Nonvertical Excitation Transfer. Activation Parameters for Endothermic Triplet Energy Transfer to the Stilbenes

Sir:

Rate constants for endothermic triplet excitation transfer, $k_{\rm et}$, are expected to obey

$$k_{\rm et} = k_{\rm dif}e^{-\Delta E_{\rm T}/RT} = A_{\eta}e^{-E_{\eta}/RT}e^{-\Delta E_{\rm T}/RT} \qquad (1)$$

where $\Delta E_{\rm T}$ is the energy difference between the 0-0 Franck-Condon (F-C) allowed $T_1 \leftarrow S_0$ transitions in the donor and acceptor and $k_{\rm dif} = A_{\eta}e^{-E_{\eta}/RT}$ is the rate constant for a diffusion-controlled process.[1] Measurement of $k_{\rm et}$ for a series of donors of varying $E_{\rm T}$ at one temperature has allowed tests of

$$\Delta \ln k_{\rm et} = -\Delta E_{\rm T}/RT \qquad (2)$$

a simpler form of eq 1. Deviations from eq 2, first noted with *cis*-stilbene as the acceptor, led to the concept of nonvertical energy transfer.[2,3] In such cases larger $k_{\rm et}$'s than predicted by eq 2 are observed suggesting attainment of a lower energy state than the F-C allowed state upon excitation transfer. For *cis*-stilbene it was proposed that this state corresponds to a partially or fully twisted geometry, ^{3}p*.[2] Since rate constants for *trans*-stilbene obey eq 2, it was supposed to function as a vertical excitation acceptor attaining a transoid geometry, ^{3}t*.[2,3]

Several views have been expressed concerning the mechanism of nonvertical energy transfer.[4] Hammond and Saltiel[2] suggested relaxation of F-C requirements owing to (a) a longer interaction time of the donor-acceptor pair in the solvent cage compared with the interaction time of a photon with a molecule and/or (b) interaction between donor and acceptor electronic systems with resulting coupling of vibrational motions in the two molecules. Bylina[5] and later Yamauchi and Azumi[6] argued that no greater twisting occurs than that expected for a nonvertical spectroscopic transition having small but finite F-C factors, Figure 1, path a. Accordingly, the energy of the lowest effective donor gives a limiting value for the 0-0 band of the $T_1 \leftarrow S_0$ transition, 42.7 kcal/mol in *cis*-stilbene.[6] At the other extreme Liu[7] proposed a "hot band" mechanism, Figure 1, path b, involving vertical excitation of torsionally excited acceptors.

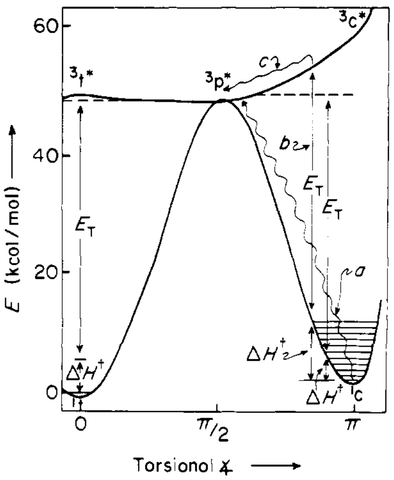


Figure 1. Possible pathways of endothermic triplet energy transfer to the stilbenes. A small intrinsic and/or medium imposed energy barrier for ^{3}t* ⇄ ^{3}p* interconversion is not shown but may be present.

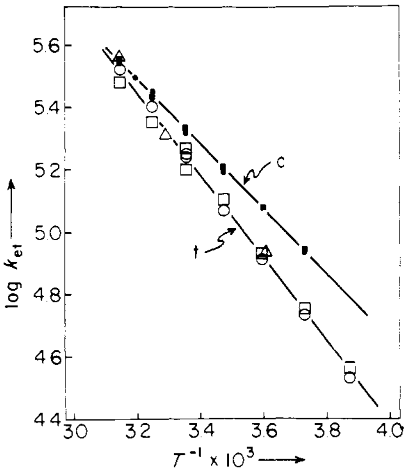
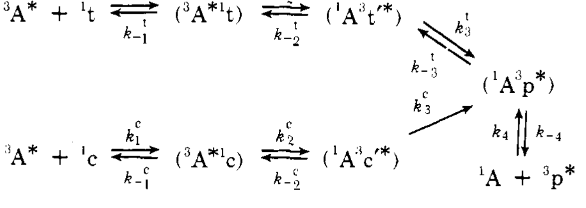


Figure 2. Arrhenius plots of rate constants of excitation transfer from anthracene to *trans*- (○, □, △) and *cis*-stilbene (●, ■). Different symbols for points indicate independent experiments.

