

## INTERSYSTEM CROSSING IN ORGANIC PHOTOCHEMICAL INTERMEDIATES

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**Abstract** - The lifetimes of a number of olefin triplets and triplet biradicals have been determined by nanosecond laser flash spectroscopy. Examples were chosen in an attempt to segregate structural features which affect intersystem crossing rates and thus determine the lifetimes. For olefin triplets, the effects of constraint to planarity, of substitution at the twisted bond for twisted triplets, of deuterium, and of polar substituents are presented. For biradicals, the main examples are derived from the Norrish II photoreaction of alkanophenones, and effects of substituent and conformational constraint are discussed. Including Norrish I biradicals of cyclohexanones, examples from zero to four carbons between the termini have been studied.

### INTRODUCTION

Photochemical reactions proceeding through triplet states of organic molecules in general involve two intersystem crossing steps. The first normally occurs in a spectroscopic state of the excited photoreactant (or photosensitizer) and is as well understood as most elementary photochemical events. The second step will in most cases occur at a point at which triplet ( $T_1$ ) and ground singlet ( $S_0$ ) surfaces approach one another closely in energy so that any energy deficit can be as small as possible. These latter geometries are termed "biradical" by most chemists if the unpaired electrons are in essentially isolated orbitals and "biradicaloid" if they are not.

Such species are now familiar intermediates in a host of organic photo-reactions, such as the Norrish I photoreactions of cyclic alkanones, Norrish II reactions of alkanophenones, triplet-state carbocyclic photoadditions, and sensitized (triplet-state) olefin *cis-trans* isomerizations among others. Until the last seven or eight years, however, they had proved elusive to detect, yielding best to indirect probes such as inference from product structures and quantum yields.

The inability to detect such species of course made studies of their lifetimes and properties more difficult and represented a gap in our general understanding of triplet state processes. The gap is particularly critical because biradical decay closely precedes product formation and is thus likely to influence the distribution, stereochemistry, regiochemistry, and efficiency of formation of photoproducts.

In 1977, Scaiano (1,2) showed that simple Norrish II biradicals were amenable to study by laser flash photolysis techniques. The Norrish II biradicals from simple valerophenone derivatives could be detected either indirectly (1) as one-electron reductant precursors to the highly colored reduced methyl viologen, or directly (2) by a near UV/VIS absorption identical to that for analogous known monoradical ketyls. Such an advance gave confidence that triplet biradicals and related species could be studied systematically and paved the way for future advances in understanding of their properties.

Also in 1977, we began a systematic study of biradicals and olefin triplets. Our approach was (and remains) to synthesize appropriate series of precursors which would permit the direct detection of the species insofar as possible and which would allow segregation of various possible structural effects from one another.

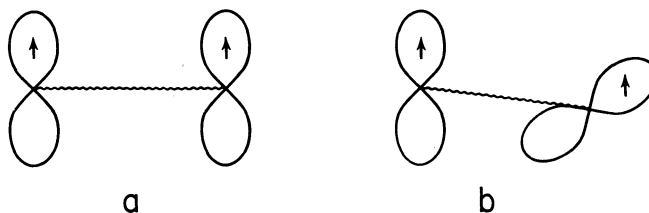
We have been guided so far by the work of Salem and Rowland (3) and of Shaik and Epiotis (4) regarding what effects might be important. In this paper we shall first briefly discuss what theory suggests, and why, before proceeding to a discussion of experiment.

### Energy gap considerations

Radiationless transitions occur more readily when the two states approach one another more closely. In the  $T_1-S_0$  process of aromatic hydrocarbons, this has been accounted for quantitatively by a dependence of Franck-Condon factor on  $E_T$  (5). The importance of vibrations involving hydrogen was demonstrated by substantial deuterium isotope effects on phosphorescence lifetimes (5). For (1,n) biradicals, average singlet-triplet energy gaps are expected to be very small, and indeed CIDNP studies clearly demonstrate that they are  $< 2 \text{ cm}^{-1}$  for  $n > 7$  (6). Franck-Condon factors in such a case must not be significantly different from unity, since bond strengths and vibrational frequencies are not likely to differ much between singlet and triplet biradical. The energy gap between singlet and triplet may still enter, however, since the weak mutual perturbation of the zero-order states will depend inversely on energy gap. The expected direction of the effect is the same in either case, i.e., a lifetime increase with increasing energy gap.

