

Negative Temperature Dependence in the Decay of Triplet Biradicals

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Abstract: The lifetimes of the 1,*n*-diphenylalkane-1,*n*-diyl triplet biradicals 3_n derived from type I photolyses of α,α' -diphenylcycloalkanones were studied by nanosecond transient absorption as a function of biradical chain length *n* and temperature. Intermediate-length biradicals $3_{5,6,9,10}$ have longer lifetimes than smaller ($3_{3,4}$) or larger ($3_{11,14}$) biradicals. The temperature dependence of the biradical lifetimes was measured in methanol and nonane solvents for biradicals $3_{5,9,11}$. For 3_5 , the Arrhenius activation energy for decay is normal. However for $3_{9,11}$ a novel *negative activation energy* has been observed in the range 0–100 °C. The results are interpreted in terms of an intrinsic relation between the sign of the high-temperature Arrhenius slope and the mechanism of intersystem crossing in the biradical.

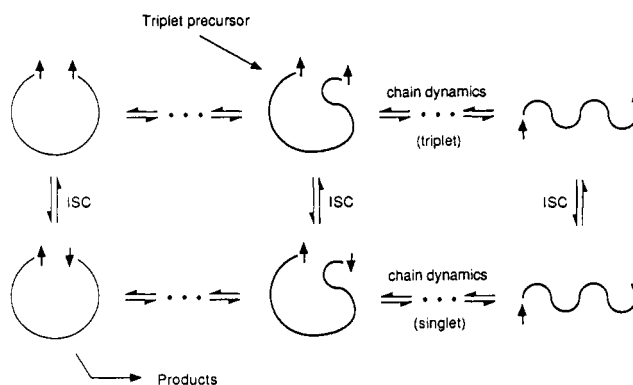
The temperature dependence of the lifetimes of a number of nonconjugated biradicals have been reported,^{1,2} many of which come from nanosecond transient UV absorption studies of flexible-chain biradicals.^{1a,b,2} The Arrhenius activation energies E_a are very small—only a few kcal/mol, and in many cases E_a is 1 kcal or less. In flexible triplet biradicals, the Arrhenius plot reveals the nature of the rate-limiting step for biradical decay.² Scheme I shows the important spin- and chain-dynamics processes of reactive polymethylene biradicals. Nanosecond experiments are able to probe intersystem crossing (ISC) and chain dynamics; product formation is subnanosecond.^{1,2} At low enough temperature, chain motions are slowed to the point where they become the rate-limiting step for biradical decay. At high temperature, chain motions are much faster and ISC becomes rate limiting. The intrinsically different temperature dependences of chain dynamics and ISC gives rise to a large curvature in the Arrhenius plot for biradical decay over a range of ca. –80 to 30 °C.²

In this paper we are particularly interested in the high temperature region (>0 °C) where rapid chain motions guarantee rotameric equilibrium of the triplet biradical prior to rate limiting ISC.² We report a study of the lifetimes of the triplet biradicals 3_n derived from type I cleavage and subsequent decarbonylation of α,α' -diphenylcycloalkanones 1_{n+1} (Scheme II)³ as a function of biradical chain length *n* and temperature. A novel *negative activation energy* for triplet biradical decay has been observed at high temperature. Our results suggest an intrinsic relation between the sign of the high-temperature Arrhenius slope and the mechanism of ISC in the biradical.

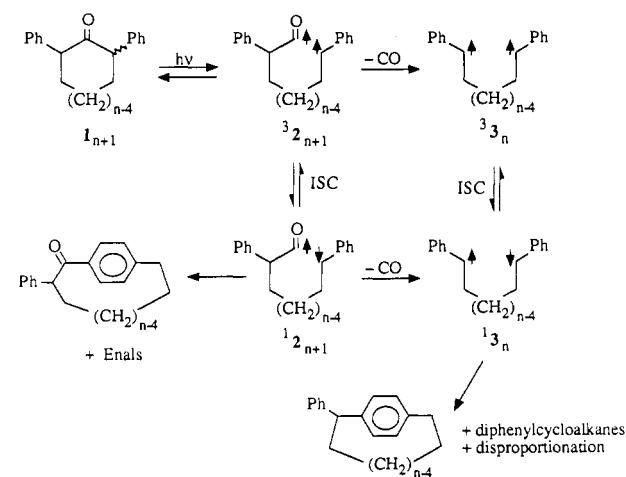
Experimental Section

Biradical lifetimes, τ , were measured by monitoring the transient absorption of the benzylic moiety at 320 nm following excitation by an excimer laser at 308 nm (fwhm ca. 18 ns) or a Nd-YAG laser at 266 nm (fwhm 6 ns), with a previously described apparatus.² Assignment of the transients was based on the transient absorption spectrum ($\lambda_{max} = 320 \pm 2$ nm) and the invariance of τ to addition of diene quencher. From –80 to 70 °C, the transient absorption spectrum was invariant and the product distribution was in accord with previous observations.⁴ The transient decays for 3_{4-6} were previously reported^{5a,6} and fit well to single-exponential decay. The decays for 3_n , $n \geq 9$, contained a small additional fast-decay component with an amplitude which increased as