Scheme I. Endothermic Excitation Transfer to the Stilbenes



In order to evaluate these proposals and to obtain additional information concerning energetics for twisting in the lowest stilbene triplet state, we have determined activation parameters for excitation transfer from anthracene triplets, $E_{\rm T}$ = 42.7 kcal/mol,[8] to the stilbenes by measuring the temperature dependence of the rate constants in toluene, Figure 2.[9] While it can readily be shown that, in addition to $\Delta E_{\rm T}$, the activation energy for viscous flow, E_{η}, must be overcome for a successful vertical endothermic excitation transfer event, this need not be the case for nonvertical excitation transfer where geometric distortion, e.g., paths a or b and c in Figure 1, may preclude freely reversible excitation transfer in the encounter complex. That this is the case in stilbene is indicated by inefficient quenching of ^{3}p* to ^{1}t by low energy acceptors; e.g., the rate constant for quenching by azulene in toluene at 30 °C is 4% the value of a diffusion-controlled process.[11] A more complete analysis can be achieved by considering Scheme I, where ^{3}t′* and ^{3}c′* represent geometries of entry from ^{1}t and ^{1}c, respectively, into the triplet-state potential energy surface. Step 3 for the cis isomer is shown irreversible since triplet excitation acceptors quench ^{3}p* only to ^{1}t. Quenching experiments[11,12] and flash-spectroscopic observations[13] suggest ^{3}p* as the lowest free-energy geometry. Applying the steady-state approximation on encounter complexes and neglecting $k_{-4}[^1\mathrm{A}]$ for low $[^1\mathrm{A}]$, gives

$$k^{\rm t}_{\rm et} = [(k^{\rm t}_1k^{\rm t}_2k^{\rm t}_3k_4)/(k^{\rm t}_{-1}k^{\rm t}_{-2}k^{\rm t}_{-3} + k^{\rm t}_{-1}k^{\rm t}_{-2}k_4 + k^{\rm t}_{-1}k^{\rm t}_3k_4 + k^{\rm t}_2k^{\rm t}_3k_4)] \qquad (3)$$

$$k^{\rm c}_{\rm et} = [(k^{\rm t}_{-1}k^{\rm t}_3k^{\rm t}_4 + k^{\rm t}_{-1}k^{\rm t}_{-2}k_4 + k^{\rm t}_2k^{\rm t}_3k_4)/(k^{\rm t}_{-1}k^{\rm t}_{-2}k^{\rm t}_{-3} + k^{\rm t}_{-1}k^{\rm t}_{-2}k_4 + k^{\rm t}_{-1}k^{\rm t}_3k_4 + k^{\rm t}_2k^{\rm t}_3k_4)] \times [(k^{\rm c}_1k^{\rm c}_2k^{\rm c}_3)/(k^{\rm c}_{-1}k^{\rm c}_{-2} + k^{\rm c}_{-1}k^{\rm c}_3 + k^{\rm c}_2k^{\rm c}_3)] \qquad (4)$$

for rate constants of excitation transfer to ^{1}t and ^{1}c, respectively. The inefficiency of excitation transfer from stilbene triplets to low energy acceptors shows that $k_4 > k^{\rm t}_{-3}$ and, since $k^{\rm t,c}_2 \ll k^{\rm t,c}_{-1}$, eq 3 and 4 reduce to

$$k^{\rm t}_{\rm et} \simeq [(K^{\rm t}_1k^{\rm t}_2)/(1 + k^{\rm t}_{-2}/k^{\rm t}_3)] \simeq K^{\rm t}_1k^{\rm t}_2 \qquad (5)$$

$$k^{\rm c}_{\rm et} \simeq [(K^{\rm c}_1k^{\rm c}_2)/(1 + k^{\rm c}_{-2}/k^{\rm c}_3)] \simeq K^{\rm c}_1k^{\rm c}_2 \qquad (6)$$

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The further simplifications hold if $^3t'^* \rightarrow {}^3p^*$ and $^3c'^* \rightarrow {}^3p^*$ relaxations are faster than back energy transfer, i.e., $k_3^{t,c} > k_{-2}^{t,c}$. Failure of appropriate acceptors to quench stilbene triplets to ^1c suggests that this relationship is valid at least for the cis isomer. In any case, since fast processes are involved, the $k_{-2}^{t,c}/k_3^{t,c}$ ratios are expected to be temperature insensitive. Assuming no exothermicity in the initial donor-acceptor encounters, $\Delta H_1^{t,c} = 0$,[14] the $K_1^{t,c}$ reflect the entropy change (cratic) for bringing two solutes together.[15]

