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Picosecond Dynamics for the Photocycloaddition of *trans*-Stilbene with Tetramethylethylene: No Evidence of an Exciplex

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Abstract: Picosecond absorption spectroscopy is used to examine the temperature dependence of the dynamics for the quenching of the first excited singlet state of *trans*-stilbene (TS*) by tetramethylethylene (TME) in hexane. The rate of quenching TS* by TME is 3.6×10^9 M^{-1}s^{-1} and it is virtually independent of temperature over the temperature range of −8.0 to 36.8 °C. There is no kinetic evidence for reversible exciplex formation.

Introduction

In 1971 Chapman and Saltiel reported a mechanistic investigation of the 2 + 2 photocycloaddition of *trans*-stilbene (TS) with tetramethylethylene (TME) in hexane.[1] They observed that the quantum yield for photocycloaddition decreases with increasing temperature, suggesting the existence of an intermediate along the reaction coordinate which is in thermal equilibrium with the first excited singlet state of TS (TS*) and TME. The intermediate was proposed to be an exciplex although no emission was observed from this species.

$$\text{TS}^{*} + \text{TME} \rightleftharpoons \text{exciplex} \rightarrow \text{cycloadduct} \tag{1}$$

This was the first evidence for the intermediacy of an exciplex in a photocycloaddition reaction although Corey had previously suggested that an oriented π complex participates in the enone photoannelation reaction.[2]

Subsequent to this initial report there appeared numerous studies of the mechanism for photocycloaddition and photodimerization reactions where exciplexes and excimers were shown to intervene. Farid and co-workers[3] observed exciplex emission in the photocycloaddition of phenanthrene with dimethyl fumarate and Caldwell[4] subsequently demonstrated the intermediacy of the exciplex along the reaction path in the phenanthrene cycloaddition. The first direct observation of an exciplex in stilbene photocycloaddition reactions was Lewis' observation[5] of exciplex emission from *trans*-stilbene and 2,5-dimethyl-2,4-hexadiene. The role of the exciplex in 2 + 2 photocycloaddition reactions received theoretical support based upon the calculation of the potential energy surfaces for the ethylene photodimerization where an excimer is shown to be an intermediate along the reaction coordinate even in the gas phase.[6] Given these and many other studies, the general consensus is that an exciplex or excimer is an intermediate in cycloaddition and cyclodimerization reactions.

Recently we reported a picosecond kinetic study for the photodimerization of TS in benzene where a transient species, presumably an exciplex, is formed at the diffusion rate and decays on the 400 ps time scale.[7] In this report we employ picosecond absorption spectroscopy to examine the temperature dependence of the kinetics for the photocycloaddition reaction of TS with TME in hexane. The aim of the study is to ascertain whether direct kinetic observations can demonstrate that the proposed exciplex is in thermal equilibrium with the first excited singlet state of TS as suggested by Chapman and Saltiel based upon quantum yield studies.[1] We find no kinetic evidence for an exciplex, and if an exciplex does exist, its lifetime must be less than 10 ps.

Experimental Section

Picosecond Absorption Spectrometer. The details of the picosecond absorption spectrometer have previously been presented.[8] A 10-Hz Nd:YAG laser system (Continuum PY61C-10) produces light pulses with a fwhm of 19 ps. The pump energy at 266 nm is 200 μJ. Single wavelength kinetics at 580 nm, resolved by a 5 nm narrow band pass filter, are obtained by monitoring the I and I_0 beams with two photodiodes (EG&G DT100) coupled to two box integrators (SRS 250) interfaced to a laboratory computer. Transient absorption spectra are obtained by passing the I and I_0 beams into a JY 200 spectrometer interfaced to a Princeton Instruments thermoelectrically cooled CCD (TE/CCD 576 EUV).

Samples. *trans*-Stilbene (Aldrich) was recrystallized twice from absolute ethanol. 2,3-Dimethyl-2-butene (Aldrich) and hexane (Aldrich) were used as received.

