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Time-Resolved Studies of Biradical Reactions in Solution[1]

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Contents

Introduction

Biradicals have been proposed as reaction intermediates in thermal and photochemical reactions for many years, but their trapping and direct detection are relatively recent. While several definitions of the term biradical are frequently used, we will adopt the one given by Berson:[2] biradicals are "even-electron molecules that have one bond less than the number permitted by the standard rules of valence". While this definition may be somewhat ambiguous at times, it is simple and adequate for most situations in organic chemistry.

Numerous reviews of various aspects of biradical chemistry have appeared in the literature.[2-20] The coverage of this review is limited to solution studies

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employing direct detection by time-resolved techniques. This excludes competitive studies even when these may lead to rate constants for biradical reactions through the educated choice of kinetic data for competitive processes. Also excluded are some CIDNP studies that involve assumptions relating to time-dependent parameters of the system. Further, studies in rigid media (e.g., low-temperature matrices) are generally not covered. In some cases we have chosen to include some examples that fall outside the scope of this review when they represent a unique or particularly significant measurement.

Our coverage excludes a few species that under certain circumstances could be regarded as biradicals or biradicaloid species. Thus, this review excludes molecular oxygen, carbenes, biradical–metal complexes, and radical pairs in constrained media, where the radical centers are maintained at a "controlled" distance by a physical boundary rather than a molecular frame.

Excited states, which frequently show radical or biradical properties, are not included, with the exception of the species (biradicals or triplet enols) produced as intermediates in the photoenolization of *o*-alkyl-substituted aromatic ketones. These transients share many of the characteristics found in Norrish Type II biradicals (vide infra).[4,17]

Numerous dinitroxide biradicals have been prepared. These are very persistent species, with stability comparable to that of typical nitroxide monoradicals. Time-resolved studies are carried out in these systems by using conventional "slow" techniques. Studies of these species include large numbers of reports on their ability to quench excited states. The reactions of these biradicals have been reviewed relatively recently[6] and will not be included here since this rather specialized topic adds little to our understanding of the chemistry of transient biradicals.

As is frequently the case with reviews of this type, the interests and expertise of the authors are probably reflected in a somewhat biased choice of examples.

Biradical Generation

Biradicals can be generated in a wide range of thermal and photochemical reactions. Their time-resolved study usually requires that the biradicals be produced in a time scale short compared with their own lifetime. In most cases this means that time-resolved studies are limited to photochemical biradical generation using pulsed light sources. It is, therefore, important to identify biradical sources that can be triggered photochemically and where the various steps leading from the starting material to the biradical occur rapidly.

In this section we outline the main characteristics of some of the most frequently encountered photoreactions leading to biradicals. We also take advantage of our first example, the Norrish Type II reaction, to illustrate the points raised above.

The mechanism for the Norrish Type II reaction of aryl alkyl ketones is illustrated in Scheme I.[3,13] The reaction occurs solely from the triplet state; the reactive triplet has been established to have n,π^* character. For ketones with low-lying π,π^* states (e.g., bearing *p*-methoxy substituents), the reactive species remains the ^{3}n,π^* state, which reacts following thermal population from the $^3\pi,\pi^*$ state.[3,13,21-23] As a result, ketones with low-lying π,π^* triplet states are considerably less reactive. For example, the lifetime for triplet valerophenone in hydrocarbons at room temperature is ~6 ns, while for *p*-methoxyvalerophenone it is 750 ns.[21] The biradicals produced from simple ketones (such as valerophenone) have lifetimes of 30–100 ns, depending on the conditions, particularly the solvent, and are extensively covered later in this review. The lifetime of the biradical is controlled by intersystem crossing; the singlet biradical, which is presumably produced on the pathway to products, has never been detected. Typical laser pulses used to initiate the reaction have durations of a few nanoseconds, so they are still short in comparison with the biradical lifetime. The Norrish Type II reaction is also faster the more labile the C–H bond at the γ-position.[3] Thus, ketones with tertiary γ-C–H bonds and n,π^* triplet states are expected to have very short triplet lifetimes, which makes them ideal rapid sources for biradical generation. γ-Methylvalerophenone, which meets all the criteria mentioned above ($\tau_T \sim 2$ ns), has been a favorite in time-resolved biradical studies.[4]

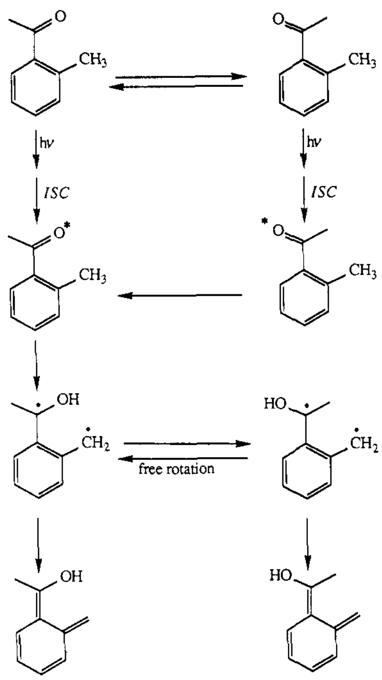
SCHEME I

Aliphatic ketones bearing γ-hydrogens also undergo the Norrish Type II reaction, but in this case the reaction can occur from both the singlet and triplet manifolds.[13] Biradical time-resolved data have only been obtained for the triplet-state reaction, and even in this case, our understanding is extremely limited.

The photoenolization of *o*-alkyl-substituted aromatic ketones occurs by essentially the same mechanism as the Norrish Type II reaction and is illustrated in Scheme II for 2-methylacetophenone.[4,18] In this case the reaction of the triplet carbonyl with the adjacent benzylic C–H bond is fast enough to make rotation around the aryl–CO bond the rate-determining step for decay of the anti conformer. Under these conditions the syn and anti conformers become kinetically distinct.[4,18,24] For the syn conformer the triplet lifetime is controlled by the hydrogen-transfer step; on the other hand, the triplet lifetime for the anti conformer is determined by the rate of bond rotation. While a number of triplet ketones adhere to the mechanism of Scheme II, we note that there are numerous exceptions that include cases of symmetry (e.g., mesitylaldehyde),[25] structurally restricted motion (e.g., tetralones),[25] or steric effects (e.g., 2,4,6-triisopropylbenzophenone).[26]

The biradicals involved in the photoenolization can also be identified as the triplet states of the corre-

SCHEME II



sponding enols.[4] These species are one and the same, and depending on the type of reaction, they may show dominant radical-like or excited-state behavior.

The Norrish Type I cleavage is a common reaction for aliphatic carbonyl compounds.[13] In the case of cycloalkanones, α-cleavage leads to the formation of 1,ω-alkyl acyl biradicals in a reaction that occurs predominantly from the triplet manifold (Scheme III).[27-30] The reaction has been extensively studied during the past few years, since it can be used as a source of biradicals of different lengths without altering the characteristics of the two ends (vide infra).

When the two α-positions to the carbonyl bear aromatic substituents, the Norrish Type I reaction is followed by rapid decarbonylation. In this case the resulting biradical is a 1,(ω − 1)-dialkyl species (e.g., 2,2,6,6-tetraphenylcyclohexanone).[31]

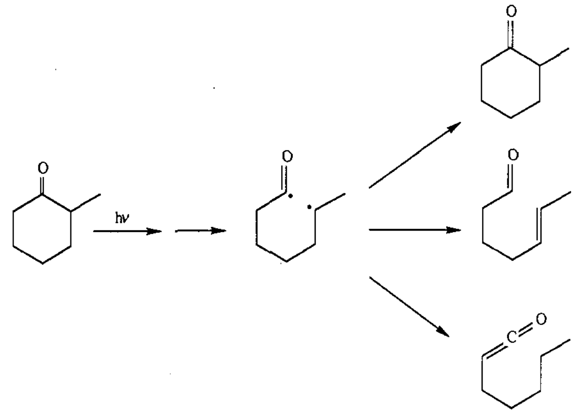
Photoinduced nitrogen loss from azo compounds has been frequently employed as a source of many biradicals.[32-34] Scheme IV illustrates the reaction for the case of a typical azoalkane.[34]

The thermolysis and photolysis of cyclic azo compounds lead to different degrees of stereospecificity,[33] suggesting the involvement of triplets in the photochemical process. High yields of triplet reaction can of course be achieved by triplet sensitization.[34]

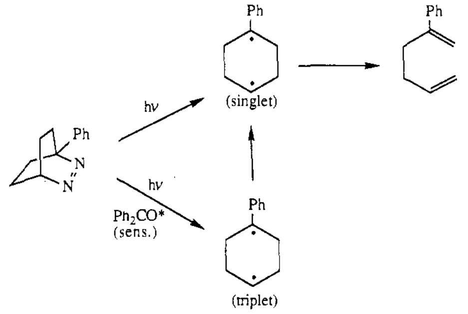
Photochemical (frequently triplet sensitized) ring cleavage has occasionally been employed. Scheme V shows examples involving intermolecular[35] and intramolecular[36] sensitization. Under these conditions the biradicals are produced initially in the triplet state.

A few other biradical sources have been employed occasionally and are listed with the individual examples.

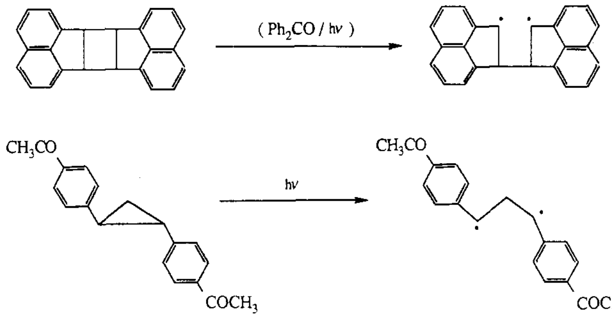
SCHEME III



SCHEME IV



SCHEME V



Time-Resolved Methods for the Study of Biradicals

At least 90% of the data included in this review have been obtained with laser flash photolysis techniques, mostly with nanosecond resolution, and in a few cases with picosecond techniques. Other methods, in particular magnetic resonance techniques, have been employed in a few cases, but, in general, time-resolved methods of this type have not been widely used.

For the reasons mentioned above we only outline here the use of laser flash photolysis techniques. The technique has been in use for over 20 years[37] and has been described in detail in the literature.[4,38-43] Briefly, a pulsed laser is used for sample excitation. Commonly employed lasers that have useful fundamental wavelengths include nitrogen (337.1 nm) and excimer (e.g., at 248 or 308 nm) gas lasers. Solid-state lasers (Nd:YAG or ruby) are also commonly employed, but in these cases the fundamental wavelength is not very useful in organic photochemistry and the various harmonics are normally used; for example, in the case of Nd:YAG lasers, from the fundamental at 1.06 μm one can obtain ~532 (double), 355 (triple), and 266 nm (quadruple). Dye lasers can also be employed in this type of work. Desirable pulse durations are ≤10 ns and energies-per-pulse should be on the order of several millijoules. Under these conditions one can typically generate transient concentrations in the 10–50 μM range in the volume probed by the monitoring beam. It should be pointed out that focusing high-powered lasers into small volumes may lead to higher transient concentrations and, thus, the attenuation of transient lifetimes. This approach has been used to estimate the rate constant for self-reaction of a Type II biradical.[10]

Transient absorption measurements require a polychromatic monitoring beam, as does any other absorption spectrometer. For nanosecond techniques this beam is normally provided by a xenon lamp (pulsed or not). In the case of picosecond studies the monitoring source is usually a delayed continuum generated when part of the laser beam is concentrated in a liquid (e.g., D_2O).[44]

The time resolution of the laser system is determined by the laser pulse duration and by the time response of the detection system. In the case of nanosecond techniques, photomultipliers with rise times of 1–3 ns are normally used for kinetic studies. Spectroscopic studies can use either the same detection as for kinetic work or a gated optical multichannel analyzer (OMA), which provides a "snapshot" of the spectrum after a given delay following laser excitation.

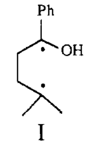
In the case of picosecond techniques, a streak camera can be used for the kinetic work and an OMA for spectroscopic studies. However, quite frequently the OMA is also employed for kinetic work by taking "snapshots" at various intervals following excitation.

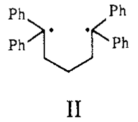
Abbreviations used throughout the review for the various techniques are lfp (laser flash photolysis), fp (conventional flash photolysis), ps (picosecond spectroscopy), KESR (kinetic ESR), and SESR (steady-state ESR).

Mechanisms for Biradical Decay: What Determines Biradical Lifetimes?

There is a considerable amount of evidence that suggests that the lifetimes of small, flexible triplet biradicals are controlled by intersystem crossing (ISC).[5,10,45–52] Thus, the rate constant for product formation from the singlet biradical is fast relative to the ISC rate constant. Most of the evidence that supports this hypothesis comes from an examination of Norrish Type I[48–52] and II[5,10,46,47] biradicals with short distances between the two termini. However, it has recently been established that under certain conditions the rate-determining step for longer chain biradicals can switch from ISC to chain dynamics.[51] Although ISC can occur by two major pathways, spin–orbit coupling (SOC) and electron–nuclear hyperfine coupling (HFC), the latter is only expected to be important in cases where the singlet–triplet energy gap is small, as, for example, in biradicals with large separations between the two radical centers.[53] In general, intersystem crossing is expected to be affected by factors such as the singlet–triplet energy gap, the distance between the two radical centers, the nuclear charge, and the orbital orientations. The experimental results that support both the intersystem crossing and chain dynamics mechanisms for controlling biradical lifetimes are discussed below.

