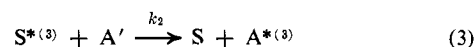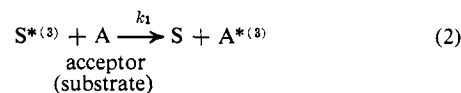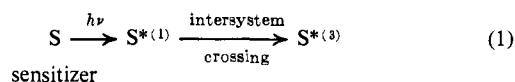# Physical and Inorganic Chemistry

Mechanisms of Photochemical Reactions in Solution. XXXIX.[1] Study of Energy Transfer by Kinetic Spectrophotometry

William G. Herkstroeter[2] and George S. Hammond

Contribution No. 3320 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California. Received April 11, 1966

Abstract: Conventional flash techniques are used to measure the acceleration of the decay of various sensitizer triplets in the presence of energy acceptors. An extensive study has been made of the stilbenes and 1,2-diphenylpropenes as acceptors. The results are correlated with those obtained earlier in studies of the photosensitized cis–trans isomerization of the same substrates. The reactivity in energy transfer remains remarkably high with these substrates even when the triplet excitation energy of the sensitizer is insufficient to produce any known optical transition of the substrates. The result is in good agreement with the hypothesis that flexible molecules can undergo "nonvertical" transitions to produce twisted geometric forms directly.

We have recently published an account of quantitative studies of several photosensitized cis–trans isomerization reactions.[3] Study of the relative rates of isomerization of the members of isomeric pairs as a function of the nature of the sensitizers yielded results not in accord with the simplest theory of energy transfer. Several speculative interpretations were advanced as extensions of the theory. Some of the proposals have since been found to be untenable,[4] but the most important, the notion that energy transfer can be synchronous with substantial distortion of the geometry of the ground state of the acceptor, has been fruitfully extended.[5-8] In all the work reported up to this time we have focused attention upon the rates of appearance of photoproducts and discussed the results in terms of the following, idealized mechanism.

$$S \xrightarrow{h\nu} S^{*(1)} \xrightarrow[\text{crossing}]{\text{intersystem}} S^{*(3)} \qquad (1)$$

$$\text{sensitizer}$$

$$S^{*(3)} + A \xrightarrow{k_1} S + A^{*(3)} \qquad (2)$$

$$\text{acceptor}$$
$$\text{(substrate)}$$

$$S^{*(3)} + A' \xrightarrow{k_2} S + A^{*(3)} \qquad (3)$$

$$A^{*(3)} \xrightarrow{k_3} A \qquad (4)$$

$$A^{*(3)} \xrightarrow{k_4} A' \qquad (5)$$

In the cases to be discussed, A and A' are cis–trans isomers and the mechanism is formulated as involving decay from a single excited state $A^{*(3)}$. Two or more excited triplets of the substrate could be fitted into the mechanism as long as rapid interconversion of the triplets is assumed. Perhaps the most desirable approach to study of the details of the reaction would be by direct observation of the excited triplet(s) of the substrate, $A^{*(3)}$. However, we have not been able to observe these species by any of the commonly available techniques.[9] The negative results probably indicate

(1) Part XXXVIII: P. J. Wagner and G. S. Hammond, J. Am. Chem. Soc., **88**, 1245 (1966).

(2) National Science Foundation Predoctoral Fellow, 1961–1965.

(3) G. S. Hammond, et al., J. Am. Chem. Soc., **86**, 3197 (1964).

(4) L. M. Coyne, D. Valentine, and J. N. Howell, unpublished results.

(5) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, J. Am. Chem. Soc., **86**, 2532 (1964).

(6) J. R. Fox and G. S. Hammond, ibid., **86**, 4031 (1964).

(7) G. S. Hammond, N. J. Turro, and R. S. H. Liu, ibid., **87**, 3406 (1965).

(8) R. S. Cole and G. S. Hammond, ibid., **87**, 3256 (1965).

(9) We have tried to use triplet–triplet absorption, emission spectroscopy, and esr spectrometry.

that the lifetimes of triplets of olefinic compounds are very short.[10]

Still another means of studying the system is provided by detection and monitoring of the sensitizer triplets, $S*^{(3)}$. Flash spectrophotometry, in which molecules are excited by an intense pulse of light followed by direct observation of the decay of the longer-lived excited states, has become a standard technique for such studies.[11] This paper reports a systematic study of the quenching of various sensitizer triplets by two pairs of substrates, the stilbenes and the 1,2-diphenylpropenes, which have shown especially interesting behavior in sensitized isomerization reactions.