Data Analysis. The time dependence of the absorbance, $A(t)$, is the result of the convolution of the molecular kinetics, $F(t)$, with the instrument response function, $I(t)$,

$$A(t) = \int_{\infty}^{t} I(\tau)\, F(t-\tau)\, \mathrm{d}\tau \tag{2}$$

where the instrument response function, $I(t)$, is produced by the convolution of the pump and probe pulse and is assumed to have the analytical form of a Gaussian,

$$I(t) = (2\pi\sigma)^{-0.5} \exp(-(t-t_0)^2/2\sigma^2) \tag{3}$$

where σ is the width of the laser pulse and t_0 is the position of the peak of the Gaussian. The value of σ is 19 ps corresponding to a full width at half maximum height of 45 ps for the instrument response function.

The deconvolution procedure for obtaining the kinetic parameters employs the Grinwald-Steinberg fast convolution algorithm[9] combined with the downhill-simplex method of Nelder and Mead[10] to accomplish

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(1) Saltiel, J.; D'Agostino, T. D.; Chapman, O. L.; Lura, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 2804. Chapman, O. L.; Lura, R. D. *J. Am. Chem. Soc.* **1970**, *92*, 6352.

(2) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.

(3) Farid, S.; Doty, J. C.; Williams, J. L. R. *J. Chem. Soc., Chem. Commun.* **1972**, 711.

(4) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45.

(5) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152.

(6) Michl, J.; Bonacic-Koutecky, V. *Electronic Aspects of Organic Chemistry*; Wiley: New York, 1990; pp 264–272.

(7) Peters, K. S.; Lee, J. *J. Phys. Chem.* In press.

(8) Peters, K. S.; Lee, J. *J. Phys. Chem.* **1993**, *97*, 3761.

(9) Demas, J. N. *Excited State Lifetime Measurements*; Academic Press: New York, 1983; p. 273.

(10) O'Neill, R. *Applied Statistics Algorithms*; Griffiths, P., Hill, I. D., Eds.; Ellis Horwood Lmt.: London, 1985.

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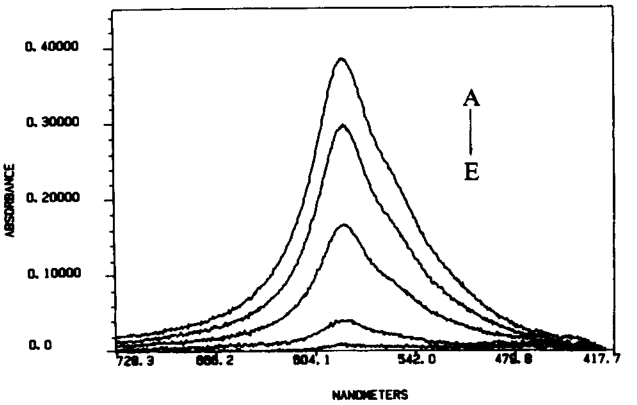

Figure 1. Transient absorption spectra following the 266-nm irradiation of 5 mM *trans*-stilbene, 2 M tetramethylethylene, in hexane at 23.8 °C: (A) 0, (B) 50, (C) 100, (D) 200, and (E) 300 ps.

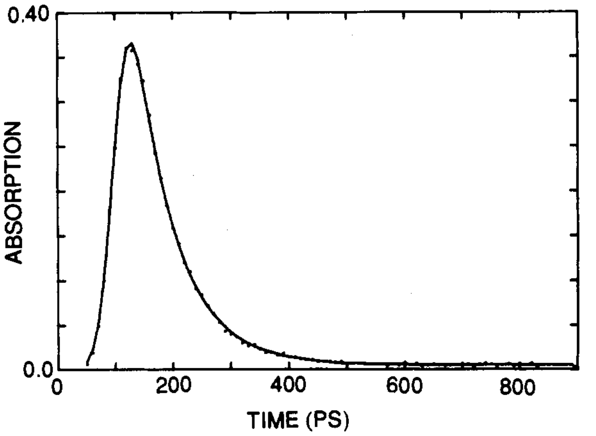

Figure 2. 580-nm dynamics following the 266-nm irradiation of 5 mM *trans*- stilbene, 2 M tetramethylethylene, in hexane at 4.0 °C: points—experimental data which are the average of 3 experiments, 10 ps time increments; solid curve—calculated kinetics, eq 2, with $k_{obs} = 1.43 \times 10^{10}$ s^{-1}.

the multidimensional parameter searching to minimize the sum of the square of the residuals, SSR.

$$\mathrm{SSR} = \sum_t (A_{\mathrm{exp}}(t) - A_{\mathrm{cal}}(t))^2 \qquad (4)$$

The function $A_{exp}(t)$ is the experimental time dependence absorbance and $A_{cal}(t)$ is the calculated time dependence absorbance, eq 2.

