Table V. Values of χ for I-TCNE Calculated Using the ω Technique

	χ_1	χ_2	Charge in one ring, %
Initial	0.777	0.443	100
After one iteration	0.779	0.469	78
After two iterations	2.376	2.061	57

ion. This situation can be simply analogized within the ω-technique framework by considering first a localized donor ion, then examining the effect of successive iterations. Hückel calculations of neutral III and its cation provide values of the charge density on all 24 atoms, which values are then used to vary α in the usual way[21] for the first ω iteration.

Results of such a calculation are shown in Table V for the first and second iterations. Clearly, extension even only this far leads to an unacceptable description. After only one iteration, however, differences in χ caused by TI are only 0.002β and 0.026β for the first and second EDA bands, respectively. From Table IV, this corresponds to an energy difference of 45 and 570 cm^{-1}. The observed difference, 200 and 1000 cm^{-1}, is somewhat higher. An increase in the overlap integrals between rings improves the fit. In fact, calculation of β between rings by application of Simonetta and Winstein's relationship between β and overlap[26] yields a calculated energy difference of 330 and 890 cm^{-1} for the two bands. This improvement is of questionable significance considering the crudity of the method, especially the rather arbitrary but convenient designation of one cycle of iteration as a measure of perturbation due to TI. Nevertheless, consideration of the unsymmetrical ion as described above does effect a reversal in the relative magnitudes of the energy differences from those calculated ignoring this feature.

The model described here clearly requires further application to demonstrate its generality or lack thereof. Its main advantage over other semiempirical SCF methods lies in its operational simplicity, which has been shown not to appreciably impair its relative ability to fit data such as are included in Figure 1.

(26) M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954).

Perdeuteriostilbene. The Triplet and Singlet Paths for Stilbene Photoisomerization[1]

Jack Saltiel

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306. *Received June 3, 1968*

Abstract: A comparative study of the direct and sensitized *trans* → *cis* photoisomerization of perhydro- and perdeuteriostilbene solutions in benzene has been carried out. Perdeuteration does not affect *cis–trans* decay ratios of stilbene S^1 and T^1 states. The effect of azulene on stationary states of the benzophenone-sensitized photoisomerization has been determined, and it is inferred that upon perdeuteration the lifetime of stilbene T^1 states increases 30% at 25 and 60°. These observations are accounted for by a modified triplet mechanism for sensitized isomerization and a new singlet mechanism for direct photoisomerization. The two mechanisms involve radiationless decay from common twisted T^1 and S^1 electronic states, respectively. Loss of triplet excitation through interaction with *trans*-stilbene ground states is shown not to occur.

Theory predicts that deuteration should decrease the rate of $T^1 \rightarrow S^0$ and $S^1 \rightarrow S^0$ radiationless transitions.[2] The deuterium effect is attributed to inhibition of a kind of tunneling between the zero vibrational level of the electronically excited state and high vibrational levels of the ground state.[2] Spectroscopic studies of rigid perhydro and perdeuterio aromatic compounds provide abundant experimental support for the theory.[3] Perdeuteration leads to large increases in T^1 lifetimes of aromatic hydrocarbons and, as expected,[2] the effect diminishes as the energy separation between electronic states decreases.[3] Corresponding deuterium effects on S^1 lifetimes and fluorescence quantum yields are not generally found.[4–6] This is because $S^1 \rightarrow S^0$ radiationless transition in rigid aromatic hydrocarbons is not an important decay process even for the perhydro compounds.[5–7] No deuterium effect on $S^1 \rightarrow T$ intersystem crossing is expected because of small energy gaps between the zero vibrational level of S^1 and lower lying triplet states.

Information concerning radiationless decay paths of electronically excited intermediates is required for a detailed understanding of the mechanisms of photochemical reactions. In this work deuteration has been utilized in evaluating the nature of the excited states and the radiationless decay paths involved in the sensitized and direct *cis–trans* photoisomerization of the stilbenes.

(1) A preliminary account of this work has been published: J. Saltiel, *J. Amer. Chem. Soc.*, **89**, 1036 (1967).

(2) G. W. Robinson and R. Frosch, *J. Chem. Phys.*, 37, 1962 (1962); 38, 1187 (1963).

(3) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).

(4) I B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965.

(5) E. C. Lim and J. D. Laposa, *J. Chem. Phys.*, **41**, 3257 (1964).

(6) J. D. Laposa, E. C. Lim, and R. E. Kellogg, *ibid.*, **42**, 3025 (1965).

(7) A. R. Horrocks, T. Medinger, and F. Wilkinson, *Photochem. Photobiol.*, **6**, 21 (1967), and references cited therein.

Results

Photostationary states were approached from *trans*-perdeuteriostilbene. Generally, irradiation was terminated when no further change in stilbene composition occurred. In many cases, *trans*-perdeuteriostilbene and *cis*- and *trans*-perhydrostilbenes were irradiated in parallel. Perdeuteriostilbene samples were analyzed when the photostationary state of the perhydrostilbenes had been reached from both sides.

Sensitized Photoisomerization. a. Photostationary states for a representative set of triplet excitation donors are shown in Table I. The values for benzophenone are the most reliable, since they were also measured independently in experiments dealing with azulene and stilbene concentration effects (see below). The small discrepancies between values found in this work and those reported in ref 8 are due to different filter systems and methods of analysis (see Experimental Section).

Table I. Stationary States of the Stilbenes with Different Sensitizers

Sensitizer, concn, *M*	% *cis* at photostationary state[a] $C_{14}D_{12}$	% *cis* at photostationary state[a] $C_{14}H_{12}$
Benzophenone, 0.050	58.3 ± 0.2	58.1 ± 0.4 (59.6 ± 0.8)[b]
9,10-Anthraquinone, 0.010	57.2 ± 0.3	(60.0 ± 1.0)
Chrysene, 0.020	75.9 ± 0.4	74.2 ± 1.0
Benzil, 0.050	93.4 ± 0.6	(92.4 ± 0.8)
Fluorenone, 0.050	86.3 ± 0.5	84.6 ± 0.6 (86.2 ± 0.5)
Pyrene, 0.020	91.9 ± 0.4	(91.5 ± 0.2)

[a] A uranium glass filter and a 200-W Hanovia high-pressure mercury lamp were employed. Stilbene concentration was 10^{-2} *M*. Errors represent average deviations for several determinations. [b] Numbers in parentheses are taken from ref 8.

b. **The effect of azulene** on the photostationary state of the benzophenone-sensitized photoisomerization was determined for perdeuteriostilbene at 25 and 60°. In order to improve the accuracy of the data and to make comparison more valid, the effect of azulene on the perhydrostilbenes was redetermined under identical conditions. The data are shown in Table II. Plots of [*trans*]/[*cis*] ratios against azulene concentration are shown in Figure 1.