Biradical decays do not usually show particularly large temperature dependence, as illustrated by the Arrhenius data for I and II: $\log A = 7.53$, $E_a = 150$ cal mol^{-1} for I in methanol;[10] $\log A = 7.1$, $E_a = 1.33$ kcal mol^{-1} for II in 1:4 benzene–methanol.[31] Neither the activation energies nor the preexponential factors are consistent with product formation as the rate-determining step. For example, for Type II biradicals, the A factors are in the $(1–3) \times 10^7\ s^{-1}$ range whereas those for the forward reaction (i.e., Type II hydrogen abstraction) are typically $10^{11}\ s^{-1}$.[10,13] However, one would expect the transition states for both biradical formation and decay to be similar, particularly since in at least nonpolar solvents, back-reaction is the major biradical decay pathway.[3] Thus, the relatively small temperature dependences have been suggested to reflect ISC control of biradical lifetimes. The observed activation energies incorporate a contribution from the Boltzmann factor necessary to achieve the most favorable conformation for ISC.[10]

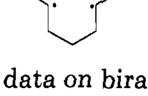

I


II

The decreased biradical lifetimes observed in the presence of free radicals and oxygen are also consistent with the importance of a spin-forbidden process.[6,10] Furthermore, the variations in product ratios that have been observed when the biradicals are generated in the presence of paramagnetic quenchers have also been rationalized in terms of the ISC mechanism.[10,45,54] Thus, the conformation from which ISC occurs is expected to differ when the process involves interaction with a paramagnetic species. If the singlet biradical lifetime is shorter than the time required for bond rotation, the products will then reflect this conformation.

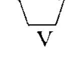
Considerably longer lifetimes are observed for 1,4-Type II and photoenol biradicals in polar solvents.[6] It has been suggested that hydrogen bonding of the biradical with the solvent modifies the biradical conformation and, thus, decreases the ISC rate.[10] The small solvent effects observed for Type I biradicals may be similarly explained. The lack of solvent effect in less polar biradicals is also consistent with this explanation.

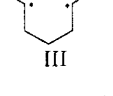
Type I biradicals have considerably shorter lifetimes than similar chain length biradicals without the acyl center.[49] These results have recently been attributed to an increased SOC contribution to ISC as a result of the acyl group.[49] It should also be pointed out that these biradicals contain a σ radical center, unlike most of the other examples, and, to our knowledge, this factor has not been examined. Similarly, the decreased lifetimes for *p*-bromo- and α-hydroxy-substituted biradical III have also been explained on the basis of increased SOC due to the substituents.[52]

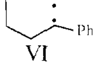

III

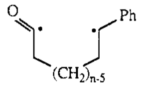
The bulk of the data on biradical lifetimes suggests that, other factors being equal, the lifetimes increase with increasing distance between the radical centers, as expected for the SOC contribution to ISC.[53] For example, the lifetimes for IV, V, III, and VI are 20, 190, 920, and 1080 ns, respectively, in acetonitrile.[52] However, a recent examination of biradicals VII, where *n*


IV


V


III

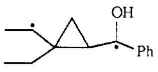

VI



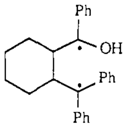
VII; n = 6-12, 15

= 6–12 and 15, in a variety of solvents indicates an increase in biradical lifetime with increasing n up to n = 9, followed by a decrease for larger biradicals.[51] It should be noted that this effect was observed for a variety of solvents of differing polarities and viscosities. The results have been interpreted in terms of the requirement for a nearly cyclic conformation with a small distance between the termini for ISC to occur via the SOC mechanism. The observed lifetime variation parallels data for cyclization rates and, thus, reflects the fraction of biradical conformers with small end-to-end distances.

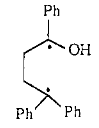
Several reports have attempted to explain the effect of conformation on the lifetimes of 1,4-biradicals. For example, the 22-ns lifetime for biradical VIII is considerably shorter than those for similar less rigid 1,4-biradicals and was attributed to a decreased end-to-end distance.[55] In contrast, biradical IX has a lifetime comparable to that of X despite the rigid conformation and shorter average distance between the biradical termini in the former.[56] It has, however, been argued that the cyclohexane ring in IX effectively prevents the eclipsed conformation in which the distance between the carbon atoms carrying the radical centers is at a minimum;[55] this conformation can be readily achieved by rotation in the case of X. It is clear from the above discussion that no concensus has been reached as to which parameters, in addition to distance between the termini, are of importance in determining biradical lifetimes in constrained systems. An alternative interpretation of the results for VIII in terms of an adiabatic decay process has also been recently suggested.[56b]



VIII



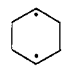
IX



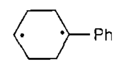
X

Recently, lifetimes for 1,3-cyclopentanediyl (XI), 1,4-cyclohexanediyl (XII), and related biradicals have been estimated by oxygen-trapping experiments.[34,57-59]

XI



XII

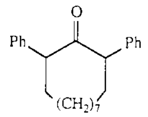


XIII

The observation of an approximately 10-fold increase in lifetime for XI compared to XII has been explained on the basis of conformational effects.[57,58] That is, the orbitals in XI are parallel whereas those in XII (in its boat conformation) are more favorably oriented for ISC, according to Salem's orbital orientation rule.[53] Similar conformational arguments have been used to explain the lengthening of the lifetime by the 1-phenyl substituent in XIII.[34]

Although magnetic field effects on biradical lifetimes have not been detected for small biradicals (e.g., Norrish Type II), they have been observed for VII (n = 10–12).[50a] For these biradicals application of a magnetic field leads to an initial increase in lifetime followed by a decrease at higher fields. The occurrence of magnetic field effects for larger biradicals is readily understood on the basis of a change in the relative contributions of SOC and HFC to the ISC mechanism. For short biradicals SOC is important due to the short end-to-end distance and the large singlet–triplet gap, which minimizes the effect of HFC interactions. However, for larger end-to-end distances, SOC becomes of minor importance and HFC takes over, giving rise to magnetic field effects.[50a] It should be noted that the observed magnetic field effects on biradical-derived CIDNP[48,60] have now been suggested to result only from conformers with large end-to-end distances and, thus, do not reflect the total biradical population.[50a] Another example of magnetic field effects on biradical lifetimes has recently been reported.[50b] In this case anomalously large effects were observed, and further studies are obviously required to establish the generality of these results.

The amount of ^{13}C enrichment has been examined for the recovered starting material and products upon photolysis of 2,11-diphenylcyclododecanone (XIV) and related ketones.[61] The smaller enrichment found in the recovered starting material suggested that the ketone was regenerated primarily from cyclic biradical conformers with short end-to-end distances, for which SOC (which does not lead to ^{13}C enrichment) was the dominant ISC mechanism. On the other hand, the rearranged ketone products were formed mostly from extended conformers that had undergone ISC via the HFC mechanism, which does lead to ^{13}C enrichment, and, therefore, showed substantial ^{13}C enrichment.



XIV

The discussion so far has dealt only with examples that are explainable on the basis of ISC control of biradical lifetimes. However, biradicals VII with n = 9, 12, and 15 have been shown to have strongly curved Arrhenius plots over a +20 to −90 °C temperature range. In the high-temperature region "normal" biradical Arrhenius parameters are observed ($\log (A/s^{-1}) \sim 8.0$ and $E_a \sim 1.0$ kcal mol^{-1}), and the lifetimes are insensitive to viscosity.[51] However, at low temperature the lifetimes are strongly viscosity and temperature dependent, with log A's of 10–11 and E_a's of 3–4 kcal mol^{-1}. It has been suggested that the rate-determining step for biradical decay changes from ISC at high temperatures to chain dynamics (i.e., conversion of extended conformers to cyclic ones from which product formation can occur) at low temperatures. Thus, at lower temperatures for larger biradicals both product formation and ISC are fast relative to chain dynamics. Biradical decay then becomes temperature and viscosity dependent and reflects the decay of an equilibrium mixture of singlets and triplets. However, at high temperature, the Arrhenius parameters are related to the temperature dependence of the conformational equilibrium constant.

The above examples have all discussed factors that control biradical lifetimes in systems where the termini are separated by aliphatic chains. However, we note that π-conjugated biradicals such as the naphthoquinodimethanes often have much longer lifetimes than other biradicals (vide infra). This may be a reflection of an increased singlet–triplet gap due to conjugation

TABLE I. Lifetimes for Type II Biradicals

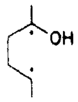
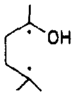
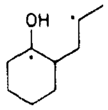
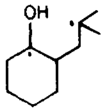
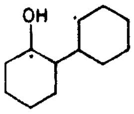
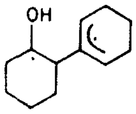
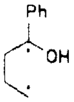
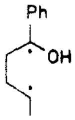
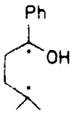
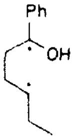
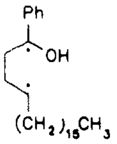
biradical	solvent	T/K	method[a]	τ/ns	ref
	acetonitrile–water	295	lfp, 337 nm, probe	2000	73
	acetonitrile	rt[r]	lgp, 226 nm	42	74
	methanol	rt		48	74
	hexane	rt		30	74
	dichloromethane	rt		33	74
	*acetonitrile*	*rt*	lfp, 266 nm	36	74
	methanol	rt		34	74
	hexane	rt		19	74
	dichloromethane	rt		17	74
 [b]	acetonitrile–water (9:1)	295	lfp, 337 nm, probe	2200	75
 [c]	acetonitrile–water	295	lfp, 337 nm, probe	3030	75
 [d]	acetonitrile–water (9:1)	295	lfp, 337 nm, probe	600	75
 [c]	acetonitrile–water (9:1)	295	lfp, 337 nm, probe	1200	75
	benzene	293	lfp, 347 nm	150	76
	benzene	293	lfp, 347 nm	60	76
		295	lfp, 347 nm	59	77
	methanol	295	lfp, 337 nm, probe	102	46
	acetonitrile–water (9:1)	295		71	46
	methanol	295	lfp, 337 or 266 nm	93	64, 66
	benzene	295		34	64
	cyclohexane	295		38[e]	64
	methanol	298	lfp, 265 nm	103 ± 7	78
	cyclohexane	298		23 ± 3[e]	78
	methanol	295	lfp, 337 nm, probe	97 ± 15	71, 79
	methanol	258–323	lfp, 337 nm, probe	97[f]	46
	acetonitrile–water	295		70	46
	toluene	302.6		25[f]	10
	methanol	295	lfp, 337 nm	97	80
	cyclohexane	295		30[e]	80
	methanol	295	lfp, 337 nm	98	64
	cyclohexane	295		37[e]	64
	acetonitrile–water (8:2)	295	lfp, 337 nm, probe[g]	81	81
	SDS micelles[h]	295	lfp, 337 nm, probe[g]	92 ± 10	82
	methanol	295	lfp, 337 nm, probe	110	46
	*n*-butyl stearate[i]	293	lfp, 266 nm	64 ± 5	83
	n-butyl stearate[j]	303		70 ± 5	83
	n-butyl acetate			68 ± 5	83

TABLE I (Continued)

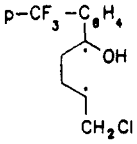
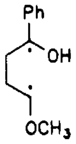
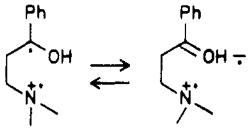
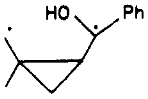
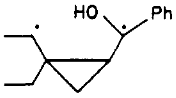
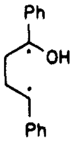
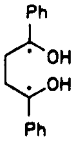
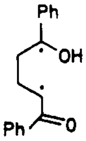
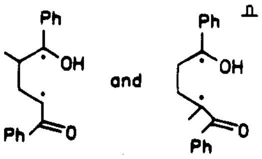
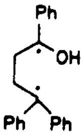
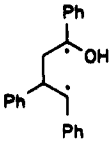
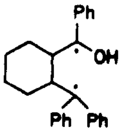
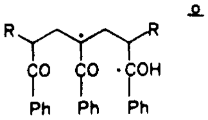
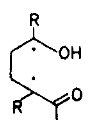
biradical	solvent	T/K	method[a]	τ/ns	ref
	benzene + 0.1 M pyridine	300	lfp, 337 nm	27	84
	methanol	295	lfp, 266 nm	70 ± 5	66
	heptane	295		30 ± 6	66
	water, pH = 11.1	295	lfp, 337 nm, probe	1200[e,k]	85
	water, pH = 8.0	295		2000[e,k]	85
	methanol-water (4:1)	295		2300[e]	85
	methanol	rt	lfp, 308 or 337 nm	~20	55
	methanol	293	lfp, 308 or 337 nm	~20	55
		211		~30	55
		rt	lfp, 308 or 337 nm, probe	~25	55
	methanol	295	lfp, 266 nm	146 ± 18	66
	heptane	295		55 ± 8	66
	methanol-water (2:1)	rt	lfp, 266 nm	125	86
	methanol-water (2:1)	rt		62[l]	86
	methanol	295	lfp, 337 nm, probe	83	46
	acetonitrile-water (9:1)	295	lfp, 337 nm	40[m]	87
 [n]	benzene	295	lfp, 337 nm	27[m]	87
	acetonitrile-water (9:1)	295		47	87
		295	lfp, 337 nm, probe	56	87
	methanol	295	lfp, 266 nm	222 ± 18	66
	heptane	295		113 ± 13	66
	methanol	295	lfp, 266 nm	166 ± 3	56a
	heptane	295		84	56a
	methanol	295	lfp, 266 nm	95	66
	methanol	295	lfp, 266 nm	242 ± 14	56a
	heptane	295	lfp, 266 nm	69 ± 5	56a
	benzene	295	lfp, 347 nm	63[p]	77
		293		60[q]	76
		293	lfp, 337 nm	67[p]	88
		295		76[q]	89

