds is not fast enough (thus inefficient) to be studied by laser techniques, although the interaction of biradicals with methyl methacrylate has been shown to initiate polymerization.^{54,55} Interaction with oxygen is believed to reflect largely its paramagnetic properties and is discussed separately.

Interaction with Paramagnetic Species. The mechanism and kinetics of the reactions mentioned above do not differ substantially from those of typical monoradicals with similar substitution at the reactive center. By contrast, the interaction of biradicals with paramagnetic species [oxygen, nitroxides, Cu(II) complexes] occurs by pathways that are characteristic of the biradical and tend to reflect spin selection rules. In 1973 we reported the first observation of such an effect:⁵⁹ the photofragmentation of γ -methylvalerophenone (1) occurs with higher quantum yields in the presence of oxygen compared to the absence of oxygen, a rather unusual observation for a reaction that occurs exclusively from the triplet state.

Laser experiments show that biradicals are efficiently scavenged by oxygen.^{18,57} Rate constants of $\sim 6.7 \times 10^9 M^{-1} s^{-1}$ can be determined either by direct scavenging¹⁸ or by monitoring the effect of oxygen on reaction 5 (i.e., with reaction 5 as a probe).⁵⁷ Similar experiments with other paramagnetic species, such as di-*tert*-butyl nitroxide or bis(acetylacetonato)copper(II),⁵⁸⁻⁶⁰ lead to the rate constants given in Table IV. While the high rate constants could be expected, it is surprising that in all these examples the chemical processes taking place are quite different from those that could be expected from

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(55) Small, R. D., Jr.; Scaiano, J. C. *Macromolecules* 1978, 11, 840-841.

(56) Grotewold, J.; Previtali, C. M.; Soria, D.; Scaiano, J. C. *J. Chem. Soc., Chem. Commun.* 1973, 207.

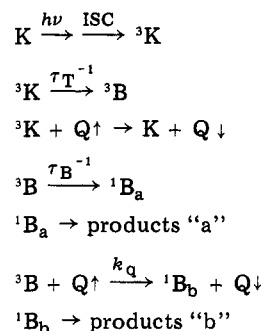
(57) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* 1977, 48, 354-357.

(58) Encinas, M. V.; Scaiano, J. C. *J. Photochem.* 1979, 11, 241-247.

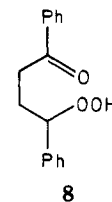
(59) For other examples involving 1,4-biradicals, see: Caldwell, R. A.; Creed, D. *J. Phys. Chem.* 1978, 82, 2644-2652.

(60) Scaiano, J. C.; Lee, C. W. B.; Chow, Y. L.; Marciniak, B. *J. Phys. Chem.*, in press.

Scheme III



typical monoradical behavior. For example, in the case of oxygen, we have shown that 75% of the quenching events leads to typical type II products⁶¹ (fragmentation and cyclization) while the other 25% leads to the formation of hydroperoxides. In the case of γ -phenylbutyrophenone, the hydroperoxide has been characterized as 8.



This behavior was found to be independent of the structure of the type II biradical and of the solvent. We have proposed that the constancy of the 3:1 ratio of products reflects the spin selection rules operative in this case; that is, two triplets (oxygen and the biradical) will lead to singlet, triplet, and quintet encounters in a 1:3:5 ratio. The hydroperoxides result from the singlet encounters and the type II products (fragmentation or cyclization and ground-state ³O₂) from triplet encounters. Thus, the product forming reactions are all spin allowed and take place with a 3:1 probability ratio; quintet encounters are assumed to be dissociative.

Similarly, in the case of di-*tert*-butyl nitroxide in nonpolar solvents the fraction of biradicals that leads to products is enhanced by addition of the scavenger. In all cases the basic explanation rests on the idea that partitioning of the biradical into products can be modified by addition of a paramagnetic quencher.