### Orbital orientation

El-Sayed's Rules (7) have long been used to rationalize the singlet and triplet lifetimes of  $n, \pi$  and  $\pi, \pi^*$  ketones and azines. Qualitatively they may be summarized as mandating a more rapid spin-forbidden process when the transition is between states which differ in orbital angular momentum. Salem and Rowland (3) pointed out years ago that, for biradicals, this devolved to a preference for intersystem crossing in conformations in which p orbitals were orthogonal, e.g. a below slower than b.

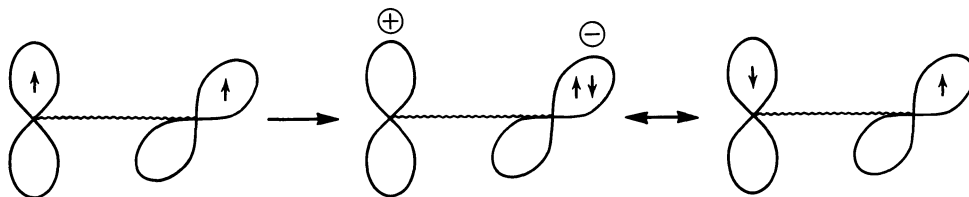


### Distance between the termini

Salem further suggested (3) that decreasing distance between the termini should make intersystem crossing faster as a result of a sharp inverse distance dependence of the relevant integrals. However, no simple prediction turned out to be possible because the increased overlap at shorter distances will in general bring the singlet substantially below the triplet and thus create an opposing energy gap effect.

### Ionic character in the singlet wave function

Finally, Salem pointed out that increasing ionic character in the singlet wave function allows intersystem crossing to proceed more rapidly. Since the triplet is always purely covalent, no net spatial redistribution of electrons (necessary to create a torque to flip the spin) is possible with a purely covalent singlet. Again, however, too much ionic character will work in the opposite direction for energy gap reasons (8).



### The role of nuclear motions

The Salem-Rowland picture of intersystem crossing is inherently static. In contrast, the dynamic (i.e. nuclear-motion induced) aspect of the problem has been discussed by Shaik and Epiotis (4). Basically, motions of certain symmetries couple triplet and singlet states and thus may induce intersystem crossing. Such motions are, for example, internal rotations and pyramidalizations. Bond stretches produce no angular momentum changes and are thus in this sense inactive.

### EXPERIMENTS

We have been fortunate to have the cooperation of the Center for Fast Kinetics Research at The University of Texas at Austin, at which we have made all our transient measurements. The majority of experiments have been performed with the 266nm fourth harmonic or 353nm third harmonic of a Nd-YAG Q-switched (or sometimes a mode-locked) laser. The extensive computerized data acquisition and analysis routines make possible the determination of lifetimes with high precision. A description of the system is given elsewhere (9).

Although we did not emphasize it initially, we have come nearly exclusively to study transients which can be directly detected and studied to remove as many experimental uncertainties as possible. This has meant that experimental designs generally assume that the absorption spectra of biradicals can be understood as the composite of the spectra of the termini which themselves are well modeled by analogous monoradicals. In our experience so far, this assumption is valid.

It is of course necessary to add standard preparative and steady-state quantitative studies of the photochemistry of the compounds in question to the transient spectroscopy. Without such studies, from which the appearance and quantum yield of the transient(s) can be inferred, assignments are that much less certain.