Results

The transient absorption spectra following the 266-nm irradiation of 5 mM TS and 2 M TME in hexane at 23.8 °C are shown in Figure 1. Within the laser pulse the absorption spectrum of the first excited singlet state of TS (TS*), λ_{max} 575 nm, appears and in turn decays on the 100 ps time scale; this absorption spectrum is identical to the absorption spectrum of TS* in the absence of TME. No new transient species, within the wavelength range of 400 to 750 nm, are observed following the decay of TS*.

The kinetics, monitored at 580 nm, for the decay of TS* in the presence 2 M TME were examined over the temperature range of −8.0 to 36.8 °C. Due to problems with water condensation on the cell windows it was not possible to probe low temperatures with the present apparatus. The kinetics were obtained over the time interval of 0–1 ns with time increments of 10 ps. The decay at 4.0 °C is shown in Figure 2. The simplest kinetic model that adequately characterizes the kinetic data assumes one exponential decay for $F(t)$, eq 2. The value for the SSR, eq 4, is 4.1×10^{-4} OD^2, corresponding to an average error in the fit of the kinetic model to the experimental data of 0.002 OD which is the estimated error for these experiments. The residuals for the kinetic analysis are given in Figure 3, and the temperature dependence of the kinetic parameters, k_{obs}, is listed in Table I.

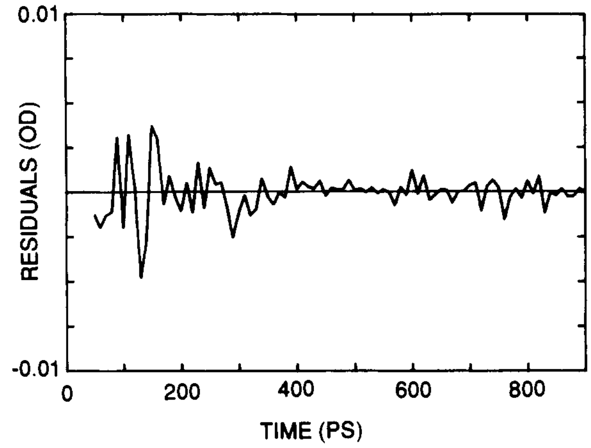

Figure 3. Residuals from the experimental and calculated decays in Figure 2.

Table I. Rate Constants for the Decay of TS* in the Presence of TME, k_{obs}, and Absense of TME, k_1, in Hexane as a Function of Temperature

temp (°C)	[TME][a]	k_{obs} ($\times 10^{-10}$ s^{-1})[b]	k_1 ($\times 10^{-10}$)[b]	k_q ($\times 10^{-9}$ M^{-1} s^{-1})[c]
−8.0	2.08	1.19	0.48	3.4
4.0	2.05	1.43	0.67	3.7
15.7	2.02	1.67	0.94	3.6
23.8	2.00	1.93	1.18	3.8
36.8	1.96	2.26	1.56	3.6

[a] Concentration of TME as a function of temperature, accounting for the temperature dependence of the density of *n*-hexane. [b] Estimated error in the rate constants is ±5%. [c] k_q is defined in eq 5.

The kinetics for the decay of TS* in the absence of TME were also obtained over the temperature range of −8.0 to 36.8 °C. Again the decays were fit to a single exponential in time. The associated rate constants for the decay of TS*, k_1, are given in Table I. Arrhenius analysis of the kinetic parameters for the decay of TS* in the absence of TME yields $E_a = 4.51 \pm 0.17$ kcal/mol and $A = 2.53 \pm 0.71 \times 10^{13}$ s^{-1}. These values differ only slightly from the activation parameters obtained by Fleming[11] through time-resolved fluorescence for the decay of TS* in hexane: $E_a = 3.9 \pm 0.3$ kcal/mol and $A = 9 \pm 4 \times 10^{12}$ s^{-1}.

