(0.39 g) at −5 °C. After it was stirred for 10 min at 0 to −5 °C the reaction mixture was diluted with ice–water and was then worked up by extraction with ether in the usual fashion. The crude product was purified by PLC (5% ethyl acetate/light petroleum) to give on recrystallization from light petroleum 27% (0.135 g) of chloride **12**: mp 135–136 °C; ^{1}H NMR δ 0.93 (s, 9 H, CMe$_3$), 1.1–2.5 (br m, 9 H, cyclohexyl protons), AA′XX′ pattern 7.76 (m, 2 H), 8.21 (m, 2 H), $J_{AX} + J_{AX'} =$ 9.0 Hz; IR (CHCl$_3$) 1600, 1510, 1395, 860 cm^{-1}; UV (EtOH) 203 nm (ϵ 1.05 × 10^4), 273 (9.1 × 10^3); mass spectrum, *m/z* 297 (M$^+$ + 2, 0.7%), 295 (M$^+$, 2), 260 (12), 239 (27), 57 (100), 41 (51).

Anal. Calcd for $C_{16}H_{22}ClNO_2$: C, 64.96; H, 7.50; N, 4.74. Found: C, 65.29; H, 7.45; N, 4.74.

Acknowledgment. We thank R. J. Smyth-King, D. G. Harle, F. Flower, B. Barnes, M. C. Harsanyi, and K. Mandla for assistance with preparation of samples and the Australian Research Grants Scheme for support (to R.K.N.), particularly for research assistantships to B.B., M.C.H., and K.M. The research at the Notre Dame Radiation Laboratory and at the National Bureau of Standards was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. This is report No. NDRL-2520.

Registry No. 1, 62558-02-5; **1**$^{-\cdot}$, 89727-61-7; **1** (benzyl radical), 89727-79-7; **2**, 40637-42-1; **2**$^{-\cdot}$, 89727-62-8; **2** (benzyl radical), 89727-80-0; **3**, 89727-55-9; **3**$^{-\cdot}$, 89727-63-9; **3** (alcohol), 61986-33-2; **4**, 62558-03-6; **4**$^{-\cdot}$, 89727-65-1; **4** (benzyl radical), 89727-81-1; **5**, 86096-90-4; **5**$^{-\cdot}$, 89727-66-2; **6**, 86983-99-5; **6**$^{-\cdot}$, 89824-63-5; **6** (benzyl radical), 89727-82-2; **7**, 66360-61-0; **7**$^{-\cdot}$, 89727-67-3; **7** (alcohol), 13629-87-3; **8**, 89727-56-0; **8**$^{-\cdot}$, 89727-68-4; **9**, 89727-57-1; **9**$^{-\cdot}$, 89824-64-6; **10**, 89727-58-2; **10**$^{-\cdot}$, 89824-65-7; **11**, 89727-59-3; **11**$^{-\cdot}$, 89727-64-0; **12**, 89727-60-6; **12**$^{-\cdot}$, 89824-66-8; **12** (benzyl radical), 89727-69-5; **13**, 78928-45-7; **13**$^{-\cdot}$, 89824-67-9; A, 89727-71-9; B, 89727-72-0; C, 89727-73-1; C (ketone), 41468-01-3; D, 52449-32-8; E, 89727-74-2; F, 89727-75-3; G, 89727-76-4; H, 89727-77-5; I, 89727-78-6; *p*-(1,2-dibromo-1,2-dimethylpropyl)nitrobenzene, 89727-70-8; α,β,β-trimethyl-*p*-nitrostyrene, 13399-43-4; *p*-nitroacetophenone, 100-19-6; 1-(4-biphenylyl)-2,2-dimethyl-1-propanone, 34546-86-6; 4-methylpivalophenone, 30314-44-4; *p*-nitrobenzaldehyde, 555-16-8; 1-pivalonaphthone, 25540-73-2; *c*-4-*tert*-butyl-*r*-1-chloro-1-phenylcyclohexane, 28140-28-5.

Nonvertical Triplet Excitation Transfer to *cis*- and *trans*-Stilbene[1]

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Received August 1, 1983. Revised Manuscript Received January 9, 1984

Abstract: Rate constants, k_{obsd}, for triplet excitation transfer from anthracene (E_T = 42.7 kcal/mol) and from 9,10-dichloroanthracene (E_T = 40.3 kcal/mol) to the stilbenes have been measured as a function of temperature in toluene. These are converted to rate constants, k_{en}, for the excitation transfer step within the donor/acceptor encounter cage by using empirical values for the rate constants of diffusion, k_{dif}, and the rate constants of back energy transfer, k_{-en}, from stilbene triplets to the donors. Activation parameters for k_{en} are as follows: for *trans*-stilbene $\Delta S^{\ddagger} = -12.3 \pm 0.1$ and -20.5 ± 0.6 eu and $\Delta H^{\ddagger} = 5.3 \pm 0.1$ and 5.2 ± 0.5 kcal/mol for anthracene and 9,10-dichloroanthracene, respectively; and for *cis*-stilbene $\Delta S^{\ddagger} = -16.3 \pm 0.1$ and -22.49 ± 0.53 eu and $\Delta H^{\ddagger} = 3.95 \pm 0.08$ and 4.30 ± 0.22 kcal/mol, in the same order. The striking result is that the difference in triplet energy between the two donors is reflected almost entirely in the activation entropy and not in the activation enthalpy in sharp contrast to predictions from recent classical and quantum mechanical treatments. This result, together with the observation that all $\Delta S^{\ddagger}$ values are smaller than expected for vertical triplet excitation transfer, strongly suggests that endothermic triplet excitation transfer is nonvertical to both stilbene isomers. It follows that twisted stilbene triplet conformations, $^3p^*$, must be lower in potential energy than either cisoid, $^3c^*$, or transoid, $^3t^*$, conformations. The same conclusions can be reached somewhat more crudely by a consideration of Arrhenius parameters obtained directly from the temperature dependence of k_{obsd}. Modified potential energy curves for twisting about the central bond of stilbene in S_0 and T_1 are proposed.

About 20 years ago it was recognized that rate constants for endothermic triplet-excitation transfer from a series of donors to *cis*-stilbene, $k_{obsd}{}^c$, far exceeded predicted values when the observed $T_1 \leftarrow S_0$ spectral origin was used to estimate the triplet energy[3] of *cis*-stilbene. Hammond and co-workers reasoned that the $T_1 \leftarrow S_0$ spectrum did not reveal the true energy of the relaxed, twisted *cis*-stilbene triplet state because of the severe Franck–Condon (F–C) restrictions on the transition. For this reason the twisted *cis*-stilbene triplet state was referred to as a phantom state. In general, a spectroscopic transition between states having different nuclear positions (and/or kinetic energies) is referred to as a nonvertical transition. A transition of this type can also be promoted by excitation transfer, and by analogy to the spectroscopic transitions the latter process is also called nonvertical although the mechanisms of the two processes may be considerably different. The concept of nonvertical excitation transfer has been applied generally to cases in which substantially different geometries between ground and excited states of either the acceptor or the donor lead to vanishingly small F–C terms that prevent direct observation of the 0–0 band of the vibronic progression.[4]

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(4) Analogy for the concept of nonvertical transitions can be found in the spectroscopic literature. For example, in discussing the spectrum of acetylene which involves "F–C forbidden transitions" from a linear ground state to a trans-bent excited state,[5] Ingold and King state that "the change in shape is so drastic that the transitions are far from being 'vertical' transitions in the Franck sense", ref 5a, p 2741.