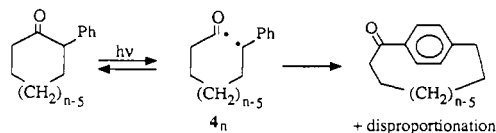
Scheme I



Scheme II



Scheme III



(1) (a) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252. (b) Caldwell, R. A. *Pure Appl. Chem.* **1984**, *56*, 1167. (c) Buchwalter, S.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857; **1979**, *101*, 4688. (d) Jain, J.; Snyder, G.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7294. (e) Sponser, M.; Jain, R.; Coms, F.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2240.

(2) Zimmt, M.; Doubleday, C.; Turro, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 3618.

(3) Syntheses of 3_n : Lei, X.; Doubleday, C.; Turro, N. J. *Tetrahedron Lett.* **1986**, *27*, 4671.

(4) Lei, X.; Doubleday, C.; Turro, N. J. *Tetrahedron Lett.* **1986**, *27*, 4675.

(5) (a) Previous report on $3_{4,5}$: Zimmt, M.; Doubleday, C.; Turro, N. J. *Chem. Phys. Lett.* **1987**, *134*, 549. (b) Report on *p*-acetyl-substituted 3_3 : Mizuno, K.; Ichinose, N.; Otsuji, Y.; Caldwell, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5797.

(6) Zimmt, M.; Doubleday, C.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6724.

n increased, from <5% for *n* = 6 up to ca. 25% for *n* = 14. All reported lifetimes in this paper correspond to the larger amplitude slow component. The temperature dependence of τ for $3_{5,9,11}$ was measured in methanol and nonane solvents over a range of –80 to 70 °C (methanol) or –50 to 100 °C (nonane).

Results and Discussion

Table I lists room temperature values of τ^{-1} as a function of the number of carbons in the biradical chain, *n*, for both the

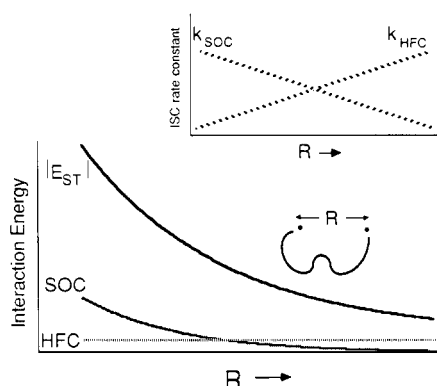


Figure 1. Qualitative dependence of the singlet-triplet energy gap and SOC and HFC matrix elements on end-to-end distance R . Upper inset: qualitative R dependence of ISC rate constants k_{SOC} and k_{HFC} , corresponding to pure SOC and HFC mechanisms, respectively. Linearity is not implied.

Table I. Rate Constants τ^{-1} ($\pm 5\%$) for Decay of Biradicals 3_n and 4_n at Room Temperature as a Function of n in Acetonitrile Solvent

n	3_n		4_n	
	$\tau^{-1} \times 10^{-6}, \text{s}^{-1}$	ref	$\tau^{-1} \times 10^{-6}, \text{s}^{-1}$	ref
3	77.0	5b		
4	5.3	5a		
5	1.07	5a		
6	0.87	6	16.4	6
7			10.6	6
8			9.4	6
9	1.56	this work	9.3	6
10	1.64	this work	10.4	6
11	3.17	this work	11.8	6
12			13.5	6
14	6.25	this work		
15			13.3	6

dibenzyl biradicals 3 and the previously reported⁶ acyl-benzyl biradicals 4 (Scheme III). The range of τ^{-1} for 3 is much greater than that for 4 , and the minimum τ^{-1} occurs around $n = 6-8$ for 3 and $n = 9$ for 4 . Where comparison can be made, for a given n , 3_n decays more slowly than 4_n . The maximum ratio is 19 for decays of 3_6 vs 4_6 .