Discussion

In the absence of TME, TS* decays principally by isomerization about the olefinic bond to produce a 90° twisted intermediate on the excited state surface which then undergoes internal conversion, partitioning between TS and *cis*-stilbene (CS).[12] In addition, TS* undergoes radiative emission with a lifetime of approximately 2 ns; the intersystem crossing of TS* at ambient temperatures is negligible.[12] The measured rate for the decay of TS, k_1, reflects the sum of rates for these processes. TS* may also react with TME, k_q, ultimately leading to cycloadduct. Assuming reversible exciplex formation does not participate in the quenching of TS*, the observed kinetics for the quenching of TS* in the presence of TME, k_{obs}, results from the contributions of both k_1 and k_q.

$$k_{obs} = k_1 + k_q[\mathrm{TME}] \qquad (5)$$

The values of k_q as a function of temperature are given in Table I. Over the temperature range of −8.0 to 36.8 °C k_q is virtually independent of temperature with an average value of 3.6×10^9 M^{-1} s^{-1}.

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(11) Courtney, S. H.; Fleming, G. R. *J. Chem. Phys.* **1985**, *83*, 215.
(12) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415.

Table II. Rate Constant k_q Obtained from the Quantum Yield Studies of Chapman and Saltiel[1]

temp (°C)	$(\tau k_q)^{-1}$ (M)[a]	k_s ($\times 10^{-9}$ s^{-1})[b]	k_q ($\times 10^{-9}$ M^{-1} s^{-1})
54	8.06	25.56	3.2
44	7.00	21.08	3.0
34	5.88	17.2	2.9
25	4.20	14.19	3.4
5	2.94	8.96	3.0
–5	1.34	7.00	5.2
–10	0.94	6.16	6.6
–22	0.28	4.49	16.0

[a] Defined in eq 6; values taken from ref 1. [b] Rate constant for decay of TS*, k_s ($1/\tau$), defined as the sum of the rate constant for isomerization of TS*, k_{tp}, and the rate constant for fluorecence, k_f, taken from ref 13.

In their analysis of the temperature dependence of the quantum yield for the photocycloaddition of TS with TME in hexane, Chapman and Saltiel found that the rate for the quenching of TS* by TME actually increases with decreasing temperature leading to a negative enthalpy of activation associated with k_q.[1] The negative temperature dependence of k_q led to the proposal that the quenching of TS* by TME occurs through reversible exciplex formation. The rate constant for the quenching of TS* by TME was obtained from the quantum yields for photocycloaddition, ϕ_{add}, as a function of the concentration of TME.

$$\phi_{add}^{-1} = 1 + (\tau k_q[\mathrm{TME}])^{-1} \qquad (6)$$

The lifetime of TS* in the absence of TME, τ, reflects the contributions of cis–trans isomerization, k_1, and temperature-independent fluorescence, k_2, where $\tau = (k_1 + k_2)^{-1}$. The value assumed for k_2 was 4×10^8 s^{-1}, and k_1 was determined as a function of temperature employing the Arrhenius parameters $A = 5.6 \times 10^{11}$ s^{-1} and $E_a = 2.84$ kcal/mol.[1] The results of their determination of k_q are reproduced in Table II. Over the temperature range of 54 to –22 °C, k_q increased from 0.93×10^9 to 8.10×10^9 M^{-1} s^{-1}.

Since the Arrhenius parameters used in determining τ in the Chapman–Saltiel experiments are substantially different from the values derived by Fleming,[11] Saltiel,[13] and the present experiment, we have rederived k_q from the photocycloaddition quantum yield study as a function of temperature using τ obtained from Saltiel's extensive study[13] of TS* isomerization in alkane solvents, Table II. Over the temperature range of 54 to 5 °C, k_q is independent of temperature with a average value of $(3.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1}. Decreasing the temperature from 5 to –22 °C, the rate for quenching increases to 16.0×10^9 M^{-1} s^{-1}. There is good argeement between the values for the rate constants determined by the picosecond absorption spectroscopy over the range of –8 to 35.8 °C and those determined from the photocycloaddition quantum yield studies over the range of 5 to 54 °C.