TABLE I (Continued)

biradical	solvent	T/K	method[a]	τ/ns	ref
 [q]	dichloromethane	rt	lfp, 265 nm	40	90

[a] Probe = methylviologen. [b] Φ(Type II biradical) = 0.03. [c] Φ(Type II biradical) = 0.022. [d] Φ(Type II biradical) = 0.02. [e] Lifetimes in other solvents are available in the original reference.[80] [f] See Table X for Arrhenius parameters. [g] Based on electron transfer to various other acceptors as well. [h] In sodium dodecyl sulfate micelles with typical surfactant concentrations of 0.2–0.25 M. [i] Isotropic phase. [j] Smectic phase. [k] Lifetimes at other pHs are available in the original reference and lead to a pK_a of 10.0 in water.[85] [l] Lifetime for the basic form of the biradical. A study of the pH dependence of the biradical lifetime leads to a value of 11.8 for the pK_a in methanol/water (2:1).[86] [m] A lifetime of microseconds has also been reported.[77] [n] The reaction yields a mixture of both species. [o] R = polymer chain. [p] Poly(phenyl vinyl ketone). [q] Polyacrylophenone. [r] rt = room temperature in this table and subsequent tables.

between the radical centers and, thus, a slower rate of ISC.

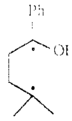
The rest of this review is divided into two main sections dealing with unimolecular and intermolecular biradical processes, respectively.

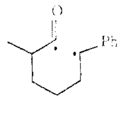
Biradical Spectroscopy and Lifetimes

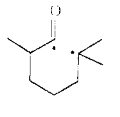
This section deals with the spectroscopy of the biradicals and their lifetimes. The data have been grouped according to the type of biradical that, unless otherwise indicated, is believed to be a triplet species. This does not necessarily mean that the triplet state is the ground state for the biradical but rather that the biradical is initially formed from a triplet and that it is believed to preserve that spin configuration for essentially all its lifetime; i.e., intersystem crossing to the singlet is in many cases followed by rapid collapse to products.

A common feature of the absorption spectra of biradicals is that they resemble very closely monoradical spectra for free radicals with similar characteristics. Thus, the absorption[31] and emission[62] spectra for II are very similar to those for diphenylmethyl radicals.[63]

The same applies to Norrish Type II and Type I biradicals, for which representative structures are shown below (I, XV, and XVI).


I


XV

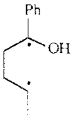

XVI

The absorption characteristics of I,[64] XV,[65] and XVI[67] closely resemble those of acetophenone ketyl,[68] benzyl,[69] and *tert*-butyl,[70] respectively. This similarity between biradicals and free radicals is also frequently reflected by their reactivity (vide infra).

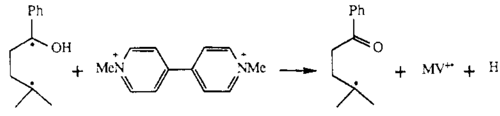
Arrhenius data on biradical decay are treated separately following the various types of biradicals.

Norrish Type II Biradicals

The spectra of the biradicals produced in the Type II reaction (see Scheme I) from aromatic ketones typically show a weak but characteristic band at ~415 nm (e.g., ϵ_{415} = 800 M^{-1} cm^{-1} for I)[64] and a stronger band in the UV region (e.g., λ_{max} at ~320 nm for XVII).[66]


XVII

Biradical lifetimes have been determined by two techniques: (a) *direct detection*, in which the biradical absorption is monitored at a convenient wavelength following laser excitation, and (b) *probe techniques*, in which a product resulting from a reaction of the biradical is the species monitored. The latter technique deserves some comment. The "probe" is a molecule that does not react thermally with the biradical precursor, is sufficiently transparent at the excitation wavelength, and reacts with the biradical to produce a new species that shows a characteristic absorption. Another desirable probe characteristic is that the product of the reaction should be sufficiently long-lived that its decay will not interfere in the kinetic measurements. The most frequently used probe for Type II biradicals is the electron acceptor methylviologen (paraquat), which upon reaction with the biradical yields its readily detectable reduced form.[46,71] The reaction, which takes advantage of the excellent electron-donor ability of the ketyl radical site,[72] is illustrated in reaction 1 for the biradical from γ-methylvalerophenone.[46] As in other


(1)

I MV^{2+} XVIII

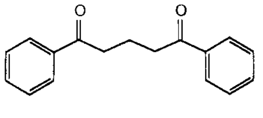
approaches to biradical studies, the biradical precursor (i.e., triplet state) has to be short-lived in comparison with the biradical lifetime. Under these conditions the formation of $MV^{\bullet+}$ follows pseudo-first-order kinetics. The experimental rate constant (k_{expt}) for this growth can be related to the rate constant of interest according to eq 2, where τ_B is the biradical lifetime and k_r is the

$$k_{expt} = \tau_B^{-1} + k_r[MV^{2+}] \qquad (2)$$

rate constant for reaction with the probe. The values of τ_B and k_r are readily obtained from a plot of k_{expt} vs $[MV^{2+}]$. This technique is advantageous when the biradical cannot be detected directly or when its spectroscopic properties are not firmly established. It was widely employed about a decade ago, before direct biradical studies became common. Naturally, the same measurements yield values of k_r, and the technique is widely used for this purpose (vide infra).

The lifetimes of Norrish Type II biradicals are summarized in Table I. In the case of the biradical from γ-methylvalerophenone, there have been extensive studies of the solvent dependence of its lifetime; a few representative values have been included in Table I, but the reader is referred to the original literature for an extensive compilation.[80] Measured lifetimes for I range from 16 ns in dibromomethane to 121 ns in pyridine. For hydrogen-bonding solvents there is a clear increase of the lifetimes with increasing hydrogen-bonding ability of the solvent. As already pointed out, the lifetimes are largely temperature independent. For biradicals derived from aromatic ketones the lifetimes are generally <200 ns.

In some cases the triplet lifetimes are sufficiently long that they interfere with studies of biradical decay. I.e., biradical formation is not sufficiently rapid compared with its own lifetime. In some of these cases it is possible to "tune" the triplet lifetime to a sufficiently short value by adding an efficient triplet quencher. The technique solves the problem at the expense of signal intensity and can only be used when the experiment can tolerate considerable signal attenuation. For example, the technique has been used for XIX.[87]

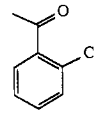


XIX

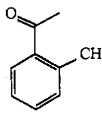
The pK_A of the Norrish Type II biradical derived from γ-phenylbutyrophenone has been determined by monitoring the biradical lifetime as a function of pH.[86] The similarity between the pK_A values for the biradical and the acetophenone ketyl radical provides additional support for the essentially independent behavior of the two biradical termini.

Photoenol Biradicals

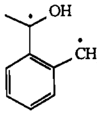
The photolysis of *o*-alkyl aromatic ketones yields biradicals and enols. The process involves complex transient phenomena that have been the subject of considerable confusion in the literature. Simple cases, such as *o*-methylacetophenone, have been understood for a number of years,[24] but for more substituted and hindered ketones, a detailed understanding of their photobehavior has been published only recently.[26] For example, in the case of *o*-methylacetophenone the transients involved include two kinetically distinct triplets (XXa and XXb), one biradical (XXI), and two enols (XXIIa and XXIIb).[25] All these species can be trapped and/or detected directly. In addition, it is reasonable to assume that two short-lived (and as yet undetected) singlets are also involved. The lifetime of the syn enol XXIIa is always shorter than that for the anti enol XXIIb and both are solvent dependent. Hydrogen bonding by solvents tends to stabilize the enols and leads to longer lifetimes than in nonpolar media. The probe technique mentioned earlier proved useful in the understanding of the complex transient phenomena in this system, since lifetime measurements do not depend on a precise understanding of the spectroscopy, although they do require some hindsight as to the lifetime of precursors (i.e., triplets) and possible reactivity of products (i.e., enols) with the probe used.



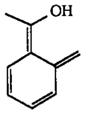
XXa



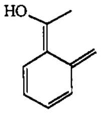
XXb



XXI



XXIIa



XXIIb

The lifetimes of photoenol biradicals compiled in Table II have been measured by both direct and probe techniques. Those biradicals for which absorption spectra are available typically exhibit λ_{max} at 320–330 nm, in good agreement with the spectra for related ketyl radicals.[68,105] For biradical XXIII there is also a long-wavelength band at 535 nm.[95]

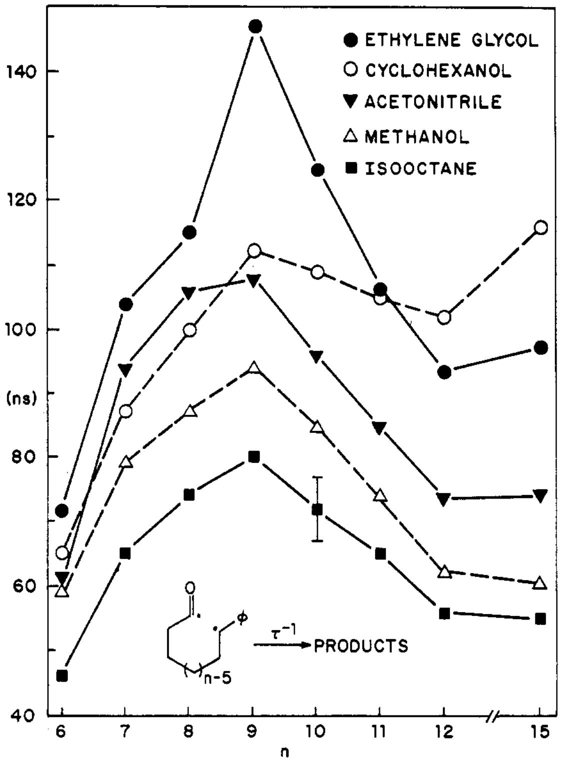
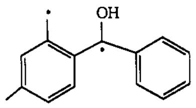


Figure 1. Lifetimes of biradicals VII as a function of chain length and solvent at 20 °C. Reprinted from ref 49; copyright 1985 American Chemical Society.



XXIII

The lifetimes for some of the biradicals in Table II are considerably longer than those for the related Type II biradicals, which are typically ≤200 ns. In this regard it may be worth noting again that the biradical is also the triplet state of the photoenol and that its lifetime may be controlled by factors similar to those that determine the lifetimes of polyene triplets.