Previous studies^{2,7a,8} have shown that above about 0°C the decays of 3 and 4 are limited by ISC. That is, $\tau^{-1} = k_{\text{ISC}}$, the rate constant for ISC from triplet to singlet biradical. Two mechanisms of ISC are important in 3 and 4 : spin-orbit coupling (SOC) and electron-proton hyperfine coupling (HFC). We estimated that SOC accounts for 86% of ISC in 4_{11} and 76% in 4_{12} , and the remainder of ISC occurs by means of electron-nuclear hyperfine coupling (HFC).^{7a,b} The absence of an acyl group in 3 suggests that the longer lifetimes are due to a small or negligible SOC contribution to ISC in 3_n , $n \geq 6$. Indeed, even though the mean square HFC in 3_n is twice that of 4_n , k_{ISC} in 3_n is much less than in 4_n . Therefore the data are consistent with dominant HFC in $3_{9-11,14}$ rather than SOC. This is corroborated by the very large magnetic field effect on τ for $3_{9,11,14}$.⁸

For a qualitative interpretation of the pattern of k_{ISC} vs n for 3_n , let us assume that k_{ISC} depends on the ISC matrix elements, consisting of SOC and HFC, and on the singlet-triplet energy gap ($E_{\text{ST}} \equiv \langle E_{\text{S}} - E_{\text{T}} \rangle$ (brackets indicate an average over conformations)). We shall consider these quantities as a function of end-to-end distance, R , since the conformational average value $\langle R \rangle$ increases as the biradical chain length n increases. These are shown qualitatively in Figure 1. Both $|E_{\text{ST}}|$ ⁹ and SOC¹⁰ are

(7) (a) Zimmt, M.; Doubleday, C.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6727. (b) In atoms, SOC increases as the fourth power of the effective nuclear charge. Delocalization of the odd electron in the acyl radical center of 4 onto oxygen is expected to give rise to significantly larger SOC in 4 than in 3 .

(8) Wang, J.; Doubleday, C.; Turro, N. J. *J. Phys. Chem.* In press.

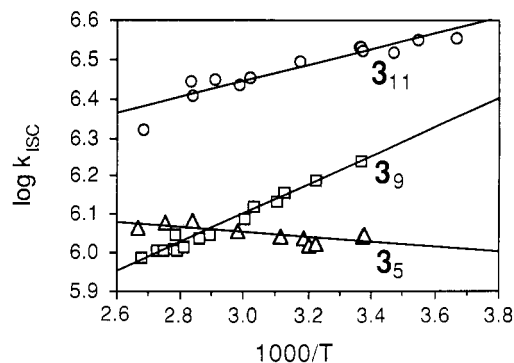


Figure 2. Arrhenius plots for the decay of 3_5 , 3_9 , and 3_{11} in nonane solvent.

Table II. High-Temperature Arrhenius Parameters for the Decay of Biradicals 3_n

biradical	methanol ^a		nonane ^b	
	$\log A^c$	E_a^d	$\log A^c$	E_a^d
3_5	6.4	0.5	6.3	0.3
3_9	4.8	-1.9	5.0	-1.7
3_{11}	5.9	-0.9	5.8	-0.9

^a Temperature range: $0-78^\circ\text{C}$. ^b $20-100^\circ\text{C}$. ^c ± 0.3 ; A in s^{-1} . ^d In kcal/mol, ± 0.2 .

expected to decay approximately exponentially with increasing R . HFC is independent of R . The upper plot in Figure 1 gives the qualitative R dependence of the ISC rate constants k_{SOC} and k_{HFC} for pure SOC and HFC mechanisms, respectively. With increasing R , k_{HFC} increases because the S-T gap gets smaller with a constant HFC. For a pure SOC mechanism, the matrix element is negligible at large R but can be very large at small R .¹¹ Thus k_{SOC} decreases as R gets larger. The contributions of SOC and HFC to τ^{-1} therefore have opposite R dependences.

In Table I, the decrease in $\tau^{-1} = k_{\text{ISC}}$ for $n = 3-6$ is the kind of change one expects from the R dependence of SOC. This pattern suggests that SOC is dominant in $3_{3,4}$ and perhaps 3_5 , which would correspond to the left side of Figure 1. At about $n = 6$, the increase in $\langle R \rangle$ may be sufficient to weaken SOC while still leaving a sizeable value of $\langle E_{\text{ST}} \rangle$. This situation—a large energy separation and a small ISC matrix element—is unfavorable for ISC, and one sees a small value of k_{ISC} for $n = 6$. For $n \geq 9$, HFC is probably the exclusive ISC mechanism since SOC is presumably very small. If $k_{\text{ISC}} \approx k_{\text{HFC}}$ for 3_n , $n \geq 9$, Figure 1 predicts that k_{ISC} should increase as $\langle R \rangle$ increases. This is just what we observe for $n \geq 9$. As the chain length n increases, $\langle R \rangle$ increases, and k_{ISC} consequently increases.