Results

The decay of triplet states in solution follows the empirical equation[12-14]

$$-\frac{d[T]}{dt} = k_1[T] + k_2[T]^2 \qquad (6)$$

The significance of the measured rate constants is not simple. Reported values of first-order rate constants vary widely. In general, exhaustive purification of the solvent leads to decreases in measured rate constants of several orders of magnitude. Livingston[15,16] has presented strong evidence that the first-order term is actually the sum of at least two terms. The first is independent, or nearly independent, of temperature and viscosity and corresponds to the true unimolecular decay rate, radiative, and nonradiative. The second term varies with temperature and viscosity and appears to be due to interaction with adventitious quenchers such as oxygen. In order to keep the rate of quenching by oxygen within reason, it is necessary to remove oxygen extensively from solution. The addition of a quencher increases the first-order term as long as the concentration of the quencher remains constant during a run. A small contribution to triplet decay may also come from the self-quenching reaction.

$$S*^{(3)} + S \xrightarrow{k_5} 2S \qquad (7)$$

Self-quenching leads to surprisingly complex kinetics, because decay of the excited state increases the concentration of ground-state molecules. If [S⁰] is set equal to the sum of [S] plus [S*$^{(3)}$], the destruction of triplets by reaction 7 can be shown to include a term involving pseudo-second-order dependence of [S*$^{(3)}$].

$$-\frac{d[S*^{(3)}]}{dt} = k_5[S^0][S*^{(3)}] - k_5[S*^{(3)}]^2 \qquad (8)$$

Consequently, the experimental value of k_1 is interpreted by

$$k_1 = k_1^0 + k_1* + k_Q[Q] + k_5[S^0] \qquad (9)$$

where k_1^0 = natural decay constant, k_1* = quenching

by adventitious impurities, and k_Q = rate constant for energy transfer to added quencher.

Although self-quenching makes a small negative contribution, the second-order term is primarily a measure of the rate of triplet–triplet annihilation,[17,18] (eq 10). In this expression $S*^{(1)}$ is an excited singlet

$$2S*^{(3)} \xrightarrow{k_6} S*^{(1)} + S \qquad (10)$$
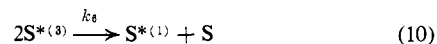
state formed by energy transfer from one sensitizer triplet to another. This excited singlet may then return to the ground state either directly or via the lowest triplet state. The rate constant, k_2, can then be written as the difference between k_6 and k_5.

$$k_2 = k_6 - k_5 \qquad (11)$$

Oscillographs recording the disappearance of triplet–triplet absorption spectra were analyzed by the method of Linschitz and Sarkanen[19] in which absorbance readings are used directly to evaluate k_1 and a second-order coefficient, β, which is proportional to k_2.[20] Since β depends upon the extinction coefficient of the absorbing species, the value varies with wavelength, and the first-order coefficient should vary with the concentration of the sensitizer. Trial studies with several substances showed sensitivity of the measured coefficients to the variables mentioned. The data shown in Table I for the decay of fluorenone triplets are representative.

Table I. Decay of Fluorenone Triplets in Benzene[a] Solution

Fluorenone concn, $M \times 10^5$	Analytical wavelength, A	k_1, 10^{-3} sec^{-1}	β, 10^{-4} sec^{-1}
4.0	6600	3.9	18
	6200	3.4	18
	5800	5.3	17
	5400	6.3	25
	5100	5.2	19
	4800	4.0	9.5
	4600	3.6	5.3
	4465	4.5	5.0
	4400	3.1	4.7
	4300	4.6	4.4
	4200	4.6	4.9
	4100	4.8	4.9
	4050	4.1	5.7
100	5800	10	15
	4800	6.4	8.7
	4465	8.1	4.4
	4400	7.1	3.5

[a] Benzene purified by conventional acid wash; see Experimental Section.

Although it may appear that the allocations of the variations of observed rates of change of absorbance to the first- and second-order terms are not perfect, it should be noted that experimental error is large, especially at wavelengths longer than 4600 A where the absorption intensity is weak and the decay has a large second-order contribution. In subsequent measurements reported here, the decay of triplet–triplet absorption of various

(10) W. J. Potts, J. Chem. Phys., 23, 65 (1955).
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(12) G. Porter and M. R. Wright, Discussions Faraday Soc., 27, 18 (1959).
(13) G. Jackson, R. Livingston, and A. Pugh, Trans. Faraday Soc., 56, 1635 (1960).
(14) H. Linschitz and L. Pekkarinen, J. Am. Chem. Soc., 82, 2411 (1960).
(15) R. Livingston and W. R. Ware, J. Chem. Phys., 39, 2593 (1963).
(16) G. Jackson and R. Livingston, ibid., 35, 2182 (1961).

(17) H. Sternlicht, G. C. Niemann, and G. W. Robinson, ibid., 38, 1326 (1963).
(18) C. A. Parker, Proc. Roy. Soc. (London), A276, 125 (1963).
(19) H. Linschitz and K. Sarkanen, J. Am. Chem. Soc., 80, 4826 (1958).
(20) $\beta = k_2/\epsilon l$ where ϵ is the extinction coefficient for triplet–triplet absorption and l is the optical path length.