It should be noted that the previous biradical assignment for 2,4,6-triisopropylbenzophenone[100] has now been revised.[26] The biradical from this ketone does not have a 5-μs lifetime in acetonitrile but, rather, is too short-lived (<100 ns) to be detectable in the presence of long-lived triplet and enol transients. Similarly long lifetimes for 4′-substituted 2,4,6-triisopropylbenzophenones are presumably also in error.[101,102]

1,*n*-Biradicals (*n* ≠ 4) Produced by Intramolecular Hydrogen Abstraction

The reactions that lead to these biradicals are analogous to the Norrish Type II process. In general, abstraction at the γ-position leading to a 1,4-biradical is favored. However, the biradicals in Table III are produced by abstractions at other positions, reflecting either the absence of γ-hydrogens or conformational or enthalpic factors that make γ-hydrogen abstraction unfavorable. It is interesting that the four 1,5-biradicals

TABLE II. Lifetimes for 1,4-Photoenol Biradicals

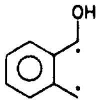
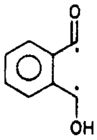
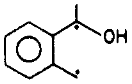
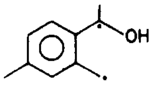
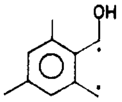
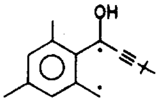
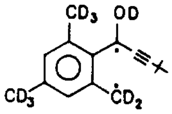
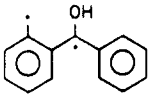
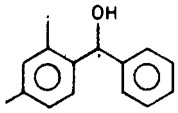
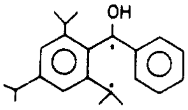
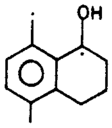
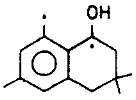
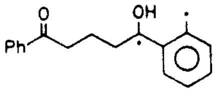
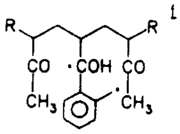
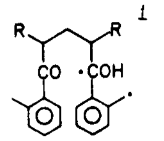
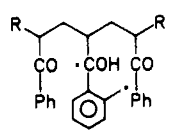
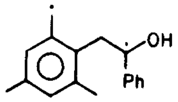
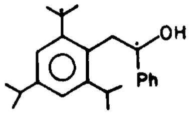
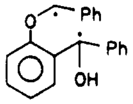
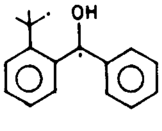
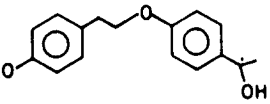
biradical	solvent	T/K	method[a]	τ/ns	ref
	acetonitrile–water	295	lfp, 337 nm, P1	1500	25
	toluene	295	lfp, 337 nm, P2	310	91
	methanol	295	lfp, 337 nm, P1	1600	92
	cyclohexane	295	lfp, 353 or 265 nm	150[b]	93
	methanol	295		1200[c]	93
	cyclohexane	295	lfp, 265 or 353 nm	130	95
	acetonitrile	295		830	95
	methanol	295		900[c]	95
	methanol	295	lfp, 337 nm, P1	300 ± 40	96
	acetonitrile–water (4:1)	295	lfp, 337 nm, P1	580	25
	methanol	300	lfp, 337 nm	480[d]	97
	toluene	295	lfp, 337 nm, P2	310	91
	2-propanol	295	lfp, 353 or 265 nm	1300[b]	93
	cyclohexane	295		700[b]	93
	acetonitrile–water (4:1)	295	lfp, 337 nm, P1	1100	25
	methanol	rt	lfp, 308 or 353 nm	38 ± 4	98
		220	lfp, 308 nm	ca. 50	98
		rt	lfp, 353 nm, P1	37 ± 2	98
	heptane	rt	lfp, 353 nm	44 ± 5	98
	acetonitrile–water (4:1)	295	lfp, 337 nm, P1	24	25
	ethanol	295	lfp, 347 nm	26	99
	ethanol	295	lfp, 265 or 353 nm	28[b]	93
	cyclohexane	295		38[b]	93
	methanol	295	lfp, 265 or 353 nm	30	95
	cyclohexane	295		30	95
	acetonitrile	295	lfp, 266 nm	*e*	100
	acetonitrile–water (4:1)	295	lfp, 337 nm, P1	930	25
	cyclohexane	295	lfp, 265 or 353 nm	230	95
	tetrahydrofuran	295		5000	95
	acetonitrile	295		3500	95
	methanol	295		5000	95
	water	295		3300	95
	acetonitrile–water (9:1)	295	lfp, 337 nm, P1	435	87
 [f]	methanol–acetone–acetonitrile (40:30:30)	295	lfp, 337 nm, P1	370	103
		295	lfp, 337 nm, P1	310	103
	benzene	295	lfp, 337 nm	320	103

TABLE II (Continued)

biradical	solvent	T/K	method[a]	τ/ns	ref
 [f]	toluene-d_8 benzene	300 300	lfp, 337 nm lfp, 337 nm	200[d] 200[g]	10 88
 [f,h]	benzene	293	lfp, 337 nm	75[i] 160[j] 250[k]	88 88 88

[a] Probes used: P1 = methylviologen; P2 = β-carotene. [b] Kinetics are taken from ref 93 using the revised transient assignments from ref 94. [c] Lifetimes in other solvents are also available in the original reference. [d] See Table X for Arrhenius parameters; see ref 104 for a related study. [e] The transient previously assigned[100] to this biradical has been shown to be the enol.[26] Similar transients for 4′-substituted triisopropylbenzophenones[101,102] are also assumed to be enols. Biradicals probably have lifetimes <<100 ns, which make them undetectable in the presence of long-lived triplet and enol signals.[26] [f] R = polymer chain. [g] Polymer molecular weight ≃ 200000. [h] Copolymers of phenyl vinyl ketone and o-tolyl vinyl ketone (TVK) with different monomer ratios. [i] 1% TVK. [j] 3% TVK. [k] 11% TVK.

TABLE III. Lifetimes for 1,n-Biradicals ($n \neq 4$) Produced by Intramolecular Hydrogen Abstraction

biradical	solvent	T/K	method	τ/ns	ref
	various[a]	rt	lfp, 337 nm	15	106
	various[a]	rt	lfp, 337 nm	40–50	106
	benzene + pyridine	rt	lfp	13	107
	methanol diethyl ether freon 113 *tert*-butyl alcohol 50% aq dioxane[b]	183–299 rt rt rt rt	lfp, 308 nm	43 ± 3 20 <6 24 32	108 108 108 108 108
	acetonitrile 2-propanol benzene dioxane	295 295 295 295	lfp, 308 nm lfp, 308 nm lfp, 308 nm lfp, 308 nm	116 85 100 147	109 109 109 109

[a] Original reference quotes the same biradical lifetimes in various solvents.[106] [b] Lifetimes in other solvents are given in the original reference.[108]

in Table III have somewhat shorter lifetimes than many 1,4-biradicals (see Table I). However, we note that these four examples have at least some bonds that can force a cisoid structure and also have resonance structures corresponding to a 1,3-biradical configuration.

The last example in Table III is unusual in that it involves abstraction from an O–H bond by a π,π^* carbonyl triplet.[109] While hydrogen abstraction is a typical reaction of $^3n,\pi^*$ states, in the case of phenols it is now well established that $^3\pi,\pi^*$ states will also react quite readily.[110]

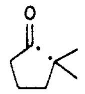
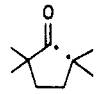
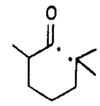
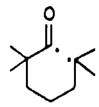
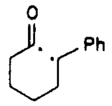
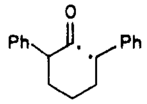
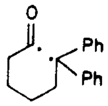
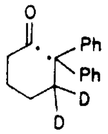
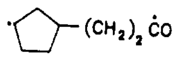
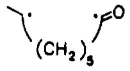
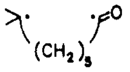
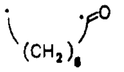
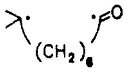
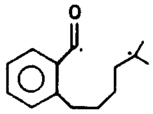
Norrish Type I Biradicals

This section deals with those systems where the Norrish Type I reaction (see Scheme III) is not followed by rapid loss of carbon monoxide. The reader should also see the section on α,ω-1,n-diyls, which includes examples of biradicals formed following loss of carbon monoxide.

The absorption spectra of these biradicals resemble closely those of the corresponding radical sites. Thus, the spectra for the series of biradicals VII[50] are in line with those of typical benzylic radicals,[69] while studies of XVI and related biradicals have taken advantage of the similarities between their spectra and that of the *tert*-butyl radical.[67,70]

The lifetimes for Type I acyl–alkyl biradicals are listed in Table IV. These generally fall within the 10–100-ns range and show less solvent dependence than Type II or photoenol biradicals. As discussed in a previous section, the study of these biradicals has contributed significantly to our understanding of the ways in which chain length, temperature, solvent viscosity, and magnetic field effects determine biradical lifetimes.[49–51] Only the parent biradical (XV) is listed in

TABLE IV. Lifetimes for Type I Biradicals

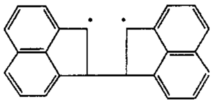
biradical	solvent	T/K	method	τ/ns	ref
	methanol	300	lfp, 308 nm	11 (±15%)	67
	isooctane	300		10 (±15%)	67
	methanol	300	lfp, 308 nm	14 (±15%)	67
	isooctane	300		13 (±15%)	67
	methanol	300	lfp, 308 nm	37 (±10%)	67
	isooctane	300		31 (±10%)	67
	methanol	300	lfp, 308 nm	45 (±10%)	67
	isooctane	300		36 (±10%)	67
	methanol	300	lfp, 308 nm	65 ± 4[a]	67
		298	lfp, 248 nm	58 ± 6[a]	49
		rt	lfp, 266 nm	50 (±5%)	56
	isooctane	300	lfp, 308 nm	47 ± 4	67
	heptane	rt	lfp, 266 nm	49 (±5%)	65
	methanol	190	lfp, 248 nm	121 ± 10	49
	methanol	rt	lfp, 265 nm	66.7 (±2%)	65
	heptane	rt		56.2 (±2%)	65
	methanol	rt	lfp, 265 nm	67.6 (±2%)	65
	heptane	rt		57.1 (±2%)	65
	not given	rt	CIDNP[b]	77 (±20%)	111
	not given	rt	CIDNP[b]	100 (±20%)	111
	not given	rt	CIDNP[b]	130 (±20%)	111
	not given	rt	CIDNP[b]	100 (±20%)	111
	not given	rt	CIDNP[b]	83 (±20%)	111
	dimethyl-d_6 sulfoxide–D_2O (4:1 (w/w))	303	CIDNP[b]	188 ± 4	112

[a] Arrhenius parameters are given in Table X. [b] Time-resolved CIDNP.

Table IV, as the effects of chain length are best illustrated pictorially (see Figure 1).[49]

α,ω-1,*n*-Diyls

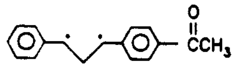
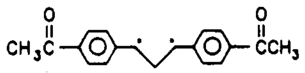
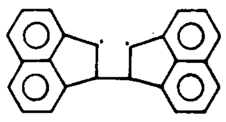
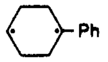
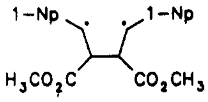
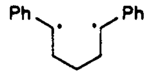
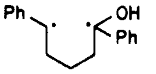
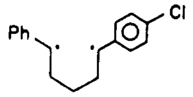
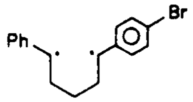
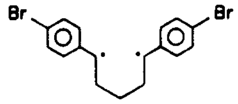
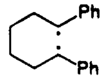
These biradicals are generally produced by α-cleavage of ketones (Scheme III) or sulfones, followed by loss of carbon monoxide or sulfur dioxide, respectively, or by photoinduced ring opening (Scheme V). Their absorption spectra are again very similar to those of the individual benzyl, diphenylmethyl, or naphthylmethyl radical centers. For example, biradical XXIV has λ_{max} at 379 nm[113] compared to 370 nm for the 1-naphthylmethyl radical in benzene.[114]



XXIV

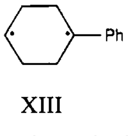
The lifetimes for α,ω-1,*n*-diyls are listed in Table V. These biradicals provide several examples of the substantial effect of chain length on biradical lifetimes. It remains to be demonstrated whether or not the maximum lifetime will occur for intermediate-sized (1,8 → 1,10) biradicals, as has been observed for 1,*n*-Type I biradicals.[49] Also of interest are the effects of bromine

TABLE V. Lifetimes for α,ω-1,n-Diyl Biradicals

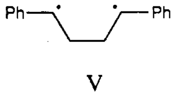
biradical	precursor	solvent	T/K	method	τ/ns	ref
	azoalkane	cyclohexane matrix	40[a]	SESR	3.4 ± 10^{11}	115
	cyclopropane	heptane	rt	lfp, 266 nm	15 ± 1	36
	cyclopropane	heptane	rt	lfp, 266 nm	14.7 ± 1	36
		methanol	rt		13.4 ± 1	36
	sulfone[b,c]	acetonitrile	rt	lfp, 312 nm	20 ± 4	52
	ketone	acetonitrile	298	lfp, 308 nm	190 (±5%)	52
	ketone	benzene–methanol (1:3)	rt	lfp, 308 or 337 nm	500 ± 100	31
	*trans*-acenaphthylene dimer[d]	benzene	293	lfp, 347 nm	330[e]	113
		bromobenzene	293		150	35
		pyridine	293		290	35
		1,4-dioxane	293		270[f]	35
	azoalkane[d]	benzene	rt	lfp, 351 nm	275 ± 15	34
		acetonitrile	rt		248 ± 15	34
	cyclobutane[d]	acetonitrile	295	lfp, 347 nm	220	118
	ketone or sulfone[b]	acetonitrile	298	lfp, 347 nm	920 ± 50	49
		methanol	298		900 ± 50	49
	ketone	methanol	298	lfp, 308 nm	360 (±5%)	52
		acetonitrile	298		320 (±5%)	52
		isooctane	298		60 (±5%)	52
	ketone	methanol	298	lfp, 308 nm	910 (±5%)	52
	ketone	methanol	298	lfp, 308 nm	280 (±5%)	52
		isooctane	298		280 (±5%)	52
	ketone	methanol	298	lfp, 308 nm	190 (±5%)	52
	ketone	benzene	300	lfp, 308 or 337 nm	900 ± 200	31
		benzene–methanol (1:4)	300		900 ± 200	31
	sulfone[a]	acetonitrile	298	lfp, 308 nm	1080 ± 50	49

[a] Rate constants for biradical decay at lower temperatures are also given in ref 115; a related study is reported in ref 116. [b] Acetone sensitized. [c] Data quoted in a footnote as preliminary experiments. [d] Benzophenone sensitized. [e] See Table X for Arrhenius data. [f] Lifetimes in other solvents are also listed in ref 113 and 117.