### RESULTS AND DISCUSSION

#### Olefin triplets

Planarity and the energy gap. The properties and lifetimes of olefin triplets have been under investigation by many groups for more than twenty years (10). These species have recently been detected by direct (11-17) and indirect flash photolysis techniques, the latter including electron transfer to methyl viologen (18-20) and excitation transfer to low-energy triplets such as certain arenes or beta-carotene (21). Because of the interest in stilbene triplets and its trans-planar triplet-twisted (phantom) triplet equilibrium (22), much thought has gone into the question of the effect of planarity on triplet lifetime. That azulene at moderate concentrations biases stilbene cis:trans photostationary states toward higher percentages of trans (10,22) is evidence that a trans triplet species is present in some reasonable fraction of the total; however, that the spontaneous decay is some 60% cis: 40% trans suggests that the twisted form dominates the decay. The twisted form is most likely dominant at equilibrium (12,22). No "azulene effect" is observed for beta-methylstyrene (23), which led us to conclude that it is essentially exclusively twisted.

More highly conjugated species, e.g. triene (24) and polyene (25,26) triplets and certain naphthylarylethylene derivatives (15,16), appear to have significantly to dominantly planar triplets at equilibrium. In the trans-planar form, the energy gap between  $T_1$  and  $S_0$  is substantial and the interconversion thereby severely hampered. We have determined the lifetimes of a few arylcycloalkenes (19), which do indeed show the expected trend. Note in Table 1 the near identity of lifetime of the anisylcycloheptene triplet with the acyclic model, the increased lifetime for the cyclohexene analogue, and the nearly thousandfold increase for the cyclopentene. The seven-membered ring triplet can adopt a geometry nearly the same as the acyclic, while the cyclopentene is necessarily nearly planar. The cyclohexene is intermediate.

Gorner (13) determined the lifetimes of di-, tri-, and tetraphenylethylene triplets and noted a trend to longer lifetime with increasing substitution which he interpreted as due to an increased contribution from the planar species. We have observed an effect of similar magnitude for methyl substitution (19,27) and reached quite a different conclusion, namely

**TABLE 1.** Cycloalkene triplet lifetimes

Triplet	Lifetime (nanoseconds, CH <sub>3</sub> OH)
3-anisyl-2-pentene	38 ± 4
anisylcycloheptene	37 ± 2
anisylcyclohexene	68 ± 7
anisylcyclopentene	29000 ± 4000

that simple alkyl-arylethylene triplets are invariably dominantly twisted unless geometrically constrained and that structural effects on lifetime are strictly effects on the twisted triplet. A rationale for this is the extreme crowding of (say) planar tetraphenylethylene, which can be relieved by twisting, plus the additional stabilization which then results from the conjugative delocalization at each terminus by the phenyls. If stilbene triplet is a mixture of planar and twisted, we feel that any more highly substituted cases must be almost completely in the twisted form.

**Structural effects on the twisted triplet lifetime.** What then is the origin of the longer lifetime for more highly substituted twisted triplets? Figure 1 provides an empirical correlation of phenyl-(or *p*-methoxyphenyl-) and alkyl-substituted alkene lifetimes via the equation (27)

$$\log \tau = \log \tau_0 + am + bn$$

where *m* and *n* are respectively the number of methyl and phenyl (anisyl) groups on the double bond. The values of *a* (0.20) and *b* (0.30) obtained by trivariate linear regression reflect the somewhat larger effect of aryl than methyl, but clearly are of the same order. It seems difficult to ascribe a much different role to the two substituents. Indeed, methyl substituted diene triplet lifetimes (20), if we assume that the second double bond counts as a phenyl group, are not far off the line. These "allylmethylene" triplets thus appear similar to correspondingly substituted styrenes.

