

bringing the methyl groups together, negative  $\tau$  to moving them apart. Note that the potentials are quite soft, the maximum change in energy being about 0.06 and 0.09 eV for EH and CNDO/2, respectively. This is consistent with the low-energy infrared twisting frequency for olefins which is  $1023\text{ cm}^{-1}$  for ethylene itself.<sup>3</sup>

The curves conform to our intuitive expectations: the methyl groups prefer to bend away rather than toward one another, thus favoring motion along path 5. The asymmetry in the torsional potential means that the time-averaged value of  $\tau$  will be negative instead of zero. Accordingly, the torsional contribution to the

rotatory strength will be negative (see Figure 1). Application of the olefin octant rule<sup>4a,b</sup> to the hypothetically chiral *cis*-pentene-2 **4** also leads to this prediction. In the case at hand then, the olefin octant rule correctly assesses the sign of the torsional rotatory strength contribution. Attempts to extrapolate this sort of reasoning to the steroidal olefins correlated by the rule would not be very meaningful owing to the many degrees of freedom present in their multicyclic frameworks. Nevertheless the possibility that torsion is important in these compounds should not be overlooked.

Recapitulating, our calculations suggest that the sign of the Cotton effect in twisted olefins such as twistene and *trans*-cyclooctene is dominated by double bond torsion. For these olefins it appears that the success of the octant rule derives from its ability to correctly predict the sense of twist from the absolute configuration of the nearest substituents. A torsion contribution may also be important in less strained olefins, but this is hard to assess with the experimental data presently available.

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## Mechanisms of Photochemical Reactions in Solution. LXVII.<sup>1</sup> Energy Wastage in Photosensitized Isomerizations of the Stilbenes<sup>2</sup>

Donald Valentine, Jr., and George S. Hammond\*<sup>3</sup>

Contribution No. 4260 from the Gates and Crellin Laboratories of Chemistry,  
California Institute of Technology, Pasadena, California 91109.

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**Abstract:** Photosensitized isomerizations of the stilbenes using high energy sensitizers, capable of exothermic triplet energy transfer to either *cis*- or *trans*-stilbene, have been investigated in detail. Our present measurements differ slightly in some cases from those reported previously. Detailed scrutiny reveals that, with sensitizers having excitation energies in the range 62–74 kcal, there is a small, but significant, variation in the final photostationary states. The variation is a systematic function of excitation energy, and  $(c/t)_{\text{ps}}$  varies from 1.3 at the high end of the energy scale to 2.0 at the low end. Careful study of energy balance in photosensitized stilbene isomerizations with acetophenone, benzophenone, and 9-fluorenone as sensitizers reveals that quenching of sensitizer triplets by stilbene does not always occur with energy transfer to stilbene. Our data indicate that about 5% of the time when acetophenone triplets are quenched by *trans*-stilbene the stilbene does not become electronically excited. Similarly 9-fluorenone triplets are quenched readily by both *trans*- and *cis*-stilbene. Triplet energy to *trans* is exothermic and occurs in about 95% of the quenching events; triplet energy transfer to *cis* is slightly endothermic and occurs in only about half of the quenching events. Various possible quenching mechanisms are discussed.

Quenching of sensitizer triplets by other substrates may in the general case involve one or more of processes 1–3, where S is the sensitizer, A is the substrate, and subscripts T<sub>1</sub> and S<sub>0</sub> refer respectively to lowest triplet and ground singlet states.

Where A is an olefin, *cis*–*trans* isomerization may

(1) Part LXVI: L. J. Sharp IV and G. S. Hammond, *Mol. Photochem.*, **2**, 225 (1970).

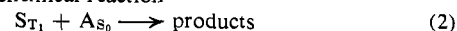
(2) Taken in part from the Ph.D. Thesis of D. Valentine, Jr., California Institute of Technology, Pasadena, Calif., 1966.

(3) Author to whom correspondence should be addressed.

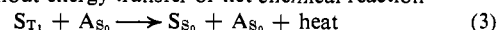
Triplet energy transfer



Quenching *via* net chemical reaction

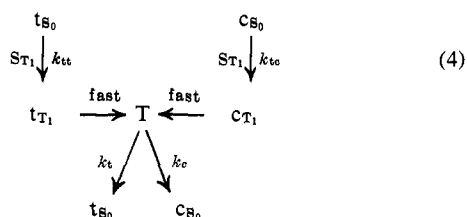


Quenching without energy transfer or net chemical reaction



follow reaction 1, providing a basis for monitoring the occurrence of reactions 1 and 3. When reaction 1 provides the only path leading to olefin isomerization, then