Table II. Azulene Effects on Benzophenone-Sensitized Photoisomerization[a]

Azulene, $M \times 10^3$	Temp, °C	% *cis* at photostationary state $C_{14}D_{12}$	% *cis* at photostationary state $C_{14}H_{12}$
0	25.0	58.3 ± 0.2	58.2 ± 0.4
0	60.0	60.5 ± 0.4	60.7 ± 0.5
1.00	25.0	35.6 ± 0.2	38.6 ± 0.4
1.00	60.0	31.0 ± 0.3	34.5 ± 0.3
2.00	25.0	25.0 ± 0.2	29.0 ± 0.3
2.00	60.0	20.7 ± 0.2	24.5 ± 0.2

[a] Irradiation as in Table I. Stilbene concentration was 10^{-2} *M* for experiments at 25.0°, and 5×10^{-3} *M* for experiments at 60.0°; benzophenone was 0.05 *M* throughout.

c. **Relative rates of conversion** were determined for the benzophenone-sensitized photoisomerization of *trans*-perdeuterio- and *cis*- and *trans*-perhydrostilbenes for benzene solutions 1.00×10^{-2} *M* in stilbene, 0.05 *M* in benzophenone, and 1.00×10^{-2} *M* in azulene. Irradiations were carried out in parallel in a merry-go-round apparatus at 25°. The results are shown in Table III.

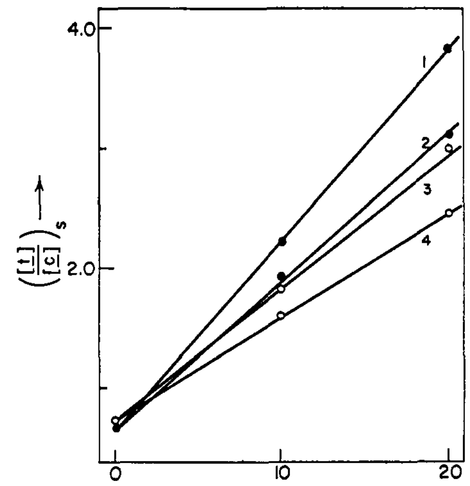

Figure 1. The effect of azulene on photostationary ratios of perhydro- and perdeuteriostilbenes; lines 1 and 3, perdeuteriostilbene; lines 2 and 4, perhydrostilbene; lines 1 and 2, effect at 60°; lines 3 and 4, effect at 25°.

Table III. Relative Rates of Benzophenone-Sensitized Photoisomerization

Stilbene	% isomerization[a]
trans-$C_{14}D_{12}$	2.40 ± 0.04
trans-$C_{14}H_{12}$	2.58 ± 0.05
cis-$C_{14}H_{12}$	4.21 ± 0.07

[a] The values given are corrected for small amount of isomer present in initial solution. The corrections were 0.08, 0.14, and 0.16%, respectively.

d. **The effect of perhydrostilbene concentration on photostationary-state compositions** was determined using benzophenone as the sensitizer. Photostationary states were approached from both sides at 25 and 60°. The concentration of benzophenone was 0.05 *M* throughout. Results for the concentration range 0.001–0.300 *M* are shown in Table IV. In addition two solutions were irradiated in parallel at 25° which were 0.600 *M* total stilbene concentration with initial compositions of 40.0 and 60.0% *cis*. After irradiation these solutions contained 44.4 and 59.7% *cis*, respectively. The extrapolated stationary state being 58.5 ± 1.0% *cis*.

Table IV. Effect of Stilbene Concentration on Photostationary-State Composition of the Benzophenone-Sensitized Isomerization

Total stilbene concn, $M \times 10^3$	% *cis* at photostationary state 25.0°	% *cis* at photostationary state 60.0°
1.00	58.5 ± 0.5	61.2 ± 0.7
5.00	58.6 ± 0.6	60.3 ± 0.6
10.0	58.2 ± 0.4	59.8 ± 0.5
50.0	58.9 ± 0.4	60.2 ± 0.5
100	58.4 ± 0.4	59.1 ± 1.0
300	58.3 ± 0.3	58.3 ± 1.0[a]

[a] This stationary state was obtained by extrapolation using the equation of Lamola and Hammond, see text and ref 27.

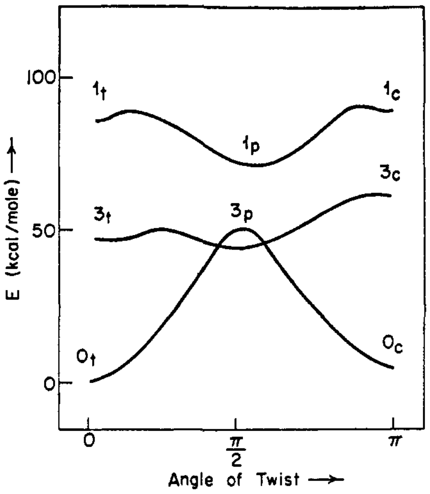

Figure 2. Possible potential energy diagram for the lowest electronic states of the stilbenes.

Direct Photoisomerization. Benzene solutions of *trans*-perdeuterio- and *trans*-perhydrostilbene, 1.00 × 10^{-2} *M*, were irradiated in parallel at 30.0° using 3130-Å light (see Experimental Section). Relative rates of approach of the photostationary states were determined by removing and analyzing tubes periodically until prolonged irradiation led to no further change in stilbene composition. The results are shown in Table V. In addition to analysis by vapor phase chromatography, ultraviolet spectra were recorded for each set of samples. Perhydro- and perdeuteriostilbene samples which had been irradiated for equal time intervals had very similar spectra and in particular the absorbance at 3130 Å was identical for each set.