Table II. Summary of Data for Quenching of Anthracene Triplets by Azulene in Benzene[a] Solution

Anthracene concn, M	Azulene concn, M	k_1, sec^{-1}	β, sec^{-1}	k_Q, M^{-1} sec^{-1}
4.0×10^{-5}	None	$1.0 \pm 0.1 \times 10^3$	$7 \pm 1 \times 10^3$	
4.0×10^{-5}	2.0×10^{-6}	$1.6 \pm 0.1 \times 10^4$	$9 \pm 3 \times 10^3$	$7.5 \pm 0.5 \times 10^9$

[a] Benzene purified by conventional acid wash; see Experimental Section.

sensitizers was monitored at a wavelength where the absorption intensity is near maximum.

Variations in first-order terms in the triplet decay of any particular sensitizer were frequently observed with different solutions of the sensitizer, and were believed due to small differences in solvent purity and the extent of oxygen removal from one run to another. In order to have a reliable reference for the first-order decay term, a sample with sensitizer alone was prepared simultaneously and under the same experimental conditions with each groups of cells containing that sensitizer and added quenchers.

The increase in the first-order rate constants upon addition of known amounts of quenchers can be measured more accurately than the parameters for decay in the absence of added quenchers. This improvement in precision arises simply from the fact that quenching by the additive can usually be made the dominant decay process. Table II shows a summary of the results obtained in a series of measurements of the quenching of anthracene triplets by azulene. The value of the quenching constant is in good agreement with that reported by Ware[21] for the same process.

The Stilbenes. The first step in the investigation was an attempt to detect stilbene triplets themselves by triplet–triplet absorption. No transient absorption could be found in the region 3420–5790 A after flashing solutions containing 1×10^{-2} and 2×10^{-4} M trans-stilbene in benzene. In similar experiments with cis-stilbene a transient absorbing in the region 4200–4900 A was found with a lifetime greater than 5 sec. This species is almost certainly the dihydrophenanthrene, first detected by Moore, Morgan, and Stermitz.[22] The intensity of absorption by the transient was increased only slightly by increasing the intensity of the flash or the concentration of cis-stilbene, confirming our belief that the compound is destroyed in a photochemical reaction.[3] We also attempted to develop spectra of stilbene triplets using fluorenone as a sensitizer. A filter solution containing trans-stilbene was used to prevent direct excitation of the stilbenes. After flashing, the spectrum was scanned from 4150 to 6000 A. The concentrations of stilbenes (10^{-2} M) was high enough to quench all triplet–triplet absorption by the the sensitizer but no absorption attributable to stilbene triplets appeared with either isomer. The results are not surprising since Porter[23] was also unable to detect stilbene triplets. In addition, kinetic arguments[3] have been used to adduce the conclusion that stilbene triplets are very short lived.

The short lifetime of the stilbene triplets, although somewhat frustrating, offers considerable advantages in the type of study reported in this paper. For example, when measuring the rate of triplet energy transfer from sensitizer to stilbene, analysis of the rate of disappearance of triplet–triplet absorption cannot be complicated by simultaneous, overlapping absorption of stilbene triplets.[25] Furthermore, we can assume that the total concentration of quenching species (cis plus trans) remains constant throughout the monitoring phase of the flash experiments. Perhaps most significant is the fact that energy transfer from stilbene triplets to sensitizer, the reverse of eq 2 and 3, does not enter into the kinetic scheme.[26]

Sensitizers having high triplet excitation energies transfer energy to the stilbene isomers with rate constants of the order of 5×10^9 M^{-1} sec^{-1}. Consequently, it was necessary to use stilbene concentrations of the order of 10^{-5} M in order to keep the decay rates of the sensitizer triplets in the region where accurate measurements could be made. Under these circumstances it was questionable whether isomeric purity in stilbene persisted after only one flash. Except where it is indicated that rate constants were measured by assuming maintenance of initial concentration conditions (pure cis or trans isomers), the kinetic measurements were made after a number of flashes to ensure establishment of stationary conditions. The kinetic parameters measured and quenching constants derived from them, for high-energy sensitizers, are shown in Table III. In calculating the rate constants for the individual isomers, we assumed that triphenylene and thioxanthone triplets transfer energy equally efficiently to the two isomers. In the remaining cases in which measurements were made at the photostationary state, we assumed that the composition of the stationary state is determined by the excitation ratio,[3] (k_1/k_2), and evaluated the individual rate constants accordingly. The same rate of quenching was achieved in solutions prepared initially from either pure cis- or pure trans-stilbene, thus indicating that a common state had been reached. Many of these solutions were concentrated by evaporation and analyzed by vapor chromatography. The cis/trans ratios found were in reasonable agreement with previously reported, stationary-state values.[3]

With sensitizers having excitation energies between 47 and 53 kcal/mole, we obtained quenching rates for initial conditions with each isomer and at the stationary states. The results are summarized in Table IV.