(4) describes the mechanism of photosensitized isom-



erization of the olefin, where c is cis olefin and t is trans olefin, and we assume that conversion of  $C_{T_1}$  and  $t_{T_1}$  to the common manifold of triplets, T, is fast compared to all other processes of  $C_{T_1}$  and  $t_{T_1}$ .<sup>4</sup> If T is converted to ground state olefins in characteristic ratios independent of its source, (5) and (6) follow, and when

$$(c/t)_{\text{pss}} = (k_{tt}/k_{tc})(k_c/k_t) \quad (5)$$

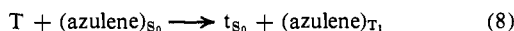
$$\phi_{t \rightarrow c} + \phi_{c \rightarrow t} = \phi_{\text{isc}} \quad (6)$$

exothermic triplet energy transfer to either olefin isomer is possible, so that  $k_{tt} \approx k_{ct} \approx k_{\text{diff}}$ , then (7) also

$$\alpha_{t \rightarrow c} + \alpha_{c \rightarrow t} = (c/t)_{\text{pss}} \quad (7)$$

follows.  $\phi_{\text{isc}}$  is the intersystem crossing yield of the sensitizer, which is assumed to be independent of the olefin.<sup>5</sup>

Mechanism 4 was tested quantitatively with several systems for which the crucial assumptions should be satisfied. Photosensitized isomerizations of  $\alpha$ -methylstilbene generally gave kinetic parameters essentially identical with those predicted by (5)–(7), and similar good agreement was observed also with the 1,3-pentadienes. For instance with benzophenone and the  $\alpha$ -methylstilbenes we found<sup>6</sup>  $\phi_{t \rightarrow c} = 0.55$ ,  $\phi_{c \rightarrow t} = 0.45$ , and  $(c/t)_{\text{pss}} = 1.22$ , thereby satisfying both (6) and (7). With the stilbenes, however, our data were not in good quantitative agreement with either (6) or (7). For benzophenone–stilbene, we found<sup>6</sup>  $\phi_{t \rightarrow c} = 0.44$ ,  $\phi_{c \rightarrow t} = 0.37$ , and  $(c/t)_{\text{pss}} = 1.48$ , giving the ratio  $\phi_{t \rightarrow c}/\phi_{c \rightarrow t} = 1.19$  and the sum  $\phi_{t \rightarrow c} + \phi_{c \rightarrow t} = 0.81$ . Similar discrepancies between prediction and experiment were observed with other high energy sensitizers. That significant discrepancies should be observed with the stilbenes was especially intriguing since in this system it was possible to show, by studying the effect of azulene on the  $(c/t)_{\text{pss}}$  values for the photosensitized isomerizations with several sensitizers, that the same stilbene intermediate, presumably T, which is quenched by azulene to give preferentially  $t_{S_0}$  (eq 8), was involved in



isomerizations with all the different sensitizers.<sup>7</sup>

The original purpose of this investigation was to explore possible explanations for the course of photosensitized isomerizations of the stilbenes. Our results serve to explain many anomalies present in our earlier

(4) It is possible to show this assumption to be valid for stilbenes (*vide infra*). It will not in general be true, particularly if the olefin localized triplet is not the lowest energy triplet of the molecule. Note that T may contain cisoid and transoid forms in addition to possible twisted forms.

(5) That is, the olefin does not quench the excited singlet states of the sensitizer.

(6) 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).

(7) We have written (8) to indicate that only  $t_{S_0}$  is produced, although our data do not actually show that (8) gives only trans. See ref 6.

Table I. Acetophenone, Benzophenone, and Fluorenone Photosensitized Stilbene Isomerizations

Sensitizer	Triplet <sup>b</sup> energy, kcal/mol	Inter-system <sup>c</sup> crossing yield	Triplet <sup>d</sup> lifetime (25°), sec	Triplet quenching <sup>e</sup> rate constants l. mol <sup>-1</sup> sec <sup>-1</sup>	Data from ref 4 <sup>a</sup>			Our present values <sup>g</sup>						
					$\phi_{t \rightarrow c}$	$\phi_{c \rightarrow t}$	$\sum \phi$	$\phi$	$\phi_{t \rightarrow c}/\phi_{c \rightarrow t}$	$(c/t)_{\text{pss}}$				
Acetophenone	73.6	1.00	$\sim 10^{-6}$	$\sim 6 \times 10^9$	(0.45)	(0.40)	(0.85)	1.1	1.48	0.52	0.37 <sup>h</sup>	0.89	1.3	1.27
Benzophenone	68.7	1.00	$\sim 10^{-6}$	$\sim 6 \times 10^9$	(0.40)	(0.37)	(0.77)	1.2	1.48 <sup>i</sup>	0.55	0.41 <sup>i</sup>	0.93	1.4	1.4
Benzophenone + $\alpha$ -methylstilbene	68.7	1.00	$\sim 10^{-6}$	$\sim 6 \times 10^9$	(0.48)	(0.41)	(0.89)	1.3	1.22	0.56 <sup>j</sup>	0.41 <sup>i</sup>	0.96	1.35	1.35
9-Fluorenone	55.3	0.93	$3 \times 10^{-4}$	$\sim 3.5 \times 10^9$	0.55	0.45	1.00	1.8	6.2	0.47	0.19	0.66	2.47	6.2
										0.43 <sup>k</sup>				