Table V. Effect of Deuteration on Relative Rate of Approach of the Photostationary State upon Direct Excitation at 3130 Å

% *cis*[a]	
$C_{14}D_{12}$	$C_{14}H_{12}$
6.24 ± 0.07	6.56 ± 0.15
39.9 ± 0.3	40.5 ± 0.2
56.9 ± 0.4	57.9 ± 0.2
88.8 ± 0.2[b]	89.3 ± 0.3[b]

[a] In the order of increasing irradiation times. [b] This is the photostationary-state composition and represents the average composition of two samples irradiated for different lengths of time.

Discussion

Triplet-State Path. Previous work on the sensitized photoisomerization with high triplet energy donors has been adequately accounted for by the following mechanism.[8,9]

$$ {}^0\mathrm{D} \longrightarrow {}^1\mathrm{D} \longrightarrow {}^3\mathrm{D} \qquad (1)$$

$$ {}^3\mathrm{D} + {}^0t \xrightarrow{k_2} {}^0\mathrm{D} + {}^3t \qquad (2)$$

$$ {}^3\mathrm{D} + {}^0c \xrightarrow{k_3} {}^0\mathrm{D} + {}^3c \qquad (3)$$

$$ {}^3c \xrightarrow{k_4} {}^3p \qquad (4)$$

$$ {}^3t \overset{K_5}{\rightleftarrows} {}^3p \qquad (5)$$

$$ {}^3t \xrightarrow{k_6} \alpha{}^0t + (1 - \alpha){}^0c \qquad (6)$$

$$ {}^3p \xrightarrow{k_7} \beta{}^0t + (1 - \beta){}^0c \qquad (7)$$

In the above, D, *t*, *c*, and *p* stand for the excitation donor, *trans*-, *cis*-, and twisted stilbenes (see Figure 2), respectively, the superscripts 0, 1, and 3 indicate S^0, S^1, and T^1 states, and the fractions of *trans* and twisted triplets decaying to *trans* S^0 are given by α and β, respectively.

A twisted (phantom) triplet state, nearly isoenergetic and in equilibrium with the *trans* triplet, was suggested as the key stilbene intermediate.[8] To account for small temperature effects on photostationary states it was assumed that the twisted triplet has higher enthalpy content than the *trans* triplet, and that radiationless decay takes place from both triplets.[8] The slight increase in *cis*/*trans* photostationary ratios at the higher temperature is accounted for since decay from the twisted triplet to *cis* S^0 is expected to be more favorable than *trans* triplet decay to *cis* S^0, *i.e.*, $\alpha > \beta$.[8,10]

Deuterium Effect on Triplet Decay Ratio. Using the steady-state assumption for excited species, eq 8

$$\frac{[t]_s}{[c]_s} = \left(\frac{k_3}{k_2}\right)\left[\frac{\alpha k_6 + \beta k_7 K_5}{(1 - \alpha)k_6 + (1 - \beta)k_7 K_5}\right] \qquad (8)$$

is obtained for the $[t]_s/[c]_s$ ratio at the photostationary state, where subscript s indicates the stationary-state condition. The stationary-state composition is determined by the excitation ratio, k_3/k_2, and the triplet decay ratio, the factor in brackets in eq 8. Triplet excitation donors with $E_T \geq 62$ kcal/mol have been shown to transfer triplet excitation with equal efficiency to either stilbene isomer.[9] For such sensitizers the excitation ratio is unity and the stationary ratio is equal to the triplet decay ratio. Since the stationary state for benzophenone, $E_T = 69$ kcal/mol,[12] is identical for perhydro- and perdeuteriostilbene, Tables I and II, it is concluded that *the triplet decay ratio is not affected by deuteration*. This result, coupled with the assumption that $\alpha > \beta$,[11] is not entirely consistent with the above mechanism for isomerization. Since the S^0–T^1 energy gap is much larger for the *trans* triplet than for the twisted triplet, Figure 2, perdeuteration should decrease k_6 more than k_7 and, consequently, decay of perdeuteriostilbene triplets should favor the *cis* isomer more than does decay of perhydrostilbene triplets. The absence of a deuterium effect leads to the conclusion that *decay from* ${}^3t$ *is negligible for both perhydro- and perdeuteriostilbene*, *i.e.*, $k_6 \ll k_7$. The decay ratio term in eq 8 is thus reduced to $\beta/(1 - \beta)$.

Sensitizers of lower E_T also lead to photostationary compositions which are, within experimental uncertainty, identical for perdeuterated and undeuterated stilbene, Table I. It follows that the excitation ratio, k_3/k_2, is similarly not affected by deuteration. The conclusion also applies in the case of sensitizers, for

---

(8) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(9) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

(10) The best estimate of the barrier to rotation about the central bond in the ground state is 52 ± 2 kcal/mol[11] whereas the energy content of ${}^3t$ is ~48 kcal/mol.[8] It is therefore, reasonable to expect that decay from ${}^3t$ should produce ${}^0t$ exclusively, *i.e.*, $\alpha = 1$.

(11) A. V. Santoro, E. J. Barrett, and H. W. Hoyer, *J. Amer. Chem. Soc.*, **89**, 4545 (1967).

(12) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

which nonvertical excitation of the *cis* isomer directly to ^3p has been postulated.[8,9] The insensitivity of k_3/k_2 to deuteration is not surprising since the electronic energy gaps between initial and final states in the energy-transfer processes are small and no deuterium effect is expected.[2] This result appears to be at variance, however, with preliminary measurements for the system 9,10-phenanthrenequinone–α,α'-stilbene-d_2.[13]

Deuterium Effect on Triplet Lifetime. The effect of azulene on the photostationary-state composition of the stilbenes has been accounted for by including reaction 9 in the mechanism.[8] If, as was concluded above,

$$^3t + {}^0\mathrm{Az} \xrightarrow{k_9} {}^0t + {}^3\mathrm{Az} \qquad (9)$$

$k_6 \ll k_7$, the photostationary law for solutions which include azulene is given by eq 10. Plots of azulene

$$\frac{[t]_s}{[c]_s} = \left(\frac{k_3}{k_2}\right)\left[\frac{\beta}{1-\beta} + \frac{k_9[\mathrm{Az}]}{k_7(1-\beta)}\right] \qquad (10)$$

concentration against $[t]_s/[c]_s$ are linear and slope to intercept ratios give $k_9/k_7\beta$.[8,14] We have used the azulene effect on the benzophenone-sensitized isomerization of the stilbenes in determining the relative lifetimes of perhydro- and perdeuteriostilbene triplets.

