Ultraviolet Spectral Measurements. Absorbance measurements were made on Cary recording spectrophotometers, Models 14 and 16.

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Deuterium Isotope Effects on the $^1T \rightarrow {}^0S$ Radiationless Decay Rate in Stilbene[1a]

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Abstract: The effect of azulene on stationary states of the benzophenone-sensitized photoisomerization of vinyl-substituted stilbene-d_2 and aromatic-substituted stilbene-d_{10} has been determined in benzene solutions at 298°K. Comparison with previous observations concerning stilbene-d_0 and stilbene-d_{12} leads to the conclusion that deuteration of the vinyl positions increases the effective lifetime of stilbene triplets by 30%, while ring deuteration has no effect. The lifetime increase is tentatively attributed to a change in the radiationless decay rate of twisted stilbene triplets. The positional dependence of the deuterium isotope effect for radiationless decay from transoid triplets has been determined by flash kinetic spectrophotometry in 3-methylpentane and isopentane–3-methylpentane glasses at 77°K and in glycerol at 195°K. Once again deuteration at the vinyl positions has the most substantial effect, but in this case some lengthening of the lifetime is also observed upon ring deuteration. This positional dependence of the deuterium isotope effect is in good agreement with previous measurements in EPA at 77°K. The experimental observations are discussed in terms of a previously proposed potential energy curve for twisting about the central bond in the lowest stilbene triplet state, and possible implications of the positional dependence of the deuterium isotope effects are considered in relation to existing theories of radiationless intersystem crossing.

The observation that longer triplet lifetimes result upon perdeuteration of aromatic hydrocarbons has played an important role in the development of theories of radiationless transitions.[2–4] More recently, measurements on partially deuterated hydrocarbons have shown that the effectiveness of deuterium substitution in decreasing the rate of radiationless $^1T \rightarrow {}^0S$ intersystem system crossing depends upon the position of substitution.[5–9] This positional dependence of the deuterium isotope effect has been proposed to provide a diagnostic tool in distinguishing between various mechanisms of intersystem crossing.[10,11]

The present paper describes the positional dependence of deuterium substitution on the decay characteristics of stilbene triplets. It complements previous observations concerning the effect of perdeuteration on the lifetime of stilbene triplets in solution at room temperature,[12] and in rigid media at low temperatures,[13] and parallels, in part, recent observations on partially deuterated stilbenes.[9]

Results

Steady-State Observations in Solution. The effect of azulene on photostationary states for the benzophenone sensitized photoisomerization of vinyl-substituted stilbene-d_2 and ring-substituted stilbene-d_{10} in benzene was determined at 25°.[14] As a check of previous observations[12] and in order to extend the azulene concentration range, additional measurements were made using stilbene-d_0. A few, less refined and probably less accurate measurements were also made at 60°. Photo-

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

Azulene, $M \times 10^2$	Temp, °C	% cis at photostationary state: Stilbene-d_0[b,c]	Stilbene-d_2[b,c]	Stilbene-d_{10}[c]
0	25 ± 1	61.5 ± 0.3 (58.5 ± 0.3)	61.4 ± 0.4 (59.6 ± 0.2)	58.7 ± 0.1
0.75		(42.0 ± 0.1)	37.9 ± 0.1	42.4 ± 0.2
1.50		(32.6 ± 0.4)	29.8 ± 0.2	33.6 ± 0.3
2.25		28.2 ± 0.1 (27.3 ± 0.3)	23.3 ± 0.2	27.8 ± 0.2
3.00		23.3 ± 0.1 (23.3 ± 0.2)	18.9 ± 0.2	23.9 ± 0.2
0	60 ± 1	61.6 ± 0.1		
0.75		39.0 ± 0.3		
1.50		29.6 ± 0.2	26.1 ± 0.1	30.9 ± 0.3[b]
2.25		22.9 ± 0.1		
3.00		19.4 ± 0.2	15.1 ± 0.1	

[a] Ranges represent average deviations for several glpc determinations. [b] Extreme care was taken to prevent loss of cis isomer during work-up. [c] Values in parentheses and values for stilbene-d_{10} were obtained using the usual work-up procedure; see ref 12 and Experimental Section.

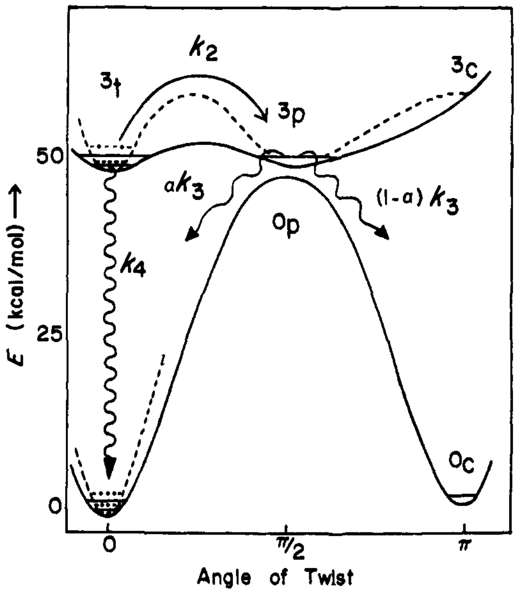

Figure 1. Possible potential energy curves for the ^{0}S and ^{1}T states of the stilbenes. Dashed lines show the effect of increased medium rigidity.

stationary states were approached from the trans isomer only, and irradiations were terminated when no further change in stilbene composition occurred. A uranium glass filter and a 200-W Hanovia high-pressure mercury lamp were employed. Stilbene and benzophenone concentrations were 0.01 and 0.05 M, respectively. The data are shown in Table I.