<sup>a</sup> The quantum yield data given below are those calculated from our original data<sup>9</sup> with correction for back reaction<sup>6</sup> and are thus different from the uncorrected data in ref 6. <sup>b</sup> From phosphorescence measurements; cf. A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Interscience, New York, N. Y., 1970, pp 92, 93. <sup>c</sup> Reference 8. <sup>d</sup> The lifetime for benzophenone is estimated by C. D. DeBoer, unpublished. The fluorenone lifetime is from ref 12. The acetophenone lifetime is from ref 22. <sup>e</sup> Reference 8. <sup>f</sup> Photosensitized state data and  $\phi_{t \rightarrow c}$  for benzophenone–stilbene were reported to be somewhat dependent on the stilbene concentration; both  $(c/t)_{\text{pss}}$  and  $\phi_{t \rightarrow c}$  seemed to increase slightly at low stilbene concentrations. No effect of sensitizer concentration was observed in any case. <sup>g</sup> Precision limits are  $\pm 0.02$  for  $\phi$  and  $\pm 0.05$  for pss measurements with acetophenone and benzophenone and  $\pm 0.5$  for the fluorenone pss. <sup>h</sup> Our value. <sup>i</sup> Reference 6. <sup>j</sup> Reference 1. <sup>k</sup> Reference 23.

work<sup>6</sup> and have revealed new and interesting aspects of energy transfer in certain sensitizer–stilbene systems.

## Results and Discussion

Meaningful kinetic analyses of photosensitized stilbene isomerizations in terms of (5)–(7) can be made only with precise and accurate data. Some quantum yields reported<sup>6</sup> were measured without correcting for back reaction.<sup>8</sup> Making the necessary correction on the original data<sup>9</sup> increased the average quantum yield by about 10%. Uncorrected values from ref 6 are given on the left side of Table I with corresponding corrected values in parentheses. Some photostationary state data reported in ref 6 were obtained using light that was in part absorbed by the stilbenes.<sup>10</sup> Consequently, the experimental measurements did not give accurate information concerning the *photosensitized* isomerization reaction. In fact, very complicated reactions occur on irradiations of various sensitizer–stilbene systems with light absorbed entirely or in part by the stilbenes.<sup>11</sup> We decided to begin by carefully measuring  $\phi_{t \rightarrow c}$ ,  $\phi_{c \rightarrow t}$ , and  $(c/t)_{\text{pss}}$  for representative sensitizer–stilbene systems using a common set of reagents and (essentially) the same experimental conditions for degassing, storage, and analysis of samples.

Quantum yields were measured using reagents and degassing procedures suitable for flash photolysis studies.<sup>12</sup> Measurement of  $\phi_{t \rightarrow c}$  for benzophenone–stilbene was calibrated against three separate actinometric systems: potassium ferrioxalate,<sup>13</sup> benzophenone photosensitized  $\alpha$ -methylstilbene *trans* to *cis* isomerization,<sup>6</sup> and benzophenone photosensitized dimerizations of 0.20 *M* cyclohexadiene-1,3 in benzene.<sup>14</sup> Measured  $\phi_{t \rightarrow c}$  values were the same within experimental error with each of these actinometers. Other quantum yields were measured using benzophenone–*trans*-stilbene as the actinometer. This was done to allow us to measure with maximum precision quantum yields relative to  $\phi_{t \rightarrow c}$  for benzophenone–

stilbene. By using the quantum yield “merry-go-round”<sup>15</sup> in such comparison experiments we could reduce the important sources of imprecision in our measurement to those involved in vpc analyses. We believe that our vpc analyses, which were made using a flame detector and disc integrator, calibrated for stilbene isomer response as a function of total sample size, were sufficiently precise to enable us to distinguish *relative* quantum yields differing by 6% or more. Thus, we agree with Cowan and Saltiel, *et al.*,<sup>6,9</sup> in finding that  $\phi_{t \rightarrow c}$  is slightly larger with benzophenone than with acetophenone as sensitizer. This very important result will be discussed later.

Clearly the most important new finding of this work is that  $\phi_{t \rightarrow c}$  values for benzophenone and the other sensitizers employed are about 15% higher than (corrected) values obtained from our earlier data and as much as 25% higher than  $\phi_{t \rightarrow c}$  values reported in ref 6.<sup>16</sup> Since this work was completed and first published<sup>2</sup> parts of these findings have been confirmed by other workers.<sup>17</sup>

Photostationary state data were obtained in essentially the same way as the quantum yields except that samples of pure *cis* and pure *trans* isomers were irradiated until no further change in  $(c/t)$  was observed. With the exception of acetophenone–stilbene as noted in ref 10,  $(c/t)_{\text{pss}}$  values measured with ( $\lambda > 345$  nm) light were essentially identical with those measured with our earlier light source which contained some ( $\lambda > 300$  nm) light. The change in  $(c/t)_{\text{pss}}$  for acetophenone–stilbene on going from  $\lambda > 300$  to  $> 345$  nm exciting light was from 1.48 to 1.27. This corresponds to a change from  $\sim 59.5\%$  to  $\sim 55.5\%$  *cis*-stilbene and lies significantly outside expected precision limits of our vpc analyses. We believe this is a measurable difference and conclude that  $(c/t)_{\text{pss}}$  is not the same for benzophenone–stilbene (1.48) as for acetophenone–stilbene (1.27). Certain other  $(c/t)_{\text{pss}}$  data reported in Table II for various sensitizer–stilbene systems were also not identical with those found earlier.<sup>6,18</sup> The differences were usually small, however, and may be attributed to differences in sensitizer purity (e.g., 10-thioxanthone, for whose exhaustive purification see ref 2) or to the likely occurrence of side reactions (e.g., with anthraquinone).<sup>19</sup>

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

(9) J. Saltiel and D. O. Cowan, unpublished results.