and α-hydroxy substitution on biradical III.[53] The lifetime of III-α-OH is considerably shorter than that of III and shows a strong temperature dependence reminescent of that for Type II biradicals. Biradical XIII is noteworthy as one of the first examples of the direct detection of a biradical in which the two termini are confined to a single ring.[34] Comparison with the related acyclic biradical V indicates that this does not have a particularly large effect.[52]



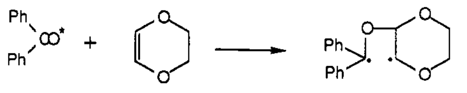
XIII



V

Paterno–Buchi Biradicals

Several 1,4-Paterno–Buchi biradicals have been produced as intermediates in the cycloaddition of triplet ketones to olefins, as illustrated in reaction 3.[119,120]

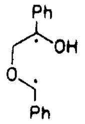
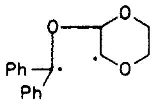
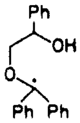
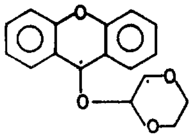


(3)

XXV

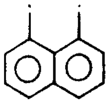
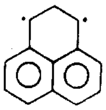
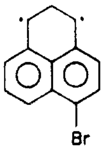
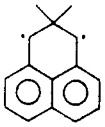
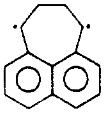
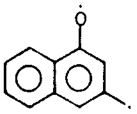
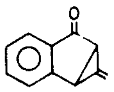
The absorption spectrum of XXV is virtually identical with that for the ketyl radical from benzophenone,[105] thus providing another example where

TABLE VI. Rate Constants for Intramolecular Decay of Paterno–Buchi Biradicals

biradical	solvent	T/K	method	τ/ns	ref
	methanol heptane	295 295	lfp, 266 nm^{a}	1.3 1.7	66 66
	acetonitrile + 1 M dioxene	295	ps, 355 nm^{b}	1.6 ± 0.2	119, 120
	methanol heptane	295 295	lfp, 266 nm^{a}	4.9 ± 1.5 6.4 ± 1.6	66 66
	acetonitrile + 1 M dioxene	rt	ps, 355 nm^{b}	6.7 ± 2.2	119

[a] Biradical produced by intramolecular Type II hydrogen abstraction. [b] Biradical produced from ketone plus olefin.

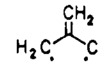
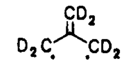
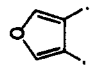
TABLE VII. Lifetimes for Naphthoquinodimethane and Related Biradicals

biradical	precursor	solvent	T/K	method	τ	ref
	diazo	hexafluorobenzene^{a} iodobenzene^{a} 2-methyltetrahydrofuran^{a}	118 118	KESR	164 ± 8 s^{b} 141 ± 6 s 208 ± 13 s	126 126 126
	hydrocarbon	1-pentanol^{a} solid polyethylene	134 134	KESR or UV UV/IR/ESR^{e}	15 ms^{b-d} 29 ms^{b,c}	127 129
	hydrocarbon	solid polyethylene	134	UV/IR/ESR^{e}	1.7 ms^{b,c}	129
	azo compound^{f} or hydrocarbon^{f}	benzene	rt	lfp, 353 nm	400 μs^{b}	130
	azo compound^{g}	h methylene bromide 0.2 M dimethylmercury in methanol	rt rt rt	lfp	200 ± 20 μs^{b,f} 20 μs 30 μs	128 128 128
 (singlet)		cyclohexane benzene acetonitrile	rt rt rt	ps, 355 nm	250 ± 100 ps 750 ± 350 ps 2.74 ± 1.1 ns	131 131 131

[a] Matrix. [b] See Table X for Arrhenius data. [c] Calculated from quoted Arrhenius parameters. [d] Biradical was originally assigned as a singlet from ESR experiments[127] but was later shown to be a triplet.[128] [e] Based on disappearance of UV, IR, and ESR signals of biradical as well as the apperance of product signals, under conditions where phenalene is the only product. [f] Benzophenone sensitized. [g] Direct or benzophenone sensitized. [h] Lifetime reported as 200 ± 20 μs in various solvents.

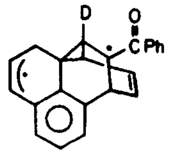
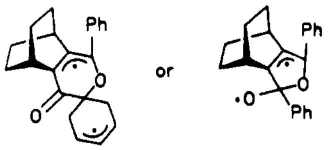
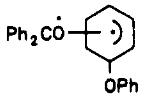
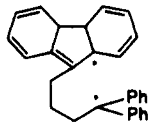
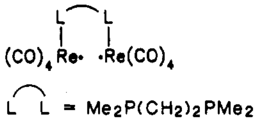
radical sites in biradicals show the same absorption properties as the same centers in monoradicals. The lifetimes of several Paterno–Buchi biradicals are summarized in Table VI. The short lifetime of these biradicals relative to other 1,4-biradicals appears to be a direct result of the presence of an oxygen atom between the termini. Four reasons have been cited as being possibly responsible for these short lifetimes: (a) large spin–orbit coupling resulting from radical interaction with oxygen;[120] (b) smaller singlet–triplet splitting due to the presence of two phenyl rings;[120] (c) reduced end-to-end distance due to contribution from the resonance structure shown in eq 4,[66] (d) reduced end-to-end distance due to reduced nonbonded interactions

TABLE VIII. Lifetimes for Trimethylenemethane and Related Biradicals

biradical	precursor	solvent	T/K	method	τ	ref
	neat	trimethylenecyclopropane[a]	135	SESR, γ-irr	530 s[b]	134
	neat	trimethylenecyclopropane-d_6[a]	135	SESR, γ-irr	510 s[b]	134
 (singlet)	diazene	chloroform-d	283	lfp, 355 nm	3-4 μs[c,d]	138

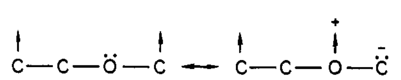
[a] Matrix. [b] Calculated from Arrhenius parameters; see Table X. [c] Singlet nature of this biradical has been confirmed by NMR.[139] [d] Lifetime may be controlled by adventitious residual oxygen.

TABLE IX. Lifetimes for Miscellaneous Biradicals

biradical	precursor	solvent	T/K	method	τ/ns	ref
 [a]	*b*	benzene	280–350	lfp, 353 nm	15	143
 [c]	*d*	methanol	295	lfp, 337 nm	16000 ± 2000	145
	*e*	diphenyl ether	295	lfp, 337 nm	13000	146
	*f*	benzene acetonitrile	rt rt	lfp, 308 + 337 nm	1100 ± 100 900 ± 100	62 62
	Re–Re cleavage			lfp, 337 nm		
L L = $Me_2P(CH_2)_2PMe_2$		decalin	rt		12	147
$Ph_2P(CH_2)_2PPh_2$		decalin	rt		36	147
cis-$Ph_2PCH{=}CHPPh_2$		decalin	rt		130	147
$Ph_2P(CH_2)_3PPh_2$		decalin	rt		36	147
$Ph_2P(CH_2)_4PPh_2$		decalin	rt		97	147
		toluene	rt		42	147
		tetrahydrofuran[g]	rt		28	147
$Ph_2P(CH_2)_5PPh_2$		decalin	rt		67	147
$Cy_2P(CH_2)_2PCy_2$		decalin	rt		290	147
		toluene	rt		130	147
		tetrahydrofuran[g]	rt		45	147

[a] Tentative transient assignment confirmed in ref 144. [b] From 8-benzoyl-9-deuterionaphtho[*de*-2,3,4]bicyclo[3.2.2]nona-2,6,8-triene. [c] Tentative transient assignment. [d] 2,3-Dibenzocyclo[2.2.2]oct-2-ene. [e] Benzophenone plus diphenyl ether. [f] Photorearrangement of $Ph_2\dot{C}(CH_2)_3\dot{C}Ph_2$. [f] Other solvents given in original reference.[147]

in the case of oxygen as compared with CH_2[31] (similar effects are well-known in free radical chemistry).[121,122]

 (4)

Among these effects, effect b is unlikely to be of importance, since increased delocalization does not normally reduce the lifetimes (vide supra). Nonbonded effects such as in effect d probably play a role, since there is no apparent reason why conformational effects present in monoradical and excited-state processes[123] involving end-to-end interactions would be absent in biradical systems. Effects a and c possibly play a role since both effects (SOC and end-to-end distance) are common factors determining biradical lifetimes. No experiments that could separate effects a and c from effect d have to date been reported.

It should be noted that an earlier report of a ~10-μs lifetime for biradical XXVI[124] has been shown to be incorrect.[125] The species detected in these experiments was $Ph_2\dot{C}OH$, not XXVI.

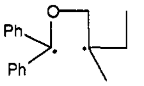
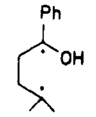
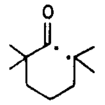
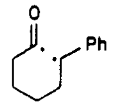
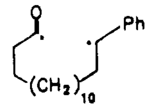
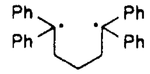
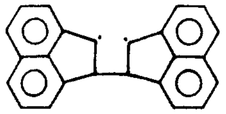
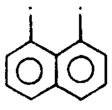
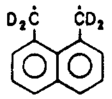
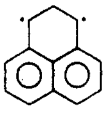
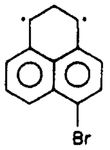
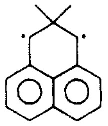
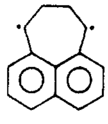
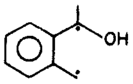
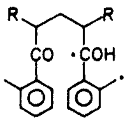
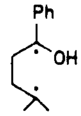
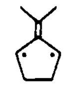
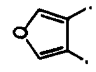
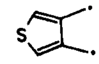
 XXVI

TABLE X. Arrhenius Parameters for Intramolecular Biradical Decay

biradical	solvent	method[a]	T/K	E_a/(kcal mol^{-1})	log (A/s^{-1})	ref
	methanol	lfp, probe	258–323	0.0 ± 0.03	7.01	146
	methanol	lfp	216–358	0.15 ± 0.15	7.20 ± 0.1	10
	toluene-d_8	lfp	216–358	0.04 ± 0.15	7.53 ± 0.15	10
	methanol	lfp	203–327	1.36 ± 0.3	8.4 ± 0.2	67
	methanol	lfp	197–329	1.19 ± 0.13	8.2 ± 0.1	67
	methanol	lfp	183–293	0.8 ± 0.2	7.7 ± 0.3	51
 [b]	methanol	lfp	263–293	1.1 ± 0.2	8.1 ± 0.3	51
	methanol	lfp	183–220	4.0 ± 0.2	10.8 ± 0.3	51
	methanol	lfp	233–333	0.85 ± 0.15	6.7 ± 0.2	49
	benzene–methanol (1:4)	lfp	213–314	1.33 ± 0.59	7.1 ± 0.5	31
	benzene[c]	lfp	279–337	0.29	6.28	113
	hexafluorobenzene[d]	KESR	110–125	6.4 ± 0.3	10.4 ± 0.4	126
	hexafluorobenzene[d]	KESR	118–134	6.0 ± 0.5	8.7 ± 0.7	126
	1-pentanol[d]	KESR	119–134	4.5 ± 0.6	4.5 ± 1	127
	solid polyethylene	UV/IR/ESR[e]	120–160	5.3 ± 1	5.1 ± 1	129
			10–100[f]	0.0 ± 0.1	-6.1 ± 0.5	129
	solid polyethylene	UV/IR/ESR[e]	120–160	5.5 ± 0.5	6.2 ± 0.5	129
			10–100[g]	0	-5.4 ± 0.5	129
	glycerol	lfp	238–273	6.84 ± 0.16	8.4 ± 0.15	130
	glycerol	lfp	298–348	1.1 ± 0.1	6.9 ± 0.3	128
	methanol	lfp	198–320	1.63	7.51	97
	toluene-d_8	lfp		~0.5		10

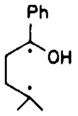
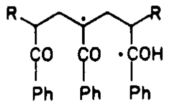
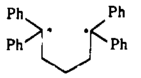
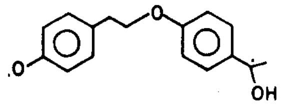
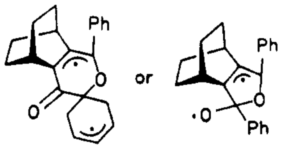
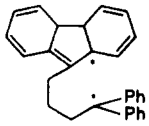
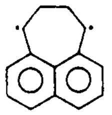
[a] Probe = methylviologen dication. [b] Arrhenius data for analogous 1,n-biradicals (n = 9, 12) in methanol and isooctane over high (263–293 K) and low 183–223 K) temperature ranges are given in ref 51. [c] Additional temperature-dependent results are given in a table in ref 117. [d] Matrix. [e] Results based on disappearance of UV, IR, and ESR signals for biradical and for appearance of product signals. Experiments were carried out under conditions where phenalene was the only product. [f] A temperature-independent region was also observed for the 2-d_2 biradical for which $k = 10^{-9.2\pm0.5}$ s^{-1}, giving k_H/k_D = 1300.[129] [g] A temperature-independent was also observed for the 2-d_2 biradical for which $k = 10^{-8.5\pm0.5}$ s^{-1}, giving k_H/k_D = 1300.[129]

TABLE XI. Rate Constants for Bimolecular Self-Reaction of Biradicals

biradical	source	products	solvent	T/K	method	$2k/(M^{-1}\ s^{-1})$	ref
	Type II	unknown	methanol	298	lfp, 337 nm	10^{10}	10
	diazene	dimers	2-propanol–1-propanol (3:2)	143.5	KESR	$(2.0 \pm 0.8) \times 10^3$	137
			2-propanol–1-propanol (3:2)[a]	143.6	KESR	(2.2 [illegible] 1.3) × 10^3	136
	diazene	dimers	acetonitrile	263	lfp, 337 nm	3.3×10^{10}	159
(singlet)			toluene	263		1.6×10^{10}	159
	diazene	dimers	acetonitrile	263	lfp, 337 nm	9.3×10^9	159
(singlet)			toluene	263		5.5×10^9	159

[a] η = 2000 cP.