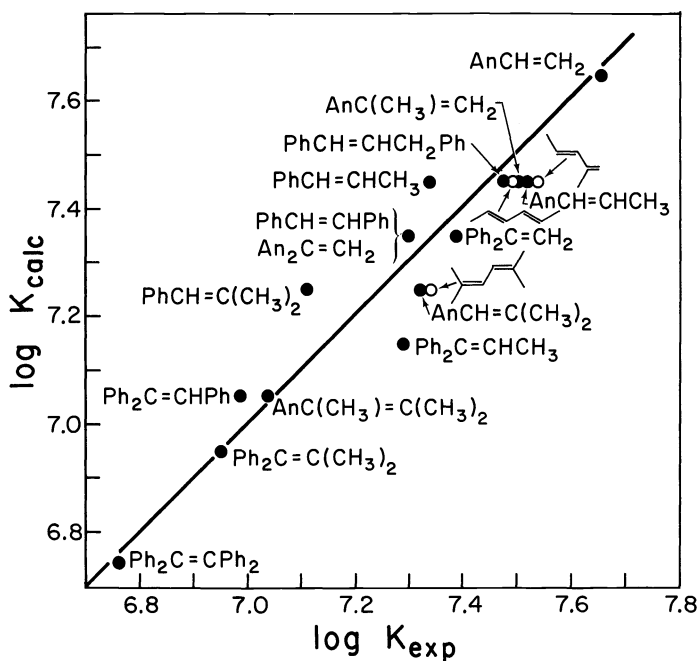


Fig. 1. Comparison of measured triplet lifetimes of olefins with lifetimes calculated from equation in text. Open circles are for diene triplets not used in regression calculation.

TABLE 2. Effect of deuterium on olefin triplet lifetime

Triplet	$k_{2H}/k_{2D}$
AnCD = CDCH <sub>3</sub> <sup>a</sup>	1.11 ± 0.07 (CH <sub>3</sub> OH)
PhCD = CDPH <sup>b</sup>	1.27 (C <sub>6</sub> H <sub>6</sub> )
Ph <sub>2</sub> C = CD <sub>2</sub> <sup>b</sup>	1.18 (C <sub>6</sub> H <sub>6</sub> )
	1.18 (CH <sub>3</sub> OH)
	1.13 (C <sub>7</sub> H <sub>16</sub> )

a. By viologen interception. b. By direct observation. Estimated error ±3%

Equally importantly, despite the rather short lifetimes of twisted olefin triplets, significant isotope effects are observed for vinyl deuterium. Table 2 shows that ( $k_H/k_D - 1$ ) is at least 5-6% and is nearly 15% per deuterium in one case. These effects are smaller than those (5) for radiationless decay of aromatic hydrocarbons (10-25% per D), but not by too much. The specific Franck-Condon effect to which the latter is ascribed would go nearly to nil at these small energy gaps, so we are forced to some alternative.

There are two which come to mind. First, some other vibrational mode dominates the Franck-Condon factor, e.g. a torsion or pyramidalization. We are currently exploring some options quantitatively, but we note that the qualitative observation that  $k_H > k_D > k_{CH_3} > k_{Ph}$  at least orders the substituents by reduced mass. Second, the Shaik-Epiotis argument (4) may apply, i.e. nuclear motions themselves may induce the intersystem crossing. The distinction between these seems likely to rest on some rather difficult calculations. However, it seems clear that the intersystem crossing rate is largely determined by the number of hydrogens on the twisted bond and not substantially by the phenyl, vinyl, or alkyl group.

**Polar substituent effects.** It appeared to us that a twisted olefin triplet could in some senses be called a "1,2-biradical" and subject to the same considerations as given earlier. We have prepared a series of ring-substituted chalcones and studied (28) the lifetimes of the corresponding triplets which we believe to be twisted. These triplets all possess a benzoyl group, which is strongly electron-attracting, at one terminus; electron-donating groups in the other ring should therefore increase the rate of T<sub>1</sub>-S<sub>0</sub> decay.

The facts, however, are quite different. Donor substituents, p-Me<sub>2</sub>N especially but also p-CH<sub>3</sub>O, increase the lifetime. A small variation in the expected direction is observed in the group of electron-attracting substituents but is not large enough to be convincing in view of the rest of the data. We have suggested that the best interpretation is the involvement of a planar, CT-type triplet with p-Me<sub>2</sub>N and to some extent with p-CH<sub>3</sub>O, but that essentially no polar substituent effect operates elsewhere. The data are presented as a Hammett plot in Fig. 2. Unless the opposing possibilities fortuitously cancel one another out, the effect of polar substituent per se on olefin triplet lifetimes appears small.