The results for the photoisomerization at 25 and 60° are shown in Table II, and the $[t]_s/[c]_s$ ratio is plotted against azulene concentration in Figure 1. Table VI shows ratios of rate constants obtained. Since perdeuteration does not affect relative rates of excitation transfer from several sensitizers to the stilbenes (see above), it seems reasonable to assume that k_9 should be the same for perhydro- and perdeuteriostilbene, *i.e.*, $k_9^{\mathrm{H}} = k_9^{\mathrm{D}}$. Since $\beta^{\mathrm{H}} = \beta^{\mathrm{D}}$ it follows that $k_7^{\mathrm{H}}/k_7^{\mathrm{D}}$ is 1.31 and 1.29 at 25 and 60°, respectively, *i.e., perdeuteration increases the lifetime of stilbene triplets 30%*.[15]

Table VI. Ratios of Rate Constants

Substrate	Temp, °C	$k_9/k_7\beta \times 10^{-2}\ M^{-1\,a}$	β^b
$C_{14}H_{12}$	25	1.20	0.417
	60	1.88	0.395
$C_{14}D_{12}$	25	1.57	0.418
	60	2.42[c]	0.395

[a] The uncertainty in these ratios is estimated to be ±5%. [b] Obtained from photostationary state in the absence of azulene, Tables I, II, and IV. [c] Note that due to computational error this value was given as 2.25 in ref 1.

The inference drawn above from decay ratios that $k_6^{\mathrm{H}} \ll k_7^{\mathrm{H}}$, $k_6^{\mathrm{D}} \ll k_7^{\mathrm{D}}$, would not be valid if isoenergetic intersystem crossing from ^3t could initially concentrate the vibrational excitation at the central bond as has been suggested.[8] If this were the case rotation might occur before vibrational relaxation and k_6, k_7, α, and β might be unaffected by deuterium substitution. The presence of a small but real increase in the lifetime of stilbene triplets upon perdeuteration is strong evidence against this view.[16] The conclusion that radiationless decay from ^3t is unimportant is strengthened, and it seems likely that the lifetime effect has been correctly related to $k_7^{\mathrm{H}}/k_7^{\mathrm{D}}$.

Striking confirmation of the above conclusion is provided by recent observations of triplet–triplet absorption spectra of *trans*-perhydro- and *trans*-perdeuteriostilbene triplets in glassy media at 87–77°K.[17a] A large deuterium isotope effect in triplet decay rates is observed, $k_{\mathrm{H}}/k_{\mathrm{D}} = 5.1$, in the highest viscosity media studied. In these media, the viscosity probably inhibits torsional displacements into nonplanar configurations and decay is mainly from ^3t. A fivefold increase in k_6 is reasonable for a $\mathrm{T}^1 \rightarrow \mathrm{S}^0$ transition for which the energy gap between the initial and final states is about 48 kcal/mol.[18] As the viscosity of the medium is decreased twisting about the central bond becomes easier and decay from twisted triplets competes with decay from ^3t. As expected the lifetime of perhydrostilbene triplets decreases (from 1.8×10^{-2} sec to less than 10^{-4} sec) as the viscosity of the medium is decreased.[17a] Correspondingly, the deuterium isotope effect on the decay rate also decreases.[17a]

The estimate of the lifetime of stilbene triplets in solution, $1/k_7 = 10^{-8}$ sec, depends on the assumption that excitation transfer from ^3t, $E_{\mathrm{T}} \approx 48$ kcal/mol,[8] to azulene, $E_{\mathrm{T}} = 31$–39 kcal/mol,[20] is diffusion controlled.[8] The assumption that the value of k_9 is close to that for a diffusion-controlled process rests on the following observations: (1) azulene quenches benzophenone,[21] $E_{\mathrm{T}} = 69$ kcal/mol, and anthracene,[20,22] $E_{\mathrm{T}} = 42$ kcal/mol, triplets at diffusion-controlled rates; (2) benzanthrone, $E_{\mathrm{T}} \approx 46$ kcal/mol, quenches stilbene triplets as efficiently as azulene.[8] According to the Debye equation for diffusion-controlled rates k_9 is expected to vary as T/η (temperature, °K, viscosity, poise),[23] so that $k_9^{60}/k_9^{25} = 1.71$.[24] This ratio and the results in Table VI give k_7^{60}/k_7^{25} values of 1.15 and 1.17 for perhydro- and perdeuteriostilbene, respectively. Although these ratios are close to unity, the excellent agreement obtained for the two substrates and the fact that estimated error is less than ±10%, lead us to the tentative conclusion that the rate of decay from ^3p is sensitive to the temperature and/or viscosity of the medium.[25]

(13) J. J. Bohning and K. Weiss, *J. Amer. Chem. Soc.*, **88**, 2893 (1966).

(14) Note that in ref 8 values of this ratio were inadvertently labeled $k_9/k_7(1-\beta)$. Using the rate constant notation of that paper, $k_5/(k_{15} + k_{19}K_{12})$ should be changed to $k_5/(k_{14} + k_{19}K_{12})$ in Table V and an analogous substitution should be made in Table IV.

(15) The uncertainty in $k_7^{\mathrm{H}}/k_7^{\mathrm{D}}$ is estimated to be less than ±10%.

(16) Obviously k_6 and/or k_7 is affected by deuteration. If α is taken to be unity[10] and the increase in lifetime is assumed to be due to a decrease in k_6, the decay ratios for perdeuteriostilbene triplets are predicted to be 0.98 and 0.82 at 25 and 60°, respectively, rather than 0.72 and 0.65, as observed.