CIDNP and CIDEP are often observed in triplet biradical reactions,¹² and the spin polarization typically develops on the order of a few nanoseconds or less. This may seem incompatible with our observation of much longer lifetimes for the biradicals. However the two observations are consistent. The rate at which the biradical wave function acquires singlet character is very fast,

(9) (a) Doubleday, C.; McIver, J. W., Jr.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533; **1985**, *107*, 7904. (b) Kaptein, R.; DeKanter, F. *J. Am. Chem. Soc.* **1982**, *104*, 4759.

(10) (a) Caracci, L.; Doubleday, C.; Furlani, T.; King, H.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 5323. (b) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(11) ISC can be viewed as a radiationless transition from the triplet to a quasicontinuum of singlet vibrational levels. k_{ISC} for an individual conformer in Scheme I is then given by a golden-rule expression proportional to the square of the ISC matrix element appropriate to that particular conformer. Cf.: Henry, B.; Siebrand, W. In *Organic Molecular Photophysics*; Birks, J., Ed.; Wiley: New York, 1973; Vol. 1, p 153.

(12) (a) Closs, G. L.; Doubleday, C. *J. Am. Chem. Soc.* **1973**, *95*, 2735. (b) Closs, G. L. *Adv. Magn. Reson.* **1975**, *7*, 1. (c) Doubleday, C. *Chem. Phys. Lett.* **1979**, *64*, 67; **1981**, *77*, 131; **1981**, *79*, 375; **1981**, *81*, 164; **1982**, *85*, 65. (d) Kaptein, R.; DeKanter, F. *J. Am. Chem. Soc.* **1982**, *104*, 4759. (f) Closs, G. L.; Redwine, O. *J. Am. Chem. Soc.* **1985**, *107*, 4543; 6131. (g) Closs, G. L.; Miller, R.; Redwine, O. *Acc. Chem. Res.* **1985**, *18*, 196. (h) Closs, G. L.; Forbes, M. *J. Am. Chem. Soc.* **1987**, *109*, 6185.

but the singlet amplitude depends on the ratio of the ISC matrix element to E_{ST} . Since optical experiments detect the entire ensemble, amplitude is the relevant quantity. The observed value of k_{ISC} varies as the square of the singlet amplitude, which can be very small if E_{ST} is large. In these terms, Table I is consistent with increasing singlet amplitude with increasing n in 3_n for $n \geq 9$.

The temperature dependence of τ for $3_{5,9,11}$ was different in the low- and high-temperature regimes, as observed previously for 4 .² When $1_{6,10,12}$ were photolyzed below about 0 °C, the transient signals decayed more slowly as the temperature was lowered. However, the assignment of these signals was complicated by an increasing amount of biradical **2** below ca. -30 °C.⁵ Above 0 °C, decarbonylation of **2** is fast and only **3** is present.⁵ Figure 2 shows high temperature Arrhenius plots of $-\log \tau$ vs $1/T$ for $3_{5,9,11}$. The Arrhenius parameters are listed in Table II. For comparison, the previously determined high-temperature Arrhenius parameters (ca. -10 to 25 °C) for $4_{6,9,12,15}$ all had $\log A/s^{-1} \approx 8$ and $E_a \approx 1$ kcal/mol.² We recently remeasured the temperature dependence for 4_{10} in a higher temperature range: 0-77 °C in methanol and 0-100 °C in nonane. The Arrhenius parameters were $\log A/s^{-1} = 8.2$, $E_a = 1.5$ kcal/mol in methanol and $\log A/s^{-1} = 8.9$, $E_a = 2.4$ kcal/mol in nonane.

