On the Rate-Determining Step for Decay of Triplet Biradicals: Intersystem Crossing vs. Chain Dynamics

Matthew B. Zimmt, Charles Doubleday, Jr.,* and Nicholas J. Turro

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received October 28, 1985

Abstract: The temperature and viscosity dependence of the lifetimes of triplet biradicals derived from 2-phenylcycloalkanones have been studied by means of nanosecond transient UV absorption. Arrhenius plots for the temperature range 20 to −90 °C are strongly curved. In the high-temperature range (ca. −10 to +20 °C) log A (s^{-1}) and E_a (kcal/mol) are ca. 8.0 and 1.0, respectively. In the low-temperature range (−50 to −90 °C) the values are ca. 10–11 and 3–4, respectively, typical of chain cyclization processes. The biradical lifetimes are strongly affected by solvent viscosity at low temperature but are nearly insensitive to viscosity at room temperature. The data suggest a transition in the rate-determining step for biradical decay from intersystem crossing control at room temperature to chain dynamics control at low temperature. At room temperature and above, the observable biradicals are almost exclusively triplets, but at low temperature one observes the decay of an approximately equilibrium mixture of singlets and triplets.

What is the rate-determining step for intramolecular decay of a triplet biradical? This is a long-standing fundamental question in biradical chemistry,[1] and the answer is expected to depend in some way on the biradical structure and on experimental conditions. In principle, the rate-determining step could be any one of the 3 processes shown in Scheme I: (1) intersystem crossing (isc) to the singlet biradical, (2) interconversion among biradical chain conformers (occurring in both singlet and triplet), and (3) product formation from a singlet biradical in a conformer poised for product formation. Current evidence[2–7] favors isc as the rate-determining step for decay of small, flexible triplet biradicals in fluid solution. In this paper we present the first evidence for *conditions which swtich the rate-determining step from isc to chain dynamics*. Under these conditions isc is fast compared to biradical decay, and one observes decay of an approximately equilibrium mixture of singlet (S) and triplet (T) biradicals, i.e., T:S ≈ 3:1. We show that the rate-determining step is related in a simple way to *biradical chain length, temperature, and solvent viscosity*. The particular biradicals used in this study have one acyl and one benzylic terminus, but the qualitative conclusions are expected to apply to all flexible-chain biradicals.

The triplet biradicals ³2 (Scheme II) were generated from ketones[8] 1 by photolysis at 308 nm with a Lamba Physik excimer laser (15 ns fwhm, <20 mJ per pulse) and their lifetimes (τ) were measured by nanosecond transient UV absorption monitored at 320 nm. The analyzing light was generated by pulsing a 450-W Xe arc lamp (PRA Model 301 power supply, PRA Model 305 pulser) and detected through an ISA H10 monochrometer using
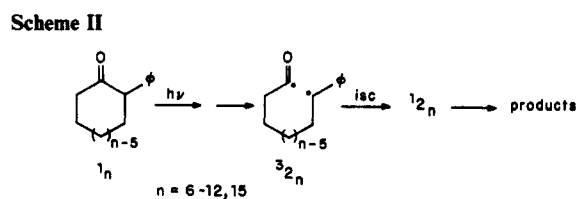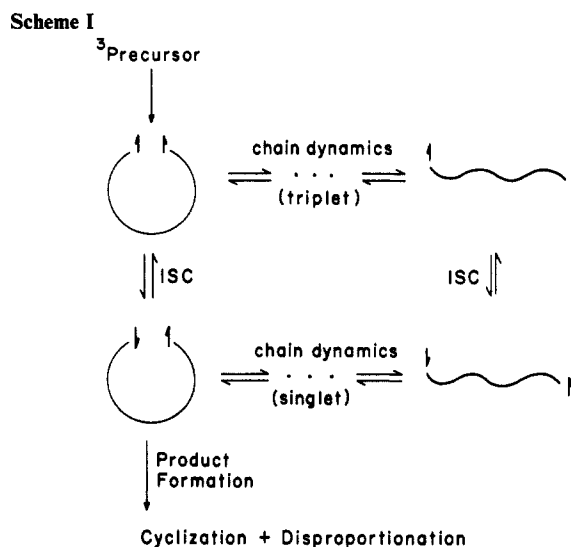
Scheme I