(17) (a) W. G. Herkstroeter and D. S. McClure, *J. Amer. Chem. Soc.*, **90**, 4522, (1968). We are grateful to these authors for a preprint of their paper.[17b] (b) H. Blume and D. Schulte-Frohlinde, *Tetrahedron Lett.*, 4693 (1967).

(18) In the case of pyrene the S^0–T^1 energy gap is about 49 kcal/mol and the effect of perdeuteration on the triplet lifetime is sixfold.[19]

(19) R. E. Kellogg and R. P. Schwenker, *J. Chem. Phys.*, **41**, 2860 (1964).

(20) A. A. Lamola, W. G. Herkstroeter, J. C. Dalton, and G. S. Hammond, *ibid.*, **42**, 1715 (1965).

(21) G. S. Hammond and P. A. Leermarkers, *J. Phys. Chem.*, **66**, 1148 (1962).

(22) W. Ware, *J. Chem. Phys.*, **37**, 923 (1962).

(23) A. D. Osborne and G. Porter, *Proc. Roy. Soc., Ser. A*, **284**, 9 (1965).

(24) The viscosity of benzene at the two temperatures was obtained by interpolation from data in N. A. Lange, Ed., "Handbook of Chemistry," 9th ed, Handbook Publishers Inc., Sandusky, Ohio, 1956, p 1958.

(25) Preliminary experiments by E. D. Megarity of this laboratory show that the effect must be ascribed at least partially to the change in solvent viscosity.[26]

(26) *Cf.*, however, P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968).

Relative Quantum Yields for the Benzophenone-Sensitized Isomerization. Relative quantum yields for the *trans* → *cis* conversion of *trans*-perhydro- and *trans*-perdeuteriostilbene, and the *cis* → *trans* conversion of *cis*-perhydrostilbene were obtained from the data in Table III. The values in Table III were corrected for the reverse reaction using eq 11, where C is conversion (*trans* → *cis* or *cis* → *trans*) without back-reaction

$$C = 2.303\gamma \log [\gamma/(\gamma - C')] \qquad (11)$$

γ is the conversion at the photostationary state, and C' the conversion measured experimentally.[27] The relative quantum yields obtained are shown in Table VII.

Table VII. Relative Quantum Yields for the Benzophenone-Sensitized Photoisomerization

Substrate	Process	Rel ϕ
$C_{14}H_{12}$	*trans* → *cis*	1.00[a]
	cis → *trans*	1.59
$C_{14}D_{12}$	*trans* → *cis*	0.92

[a] Assumed.

Previous measurements of the quantum yields of sensitized stilbene photoisomerization are anomalous in that the ratio of the quantum yields does not equal the ratio of the concentrations of the isomers at the stationary states as is expected from the mechanism, eq 12.[8,28] The discrepancy was attributed in part

$$\frac{\phi_{c\to t}}{\phi_{t\to c}} = \frac{[t]_s}{[c]_s} \qquad (12)$$

either to quenching by impurities in the *trans*-stilbene samples, *e.g.*, eq 9, or to self-quenching by *trans*-stilbene, eq 13.[8] To avoid previous difficulties,[8] relative

$$^3t + {}^0t \to 2{}^0t \qquad (13)$$

quantum yields were determined in the presence of a known amount of azulene. Under these conditions all bimolecular quenching processes should be unimportant relative to quenching by azulene, eq 9. The results show that in the presence of azulene the system exhibits no anomalies. The observed ratio of $\phi_{c\to t}/\phi_{t\to c} = 1.59$ for perhydrostilbene agrees exactly with the ratio of the concentrations of the isomers at the stationary state, Table II. According to the proposed mechanism eq 14 should also hold. Using the ratios of rate constants in Table VI eq 14 gives $\phi_{c\to t}/\phi_{t\to c} =$

$$\frac{\phi_{c\to t}}{\phi_{t\to c}} = \frac{\beta}{1-\beta}\left(1 + \frac{k_9[\mathrm{Az}]}{\beta k_7}\right) \qquad (14)$$

1.57, in excellent agreement with the observed value.

In the presence of 10^{-2} *M* azulene $\phi_{t\to c}{}^{\mathrm{D}}/\phi_{t\to c}{}^{\mathrm{H}} = 0.92$, Table VII. If it is assumed that the sum of the *trans* → *cis* and the *cis* → *trans* quantum yields is not affected by deuteration, then the ratio of the *trans* → *cis* quantum yields is given by eq 15. Since $\beta^{\mathrm{H}} = \beta^{\mathrm{D}}$, Table VI,

$$\frac{\phi_{t\to c}{}^{\mathrm{D}}}{\phi_{t\to c}{}^{\mathrm{H}}} = \left(1 + \frac{[t]_s{}^{\mathrm{H}}}{[c]_s{}^{\mathrm{H}}}\right)\left(1 + \frac{[t]_s{}^{\mathrm{D}}}{[c]_s{}^{\mathrm{D}}}\right)^{-1} \qquad (15)$$

it can be shown that eq 16 should also hold. Substitution of the appropriate stationary-state ratios, Table II, and rate constant ratios, Table VI, into eq 15 and 16 yields $\phi_{t\to c}{}^{\mathrm{D}}/\phi_{t\to c}{}^{\mathrm{H}}$ ratios of 0.92 and 0.91, respectively, in excellent agreement with the observed value

$$\frac{\phi_{t\to c}{}^{\mathrm{D}}}{\phi_{t\to c}{}^{\mathrm{H}}} = \left(1 + \frac{k_9{}^{\mathrm{H}}}{k_7{}^{\mathrm{H}}}[\mathrm{Az}]\right)\left(1 + \frac{k_9{}^{\mathrm{D}}}{k_7{}^{\mathrm{D}}}[\mathrm{Az}]\right)^{-1} \qquad (16)$$

Thus, the ratio reflects the difference in lifetimes of perhydro- and perdeuteriostilbene triplets and it can be inferred that in the absence of azulene $\phi_{t\to c}{}^{\mathrm{D}} = \phi_{t\to c}{}^{\mathrm{H}}$.