(10) Data reported in ref 6 for acetophenone–stilbene, benzophenone–stilbene, and pyrene–stilbene were obtained using light filtered through Pyrex in such a manner that about 10% of the light absorbed by the solution was at 313 or 334 nm, the rest being at 350–370 nm and longer wavelengths. Because stilbene can be photoisomerized by direct irradiation,  $(c/t)_{\text{pss}}$  values representative of the photosensitized isomerization can be obtained only with exciting light having only wavelengths longer than 345 nm. We ensured this by using a uranium glass or 365-nm interference filter in all experiments. The experimental manifestation of the effect of direct absorption by the stilbenes in competition with acetophenone was an increase in the observed  $(c/t)_{\text{pss}}$  from 1.27 to 1.45 on going from uranium glass to Pyrex filtered light. Little change was observed with benzophenone, which unlike acetophenone absorbs strongly near 360 nm. With pyrene, it was reported<sup>6</sup> that  $(c/t)_{\text{pss}}$  decreased as the sensitizer concentration decreased. We suspected that this was due to the fact that  $(c/t)_{\text{pss}}$  for the direct photoisomerization of stilbene was less than that for the pyrene sensitized isomerization and that the direct photoisomerization was simply becoming progressively more important as the sensitizer concentration (and absorbance) decreased. Pyrene photosensitized isomerization of stilbene with ( $\lambda > 345$  nm) exciting light had  $(c/t)_{\text{pss}}$  values which increased as the sensitizer concentration decreased, as expected on the basis of reduced reverse triplet energy transfer from T to pyrene as explained in ref 6.

(11) D. Valentine, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, to be submitted for publication.

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

(13) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(14) G. F. Vesley, Ph.D. Thesis, California Institute of Technology, Pasadena, 1968. The quantum yield for photodimerization of cyclohexadiene (0.2 *M*) with benzophenone as sensitizer was assumed to be  $0.89 \pm 0.02$ .

(15) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

(16) We are unaware of any obvious reasons for this difference, although we suspect that vpc analytical techniques may be the cause. The relative detector response of the stilbene isomers is dependent on the sample size and, for a given detector, on the amount of ash on the filament.

(17) H. A. Hammond, D. E. DeMeyer, and J. L. R. Williams, *J. Amer. Chem. Soc.*, **91**, 5180 (1969).

(18) J. Saltiel, Ph.D. Thesis, California Institute of Technology, Pasadena, 1964.

(19) The range of sensitizers suitable for photosensitized stilbene isomerization experiments of the type described here is limited in number and especially in range of functional types by the requirements that  $E_{T_1 \rightarrow S_0}$  exceed ca. 62 kcal/mol and that absorption at 365 nm be appreciable. To increase the available range to include “sensitizers” which satisfy the first but not the second requirement, an indirect method was tried. This was to use a ketone (acetophenone or benzophenone) to absorb 365-nm light then transfer triplet excitation to the intended sensitizer (0.10 *M*) whose triplets are then expected to be quenched by the stilbenes (0.005 *M*). Because the ratio of “sensitizer” to stilbene is ca. 20:1, about 95% of the energy in the ketone will be transferred to the stilbenes and, hence, the observed  $(c/t)_{\text{pss}}$  will be mostly characteristic of the sensitizer not the absorbing species. Some data obtained this way are included in Table II. These data are not very precise due to the necessity for alumina chromatography of irradiated solutions to remove ketone (and sometimes “sensitizer” also) before vpc analysis.

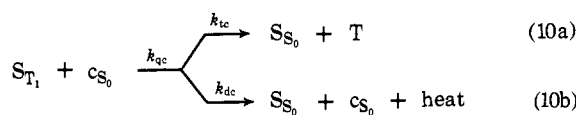
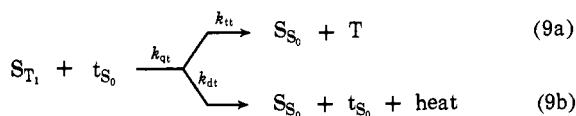
Table II. Photostationary States for High Energy Donor-Stilbene Systems

