

Transient spectroscopy (mode-locked Nd-YAG laser, fourth harmonic, 266 nm, fwhm 1.75 ns including broadening by detection electronics, unfocused, ca. 20 mJ/pulse) afforded strong signals identical in lifetime,  $\lambda_{\max}$ , and OD from either **1** or a **1-2** mixture containing >90% **2** in which **2** absorbs >92% of the 266-nm excitation. Were the signal only derived from **1**, its intensity in the irradiation of the mixture would have been ca. tenfold less. With 1 M isoprene, the lifetime of the signal from **1** in heptane was unaffected; its OD was attenuated almost precisely by the amount expected based on the relative extinction coefficients of **1** and isoprene at 266 nm. Lifetimes from **1** (or the **1-2** mixture) were as follows: heptane,  $14.7 \pm 1$  ns; methanol,  $13.4 \pm 1$  ns ( $13.0 \pm 1.5$  ns). Absorption maxima were 320 nm in heptane and 327 nm in methanol ( $\pm 5$  nm).

Similar results were obtained for *trans*-1-(4-acetylphenyl)-2-phenylcyclopropane (**4**),<sup>17</sup>  $\tau = 15.0 \pm 1$  ns in heptane ( $\lambda_{\max}$  311 nm), unaffected by isoprene except by competitive absorption of 266-nm excitation. However, *trans*-1,2-dianisylcyclopropane (**5**)<sup>17</sup> afforded only a modest fluorescence and no observable absorption signal.

We assign triplet multiplicity to the absorbing transients in view of the very fast ISC expected for substituted acetophenones.<sup>18</sup> The absence of isoprene quenching rules out the spectroscopic states <sup>3</sup>1, <sup>3</sup>2, or <sup>3</sup>4. The identical nature of the transient from **1** and from the **1-2** mixture demonstrates that it is a stereorandomized species. The transient is not the diarylpropene triplet <sup>3</sup>3, since irradiation of **3** in CH<sub>3</sub>OH affords a transient,  $\lambda_{\max}$  310 nm, with a different lifetime,  $\tau = 29 \pm 1$  ns. This value agrees well with previously reported lifetimes<sup>20</sup> for 1,3-diarylpropene triplets in methanol. The results are best consistent with assignment of the transient from **1** or **2** as <sup>3</sup>BR, particularly since the absorbance maxima are in excellent accord with expectation for benzylic biradical termini.<sup>21</sup>

That isoprene fails to quench <sup>3</sup>1, <sup>3</sup>2, and <sup>3</sup>4 is presumably due to their extremely short lifetimes. Allowing 10% error in OD measurement and assuming diffusion-controlled quenching suggests a maximum lifetime  $\approx 20$  ps for any quenchable precursor of the observed transients. The extreme reactivity of the spectroscopic triplets toward central C-C bond scission can be expected from the extreme exothermicity (ca. 40 kcal/mol<sup>22</sup>) of the <sup>3</sup>1  $\rightarrow$  <sup>3</sup>BR reaction.

That mono- and diacetyl 1,3-diphenylpropane-1,3-diyls have identical lifetimes is presaged by the lack of a polar substituent effect on olefin triplet lifetimes<sup>23</sup> and the small effect on Norrish II biradicals.<sup>7</sup> An expectation based on the work of Salem and Rowland,<sup>1</sup> that polar contribution to the singlet biradical should increase the ISC rate, is not followed. It would predict that the asymmetric 4-derived biradical would have the shorter lifetime.

Lifetimes for 1,3-diarylpropane-1,3-diyls at  $\sim 15$  ns are shorter than diarylalkene triplets at ca. 60 ns,<sup>24</sup> triplet 1,1,4,4-tetra-phenyl-1,4-butanediyl ( $500 \pm 100$  ns),<sup>3</sup> and triplet 1,1,5,5-tetra-phenyl-1,5-pentanediyyl ( $900 \pm 200$  ns).<sup>3</sup> We believe this is a useful series for examination since the number of aryl groups at biradical termini has only a small effect on the lifetime.<sup>2,8</sup> The effect of interterminal distance on ISC rate (i.e., triplet biradical lifetime) is a blend of two factors. As the chain length between the termini increases, the lifetime will be shortened by a decreasing  $\Delta E_{ST}$

resulting from a diminishing exchange integral but lengthened by diminishing spin-orbit coupling.<sup>1</sup> Perhaps not surprisingly, the results show that 1,3 and the longer biradicals follow expectation based on diminution of spin-orbit coupling with distance.