When a negative activation energy is encountered, it is usual to consider a mechanism in which the monitored species rapidly and reversibly form an intermediate complex lower in energy than the reactants. The complex then proceeds to products over a barrier lower than that required for return to reactants.¹³ For example, the two phenyl groups in **3** might form a shallow π -complex prior to cyclization. However, the negative activation energies for $3_{9,11}$ occur at high temperature, where ISC is rate limiting. ISC in flexible biradicals is not known to have intrinsic barriers, and a π -complex would presumably be formed after the ISC step.¹⁴ This forces us to examine other mechanistic possibilities. Of all the flexible triplet biradicals for which the temperature dependence of τ has been reported,^{1,2} $3_{9,11}$ are the only ones with negative activation energies and the only ones in which ISC is dominated by the HFC mechanism. In our opinion this is not a coincidence. We shall show that our discussion above of the relation between k_{ISC} and $\langle R \rangle$ for 3_n , $n \geq 9$, implies negative activation energies for $3_{9,11}$.

In the following discussion it is important that rapid conformational equilibration requires k_{ISC} to be a conformational average: $k_{ISC} = \sum_i f^i k_{ISC}^i$, where f^i is the equilibrium mole fraction of triplet conformer i and k_{ISC}^i is the ISC rate constant for conformer i (see Scheme 1). We can use this assumption together with Figure 1 to examine the temperature dependence of k_{ISC} , dk_{ISC}/dT . For a qualitative understanding of dk_{ISC}/dT it is convenient to consider k_{ISC} as a function of T and $\langle R \rangle$. Chain-rule differentiation of $k_{ISC}(T, \langle R \rangle)$ gives

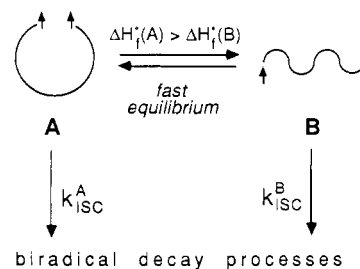
$$\frac{d}{dT} k_{ISC} = \left(\frac{\partial k_{ISC}}{\partial T} \right)_{\langle R \rangle} + \left(\frac{\partial k_{ISC}}{\partial \langle R \rangle} \right)_T \frac{d\langle R \rangle}{dT} \quad (1)$$

For a given biradical conformation, the explicit T dependence of ISC (first term of eq 1) is expected to be small. To a first approximation we ignore it and concentrate on the chain-rule product. To understand the sign of the high-temperature Arrhenius slope, we need to know the sign of each of the two derivatives.

The $\partial k_{ISC}/\partial \langle R \rangle$ term is qualitatively given in the upper plot in Figure 1. For $3_{9,11}$, $k_{ISC} \approx k_{HFC}$, and for 4_n , $k_{ISC} \approx k_{SOC}$.^{7a} The sign of this term is therefore positive for $3_{9,11}$ and negative for 4_n . For $d\langle R \rangle/dT$, we note that a close approach of the two ends

(13) For an example of such a mechanism in radical recombination, see: Olson, J.; Koch, T. *J. Am. Chem. Soc.* **1986**, *108*, 756.

(14) A referee has suggested that a triplet π -complex may be formed, by analogy with triplet excimers. At present the nature of triplet exciplexes is open to discussion. The interactions leading to complex formation typically lower the HOMO and raise the LUMO of the complex, which favors the singlet state, not the triplet. It is conceivable that in a specific geometry electron correlation could overcome the singlet preference. For the present, we shall note the possibility and proceed with the analysis.



HFC: $k_{ISC}^A < k_{ISC}^B$ negative activation energy

SOC: $k_{ISC}^A > k_{ISC}^B$ positive activation energy

Figure 3. Simplified version of a triplet biradical kinetic scheme capable of giving either positive or negative activation energies, depending on the relative values of the conformational ISC rate constants.

of the biradical requires an enthalpically unfavorable situation of several gauche interactions within the chain. On average, a smaller value of R is associated with a greater number of gauche interactions (higher enthalpy). Experimentally, Flory showed that larger $\langle R \rangle$ is favored by lower temperature in polyethylene,^{15a-c} and similar results were deduced from ESR of flexible nitroxide biradicals.^{15d} Thus $d\langle R \rangle/dT$ is negative.

Now we have the information needed to evaluate the sign of the chain-rule product in eq 1. For $3_{9,11}$ one gets (+)(-) = (-), and for 4_n , (-)(-) = (+): a negative temperature dependence for $3_{9,11}$ and a positive one for 4_n . This analysis suggests that the sign of the high-temperature Arrhenius slope is diagnostic for the dominant ISC mechanism. A positive activation energy implies that ISC is favored in conformers with small R , which implies that SOC is the dominant ISC mechanism. A negative activation energy implies that ISC is faster in conformers with large R , and HFC is the dominant mechanism. The hypothesis can be tested in the 3_n series, because the smaller members are dominated by SOC and the sign of E_a should be positive. This is in fact observed for 3_5 (Table II, Figure 2). From the Arrhenius parameters together with the discussion of Table I, we conclude that HFC and SOC both contribute to ISC in 3_5 , but that SOC is dominant.