In contrast, rate constants, $k_{\text{obsd}}^{\text{t}}$, measured for a series of donors of varying triplet energy, E_T, with use of *trans*-stilbene as the acceptor are in good agreement with values based on the $T_1 \leftarrow S_0$ or $T_1 \rightarrow S_0$, spectra of *trans*-stilbene, which was consequently supposed to function as a vertical excitation acceptor.[3]

Several views have been expressed concerning the mechanism of nonvertical energy transfer.[6] Hammond and Saltiel[3a] 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 of a photon with a molecule and/or (b) interaction between donor and acceptor electronic systems with resulting coupling of vibrational motions of the two molecules. An elaboration of b has been discussed by Turro, who suggested a triplet exciplex as the intermediate in the excitation transfer process.[7] Bylina,[8] and later Yamauchi and Azumi,[9] from a comparison of the dependence on energy of $k_{\text{obsd}}^{\text{t,c}}$ and molar absorptivities in the $T_1 \leftarrow S_0$ spectra, argued that nonvertical energy transfer involves no greater twisting than that expected for the corresponding spectroscopic transitions for which F–C factors, though small, are finite. Also stemming from analogy with spectroscopy is Liu's "hot band" mechanism, as elaborated on by Lamola,[6a] Liu,[10a] and others,[10b–d] and more forcefully perhaps by Wagner and Scheve.[10b] According to this mechanism nonvertical excitation transfer is the result of excitation transfer to acceptor molecules which are thermally excited along the relevant distortion coordinate (torsional for the stilbenes) as expected from the Boltzman distribution law. Finally, two important recent papers by Balzani, Orlandi, and co-workers describe a classical treatment claimed to be generally applicable to vertical or nonvertical triplet energy transfer[11a,b] and a quantum mechanical treatment applied specifically to the stilbenes.[11c] In both these papers, it is concluded that the excitation transfer events are completely analogous to spectroscopic transitions.

In order to evaluate the various proposals and to gain further insight into the mechanism of nonvertical triplet excitation transfer, we had initiated a study of the temperature dependence of rate constants for endothermic triplet excitation transfer to the stilbenes.[1b] It was also anticipated that this work would lead to additional information concerning the energetics for twisting in the lowest stilbene triplet state. In this paper we present results for the triplet energy donors anthracene (A, E_T = 42.7 kcal/mol[12]) and 9,10-dichloroanthracene (DCA, E_T = 40.3 kcal/mol[12]).

Results

The decay of A or DCA triplets in solution can be expressed (for A) as

$$-\mathrm{d}[{}^3\mathrm{A}^*]/\mathrm{d}t = k_1[{}^3\mathrm{A}^*] + k_2[{}^3\mathrm{A}^*]^2 \qquad (1)$$

where k_1 represents all first-order and pseudo-first-order decay processes and k_2 is the effective rate constant for triplet–triplet annihilation. In each experiment, the decay of the donor triplets was measured at several temperatures in degassed toluene, the stilbene quencher was then admitted into the solution through a break-seal, and decay measurements for several temperatures were repeated. The quencher increases k_1 to k_1',

$$k_1' = k_1 + k_{\text{obsd}}[\text{St}] \qquad (2)$$

where k_{obsd} is the effective triplet excitation transfer rate constant. Analysis of the transient absorption kinetics data was as previously described.[13] Interpretation of k_2 values obtained from this work for A has been published separately,[13] and the analogous data for DCA will also be presented in a separate publication. At the concentrations of A employed, 3.0–7.5 × 10^{-5} M, self-quenching of ^{3}A* by ^{1}A is negligible and expected k_1 values are in the 50–75-s^{-1} range.[14] Values obtained in this work were generally larger, <10^2 to 10^3 s^{-1}, and were not reproducible from experiment to experiment. However, k_{obsd} values for A calculated by using eq 2 and density adjusted stilbene concentrations[15] were nicely reproducible; since an Arrhenius treatment of these data has been published,[1b] they are not reproduced here, see Table I-S (supplementary material). Generally, transient decay was monitored at 25 °C at the beginning of each run and again toward the end of the run. Reproducibility of the early and late 25 °C measurements was used as a criterion in evaluating the quality of the data. In the case of DCA, substantially larger k_1 values were obtained that were generally reproducible. Some of these are reported in Table I along with k_1' and k_{obsd} values; a more extensive set of k_1 values was used for interpolations (see Appendix). In the absence of the quencher, DCA solutions were stable to excitation from repeated flashes or prolonged exposure to the monitoring beam. This turned out to be the case in the presence of *cis*-stilbene as well (duplicate temperatures in Table I are from the beginning and the end of the run). However, in the presence of *trans*-stilbene repeated flashing caused a gradual increase in k_1'; late measurements at 25 °C always gave 10–20% larger k_1' values than initial measurements. This difficulty was overcome by varying the initial temperature from run to run, and by using decay data from no more than the first 20 flashes. Flash excitation energies were kept constant by using the same capacitor voltage for each flash. Since the half-width of the pulse, ~20 μs, is small compared to monitored ^{3}DCA* lifetimes, initial ^{3}DCA* concentrations could be estimated to within ±10% by extrapolation of monitored light transmittance to "zero time". No change in $[{}^3\text{DCA}^*]_0$ could be discerned, within this uncertainty range, upon admitting either stilbene quencher into the DCA solutions (none for trans, ~6% quenching for cis). Thus, despite the high stilbene concentrations employed, quenching of DCA triplets higher than T_1 is negligible.[16] Furthermore, qualitative experiments showed that *trans*-stilbene is an inefficient quencher of DCA fluorescence; Stern–Volmer constants reveal a pronounced negative temperature dependence (K_{SV} = 0.9, 0.3, and 0.09 M^{-1} at 0, 28, and 55 °C, respectively). Although at [t-St] = 0.3 M as much as a 3–25% decrease in $[{}^3\text{DCA}^*]_0$ could have been attributed to ^{1}DCA* quenching alone, this decrease was not detected.

No change in the triplet–triplet absorption spectrum of DCA was observed upon admitting the stilbene quenchers into the DCA solutions. This possibility was not examined in the case of A.

Discussion

Kinetic Treatment. Analysis of excitation transfer rate constants from donor triplet, ^{3}D*, to acceptor singlet ground state, ^{1}A, in solution can be based generally on the sequence

$${}^3\mathrm{D}^* + {}^1\mathrm{A} \underset{k_{-\mathrm{dif}}}{\overset{k_{\mathrm{dif}}}{\rightleftharpoons}} ({}^3\mathrm{D}^*\ {}^1\mathrm{A}) \underset{k_{-\mathrm{en}}}{\overset{k_{\mathrm{en}}}{\rightleftharpoons}} ({}^1\mathrm{D}\ {}^3\mathrm{A}^*) \underset{k_{\mathrm{dif}}}{\overset{k_{-\mathrm{dif}}}{\rightleftharpoons}} {}^1\mathrm{D} + {}^3\mathrm{A}^* \qquad (3)$$

where k_{dif} and $k_{-\text{dif}}$ are diffusion rate constants for association and dissociation of donor/acceptor pairs and k_{en} and $k_{-\text{en}}$ are excitation

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Table I. Decay and Effective Excitation Transfer Rate Constants from ^{3}DCA* to the Stilbenes in Toluene[a]