The effect of halogen substituents, however, can be large. Note in Fig. 2 that p-Br sharply decreases the lifetime, by about threefold, while m-Br causes a smaller decrease. We attribute this to a heavy atom effect which is positionally sensitive, being large only when the heavy atom is at a position of significant spin density in the triplet.

A chlorine substituent normally does not exert a very large heavy atom effect, and indeed the p-Cl falls nicely on the line in Fig. 2. We were therefore surprised by our observation in another case (27) that a vinyl chloride derivative had an immeasurably short lifetime. Although other 1,1-diphenylethylene derivatives, both in our hands and Gorner's (13), give good triplet signals on benzophenone sensitization, the compounds 1,1-diphenyl-2,2-dichloroethylene and 1,1-diphenyl-2-chloropropene afford no detectable transient with lifetime > 1 nsec at wavelength > 330 nm. By comparison, under similar conditions diphenylethylene triplet is readily detected as strong (OD > 0.2) end absorption at 385 nm.

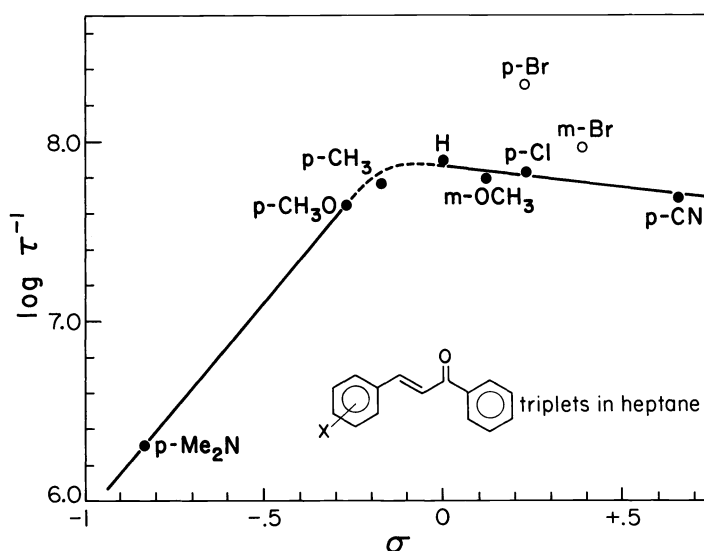


Fig. 2. Hammett plot of decay rates of substituted chalcone triplets. Bromine compounds not used in calculation of slope.

We suggest that the anomalously short lifetime may be due to a hyperconjugatively enhanced spin density at the chlorine nucleus. In the other cases, the halogen nucleus is in the nodal plane of the  $\pi$  system bearing the unpaired electron. In the twisted olefin triplet, as Fig. 3 shows, the C-X bond can overlap moderately well with the p orbital on the other carbon atom. This overlap is apparently enough to affect the triplet lifetime drastically, although not enough to produce any C-Cl fission since no such chemistry is observed.

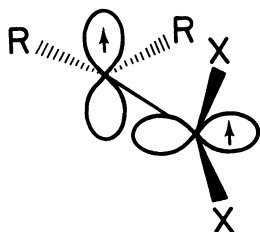


Fig. 3. Sketch of a twisted olefin triplet.

**Alkyne triplets.** We have observed remarkably strong transients with absorption maxima at 410-420 nm, on both benzophenone-sensitized and direct irradiation of tolan. Lifetimes are in the seventy microsecond range, which may be a minimum estimate since in this range impurity quenching can become important. Evidently any geometry difference between the relaxed tolan triplet and the ground state molecule is insufficient to allow the  $T_1$  and  $S_0$  surfaces to approach at all closely. With such a long lifetime it is surprising that there is not more photochemistry reported for acetylenes and derivatives.