Temperature and Concentration Effects on Stilbene Triplet Decay. There are conflicting reports in the literature concerning the effects of temperature and stilbene concentration on stationary states obtained with benzophenone as triplet excitation donor. Malkin and Fischer report that stationary states are independent of changes in either of these variables,[29] whereas Hammond and coworkers find small concentration effects which were attributed, at least in part, to self-quenching, eq 13, and a small temperature effect which was attributed to a change in *cis*/*trans* decay ratio from stilbene triplets.[8] The present results, Table II, indicate that photostationary mixtures become richer in *cis*-stilbene as the temperature is raised and seem to confirm the presence of a small temperature effect. The effect is the same for perhydro- and perdeuteriostilbene and, since it has been inferred that $k_7 \gg k_6$, it can no longer be assumed that it reflects the difference in free energy between ^3p and ^3t.[8] Although we have attributed the effect to a change in β, Table VI,[30] another possible explanation has been suggested involving the self-quenching process, eq 13.[34] It can readily be seen that if eq 13 were important, changes in the lifetime of ^3p or ^3t should lead to changes in the fraction of triplets which decay by interaction with ground-state *trans*-stilbene. If at higher temperatures stilbene triplets undergo faster unimolecular decay, stationary states would become richer in *cis*-stilbene as is observed.

Inclusion of the self-quenching process in the mechanism predicts that stationary states should depend on the concentration of *trans*-stilbene, eq 17.[8] Although a

$$\frac{[t]_s}{[c]_s} = \frac{k_3}{k_2}\left(\frac{\beta k_7 + k_{13}[t]_s}{(1-\beta)k_7}\right) \qquad (17)$$

small dependence of this type was previously reported[8] the results in Table IV show that stationary states are independent of *trans*-stilbene concentration. Furthermore, the temperature effect is not diminished as the concentration of stilbene is decreased. We conclude that eq 13 does not obtain and that the temperature effect can be, tentatively, attributed to a change in β.

Singlet-State Path. Evidence has been presented which suggests that, contrary to prevalent views, the mechanism of the direct *cis–trans* photoisomerization of the stilbenes bypasses the triplet states.[35] It was

---

[27] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[28] Part of the discrepancy is due to the fact that eq 11 had not been used to correct for back-reaction.

[29] S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).

[30] Temperature effects have been observed in the direct photoisomerization of several olefins by Olson and coworkers. The results have been similarly attributed to changes in decay ratios and have been discussed in terms of excited-state potential energy curves.[31-33]

[31] A. R. Olson, *Trans. Faraday Soc.*, **27**, 69 (1931).

[32] A. R. Olson and F. L. Hudson, *J. Amer. Chem. Soc.*, **55**, 1410 (1932).

[33] A. R. Olson and W. Maroney, *ibid.*, **56**, 1320 (1934).

[34] D. Schulte-Frohlinde and H. Güsten, *Z. Phys. Chem.* (Frankfurt am Main), **45**, 209 (1965).

concluded that the Lewis mechanism in which molecules pass through a condition of free rotation following $S^1 \rightarrow S^0$ conversion[36] obtains. The activated process which, for the *trans* isomer, competes with fluorescence[29,37] was assumed to be $S^1 \rightarrow S^0$ conversion, the photochemically active state being a vibrationally excited ground state.[35]

Potential energy curves for the lowest singlet states of the stilbenes which are consistent with the Lewis mechanism[36] for the direct photoisomerization are shown in Figure 3. An important feature of this mechanism is the large barrier to *cis–trans* isomerization in the S^1 state. Vibrational analysis of low-temperature absorption spectra of the stilbenes in solid matrices seems to provide substantiation for this feature.[37] Large stretching frequencies have been assigned to the central bond of the S^1 state of *trans*- and *cis*-stilbenes, 1599 and 1680 ± 100 cm^{-1}, respectively, which lead to an estimated value of 40 kcal/mol for the barrier to rotation in this state.[37] Such a barrier would account for the observation that excitation of *cis*-stilbene yields no *trans*-stilbene fluorescence.[29,37] The major assumption of the Lewis mechanism is that, upon internal conversion to highly excited vibrational levels of S^0 states, intramolecular concentration of vibrational excitation at the appropriate rotational mode can be so efficient that rotation may occur faster than vibrational relaxation.[8,38]

The Lewis mechanism is described by eq 18–22.[41] The mechanism yields stationary-state relationship 23

$$^0c \xrightarrow{h\nu} {}^1c \tag{18}$$

$$^0t \xrightarrow{h\nu} {}^1t \tag{19}$$

$$^1t \xrightarrow{k_{20}} {}^0t + h\nu \tag{20}$$

$$^1t \xrightarrow{k_{21}} \gamma^0t + (1 - \gamma)^0c \tag{21}$$

$$^1c \xrightarrow{k_{22}} \delta^0t + (1 - \delta)^0c \tag{22}$$

$$\frac{[t]_s}{[c]_s} = \left(\frac{\epsilon_c}{\epsilon_t}\right)\left(\frac{\gamma}{1 - \delta}\right)\left(1 + \frac{k_{20}}{k_{21}}\right) \tag{23}$$

where ϵ_c and ϵ_t are extinction coefficients of *cis*- and *trans*-stilbenes at the exciting wavelength.[35] In eq 23 the term which should be most sensitive to perdeuteration is k_{20}/k_{21}. The value for this ratio can be estimated for perhydrostilbene from the relative quantum yields of fluorescence and isomerization. In nonviscous solvents at 25°, $k_{20}/k_{21} = 0.07$.[43,44] The rate of radioactive decay from ^1t should be the same for perdeuterio- and perhydrostilbene, *i.e.*, $k_{20}{}^{\text{H}} = k_{20}{}^{\text{D}}$, since the $S^0 \rightarrow S^1$ absorption spectrum of *trans*-stilbene is essentially unaffected by perdeuteration (see Experimental Section). The $S^0 \rightarrow S^1$ energy gap for near-planar *trans*-stilbene should be given approximately by the 0–0 band in the absorption spectrum, ~85 kcal/mol. It follows that for isoenergetic radiationless $S^1 \rightarrow S^0$ internal conversion vibrational overlap would involve large numbers of quanta and, therefore, carbon–hydrogen vibrations should be most important.[2] A large deuterium isotope effect on k_{21} is expected, $k_{21}{}^{\text{H}} \gg k_{21}{}^{\text{D}}$, and as a consequence perdeuteration should lead to photostationary states which are much richer in *trans*-stilbene.