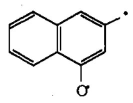
TABLE XII. Rate Constants for the Interaction of Triplet Biradicals with Ground-State Doublets in Solution at Room Temperature

biradical	source	quencher	solvent	method	$k_q/(M^{-1}\ s^{-1})$	ref
	Type II	$Bu^t_2NO^\bullet$	methanol	lfp, 337 nm	2.5×10^9	54
			methanol	lfp, 337 nm	1.94×10^9	10
			benzene	lfp, 337 nm	1.2×10^9	54
		$Cu(acac)_2$	methanol	lfp, 337 nm	1.98×10^9	160
			acetonitrile–water (9:1)	lfp, 337 nm	5×10^8	160
	Type II	$Bu^t_2NO^\bullet$	benzene	lfp, 337 nm	7.5×10^{8} [a]	89
		$NO^\bullet$	benzene	lfp, 337 nm	1.7×10^{7} [a,b]	89
	Type I	$Bu^t_2NO^\bullet$	benzene	lfp, 308 or 337 nm	$(2.1 \pm 0.3) \times 10^9$	31
	Type I	$Bu^t_2NO^\bullet$	benzene	lfp, 308 or 337 nm	$(1.36 \pm 0.03) \times 10^9$	31
	remote H abstraction	TEMPO	*c*	lfp, 337 nm	3.2×10^9	109
	photorearrangement	$Bu^t_2NO^\bullet$	methanol	lfp, 337 nm	1.8×10^{9} [d]	145
	photorearrangement of $Ph_2\dot{C}(CH_2)_3\dot{C}Ph_2$	$Bu^t_2NO^\bullet$	benzene	lfp, 308 + 337 nm	$(1.25 \pm 0.04) \times 10^{9}$ [d]	62
	cleavage of azoalkane	$NO^\bullet$	methanol[e]	lfp	$(2.5 \pm 0.5) \times 10^{10}$	128

[a] Polyacrylophenone, MW = 1.3×10^5. [b] Based on τ = 59 ns for a partial pressure P_{NO} = 39 Torr. [c] Unpublished; no solvent given in original report. [d] Tentative assignment of structure. [e] Solvent assumed to be methanol based on other experiments in the same report.

Naphthoquinodimethane and Related Species

These biradicals have usually been generated by either direct or sensitized photolysis of azo compounds or strained hydrocarbons. Some of the naphthoquinodimethanes (Table VII) have been examined only at low temperature. Those for which spectra are available[128,130] show λ_{max} at approximately 340 nm, which is somewhat shifted from that of the 1-naphthylmethyl radical.[114] Both singlet and triplet biradical spectra have been reported for biradical XXVII;[131,132] for the singlet λ_{max}



XXVII

TABLE XIII. Rate Constants for the Interaction of Biradicals with Oxygen in Solution at Room Temperature

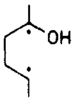
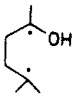
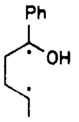
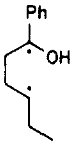
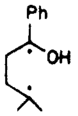
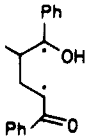
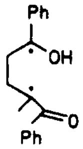
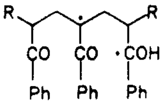
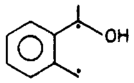
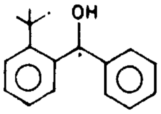
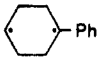
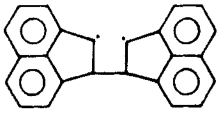
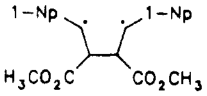
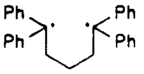
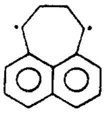
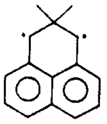
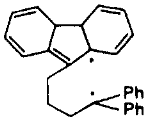
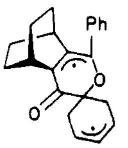
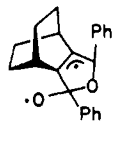
biradical	source	solvent	method	$k_{O_2}/(M^{-1}\ s^{-1})$	ref
	Type II	methanol hexane[b]	lfp, 226 nm	4.2×10^{10} [a] 1.5×10^{10} [a]	74 74
	Type II	methanol hexane[b]	lfp, 266 nm	3.9×10^{10} [a] 1.6×10^{10} [a]	74 74
	Type II	methanol	lfp, 337 nm	6.2×10^{9}	46
	Type II	methanol	lfp, 337 nm	6.2×10^{9}	46
	Type II	methanol	lfp, 337 nm, probe lfp, 347 nm	6.5×10^{9} 6.7×10^{9}	162 64
 and 	Type II	acetonitrile–water	lfp, 337 nm	6.8×10^{9}	87
	Type II	benzene	lfp, 337 nm	1×10^{9} [c]	89
	photoenolization	methanol cyclohexane	lfp, 337 nm fp	4.6×10^{9} 1.3×10^{9}	96 94
	1,5-H abstraction	methanol	lfp, 308 nm	$\sim 7 \times 10^{9}$ [a]	108
	sensitized cleavage of azoalkane	acetonitrile benzene	lfp, 351 nm	$(2.2 \pm 0.2) \times 10^{10}$ $(1.6 \pm 0.1) \times 10^{10}$	34 34
	sensitized ring cleavage	benzene	lfp, 347 nm	9×10^{9}	113
	sensitized ring cleavage	acetonitrile	lfp, 347 nm	2.1×10^{10}	118
	Type I	benzene	lfp, 308 or 337 nm	$\sim 5 \times 10^{9}$ [a]	31
	cleavage of azoalkane	methanol[d]	lfp	$(1.3 \pm 0.3) \times 10^{10}$	128
	sensitized cleavage of azoalkane	benzene	lfp, 353 nm	$\sim 1 \times 10^{9}$ [a]	130
	photorearrangement of $Ph_2\dot{C}(CH_3)_2\dot{C}Ph_2$	benzene	lfp, 308 + 337 nm	$\sim 5 \times 10^{9}$ [a]	62

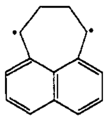
TABLE XIII (Continued)

biradical	source	solvent	method	k_{O_2}/(M^{-1} s^{-1})	ref
 or 	photorearrangement	methanol	lfp, 337 nm	5.7×10^8 [e]	145

[a] Based on a single oxygen concentration. [b] Rate constants in other solvents are also available. [c] For polyacrylophenone with MW = 1.3×10^5. [d] Solvent assumed to be methanol based on other experiments in the same report. [e] Transient assignment tentative.

is 490 nm in cyclohexane and <450 nm in acetonitrile[131] while the triplet is shifted to longer wavelength (λ_{max} at 437, 404, and 500 nm).[132] Again the spectra are not those expected for the individual radical centers.[133]

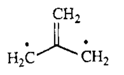
The lifetimes for naphthoquinodimethane biradicals are unusually long (>100 μs) in solution at room temperature. Although it may be tempting to attribute these lifetimes to steric hindrance to product formation, the substantially shorter lifetime for XXVIII in a heavy-atom solvent suggests that ISC is still an important factor.[128] Possibly an increased singlet–triplet gap resulting from communication between the two radical centers leads to a slower ISC rate. In contrast to the naphthoquinodimethanes, singlet XXVII has a lifetime of ~1 ns in a variety of solvents. In this case, the lifetime is determined by ISC to the triplet biradical, which has been reported to be stable on a nanosecond time scale.[131]



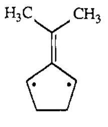
XXVIII

Trimethylenemethane and Related (Non-Kekulé) Biradicals

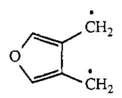
Included in this group are biradicals such as XXIX–XXXI. Trimethylenemethane biradicals (e.g., XXIX and XXX)[134-137] have been examined by using steady-state ESR techniques, and their decay can be dominated by first-order (XXIX) or second-order (XXX) processes. The lifetime data available for XXIX and its deuterated analogue are included in Table VIII.[140]



XXIX



XXX



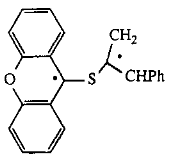
XXXI

Biradical XXXI has been established to have a ground-state singlet.[139] Its absorption spectrum shows λ_{max} ~560 nm;[138] no monoradicals of similar structure appear to have been reported, but it would be rather surprising if they absorbed at such a long wavelength.

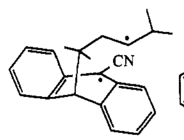
Miscellaneous Biradicals

A variety of biradicals that do not fit into any of the foregoing categories are compiled in Table IX. For many of these, the transient assignment should be regarded as tentative. The rhenium-centered biradicals are particularly interesting since they provide one of the first examples of direct detection of metal-centered biradicals.

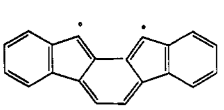
Several other tentative biradical assignments have been reported in the literature; among these we find that XXXII–XXXIV could be interesting subjects for further study.[148-150]



XXXII



XXXIII



XXXIV

Temperature Dependence of Biradical Lifetimes

The Arrhenius parameters for biradical decay have only been examined in a few cases and have been summarized in Table X. As already discussed in an earlier section, the low activation energies and *A* factors frequently reflect the importance of intersystem crossing processes in determining biradical lifetimes.

It should be noted that some of the Arrhenius data have been acquired over relatively narrow temperature ranges (see Table X); in these cases, the linearity of the plot could be limited to a small temperature range, and extrapolation of the data outside the measurement range may not be justified. Matrix effects may play a role in some cases. For example, some of the low-temperature data over small temperature ranges provide the only examples of relatively high activation energies (see Table X).

Indirect Determination of Biradical Lifetimes

Numerous competitive studies of biradical reactions have been reported in the literature.[2,3,7,13] While these are not the subject of this review, there are two main reasons for presenting a few examples: First, competitive studies have played a crucial role in leading to our current understanding of biradical mechanisms and kinetics. Indeed, for biradicals that have not been detected directly, competitive techniques (e.g., using oxygen trapping; vide infra) remain extremely useful. Second, competitive studies that have been carried out under conditions that match or closely approach those of the time-resolved work can be used to obtain absolute rates by combination of the two types of data.

In 1972, Wagner et al.[151,152] reported the trapping of the Norrish Type II biradicals from valerophenone