Flash Kinetic Observations in Rigid Media. Triplet–triplet absorption decay rate constants for *trans*-stilbene and deuterated derivatives were recorded at low temperature in several rigid media. The decay was first order in all cases and the rate constants are shown in Table II, together with selected previously published vaules.[9,13,15]

Table II. First-Order Rate Constants for ^{1}T – ^{0}S Decay in *trans*-Stilbene and Deuterated Derivatives in Rigid Media[a]

Stilbene	k, sec^{-1}: IPMP, 77°K	MP, 77°K	EPA, 77°K	G, 195°K
d_0	190,[b] 230,[c] 190	56,[b] 56	45.5[d]	110,[c] 77
d_2	150	31	18.9[d]	45, 45
d_{10}	180	51	38.5[d]	78,[c] 72
d_{12}	88[b]	11[b]	10.9[d]	21

[a] Abbreviations for media: IPMP, 6:1 by volume isopentane–3-methylpentane; MP, 3-methylpentane; EPA, a 5:5:2 mixture of diethyl ether, isopentane, and ethanol; G, glycerol. [b] Reference 13. [c] May reflect incomplete cooling of the glassy medium. [d] Reference 9.

Discussion

$$^3\text{c} \xrightarrow{k_1} {}^3\text{p} \tag{1}$$

$$^3\text{t} \underset{}{\overset{K_2}{\rightleftarrows}} {}^3\text{p} \tag{2}$$

$$^3\text{p} \xrightarrow{k_3} \alpha{}^0\text{t} + (1-\alpha){}^0\text{c} \tag{3}$$

Observations concerning the cis–trans photoisomerization of the stilbenes sensitized by benzophenone and other high triplet excitation donors are adequately accounted for by a mechanism involving formation of stilbene triplets which decay as shown in eq 1–3, where ^{3}t, ^{3}c, and ^{3}p represent transoid, cisoid, and twisted conformations of stilbene triplets, respectively, and α is the fraction of twisted triplets decaying to the trans ground state, ^{0}t.[12,16–18] The proposed potential energy curves for twisting about the central bond in the lowest triplet state and in the ground state shown in Figure 1 represent a more explicit formulation of this mechanism.[19] These curves provide the model for the interpretation of deuterium isotope effects on triplet decay rates.

Stilbene Triplet Decay in Solution. Since no reversible excitation transfer could be detected from ^{3}c to donors whose triplet energy is in the 51–57-kcal/mol range,[16] it has been inferred that ^{3}c is extremely short-lived and represents a higher vibrational level of ^{3}p. Reversible excitation transfer from ^{3}t has been shown to be important for donors whose triplet excitation energy is less than or equal to 49 kcal/mol, the energy of the lowest spectroscopically observed ^{1}T ← ^{0}S transition[20–23] of *trans*-stilbene. This fact supports the con-

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Table III. Ratios of Rate Constants at 25° [a]

Stilbene-d_n n	$10^{-2}k_5/K_2k_3\alpha$, M^{-1}	α	$10^8(K_2k_3)^{-1}$,[b] sec^{-1}	$k_3^{d_0}/k_3^{d_n}$
0	1.2_0,[c] 1.1_6,[d] 1.4_3[e]	0.42,[c] 0.42,[d] 0.38[e]	1.0_0,[c] 0.99,[d] 1.0_9[e]	1.00
2	1.8_4	0.39	1.4_5	1.33
10	1.1_4	0.42	0.96	0.98
12	1.5_7	0.42	1.3_1	1.31

[a] In each of the first three columns the entry for each deuterated stilbene should be compared with the entry for stilbene-d_0 immediately above it. The differences are due to different sample concentration procedures prior to glpc analysis (see Experimental Section). [b] Based on $k_5 = 5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. [c] Reference 12. [d] Work-up procedure 1. [e] Work-up procedure 2.

clusions, reached independently from a study of the dependence of triplet excitation transfer rate constants to *trans*-stilbene upon the energy of the donor,[16,17] that the 0–0 band of the $^0t \rightarrow {}^3t$ transition must be close to 49 kcal/mol, and that the energy of the planar configuration must be close to the minimum possible energy for the stilbene triplet. Perdeuteration does not affect the cis/trans decay ratio of stilbene triplets in solution suggesting that $^1T \rightarrow {}^0S$ decay directly from ^3t to ^0t, eq 4,

$$^3t \longrightarrow {}^0t \qquad (4)$$

does not compete with decay from ^3p in either stilbene-d_{12} or -d_0.[12]

