DOES INTERSYSTEM CROSSING IN TRIPLET BIRADICALS GENERATE SINGLETS WITH CONFORMATIONAL MEMORY?

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Abstract—The effect of temperature, concentration, external magnetic fields and paramagnetic quenchers on the lifetime of biradicals produced in the Norrish Type II reaction has been examined. Analysis of this data and that available from earlier reports leads to the conclusion that in addition to controlling the biradical lifetimes, intersystem crossing in triplet-derived biradicals plays a critical role in determining the behaviour and products which result from singlet biradical reactions. The effect is attributed to conformational memory in the singlet biradical which reflects its short lifetime.

Recent research on biradical behaviour supports the idea that in many cases the lifetime of triplet-derived biradicals is controlled by the rate at which they undergo intersystem crossing (ISC).[2–8] That is, their lifetime is simply a measure of how fast they interconvert irreversibly to the singlet biradical that then yields products in a fast process. In this paper we put forward the idea that not only does ISC determine the biradical lifetime, but in addition it exerts considerable control on the partition of the singlet biradical into products. In other words, the nature and ratio of products generated from the singlet biradical can be controlled by interactions at the triplet manifold level. This naturally requires some triplet control on the conformation (and thus reaction pathways) of the singlet biradical.

While no attempt seems to have been made to explain the many unusual features of biradical behaviour on the basis of this model, the literature does contain recurrent reports suggesting this possibility. For example Caldwell and Creed[5] used a model of this type to explain the effect of paramagnetic quenchers on the biradicals produced by addition of triplet phenanthrene to dimethyl fumarate and suggested that they could be trapped before conformational equilibration was achieved. Our own results[6] on Norrish Type II biradicals have suggested that the preferred conformation for ISC is different for the spontaneous decay and for the decay induced by paramagnetic species and that this is reflected in the product ratios. Ito *et al.*[9] have shown that the biradical from valerophenone behaves differently depending on whether the generating reaction is the Norrish Type II process[10,11] or the sensitized decomposition of valerophenone diperoxide. A recent CINDP study by Doubleday[8] suggests that ISC in the biradicals from the photocleavage of cyclohexanones is to some extent involved in determining product ratios. In a recent study of the temperature dependence on the photochemistry of *o*-methylacetophenone[12] we suggested that the lowest energy conformation for the biradical is different from the conformation for which the probability for ISC is a maximum.

This paper reports the results of a series of experiments on the effect of temperature, concentration, external magnetic fields and paramagnetic species on the lifetimes of triplet-derived biradicals. All experiments were carried out using laser flash photolysis techniques

and in most of them we use the biradical from the Norrish Type II reaction of *γ*-methylvalerophenone, which we have characterized in earlier work.[2, 13–15] These experiments were designed so as to test the ideas put forward in this work; however, it should be noted that a considerable fraction of the information necessary to provide support to this model is already available in the literature, but the data has never been analyzed in the light of a model that would provide a comprehensive explanation to the many unusual features of biradical behaviour.

It is interesting to note that the chemistry of biradicals can be easily understood as long as one considers exclusively reactions with diamagnetic species or processes that reflect the chemistry of only one radical-site. Thus, hydrogen abstraction,[16, 17] electron transfer,[2, 13,18] intramolecular rearrangements,[19] elimination reactions[20] and probably addition to double bonds[21] all occur with rate constants characteristic of typical monoradicals with similar substitution at the reactive center. The situation is entirely different when one considers reactions with paramagnetic species, or internal or external effects where the multiplicity of the biradical can be expected to be important; thus, the factors that control lifetimes,[2,4,8] the effect of magnetic fields,[4,8] the interaction with free radicals,[5,6] with oxygen[3,5,22,23] and probably with paramagnetic transition metal complexes,[24] all show a behaviour that is characteristic of the biradical and in most cases does not parallel that of free radicals.

In trying to understand the interrelation between triplet and singlet biradical behaviour we have concentrated in the second group mentioned above, since there would be little to be learned about this problem from processes that reflect typical monoradical behaviour. The Discussion Section is really an analysis of the data available on the problem, naturally including the new results reported here.

EXPERIMENTAL

All the experiments reported in this paper were carried out using laser flash photolysis techniques and using the pulses (337.1 nm–8 ns, up to 10 mJ) from a Molectron UV-24 nitrogen laser for excitation. Our system has been fully interfaced with a PDP-11/03L computer that controls the experiment, gathers data and provides suitable storage and processing facilities. Further details have been given elsewhere.[25]

Experiments using an external magnetic field were carried out using a home built magnet capable of fields of up to 2500 Gauss. It was calibrated using a Varian E500 NMR Gaussmeter.