Scheme II

Table I. Limiting Arrhenius Parameters for Decay of 2_6, 2_9, 2_{12}, 2_{15}

temp region	n	methanol		isooctane	
		log A^a	$E_a{}^b$	log A^a	$E_a{}^b$
high	6	7.7	0.8		
high	9	8.1	1.5	7.9	1.0
high	12	8.1	1.2	8.0	1.1
high	15	8.1	1.1	7.9	0.8
high	15^c			8.1^c	1.1^c
low	6	7.7	0.8		
low	9	8.8	2.2	9.6	2.9
low	12	10.6	3.6	10.0	3.1
low	15	10.8	4.0	10.0	3.2
low	15^c			9.0^c	2.2^c

^{a} ±0.3; A in s^{-1}. ^{b} In kcal/mol, ±0.2. ^{c} Isoviscous, η = 1.00 ± .05 cP, in alkane solvents, pentane to pentadecane.

6 dynodes of an RCA 4840 photomultiplier tube. Signals were digitized with either a Biomation 4500 digital oscilliscope or a Tektronix 7912AD programmable digitizer. Data analysis was performed on a dedicated PDP 11/23 minicomputer. The excitation geometry was right-angle. Variable-temperature studies

(1) Wagner, P. J. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; p 381.

(2) (a) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252. (b) Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819. (c) Scaiano, J. C.; Lee, C.; Chow, Y.; Marciniak, B. *J. Phys. Chem.* **1982**, *86*, 2452.

(3) (a) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629. (b) Caldwell, R. A.; Creed, D. *J. Phys. Chem.* **1978**, *82*, 2644. (c) Caldwell, R. A.; Sakuragi, H.; Majima, T. *J. Am. Chem. Soc.* **1984**, *106*, 2471.

(4) (a) Closs, G.; Doubleday, C. *J. Am. Chem. Soc.* **1973**, *95*, 2735. (b) Closs, G. *Adv. Magn. Reson.* **1975**, *7*, 1. (c) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 3586. (d) Closs, G. L.; Miller, R.; Redwine, O. D. *Acc. Chem. Res.* **1985**, *18*, 196. (e) Closs, G. L.; Redwine, O. D. *J. Am. Chem. Soc.* **1985**, *107*, 4543, 6131.

(5) (a) Doubleday, C. *Chem. Phys. Lett.* **1979**, *64*, 67. (b) Doubleday, C. *Ibid.* **1981**, *77*, 131. (c) Doubleday, C. *Ibid.* **1981**, *79*, 375. (d) Doubleday, C. *Ibid.* **1981**, *81*, 164. (e) Doubleday, C. *Ibid.* **1982**, *85*, 65.

(6) (a) DeKanter, F.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4759. (b) DeKanter, F.; den Hollander, J.; Huizer, A.; Kaptein, R. *Mol. Phys.* **1977**, *34*, 857.

(7) (a) Bartlett, P.; Porter, N. *J. Am. Chem. Soc.* **1968**, *90*, 5317. (b) Schultz, P.; Dervan, P. *J. Am. Chem. Soc.* **1982**, *104*, 6660. (c) Dervan, P. B.; Dougherty, D. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1981; pp 107–149.

(8) Synthetic sequence starting with the parent cycloalkanone: (1) PhLi; (2) TsOH; (3) B$_2$H$_6$, then H$_2$O/NaOH; (4) pyridinium chlorochromate.

Rate-Determining Step for Decay of Triplet Biradicals

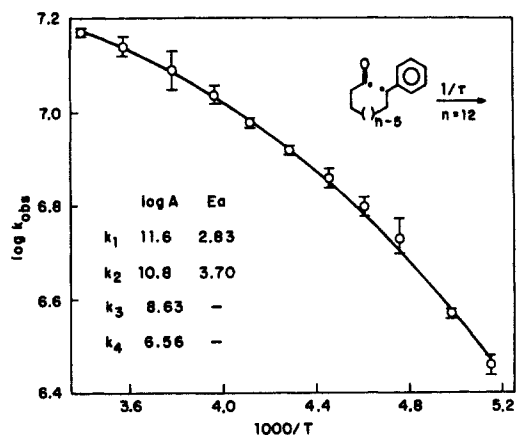*J. Am. Chem. Soc., Vol. 108, No. 13, 1986* 3619