Donor	Donor $E_{T_1 \rightarrow S_0}$ , kcal/mol	(c/t) <sub>pss</sub>	$\phi_{t \rightarrow c}$	$\phi_{c \rightarrow t}$
Acetophenone	73.6 <sup>a</sup>	1.27 ± 0.03	0.52 ± 0.03	0.37 ± 0.03
Propiophenone	73	1.27 ± 0.03	0.52 ± 0.03	0.37 ± 0.03
Isobutyrophenone	72.2	1.29 ± 0.03		
Cyclopropyl phenyl ketone	72 <sup>b</sup>	1.26 ± 0.01 <sup>e</sup>		
Deoxybenzoin	72 <sup>b</sup>	1.27 ± 0.03		
Carbazole	70.1	5.7 ± 0.3 <sup>d</sup>		
Diphenylene oxide <sup>e</sup>	70.1	1.47 ± 0.03		
Dibenzothiophene	69.7	1.82 ± 0.03 <sup>f</sup>		
<i>o</i> -Dibenzoylbenzene	68.7	1.56 ± 0.09		
<i>p</i> -Bromobenzophenone	68.7	~0 <sup>g</sup>		
Benzophenone	68.5	1.45 ± 0.03	0.55 ± 0.02	0.38 ± 0.03
1,4-Diacetylbenzene	67.7	1.46 ± 0.02 <sup>h</sup>	0.52 ± 0.02	0.37 ± 0.03
Fluorene <sup>e</sup>	67.6	3.4 ± 0.2		
9-Benzoylfluorene	66.8	2.2 ± 0.2 <sup>e</sup>		
Triphenylene <sup>e, i</sup>	66.6	~1.4		
<i>p</i> -Cyanobenzophenone	66.4	1.55 ± 0.1		
1,3,5-Triacetylbenzene	66(?) <sup>k</sup>	1.51 ± 0.1		
Thioxanthone	65.5	1.47 ± 0.03	0.49 ± 0.02	0.33 ± 0.02
Anthraquinone	62.4	1.73 ± 0.06	0.51 ± 0.02	0.28 ± 0.02
Phenanthrene <sup>j</sup>	62.2	1.82 ± 0.06		
Flavone	62.0	1.64 ± 0.10		
2-Acetylfluorene	62.0	1.83 ± 0.10		

<sup>a</sup> All  $E_{T_1 \rightarrow S_0}$  values are from Lamola and Turro (Table I, footnote b). <sup>b</sup> Estimated value. <sup>c</sup> Sensitizer decomposed partially. <sup>d</sup> Solutions had permanent yellow cast. <sup>e</sup> Measured by indirect method described in Experimental Section. <sup>f</sup> For direct illumination of dibenzothiophene. A higher (cis/trans)<sub>pss</sub> ratio was obtained using the indirect method. <sup>g</sup> Variable values in the range 0-0.2 were obtained. This donor liberates Br atoms. <sup>h</sup> Solutions were chromatographed on alumina to remove *p*-CH<sub>3</sub>COC<sub>6</sub>H<sub>4</sub>COCH<sub>3</sub> before vpc analysis. <sup>i</sup> L. Coyne, Ph.D. Thesis, California Institute of Technology, Pasadena, 1967. <sup>j</sup> Slightly yellow solutions after long photolysis.

Earlier, we reported<sup>6</sup> that for sensitizers having  $E_{T_1 \rightarrow S_0}$  greater than 62 kcal/mol and not subject to unusual steric constraints on orientations for energy transfer,<sup>20</sup> (c/t)<sub>pss</sub> was not dependent on the sensitizer and, in particular, was independent of sensitizer  $E_{T_1 \rightarrow S_0}$  as required by (4) and explained in the introductory section. Our present expanded set of data, given in Table II, shows this to be only an approximation. In fact, with sensitizers having  $E_{T_1 \rightarrow S_0} \cong 74$  kcal/mol we obtain (c/t)<sub>pss</sub>  $\cong 1.3$ , while with sensitizers having  $E_{T_1 \rightarrow S_0} \cong 62$  kcal/mol we obtain (c/t)<sub>pss</sub>  $\cong 1.7$ . With a few exceptions, which we believe to have resulted from the occurrence of side reactions, data in Table II suggest that (c/t)<sub>pss</sub> does not depend on the functional type of the sensitizer in the  $E_{T_1 \rightarrow S_0}$  range of 62-74 kcal/mol, and our data provide no further evidence for steric hindrance to energy transfer from high energy sensitizers.

That (c/t)<sub>pss</sub> values for high energy sensitizers should depend on sensitizer energy is probably in general the result of energy wastage during the triplet quenching processes 9 and 10. This may be illustrated by dis-



cussing our results for benzophenone-stilbene, acetophenone-stilbene, and 9-fluorenone-stilbene.

**A. Benzophenone-Stilbene.** For benzophenone,  $E_{T_1 \rightarrow S_0} = 68.7$  kcal/mol,  $\phi_{isc} = 1.00$ ,<sup>8</sup> the singlet state

(20) W. G. Herkstroeter, L. B. Jones, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4777 (1966).

lifetime is a few picoseconds.<sup>21</sup> According to our present values,  $\phi_{t \rightarrow c} + \phi_{c \rightarrow t} = 0.96 \pm 0.04$  which cannot be said to be different from unity in view of our experimental uncertainties.<sup>22</sup> Also,  $\phi_{t \rightarrow c}/\phi_{c \rightarrow t} = (c/t)_{pss}$  within experimental uncertainties. Hence, for this system, mechanism 4 appears to be nearly correct quantitatively in the limit of present experimental uncertainties. This means that in (9) and (10)  $k_{dt} \ll k_{tt} \cong k_{qt}$ ,  $k_{dc} \ll k_{tc} \cong k_{qc}$ , and  $k_{qt} \cong k_{qc}$ .