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### Cyclization Dynamics of Polymers. 18. Capture Radius Effects in the End-to-End Cyclization Rate of Polymers, Excimers vs. Exciplexes

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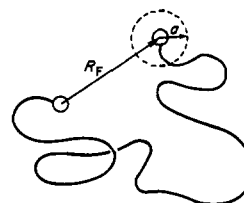
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The theory of diffusion-controlled cyclization of polymers makes an unusual prediction.<sup>1-3</sup> It suggests that the size of the capture radius  $a$  affects the cyclization rate constant,  $k_{cy}$ , when polymer chains are short but that this dependence disappears for longer chains. The important parameter is the ratio  $a/R_F$ , where  $R_F$  is the root-mean-squared end-to-end distance of the chain.  $R_F$  increases, of course, as the chain gets longer.



These predictions are based upon the Rouse-Zimm (bead and spring) model for polymers.<sup>4</sup> Here the polymer is envisioned as a series of beads connected by harmonic springs. The beads contain the mass of the polymer and serve as friction centers for interaction with solvent. This model, in spite of its simplicity, is remarkably successful in describing such properties of polymers as translational and rotational diffusion and intrinsic viscosity.<sup>4</sup>

This peculiar sensitivity of  $k_{cy}$  to the distance between the end groups at which cyclization is detected has attracted considerable attention among various theoretical research groups.<sup>2,5</sup> An excellent review has appeared.<sup>3b</sup> Nonetheless one knows that the concept of a capture radius is an artifact of convenience: real chemical reactions have distance-dependent rate constants. The distance dependence of chemical reaction rates can vary signif-

(18) A referee has suggested that more physical evidence regarding the multiplicity of the biradical is necessary to turn a "good argument" into proof. We cannot disagree with the general desirability of having as much data as possible in support of transient assignments, and do plan further physical characterization, but we find the present data convincing. To our knowledge there are no known singlet photoreactions of *p*-alkylacetophenones nor is there any cogent evidence given recent thermochemical work<sup>19</sup> that simple singlet 1,3-biradicals are barrier protected, as would be necessary if the 15-ns lifetime does not reflect spin protection.

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(22) Cleavage of a C-C bond (85 kcal/mol) is facilitated by generation of two benzylic radical sites (25 kcal/mol) and release of 27 kcal/mol of ring strain. Given  $E_T$  for an acetophenone 72 kcal/mol, <sup>3</sup>1  $\rightarrow$  <sup>3</sup>BR is exothermic by some (72 + 25 + 27 - 85) = 39 kcal/mol.

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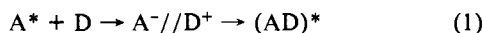
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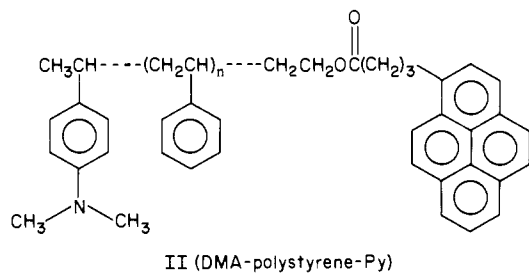
icantly. Thus it should be possible, by careful choice of the end groups on a polymer chain, to affect the end-group separation at which cyclization is detected experimentally. Under these circumstances, aspects of the theoretical predictions about cyclization dynamics can be examined.

Several years ago we reported on the use of pyrene excimer formation to determine cyclization rates of polystyrene.<sup>6,7</sup> Polymers of varying chain lengths and narrow molecular weight distribution (MWD) were prepared, each substituted with pyrene groups at both chain ends (I).<sup>6</sup> Steady-state and fluorescence-decay experiments allowed the (experimental) rate constant for cyclization ( $\langle k_1 \rangle$ ) to be evaluated. The angle brackets serve as a reminder that the experimental values represent averages over the narrow but finite MWD's in each sample. Beginning from the point of view that excimer formation between the pyrene groups required proximity, we considered alternative end labels whose interaction might reasonably occur over larger distances. The excimer data would serve as a reference point for comparison of the two sets of cyclization rate constants.

There has very recently been evidence presented that exciplex formation, in certain cases, is preceded by electron transfer to generate solvent-separated ion pairs.<sup>8,9</sup> These ion pairs subsequently collapse to yield exciplexes. For this mechanism to operate, electron transfer has to be sufficiently exergonic.<sup>10</sup>



In order for a polymer to cyclize to form an exciplex, the end groups must be different. Preparation of polymer of the form  $A \sim D$  is not easy. By treating 1-(4-(dimethylamino)phenyl)-1-ethoxyethane with potassium metal in THF, we generated a carbanion which served to initiate styrene polymerization. The reaction was terminated with ethylene oxide, and the polymers, after purification, were converted to esters of 4-(1-pyrene)butyric acid.<sup>11</sup> The final samples, of  $M_n = 3000$ – $28\,000$ , had  $M_w/M_n \leq 1.2$ .