Figure 1. Arrhenius plot (4–6 measurements per point) for decay of 2_{12} in MeOH. τ is the biradical lifetime. The line is the best fit of the data to Scheme III, obtained with the parameters shown (see text). Errors are ±2 standard deviation.
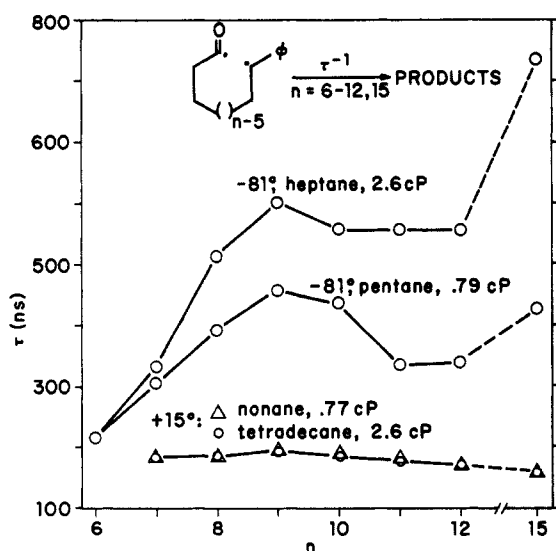

Figure 2. Viscosity dependence of the biradical lifetimes at −81 and +15 °C. Each point is an average of 3 measurements at −81° and 5 at 15°. Typical errors (±2σ) are ±5%.

Figure 3. Qualitative representation of the dependence of the rate-determining step for biradical decay (isc vs. chain dynamics) upon viscosity η, temperature T, and biradical chain length.

Scheme III

were performed with use of an optical dewar (three quartz windows positioned at 90° intervals) and chilled or heated with N_2 gas. Temperature readings were made on an Omega Digicator with constantan thermocouple, which was attached directly to the cell holder in the dewar. All biradicals were characterized by their transient UV spectra in MeOH (λ_{max} = 320 ± 2 nm)[9] and by the invariance of τ to isoprene quenching, both at 20 and at −80 °C.[10]

The temperature dependence of τ was measured for 2_6 in MeOH and for 2_9, 2_{12}, and 2_{15} in MeOH and isooctane (2,2,4-trimethylpentane) from 20 to −85 or −95 °C, depending on solvent. An Arrhenius plot of −log τ vs. $1/T$ is linear for 2_6, curved for 2_9, and *strongly curved* for 2_{12} and 2_{15}. Figure 1 shows the experimental points for 2_{12} in MeOH. Table I lists the limiting values of the Arrhenius parameters in the high- (ca. −10 to 20 °C) and low- (ca. −90 to −50 C) temperature regions. Because of the limited temperature range, these may not be the true asymptotic values.

Table I includes the results of an isoviscous Arrhenius plot for 2_{15}, obtained by measuring each experimental point in a different alkane solvent (pentane to pentadecane) at a temperature selected to hold the viscosity constant at η = 1.00 ± 0.05 cP. The effect of viscosity was examined further by measuring τ at −81° in

pentane (0.79 cP)[11] and heptane (2.6 cP)[11] and at +15° in nonane (0.77 cP)[11] and tetradecane (2.6 cP).[11] The results (Figure 2) show a pronounced viscosity dependence at −81 °C but a negligible one at 15 °C.

The data in Figures 1 and 2 and Table I are consistent with a *change in rate-determining step for biradical decay from isc at high temperature to chain dynamics at low temperature.* This situation is easily understood in terms of Scheme I. At 25 °C in fluid solution, isc is typically the rate-determining step for biradical decay,[2–7] chain dynamics is faster, and product formation is fastest of all.[6,7] To a first approximation isc is expected to be independent of both the temperature T and solvent viscosity η. On the other hand, conversion of an extended to a nearly cyclic conformer has an activation energy of ca. 2–4 kcal/mol[12] and is slowed down by increasing η[12,13] as a result of frictional forces exerted by the solvent.[14] As one increases η/T, either by increasing η or decreasing T, chain dynamics is slowed to the point where it becomes the rate-determining step. In general, with increasing biradical chain length n the change from isc to chain

(9) Gould, I.; Zimmt, M.; Turro, N.; Baretz, B.; Lehr, G. *J. Am. Chem. Soc.* **1985**, *107*, 4607.