**B. Acetophenone-Stilbene.** For acetophenone,  $E_{T_1 \rightarrow S_0}$  is 73.6 kcal/mol and  $\phi_{isc}$  is 1.00.<sup>8</sup> The singlet lifetime is almost certainly too short to allow bimolecular quenching of singlets. Lutz and Lindqvist<sup>23</sup> reported the acetophenone triplet lifetime to be about  $3 \times 10^{-6}$  sec so that concentrations of stilbene (0.05 M) used in this work are adequate to ensure that diffusion limited quenching of acetophenone triplets by *cis*- or *trans*-stilbene will be more than 99% efficient. In view of this, our findings that (a) material balance is maintained even for prolonged irradiations; (b)  $\phi_{t \rightarrow c} + \phi_{c \rightarrow t} = 0.93 \pm 0.04$  and  $\phi_{t \rightarrow c}$  for acetophenone is definitely less than for benzophenone (*vide supra*); and (c)  $(\phi_{t \rightarrow c}/\phi_{c \rightarrow t}) = (c/t)_{pss}$  within experimental uncertainty can be rationalized most convincingly by postulating that in (9) and (10)  $k_{qt} \cong k_{qc}$  and  $k_{dc} \ll k_{tc}$ , but  $k_{dt}$  is not negligible compared to  $k_{tt}$  and in fact  $k_{dt}$  is about  $0.05k_{tt}$ . That is, acetophenone triplets are quenched by *trans*-stilbene and *cis*-stilbene at the same, presumably encounter limited rate but when *trans*-stilbene is the quencher, triplet energy is transferred about 95% of the time.

(21) M. M. Malley and P. M. Rentzepis, *Chem. Phys. Lett.*, **3**, 534 (1969).

(22) Note that these uncertainties are in comparison with the actinometric systems (whose quantum efficiencies are known only to ca.  $\pm 1\%$  at best), and these uncertainties should not be present in measurements of relative quantum yields.

(23) H. Lutz and L. Lindqvist, *J. Chem. Soc. D*, 493 (1971).

**C. 9-Fluorenone-Stilbene.** While triplet energy wastage is relatively unimportant with acetophenone, dramatic, easily observed effects appear with 9-fluorenone for which ( $E_{T_1 \rightarrow S_0} = 53$  kcal/mol,  $\phi_{isc}(\text{benzene}) = 0.93$ ,<sup>24a</sup> and the triplet lifetime in benzene is about  $10^{-4}$  sec.<sup>12</sup> For fluorenone-stilbene we showed earlier that  $k_{qt} + k_{qc} > 10^9$  l. mol<sup>-1</sup> sec<sup>-1</sup> so 0.05 *M* stilbene guarantees quenching of more than 99.8% of fluorenone triplets by stilbene. Fluorenone fluorescence is not quenched significantly by either *trans*-stilbene (0.10 *M*)<sup>24a</sup> or *cis*-stilbene (0.05 *M*).<sup>24b</sup> Hence, inefficiencies observed for fluorenone-stilbene result from quenching of fluorenone triplets without energy transfer to stilbene.

For fluorenone-stilbene we find  $\phi_{t \rightarrow c} = 0.47$  which is somewhat lower than the value of  $\phi_{t \rightarrow c} = 0.51$  obtained by substitution in (11). We calculate on this basis that in this system  $k_{dt} \cong 0.08k_{tt}$ .<sup>25</sup> We find that  $\phi_{c \rightarrow t} =$

$$\phi_{t \rightarrow c} = \phi_{t \rightarrow c}(\text{benzophenone})\alpha_{isc}(\text{sensitizer}) \quad (11)$$

$0.21 \pm 0.02$ <sup>26</sup> and that  $(c/t)_{pss} = 6.2$ .

The ratios  $k_{qt}/k_{tt}$  and  $k_{qc}/k_{tc}$  are already known from the quantum yields and  $k_{tt}/k_{tc}$  can be obtained from (12)

$$(c/t)_{pss} = (k_c/k_t)(k_{tt}k_{tc}) \quad (12)$$

since the ratio  $k_c/k_t \cong 1.4$  obtained with benzophenone as sensitizer is valid for fluorenone also because the same effect of azulene on  $(c/t)_{pss}$  was observed.<sup>6</sup> We calculate  $k_{tt}/k_{tc} = 4.3$ . Since  $k_{tc} = 1.1k_{dc}$  and  $k_{tt} \geq 20k_{dt}$  we obtain the result that  $k_{qt} \cong 2k_{qc}$  in this system, despite the fact that (9a) is  $\sim 3$  kcal/mol *exothermic* while (10a) is  $\sim 4$  kcal/mol *endothermic*. The endothermic and exothermic systems are thus different in the fraction of quenching events which involve energy transfer, but there is not a dramatic difference in total quenching rates.