The rates of quenching of sensitizers having excitation energies below 47 kcal/mole were small. Consequently, large amounts of the stilbene isomers had to be used to obtain satisfactory values of the quenching constants and it was not attempted to flash the solutions a sufficient number of times to bring the systems to stationary

(21) W. R. Ware, *J. Chem. Phys.*, 37, 923 (1963).
(22) W. M. Moore, D. D. Morgan, and F. R. Stermitz, *J. Am. Chem. Soc.*, 85, 829 (1963).
(23) Unpublished results quoted in ref 24.
(24) D. Schulte-Frohlinde, H. Blume, and H. Güsten, *J. Phys. Chem.*, 66, 2486 (1962).

(25) It is also important to note that no dihydrophenanthrene[3,22] is formed when cis-stilbene is activated by energy transfer.
(26) A detailed presentation of the complications introduced by reversible energy transfer is given by Sandros.[27]
(27) K. Sandros, *Acta Chem. Scand.*, 18, 2355 (1964).

Table III. Quenching of High-Energy Triplets by the Stilbenes[a,b]

Sensitizer (E_T)[c]	Sensitizer concn, M $\times 10^6$	Stilbenes concn, M $\times 10^6$	Stilbene isomer initially present	k_1, 10^{-3} sec^{-1}	$k_{Q\ cis}$, 10^{-8} M^{-1} sec^{-1}	$k_{Q\ trans}$, 10^{-8} M^{-1} sec^{-1}
Triphenylene (66.6)	40	None	...	1.6 ± 0.3	...	...
		8.6	cis	59 ± 1	66	66
		5.0	trans	40 ± 2	76	76
Thioxanthone (65.5)	60	None[d]	...	13 ± 1	...	...
		5.4[d]	cis	39 ± 1	48	48
		5.0[d]	trans	39 ± 2	52	52
Phenanthrene (61.8)	60	None	...	9.0 ± 0.3	...	...
		8.6	cis	32 ± 1	40	49
		5.0	trans	28 ± 1	36	43
2-Acetonaphthone (59.3)	40	None	...	3.3 ± 0.2	...	...
		8.6	cis	35 ± 2	33	47
		5.0	trans	23 ± 2	35	51
1-Naphthyl phenyl ketone (57.5)	40	None	...	1.1 ± 0.1	...	...
		8.6	cis	27 ± 2	25	43
		5.0	trans	17 ± 1	27	46
	100	None[d]	...	1.8 ± 0.3	...	...
		11[d]	cis	36 ± 3	26	44
		10[d]	trans	54	...	52[f]
		None	...	1.6 ± 0.2	...	...
		11	cis	32 ± 2	23	39
		10	trans	30 ± 2	24	40
Chrysene (56.6)	40	None	...	2.0 ± 0.3	...	...
		11[d]	cis	35 ± 2	24	49
		10[d]	trans	58 ± 1	...	56[f]
		11	cis	36 ± 3	25	50
		10	trans	34 ± 2	26	51
Fluorenone (53.3)	40	None	...	3.0 ± 0.4	...	...
		22	cis	29 ± 2	8.7	33
		10	trans	17 ± 1	10	38
	200	None[e]	...	6.3 ± 0.3	...	...
		22[e]	cis	34 ± 3	9.3	36
		10[e]	trans	19 ± 1	9.3	36

[a] Benzene solution, trans-stilbene sample no. 1 (see Experimental Section). [b] Rates in the presence of sensitizers were in each case measured in experiments parallel to those without sensitizer listed immediately above in the table. [c] E_T is the excitation energy of the sensitizer triplet; a discussion of these energy values follows. [d] The outer jacket of the absorption cell was filled with a solution (6 mm thick) of 2.1 $\times 10^{-3}$ M trans-stilbene in benzene. [e] A solution of 1.2 $\times 10^{-4}$ M trans, trans-1,4-diphenyl-1,3-butadiene in benzene was used as a filter. [f] Calculated on the assumption that initial concentration conditions are maintained.

states. Results obtained with low-energy sensitizers are shown in Table V. Since the quenching activity of the stilbenes toward low-energy sensitizers is small, one can readily conceive of obtaining entirely spurious results if the stilbene samples contained even small amounts of active quenchers as impurities. This possi-
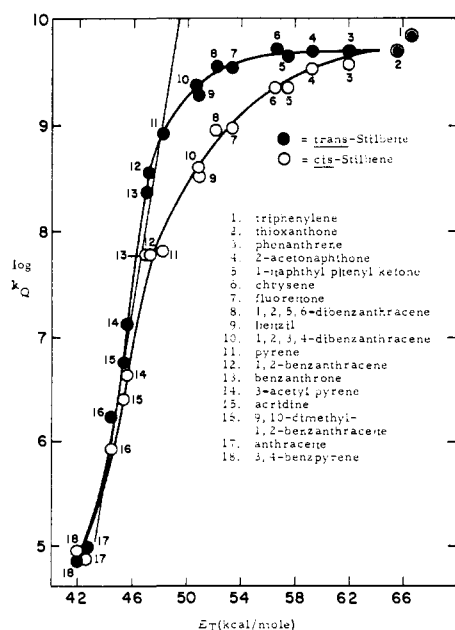