As far as we are aware, the mechanism proposed to give rise to negative activation energies in $3_{9,11}$ is unprecedented. The essential elements are summarized in Figure 3. Triplet biradical conformers A with short R are in rapid equilibrium with conformers B with long R , and B is favored enthalpically. The rate constant for decay of A + B is given by the Winstein-Holness relation,¹⁶ $\tau^{-1} = f^A k_{ISC}^A + f^B k_{ISC}^B$, where $f^{A,B}$ are equilibrium mole fractions. The unique feature of this mechanism is that the decays of A and B via ISC are assumed to have no activation barrier; they are slower than A/B interconversion because of the low Arrhenius A factors associated with ISC. The temperature dependence of τ^{-1} comes from the temperature dependence of the A/B equilibrium, which favors B at lower temperature.¹⁷ Actually, the kinetic scheme in Figure 3 bears a formal similarity to the usual mechanism leading to a negative E_a , in which two reactants form an intermediate complex lower in energy than the reactants, followed by a fast product forming step.¹³ The reactants and complex of the standard mechanism would correspond to A and B, respectively, in Figure 3.

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(16) Winstein, S.; Holness, N. J. *J. Am. Chem. Soc.* **1955**, *77*, 5562.

(17) The Winstein-Holness relation, not the related Curtin-Hammett principle, is the proper mechanistic framework for Figure 3. The Curtin-Hammett principle deals with a rate ratio or product distribution rather than with the total rate constant for decay. These issues are discussed in the following: (a) Eliel, E. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962. (b) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970. (c) DeTar, D. F. *J. Org. Chem.* **1986**, *51*, 3749.

Negative activation energies are not common, but for certain types of reactions they are the rule rather than the exception. It has long been known that the activation energy for gas-phase diatomic dissociation is smaller than the bond-dissociation energy.¹⁸ The associated negative temperature dependence for diatomic recombination can be viewed as a variation of the standard mechanism, in which the atoms reversibly form a vibrationally excited diatomic, followed by collisional deactivation. In general, a negative temperature dependence can be observed if recombination is more efficient for molecules with less than the average thermal energy.¹⁹ In solution, a variety of fast bimolecular reactions exhibit negative activation energies. Recent examples from this laboratory include reactions of olefins with singlet carbenes²⁰ and nitrile ylides,²¹ which are readily interpreted by the standard mechanism. Another interpretation of negative activation energies has developed from the observation that, for reactions with very small or zero potential energy barriers, conventional transition-state theory is inadequate and a variational approach must be used.²² These ideas have been applied to alkyl radical recombinations,²³ many of which exhibit a negative temperature dependence.²⁴ They have also been applied to intramolecular singlet biradical reactions²⁵ and singlet carbene addition

to olefins.²⁶

In general, the analysis in terms of eq 1 should apply to any flexible triplet biradical, but not necessarily to biradicals with restricted geometries. For example, a rigid triplet biradical (only one local biradical energy minimum) with HFC as the major ISC mechanism would have a positive activation energy if nuclear motion brought the singlet and triplet levels closer together. A caveat for our interpretation is that we have ignored the explicit T dependence in eq 1. A theoretical analysis of the two state curve crossing problem has revealed circumstances in which the T dependence of ISC may be observed if the T range is large enough,^{27a} and benzene and derivatives in the gas phase under isolated-molecule conditions exhibit a strong energy dependence of ISC.^{27b-d} It appears that neither of these situations applies to flexible biradical ISC, but an intrinsic T dependence may nevertheless exist. We shall be testing our interpretation on other biradicals.

Conclusion

Evidence presented here suggests that the high-temperature Arrhenius parameters for biradical decay depend on both the equilibrium distribution of triplet conformers and the relative contributions of SOC and HFC to the total ISC of the biradical. In a previous study,² we showed that the temperature dependence allows one to monitor a change in the rate-limiting step for biradical decay, between ISC and chain dynamics. The temperature dependence is therefore not simply a routine experiment for determining "barriers", but is extraordinarily rich in information about chain motions, chain equilibria, and spin dynamics.

Acknowledgment. C.D. thanks the National Science Foundation, Grant No. CHE-8721164, for support. J.W. and N.J.T. thank the NSF, the Department of Energy, and the Air Force Office of Scientific Research for support.

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