#### Norrish II biradicals

Many investigators over the years have studied Norrish II photochemistry with an eye to understanding the behavior of biradicals in general (29-31). The quantitative intersystem crossing and facile gamma-hydrogen abstraction of phenyl ketones makes Norrish II photochemistry nearly ideal for biradical generation. The strong absorption of benzylic radicals near 300 nm

means that almost any phenyl ketone can be made amenable to transient studies.

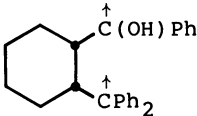
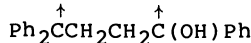
We wished to examine several aspects of biradical behavior via transient spectroscopy of Norrish II biradicals.

**The role of conformation.** Several suggestions have been made (31,32) that *gauche* conformations of biradicals will have shorter lifetimes than the corresponding *anti* conformations for reasons of stronger interaction between the termini. We examined the effect of conformation carefully in one system (33) and in fact found this not to be the case.

The photochemistry of and the biradicals from *gamma*, *gamma*-diphenylbutyrophenone and *cis*-1-benzoyl-2-benzhydrylcyclohexane were studied. For the former, essentially exclusive fragmentation to acetophenone and 1,1-diphenylethylene results, as would be expected from the *anti* biradical conformation which simple steric grounds would predict to dominate heavily. For the latter, a good yield of the ring-closed cyclobutanol results in hexane-benzene, with a moderate yield of the same product in methanol accompanied by a set of products which suggest that ring hydrogen abstraction competes with benzhydryl hydrogen abstraction in this solvent. The biradical of interest, that derived from benzhydryl hydrogen abstraction, is *gauche*-locked.

The lifetimes of the benzhydryl-derived biradical can in any case be deduced from the decay profile at 330 nm, a wavelength at which the ring abstraction derived biradicals are expected to absorb only weakly. Those lifetimes are given in Table 3 for both compounds. It is clear that, in heptane, almost no difference in lifetime exists between the two biradicals, and, in methanol, the *gauche*-constrained one is even longer-lived. The observation cautions against overreliance on the simple proximity of the termini as a criterion which determines biradical lifetime.

TABLE 3. Lifetimes of conformationally constrained or biased biradicals.

	Methanol (nanoseconds)	Heptane (nanoseconds)
	242±14 <sup>a</sup>	69±5 <sup>a</sup>
	166±8 <sup>a</sup>	84

a. Errors ±2 standard deviations.

It would be tempting to use the constraints of the cyclic system to address the question of orbital orientation. Indeed, in one likely conformation of the biradical the orbitals are oriented in close to a perpendicular arrangement, which should maximize the intersystem crossing rate. If this were the dominant biradical conformation, one would have to say that orbital orientation is not the important feature it is expected to be, since the lifetime is not particularly shortened. However, since there are other comparably likely conformations, no rigorous statement can be made.

**Polar effects.** If the expected polar effects were not manifested in twisted olefin triplets, we thought that they might well be in Norrish II biradicals. Accordingly, we prepared a series of *gamma*-phenylbutyrophenone derivatives substituted in the *gamma* phenyl ring with polar substituents (34). The benzylic hydroxyl group in the biradical defines that terminus as the "donor" end, and consequently electron-attracting groups in the other ring should shorten the lifetime if polar effects are important. Data are presented as Hammett plots in Fig. 4. In heptane, a reasonable Hammett plot results,  $\rho = -0.43$ , while in methanol, the value of  $\rho = +0.02$  shows that polar substituent effects are nonexistent. In both cases a *p*-Br shows a small heavy atom effect.