TABLE XIV. Electron-Transfer Reactions of Triplet Biradicals

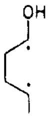
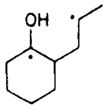
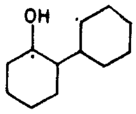
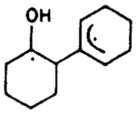
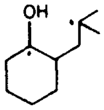
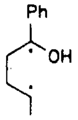
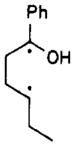
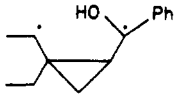
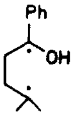
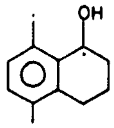
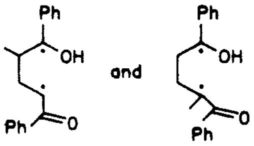
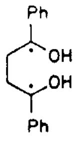
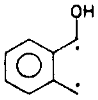
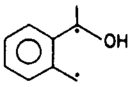
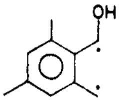
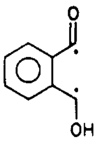
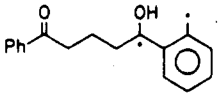
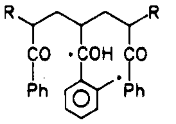
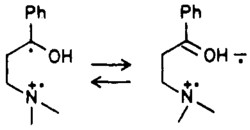
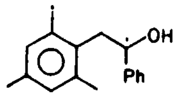
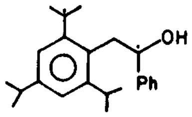
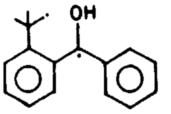
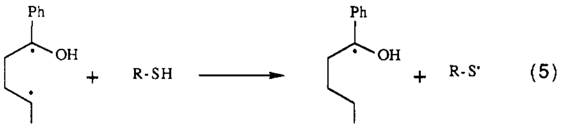
biradical	source	electron acceptor	solvent	T/K	method	$k_{et}/(M^{-1}\ s^{-1})$	ref
	Type II	MV^{2+}	acetonitrile–water (9:1)	295	lfp, 337 nm	3.7×10^9	73
		INA^+	acetonitrile–water (9:1)	295	lfp, 337 nm	1×10^9	73
	Type II	MV^{2+}	acetonitrile–water (9:1)	295	lfp, 337 nm	3.6×10^9	75
	Type II	MV^{2+}	acetonitrile–water	295	lfp, 337 nm	5.5×10^9	75
	Type II	MV^{2+}	acetonitrile–water (9:1)	295	lfp, 337 nm	2.7×10^9	75
	Type II	MV^{2+}	acetonitrile–water (9:1)	295	lfp, 337 nm	4.2×10^9	75
	Type II	MV^{2+}	methanol	295	lfp, 337 nm	3.6×10^9	46
			acetonitrile–water (9:1)	295	lfp, 337 nm	2.4×10^9	46
	Type II	MV^{2+}	methanol	295	lfp, 337 nm	3.5×10^9	46
	Type II	MV^{2+}	methanol	rt	lfp, 308 or 337 nm	3.8×10^9	55
	Type II	BPY^{2+}	acetonitrile–water (8:2)	295	lfp, 337 nm	1.4×10^9	81
		MV^{2+}	methanol	295	lfp, 337 nm	3.8×10^{9} [a]	46
		MV^{2+}	methanol	295	lfp, 337 nm	$(4.6 \pm 1.0) \times 10^{9}$ [b]	71
		MV^{2+}	acetonitrile–water (8:2)	295	lfp, 337 nm	3.2×10^9	81
		MV^{2+}	acetonitrile–water (9:1)	295	lfp, 337 nm	2.4×10^9	46
		HV^{2+}	acetonitrile–water (8:2)	295	lfp, 337 nm	4.0×10^9	81
		BV^{2+}	acetonitrile–water (8:2)	295	lfp, 337 nm	3.9×10^9	81
		DQ^{2+}	acetonitrile–water (8:2)	295	lfp, 337 nm	2.6×10^9	81
		DNBA	acetonitrile–water (8:2)	295	lfp, 337 nm	7.6×10^8	81
		INA^+	acetonitrile–water (8:2)	295	lfp, 337 nm	1.7×10^8	81
		PhN_2^+	methanol	300	lfp, 337 nm	$(3.3 \pm 0.5) \times 10^9$	164
		$PMBO^+$	methanol	300	lfp, 337 nm	$(5.5 \pm 1.8) \times 10^9$	164
	Type II	MV^{2+}	acetonitrile–water (4:1)	295	lfp, 337 nm	5.6×10^9	25
	Type II	MV^{2+}	acetonitrile–water (9:1)	295	lfp, 337 nm	4.2×10^9	87
	Type II	MV^{2+}	methanol	295	lfp, 337 nm	9×10^9	46
	photoenolization	MV^{2+}	acetonitrile–water	295	lfp, 337 nm	6.2×10^9	25

TABLE XIV (Continued)

biradical	source	electron acceptor	solvent	T/K	method	k_{et}/(M^{-1} s^{-1})	ref
	photoenolization	MV^{2+}	methanol	295	lfp, 337 nm	$(4.8 \pm 1.0) \times 10^9$	25, 96
			acetonitrile–water (4:1)	295	lfp, 337 nm	6.5×10^9	25
		INA^+	acetonitrile–water (4:1)	295	lfp, 337 nm	4.9×10^9	25
	photoenolization	MV^{2+}	acetonitrile–water (4:1)	295	lfp, 337 nm	5.2×10^9	25
	photoenolization	MV^{2+}	methanol	295	lfp, 337 nm	7.6×10^8	92
	photoenolization	MV^{2+}	acetonitrile–water (9:1)	295	lfp, 337 nm	6×10^9	87
	photoenolization	MV^{2+}	methanol–acetone–acetonitrile (4:3:3)	295	lfp, 337 nm	1.7×10^9 [d]	103
	intramolecular electron transfer	BPY^{2+}	methanol–water (4:1), 0.1 M AcOH	295	lfp, 337 nm	7.5×10^9	85
		MV^{2+}	water, pH = 11.1	295	lfp, 337 nm	4.7×10^9	85
			water, pH = 10.3			3.8×10^9	85
			water, pH = 9.6		06	2.5×10^9	85
			water, pH = 9.0			1.8×10^9	85
			water, pH = 8.0			1.7×10^9	85
		MV^{2+}	methanol–water (4:1), 0.1 M AcOH	295	lfp, 337 nm	9.0×10^8	85
			methanol–water (4:1)	295	lfp, 337 nm	9.6×10^8	85
			methanol–water (4:1), 0.1 M NaOAc	295	lfp, 337 nm	2.0×10^9	85
		INA^+	methanol–water (4:1), 0.1 M NaOH	295	lfp, 337 nm	1.9×10^9	85
		BV^{2+}	water, pH = 11.1	295	lfp, 337 nm	3.6×10^9	85
			water, pH = 8.0			1.4×10^9	85
			methanol–water (4:1), 0.1 M NaOAc	295	lfp, 337 nm	2.0×10^9	85
		DNBA	water, pH = 11.1	295	lfp, 337 nm	3.6×10^9	85
			methanol–water (4:1), 0.1 M NaOH	295	lpf, 337 nm	3.2×10^9	85
	intramolecular H abstraction	MV^{2+}	not given	rt	lfp, 337 nm	$>10^9$	106
	intramolecular H abstraction	MV^{2+}	not given	rt	lfp, 337 nm	$>10^9$	106
	intramolecular H abstraction	MV^{2+}	methanol	rt	lfp, 337 nm	9×10^8	108

[a] See Table XVII for Arrhenius parameters. [b] See ref 165 for quantum yield data. [c] Two-step trapping; the second step (i.e., monoradical trapping) occurs with $k_{et} = 4.8 \times 10^9$ M^{-1} s^{-1}. [d] Copolymer of methyl vinyl ketone and *o*-tolyl vinyl ketone containing 15% of the latter.

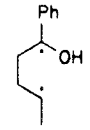
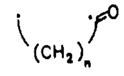
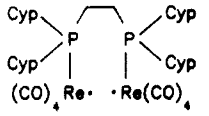
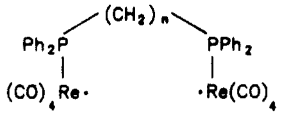
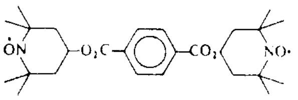
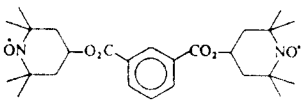
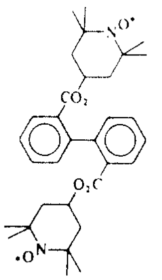
(XVII) and γ-methoxyvalerophenone by thiols according to reaction 5. Thus, biradical trapping by thiols



XVII XXXV

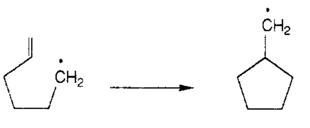
leads to XXXV and as a result prevents the formation of normal Type II products such as acetophenone. Quenching studies based on reaction 5 led to $k_5\tau_B = 1.8$ M^{-1} for valerophenone in benzene containing pyridine, where τ_B is the biradical lifetime. On the basis of the limited knowledge on radical trapping by thiols, the authors estimated $\tau_B \sim 1$ μs. This lifetime is about an order of magnitude longer than values obtained by laser flash photolysis (see Table I). It should be noted that time-resolved studies of the same system have shown that the difference was entirely due to the uncertainty on the estimation of k_5.[153]

TABLE XV. Intermolecular Atom-Transfer Reactions of Biradicals

biradical	source	atom donor[a]	solvent	method	$k_q/(M^{-1}\ s^{-1})$	ref
	Type II	$n\text{-}C_8H_{17}S\mathit{H}$	benzene with 1.2 M pyridine	lfp, 337 nm	1.13×10^{7} [b]	153
	Type II	$n\text{-}C_8H_{17}S\mathit{H}$	benzene with 1.2 M pyridine	lfp, 337 nm	9.0×10^{6} [b]	153
		$(n\text{-}C_4H_9)_3Sn\mathit{H}$	benzene with 1.2 M pyridine	lfp, 337 nm	1.1×10^{6} [b]	153
 n=6,7,8,10	Type I	$(CH_3)_3CS\mathit{H}$	dichloromethane	CIDNP	5.0×10^{7}	166
	Re–Re cleavage	$C\mathit{Cl}_4$		lfp, 337 nm	1.6×10^{8} [b]	147
		$CH_2\mathit{Br}_2$		lfp, 337 nm	1.8×10^{7} [b]	147
	Re–Re cleavage	$C\mathit{Cl}_4$		lfp, 337 nm	5.4×10^{8} ($n = 3$)[b]	147
				lfp, 337 nm	9.3×10^{8} ($n = 4$)[b]	147
		$CH_2\mathit{Br}_2$		lfp, 337 nm	2.2×10^{8} ($n = 3$)[b]	147
					2.9×10^{8} ($n = 4$)[b]	147
	persistent	$PhCH_2CH_3$	ethylbenzene	ESR	6.45×10^{-6} [c]	167
	persistent	$PhCH_2CH_3$	ethylbenzene	ESR	6.45×10^{-6} [c]	167
	persistent	$PhCH_2CH_3$	ethylbenzene	ESR	1.6×10^{-5} [c]	167

[a] Atom transferred is italicized. [b] Room temperature. [c] 400 K; Arrhenius data in Table XVII.

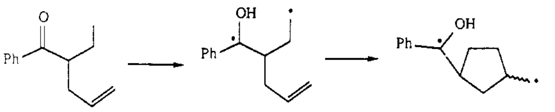
Radical clocks[154] are widely used in kinetic studies in free radical chemistry. If the assumption that radical centers in biradicals and in monoradicals show the same reactivity is valid, then it should be possible to incorporate these features (i.e., biradical reactivity and a radical clock) into the same molecule. These ideas have been used in a number of cases, which we would like to illustrate with an example reported by Wagner and Liu.[155] 5-Hexenyl radicals are known to cyclize to cyclopentylmethyl radicals (reaction 6) in a process for which the kinetics have been examined in detail.[156]



XXXVI XXXVII (6)

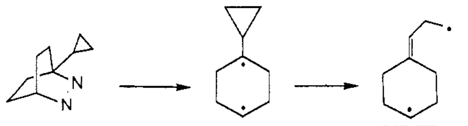
The biradical from α-alkylbutyrophenone (XXXVIII) incorporates the same features as XXXVI and undergoes the Type II reaction or cyclizes according to reaction 7.[155]

From a study of the reaction products it was possible to estimate a biradical lifetime of ca. 300 ns.



XXXVIII XXXIX XL (7)

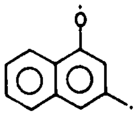
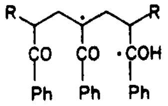
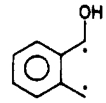
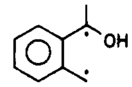
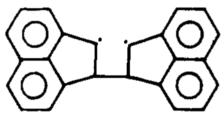
A second example of the use of the radical clock approach is provided by the direct and sensitized photolysis of azo compound XLI to generate biradical XLII, which can then undergo cyclopropylcarbinyl rearrangement to XLIII (reaction 8).[157,158] A combination of product ratios and a rate of rearrangement based on measurements for similar monoradicals allowed estimates of lifetimes of ≤2.3 and 28 ns for singlet and triplet XLII, respectively.[157] Additional trapping experiments suggested a lifetime of 360 ns for XLIII.[158] However, the authors have noted that a number of assumptions are involved in determining these numbers.



XLI XLII XLIII (8)

Recently, Adam, Wilson, et al. have reported the use of quantitative oxygen-trapping techniques in determining lifetimes for alkyl biradicals that are not readily

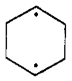
TABLE XVI. Miscellaneous Intermolecular Reactions of Biradicals

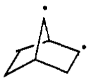
biradical[a]	source	scavenger	solvent	T/K	method	k_q/(M^{-1} s^{-1})	ref
 (singlet)	diazene	$CH_2{=}CHCN$	hexane	285	ps fluorescence	8×10^8	141
	diazene		2-propanol-1-propanol (3:2)[b]	143.5	KESR	0.16	136, 137
		trans-$CH_3O_2CCH{=}CHCO_2CH_3$				3.2	137
		trans-$NCCH{=}CHCN$				1.0	137
		$PhCH{=}CH_2$				0.12	136, 137
		$CH_2{=}CHCN$				0.21[c]	136, 137
 (singlet)	rearrangement	CH_3OH	not given	rt		3.6×10^8	131
	Type II	SO_2	benzene	295	lfp, 337 nm	9×10^8 [d]	89
	photoenolization	β-carotene	toluene	295	lfp, 337 nm	4.1×10^9 [e]	91
	photoenolization	β-carotene	toluene	295	lfp, 337 nm	4.1×10^9 [e]	91
	sensitized ring cleavage	C_2H_5I	benzene	293	lfp, 347 nm	6×10^6	35
		$(C_2H_5)_2Hg$	benzene	293	lfp, 347 nm	3.7×10^7	35

[a] Triplet unless otherwise indicated. [b] η = 2000 cP at 143.5 K. [c] See Table XVII for Arrhenius data. [d] Polyacrylophenone, MW = 1.3×10^5. [e] Energy transfer.

detectable by spectroscopic methods.[34,58-59] The technique requires the measurement of product ratios as a function of oxygen concentrations as well as the rate constant for reaction (both by chemical trapping and assisted intersystem crossing) of the biradical with oxygen.[57] Lifetimes for biradicals XI and XII have been estimated as 115 ± 20 and 10–20 ns, respectively,[58] whereas XLIV was not trappable, suggesting that its lifetime is <0.1 ns.[57,58] The variation in lifetime has been rationalized on the basis of conformational effects which prevent the proper orbital orientation required for ISC via the SOC mechanism.[57,58] The technique has also been recently used to estimate lifetimes for biradicals XLV (X = CH_2, $CH_2{=}C$, 1,1-cyclopropyl), all of which are substantially shorter-lived than XI.[59]

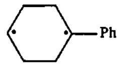

XI


XII


XLIV

XLV

Although oxygen trapping has provided a number of biradical lifetimes that are not easily measured by direct techniques, the selection of the rate constant for reaction of oxygen (k_{O_2}) with the biradical can cause a wide variation in the values obtained. We note that there is excellent agreement between the lifetimes measured for XIII by the direct (243 ± 15 ns) and trapping (280 ± 40 ns) methods.[34] However, in this case k_{O_2} was measured directly, thus eliminating one substantial source of error.