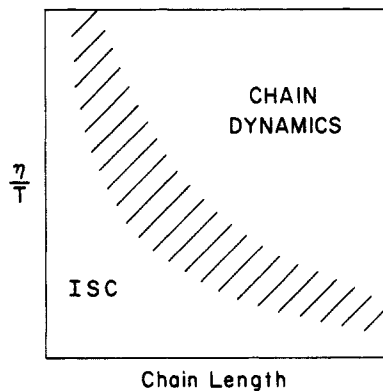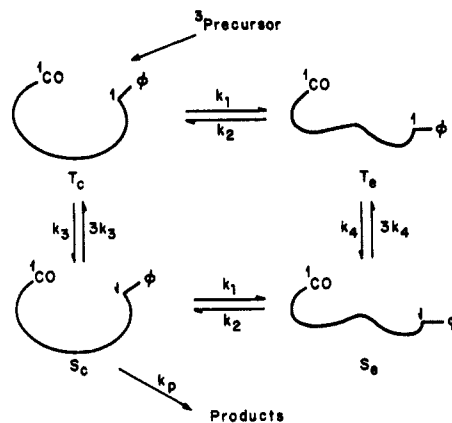(10) At 20 °C up to 0.01 M isoprene was used and at −80 °C up to 0.4–0.8 M isoprene.

(11) Rossini, F.; Pitzer, K.; Arnett, R.; Braun, R.; Pimentel, G. *Selected Values of Physical and Thermodynamical Properties of Hydrocarbons and Related Compounds*; Carnegie Press: Pittsburgh, 1953; p 226.

(12) (a) Redpath, A.; Winnik, M. *J. Am. Chem. Soc.* **1982**, *104*, 5604. (b) Winnik, M. *Chem. Rev.* **1981**, *81*, 491. (c) Goldenberg, M.; Emert, J.; Morawetz, H. *J. Am. Chem. Soc.* **1978**, *100*, 7171. (d) Nairn, J.; Braun, C. *J. Chem. Phys.* **1981**, *74*, 2441. (e) Nairn, J.; Braun, C.; Caluwe, P.; Szwarc, M. *Chem. Phys. Lett.* **1978**, *54*, 469.

(13) (a) Yang, N. C.; Neoh, S.; Naito, T.; Ng, L.-K.; Chernoff, D.; McDonald, D. *J. Am. Chem. Soc.* **1980**, *102*, 2806. (b) Zachariasse, K.; Duvenek, G.; Busse, R. *J. Am. Chem. Soc.* **1984**, *106*, 1045 and references therein. (c) Morawetz, H. *Pure Appl. Chem.* **1980**, *52*, 277. (d) Perchak, D.; Weiner, J. *Macromolecules* **1981**, *14*, 785.

(14) (a) Montgomery, J., Jr.; Chandler, D.; Berne, B. *J. J. Chem. Phys.* **1979**, *70*, 405. (b) Grote, R.; Hynes, J., *J. Chem. Phys.* **1980**, *73*, 2715; **1981**, *74*, 4465. (c) Berne, B.; Skinner, J.; Wolynes, P. *J. Chem. Phys.* **1980**, *73*, 4314. (d) Jasha, D.; Eguchi, T.; Jonas, J. *J. Am. Chem. Soc.* **1982**, *104*, 2290. (e) Vesko, S.; Waldeck, D.; Fleming, G. *J. Chem. Phys.* **1983**, *78*, 249.

3620 *J. Am. Chem. Soc., Vol. 108, No. 13, 1986*

Zimmt et al.

dynamics occurs at lower values of η/T. This is summarized qualitatively in Figure 3, which shows how the rate-determining step depends upon T, η, and n. The transition zone between isc and chain dynamics is broad, corresponding to the large temperature range separating the two limiting regimes. All our data are accommodated by this qualitative model. 2_6 corresponds to the left side of Figure 3, since the linear Arrhenius plot implies that even at -80 °C the biradical is in the low η/T isc-limited regime. 2_{12} and 2_{15} correspond to the right side of Figure 3—their low-T Arrhenius parameters are typical of chain cyclizations.[12] The large effect of η at -81 °C and the negligible effect at 15 °C corroborate the change in rate-determining step for 2_{12} and 2_{15} on going from high to low T.

For quantitative modelling, Scheme III (a special case of Scheme I) is the simplest model that exhibits a change in rate-determining step and a curved Arrhenius plot. Biradicals are divided into two classes: nearly cyclic triplet/singlet conformers (T_c, S_c) with small end-to-end distances R and extended conformers (T_e, S_e) with large R. The factor of 3 in the isc rate constants guarantees that T:S = 3:1 at equilibrium. The kinetic equations were solved exactly, subject to $k_p \gg k_{1-4}$[6,7] and initial formation of T_c, to obtain k_{obsd} ($=\tau^{-1}$), the rate constant for disappearance of $T_c + T_e + S_c + S_e$. In the resulting tetraexponential, k_{obsd} corresponds to the slowest decay. The temperature dependence was simulated in a six-parameter fit by putting $k_1 = A_1 \exp(-E_1/RT)$, $k_2 = A_2 \exp(-E_2/RT)$, with k_3 and k_4 T independent.