The discovery of energy wastage in photosensitized isomerizations of the stilbenes cannot be considered particularly surprising in view of present-day experience. Numerous examples of the quenching of excited singlet states without electronic excitation transfer to the quencher have been reported.<sup>27</sup> We are apparently seeing a similar phenomenon in triplet decay. While we know of no data which conclusively eliminate chemical reaction of excited sensitizer with stilbene to give an unstable adduct which reverts to ground state sensitizer and stilbene,<sup>28</sup> we prefer to conceive of (9b) and (10b) as catalysis by stilbene of nonradiative decay of sensitizer triplets. As with catalyzed nonradiative decay of excited singlet states the triplet quencher might cooperate in internal conversion by providing vibrational modes especially appropriate for accepting excitation converted from electronic to vibrational form. This mode of decay is expected to operate in a weakly bound exciplex.<sup>29</sup>

(24) (a) R. P. Gajewski and R. A. Caldwell, *J. Amer. Chem. Soc.*, **93**, 532 (1971); (b) W. G. Herkstroeter, private communication.

(25) Caldwell and Gajewski<sup>24a</sup> report for fluorenone-stilbene  $\phi_{t \rightarrow c} = 0.43$ , which would lead to the conclusion that  $k_{dt} \cong 0.19k_{tt}$ .

(26) This value represents the average of  $\phi_{c \rightarrow t} = 0.23$  obtained by Cowan<sup>9</sup> and  $\phi_{c \rightarrow t} = 0.19$  obtained in this work.

(27) *E.g.*, L. M. Stephenson, D. G. Whitten, and G. S. Hammond, "The Chemistry of Ionization and Excitation," Butterworths, Washington, D. C., 1967, p 35.

(28) Arguments are given in ref 24a to indicate the unlikelihood of such chemical reactions of fluorenone with *trans*-stilbene.

(29) A similar proposal was made in ref 24a. Triplet exciplexes have been discussed by T. Förster, *Angew. Chem., Int. Ed. Engl.*, **8**, 333 (1969).

Energy wastage has been found to appear in just those cases where one might expect it. The rate of energy transfer might be expected to be a maximum when the energetics are closest to perfect resonance in electronic excitation alone.<sup>30</sup> Where there is a large energetic mismatch, with the acceptor requiring much less energy than is available in the donor, conversion of a significant amount of electronic to vibrational energy is required. This process should begin to be slow for the same reasons that delay nonradiative decay of fluorescent and phosphorescent species.<sup>30</sup> The fact that another route is found when high energy sensitizers are quenched by *trans*-stilbene may well be due to the large energy gap involved in pure electronic energy transfer. On the other hand, transfer from fluorenone triplets to *cis*-stilbene is endothermic unless the acceptor undergoes some geometric relaxation during transfer.<sup>6</sup> Since another mechanism for quenching apparently exists, it is not surprising that it makes a contribution to the overall process.

In view of the above arguments, it is reasonable that energy wastage should appear in quenching of acetophenone triplets ( $E_{T_1 \rightarrow S_0} = 73.6$  kcal/mol) by *trans*-stilbene ( $E_{S_0 \rightarrow T_1} \geq 57$  kcal/mol<sup>6</sup>). That quenching of fluorenone triplets by *trans*-stilbene should also involve energy wastage is not expected, however.

Finally, we note that the data given in this paper indicate clearly the dangers of associating *quenching* of triplet excited states of the sensitizer with *triplet energy transfer* to the acceptor. There is no necessary connection.

## Experimental Section

**Materials.** *trans*-Stilbene used in photostationary state determinations was MCB scintillation grade which was twice recrystallized from ethanol and sublimed under vacuum at about 80° (1 mm). The melting point of this sample was 125.6–125.8°.

*trans*-Stilbene used for quantum yields and some photostationary states had been zone defined by Dr. J. Hinton, Valparaiso, Fla., and used as received. It contained 0.08% *cis*-stilbene (vpc) and melted at 125.9–126.0°.

*cis*-Stilbene for use in most of the experiments described in this work was prepared and purified by Dr. K. R. Kopecky and was shown to contain 0.16% *trans*-stilbene (vpc).

Benzene (MCB analytical reagent) was stirred over sulfuric acid layers until the acid layer was not discolored, washed with distilled water, dried over potassium carbonate, and distilled from phosphorus pentoxide through a column packed with glass helices. A middle fraction, bp 79.9–80.0°, was collected. The benzene was redistilled if the phosphorus pentoxide layer was discolored during the final distillation. Benzene prepared in this way was satisfactory for use in flash photolysis and was used throughout this work.

Sensitizers were prepared and purified as previously described.<sup>31</sup>

**Determination of Photostationary States for Stilbene Isomerizations.** Several procedures were used to determine photostationary states for the sensitized isomerization of the stilbenes.

The general method was to introduce benzene solutions of the stilbenes and sensitizers in the proper concentrations into clean Pyrex tubes constricted near the top. The solutions were then degassed, sealed under vacuum, and irradiated with a 450-W Hanovia lamp housed in a quartz immersion well. A number of different filter systems were employed. Analysis of the photostationary compositions was carried out using standard vpc techniques.

Test tubes for stationary state determinations were washed with aqueous solutions of Orvus, scrubbed carefully with a test tube brush, rinsed many times with distilled water, and dried several

(30) *E.g.*, G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **38**, 1187 (1963).

(31) For purification of thioxanthone *cf.* ref 2; for others *cf.* ref 2, 12, and 17 and W. G. Herkstroeter, Ph.D. Thesis, California Institute of Technology, Pasadena, 1966.

hours in the oven at 110°. Tubes prepared in this way were wet entirely by a single drop of water. The outsides of sealed tubes were washed previous to irradiation.