Transfer of triplet excitation from ^3t occurs also to compounds whose triplet excitation energies are so low that they do not function as sensitizers for the cis–trans isomerization of the stilbenes. Azulene, E_T = 30 kcal/mol,[24] has been the most thoroughly studied acceptor of this type.[16,18] Its effects on trans/cis photostationary ratios and on initial isomerization quantum yields for the sensitized isomerization of the stilbenes are quantitatively accounted for by including eq 5 in the mechanism, assuming no azulene interference with the $^3c \rightarrow {}^3p$ conversion and complete equilibration between ^3p and ^3t.[18] Photostationary trans/cis ratios are predicted to be linearly dependent upon the azulene concentration with slope/intercept ratios giving $k_5/K_2k_3\alpha$.[16,18] Several experimental observations, the most convincing of which is a large solvent viscosity effect on $k_5/K_2k_3\alpha$, suggest that the value of k_5 in benzene is very nearly that for a diffusion controlled process.[18] Assuming $k_5 = 5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ at 25°[17] and using the known value of $\alpha = 0.41$[16,18] allow the calculation of $(K_2k_3)^{-1}$, the effective lifetime of stilbene triplets.

$$^3t + {}^0Az \xrightarrow{k_5} {}^0t + {}^3Az \qquad (5)$$

The benzophenone sensitized cis–trans photoisomerization of stilbene-d_{12} has been shown to be more sensitive to azulene than the sensitized photoisomerization of stilbene-d_0 at both 25 and 60°.[12] We have now studied the effects of azulene on the benzophenone sensitized photoisomerization of stilbene-d_{10} and stilbene-d_2.[14] The [t]/[c] photostationary ratios obtained at 25° in this and the previous work[12] are plotted against azulene concentration in Figure 2. It can be seen that within experimental uncertainty the points for stilbene-d_0 and -d_{10} fall on a single straight line while the points for stilbene-d_2 and -d_{12} fall along a second straight line. The fact that these two lines have very nearly the same intercept demonstrates the absence of a deuterium effect on the decay fraction α.[12,25] Since perdeuteration does not affect relative rates of excitation transfer from several triplet energy donors to the stilbenes,[12,25] it seems likely that k_5, the rate constant for exothermic transfer of triplet excitation from ^3t to azulene, will also be independent of deuterium substitution. Thus, the difference in the slopes of the lines in Figure 2 can be attributed to changes in the effective lifetime of stilbene triplets $(K_2k_3)^{-1}$. Since no deuterium isotope effect on the equilibrium constant K_2 is expected, deuterium isotope effects on effective lifetimes reflect changes in the rate constant for radiationless decay of twisted stilbene triplets, k_3. The observations at 25° are interpreted in this way in Table III. Clearly, the 30% increase in stilbene triplet lifetime observed for perdeuteriostilbene[12] is due exclusively to deuterium substitution at the olefinic positions. Deuteration at the aromatic positions does not affect the decay rate of ^3p.[26]

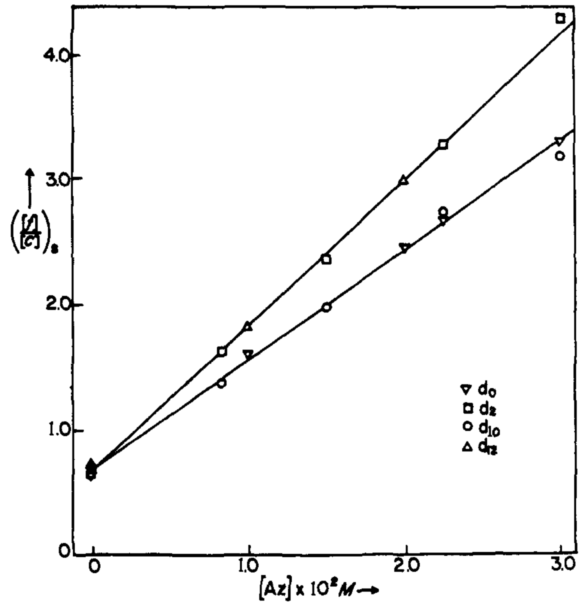

Figure 2. The azulene effect on the benzophenone sensitized photoisomerization of the stilbenes-d_0, -d_2, -d_{10}, and -d_{12} at 25°.

The observations at 60° can be readily fitted to the model in Figure 1. The increased sensitivity of [t]/[c] photostationary ratios to azulene is ~15% smaller than predicted for the increase in the diffusion-controlled

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[24] P. M. Rentzepis, *Chem. Phys. Lett.*, 3, 717 (1969).

[25] *Cf.* also R. A. Caldwell, G. W. Sovocool, and R. J. Peresie, *J. Amer. Chem. Soc.*, 93, 779 (1971), for similar observations in the case of β-methylstyrene.

[26] Actually, the data suggest a slight acceleration of the decay rate of ^3p upon deuteration of the aromatic positions, but the difference is smaller than the expected experimental uncertainty.

rate constant k_5 using the Debye equation,[11] suggesting a somewhat smaller effective lifetime for stilbene triplets at 60°. It is tentatively assumed that this lifetime change is due to the temperature dependence of K_2 and reflects a slightly higher free energy for ^{3}p than for ^{3}t. Since the decay ratio from ^{3}p is assumed to be temperature independent,[27,28] the observation that the ratio of effective triplet lifetimes for stilbene-d_0 and -d_{10} at 60° is 1.29[12] suggests that the effect of perdeuteration on k_3 is also temperature independent and is consistent with the assumption that deuterium substitution does not affect K_2. The limited observations in Table I for stilbene-d_2 and -d_{10} at 60° demonstrate that, at this temperature also, only deuteration of the olefinic positions brings about a lengthening of the stilbene triplet lifetime.