The samples, usually lmL, were contained in suprasil cells and deaerated by bubbling oxygen-free nitrogen. The sources of materials and purification procedures were the same employed in earlier work.[2,26]

RESULTS

Temperature dependence of biradical lifetimes. These experiments were carried out using γ-methyl-valerophenone (1), which upon excitation produces the biradical 2, via the intermediary of a short lived ($\tau_T \sim$ 2 ns in benzene) triplet, reaction 1.[10,11]
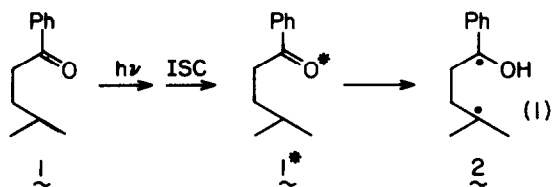
The solvents chosen were methanol and toluene-d_8, both of which are relatively unreactive towards the short lived triplet state of γ-methylvalerophenone and are liquids over a wide temperature range. In both cases the decay of the biradical was monitored at 415 nm and is virtually temperature independent, see Table 1. Arrhenius treatment of the data yields:

$$\log(1/\tau_B) = (7.53 \pm 0.15) + (40 \pm 150)/\theta \text{ in toluene-}d_8$$
$$\log(1/\tau_B) = (7.20 \pm 0.10) - (150 \pm 150)/\theta \text{ in methanol}$$

where $\theta = 2.3RT$ has been expressed in cal/mol and τ_B in seconds. Typical decay traces are shown in Fig. 1.

The results obtained in methanol are entirely consistent with our earlier measurements;[2] however, we felt it was important to complete those earlier studies (where
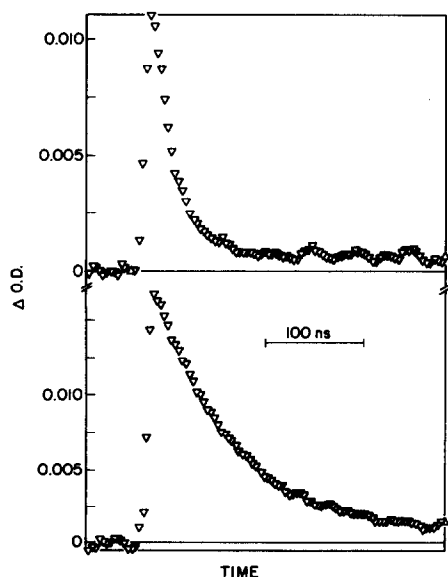
Table 1. Temperature dependence of the lifetime of the biradical from γ-methylvalerophenone

Solvent	T/°K[a]	τ_B/ns[b]
Toluene-d_8	216.2	28.4
	226.5	27.4
	262.0	23.5
	302.6	25.4
	337.7	31.2
	357.5	27.7
Methanol	215.9	102
	249.4	99
	273.2	91
	293.2	94
	327.3	90
	333.0	92

[a] Typical error ± 0.4°K.

[b] Error ± 3 ns.

the lifetimes were based on an extrapolation) using direct detection, covering a wider temperature range, and, in particular using a solvent like toluene were only a fraction of the biradicals leads to products.[10,11]

A few experiments were also carried out on the biradical from poly (o-tolyl vinyl ketone),[26] 3, which has a lifetime of 200 ns at room temperature. The data is less accurate in this case, but it suggests a slight inverse temperature dependence (Ea ~ -0.5 kcal/mol) in toluene-d_8.
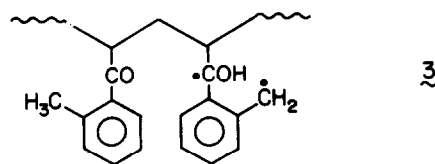
Biradical quenching by di-t-butylnitroxide. We have shown in earlier work that the biradicals produced in the Norrish Type II reaction can be scavenged by the free radical di-t-butylnitroxide (DTN) in a process that promotes biradical fragmentation. We have now examined the temperature dependence of this process for the biradical from γ-methylvalerophenone(2). The rate constants at each temperature were determined from plots of the rate of biradical decay as a function of DTN concentration, as reported earlier. The Arrhenius plot obtained in methanol as solvent is shown in Fig. 2, and leads to:

$$\log(k_{DTN}/M^{-1}s^{-1}) = (10.53 \pm 0.10) - (1700 \pm 200)/\theta.$$

Effect of external magnetic fields. These experiments were carried out in the 0–2000 G field region, and due to
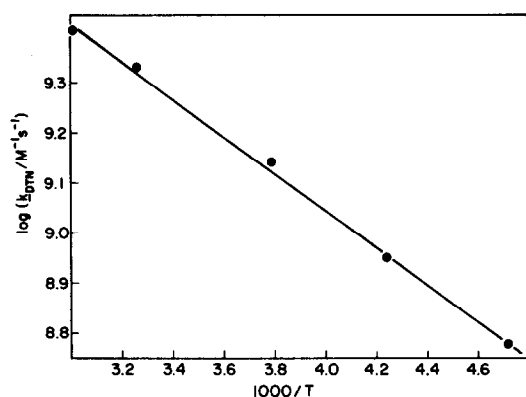
Fig. 1. Typical decay traces for biradical 2 in toluene-d_8 (top) and in methanol at 26°.

Fig. 2. Arrhenius plot for the quenching (k_{DTN}) of 2 by DTN in methanol.


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experimental reasons measurements could only be made at room temperature. Once again we examined biradical 2 in this case in benzene and methanol and we find that the lifetimes are essentially insensitive to the application of a field. The only changes detected were a ca 4% decrease in biradical lifetime, which regardless or whether it is real or not is certainly within the experimental error. In summary, the changes, if any, do not exceed 10%. By contrast, ISC rates for confined radical-pairs (e.g. in solium dodecyl sulfate micelles) are very sensitive to moderate magnetic fields.[27-30]

The intermolecular rate constant for biradical quenching by DTN was also found to be insensitive to the application of an external magnetic field.

Biradical-biradical annhilation. When the lifetime of 2 is measured at relatively high ketone concentration (0.1–0.4 M) and with the laser beam highly concentrated, it is possible to detect changes in lifetime with light intensity. In these experiments the biradical lifetime was measured in methanol at 25° changing the laser dose with suitable neutral density filters. The plot of initial rate of decay vs dose extrapolates at dose→0 to the lifetime given in Table 1. We find that at the maximum available dose the experimental lifetime is reduced by 20%, which taking into consideration the experimental optical density and an extinction coefficient of $800\,M^{-1}\,cm^{-1}$ (at 415 nm)[14] for the biradical leads to an estimate of $\sim 10^{10}\,M^{-1}s^{-1}$ for the rate of biradical annhilation. The error in this value could be as large as a factor of two.

DISCUSSION

It should probably be emphasized that while the ideas discussed herein seem at this point to apply to a variety of biradicals in solution they may not be of universal applicability. The analysis which follows centers on biradicals generated in the Norrish Type II reaction (5), on the opening of cycloalkanones (6), on the interaction of phenanthrene with dialkyl fumarates (7) and on the photoenolization of o-alkyl substituted carbonyl compounds (8).

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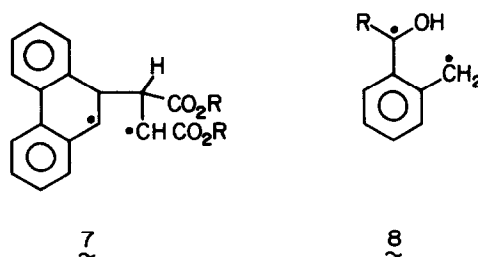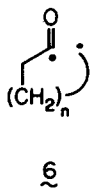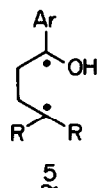
As pointed out earlier, the results reported here, simply add to what is already known about these species. Biradical lifetimes seem to be controlled by the rate of intersystem crossing in the triplet biradical. This is supported by (a) the lifetimes are temperature independent (e.g. 2) or show only a small dependence (e.g. 3 and 8).[12] (b) The lifetimes seem to be independent of the enthalpy change associated with decay,[2] even when product ratios do show temperature dependence.[31] (c) The interaction of biradicals with free-radicals, DTN in particular, suggests that the main role of DTN centers on a relaxation of the spin restrictions associated with biradical decay.[5,6] (d) The interaction with oxygen is similar to the case of free-radicals, but, in addition spin selection rules can be reflected in the ratios of final products.[3] (e) The results of magnetic field dependent CINDP are consistent with ISC as the factor controlling biradical decay.[4,8] (f) The pre-exponential factors associated with the decay [see also point (a)] are much lower than could be expected if singlet–triplet equilibration occured and, (g) biradical–biradical annhilation kinetics are consistent with values usually found for T–T processes. In fact, the idea that biradical lifetimes could be controlled by ISC had been proposed by Bartlett and Porter[32] on the basis of their studies of the photodecomposition of cyclic azo-compounds long before the studies mentioned above were carried out.