XIII

Intermolecular Biradical Reactions

This section deals with various types of biradical reactions that have been classified by the type of reactivity rather than by the type of biradical as in earlier sections. Among the processes listed, biradical self-reaction is the only one that depends upon the knowledge of the extinction coefficient for the biradical.

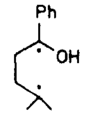
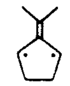
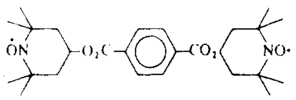
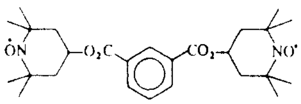
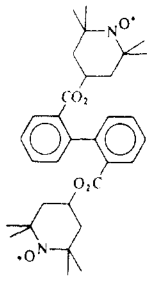
Biradical Self-Reactions

Self-reactions of biradicals have been examined in very few examples, which are summarized in Table XI.

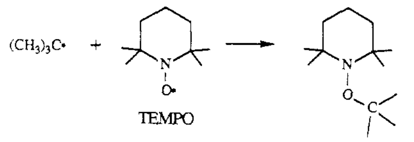
Interaction of Biradicals with Paramagnetic Substrates

Biradicals show a high reactivity toward paramagnetic substrates such as oxygen, nitroxides, and Cu(II) derivatives. While essentially all other intermolecular reactions of biradicals appear to reflect the reactivity of the individual free radical centers (vide supra), their

TABLE XVII. Arrhenius Parameters for Intermolecular Biradical Reactions

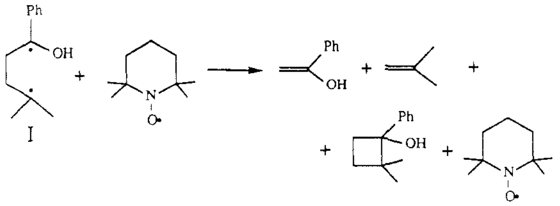
biradical	scavenger	solvent	method	T/K	E_a/ (kcal mol^{-1})	log (A/ (M^{-1} s^{-1}))	ref
	$Bu^t_2NO^\bullet$	methanol	lfp	210–333	1.7 ± 0.2	10.53 ± 0.1	10
	MV^{2+}	methanol	lfp	258–323	2.5	11.4	46
	$CH_2{=}CHCN$	2-propanol-1-propanol (3:2)	KESR	120.8–143.5	6.3	8.9	137
				120.8–143.6	6.0	8.7	136
	$PhCH_2CH_3$	ethylbenzene	ESR	373–463	15.5	3.3	167
	$PhCH_2CH_3$	ethylbenzene	ESR	373–463	15.5	3.3	167
	$PhCH_2CH_3$	ethylbenzene	ESR	373–433	9.99	0.68	167

interaction with paramagnetic centers is exceptional in that the reactivity usually has a different origin than that for the corresponding monoradicals (see Table XII). For example, in the case of a nitroxide such as TEMPO, its reactivity toward monoradicals is the direct consequence of C–O bond formation.[161] For example, in the case of the *tert*-butyl radical



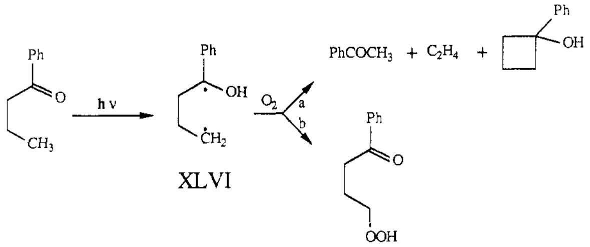
(9)

In contrast with this behavior, the interaction of TEMPO with biradicals frequently leads to assisted intersystem crossing accompanied by a shortening of the biradical lifetime and some changes in product distribution.[10] Normally the nitroxide quencher is not incorporated into the products. For example, in the case of γ-methylvalerophenone (note the presence of a *tert*-alkyl center)[10,54]



(10)

In this sense, the paramagnetic quencher is simply a catalyst for the reaction. Even oxygen frequently behaves in this manner (see Table XIII). In the case of biradicals derived from a series of phenyl alkyl ketones, the products are a mixture of normal Type II products and a hydroperoxide produced by chemical trapping by oxygen; e.g., in the case of butyrophenone[47]



(11)

It was observed that in all the systems examined the products resulting from reaction paths a and b were formed in a 3:1 ratio.[47] It has been suggested that the product ratio is determined by spin selection rules, i.e., path a reflecting triplet encounters and path b reflecting singlet encounters. In a triplet–triplet encounter, spin statistics lead to $^1/_9$ singlets, $^3/_9$ triplets, and $^5/_9$ quintets; this last group of encounters is believed to be dissociative.[47] While spin statistical control appears to apply for Norrish Type II biradicals, there are other systems where oxygen chemical trapping is essentially quantitative.[57]

In the case of the Norrish Type II reaction, paramagnetic quenchers also change the cyclobutanol-to-fragmentation ratio, generally favoring cyclobutanols. It has been suggested that the products from 1,4-biradicals reflect the conformation at which intersystem crossing occurs (i.e., singlet biradicals may be short-lived in the time scale for bond rotation).[10,160]

Electron-Transfer Reactions of Biradicals

This type of reaction represents the largest group of biradical processes examined. The biradicals generated in intramolecular abstraction by excited carbonyl compounds are excellent electron donors, reflecting the presence of a ketyl radical site.[72] Reaction 12 illustrates

(12)

the reaction of a ketyl site with the electron acceptor methylviologen, MV^{2+} (see Chart I).[72] The reduced form, $MV^{\bullet+}$ has two strong absorption maxima at 398 and 603 nm and is readily detectable in flash photolysis experiments.[163] Table XIV summarizes the values reported for various electron-transfer reactions of biradicals, while Chart I shows the structures and abbreviations for the electron acceptors employed. The reader may be surprised by the abundance of data for MV^{2+}, which, in fact, is rather uninformative, since most numbers for simple systems are quite similar. Most of these data were obtained while determining biradical lifetimes using electron-transfer techniques and are a byproduct of these studies. Just as in the case of other studies involving diamagnetic quenchers, biradical reactivities are comparable with those for free radicals having the same radical sites.

Biradical zwitterions derived from β-(dimethylamino)propiophenone behave similarly to Norrish Type II biradicals.[85] Their reactivity is pH dependent, and this characteristic has been employed as a probe to determine a pK_a of 10.0 for the biradical.

Intermolecular Atom-Transfer Reactions of Biradicals

In the case of biradicals with carbon-centered radical sites, only the reactions of Type II biradicals with the S–H and Sn–H bonds have been examined.[153] The essential conclusion that arises from these results is that radical centers in biradicals react with atom donors, in particular hydrogen donors, with similar kinetics to monoradicals with comparable radical sites. For example, the biradical from γ-methylvalerophenone (tertiary site) and the *tert*-butyl radical react with Bu_3SnH with rate constants of 1.1×10^6 and 1.8×10^6 M^{-1} s^{-1}. The same conclusion can be derived from the reactivity toward thiols as well as from studies of electron transfer (vide supra) and intramolecular rearrangements. This characteristic of biradical behavior can and has been used to estimate biradical lifetimes from competitive studies.

Table XV summarizes the limited data available on atom-transfer reactions. The data on nitroxide systems have been obtained by steady-state techniques since these are stable biradicals.

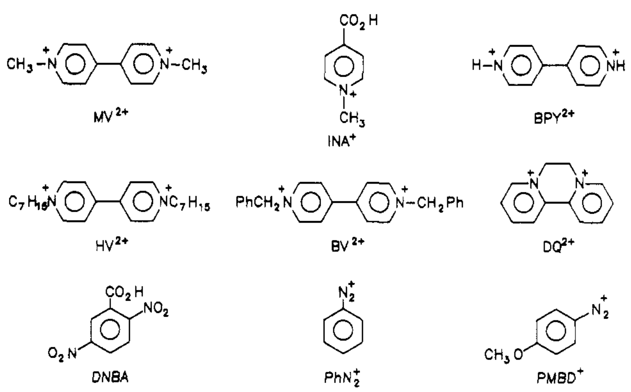
Miscellaneous Intermolecular Reactions of Biradicals

In addition to the reactions illustrated above, biradicals undergo a variety of other reactions, which include additions to unsaturated systems. For example, Type II biradicals add to SO_2.[89] While there are no kinetic studies of addition of Type II biradicals to C=C bonds, their ability to initiate vinyl polymerization has been demonstrated.[168]

Biradicals of the trimethylenemethane type (see Table XVI) add quite readily to unsaturated systems leading to cycloadducts.[2,136,137]

The interaction of biradicals derived from photoenolization reactions with β-carotene is particularly interesting.[91] While other reactions of these species are dominated by their radical-like properties, the reaction with β-carotene involves triplet energy transfer to yield the triplet state of the acceptor. This demonstrates that photoenol biradicals and triplet enols are indeed the same intermediates. Further, the β-carotene reaction puts a lower limit of 19 kcal mol^{-1} for the triplet energy of the enol.[169]

CHART I



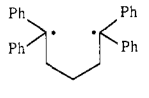
Temperature Dependence of Intermolecular Biradical Reactions

The limited information available is summarized in Table XVII. We note that in the case of the reaction of the biradical from γ-methylvalerophenone (I) with methylviologen, the reaction is very fast and the Arrhenius parameters may partially reflect the diffusional parameters of the solvent. The last three entries in Table XVII are stable biradicals.

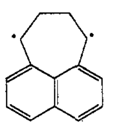
Conclusions and Final Comments

In spite of the 17 tables included in this review, an understanding of some aspects of the chemistry of biradicals remains very limited. Some techniques for their study have only been applied to a few examples, which mostly serve to establish their usefulness.

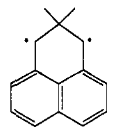
Excited biradicals have not been covered in this review, but a few examples have been reported in the past few years. The wide use of lasers has triggered considerable interest in photochemical processes involving sequential absorption of two photons.[170] In particular, the fluorescence spectra and lifetimes have been reported for II,[62] XXVIII,[128] XLVII,[130] and XXX.[141]



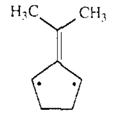
II



XXVIII



XLVII



XXX

The excited biradical II* has a lifetime of 2.5 ns in solution at room temperature, and its fluorescence spectrum is very similar to that for diphenylmethyl radicals.[62] Fluorescence lifetimes of 190 (77 K), 560 (77 K), and 0.28 ns (room temperature) have been reported for XXVIII,[128] XLVII,[130] and XXX,[141] respectively.

Singlet biradicals remain as elusive as ever, and while most reactions of triplet biradicals involve ISC to the singlets, the latter have usually escaped detection. A notable exception has recently been provided by Berson's characterization of several biradicals with singlet ground states.[138,159] As part of this project Zilm et al. have succeeded in recording for the first time the ^{13}C NMR spectrum of matrix-isolated XXXI.[139] Information of this type would be extremely useful in a wide range of examples.

Closs and Redwine have recently reported time-resolved CIDNP studies of Norrish Type I biradicals (see Table IV) with 25-ns resolution.[111] This technique adds new possibilities in the study of the kinetics of biradical reactions and hopefully will be applied to other systems, in particular those where the biradical does not contain a suitable chromophore for optical detection.

The study of magnetic field effects, which has already been discussed in this review, has added a new dimension to biradical work.[50] These studies provide unique insights into the mechanisms by which ISC occurs as the possibilities for end-to-end approach change due to chain length and/or media effects.

In conclusion, a large volume of data on biradical lifetimes and reactivities has been obtained by time-resolved spectroscopic techniques. However, it should also be pointed out that kinetic data alone are not sufficient to completely understand the chemistry in any particular biradical reaction. A variety of product and trapping studies also contribute to the final mechanistic picture. The challenges for future time-resolved work include extending our knowledge of those systems such as trimethylenemethanes and saturated hydrocarbon-derived biradicals that have not yet been extensively examined spectroscopically at room temperature as well as finding systems that produce biradicals designed to answer some of the remaining questions on what determines biradical lifetimes.

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