Stilbene Triplet Decay in Rigid Media. Since no phosphorescence from stilbene triplets has been observed, the first-order decay rate constants, k, in Table II can be represented as the sum of the rate constants for all radiationless processes leading to decay of transoid triplets, eq 6.[29] The potential energy barrier for

$$k = k_2 + k_4 \tag{6}$$

twisting from ^{3}t → ^{3}p in Figure 1 was chosen arbitrarily. The thermal barrier, E_t, must be at least as large as the energy difference between ^{3}t and ^{3}p, and by analogy with the corresponding conversion in the ^{1}S state, ^{1}t → ^{1}p, an additional medium dependent barrier, E_v, is expected in the temperature region for which solvent relaxation rates are slower than the rate of the twisting process in the absence of medium restrictions.[31-33] For example, the E_v value for the ^{3}t → ^{3}p conversion at −78° in glycerol can be expected to be considerably larger than 6.2 kcal/mol, the E_v value for the ^{1}t → ^{1}p conversion at 20°.[33] Since perdeuteration alters neither the trans → cis quantum yield for direct stilbene excitation nor the fluorescence quantum yield of *trans*-stilbene down to −180°,[12,34] deuterium substitution does not affect the twisting process in ^{1}S. It is expected, therefore, that k_2 should be likewise insensitive to deuterium substitution. The relatively large deuterium isotope effects on stilbene triplet decay rate constants reported in Table II must therefore be associated with changes in k_4, the rate constant for radiationless decay of ^{3}t to ^{0}t. The largest deuterium isotope effects in the triplet decay rate constants, $k^{d_0}/k^{d_{12}} \sim 5$, are observed in the most rigid media employed at 77°K, MP and EPA. In these rigid media torsional displacements into nonplanar configurations are expected to be severely inhibited and decay should be mainly according to eq 4 (see dotted lines in Figure 1). The fivefold decrease in k upon perdeuteration is comparable to the sixfold change in triplet decay rate observed in pyrene for which the ^{1}T–^{0}S energy gap is also ~49 kcal/mol.[35] The decay rate constants obtained for stilbene-d_2 and stilbene-d_{10} in the media we studied reveal the trend which was previously observed in EPA[9] and support the conclusion that olefinic C–H vibrations are much more effective in promoting the ^{3}t → ^{0}t conversion than are aromatic C–H vibrations.[9] The small but measurable increase in the lifetime of ^{3}t caused by deuteration of the aromatic positions further delineates the low temperature observations from those obtained in solution, and is consistent with the notion that decay in solution is from a different stilbene conformation, namely ^{3}p.

A more quantitative evaluation of the positional dependence of the deuterium isotope effect can be attempted using the procedure employed by Watts and Strickler[7] in the case of naphthalene.[36] The observed decay rate constants are expressed in terms of sets of simultaneous equations of form 7, where $k^{d_{12}}$ is the rate

$$k = k^{d_{12}} + n_{\mathrm{O}}k_4{}^{\mathrm{O}} + n_{\mathrm{A}}k_4{}^{\mathrm{A}} \tag{7}$$

constant for stilbene-d_{12} triplet decay, eq 8, n_{O} and n_{A}

$$k^{d_{12}} = k_2 + k_4{}^{d_{12}} \tag{8}$$

are the number of olefinic and aromatic protons, respectively, and $k_4{}^{\mathrm{O}}$ and $k_4{}^{\mathrm{A}}$ represent the change in the nonradiative rate constant when a proton is substituted for a deuteron in an olefinic or an aromatic position, respectively. In eq 8 $k_4{}^{d_{12}}$ is the nonradiative rate constant for stilbene-d_{12}. The radiative rate constant is assumed to be negligible throughout.[29] Calculated values for $k_4{}^{\mathrm{O}}$ and $k_4{}^{\mathrm{A}}$ and their ratios are shown in Table IV. It can be seen that on the average olefinic C–H vibrations are ten times more effective in promoting radiationless ^{3}t → ^{0}t intersystem crossing than are aromatic C–H vibrations. Interestingly, the relative contribution of the aromatic C–H vibrations in this process seems to increase as the viscosity of the medium is decreased.

Table IV. Positional Dependence of Deuterium Substitution in Stilbene Triplet Decay in Rigid Media[a]

Medium (°K)	Log η,[a] P	$k_4{}^{\mathrm{O}}$, sec^{-1}	$k_4{}^{\mathrm{A}}$, sec^{-1}	$k_4{}^{\mathrm{m}}$, sec^{-1}	$k_4{}^{\mathrm{O}}/k_4{}^{\mathrm{A}}$	$k_4{}^{\mathrm{O}}/k_4{}^{\mathrm{m}}$
IPMP (77)[b]	6.8	46	6.2	15.5	7.4	3.0
G (195)	10	25.5	2.4	6	11	4.3
MP (77)[b]	12.5	20	2.0	5	10	4.0
EPA (77)[9,b]		13.8	0.8	2	17.2	6.9

[a] IPMP and MP viscosities from A. C. Ling and J. E. Willard, *J. Phys. Chem.*, **72**, 1918 (1968); G viscosity extrapolated from data given by T. A. Litovitz, *J. Chem. Phys.*, **20**, 1088 (1952). [b] Partial rate constant changes calculated from stilbene-d_0, -d_{10}, and -d_{12} data in Table II.