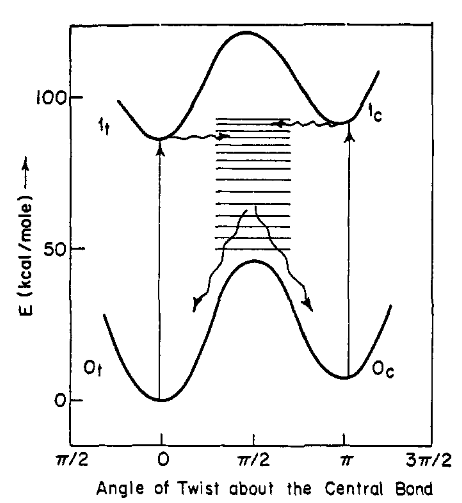

Figure 3. Potential energy curves for the lowest singlet states of the stilbenes which are consistent with the Lewis mechanism.

The results in Table V show that benzene solutions of *trans*-perdeuterio- and *trans*-perhydrostilbene, irradiated in parallel, approach photostationary states of the same composition at rates which are identical within experimental uncertainty. *Deuterium substitution does not alter cis → trans and trans → cis quantum yields.*[45] We conclude that the process which competes with *trans*-stilbene fluorescence and leads to isomerization cannot be $S^1 \rightarrow S^0$ radiationless conversion and that *the Lewis mechanism for the isomerization does not obtain.*

Since the energy gap between S^1 and available triplet states is very small[47] no deuterium effect on intersystem crossing is expected. The Förster mechanism[8,46,48] in which the stilbene isomers lose their identity after $S^1 \rightarrow T$ intersystem crossing accounts for the absence of a deuterium effect on the direct photoisomerization.[49] However, appreciable involvement of triplet states is rendered highly improbable by the absence of the expected azulene effect on photostationary states produced by direct irradiation.[35] We, therefore, propose a mechanism involving rotation of the central bond in S^1 to a common twisted singlet state, ^1p (Fig-

---

(35) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *J. Amer. Chem. Soc.*, **88**, 2386 (1966).

(36) G. N. Lewis, T. T. Magel, and D. Lipkin, *ibid.*, **62**, 2973 (1940).

(37) H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(38) Although this view has been criticized on theoretical grounds,[39] there is evidence that the mechanism of the *cis–trans* isomerization of nitrous acid which is caused by absorption of infrared light involves a highly efficient intramolecular transfer of energy between vibrational modes.[40]

(39) G. Zimmerman, L. Chow, and V. Paik, *J. Amer. Chem. Soc.*, **80**, 3528 (1958).

(40) R. T. Hall and G. C. Pimentel, *J. Chem. Phys.*, **38**, 1889 (1963).

(41) The reversible formation of a small amount of dihydrophenanthrene[42] is neglected because the filter system used in our experiments minimized its steady-state concentration.

(42) K. A. Muszkat and E. Fischer, *J. Chem. Soc.*, *B*, 662 (1967).

(43) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, **90**, 12 (1968).

(44) J. Saltiel, O. C. Zafiriou, E. D. Megarity, and A. A. Lamola, *ibid.*, **90**, 4759 (1968).

(45) These results have been confirmed and similar results obtained in a wide temperature range, down to −180°, both for $\phi_{t\rightarrow c}$ and ϕ_F.[46]

(46) K. A. Muszkat, D. Gegiou, and E. Fischer, *J. Amer. Chem. Soc.*, **89**, 4814 (1967).

(47) D. L. Beveridge and H. H. Jaffé, *ibid.*, **87**, 5340 (1965).

(48) Th. Förster, *Z. Electrochem.*, **56**, 716 (1952).

(49) In the preliminary communication of this work,[1] the absence of a deuterium effect was not suggested as evidence againt the triplet mechanism as indicated in ref 46.

ure 2, eq 24–26). A small activation energy, ~2

$$^1t \longrightarrow {}^1p \tag{24}$$

$$^1c \longrightarrow {}^1p \tag{25}$$

$$^1p \longrightarrow \mu^0t + (1 - \mu)^0c \tag{26}$$

kcal/mol, for $^1t \rightarrow {}^1p$ rotation would account for the temperature effects on ϕ_F and $\phi_{t\rightarrow c}$.[29,37,43,50] The absence of *trans*-stilbene fluorescence from *cis*-stilbene is accounted for if the energy of ^1p is low relative to the energy of ^1t.

SCF molecular orbital calculations of potential energy curves for ground and excited states of the stilbenes have also led to the conclusion that following direct excitation the two isomers first lose their identity by twisting about the central bond in the S^1 state.[51] The predictions that twisted configurations represent minima in energy for T^1 and S^1 agree with our conclusions. There are, however, significant discrepancies between the theoretical curves and experimental findings.[52]

Since *cis*/*trans* decay ratios from stilbene excited states involved in the direct and sensitized photoisomerizations are identical, it has been suggested that there is a crossing of the paths of the two reactions.[8] We suggest that if there is such crossing, it arises in vibrationally excited S^0 states.[54] Since the geometries of ^1p and ^3p should be similar, crossing of their decay paths in the ground state seems likely.

The large stretching frequencies assigned to the central bond of the stilbenes[37] are not consistent with the proposed mechanism which involves facile rotation to a common singlet state, ^1p. These assignments, however, were based on low-temperature absorption spectra in solid matrices and their relevance to stilbene molecules under isomerization conditions is questionable. Room temperature spectra of *trans*-stilbene solutions show a fairly well-defined vibrational progression.[37] The gap between absorption maxima is about 1400 cm^{-1}.[37] If these vibrational bands are related to the stretching motion of the central bond, a considerable reduction in the strength of this bond under the conditions of the photochemical measurements is indicated.