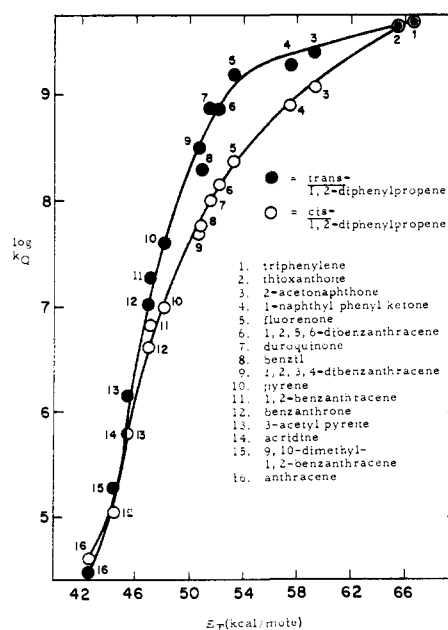Figure 1. Rate constants for quenching of sensitizers by the stilbenes.

Figure 2. Rate constants for quenching of sensitizers by the 1,2-diphenylpropenes.

Table IV. Quenching of Triplets Having Intermediate Excitation Energies[a]

Sensitizer (E_T)	Sensitizer concn, $M \times 10^6$	Stilbenes concn, $M \times 10^6$	Original isomer	k_1, 10^{-3} sec^{-1}	$k_{Q\ cis}$, 10^{-8} M^{-1} sec^{-1}	$k_{Q\ trans}$, 10^{-8} M^{-1} sec^{-1}
1,2,5,6-Dibenzanthracene (52.2)	40	None	...	0.73	...	...
		27[b]	cis	33[e]	8.4	35
		15[b]	trans	21[e]	9.4	39
		None[b]	...	0.82	...	...
		27[b]	cis	26[f]	9.3	...
		10[b]	trans	33[f]	...	32
		27[b]	cis	33[e]	8.4	35
		10[b]	trans	12[e]	7.8	33
Benzil (50.9)	1000	None[b]	...	17	...	...
		43[b]	cis	35[e]	2.8	20
		50[b]	trans	39[e]	2.9	21
	100	None[c]	...	17	...	...
		54[c]	cis	31[f]	5.7	...
		50[c]	trans	87[f]	...	17
		54[c]	cis	37[e]	2.5	18
		50[c]	trans	36[e]	2.5	18
1,2,3,4-Dibenzanthracene (50.8)	100	None[b]	...	1.2	...	...
		54[b]	cis	23[f]	4.1	...
		None[c]	...	1.1	...	...
		15[c]	trans	29[f]	...	19
		54[c]	cis	31[e]	3.8	24
		15[c]	trans	10[e]	4.1	26
Pyrene (48.2)	40	None	...	0.65	...	...
		86[d]	cis	7.5[f]	0.79	...
		50[d]	cis	10[e]	0.69	8.1
		86[d]	trans	8.0[e]	0.95	11
	500	None[b]	...	0.32	...	...
		110[b]	cis	5.0[f]	0.43	...
		None[c]	...	0.12	...	...
		25[c]	trans	28[f]	...	11
		110[c]	cis	7.4[e]	0.37	4.3
		25[c]	trans	3.6[e]	0.62	7.4
1,2-Benzanthracene (47.2)	40	None	...	0.22	...	...
		86[c]	cis	6.5[f]	0.73	...
		86[c]	cis	7.6[e]	0.59	3.3
		50[c]	trans	5.1[e]	0.67	3.8
		None[b]	...	0.35	...	...
		110[b]	cis	6.5[f]	0.55	...
		50[b]	trans	22[f]	...	4.2
		110[b]	cis	9.2[e]	0.55	3.1
		50[b]	trans	4.7[e]	0.59	3.3
Benzanthrone (47.0)	40	None	...	0.73	...	...
		220	cis	13[f]	0.55	...
		150	trans	27[f]	...	1.7
		220	cis	19[e]	0.58	2.4
		150	trans	16[e]	0.71	3.0

[a] See footnotes to Table III. [b] trans,trans-1,4-Diphenyl-1,3-butadiene (1.2 × 10^{-4} M) in benzene as a filter. [c] trans-Stilbene (2.1 × 10^{-3} M) in benzene as a filter. [d] trans-Stilbene (1.4 × 10^{-4} M) in benzene as a filter. [e] Rates measured after repeated flashing. [f] Rates measured after first flash.

bility was studied by using four different samples of trans-stilbene as quenchers for anthracene. Each stilbene sample has been carefully purified but by significantly different procedures. The same results, within normal experimental error, were obtained with all four samples.

1,2-Diphenylpropenes. The cis and trans isomers of 1,2-diphenylpropene (α-methylstilbene) were studied in virtually the same way as the stilbenes. The values for quenching constants obtained with various sensitizer triplets are summarized in Table VI. The kinetic results are not reported in detail since they are in all respects similar to those reported for the stilbenes.