In the above treatment all aromatic positions are assumed to be equivalent. The results of Heinrich, *et al.*,[9] however, suggest that, at least in EPA, the only aromatic C–H vibrations which are effective in pro-

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(27) The temperature dependence of the effective stilbene triplet lifetime over a wide temperature region is being investigated by A. D. Rousseau of this laboratory. Preliminary observations support the above interpretation.

(28) The assignment of the temperature dependence in ref 12 to changes in k_3 was due to the inadvertent omission of K_2 from the equation describing the azulene effect (compare eq 10 in ref 12 with eq 8 in ref 18).

(29) Radiative rate constants from aromatic hydrocarbon triplets are generally expected to be much smaller than the first-order rate constants in Table II.[30]

(30) B. R. Henry and W. Siebrand, *J. Chem. Phys.*, **51**, 2396 (1969), and references cited therein.

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

(32) S. Sharafy and K. A. Muszkat, *ibid.*, **93**, 4119 (1971).

(33) J. Saltiel and J. T. D'Agostino, *ibid.*, **94**, 6445 (1972).

(34) K. A. Muszkat, D. Gegiou, and E. Fischer, *ibid.*, **89**, 4814 (1967).

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

(36) See ref 9 for a similar procedure applied to the stilbene data in EPA.

moting the ^{3}t → ^{0}t radiationless transition are those at the meta positions. Specifically, *trans-p,p'*-stilbene-d_2 and *trans-o,o'*-stilbene-d_2 triplets have exactly the same decay rate constant in EPA as do *trans*-stilbene-d_0 triplets. The observed decrease in the decay rate constant of *trans*-stilbene-d_5 in which all the positions of one of the rings are deuterated could, therefore, be due to substitution at the two meta positions. An alternative tentative interpretation of the data was therefore carried out by replacing the $n_A k_4^A$ term in eq 7 with $n_m k_4^m$, where n_m is the number of meta protons and k_4^m represents the change in the nonradiative rate constant when a proton is substituted by a deuteron at a meta aromatic position. The resulting k_4^m values are listed in Table IV.

The variation of decay rate constants in Table II shows that most and perhaps all the observed changes are associated with changes in medium viscosity rather than with temperature changes (compare, especially, the observations in G at 195°K with those in IPMP and MP at 77°K). They further suggest strongly that both k_2 and k_4 are sensitive to medium rigidity. According to eq 7 the difference between k^{d_0} and $k^{d_{12}}$ in a particular medium provides a good measure of k_4 for stilbene-d_0 triplets in that medium. The data in Table II show that at 77°K $k^{d_0} - k^{d_{12}}$, and therefore k_4, increases from 35.6 sec^{-1} in EPA to 122 ± 20 sec^{-1} in IPMP. Comparison of eq 7 and 8 shows that of the stilbenes studied the decay rate constants for stilbene-d_{12} triplets, $k^{d_{12}}$, should be most sensitive to changes in k_2. In agreement with this expectation, the change in $k^{d_{12}}$ in going from IPMP to MP at 77°K is eightfold whereas the corresponding change in k^{d_0} is only fourfold. It is likely, therefore, that k_2 represents a significant portion of $k^{d_{12}}$.[37]

A qualitative explanation of the effect of increased medium viscosity on k_2 and k_4 is suggested in Figure 1. The change in k_2 is attributed to the increased potential energy barrier to twisting about the central bond in the triplet state (dotted lines). Associated with this increased potential energy barrier to twisting is a steepening of the potential energy walls in the region of transoid stilbene conformations in both ^{1}T and ^{0}S. Torsional displacement about the central bond decreases the ^{1}T–^{0}S energy difference because the energy of the ground state increases with twisting more than that of the triplet state.[12] Since this energy difference is largest in the more viscous media where torsional motions are confined to smaller displacements, k_4 decreases as the rigidity of the medium is increased; correspondingly, the deuterium isotope effect on k_4 is expected to increase because the Franck–Condon overlap involves more quanta rendering the high frequency C–H and C–D stretching vibration more important as acceptor modes.