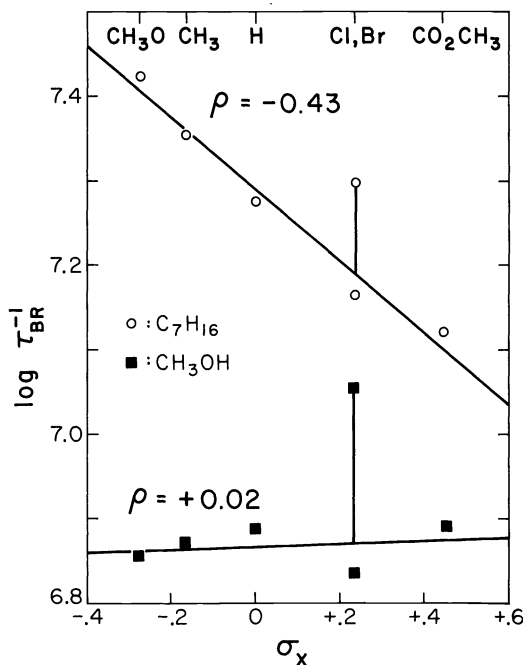


Fig. 4. Hammett plot of inverse lifetimes of gamma-phenylbutyrophenone derived biradicals substituted in the gamma phenyl ring. Bromine compound not used in calculation of slope.

The negative  $\rho$  value in heptane is in the direction opposite to our expectation. The result is better in accord with an increase in T-S separation as polar terms increase the stability of the singlet biradical. Interestingly, Ito, Nishimura, Matsuura, and Hayashi (35) have determined the photoenol triplet biradical lifetimes from 2,4,6-triisopropylbenzophenones as a function of polar substituent in the ring which does not contain the isopropyls. We calculate a Hammett  $\rho$  of  $-0.41$  for their data. This is identical in sign and magnitude to ours even though the argument above would suggest an opposite sign! In this case it is even possible that which terminus is actually the "donor" may depend on substituent. The synthesis of both sets of data suggests that substituents which push electron density toward the center of the biradical shorten the lifetime, while those which pull electron density away lengthen it. This appears to be largely a through-bond phenomenon in view of the through-space study of the previous section.

The reason for the absence of a polar effect in methanol is not clear. However, the sharply longer lifetime of Norrish II biradicals in solvents such as methanol which can accept a hydrogen bond from their acidic hydrogens has been known for some time (36). Taken together, the two experiments now seem to suggest a different detailed mechanism for T-S interconversion in methanol, which replaces the one operative in hexane because it is slowed down too much in methanol.

Another sort of "substituent" effect consistent with the electron-density hypothesis is the effect on lifetime of deprotonation of a Norrish II biradical. We have determined the  $pK_a$  of the biradical from gamma-phenylbutyrophenone to be 11.8, with a lifetime of 125 nsec for the acidic form and 62 nsec for the deprotonated form (37). The shorter lifetime for the latter would be consistent with the greater electron-releasing ability of the anion compared to the hydroxyl group.

**Isotope effects.** Since nuclear motions appeared to be important in the decay of olefin triplets, we thought it important to examine deuterium isotope effects on Norrish II biradical lifetimes in order to search for similar effects in that case. However, study of the gamma-phenylbutyrophenone-derived biradical under the following circumstances produced no difference ( $\pm 3\%$ , the experimental error) in lifetime under deuterated or undeuterated conditions: (1) unlabeled ketone in either 4:1 acetonitrile : H<sub>2</sub>O or 4:1 acetonitrile : D<sub>2</sub>O; (2) fully aliphatic-deuterated ketone



PhCD<sub>2</sub>CD<sub>2</sub>CD<sub>2</sub>COPh or unlabeled ketone in heptane (34). Neither labeled solvent nor labeled precursor thus gives any evidence that hydrogens in the system are actually involved themselves in the decay.

**Oxygen-containing Norrish II biradicals.** The effect of oxygen between the termini of Norrish II biradicals is exemplified by the lifetime of the biradical derived from benzhydryl phenacyl ether (32). Although photolysis products and quantum yields are unexceptional, the lifetime at ca 5 nsec is at least thirty times shorter than expected. We have suggested that the intervention of a resonance form suggesting that this is partly a 1,3-biradical shortens the lifetime. However, with the similarity in lifetime of biradicals ranging from "1,2" (olefin triplets) to 1,6 (vide infra) we have observed in other cases, such an explanation now seems less likely. It is interesting that the electronegativity of oxygen would presumably increase electron density between the termini, and the short lifetime would on this basis fit with the previous argument. However, again, we consider this explanation tentative until and unless we are able to develop a theoretical justification for it.