In the analysis of the picosecond kinetic data it is assumed that the quenching of TS* by TME does not produce a reversible exciplex, eq 5. If a reversible exciplex were to be formed upon quenching of TS* by TME it is of interest to establish the limits of the lifetime of the exciplex that would lead to the appearance of a single exponential decay characterizing the picosecond data for the quenching of TS*. The following kinetic scheme is used for this analysis.

$$\mathrm{TS + CS} \xleftarrow{k_1} \mathrm{TS^* + TME} \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \text{exciplex} \xrightarrow{k_4} \text{product} \qquad (7)$$

The time dependence of TS*, TS*(t), is then expressed as[14]

$$\mathrm{TS}^*(t) = C_1 \exp(-\lambda_1 t) + C_2 \exp(-\lambda_2 t) \qquad (8)$$

where

$$\lambda_{2,1} = {}^1/_2[k_1 + k_2[\mathrm{TME}] + k_3 + k_4 \pm \{(k_3 + k_4 - k_1 - k_2[\mathrm{TME}])^2 + 4k_2k_3[\mathrm{TME}]\}^{1/2}]$$

and

$$C_1 = [(\lambda_2 - X)/(\lambda_2 - \lambda_1][\mathrm{TS}^*]_0; \quad C_2 = 1 - C_1; \quad x = k_1 + k_2[\mathrm{TME}]$$

Also, assuming that the steady state approximation holds for the time dependence of the exciplex concentration, the rate of the quenching k_q, determined in eq 5, can be related to k_2, k_3, and k_4 by

$$k_q = (k_2k_4)/(k_3 + k_4) \qquad (9)$$

Equation 9 was presented by Chapman and Saltiel in the analysis of their data.[1] Rearrangement yields

$$k_3/k_4 = (k_2 - k_q)/k_q \qquad (10)$$

The picosecond experiments have determined the values of k_1 and k_q. If a value for quenching of TS* by TME, k_2, is approximately diffusion limited, then it is possible to determine the limit to the rate constants k_3 and k_4 which leads to the appearance of a single exponential decay for TS*. For example, at 23.8 °C if $k_2 = 1 \times 10^{10}$ M^{-1} s^{-1}, then $k_3 = 1.7k_4$. If $k_4 = 10^{10}$ s^{-1}, the time dependence for the decay of TS* is expressed as

$$\mathrm{TS}^*(t) = 0.435 \exp[(-1.1 \times 10^{10}\ \mathrm{s}^{-1})t] + 0.654 \exp[(-4.8 \times 10^{10}\ \mathrm{s}^{-1})t] -$$

The decay of TS* would clearly appear as the decay of two exponentials, contrary to experimental observation. Increasing k_4 to a value of 5×10^{10} s^{-1}, the time dependence of TS* has the form of

$$\mathrm{TS}^*(t) = 0.89 \exp[(-1.7 \times 10^{10}\ \mathrm{s}^{-1})t] + 0.11 \exp[(-1.49 \times 10^{11}\ \mathrm{s}^{-1})t]$$

Computer simulations reveal that, given the noise of the experiment, the decay of TS* would appear as a single exponential for $k_4 = 5 \times 10^{10}$ s^{-1}. Thus if $k_2 = 1 \times 10^{10}$ M^{-1} s^{-1}, the limit on the lifetime of the exciplex is 7.4 ps.

Similar arguments can be advanced for values of k_2 ranging from 5×10^9 to 2×10^{10} M^{-1} s^{-1}. In each instance, for the decay of TS* to appear as a single exponential as shown in Figure 2, the lifetime of the exciplex would need to be less than 10 ps. If the value of k_2 were the same as k_q, 3.6×10^9 M^{-1} s^{-1} so that $k_3 = 0$, then a reversible exciplex would not be formed. Although in principle the existence of exciplex with a lifetime of less than 10 ps cannot be excluded from the reaction mechanism, there is no compelling evidence for the existence of an exciplex that is in thermal equilibrium with TS* and TME.