Electron transfer between excited pyrene and *p*-dimethyl-toluidine is predicted to be exergonic by ca. 10 kcal/mol.<sup>8b,12</sup> This prediction is based upon oxidation and reduction potentials measured in acetonitrile plus the singlet energy of pyrene. In less polar solvents, solvation should affect these redox potentials so as to lower exergonicity of the process.

Cyclization rates measured in cyclohexane at 34.5 °C for eight different samples of II were identical within 10% with those previously determined for samples of I of similar molecular weight.

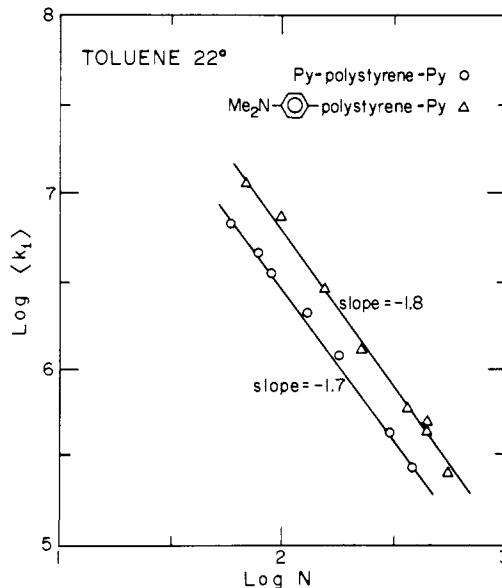
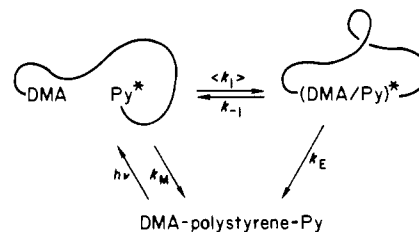


Figure 1. Plot of  $\log \langle k_1 \rangle$  vs.  $\log N$  (number of backbone bonds) for DMA-polystyrene-Py ( $\Delta$ ) and Py-polystyrene-Py ( $\circ$ ) in toluene at 22 °C. The upper line has slope  $-1.8$ ; the lower line,  $-1.7$ .

#### Scheme I



These results suggest that the energetics of the exciplex process have shifted so that electron transfer to generate the solvent-separated ion pair no longer competes with end-group encounter to form the exciplex directly.

Quite different results are obtained for experiments in toluene at 22 °C. Here there is no doubt (Figure 1) that cyclization to form the exciplex for II is substantially more rapid than excimer formation in I.

Rate constants in these experiments were determined both from analysis of the pyrene [ $I_m(t)$ ] and exciplex [ $I_E(t)$ ] fluorescence decay profiles and also from measurements of the steady-state intensity ratios,  $I_E/I_M$ . The data were treated exactly as reported in detail for the polymers I.<sup>7</sup>

We attribute the larger rate constants ( $\langle k_1 \rangle$ ) (Scheme I) for exciplex formation to a larger effective capture radius  $a$  than is operative for excimer formation. Whether solvent-separated ion pairs are actually formed in the photocyclization of II and whether they can be detected are questions for future experimental investigations. We do, however, believe that we have confirmed another aspect of the elegant theory<sup>1-3</sup> describing the cyclization dynamics of polymers.

The experimental results in Figure 1 refer to chains of molecular weights ranging from 3000 to 28 000. The theory<sup>1-3</sup> does not yet address the question of the proper dependence on chain length in good solvents, where the chain dimensions are swollen. One anticipates that  $k_{cy} \sim N^{-\gamma}$  in the limit of long chain lengths. There is a theory for cyclization equilibria in good solvents.<sup>14</sup> These equilibrium constants are predicted to decrease as  $K_{cy} \sim N^{-1.92}$ . We find a slope of  $-1.7$  in the plot of  $\log \langle k_1 \rangle$  vs.  $\log N$  for excimer formation for samples up to  $M = 28\,000$ , with a suggestion of downward curvature at higher molecular weights, where, unfor-

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unately, the excimer data are less reliable. The steeper slope of  $-1.8$  for exciplex formation is consistent with the idea that a larger capture radius enhances cyclization preferentially for shorter chains, which would affect the magnitude of the exponent. Unfortunately the differences in slope over this limited range of molecular weights are too small to be taken seriously. Further experiments are needed, particularly with a focus on longer chain lengths.