### Other biradicals

**Norrish I biradicals.** The facile triplet state Norrish I cleavage of cycloalkanones provides a chemically different series of biradicals. We have so far (38) studied the six-membered ring compounds 2-phenylcyclohexanone and 2,2-diphenylcyclohexanone. Fragmentation readily affords strong transients with the expected spectra. The lifetimes in this case are nearly insensitive to solvent (heptane or methanol) and are 50-60 nsec.

We had expected that, with four carbons between the termini, the lifetime would become quite long. In fact, given that 50 nsec is a good guess as to the lifetime of a typical trisubstituted olefin triplet and also to a Norrish II biradical in hydrocarbon solvent, the evidence suggests that lifetimes are essentially independent of whether 0, 2, or 4 carbons intervene between the termini. Presumably this is due to the balancing of the two factors mentioned at the first: longer chain biradicals show less spin-orbit coupling but the triplet and singlet are less separated in energy.

**Isotope effects on Norrish I biradicals.** Additionally, we have replaced the hydrogen eventually transferred to form product (unsaturated aldehyde) by deuterium in 2,2-diphenylcyclohexanone and note a negligible effect (< 2%) on biradical lifetime but a significant isotope effect (ca 40%) on the quantum yield of product formation (38). This immediately points out two important features. First, there must be an intermediate subsequent to the triplet biradical to explain the product isotope effect. This is not surprising since we expected rate-limiting T - S intersystem crossing, with production of a very short-lived singlet biradical immediately to precede product formation. The product isotope effect merely reflects the chemical partitioning from the singlet biradical.

Second, the lifetime isotope effect, as for the Norrish II biradicals, shows that transfer of the hydrogen does not occur prior to or concomitant with T - S interconversion. We believe that this is to be expected, at least partly because such atom transfers should occur in linear or nearly linear fashion, and this is not a motion which will couple efficiently with a change in orbital angular momentum per Shaik and Epiotis.

**Biradicals in carbocyclic cycloadditions and fragmentations.** A limited number of biradicals in carbocyclic cycloadditions and fragmentations have been studied. We obtained an indirect and imprecise estimate of the lifetime of that in the cycloaddition of triplet phenanthrene and dimethyl fumarate as 20-70 nsec several years ago (39). Takamuku and Schnabel (40) determined a lifetime of 220 nsec for the biradical 1,4-bis-(alpha-naphthyl)-2,3-bis(methoxycarbonyl)butane-1,4-diyl. These lifetimes are not unreasonable, given the substituents on the termini, in comparison to the more extensively studied Norrish II biradicals. Additionally, Paterno-Buchi biradicals (32,41) have lifetimes in the 1-4 nsec range, which are thus quite similar to the Norrish II biradical lifetimes of phenacyl ethers (32) as a result of the common structural feature  $\uparrow C-C-O-C\uparrow$ . Accordingly, we believe that structural effects in biradical chemistry generally should be well modelled by the latter reaction. However, more examples are needed.

## CONCLUSIONS

Unfortunately, we are still a substantial distance from the goal of full understanding of the factors which enhance intersystem crossing in biradical and biradicaloid intermediates in organic photochemistry. While energy gap effects are in some cases clearly documented, and in no case contravened, studies of structural effects such as polar effects or the effect of interterminal distance have led to ambiguous conclusions. The role of vinyl hydrogens in the intersystem crossing of olefin triplets seems clear, however. One correlation which so far appears to have some generality is the tendency for biradicals with greater buildup of electron density at or between the terminals to exhibit shorter lifetimes. This can be subjected to further experimental tests, fortunately, and should be before it is accepted. Finally, recent theoretical studies of biradicals (42) afford hope that, before long, the correlative results which have been obtained can be properly interpreted.

## ACKNOWLEDGEMENT

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