T, K	$10^{-3}k_1$, s^{-t}	$10^{-3}k_1'$, s^{-1}	$10^{-3}k_{obsd}$, $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$	10^{-4}-k_{en},[b] s^{-1}
		trans-Stilbene[c]		
run 1				
271.3	*1.890*	2.170 (22)	1.18 (18)	1.26
271.7	1.900 (55)			
283.8	1.934 (5)			
298.0	*2.011*	2.724 (25)	3.10 (20)	3.20
298.5	1.995 (74)			
303.9	2.059 (9)			
312.8	2.088 (54)			
325.5	2.257 (17)			
run 2				
300.2	2.017 (50)			
305.8	2.048 (65)			
330.8	2.208 (74)			
334.7	2.288 (75)	4.599 (68)	9.79 (43)	9.61
run 3				
271.7	1.818 (19)			
298.1	*2.008*	2.752 (122)	2.80 (48)	2.89
298.8	1.994 (36)			
327.4	*2.234*	4.413 (139)	8.45 (56)	8.37
run 4				
271.6	*1.849*	2.112 (18)	1.18 (18)	1.26
283.4	*1.914*	2.325 (22)	1.87 (20)	1.97
298.3	*2.009*	2.527 (96)	2.40 (48)	2.47
run 5				
303.2	1.986 (34)	2.978 (84)	3.43 (32)	3.51
313.2	2.245 (40)	3.681 (87)	5.00 (34)	5.05
323.2	2.498 (103)	4.382 (112)	6.66 (54)	6.63
333.2	2.639 (51)	5.153 (24)	8.98 (55)	8.83
run 6				
303.2	3.328 (120)	4.381 (17)	3.07 (43)	3.14
313.2	4.021 (95)	5.819 (85)	5.29 (37)	5.34
323.2	4.592 (127)	6.711 (89)	6.31 (46)	6.29
		cis-Stilbene[d]		
run 1				
267.9	*1.830*	2.374 (9)	1.98 (18)	2.13
272.2	1.854 (59)			
283.5	*1.915*	2.735 (32)	3.03 (24)	3.18
284.0	1.879 (29)			
297.8	2.054 (2)			
298.5	*2.011*	3.107 (25)	4.12 (19)	4.24
304.0	2.100 (91)			
304.1	*2.050*	3.443 (35)	5.26 (19)	5.38
312.5	2.128 (125)	3.987 (43)	7.10 (50)	7.18
327.7	2.241 (117)	5.463 (85)	12.49 (56)	12.37
327.9	*2.238*	5.467 (110)	12.52 (45)	12.40
run 2				
264.1	*1.812*	2.338 (48)	1.70 (20)	1.82
281.2	1.843 (28)			
282.5	*1.909*	2.701 (48)	2.61 (20)	2.75
297.5	2.016 (69)			
298.1	*2.008*	3.335 (31)	4.45 (16)	4.59
304.3	*2.051*	3.723 (45)	5.65 (20)	5.78
304.7	2.055 (47)			
312.6	2.125 (27)	4.471 (87)	7.98 (32)	8.06
327.7	*2.236*	5.635 (263)	11.76 (92)	11.65
327.7	*2.236*	5.687 (168)	11.94 (60)	11.83
run 3				
263.2	1.76 (2)	2.32 (6)	2.02 (22)	2.18
273.2	1.82 (4)	2.55 (4)	2.65 (21)	2.82
283.2	1.98 (2)	2.87 (4)	3.27 (16)	3.44
293.2	1.98 (2)	3.30 (4)	4.91 (17)	5.09
293.2	*1.98*	3.42 (4)	5.35 (17)	5.55
303.2	2.08 (3)	3.79 (10)	6.43 (38)	6.58
313.2	2.13 (4)	4.39 (13)	8.59 (53)	8.68
323.2	2.32 (9)	4.99 (23)	10.27 (96)	10.23

[a] [DCA] = 1.14 × 10^{-4} M, throughout; numbers in parentheses are average deviations of triplicate traces; numbers in italics are interpolated, see text. [b] From eq 11, see text. [c] [t-St] = 0.230, 0.245, 0.266, 0.216, 0.291, and 0.345 M, 25 °C, for runs 1–6, respectively. [d] [c-St] = 0.271, 0.298, and 0.268 M, 25 °C, for runs 1–3, respectively.

transfer rate constants in both directions within the encounter cage. When essentially all $^3D^*$ are deactivated by interaction with ^1A but all free $^3A^*$ decay before they can be intercepted by ^1D, conditions usually fulfilled when high [^1A] and low [^1D] are employed, effective excitation transfer rate constants are given by[11a,b]

$$k_{obsd} = k_{dif}[1 + (k_{-dif}/k_{en})(1 + k_{-en}/k_{-dif})]^{-1} \qquad (4)$$

One can generally divide triplet excitation transfer processes into two cases: (a) exothermic transfer $E_T(D) - E_T(A) > 0$ kcal/mol and (b) endothermic transfer $E_T(D) - E_T(A) < 0$ kcal/mol. In the latter case the energy deficit is made up by thermal activation. For case a k_{obsd} has the functional form of the Arrhenius equation and is very close to the diffusion rate constant k_{dif}. Reduction of eq 4 to the form $k_{obsd} = k_{dif}$ requires the assumptions that $k_{-en} \ll k_{-dif}$ and that $k_{-dif} < k_{en}$. These assumptions appear to be reasonable for exothermic transfer since k_{en} is expected to be large and k_{-en} relatively smaller. For case b, endothermic transfer, it has also been observed that k_{obsd} has the functional form of the Arrhenius equation;[1b] however, there are two sets of assumptions that simplify eq 4 to such a form. The two limiting subclasses for case b depend on the relative magnitude of k_{-en} and k_{-dif}. If $k_{-en} \ll k_{dif}$ (case b′) then $k_{obsd} = K_{dif}k_{en}$, and if $k_{-en} \ll k_{-dif}$ (case b″) then $k_{obsd} = k_{dif}K_{en}$. While a priori one does not know the relative magnitude of k_{-en} and k_{-dif}, rate constants for endothermic triplet excitation transfer often conform to case b″ and obey

$$k_{obsd} = k_{dif}e^{-\Delta E_T/RT} \qquad (5)$$

where $\Delta E_T = E_T(A) - E_T(D)$ is the energy difference between the 0–0 $T_1 \leftarrow S_0$ transitions in the acceptor and donor, respectively.[17] Adherence to eq 5 has been employed as the chief criterion for designating a transfer process as vertical.[3] It was deviations from eq 5, first noted with *cis*-stilbene as the acceptor, that led to the concept of nonvertical energy transfer.[3]

In the preliminary interpretation, values of k_{obsd} for anthracene were treated by using $k_{obsd}^{t,c} = K_{dif}k_{en}^{t,c}$ (case b′) because excitation transfer from stilbene triplets to low-energy acceptors is inefficient, $k_{-dif} > k_{-en}^{t}$. Arrhenius treatment of the k_{obsd} values for anthracene gave log A_{obsd} values of 9.66 ± 0.30 and 8.80 ± 0.13 and E_{obsd} values of 6.03 ± 0.30 and 4.74 ± 0.20 kcal/mol for ^{1}t and ^{1}c, respectively;[1b] Arrhenius treatment of the k_{obsd} values for DCA (Table I) gives log A_{obsd} values of 7.84 ± 0.19 and 7.46 ± 0.16 and E_{obsd} values of 5.93 ± 0.27 and 5.11 ± 0.22 kcal/mol in the same order. The difference in endothermicity between the two donors (~2.4 kcal/mol) is reflected almost entirely in the preexponential factor and not in the activation energies *for both isomers*, in sharp contrast to predictions from recent classical and quantum mechanical treatments (see below).[11] The major conclusion from this work, that *the transfer is nonvertical to both isomers*, can thus be drawn from this crude treatment.

To achieve a more definitive interpretation of the activation parameters obtainable from k_{obsd}, we have sought to use eq 4 directly by using estimates of k_{-dif} and k_{-en} from previous work. This allows determination of the absolute values of k_{en} and thereby the activation parameters for the energy transfer step isolated from the diffusional and back energy transfer steps.

Two specific studies of exothermic triplet excitation transfer are of special interest here. The first concerns excitation transfer from indeno[2,1-*a*]indene, In, a rigid *trans*-stilbene analogue, E_T = 46.9 kcal/mol,[18] to a similarly rigid acceptor, azulene, Az, E_T = 39 kcal/mol.[19] Rate constants for this process, measured flash kinetically, have been shown to be fully diffusion controlled over a 70 °C temperature range in several solvents, toluene included.[15] In addition to providing an empirical measure for k_{dif}, this study shows that $k_{en} \gg k_{-dif}$, eq 5, when electronic transitions in donor and acceptor are π,π^*, and molecular rigidity constraints require relatively vertical transitions in both molecules. The second study,