Mechanism of the Deuterium Isotope Effects. The theory for radiationless intersystem crossing in aromatic hydrocarbons developed by Henry and Siebrand[10] focuses on three mechanisms for ^{1}T → ^{0}S decay. These are (1) spin–orbit coupling only, in systems where the transition is orbitally allowed, (2) vibronically induced spin–orbit coupling governed by spin–orbit coupling between π states, and (3) diabatic (non-Born–Oppenheimer) coupling caused by the nuclear momenta and governed by spin–orbit coupling between π and σ states.[38] All three of these mechanisms allow for a deuterium isotope effect *via* the Franck–Condon factors, but since these factors are supposed to be sensitive only to the number of deuterium substituents and not to their positions, no positional dependence of the deuterium effect is expected in the functioning of C–H and C–D vibrations as accepting modes.[10] The second and third mechanisms involve vibronic induction and allow for additional sensitivity to deuterium substitution due to deuterium effects on the electronic integrals. The additional effect of deuteration in the second mechanism is expected to be comparable to the effect of deuteration on C–C stretching modes (2–3% for perdeuteration). Of particular interest is the third mechanism in which out-of-plane C–H vibrations are expected to be important as inducing modes. Since the frequency of these modes decreases by ~15% (the frequency of the olefinic out-of-plane vibrations of *trans*-stilbene decreases by 26%, see Experimental Section) the partial rate constant for ^{1}T → ^{0}S associated with the third mechanism could decrease by an additional factor of 2 for a perdeuterated molecule. Furthermore, the additional deuterium effect in mechanism 3 is expected to show positional sensitivity because its matrix elements are largest when the highest local π-electron density coincides with the largest local out-of-plane amplitude; the deuterium effect is smallest when the deuteria are substituted at positions of lowest π-electron density.

The positional dependence of the deuterium isotope effect has therefore been suggested as one of the principal criteria for determining which of the three mechanisms dominates in each particular case.[10] For example, in the case of naphthalene where mechanism 1 is ruled out because the ^{1}T → ^{0}S transition is orbitally forbidden, the small difference in sensitivity of the deuterium isotope effect to α *vs.* β substitution, $k^\alpha/k^\beta = 1.7$,[7] has been used as a criterion for selecting mechanism 3 as dominant. The positional dependence in the ^{3}t → ^{0}t transition in stilbene could therefore imply that C–H out-of-plane vibrations in the excited state function as inducing modes in this case also. Henry and Siebrand used Hückel MO coefficients in predicting the α/β positional dependence in naphthalene. Absolute values of the coefficients of the highest occupied and lowest unoccupied Hückel MO's of stilbene are: $C_{\text{ol}} = 0.4382$, $C_{\text{p}} = 0.3138$, $C_{\text{o}} = 0.2738$, and $C_{\text{m}} = 0.0791$.[39] In terms of mechanism 3, the large coefficients for the olefinic positions are consistent with the observation of greatest effectiveness for olefinic C–H vibrations in enhancing the ^{3}t → ^{0}t transition. The small meta coefficients, on the other hand, would lead us to expect that deuterium substitution at the meta positions should have the smallest effect on the stilbene triplet lifetime. It seems likely, therefore, that the inference drawn from the data in ref 9 concerning the special effectiveness of meta C–H vibra-

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(37) This follows since the medium sensitivity of $k_4^{d_{12}}$ is not likely to be larger than the medium sensitivity of $k_4^{d_0}$. An attractive possibility is that $k_4^{d_{12}}$ is important only in the most rigid media, *e.g.*, MP and EPA at 77°K.

(38) Sharf[11] has recently claimed that a mechanism for intersystem crossing which depends on nuclear motions like Siebrand and Henry's mechanism (3) does not exist.

(39) The more refined coefficients obtained by Whitten and Pedersen using CNDO/2 calculations agree well with the Hückel coefficients. We thank Professor D. G. Whitten for sending us these results.

tions in enhancing the ^{3}t → ^{0}t transition is incorrect. The data in ref 9 may suggest instead that, as in the case of benzene,[40] the effects of deuterium substitution in the aromatic positions of *trans*-stilbene are not additive.[41]

It should also be pointed out that in the ^{0}t → ^{3}t absorption spectrum of crystalline *trans*-stilbene the normal mode which appears to be most important in inducing radiative spin–orbital coupling in the lowest triplet state has a frequency of 308 cm^{-1} and has been tentatively assigned to an out-of-plane vibration.[42] In the ^{0}t → ^{1}t absorption spectrum this mode appears as a rather intense progression with intervals of 298 cm^{-1}. It has been assigned to an out-of-plane vibration, possibly involving the out-of-plane motion of the central double bond, because it undergoes a large deuterium shift to 249 cm^{-1} in the spectrum of *trans*-stilbene-d_{12}.[42,43] This mode could also be important in inducing the radiationless ^{3}t → ^{0}t transition.

Points of concern with respect to the above discussion are: (a) in contrast to the case of naphthalene, the ^{1}T → ^{0}S transition in *trans*-stilbene is orbitally allowed and there is no *a priori* reason for not expecting mechanism 1, direct spin–orbit coupling, to be important, and (b) the positional sensitivity encountered in the ^{3}t → ^{0}t process, Table IV, is much larger than twofold, the maximum factor expected for mechanism 3.[10]

A theoretical treatment for radiationless decay from ^{3}p was recently presented[44] and it was concluded that the torsional mode of the central double bond should serve as a primary acceptor of electronic energy. As a consequence a notable absence of a deuterium isotope effect on the rate of deactivation of ^{3}p was predicted. The observation of no deuterium isotope effect upon substitution of the aromatic positions is in accord with this prediction and shows that very little, if any, of the excitation is concentrated into C–H stretching vibrations. The significant effect of deuteration in the olefinic positions suggests that some form of Henry and Siebrand's third mechanism may also be operative in the case of ^{3}p decay.[11] It should be noted here that the Henry and Siebrand theory was formulated for planar aromatic hydrocarbons and that the effect of nonplanarity on the mechanism of ^{3}p decay is open to some speculation.