Ideally, each Arrhenius plot should yield four parameters: a slope and intercept at high T and at low T. In practice, one must be sure that one's temperature range reaches into the asymptotic high- and low-T limits. This condition is probably fulfilled for 2_{15}, is probably not fulfilled for 2_9, and is borderline for 2_{12}. In any case the Arrhenius plot alone is not sufficient to determine the six parameters A_1, E_1, A_2, E_2, k_3, and k_4. However, for the case of 2_{12} in MeOH, we have also measured the magnetic field dependence of τ.[15b] This yields additional constraints, such as the ratio of τ at zero field vs. high field.[15b] (There is excellent reason to assume that the magnetic field affects only the extended conformers and that isc is decreased by a factor of 3 on going from zero to high field, where the Zeeman splitting isolates the $T_{\pm1}$ states.[15b]) Application of this constraint to a least-squares fit yields the solid line in Figure 1 with the parameters as shown. The fit has a mean deviation from experiment of 1.9%, and the quality of the fit is sensitive to all six parameters. A wide variety of starting guesses in the least-squares fit were tried, but the parameters shown produce by far the best fit. The main conclusions we draw from the fit are the following: (1) Scheme III is a reasonable framework within which to discuss the results, and (2)

the parameters are qualitatively reasonable. No magnetic field studies of 2_6, 2_9, and 2_{15} have yet been done. Therefore these fits, though all within experimental error, are not unique.

One must keep in mind that the "nearly cyclic" and "extended" conformers of Scheme III each represent an average of a whole family of conformers. We have singled out the nearly cyclic and extended classes of conformers for special attention, because isc is strongly tied to the biradical geometry, in particular to the end-to-end distance.[15,16] We[15] and Closs[4e] have pointed out that spin–orbit coupling dominates isc in biradicals derived from cycloalkanones. It does so because the nearly cyclic conformers, with small end-to-end distances, are associated with very large spin–orbit coupling.[16] This leads us to expect $k_3 \gg k_4$ in Scheme III, which is corroborated by the fitting parameters in Figure 1. At high temperature (>260 K) T_e-T_c interconversion is fast[12] compared to isc, and equilibrium is reached among triplet conformers prior to isc. Thus at high temperature τ^{-1}, the conformationally averaged rate constant for isc *depends on the equilibrium ratio* T_c/T_e. *The high-temperature Arrhenius slope is related not to an activation energy for a rate process but to the temperature dependence of the* T_c/T_e *equilibrium constant.*

For 2_n ($n \geq 9$) at low temperature, T_e/T_c interconversion becomes slower than isc. The time-dependent solution to Scheme III suggests that, on a time scale too short for us to monitor at present, part of the initially formed T_c is lost via isc to S_c, and the rest is converted to T_e, whose subsequent decay we measure. For 2_{12} at -80 °C, the fitting parameters of Figure 1 imply that T_e and S_e equilibrate almost completely (T_e:S_e = 78:22, virtually the same as the 75:25 equilibrium mixture) before conversion to T_c and S_c. *Thus for the large biradicals at low temperature one monitors the decay of an approximately equilibrium mixture of singlets and triplets.* Irrespective of spin state, low-temperature decay is limited by passage from extended to cyclic conformers, and the calculated k_{obsd} is very close to k_2.

The viscosity effects reported here have literature precedent. Yang[13a] studied intramolecular exciplex formation in 3-(9-anthryl)-1-(*N*-phenyl-*N*-methylamino)propane, and found that increased solvent viscosity retards the *rates* of formation and dissociation of the exciplex but has almost no effect on the *equilibrium constant*. This is precisely the model we advocate. At high T, τ is insensitive to η, because τ is controlled by isc, which depends on the T_c/T_e equilibrium. At low T, τ responds to η because τ depends on chain dynamics.

(15) (a) Zimmt, M.; Doubleday, C.; Gould, I.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6724. (b) Zimmt, M.; Doubleday, C.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6726.

(16) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.