The results can be best summarized graphically, as has been done in Figures 1 and 2. When a sensitizer triplet has insufficient excitation energy to promote an acceptor to its triplet state, one might expect that the energy deficiency would be supplied as an activation energy. The decrease in transfer efficiency as a function

of the excitation energy of the sensitizer would then be given by

$$\frac{\Delta \log k}{\Delta E_T} = -\frac{1}{2.303RT} \quad (12)$$

The straight line drawn through the data for trans-stilbene in Figure 1 has the slope indicated by eq 12. Obviously the simple theory for endothermic energy transfer predicts the decrease in reactivity adequately for that acceptor. The best spectroscopic value for the vertical excitation energy of trans-stilbene is about 50 kcal per mole,[28, 29] so the decrease in rate also begins, as would be anticipated, with sensitizers having excitation energies a little more than 50 kcal/mole. trans-Stilbene is, therefore, tentatively regarded as a "classical" acceptor. Figure 3 shows the comparison between

(28) D. F. Evans, J. Chem. Soc., 1351 (1957).
(29) R. H. Dyck and D. S. McClure, J. Chem. Phys., **36**, 2326 (1962).

Table V. Quenching of Low-Energy Triplets[a]

Sensitizer (E_T)	Sensitizer concn, $M \times 10^6$	Stilbene concn, $M \times 10^6$	Original isomer	k_1, 10^{-3} sec^{-1}	$k_{Q\ cis}$, 10^{-8} M^{-1} sec^{-1}	$k_{Q\ trans}$, 10^{-8} M^{-1} sec^{-1}
3-Acetylpyrene (45.5)	40	None	...	0.69	...	...
		6100[b]	cis	26	0.043	...
		3000[b]	trans	39	...	0.13
	500	None[c]	...	0.80	...	...
		3000[c]	trans	43	...	0.14
	5000	None[c]	...	0.99	...	...
		3000[c]	trans	42	...	0.14
Acridine (45.3)	40	None	...	2.5	...	...
		5900[b]	cis	17	0.025	...
		3000[b]	trans	20	...	0.058
9,10-Dimethyl-1,2-benzanthracene (44.3)	40	None[c]	...	0.62	...	...
		9400[c]	cis	8.7	0.0086	...
		8000[c]	trans	14	...	0.016
Anthracene (42.6)	40	None[c]	...	2.7	...	...
		21000[c]	cis	4.3	0.00076	...
		40000[c]	trans	6.6	...	0.00097
		None[c]	...	1.5	...	...
		40000[c]	trans	6.3	...	0.0012
		40000[c,d]	trans	5.4	...	0.00098
		40000[c,e]	trans	5.8	...	0.0011
		32000[c,f]	trans	4.9	...	0.0011
3,4-Benzpyrene (41.9)	40	None[c]	...	0.72	...	...
		39000[c]	cis	4.1	0.00087	...
		40000[c]	trans	3.7	...	0.00075

[a] See footnotes to Table III; trans-stilbene was sample no. 1 except where otherwise noted. [b] Filter was 1.4×10^{-4} M trans-stilbene in benzene. [c] Filter was 1.2×10^{-4} M trans,trans-1,4-diphenyl-1,3-butadiene in benzene. [d] Stilbene sample no. 2. [e] Stilbene sample no 3. [f] Stilbene sample no. 4.

trans-stilbene and another classical acceptor, biacetyl, which was studied by Sandros[27] using the sensitized phosphorescence of biacetyl.
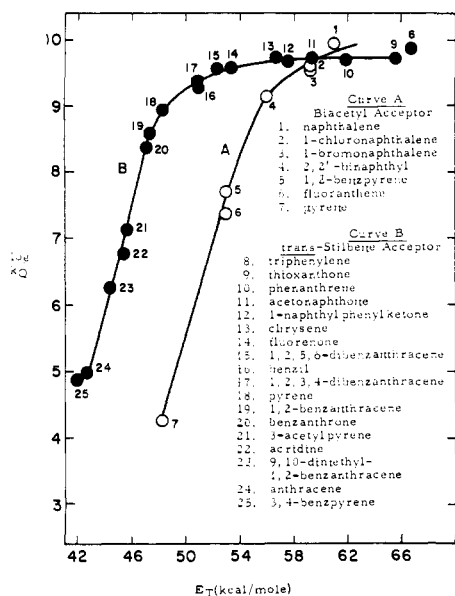

Figure 3. Comparison of rate constants for triplet transfer to biacetyl and to trans-stilbene.

cis-Stilbene has a vertical excitation energy of 57 kcal/mole.[29] The first decrease in excitation energy is unexceptional, but it is obvious that the behavior of the compound with sensitizers having excitation energies between 42 and 58 kcal/mole is definitely nonclassical. As was inferred from the study of stationary states,[3] energy transfer to cis-stilbene remains remarkably efficient even with sensitizers that are apparently