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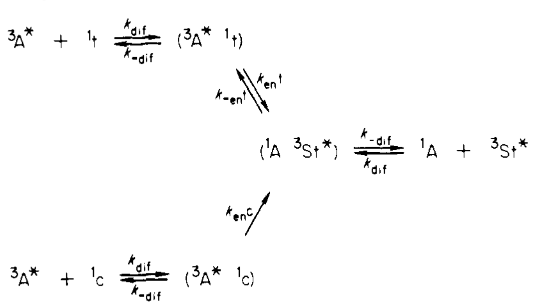
Scheme I. General Mechanism for Endothermic Energy Transfer to the Stilbenes



based primarily on steady-state observations, concerns the temperature dependence of the azulene effect on the photoisomerization of triplet stilbene.[20] Estimated k_{en}/k_{-dif} ratios close to 0.1 for this case provide direct evidence of the dramatic decrease in k_{en} that accompanies elimination of structural constraints and assumption by the donor stilbene triplet of an equilibrium geometry that differs markedly from the geometry of the ground singlet state. It is generally agreed that ~90° rotation about the central bond of stilbene accounts for the major geometry change, i.e., $^3p^*$ is the dominant geometry of thermally equilibrated stilbene triplets.[3,20b,21] Nonetheless, since the chemical consequence of stilbene triplet interaction with azulene is formation of the trans ground state exclusively, more detailed interpretations of k_{en} converge on the same final step—excitation transfer from transoid triplets to azulene. What is not clear is whether this is a consequence of the presence of a small equilibrium concentration of transoid triplets in solution or whether the transoid geometry, t, is achieved in a transition state for excitation transfer from $^3p^*$.[20b,21] It suffices at this point to consider a general mechanism for the azulene effect

$$^3St^* + Az \underset{k_{-dif}}{\overset{k_{dif}}{\rightleftharpoons}} ({}^3St^*Az) \xrightarrow{k_{en}} (t{}^3Az^*) \xrightarrow{k_{-dif}} t + {}^3Az^* \qquad (6)$$

in which $^3St^*$ includes the range of geometries available to thermally equilibrated stilbene triplets.[20b] Back energy transfer from $^3Az^*$ to t is neglected because $^3Az^*$ are too short lived, τ = 3–5 μs,[22] to participate in this highly endothermic process. Since the anthracenes and azulene have almost identical effects on the photoisomerization of stilbene triplets,[16] the anthracenes can be substituted for azulene in eq 6. Thus, experimental k_{en} values for eq 6 afford excellent estimates of k_{-en} in the present study (see below).

The simplest mechanism which allows treatment of the rate constants in Tables I and I-S is analogous to eq 6, and is shown in Scheme I for anthracene. The energy transfer step on the cis side is shown to be irreversible, $k_{-en}^c = 0$, because triplet excitation acceptors quench stilbene triplets only to ^1t, e.g., eq 6. Applying the steady-state approximation on all excited species, and neglecting $k_{-dif}[^1A]$ for low $[^1A]$, gives

$$k_{obsd}^t = k_{dif}k_{en}^t/(k_{-dif} + k_{en}^t + k_{-en}^t) \simeq k_{dif}k_{en}^t/(k_{-dif} + k_{-en}^t) \qquad (7)$$

$$k_{obsd}^c = k_{dif}k_{en}^c/(k_{-dif} + k_{en}^c + k_{-en}^t) \simeq k_{dif}k_{en}^c/(k_{-dif} + k_{-en}^t) \qquad (8)$$

The more exact treatment of the data is achieved by using the experimental efficiency of excitation transfer from $^3St^*$ to azulene to correct for back excitation transfer to the anthracenes. The azulene effect on sensitized stilbene photoisomerization is characterized by the quantity K_{az} which, using eq 6, is defined as

$$K_{az} = k_{dif}k_{-en}^t[k_d(k_{-en}^t + k_{-dif})]^{-1} \qquad (9)$$

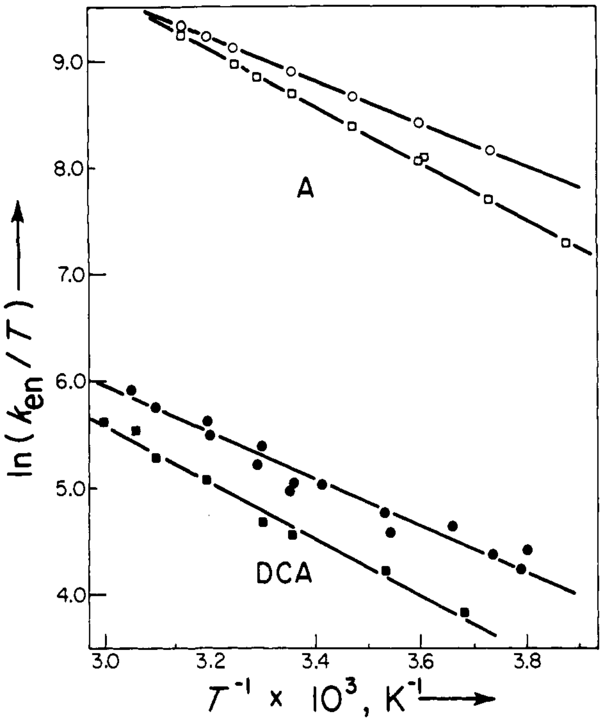


Figure 1. Plot of T^{-1} vs. ln (k_{en}/T). Where more than one experimental k_{en} was available for the same T, the average value was plotted: circles for c-St, squares for t-St, open symbols for A, closed symbols for DCA.

Table II. Activation Parameters for Endothermic Triplet Excitation Transfer to the Stilbenes

donor (E_T, kcal/mol)	*trans*-stilbene $\Delta H^{\ddagger}$, kcal/mol	 $\Delta S^{\ddagger}$,[a] eu	*cis*-stilbene $\Delta H^{\ddagger}$, kcal/mol	 $\Delta S^{\ddagger}$,[a] eu
A (42.7)				
exptl[b]	5.3 (1)	−12.2 (1)	4.0 (1)	−16.3 (1)
calcd, C[c]	6.02	−12.78	6.54	−12.78
calcd, QM[d]	5.21	−15.59	4.74	−17.63
DCA (40.3)				
exptl[b]	5.2 (5)	−20.5 (6)	4.3 (3)	−22.5 (5)
calcd, C[c]	8.34	−12.78	8.55	−12.78
calcd, QM[d]	8.02	−14.11	6.92	−16.56

[a] Actually this represents the sum $R \ln \kappa_{en} + \Delta S^{\ddagger}$, see text.
[b] From k_{en} in Tables I and I-S, using eq 12 but see footnote *a*; numbers in parentheses are uncertainties in last digit shown.
[c] Calculated by using classical treatment in ref 11a, see text.
[d] Calculated by using quantum mechanical treatment in ref 11c, see text.

where k_d is the known,[21] temperature-independent, effective decay rate constant of stilbene triplets.[20b] Combining eq 7 or 8 with eq 9 gives

$$k_{obsd}^{t,c} = k_{en}^{t,c}(k_{dif}/k_{-dif})(1 - K_{az}k_d/k_{dif}) \qquad (10)$$

which can be solved for $k_{en}^{t,c}$ to give

$$k_{en}^{t,c} = k_{obsd}^{t,c}(k_{-dif}/k_{dif})(1 - K_{az}k_d/k_{dif})^{-1} \qquad (11)$$

Values of k_{en}^t and k_{en}^c calculated from eq 11 by using k_{obsd} in Tables I-S and I and experimental values for K_{az},[20b] k_{dif},[15] and k_d[21] and by assuming (k_{-dif}/k_{dif}) = [S], the molarity of the solvent,[15] are shown in Tables I-S and I.[23] Ratios k_{en}/k_{obsd} are roughly equal to 10 M which is close to [S]; the contribution of the K_{az} term in eq 14 is minor, increasing k_{en} by ~10%, and is not sensitive to a possible small decrease in k_{dif} when DCA is

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(20) (a) Saltiel, J.; Chang, D. W.-L.; Megarity, E. D.; Rousseau, A. D.; Shannon, P. T.; Thomas, B.; Uriarte, A. K. *Pure Appl. Chem.* **1975**, *41*, 559. (b) Saltiel, J.; Rousseau, A. D.; Thomas, B. *J. Am. Chem. Soc.* **1983**, *105*, 7631.

(21) Görner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1981**, *85*, 1835.

(22) Görner, H.; Schulte-Frohlinde, D. *J. Photochem.* **1981**, *16*, 169.