While it seems essential to invoke ISC as the rate determining step in order to understand biradical behaviour, there are a number of unusual features which require a more sophisticated model.

For example, when DTN interacts with 5 or 7, the ratios of products which result from the competition of cyclization, fragmentation and reabstraction (in the case of 5) are drastically modified;[5,6] however, ISC is a requirement for all of these processes and thus, the mere fact that is rate determining would not necessarily affect product ratios. Statistically, of the encounters between the triplet biradical and the free radical, two thirds will be accounted by quartets which are expected to be dissociative and one-third by doublets and can lead to assisted biradical ISC. Two mechanisms can be proposed: in one the biradical and quencher form a complex; biradical decay (and therefore product formation) occurs from this complex which can naturally have a different reaction pattern than that for the free biradical. The second explanation does not require direct bonding between the biradical and quencher. The differences in chemical behaviour are assumed to result from changes in the conformation for ISC, differences which are preserved by the singlet biradical and eventually reflected in the products.[5] We are now inclined to favor the second mechanism: as pointed out by Caldwell and ourselves,[5,6] the reaction path promoted by DTN changes from system to system. For example, while cyclization is enhanced at the expense of fragmentation in

the case of 7, in the case of 5 fragmentation increases at the expense of reabstraction and cyclization shows a moderate increase. It is particularly difficult to see how a bonding interaction could promote cyclization, which requires the interaction of the two radical centers.[33] Further, the Arrhenius parameters obtained for the quenching are very similar to those obtained for the quenching of phenanthrene triplets by a related free radical,[34] tetramethylpiperidine–N-oxide, a process that occurs with a similar rate constant. In particular, the similarity of the A-factors $[(\log A/M^{-1}s^{-1}) = 10.13 \pm 0.15$ in the phenanthrene system][34] can be taken as an indicator that transition state requirements are not very different.

In the related example of oxygen quenching of biradicals the formation of oxygen containing products reveals the involvement of chemical bonding in the singlet encounters,[3] but this could be an end result of the process, rather than its driving force. There is no direct evidence for chemical bonding in the case of triplet encounters. The fact that product ratios reflect spin statistical factors seems to suggest that in this system the interaction in singlet and triplet encounters takes place over similar distances.

We have recently observed that the paramagnetic complex $Cu(acac)_2$ also quenches 2 with $k_q \sim 2 \times 10^9 M^{-1}s^{-1}$ in methanol,[24] although at this point it has not been confirmed that the process is paramagnetic quenching (as opposed to e.g. charge transfer).

How can DTN and other paramagnetic quenchers affect the ratios of products which undoubtedly result via the singlet biradical, without forming a bond with one of the radical centers? As pointed out above, and in agreement with Caldwell's explanation[5] and our own results,[6] we suggest that the conformation from which ISC occurs is probably different when the process involves interaction with a paramagnetic quencher. Thus, the nascent singlet biradical will have a different conformation depending on the interactions which promoted ISC. *This would have no effect on the products unless the singlet biradical can effectively "remember" this conformation.* The only simple way in which one can conceive such a memory is if the singlet biradical lifetime is

short enough that bond rotation will not occur; that is, singlet biradical decay has to occur from a semi-frozen conformation. We believe that this is indeed the explanation for the unusual features of biradical behaviour. In the case of Norrish Type II biradicals the preferred conformations will be different for fragmentation (transoid and partially from cisoid), cyclization (cisoid with the two half-occupied orbitals in the same plane) and reabstraction (skew, with the hydroxylic hydrogen interacting with the γ-radical site).

The mechanism suggested above is consistent with the temperature independent biradical lifetimes reported herein and elsewhere,[2] with the need to propose biradicals with conformational memory (or a pseudo-concerted process) in singlet state reactions in aliphatic ketones[11] and with the paramagnetic quenching and its effect on product ratios.

