Negative Temperature Dependence in the Decay of Triplet Biradicals

Jinfeng Wang, Charles Doubleday, Jr.,* and Nicholas J. Turro

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received October 3, 1988

Abstract: The lifetimes of the 1, n-diphenylalkane-1, n-diyl triplet biradicals 3, derived from type I photolyses of \( \alpha, \alpha'- \)diphenylcycloalkanes were studied by nanosecond transient absorption as a function of biradical chain length \( n \) and temperature. Intermediate-length biradicals \( 3_{3-8,10} \) 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 \( 3_{3,11} \). For \( 3_{n} \), the Arrhenius activation energy for decay is normal. However for \( 3_{11} \), 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.\(^{1,2} \) 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 -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 \( \alpha, \alpha'- \)diphenylcycloalkanes \( 1_{n+1} \) (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, \( \tau \), 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 325 nm (fwhm 6 ns), with a previously described apparatus.\(^{7} \) Assignment of the transients was based on the transient absorption spectrum (\( \lambda_{\text{max}} = 320 \pm 2 \) nm) and the invariance of \( \tau \) 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.\(^{8} \) The transient decays for \( 3_{3,4} \) were previously reported\(^{8,9} \) 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 \( n \) 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 the biradical lifetimes was measured in methanol and nonane solvents over a range of -80 to 100 °C (methanol) or -50 to 100 °C (nonane).

Results and Discussion

Table I lists room temperature values of \( \tau_{1} \) as a function of the number of carbons in the biradical chain, \( n \), for both the

---

*Corresponding author.


Negative Temperature Dependence of Triplet Biradical Decay

![Graph](image)

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.

For a qualitative interpretation of the pattern of $k_{SOC}$ vs $n$ for $3_a$ let us assume that $k_{SOC}$ depends on the ISC matrix elements, consisting of SOC and HFC, and on the singlet-triplet energy gap ($E_{ST} = E_S - E_T$) (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 ($R$) increases as the biradical chain length $n$ increases. These are shown qualitatively in Figure 1. Both $E_{ST}^{(R)}$ and SOC$^{(R)}$ are 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 $R$. Thus $k_{SOC}$ decreases as $R$ gets larger. The contributions of SOC and HFC to $r^{-1}$ therefore have opposite $R$ dependences.

In Table I, the decrease in $r^{-1} = k_{SOC}$ 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 $3_a$ and perhaps $3_b$, which would correspond to the left side of Figure 1. At about $n = 6$, the increase in ($R$) may be sufficient to weaken SOC while still leaving a sizeable value of ($E_{ST}$). 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 $k_{SOC} = k_{HFC}$ for $3_a$, $n \geq 9$, Figure 1 predicts that $k_{HFC}$ should increase as ($R$) increases. This is just what we observe for $n \geq 9$. As the chain length $n$ increases, ($R$) increases, and $k_{SOC}$ consequently increases.

CIDNP and CIDEP are often observed in triplet biradical reactions, 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,
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 a relevant quantity. The observed value of $k_{ISC}$ varies as the square of the singlet amplitude, which can therefore 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 $r$ for $3_{9,11}$ was different in the low- and high-temperature regimes, as observed previously for $3^{12}$. When $t_{4_{9,10,12}}$ 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. Above 0 °C, decay of signal 2 is fast and only 3 is present. Figure 2 shows high temperature Arrhenius plots of $-\log k_{ISC}$ vs 1/T for $3_{9,11}$. The Arrhenius parameters are listed in Table II. For comparison, the previously determined high-temperature Arrhenius parameters (ca. -10 to 25 °C) for $4_{9,8,12,15}$ all had $A/s^{-1} \approx 8$ and $E_a = 1$ kcal/mol. 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 $A/s^{-1} = 8.2, E_a = 1.5$ kcal/mol in methanol and $A/s^{-1} = 8.9, E_a = 2.4$ kcal/mol in nonane. When a negative activation energy is encountered, it is useful to consider a mechanism in which the monitored species rapidly equilibrates with 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. For example, the two phenyl groups in 3 might form a shallow barrier lower than that required for return to reactants. For a qualitative understanding of d$k_{ISC}$/dT it is convenient to consider $k_{ISC}$ as a function of $T$ and ($R$). Chain-rule differentiation of $k_{ISC}(T, R)$ gives

$$\frac{d}{dT} k_{ISC} = \left(\frac{\partial k_{ISC}}{\partial T}\right)_R + \left(\frac{\partial k_{ISC}}{\partial R}\right)_T \frac{d(R)}{dT}$$

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 $\partial k_{ISC}/\partial R$ term is qualitatively given in the upper plot in Figure 1. For $3_{9,11}$, $RISC = k_{ISC}$, and for $4_{9,11}$, $k_{ISC} = k_{SOC}$. The sign of this term is therefore positive for $3_{9,11}$ and negative for $4_{9,11}$. For $d(R)/dT$, we note that a close approach of the two ends 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 ($R$) is favored by lower temperature and, because the smaller members are dominated by SOC and the sign of $E_a$ should be positive. This is in fact observed for $3_{9,11}$ (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 $3_{9,11}$, 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 $B$ with long $R$, and $B$ is favored enthalpically. The rate constant for decay of $A + B$ is given by the equation $k_{ISC} = k_{SOC} = k_{SOC}$. 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 factors associated with ISC. The temperature dependence of $R^+1$ comes from the temperature dependence of the $A/B$ equilibrium, which favors $B$ at lower temperature. 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. The reactants and complex of the standard mechanism would correspond to $A$ and $B$, respectively, in Figure 3.
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. 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. In solution, a variety of fast bimolecular reactions exhibit negative activation energies. Recent examples from this laboratory include reactions of olefins with singlet carbene and nitrile ylides, 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. These ideas have been applied to alkyl radical recombinations, many of which exhibit a negative temperature dependence. They have also been applied to intramolecular singlet biradical reactions and singlet carbene addition to olefins.

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 contribution of SOC and HFC to the total ISC of the biradical. In a previous study, 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-871164, 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.