The quantum yield studies of Chapman and Saltiel do not provide unequivocal support for the intervention of an exciplex as previously proposed.[1] If an exciplex that is in thermal equilibrium with TS* and TME is postulated, then the relationship derived in eq 10 should be valid. Furthermore, the ratio of the rate constants k_3 and k_4 is related to the difference in the free energy change for activation through the relationship[15]

$$\log(k_3/k_4) = \Delta\Delta G^{\ddagger}/2.303RT \qquad (11)$$

and from the identity in eq 10

$$\log((k_2 - k_q)/k_q) = \Delta\Delta G^{\ddagger}/2.303RT \qquad (12)$$

Thus there should be a linear correlation of $\log((k_2 - k_q)/k_q)$ with $1/T$ providing k_2 can be defined. However, given that k_q is virtually independent of temperature over the range of 54 to 5 °C and then becomes strongly temperature dependent from 5

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[13] Saltiel, J.; Waller, A. S.; Sears, D. F., Jr.; Garrett, C. Z. *J. Phys. Chem.* **1993**, *97*, 2516–2522.

[14] Ware, W. R.; Watt, D.; Holmes, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 7853.

to −22 °C, Table II, it is not possible to derive a function for k_2 that is either linear in temperature, appropriate for a modified Debye diffusion equation,[15] or exponential in temperature, appropriate for a thermally activated process. The origin of the rather unusual temperature dependence of k_q obtained from the quantum yield studies is unclear.

Thus the question arises as to whether k_q, as defined in eq 5, can represent a distinct chemical transformation given that the kinetic process is virtually temperature independent. Analysis of the temperature dependence of k_q within the framework of Eyring transition state theory provides both the enthalpy and entropy of activation. The analysis of the kinetic data for k_q given in Table I yields an enthalpy of activation of $\Delta H^{\ddagger} = -403 \pm 149$ cal/mol and an entropy of activation of $\Delta S^{\ddagger} = -16.1 \pm 0.6$ eu.

The apparent lack of a temperature dependence in k_q is rather surprising given that most translational diffusion processes are dependent upon temperature. However, at 2 M TME, the ratio of TME to the solvent molecule, hexane, is approximately 1:2.8. It is estimated that the number of molecules solvating TS in the first shell has as a lower limit 8 and more likely is of the order of 10. Assuming that there are 8 molecules within the first shell, on average TS will have 6 hexane and 2 TME molecules surrounding it. Thus there is no need for TME to diffuse into the first solvent shell for the reaction to occur. Consequently, translational diffusion should contribute only to a minor extent to the overall kinetic process. The rate-limiting process for reaction, perhaps reflected as k_q, is reorientation of TS with respect to TME within the first solvent shell to obtain a reaction complex configuration; this is basically an entropic process with little enthalpic contribution and therefore should have only a minor temperature coefficient.

There is an extensive literature detailing chemical processes with negative enthalpies of activation. These processes include the reactions of halocarbenes,[16] singlet oxygen,[17] and nitrile ylides[15] with alkenes as well as the Diels–Alder reaction.[18] In each instance the observed negative enthalpy of activation has led to the proposal that the reaction proceeds through a π-complex or charge-transfer complex that is in thermal equilibrium with the reactants, similar to the proposal of Chapman and Saltiel.[1] However, Houk has provided an alternative rational for the halocarbene reactions with olefins based upon theoretical calculations.[19] Employing *ab initio* RHF calculations for the reactions of dichlorocarbene and dibromocarbene with isobutene and tetramethylethylene, Houk finds there are no enthalpy barriers for these carbene reactions; the reactions are entropically controlled. Furthermore, there is no evidence of an intervening π-complex along the reaction coordinate. Indeed, the reactions may be described as a concerted addition of the carbene to the alkene. Houk notes that "negative activation energies are likely to be a general feature of reactions of very energetic species".[19]

In view of the foregoing discussion, the results from the present picosecond kinetic study of the photocycloaddition of TS with TME are consistent with a concerted cycloaddition of TME with TS*. Although the intervention of a exciplex with a 10-ps lifetime cannot be unequivocally discounted, there is no direct experimental evidence for the participation of an exciplex in the photocycloaddition of TS with TME.

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(15) Padwa, A.; Rosenthal, R. J.; Dent, W.; Filho, P.; Turro, N. J.; Hrovat, D. S.; Gould, I.R. *J. Org. Chem.* **1984**, *49*, 3174.

(16) Giese, B.; Meister, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 595.

(17) Schuster, G. B.; Hurst, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6854. Gorman, A. A.; Lovering, G.; Rodgers, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 3050.

(18) Kiselev, V. D.; Miller, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 4036.

(19) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555.