Experimental Section

Materials. The synthesis of *trans*-stilbene-d_{10} has been described.[45] *trans*-Stilbene-d_0, K & K scintillation grade, was recrystallized from ethanol and sublimed. *trans*-Stilbene-d_0 was converted to the diphenylacetylene *via* the dibromide as described by Fieser.[46] Diphenylacetylene (601 mg) in 35 ml of methanol was allowed to react with deuterium (90 ml, 1 atm, 25°) over Lindlar catalyst (30 mg). A mixture of *cis*-stilbene-d_2 and bibenzyl-d_4 resulted which was refluxed in benzene for 12 hr with a large iodine crystal. Separation of *trans*-stilbene-d_2 from bibenzyl-d_4 was effected by chromatography on alumina using *n*-pentane as eluent, and the *trans*-stilbene-d_2 was sublimed prior to use, mp 125–126° (uncor). Azulene, Baker reagent grade, was sublimed twice. Benzophenone was zone-refined from Columbia Chemical Co. Benzene, Baker reagent grade, was purified by the Steinmetz procedure as previously described.[12] Small samples of *cis*-stilbene-d_2 and -d_{10} were prepared from the trans isomers by photoisomerization using pyrene as the sensitizer.[12]

Isotopic Purity of the Stilbenes. Low-resolution mass spectroscopic data for the *trans*-stilbenes obtained at low electron beam energy (12 eV) in the region of the molecular ion are shown in Table V. Although the presence of a large M − 1 peak in the mass spectrum of *trans*-stilbene-d_0 makes interpretation of the data in Table V less than straightforward,[47] it is clear that the deuterated stilbenes are of very high isotopic purity. That the M − 1 peak in the stilbene-d_2 spectrum is due primarily to loss of an aromatic proton rather than to contamination by stilbene-d_1 is confirmed by the pmr spectrum of *trans*-stilbene-d_2 in which olefinic protons are entirely absent ($\lesssim$1% olefinic hydrogen). Similarly, the pmr spectrum of *trans*-stilbene-d_{12} measured relative to *tert*-butyl alcohol as internal standard shows no stilbene protons ($\lesssim$2% hydrogen). In this case the M − 2 peak is probably due to loss of a deuteron from the parent ion but the M − 1 peak is clearly due to stilbene-d_{11} contamination (~15%). In the spectrum of *trans*-stilbene-d_{10} a major fraction of the M − 2 peak can probably be attributed to loss of a deuteron, while the M − 1 peak indicates ~14% stilbene-d_9 contamination. The high isotopic purity of the stilbene-d_{10} sample is confirmed by the pmr spectrum in which only olefinic proton absorption could be observed ($\lesssim$1% aromatic hydrogen). All pmr spectra were measured using a Varian A-60 spectrometer.

Table V. Molecular Ion Region in the Mass Spectra of the *trans*-Stilbenes[a]

Stilbene-d_n n (M = m/e)	(M + 1) 100%/M[b]	M 100%/M	(M − 1) 100%/M	(M − 2) 100%/M
0 (M = 180)	15.4	100	27.8	7.0
2 (M = 182)	19.1	100	20.0	6.7
10 (M = 190)	19.1	100	15.9	12.3
12 (M = 192)[c]	15.7	100	17.5	5.4

[a] Unless otherwise noted, mass spectra were recorded using a Nuclide Model 12-90 G 1.5 mass spectrometer. [b] Theoretical for $C_{14}H_{12}$ is 15.3%. [c] Reference 12.

Infrared spectra of CS_2 and CCl_4 solutions of the stilbenes were recorded using a Perkin-Elmer Model 137 Infracord. Deuteration caused major changes in the regions of C–H absorption. Frequencies of some major C–H and C–D vibrations for which a tentative assignment[49] could be ventured are shown in Table VI.

Analytical Procedures. Benzophenone was removed prior to glpc analysis by chromatography on alumina. Stilbene samples were concentrated and benzene was replaced with CCl_4 as solvent on a hot-plate under a stream of N_2. In work-up procedure 1 the stream of nitrogen was sufficiently fast to prevent the solutions from warming up. In work-up procedure 2 a slower stream of nitrogen was used and the solutions were maintained at reflux temperature throughout the concentration and solvent exchange step. Control experiments showed that the second procedure did not change cis/trans ratios, while the first resulted in small losses of cis isomer ($\lesssim$1%). Gas chromatographic conditions were as previously described.[18]

Irradiation Procedure. Samples (2 ml) of benzene solutions containing benzophenone (0.05 *M*), *trans*-stilbene (0.01 *M*) and azulene (0–3 × 10^{-2} *M*) were introduced into 13 × 60 mm Pyrex ampoules equipped with grease traps and 10/30 female joints. Prior to use the ampoules were washed first with concentrated NH_4OH and second with distilled water, and oven-dried. The solutions were degassed using three–four freeze–pump–thaw cycles to about 10^{-6} Torr, and the ampoules were flame sealed at a constriction. The ampoules were strapped to the outer wall of a Hano-

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[40] See Martin and Kalantar, ref 10.