(23) Values of K_{az} were interpolated from $\ln K_{az} = 7.827 - (1.1337 \times 10^3)/T$;[20b] k_{dif} from $\ln k = 27.585 - (1.369 \times 10^3)/T$;[15] the benzene value[20b,21] of $k_d = 1.61 \times 10^7$ s^{-1} was used; [S] was corrected for density changes.[15]

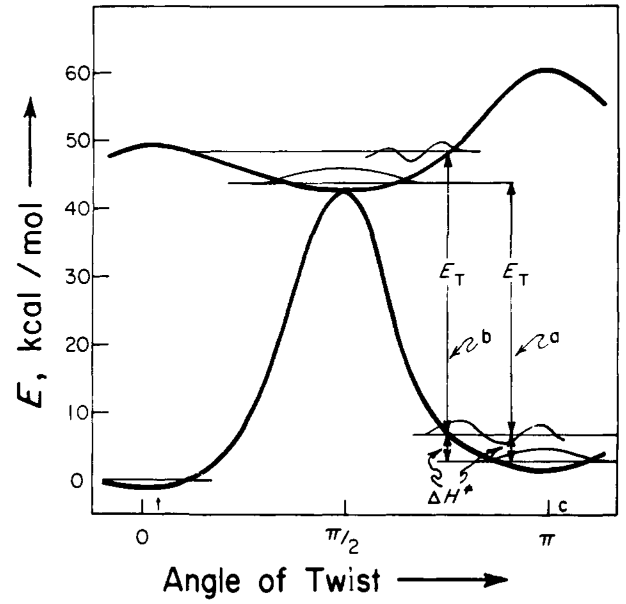

Figure 2. Possible potential energy curves for twisting about the central bond in the S_0 and T_1 states of stilbene.

substituted for A.[24] The rate constants k_{en} and k_{-en} can be expressed in terms of transition state theory as[11a,b]

$$k_{en} = \kappa_{en}(kT/h)e^{\Delta S^\ddagger/R}e^{-\Delta H^\ddagger/RT} \tag{12}$$

$$k_{en}/k_{-en} = e^{\Delta S/R}e^{-\Delta H/RT} \tag{13}$$

where κ_{en} is the transmission coefficient and $\Delta S^\ddagger$ and $\Delta H^\ddagger$ and ΔS and ΔH are the entropy and enthalpy of activation and the standard entropy and enthalpy changes for the forward energy transfer step, respectively.

The k_{en} values adhere nicely to eq 12 (Figure 1) and give the activation parameters listed in Table II. Strictly speaking, the intercepts in Figure 1 give the sum ($\Delta S^\ddagger + R \ln \kappa_{en}$) instead of $\Delta S^\ddagger$, as listed. In fact, in recent proposals for the calculation of k_{en} it has been argued that $\Delta S^\ddagger = 0$ and that small κ_{en} values account for deviation of the preexponential term in eq 12 from kT/h (see below).[11] However, the lower limit of $k_{en} \geq 2 \times 10^{12}$ s^{-1}, estimated for the In/Az system in which one of the partners, albeit rigid, is electronically the same as *trans*-stilbene and π,π^* transitions are involved in the donor and acceptor, suggests strongly that κ_{en} must be close to unity. Accordingly, $\ln \kappa_{en} = 0$ is assumed in Table II;[25] however, in the following it is not important whether the small intercepts in Figure 1, associated with molecular flexibility and nonplanar geometries in one of both partners, reflect decreases in $\Delta S^\ddagger$ or in κ_{en}.

Activation Parameter Interpretation. Depending upon the geometry of the stilbene triplet at the transition state for the excitation transfer event, we may distinguish broadly between two general mechanisms for nonvertical energy transfer. The first case we designate as the *common entry* (*threshold*) *geometry* mechanism. The degree of distortion at the transition state for this case is a property inherent in the partner undergoing the nonvertical transition and does not in any significant way depend on the magnitude of $\Delta H^\ddagger$. In the case of *cis*-stilbene, for example, the geometry of the stilbene moiety at the transition state would be the same, or nearly so, independent of the size of $\Delta H^\ddagger$ for the excitation transfer event; in other words, provided that the transfer is endothermic, a common stilbene geometry serves as the entrance into the triplet state potential energy surface. This mechanism requires that changes in $E_T(D)$ be reflected in essentially complementary changes in $\Delta H^\ddagger$; i.e., $E_T(D) + \Delta H^\ddagger$ = constant with a value equal to the difference between the energy of the vibrationless ground state acceptor and the energy of the nascent distorted triplet acceptor. In the case of *cis*-stilbene the minimum value for this constant is $\Delta E_{^1c \to ^3p^*}$, Figure 2, path a.

The second case we designate as the *variable entry geometry* mechanism. In this mechanism the degree of distortion (the greater the distortion the more nonvertical the process) of the nascent excited acceptor increases with decreasing $E_T(D)$. Accordingly, the sum $E_T(D) + \Delta H^\ddagger$ will vary, approaching a minimum value of $\Delta E_{^1c \to ^3p^*}$ at low $E_T(D)$ in the case of *cis*-stilbene. The "hot-band" mechanism[6,10] in which torsionally excited ground state cis molecules accept electronic energy from the donor and reach vertically a point in the potential energy surface of the acceptor, Figure 2, path b, is a mechanism of the variable entry geometry type. More complex mechanisms involving a coupling of vibrational motions in donor and acceptor and/or exciplex intermediates should also yield sums of $E_T(D) + \Delta H^\ddagger$ that change with $E_T(D)$.

The experimental activation parameters in Table II strongly support a variable entry geometry mechanism for nonvertical energy transfer. Most, if not all, of the additional 2.4-kcal/mol energy deficiency in substituting $^3DCA^*$ for $^3A^*$ as the donor is expressed in a decrease of $\Delta S^\ddagger$ and/or $\ln \kappa_{en}$ rather than in an increase in $\Delta H^\ddagger$. The "hot-band"-type mechanism is accordingly considered the most attractive, although the donor/acceptor interaction (exciplex?) may reduce the enthalpy requirements for torsional displacement in the stilbene partners. The magnitude and changes in the activation parameters are strikingy similar for the two isomers; the DCA results confirming the conclusion based on the earlier A observations[1b] that the transfer is nonvertical, not only for the cis isomer but for the trans as well. This may at first appear surprising because of the good adherence of $k_{obsd}{}^t$ to eq 5. Suffice it to say that such adherence, though a necessary condition, is not sufficient to ensure vertical excitation transfer behavior, because k_{obsd} measurements at a single temperature will not always reveal consequences of strong compensation between changes in the activation parameters $\Delta S^\ddagger$ and $\Delta H^\ddagger$ for k_{en}. It should be noted that the criterion of associating large negative $\Delta S^\ddagger$ values with nonvertical excitation transfer was first applied to interpret activation parameters for intramolecular triplet energy transfer from triplet metalloporphyrins to azastilbene-type ligands.[27]

We now consider the significance of the experimental $\Delta S^\ddagger$ values in Table II, within the framework of the variable entry excitation transfer mechanism. It is first important to recognize that the requirement of large torsional distortions in the transition state is not, of itself, expected to contribute significantly to $\Delta S^\ddagger$. Thermal cis → trans isomerizations of olefins and of stilbene, in particular, exhibit large preexponential Arrhenius factors reflecting small entropies of activation in achieving a transition state in which the olefin, isolated or in solution, undergoes a $\pi/2$ rotation about the central bond.[28] The large negative $\Delta S^\ddagger$ values obtained in this work can be attributed to at least two factors. The first has to do with the donor–acceptor interaction. It is recognized that, to be efficient, Dexter's exchange mechanism for electronic energy transfer requires overlap between the π-electron clouds of the donor/acceptor pair.[29] An intimate association of the two partners in the encounter cage is therefore envisioned. It follows that the larger the distortion required of the acceptor in order to achieve the optimum energy difference between ground and triplet potential energy surfaces, the greater should be the steric interaction with the donor and the poorer the π-cloud overlap. The second,

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[24] Smaller oxygen quenching rate constants for $^1DCA^*$ than for ^1A and other aromatic hydrocarbons may reflect a smaller diffusion coefficient for DCA, see: Smothers, W. K.; Meyer, M. C.; Saltiel, J. *J. Am. Chem. Soc.* **1983**, *105*, 545 and references cited therein.

[25] Note that $\kappa = 1$ is one of the major assumptions of transition-state theory.[26]

[26] (a) Moore, J. W.; Pearson, R. G. "Kinetics and Mechanism"; John Wiley & Sons: New York, 1981, p 166. (b) Miller, W. H. *Acc. Chem. Res.* **1976**, *9*, 306.

[27] Whitten, D. G.; Wildes, P. D.; DeRosier, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 7811.

[28] For a review, see: Saltiel, J.; Charlton, J. L. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 25.