The lines in Figure 2 give log A values of 9.66 ± 0.30 and 8.80 ± 0.13 and E values of 6.03 ± 0.30 and 4.74 ± 0.20 kcal/mol for ^1t and ^1c, respectively. Both A factors are smaller than 10^{12} s^{-1}, the value expected for a strictly vertical excitation transfer, eq 1.[16] Converting E values to activation enthalpies gives $\Delta H_2^t = 5.4 \pm 0.3$ kcal/mol and $\Delta H_2^c = 4.1 \pm 0.2$ kcal/mol, invalidating the postulation[6] that the 0-0 band in the $T_1 \leftarrow S_0$ transition requires no more than 42.7 kcal/mol for ^1c. Finite activation enthalpies also invalidate Bylina's mechanism[5] which ascribes all inefficiency in the excitation transfer process to the magnitude of F-C overlap factors. The ΔH_2 values, E_T for anthracene, and the 2.3-kcal/mol enthalpy difference[17] between ^1t and ^1c give 48.1 and 49.1 kcal/mol as the energies of $^3t'^*$ and $^3c'^*$, respectively.[14,18] The energy of $^3t'^*$ is very near that of the F-C allowed spectroscopic $^3t^*$-^1t transition, ~49 kcal/mol.[4,19] In contrast, the energy of $^3c'^*$ is substantially lower than that of $^3c^*$, ~59 kcal/mol,[4] but very close to that expected for $^3p^*$,[11] suggesting sufficient distortion in the excitation transfer process to achieve nearly all possible energy stabilization.[20] The low A_t value, compared with the 10^{12} s^{-1} predicted by eq 1,[16] appears to contradict the conclusion that excitation transfer is vertical for ^1t. Since A_t is approximately equal to k_{dif} at room temperature, a transition from vertical to nonvertical energy transfer would not be reflected in deviation from eq 2. Alternatively, if distortion of $^3t^*$ offers no enthalpy advantage, vertical excitation transfer may be followed by an entropy-driven twisting to $^3p^*$ which diminishes back energy transfer.[21]

Experiments with other donors and acceptors are in progress.

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(9) Anthracene triplet decay was measured at 430 nm using a Northern-Precision kinetic flash spectrometer. A 1,4-diphenyl-1,3-butadiene-methanol solution was circulated through the triple jacketed cell to provide temperature control and prevent excitation of the sample below 330 nm. Emission measurements were simultaneously made to correct for delayed fluorescence effects. Absorption decay was analyzed for first- and second-order decay components using GENLSS.[10]
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(14) In cases involving triplet exciplex formation $\Delta H_1 < 0$ and $E = \Delta H_1 + E_2$ is expected. The large activation energies observed support the notion that $\Delta H_1 \sim 0$ in our systems.
(15) For a net change of one solute the cratic part of the entropy is $-R \ln [M]$ where [M] is the molarity of the solvent; thus, $K_1^{t,c} = 1/[M]$. For toluene at 20 °C $[M] \simeq 9.4$. See R. W. Gurney, "Ionic Processes in Solution", McGraw-Hill, New York, 1953.
(16) Activation parameters for exothermic triplet excitation transfer from indeno[2,1-*a*]indene to azulene in toluene give log $A_\eta = 12.0$ and $E_\eta = 2.70$ kcal/mol.[11]
(17) G. Fischer, K. A. Muszkat, and E. Fischer, *J. Chem. Soc. B*, 1156 (1968).
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(19) Phosphorescence from $^3t^*$ has been observed: J. Saltiel, G.-E. Khalil, and K. Schanze, unpublished results.
(20) For a related intramolecular study, see D. G. Whitten, P. D. Wildes, and C. A. DeRosier, *J. Am. Chem. Soc.*, **94**, 7811 (1972).
(21) The latter interpretation is suggested by the treatment of the temperature dependence of azulene quenching of stilbene triplets.[11] However, this treatment is in doubt since it omitted an explicit step for excitation transfer.
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Photochemically Generated Silicon-Carbon Double-Bonded Intermediates. 9. Synthesis, Reactions, and Molecular Structure of a 1,2-Disilacyclobutane

Sir:

Small-ring systems involving a silicon-silicon bond in the ring are interesting because of their high strain energy. Only a few examples for the formation of 1,2-disilacyclobutanes have been reported to date[1-4] with limited information about their chemical behavior. We report here the formation and reactions of a novel 1,2-disilacyclobutane and preliminary results of X-ray diffraction study of this compound.

When a solution of 1.51 g (2.95 mmol) of trimethylsilyl(1,1-diphenyltrimethyldisilanyl)acetylene (**1**)[5] in 80 mL of dry benzene was photolyzed by irradiation with a low-pressure mercury lamp bearing a Vycor filter for 5 h, yellow crystals of 1,1,2,2-tetraphenyl-3,4-bis[bis(trimethylsilyl)-methylene]-1,2-disilacyclobutane (**2**) were formed which could be readily isolated by evaporation of the solvent from the resulting mixture (18% yield after recrystallization from hexane, mp 199 °C dec, UV λ_{max} 420 nm). The formation of **2** can be explained