All samples were degassed using a vacuum line which achieved a pressure of  $<5 \times 10^{-4}$  mm. Three freeze-thaw cycles were used with cooling in liquid nitrogen.

Irradiations of samples were carried out using the "merry-go-round."<sup>15</sup> Several different filter systems were employed: (a) 366-nm filter (this was a Corning filter which transmitted about 20% of the incident irradiation at 365 nm (band width  $\sim 10$  nm) and effectively no irradiation at other wavelengths); (b) uranium glass filter (this filter was constructed of 0.25-cm thick uranium glass and transmitted only wavelengths longer than 340 nm; its use was equivalent to using the 366-nm filter); (c) Pyrex filter (this filter was a 0.25-cm thick sheet of Pyrex and transmitted about 1% of the light at 280 nm, 75% at 334 nm, and  $>90\%$  at 366 nm).

Determinations of stilbene isomer compositions at the photostationary states were made by vpc analysis using either a Loenco Model 15B vpc with a thermal conductivity detector or a Loenco Model 70B with dual flame ionization detectors. In both cases equimolar solutions of the stilbenes gave peaks with relative areas  $\sim 1:1$  and results obtained with either vpc agreed with those obtained by Saltiel<sup>6,9</sup> using spectrophotometric analysis. Periodic checks were run to insure that the detector responses were invariant with time and linear for all attenuations. The system used for this purpose was the photostationary state mixture obtained with 0.05 *M* stilbene and 0.05 *M* benzophenone. In every case the photostationary states were approached from both sides and duplicate samples were measured at 1-day intervals in the irradiation to insure that the actual stationary composition had been reached.

The uncertainties given in the analytical measurement of the percent *cis* represent only the precision of the vpc analysis (average of three or more determinations) and obviously do not measure the real errors in the determinations. Because of this fact several of the stationary states were redetermined; in these cases duplicate values are reported. In every case investigated the average values of two determinations differed by less than the measured uncertainty in either value.

In cases where the sensitizer, because of retention time comparable to that of the stilbenes, interfered with analysis of the stationary state, the reaction mixtures were chromatographed on alumina with benzene as eluent. Since the offending sensitizers were generally ketones it was usually sufficient to continue the chromatography until no more stilbene was eluted, and then analyze the combined fractions containing stilbene. This procedure was tried on several sensitizers for which the sensitizer did not interfere with vpc analysis and the same stationary states were obtained before and after the alumina chromatography.

**Indirect Determination of Photostationary States.** To permit measurement of stilbene photostationary states for sensitizers which did not absorb sufficiently well at long wavelengths ( $>340$  nm), the following indirect technique was employed. Solutions in

benzene were prepared to be 0.05 *M* in benzophenone (or 1.0 *M* in acetophenone), 0.1 to 0.2 *M* in the intended sensitizer, and 0.005 *M* in total stilbenes. Preparation, irradiation, and analysis of these solutions were then accomplished as described in the previous section.

**Determination of Quantum Yields. A. Preparation of Samples.** Benzene solutions of the stilbene and appropriate sensitizer were delivered by calibrated syringe into constricted Pyrex test tubes surmounted by a grease trap and ground glass joint by which the tube was attached to the vacuum line. The grease trap consisted of a glass partition broken only by a small opening in the center.

Three degassing procedures were used. In a few cases tubes without the grease traps were degassed by the procedures previously described for photostationary state determinations. A second procedure involved degassing by three freeze-thaw cycles on the vacuum line used for flash photolysis experiments, but without the diffusion pump. The third method was the best. The vacuum line used for method two was used with the diffusion pump, giving ultimate vacuums of  $0.5\text{--}1.0 \times 10^{-6}$  mm. Three freeze-thaw cycles with the forepump were followed by three freeze-thaw cycles with the diffusion pump.

**B. Irradiation of Samples.** Considerable care was taken to ensure that the solutions for quantum yield measurements were not exposed to light except during the desired period of irradiation. For measurement of quantum yields for the sensitized reaction alone, irradiation was with a 450-W Hanovia medium pressure mercury arc through Corning 737 and 052 filters. This filter system admits only a narrow band of light of wavelengths equal to  $365 \pm 5$  nm and has been described elsewhere.<sup>4</sup>

The irradiations were carried out in the "quantum yield merry-go-round" which ensured equivalent radiation of each sample.<sup>15</sup> To simplify calculations and permit accurate, direct comparisons of results, as many determinations as possible were carried out at one time. Checks were run to insure that the values so obtained allowed repetition.

**Actinometry for Quantum Yields.** For all measurements potassium ferrioxalate actinometry was used to determine the quantum yield for the isomerization of *trans*-stilbene sensitized by benzophenone; then all the other measurements were made by comparison with this system.

**Analysis of Quantum Yield Data.** Two aliquots of each solution for a particular determination, occasionally three, were analyzed on a Loenco dual flame vpc with integrating recorder as described earlier. Corrections were made for back reaction using the equation derived by Lamola.<sup>8</sup> The errors reported represent precision limits of the analysis of the stilbene solutions by vpc and do not, therefore, necessarily represent the actual errors in the measurement.

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