[29] (a) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836. (b) Davidovich, M. A.; Knox, R. S. *Chem. Phys. Lett.* **1979**, *68*, 391.

and more important factor is that, as the torsional state quantum number corresponding to the transition state increases, F–C overlap factors are expected to decrease. The question of whether such quantum mechanical probability factors should be included in κ_{en} instead of in $\Delta S^{\ddagger}$ is, in our view, less than trivial. Although others[11] have attributed impediments to progress through the transition state imposed by restrictions such as multiplicity changes and F–C factors to diminution in κ, we prefer to assign them to unfavorable entropy requirements. Transmission coefficients less than one arise when there is reflection back through the transition state. For polyatomic molecules, in which there is a high density of coupled vibrational states, rapid deactivation of the nascent product effectively prevents such reflection. We therefore regard the quantum mechanical probability factors as contributions to the entropy of activation. However, as pointed out earlier, empirically it makes little difference whether the nonenthalpic factor is assigned to $\Delta S^{\ddagger}$ or κ_{en}.

Theoretical Predictions for k_{en}. A general classical treatment, CT, for exchange energy transfer processes in solution has been proposed, which parallels that used for electron transfer interactions.[11a,b] Starting with eq 3 and 4, taking $\Delta G \simeq \Delta H = \Delta E_T$ for eq 13, and applying the Agmon and Levine expression for electron transfer[30] to calculate $\Delta G^{\ddagger}$ in eq 12, we can transform eq 4 to

$$k_{obsd} = k_{dif}[1 + \exp(\Delta G/RT) + (k_{-dif}/k_{en}^{\circ}) \exp\{\Delta G + (\Delta G^{\ddagger}_{o}/\ln 2) \ln [1 + \exp(-\Delta G(\ln 2)\Delta G^{\ddagger}_{o})]\}/RT]^{-1} \quad (14)$$

where $k_{en}^{\circ} = \kappa kT/h$ and the parameter $\Delta G^{\ddagger}_{o}$ is defined as the reorganizational energy for the donor/acceptor pair. Herkstroeter and Hammond's experimental $k_{obsd}^{t,c}$ as a function of $E_T(D)$[3c] were fitted to eq 14 by developing a family of curves for different values of $\Delta G^{\ddagger}_{o}$ and k_{en}°, using $k_{-dif} = 1.16k_{dif}$ throughout. "Best fitting curves" selected in this way were obtained for $k_{en}^{\circ} = 1 \times 10^{10}$ s^{-1}, E_T^{∞}(trans) = 48.6 kcal/mol, E_T^{∞}(cis) = 48.3 kcal/mol, $\Delta G^{\ddagger}_{o}$(trans) = 1.43 kcal/mol, and $\Delta G^{\ddagger}_{o}$(cis) = 2.86 kcal/mol.[31] From these values, it is a simple matter to calculate predicted activation parameters for k_{en} for the two donors employed in this work, Table II. The calculated k_{en} values are significantly and, as will be shown below, artificially lower than the experimental values over the entire temperature range employed. More significant is the fact that changes in donor and acceptor energies are reflected only in the calculated $\Delta H^{\ddagger}$. According to ref 11a $\Delta S^{\ddagger} \simeq 0$ for all donor–acceptor combinations and $R \ln \kappa_{en} = -12.78$ independent of the magnitude(s) of distortions and/or the "reorganizational energies". While this method holds promise for predicting k_{obsd} values when applied to vertical excitation transfer, it is inadequate when applied to nonvertical excitation transfer due to neglect of the contribution of $\Delta S^{\ddagger}$. For the same reason it may also be inappropriate for nonverticl electron transfer processes.

As noted above part of the discrepancy between calculated and experimental k_{en} values is artificial. It arises because in fitting eq 14 to experimental data the choice of k_{en}° is coupled to the choice of k_{-dif}. Fixing k_{-dif} to values nearly an order of magnitude smaller than those used in our treatment results in a corresponding decrease in k_{en}°. The low ratio of k_{-dif}/k_{dif} employed in ref 11 was based on Eigen's equation,[33] $k_{-dif} = k_{dif}(3000)/(Nr^3 4\pi)$, with a rather large encounter radius, $r = 0.7$ nm. This procedure is consistent with empirical observations concerning exciplex dissociation rate constants.[34] Extrapolation from such empirical correlations has been suggested as a method for estimating k_{-dif} in systems lacking Coulombic attraction.[34c] Triplet excitation transfer encounter complexes are expected to fall in this category. We have based (k_{-dif}/k_{dif}) = [S] on the cratic part of the entropy change for bringing two solutes together in solvent S.[15,35] Experimental justification for our approach can be found in triplet excitation transfer observations and requires no extrapolation. In a pioneering study Wagner and Kochevar have estimated $k_{en} \simeq 10^{11}$ s^{-1} for triplet energy transfer from valerophenone triplets to 1,3-dienes (used as solvent),[36a] a k_{en} magnitude confirmed by direct transient measurements for benzophenone triplets transferring energy to the 1,3-pentadienes and to 1-methylnaphthalene.[37] Since, as is known,[36] $k_{obsd} \simeq {}^1/_2 k_{dif}$ for energy transfer from n,π^* ketone triplets to π,π^* acceptors in dilute quencher solutions in benzene,[3c,15,36] it follows that $[k_{en}/(k_{en} + k_{-dif})] \simeq {}^1/_2$ so that $k_{-dif} \simeq k_{en} \simeq 10^{11}$ s^{-1} and $(k_{-dif}/k_{dif}) \simeq 10$ M $\simeq$ [S].

A more ambitious undertaking has been the calculation of k_{en} based on an extension of Ulstrup and Jortner's quantum mechanical description of electron transfer reactions[38] to triplet energy transfer.[11c] According to this quantum mechanical treatment, QM, k_{en} is the product of an electronic (E) and a nuclear (N) term, $k_{en} = EN$. The electronic term is given by $E = V^2$ where V is the electron exchange matrix element between donor and acceptor, and the nuclear term is approximated by

$$N = \left[\frac{\pi}{\hbar^2 kT(E_S + 2\Delta)}\right]^{1/2} \exp[-(\gamma_A + \gamma_D)] \sum_{\nu_A=-\infty}^{+\infty} \sum_{\nu_D=-\infty}^{+\infty} (|\nu_A|!)^{-1}\gamma_A^{|\nu_A|}(|\nu_D|!)^{-1}\gamma_D^{|\nu_D|} \exp\left[-\frac{1}{2RT}\{(\nu_A + |\nu_A|)\hbar\omega_A + (\nu_D + |\nu_D|)\hbar\omega_D\}\right] \exp[-\{\Delta E_T - (E_S + 2\Delta) + \nu_A\hbar\omega_A + \nu_D\hbar\omega_D\}^2\{4RT(E_S + 2\Delta)\}^{-1}] \quad (15)$$

where E_S is the reorganizational energy, Δ is a parameter which determines the width of a vibronic band, $\hbar\omega_D$ and $\hbar\omega_A$ correspond to high frequency stretching vibrations for donor and acceptor, respectively, γ_D and γ_A are displacement parameters, and the other quantities have their usual meanings.[39] N is supposed to represent a thermally averaged summation over all the vibronic transitions of the donor/acceptor encounter complex, each proportionally weighted by its F–C factor.[11] The evaluation of this approach and of the methods used in assigning values to the parameters is beyond the scope of this paper. Suffice it to state that using $V = 8$ cm^{-1}, $E_S = 300$ cm^{-1}, and 2200 cm^{-1} for *trans*- and *cis*-stilbene, respectively, $\Delta = 150$ cm^{-1}, $\hbar\omega_A = 1500$ cm^{-1}, $\hbar\omega_D = 1400$ cm^{-1}, $\gamma_D = 1$, $\gamma_A = 2$, and $-5 \leq \nu_A$ and $\nu_D \leq 5$ excellent agreement between calculated and observed rate constants was obtained[11c] for Herkstroeter and Hammond's k_{obsd} values as a function of $E_T^{\infty}(D)$[3c] and our own initial k_{obsd} values for A as a function of T.[1b] $E_T^{\infty}(A) = 48.6$ and 47.7 kcal/mol for *trans*- and *cis*-stilbene, respectively were used in ref 11c. We have reproduced these calculations for A and find that the calculated k_{en} values are in exact agreement with eq 12 and give the activation parameters shown in Table II. What is significant here is that calculated and experimental $\Delta H^{\ddagger}$ values are in very good agreement; experimental and QM k_{en} lines are nearly parallel. The major discrepancy in the actual values once again can be traced to the different assumptions made about k_{-dif}. Since all the parameters were defined in ref 11c and no distinction was made between a whole family of diverse donors, our DCA data provide a stringent test of this approach. The only parameter change is an increase of 2.4 kcal/mol in ΔE_T. Activation parameters for

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(30) (a) Agmon, N.; Levine, R. D. *Chem. Phys. Lett.* **1977**, *52*, 197. (b) Agmon, N. *J. Chem. Soc., Faraday Trans. 2*, **1978**, *74*, 388. (c) Agmon, N,; Levine, R. D. *Isr. J. Chem.* **1980**, *19*, 330.