While assisted intersystem crossing is an essential ingredient of any explanation of these effects, it should be noted that all modes of biradical decay (assisted or not) require intersystem crossing. In other words, the fact that intersystem crossing is rate determining does not mean that product ratios will change if the rate of intersystem crossing is modified. We have proposed¹⁹ that singlet biradicals can remember the conformation at which intersystem crossing took place; further, the singlet biradical being very short lived (subnanosecond) preferentially leads to those products for which the nascent singlet biradical is already "preset". Thus, any interaction capable of changing the average conformation from which intersystem crossing takes place would be expected to exert some control on the product ratios. Quenching by paramagnetic species provides one example of such an interaction; very strong magnetic

(61) Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* 1978, 100, 4512-4519.

fields⁶² or magnetic isotope substitution at the radical sites may be other examples where product control can be exerted at the triplet manifold level by controlling the conformations at which intersystem crossing takes place. From a mechanistic point of view, *singlet biradicals generated by different intersystem crossing mechanisms should be regarded as different species*; Scheme III illustrates an example where 1B_a and 1B_b represent singlet biradicals produced via spontaneous and assisted intersystem crossing, respectively, and lead to different products, or the same products in different ratio ("a" or "b"); $Q\uparrow$ represents a paramagnetic quencher.

The case of paramagnetic quenchers provides a good example where laser techniques can provide valuable information but emphasizes the need to complement laser studies with product and quantum yield data.

Biradical-Biradical Reactions. Given the short biradical lifetimes, we should not be surprised that almost nothing is known about their self-reactions. In a recent study,¹⁹ we have shown that self-termination of 2 occurs with $2k_t \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, but no product studies have been carried out.

Biradicals in Polymer Systems

The Norrish type II reaction is a common process in carbonyl-containing polymers.^{63,64} Faure⁶⁵ was the first to detect biradicals of this type in the photochemistry of poly(phenyl vinyl ketone) (PPVK). This study also showed that the spectroscopic properties of biradicals are quite similar to those of the analogous monoradicals. The lifetimes of type II macrobiradicals are usually similar to or slightly longer than those observed in small molecules.¹³ Intermolecular reactions also show a similar pattern, with smaller rate constants in the case of polymers.^{55,66}

The background on the measurement of τ_B for PPVK is particularly interesting, because it emphasizes the importance of carrying out the measurements under conditions where the triplet lifetime is considerably shorter than τ_B . Faure⁶⁵ reported $\tau_B = 70 \text{ ns}$ in benzene, while our studies led to 76⁵⁵ and 65 ns,¹³ respectively, under similar conditions. Reported triplet lifetimes for PPVK range from 7 to 100 ns, with a recent detailed

study leading to 57 ns at 20 °C in toluene- d_8 for quencher-free macromolecules.⁶⁷ Thus, the triplet lifetime is not substantially shorter than τ_B . However, reexamination of the samples and results from our early experiments indicate that they had incorporated quencher end groups (produced in the type II reaction),⁶⁸ which led to a considerable shortening of the triplet lifetime. Thus, even if we were not aware of it, we were "tuning" the triplet lifetime to a suitably short value. We believe that the same explanation must apply to Faure's results,⁶⁵ whose data clearly show that the species monitored was the biradical, as proposed. In later experiments, with "better" samples, we had to add dienes to achieve essentially the same effect.^{13,69}

In the case of photoenolizations, macrobiradicals again show behavior much the same as that shown in the case of small molecules.^{13,66,69} Reactions of this type have been proposed to serve the purpose of photostabilization because of their ability to behave as an energy sink.⁷⁰

Concluding Remarks

Biradicals produced as intermediates in the Norrish type II reaction and in the photoenolization of *o*-alkyl-substituted carbonyl compounds show typical monoradical behavior in their reactions with diamagnetic substrates. Their reactions with paramagnetic species show characteristic behavior that reflects the operation of spin selection rules and the importance of intersystem crossing processes in biradical chemistry.

I have attempted to illustrate in this Account studies in which laser techniques have proved extremely useful. Laser techniques should prove useful in the solution of many other problems in organic chemistry. A few other systems, including alkoxy radicals, group 4 radicals, carbenes, and various ylides, have been investigated in recent laser studies. Many other problems in organic chemistry will probably be examined by means of laser flash photolysis during the next few years.

I am grateful to the many colleagues who collaborated in this project and whose names appear in the references. This work was started at the Notre Dame Radiation Laboratory with support from the U.S. Department of Energy and is now being continued at the National Research Council of Canada.

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