In trying to plan experiments to test this model, we find that many have already been carried out, although they have not been interpreted on the basis of a model of this type. For example, one obvious test would be to generate the same singlet biradical from different sources. Ito *et al.*[9] have recently examined the direct and sensitized decomposition of valerophenone diperoxide (9) and found that product ratios are definitely different from those obtained from the same biradical in the direct photolysis of valerophenone (10) in the absence[10,11] or presence of oxygen[3,23] (Scheme I). Our model provides a straightforward explanation for the differences in cyclization, fragmentation and reabstraction ratios which result from the singlet biradical (12). Quite simply different sources produce 12 in different initial conformations and the fast collapse of 12 into products favours those reaction paths for which the transition configuration resembles the geometry of the nascent singlet biradical.

A similar analysis could be performed for the biradicals from 2-hexanone depending on whether they are produced in the Norrish Type II reaction[11] or in the thermal decomposition of cyclobutanols,[35] although in this case the experimental conditions used for both experiments are quite different.

Another possible test would be the effect of magnetic
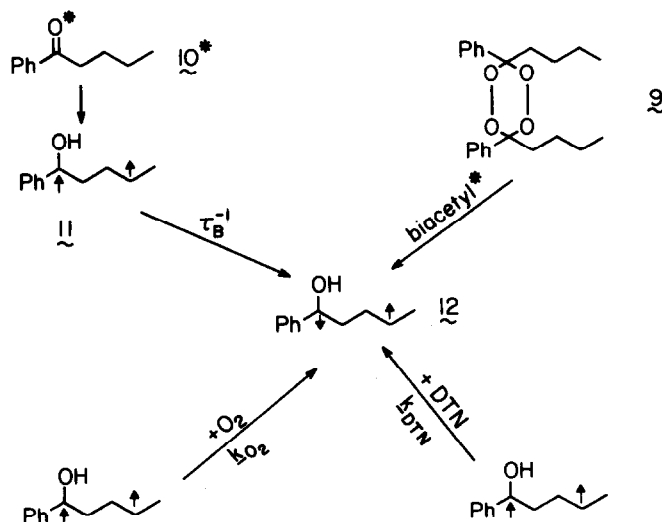
Scheme 1.

fields, which in the case of radical-pairs confined to micelles produce drastic changes in the rates of ISC as a result of Zeeman splitting of the triplet levels.[27-30] In Type II biradicals we find that magnetic fields (H ⩽ 2000 G) have no detectable (less than± 10%) effect on the biradical lifetimes in methanol and benzene. We conclude that in this particular case, the field applied is not large enough to make the Zeeman splitting comparable to the singlet–triplet energy gap in the biradical. In principle one would expect an enhancement of the rate of biradical decay as this condition is approached and a decrease at higher fields. In a recent study Doubleday[8] examined the magnetic field dependence of CINDP from 1,6-biradicals generated in the Norrish Type I cleavage of substituted cyclohexanones. In addition to being able to apply higher fields, these studies were carried out with 1,6-biradicals which are expected to move the region of interest toward lower fields.[4,36] Interestingly the fd (field dependence) curves obtained were different for different products; Doubleday[8] points out that "to the extent that they produce different fd curves they do not come from the same biradical at all," and goes on to suggest that there may be some control of ISC on the product distribution. These results can all be explained on the basis of the same model given above. The singlet biradical decays occurs preferentially by the reaction path for which the nascent biradical is already "preset". While it is difficult to make a quantitative evaluation at this point, it is possible that the different reaction paths barely mix at all.

Since magnetic fields seem to affect product and product ratios from biradical reactions, one could conceive that magnetic isotopes could play a similar role. An intriging question is whether CINDP studies based on ^{13}C enhanced emission and absorption reflect the behaviour of the "bulk" biradicals or simply of those preselected by the technique on the basis of their ^{13}C content. If this was the case biradical conformational effects could provide yet another route for isotope enrichment, similar to those proposed by Turro.[29]

Another possible test of our model would be the examination of molecules where their structure places a restraint in the relative motion of the two radical centers. There are really no experiments of this type in the literature, at least none where the biradical lifetimes have been determined.[37] In this report, we note that biradicals such as 5 and 8 are not directly comparable, because the latter can also be regarded as the first excited state of the enol, 13.[38,39]
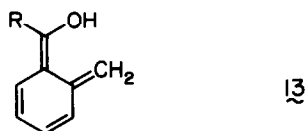
97 ns. We believe that the difference in structure, i.e. the increased proximity of the two radical sites is largely responsible for the decrease in lifetime, although other factors related to the cyclopropyl ring structure cannot be entirely ruled out at this point.