(31) Using the general least-squares program BMDPAR,[32] we obtained the following best-fit parameters: for *trans*-stilbene $(k_{-dif}/k_{en}^{0}) = 0.614$, E_T^{∞}(trans) = 45.6 kcal/mol and $\Delta G_0^{\ddagger}$(trans) = 2.80 kcal/mol; for *cis*-stilbene $(k_{-dif}/k_{en}^{0}) = 0.170$, E_T^{∞}(cis) = 36.4 kcal/mol, and $\Delta G_0^{\ddagger} = 7.86$ kcal/mol. Because of scatter in k_{obsd}, the improvement in the fit to eq 14 over that obtained in ref 11b is probably not significant.

(32) Dixon, W. I.; Brown, M. B. "BMPD Biomedical Computer Programs P-series"; 1979 ed.; University of California Press: Los Angeles, 1979.

(33) Eigen, M. *Z. Phys. Chem.* (*Frankfurt am Main*) **1954**, *1*, 176.

(34) (a) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834. (b) *Isr. J. Chem.* **1970**, *8*, 259. (c) Weller, A. *Z. Phys. Chem.* (*Wiesbaden*) **1982**, *130*, 129.

(35) Gurney, R. W. "Ionic Processes in Solution"; McGraw-Hill: New York, 1953.

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(38) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358.

(39) In ref 11c the $\nu_A\hbar\omega_A$ and $\nu_D\hbar\omega_D$ quantities in the last term of eq 15 are assigned the wrong sign.

calculated k_{en} values for DCA are also listed in Table II. As with the classical treatment the additional energy deficiency shows up primarily in the calculated ΔH^{*}. Furthermore, in this case, ΔS^{*} becomes more positive in going from A to DCA for both isomers in sharp contrast with the experimental results. We conclude that both theoretical approaches to k_{en}, in their present form, fail to account for nonvertical energy transfer to the stilbenes.

Different assumptions about k_{-dif} aside, Figure 1 illustrates another pitfall in using eq 14 to relate k_{obsd} to k_{en} for nonvertical excitation transfer. It is assumed in deriving eq 14 that there is an equilibrium between donor/acceptor complexes having the excitation localized in the donor or the acceptor. Since, in cases involving nonvertical energy transfer, the equilibrium geometry of the excited acceptor state differs significantly from the equilibrium geometry of the ground state of its origin, it cannot a priori be assumed that upon reverse energy transfer the acceptor will return to the original ground state. The stilbenes provide an excellent illustration of this point. Here, excitation transfer to the cis isomer gives a twisted excited state which upon back energy transfer returns to the ground state surface on the trans side, Figure 2. This circumstance was taken into account in our calculations of experimental k_{en} values, eq 7–11, but not in ref 11. It provides the explanation for the seeming contradiction of our derivation of experimental k_{en} values from k_{obsd} such that $(k_{en}^{t}/k_{en}^{c}) < 1$ and the need in ref 11c of $(k_{en}^{t}/k_{en}^{c}) > 1$ in order to predict the same k_{obsd} values, cf. Figure 1 of this work and Figures 1 and 2 in ref 11c.

Potential Energy Curves for Twisting. Previous versions of potential energy curves for twisting about the central bond of the lowest stilbene triplet state have generally shown $^3p^*$ nearly isoenergetic with $^3t^*$.[1b,3,6,11,20a,21,28] The latter has often been placed at an energy minimum on the potential energy surface, preferably lower than $^3p^*$ in enthalpy if not in free energy content.[20a] Such curves were consistent with the formation of *trans*-stilbene when stilbene triplets are quenched by low triplet energy acceptors[3,21,28] and the apparent functioning of *trans*-stilbene as a vertical acceptor of triplet energy.[3c] We have recently shown that $^3t^* \rightleftarrows {}^3p^*$ equilibration and quenching of $^3t^*$ only is not a unique mechanism for the interpretation of the temperature dependence of the azulene effect on stilbene triplet decay.[20b] An alternative mechanism involving nonvertical quenching of $^3p^*$ to ^1t adequately accounts for the data. This latter mechanism is strongly supported by the conclusion that both stilbene isomers are nonvertical acceptors of triplet energy. Accordingly, the potential energy curves in Figure 2 depart from previous versions in only one important feature—the energy of perpendicular stilbene in the ground and triplet states. As before,[28] the energies of $^3t^*$ and $^3c^*$ are based on $T_1 \leftarrow S_0$ spectra[40] and in the case of $^3t^*$ on the $T_1 \rightarrow S_0$ spectrum,[19] as well. The enthalpy of activation for the quenching of $^3p^*$ by azulene is 2.1 kcal/mol.[20b] By setting the energy of $^3p^*$ at ~44 kcal/mol we have made the energy (~46 kcal/mol relative to ^1t) of the transition state for nonvertical deactivation of $^3p^*$ to ^1t by Az essentially isoenergetic with the transition state for nonvertical activation of ^1t to $^3p^*$ with $^3DCA^*$. As an exit point on the trans side of $^3p^*$ an energy of 46 kcal/mol relative to ^1t is consistent with the slow decrease in efficiency noted when the acceptor E_T is increased in the 45–47-kcal/mol range.[3b,41]

The triplet curve on the cis side is somewhat more tentative because of uncertainty in the energy of ^1c; values of 2.3 kcal/mol in toluene[43a] and 5.7 kcal/mol[43b] in acetic acid have been reported. What seems clear is that the transition state energy with $^3DCA^*$ as the donor places the entry point energy on the cis side of the triplet potential energy surface at about 45 kcal/mol above ^1c. Since this transition state does not function as an exit from the excited state surface when $^3p^*$ is quenched, it must be at least 2 kcal/mol higher in energy than the transition state for exit on the trans side. This sets a minimum value of ~48 kcal/mol relative to ^1t for the $^3DCA^*$ transition state on the cis side, suggesting a minimum of 3 kcal/mol for the energy of ^1c. The activation enthalpy for thermal $^1c \rightarrow {}^1t$ isomerization must be added to the energy of ^1c to locate the energy of ^1p in the diagram. Experimental values for the Arrhenius activation energy of this process in the vapor phase, 42.8 ± 2,[44a] 42.6 ± 1,[44b] and 46 ± 2[44c] kcal/mol,[45] allow considerable latitude in selecting this energy. In keeping with previous practice and in agreement with recent theoretical calculations[46] we have made $^3p^*$ and ^1p nearly isoenergetic.

Experimental Section

Materials. The sources and purification of toluene,[13] anthracene,[13] 9,10-dichloroanthracene,[47] and the stilbenes[48] have been reported. In the later stages of the work DCA was further purified by recrystallization from toluene followed by sublimation. This procedure did not affect k_1 values. Also, in the later stages of the work, benzophenone was substituted for pyrene as the sensitizer for *cis*-stilbene formation from the trans isomer.