Table VI. Quenching of Sensitizer Triplets by cis- and trans-1,2-Diphenylpropene[a]

Sensitizer (E_T)	$k_{Q\ cis}$, 10^{-9} M^{-1} sec^{-1}	$k_{Q\ trans}$, 10^{-9} M^{-1} sec^{-1}	Basis of calculation[b]
Triphenylene (66.6)	5.0	5.0	PSS
Thioxanthone (65.5)	4.5	4.5	PSS
2-Acetonaphthone (59.3)	1.2	2.6	PSS
1-Naphthyl phenyl ketone (57.5)	0.78	1.9	PSS
	0.73	...	PI
Fluorenone (53.3)	0.23	1.6	PSS
	0.27	...	PI
1,2,5,6-Dibenzanthracene (52.2)	0.15	0.78	PSS
	0.15	0.73	PI
Duroquinone (51.6)	0.099	0.75	PSS
Benzil (50.9)	0.055	0.21	PSS
	0.058	0.20	PI
1,2,3,4-Dibenzanthracene (50.8)	0.049	0.32	PSS
	0.056	0.32	PI
Pyrene (48.2)	0.011	0.044	PSS
	0.0081	0.033	PI
1,2-Benzanthracene (47.2)	0.0066	0.0171	PI
Benzanthrone (47.0)	0.0043	0.0101	PI
3-Acetylpyrene (45.5)	0.00065	0.00141	PI
Acridine (45.3)	0.00066	0.00065	PI
9,10-Dimethyl-1,2-benzanthracene (44.3)	0.00011	0.00019	PI
Anthracene (42.6)	0.000042	0.000029	PI

[a] Benzene solution; see footnotes to Table III. [b] PSS indicates that the kinetic measurement was made at the stationary state; PI indicates that the rate was measured after the first flash in solutions originally containing a pure isomer.

deficient in energy by more than 10 kcal/mole. The previously suggested explanation that cis-stilbene undergoes a nonvertical transition to a twisted form continues to be an attractive explanation of the nonclassical behavior.
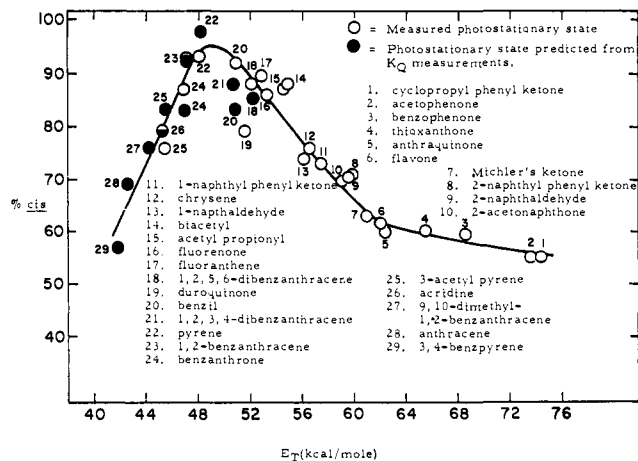
Figure 4 legend:

O = Measured photostationary state
● = Photostationary state predicted from KQ measurements.

1. cyclopropyl phenyl ketone
2. acetophenone
3. benzophenone
4. thioxanthone
5. anthraquinone
6. flavone
7. Michler's ketone
8. 2-naphthyl phenyl ketone
9. 2-naphthaldehyde
10. 2-acetonaphthone
11. 1-naphthyl phenyl ketone
12. chrysene
13. 1-napthaldehyde
14. biacetyl
15. acetyl propionyl
16. fluorenone
17. fluoranthene
18. 1,2,5,6-dibenzanthracene
19. duroquinone
20. benzil
21. 1,2,3,4-dibenzanthracene
22. pyrene
23. 1,2-benzanthracene
24. benzanthrone
25. 3-acetyl pyrene
26. acridine
27. 9,10-dimethyl-1,2-benzanthracene
28. anthracene
29. 3,4-benzpyrene

E_T(kcal/mole)

Figure 4. Measured and predicted photostationary states for the stilbenes.

Figure 5 legend:

1. acetophenone
2. benzophenone
3. 9,10-anthraquinone
4. Michler's ketone
5. 2-acetonaphthone
6. 1-naphthyl phenyl ketone
7. fluorenone
8. 1,2,5,6-dibenzanthracene
9. duroquinone
10. benzil
11. 1,2,3,4-dibenzanthracene
12. pyrene
13. 1,2-benzanthracene
14. benzanthrone
15. 3-acetyl pyrene
16. acridine
17. 9,10-dimethyl-1,2-benzanthracene
18. anthracene

O = Measured photostationary state
● = Photostationary state predicted from KQ measurements

E_T (kcal/mole)

Figure 5. Measured and predicted photostationary states for the 1,2-diphenylpropenes.