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### Temperature Dependence of the Transition-State Structure for the Disproportionation of Hydrogen Atom with Ethyl Radical

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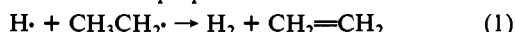
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We present preliminary computational results for one of the simplest radical-radical disproportionation reactions:



Three important conclusions emerge from our studies. (1) The reaction appears to have a small potential energy (PE) barrier. (2) The structure of the transition state (TS) is strongly temperature dependent. (3) Above room temperature, conventional transition-state theory (TST) becomes increasingly inadequate for predicting activation parameters for the low-barrier radical-radical reactions. This is in accord with previous results for biradical reactions.<sup>1</sup>

Ab initio calculations were performed with the 4-electron-4-orbital complete active space MCSCF (CASSCF) wave function.<sup>2</sup> This corresponds to a complete CI (20 singlet configurations) within the space of the electrons and orbitals involved most prominently in changes in bonding, and it provides an even-handed description of the entire interaction region. Geometry optimization and force constants were calculated by using the 3-21G basis set.<sup>3a</sup> Energies and gradients of selected geometries were recalculated with 6-31G\*\*.<sup>3b</sup>

The saddle point for the reaction was located (see Figure 1) and was found to lie 3.9 kcal/mol above the reactants (both energies calculated with the 6-31G\*\* basis set). This energy difference becomes 4.4 kcal/mol with the zero point energy correction included. The force constant matrix has one negative

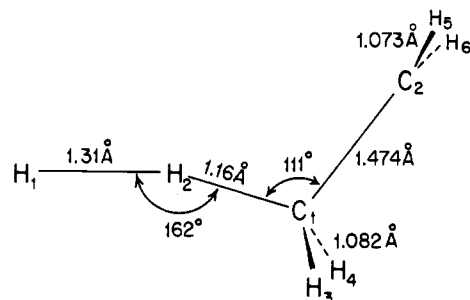


Figure 1. Geometry of the saddle point of the PES for reaction 1 ( $C_2$  symmetry).

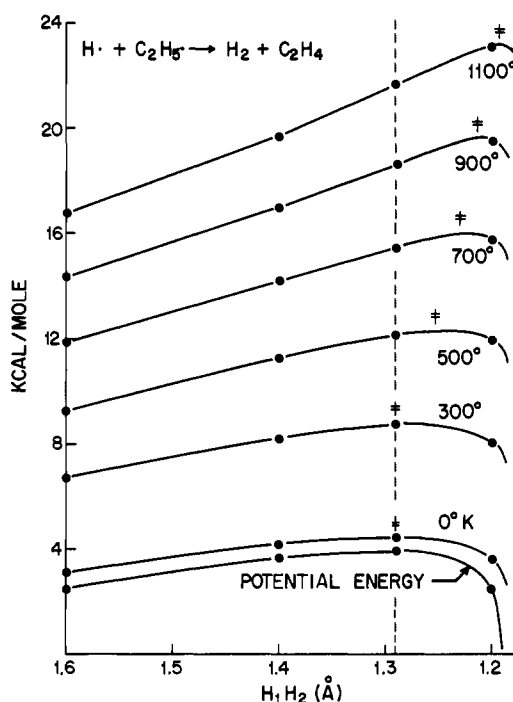


Figure 2. Free energy curves (1 M standard state) for reaction 1 as a function of temperature (K). Each curve is separately referenced to the free energy of reactants at the given temperature. The PE curve was recalculated with the 6-31G\*\* basis set. The saddle point is indicated by the vertical dotted line.

eigenvalue ( $1142i \text{ cm}^{-1}$ ) corresponding to the asymmetric  $\text{H}_1\text{H}_2\text{C}_1$  stretch. We are not aware of any kinetic studies of reaction 1, but such a high barrier is unprecedented for small radicals. Although this barrier height may be an artifact of the basis set and limited CI, our present purpose concerns the *temperature dependence* of the TS geometry.

A conventional TST calculation of the rate constant<sup>4</sup> would use the vibrational frequencies of the saddle point to calculate the free energy of activation. Our experience with tetramethylene<sup>1</sup> has shown that this can give misleading results. A more appropriate choice of TS structure is at the top of the "free energy" barrier.<sup>5,6</sup> Truhlar<sup>6</sup> has given a convenient computational for-

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