Another intriguing area of biradical behaviour are the solvent effects that are observed in the Norrish Type II reaction[10,11] and in the photoenolization of *ortho*-alkyl substituted carbonyl compounds.[41] For example, in the case of valerophenone the sum of the quantum yields of photofragmentation and photocyclization is 0.36 in benzene and increases to close to 1.0 in H-bonding media.[10,11] It is widely recognized that the affect is the result of the engagement of the OH group (from the ketyl center) in H-bonding, thus preventing the reabstraction.[10,42] At the same time the biradical lifetime increases, and is 30, 97 and 121 ns in benzene, methanol and pyridine; respectively.[15] It is tempting to try to correlate these two effects by simply stating that the biradical lifetime increases because of the slow down (or complete shut-off) of one of its reactions, i.e. the reabstraction. However, this is not consistent with the ISC model which requires the biradical lifetime to be controlled by ISC and not by chemical reaction paths. The model presented here provides a simple explanation: H-bonding solvents shut-off the reabstraction path, but in addition they change the conformational distribution in the triplet biradical and it is this that leads to the increase in lifetimes.[43] In addition, since singlet biradicals will now be formed in somewhat different conformations the cyclization-to-fragmentation ratios can be expected to change. If we assume that the short biradical lifetime obtained for 15 is the result of proximity, one would conclude that H-bonding solvents tend to separate the radical sites. Since cyclization must obviously require a cisoid conformation, one would predict a decrease in cyclization-to-fragmentation ratio with increased solvent H-bonding character. This is entirely consistent with experiment; for example the percentage of cyclobutanols from valerophenone is 18% in benzene and 12% in alcohols. Other ketones show similar features.[11]

How short does the singlet biradical lifetime need to be in order to be consistent with the mechanism proposed? Quite clearly biradical decay has to be faster than rotation around the 2,3-bond in a biradical such as 5. In the case of 17, if we combine experimental yields with biradical lifetimes one can estimate a barrier to rotation of 4–5 kcal/mol and a rotational time in the neighborhood of ∼ 4 ns.[11,44]

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We have recently examined the photochemistry of 14,[40] which yields biradical 15, which in turn cleaves to 16. We find that the lifetime of 15 is only 17 ns in methanol, under conditions where 2 and 11 have $\tau_B \sim$

On this basis we estimate that the singlet biradical lifetime has to be shorter than 1 ns. A crude estimation of the expected singlet lifetime can also be obtained by estimating the pre-exponential factor for decay via the reabstraction raction. If we assume that the transition

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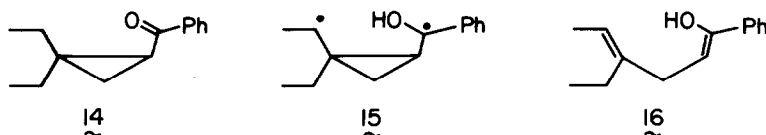
state for reabstraction is not substantially different from that for the Norrish Type II initial step, then, it is possible to use group additivity rules in the same way as reported for the forward reaction.[45] A crude estimation leads to log $(A/s^{-1}) \sim 10.5$. This combined with a very small activation energy (as expected for radical disproportionation) of 1–2 kcal/mol, and taking into consideration that other reaction paths also contribute (e.g. fragmentation), would suggest that singlet biradical lifetimes for the Norrish Type II reaction can be expected to be in the 10–500 ps range. This is naturally consistent with the fact that all attempts to detect and/or trap singlet biradicals have so far been fruitless, as well as with estimates based on CINDP studies.[4]

CONCLUSION

A model is proposed in which the lifetimes of triplet-derived biradicals in fluid media are controlled by the rate of ISC to the singlet manifold. Different biradical conformations have different abundances and different rates of ISC. The lifetime of the singlet biradical is much shorter than that required for rotational equilibration, and it collapses by the reaction path more suitable for the conformation in which the nascent singlet species is formed. As a result the nature and yields of products can be controlled by interactions at the triplet manifold level. The mechanism provides a straightforward explanation for the effect of paramagnetic species, solvents and conformational restrictions on the biradical lifetimes, as well as for their insensitivity to temperature. Product ratios are directly controlled by the conformational memory mentioned above.

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