Flash Kinetic Analysis. A Northern-Precision kinetic flash photolysis apparatus and a Bausch and Lomb monochromator with a 33-86-07 UV–vis grating having a reciprocal dispersion of 7.4 nm per 1 mm were employed. Triple-jacketed Pyrex cells, l = 15.0 cm, similar to that described by Jackson and Livingston[49] were used. A constant-temperature 1,4-diphenyl-1,3-butadiene/methanol solution was circulated through the outer jacket, to provide temperature control to ±0.5 °C and prevent excitation of the sample below 330 nm, for the anthracene experiments. Two air-discharge lamps parallel to the cell were flashed simultaneously so that excitation was perpendicular to the monitoring beam. Procedures used for the anthracene experiments and data analysis have been described;[1b,13,15] the monochromator was set for 20-nm band-pass for the monitoring beam, centered at 430 nm.[13] In the case of DCA the flash lamps were jacketed with filter solution holders containing a $CuSO_4/NH_4OH/H_2O$ solution which transmitted $\lambda \geq 340$ nm. Initial measurements were carried out using the 20-nm band-pass for the monitoring beam centered at 425 nm. Final experiments were carried out with use of narrower slits (1.8-mm entrance, 1.0-mm exit) so that the band-pass at $^1/_2$ intensity was 7 nm. In these experiments *trans*-stilbene in *n*-propyl alcohol (1 g/L) was circulated through the outer cell jacket. In some experiments with the DCA/*trans*-stilbene system a Corning CS-052 glass filter, transmitting $\lambda \geq 330$ nm, was placed between the monitoring beam and the cell. Most of the DCA experiments were carried out with use of a Nicolet Explorer I digital storage oscilloscope to monitor decay signals. Although this method made data treatment less cumbersome,[14] results obtained were indistinguishable from those from the earlier previously described procedure.[13,15] The quenchers were admitted into the cells via a break seal and a fritted-disk filter, which prevented glass fragments from entering the cell. Stilbene concentrations were determined from the dilution factor in the case of A and UV analyses at the end of the experiment in the case of DCA. Solutions were checked for stilbene photoisomerization by GLC;[48] up to 15% trans → cis conversion was observed with A, but in the case of DCA, where stilbene concentrations were higher and cell exposures to light were lower, isomerization conversions were negligible.

Fluorescence Measurements. A Perkin-Elmer Hitachi MPF-2A spectrophotometer was employed as previously described.[47]

Appendix

^{3}DCA* Decay Rate Constants. Since repeated flashing caused k_1' values for the DCA/t-St system to increase gradually, several

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(40) (a) Evans, D. F. *J. Chem. Soc.* **1957**, 1351. (b) Dyck, R. H.; McClure, D. S. *J. Chem. Phys.* **1962**, *36*, 2326.

(41) The effect reported for pyrene ($E_T \simeq 48$ kcal/mol) quenching of $^3p^*$ in ref 3b was due to improper light filters.[42]

(42) Valentine, D., Jr.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 3449.

(43) (a) Fischer, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Soc. B* **1968**, 156. (b) Williams, R. B. *J. Am. Chem. Soc.* **1942**, *64*, 1395.

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(45) Subtract $RT \simeq 0.7$ kcal/mol to obtain ΔH^{*}.

(46) (a) Gregory, R. A.; Williams, D. F. *J. Phys. Chem.* **1979**, *83*, 2652 (includes a review of earlier work). (b) Orlandi, G.; Palmiery, P.; Poggi, G. *J. Am. Chem. Soc.* **1979**, *101*, 3492.

(47) Smothers, W. K.; Meyer, M. C.; Saltiel, J. *J. Am. Chem. Soc.* **1983**, *105*, 545.

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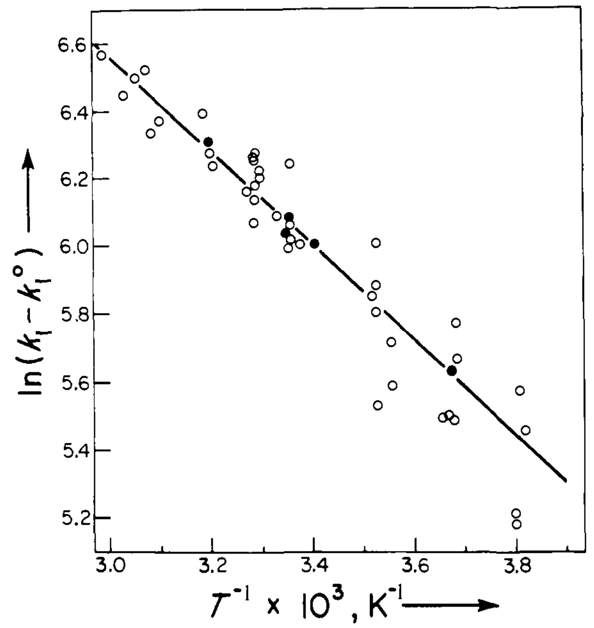

Figure 3. Adherence of DCA k_1 values to eq 17; closed symbols indicate coincidence of 2–5 independent measurements.

initial data sets had artificially high k_1'''s and were discarded. Corresponding k_1's did not change with light exposure and were, therefore, used together with those given in Table I to obtain parameters for k_1 interpolations. It was assumed that k_1 consisted of a temperature and viscosity independent unimolecular decay part, k_1°, which is augmented by bimolecular quenching contributions. The k_1° value was determined by fitting[32] the k_1's to

$$k_1 = k_1^\circ + mT/\eta \tag{16}$$

with use of T/η sources given in ref 15: $k_1^\circ = 1576 \pm 20$ s^{-1}, $m = (7.96 \pm 0.36) \times 10^{-3}$ P·K^{-1} s^{-1}. With $k_1^\circ = 1576$ s^{-1} fixed, the k_1's were then fitted[32] to

$$k_1 = k_1^\circ + b\exp(-E_q/RT) \tag{17}$$

leading to $b = (4.75 \pm 0.96) \times 10^4$ s^{-1} and $E_q = 2.78 \pm 0.12$ kcal/mol, Figure 3. The interpolated k_1 values in Table I were obtained by using eq 17.

The 30-fold increase of k_1° relative to the corresponding constant in A is attributed to heavy-atom-enhanced spin–orbit coupling on both the radiative and nonradiative rate constants for the $T_1 \rightarrow S_0$ transition.[49] Our k_1° value, being somewhat lower than that previously reported, falls exactly on a line relating triplet decay rate constants for a series of halogen-substituted anthracenes to spin–orbit coupling factors.[49a] The explanation usually favored for the behavior reflected in the second term of eq 16 or 17 is that it represents quenching by impurities adventitiously present in the solute and/or the solvent.[14,50] Since our measurements were carried out by different investigators over a period of years employing different batches of materials and different purification techniques, we tend to discount this interpretation, unless the impurity is residual oxygen. Diffusion-controlled quenching by an impurity Q would be consistent with E_q because it is nearly identical with the activation energy for viscous flow in toluene,[15] and would account for b if [Q] were $\sim 5 \times 10^{-8}$ M. An alternative interpretation is provided by the self-quenching of ^{3}DCA* by ^{1}DCA. With use of [DCA] = 1.15×10^{-4} M, the value of b gives $A = 4.1 \times 10^8$ s^{-1} which is almost identical with $A_{sq} = 3.9 \times 10^8$ s^{-1}, the Arrhenius preexponential factor for self-quenching in A.[14] We anticipate testing this interesting possibility by determining the dependence of b on [DCA].

Registry No. Anthracene, 120-12-7; 9,10-dichloroanthracene, 605-48-1; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0.

Supplementary Material Available: Table I-S, listing k_{obsd} and k_{en} values for A (1 page). Ordering information is given on any current masthead page.

Muonium Addition Reactions to Aromatic Solutes

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Abstract: Reaction rate constants of 0.3×10^{10}–1.1×10^{10} M^{-1} s^{-1} were determined for the reaction of muonium (μ^+e^-, Mu) with seven aromatic solutes in dilute aqueous solution at ~295 K. The reaction was deduced to be that of addition to the benzene ring to form cyclohexadienyl radicals. On comparison with the analogous H-atom reactions, the kinetic isotope effects were generally about 3, equal to the mean thermal velocity ratio of Mu/H. When analyzed through the Hammett equation there were serious discontinuities but a small positive ρ value was evident, not inconsistent with attack by a mildly electron-donating neutral atom forming only free radical intermediates.

A convenient and sensitive method of studying both hydrogen atom reactions and kinetic isotope effects is to study the reactions of muonium (Mu). This is the light atom ($^1/_9$ the mass of ^{1}H) which differs from hydrogen in having a positive muon rather than a proton as its nucleus. As the muon is unstable and spin polarized its chemical fate can be investigated by the muon spin rotation method (μSR) using nuclear physics counting techniques.[1-3] A variety of muonium reaction types in aqueous solution have been studied[3,4] including the following: addition, abstraction, substitution, electron spin exchange, redox, and acid–base reactions. For addition reactions, Mu has been observed to add cross C=C

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