Experimental Section

Materials. Substrates. *trans*-Perdeuteriostilbene was synthesized from *cis*-perhydrostilbene, 2 g, by four exchanges with heavy water, 10 ml per exchange, over reduced platinum oxide, 150 mg, at about 200° for 1 week. The final reduction of the platinum oxide was with deuterium gas. Exchanges were carried out in sealed heavy-walled glass tubes. Accompanying reactions were *cis* → *trans* isomerization and disproportionation to bibenzyl and phenanthrene (products identified only by glpc retention time). Since exchange of the α-hydrogens of the *trans* isomer was very slow,[55] following each exchange stilbene was photoisomerized to the *cis* isomer using pyrene as the sensitizer. Pyrene was separated from *cis*-stilbene by chromatography on alumina. After the fourth exchange *cis*-stilbene and bibenzyl were separated from *trans*-stilbene, phenanthrene, and pyrene by alumina chromatography. The *cis*-stilbene and bibenzyl mixture was dissolved in benzene containing a few crystals of iodine. The solution was refluxed for 1 hr on a hot plate. The treatment isomerized *cis*-stilbene to the *trans* isomer[56] which was separated from bibenzyl by chromatography on alumina. The over-all yield after recrystallization from ethanol was 15%, hot stage, mp 125.5–126.0° (uncor). Mass spectroscopic analysis showed the *trans*-perdeuteriostilbene to be 80% d_{12}, 14% d_{11}, 4.3% d_{10}, and 1% d_9.[57] The infrared spectrum in carbon tetrachloride showed the following strong maxima (μ): 4.39, 6.39, 7.18, 7.56, 11.84, 12.13, and 14.05. The ultraviolet spectrum in benzene was very similar to that of *trans*-perhydrostilbene. It showed a shoulder at 3231 Å (ϵ 1.65 × 10^4) and maxima at 3100 Å (ϵ 2.71 × 10^4) and 2976 Å (ϵ 2.70 × 10^4). At 3130 Å the ratio of extinction coefficients of *trans*-perhydro- to *trans*-perdeuteriostilbene is 1.03. The infrared spectrum of *cis*-perdeuteriostilbene was also recorded in carbon tetrachloride. It was much more complex than the spectrum of the *trans* isomer and showed the following strong maxima (μ): 4.38, 6.40, 7.20, 7.33, 7.56, 8.12, 9.74, 11.81, 12.16, and 14.77.

trans-Perhydrostilbene was K & K scintillation grade and was recrystallized from ethanol and sublimed before use. The *cis* isomer was prepared by photoisomerization of *trans*-stilbene and was purified by chromatography on alumina and distillation under reduced pressure.

Sensitizers. Pyrene was K & K reagent grade. It was chromatographed twice on alumina, pentane eluent, and recrystallized from ethanol. Fluorenone, K & K reagent grade, was chromatographed on alumina, benzene eluent, and recrystallized from cyclohexane. Benzil, Baker reagent grade, was chromatographed on alumina, benzene, eluent, and recrystallized from cyclohexane. Chrysene, Baker reagent grade, was chromatographed on alumina, 20% benzene in pentane followed by pure benzene eluent, and was recrystallized from benzene. 9,10-Anthraquinone, Baker reagent grade, was recrystallized from glacial acetic acid. Benzophenone, Fisher reagent grade, was sublimed under reduced pressure.

Quencher. Azulene was Baker reagent grade and was sublimed before use.

Solvent. Benzene, Baker reagent grade, was purified by a procedure recommended by Dr. R. Steinmetz.[9] Chloranil was dissolved in the benzene, 2 g/l., and the solution irradiated for a week through Pyrex glass with a Hanovia 450-W, high-pressure mercury lamp. The chloranil was replenished daily. The disappearance of impurities was followed by glpc. The solution was then passed through alumina. Benzene purified in this way was then distilled through a 4-ft column packed with Heli-Pak 2917, Podbielniak Co. (estimated efficiency, 100 plates), and a middle cut retained for use.

Analytical Procedures. Ketone sensitizers were separated from the stilbenes by chromatography on alumina. Stilbene mixtures were analyzed by glpc (5 ft × 1/8 in. column of 5% SE-30 on Chromosorb W) using Aerograph Model 600 Hy-Fi gas chromatographs. Direct irradiation samples were also analyzed by ultraviolet absorption using a Cary 14 spectrophotometer. The optical density at 3130 Å was identical for perdeuterio- and perhydrostilbene samples.

Irradiation Procedure. Irradiations were carried out in a quantum yield merry-go-round apparatus.[27] A 200-W, Hanovia (654A) high-pressure mercury lamp was used throughout. For sensitized isomerizations a Uranium glass tube which transmitted light of wavelengths longer than 3300 Å was used to filter the light source. In experiments in which the stilbene concentration was varied Corning Filter 7-37 was also used (transmitted radiation mainly 3660 Å). For direct irradiation the group of mercury lines at 3130 Å was isolated with a filter solution of potassium dichromate, 0.004 *M*, and potassium carbonate, 0.011 *M*. This solution transmits light of wavelengths longer than 4300 Å, and its use leads to very low steady-state concentrations of dihydrophenanthrene (λ_{max} 4550 Å).[42] Samples were placed in 13-mm Pyrex test tubes which had been sealed to 10/30 Pyrex standard taper joints and were provided with a constriction for sealing. They were degassed by three to four freeze–degas–thaw cycles and sealed under vacuum (0.2 μ pressure or less).

Acknowledgment. This research was supported in part by a grant from the Research Corporation and Grant GP-5159 from the National Science Foundation.

---

(50) Preliminary observations lead us to suggest that the viscosity dependence of $^1t \rightarrow {}^1p$ rotation accounts for the recent observations of Fischer and coworkers.[44]

(51) P. Borrell and H. H. Greenwood, *Proc. Roy. Soc., Ser. A*, **298**, 453 (1967).

(52) A slightly twisted ^0c is predicted to be more stable than ^0t, and no energy minimum is predicted close to the *trans* planar geometry of the triplet state (^3t).[53]

(53) *Cf.*, however, unpublished calculations by C. H. Ting and D. S. McClure mentioned in ref 17a.

(54) This possibility was emphasized in ref 8.

(55) J. L. Garnett and W. A. Sollich-Baumgartner, *J. Phys. Chem.*, **69**, 3526 (1965).

(56) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964).

(57) We thank Mr. David Weiss and Professor N. J. Turro for the mass spectroscopic data.