[41] As a partial test of this possibility we plan to synthesize *trans-m,m'*-stilbene-d_2.

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[46] L. F. Fieser, "Organic Experiments," D. C. Heath, Boston, Mass., 1964, pp 222–224. We thank Dr. H. C. Curtis for carrying out this synthesis.

[47] At 15 eV, loss of a proton has been shown to follow hydrogen randomization in the stilbene parent ion.[48]

[48] P. F. Donaghue, P. Y. White, J. H. Bowie, B. D. Roney, and H. J. Rodda, *Org. Mass Spectrom.*, 2, 1061 (1969).

[49] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958.

Table VI. Frequencies of Some Major C–H and C–D Stilbene Vibrations[a]

Stilbene-d_0		Stilbene-d_2		Stilbene-d_{10}		Stilbene-d_{12}		Tentative assignment[b]
Trans	Cis	Trans	Cis	Trans	Cis	Trans	Cis	
3040 (sh)	3040	3021	3040	*2272*	*2272*	*2273*	*2283*	Ar stretch
		2994	3012					
3012	3000	*2222*	*2237*	3010	3000	*2237*	*2247* (*sh*)	Ol stretch
1067	1068	1075	1071	*845*	*861*	*845*	*847*	Ar in-plane bend
1030	1025	1027	1022	*824*	*820*	*824*	*823*	
756	693	758	693					Ar out-of-plane bend
686		684						
960		*710*		960		*712*		Ol out-of-plane bend

[a] Frequencies in cm^{-1}, estimated accuracy ± 5 cm^{-1}. Frequencies for C–D vibrations are given in italics. [b] Aromatic and olefinic are abbreviated as Ar and Ol, respectively.

via probe and immersed in a water bath whose temperature was kept at 25 ± 1 or 60 ± 1°. A 200-W Hanovia high-pressure mercury lamp, whose output was filtered with a cylindrical uranium glass tube transmitting light of wavelengths longer than 320 nm, was employed.

Flash Kinetic Spectrophotometry. The apparatus for triplet lifetime measurements by flash kinetic spectrophotometry is similar to that used in earlier investigations.[13,50] Two xenon flashlamps (Model W3G20, Kemlite Laboratories) were connected in series and located on opposite sides of a cylindrically shaped, quartz dewar having plane windows on the bottom. The lower half of the dewar was transparent to the excitation light. The energy output of the flash lamps was variable between 200 and 400 J by selection of voltage on a 2-μF, low inductance, storage capacitor. Between the dewar and the flash lamps were positioned glass color filters (Corning 9863). The dc monitoring source was a 100-W high-intensity, point source, mercury arc lamp (Osram, HBO 100 W/2). Sample solutions were contained in cylindrical quartz cells having plane windows on the ends and positioned vertically in the center of the dewar and were cooled with either liquid nitrogen or a Dry Ice–acetone slurry. The dimensions of the cells were 100-mm optical length and 13-mm i.d. The cells were connected to bulbs where the solutions were contained during the degassing procedure. The collimated monitoring light reflected 90° from a plane mirror, passed through the sample cell, the bottom of the dewar, again reflected 90° from a plane mirror and focussed on the entrance slit of a Jarrell-Ash 0.25-m grating monochromator. An RCA 4463 photomultiplier tube, mounted on the exit of the monochromator, served as detector. The signal from the detector was dc coupled through a cathode-follower amplifier to a Tektronix Model 555 wide-band oscilloscope where it was displayed and recorded photographically.

The oscilloscope transparencies were enlarged in order to facilitate more precise measurement of the transient kinetics. The lifetimes of the transient species were measured by the recovery rate of the monitoring beam following completion of the excitation flash. Kinetic analysis was by the method of Linschitz and Sarkanen.[51]

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Primary Interaction between Diaryl Ketone Triplets and Simple Alkenes. Isotope Effects

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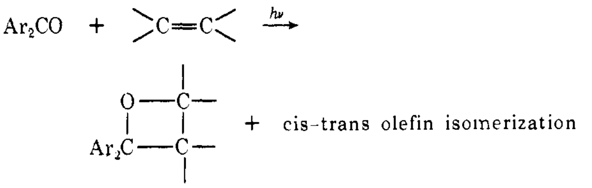
Abstract: The primary interaction between benzophenone triplet and simple alkenes is shown to be irreversible formation of a complex. The complex possesses substantial change-transfer character, with olefin as donor and ketone as acceptor. The complex has a finite (though undetermined) lifetime. Support for these conclusions derives from kinetic and quantum-yield studies with the isomeric butenes, and most importantly from the comparison of the results of an extensive study of secondary deuterium isotope effects with mechanistic models.

The photocycloaddition of aromatic carbonyl compounds to simple olefins, affording oxetanes, is an interesting and useful application of photochemistry to organic synthesis.[1–3] It is now a well-established reaction of broad scope. Several reviews of its applications and of related mechanistic studies are available.[4,5]

It is clear that several different mechanisms are possible. Ketone singlets can form oxetanes with olefins.[6–9] Although in some cases π,π^* ketone excited



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