The data for the diphenylpropenes, shown in Table VI and Figure 2, indicate that neither the cis nor the trans isomer is classical in its behavior. We conclude that both isomers can undergo nonvertical transitions requiring less energy input than the transitions that adhere to the Franck–Condon principle.

It is interesting to see how well the quenching constants determined by flash spectrophotometry predict stationary states, if we assume that variations in the latter are determined only by the relative reactivity of the isomeric substrates in energy transfer. Figures 4 and 5 show Saltiel plots in which data from measurements of stationary states are intermingled with predictions based upon quenching constants measured in the flash studies. The correlation is excellent. In our earlier report[3] we described two phenomena that do not appear in Figures 4 and 5. There were two minima for sensitizers of intermediate energy; 1,4-naphthoquinone and 1,4-benzoquinone, and two very low-energy sensitizers, eosin and 9,10-dibromoanthracene, gave stationary states that corresponded closely to the thermodynamic equilibrium compositions. The quinone sensitizers were not investigated by the flash method because no triplet–triplet absorption spectra could be found. Measurement of quenching constants with eosin and 9,10-dibromoanthracene was not attempted, because of the combination of very short lifetimes of sensitizer triplets and expected inefficient energy transfer to stilbene. However, other studies which will be reported in the near future[4] indicate that the significance of the anomalous points is not that originally suggested. We now regard Figures 4 and 5 as being more or less typical Saltiel plots for sensitizer–substrate systems in which there are no special effects arising from formation of strong complexes in excited states, generation of new sensitizers by photochemical reactions, transfer of singlet excitation, or production of substances that catalyze thermal isomerization.

Triplet Potential Surfaces. Adoption of the rationale presented above leads to interesting conclusions concerning the nature of the triplets reached by nonvertical excitation. The classical behavior of trans-stilbene implies that this compound can find no excitation path with energy requirements significantly lower than that for vertical excitation. Therefore, if there is a minimum in the triplet potential function when the angle of twist
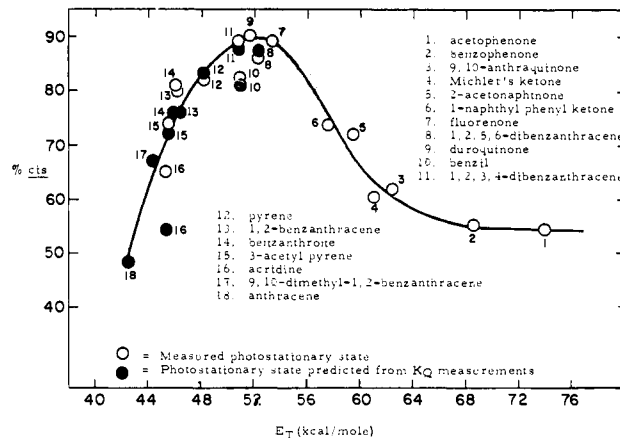
about the central bond is approximately 90°, the twisted state is probably close to isoenergetic with the planar trans configuration. On the other hand, scrutiny of Figure 2 shows that neither of the isomers of diphenyl propene behaves classically. Apparently both isomers can undergo nonvertical transition to one or more species that are at lower energy levels than the states reached by Franck–Condon transitions. Consequently, we infer that in this system a twisted triplet is more stable than either planar form. The result is reasonable since even the planar trans form is subject to substantial steric strain arising from nonbonded repulsion between the methyl group and the phenyl group that is cis to it.
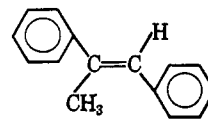
trans-1,2-diphenylpropene

Triplet Excitation Energies. The sources of triplet energies used throughout the text deserve some comment. Since all experiments were run at room temperature with benzene solvent, it would be desirable to base triplet energy assignments on phosphorescence spectra taken under the same conditions. Phosphorescence spectra are usually recorded in rigid media at low temperatures; only a limited number of sensitizers are known to phosphoresce in benzene solution. As shown in Table VII, there is, with the exception of benzil, good agreement between the energies of phosphorescence under the two different conditions. It appears that, at least for substances with $\pi-\pi^*$ lowest triplet states, triplet energy assignments from low-temperature phosphorescence spectra are good approximations to triplet energies in benzene solution. Listed in Table VIII are many of the sensitizer triplet energies used in evaluating the kinetic data along with the corresponding reference and solvent employed. The triplet energy of benzil was taken as 50.9 kcal/mole[30,31] rather than 53.7 kcal/mole,[32] because the former value was determined under experimental conditions similar to those of the kinetic measurements.

(30) See footnote h, Table VII.
(31) See footnote i, Table VII.
(32) See footnote e, Table VII.

Table VII. Phosphorescence in Rigid and Fluid Solvents

Substance	E_T,[a] kcal/ mole	Solvent	Temp	Ref
2,2'-Binaphthyl	55.9	EPA[b]	77 °K	c
2,2'-Binaphthyl	56.1	Benzene	20 °C	27
Naphthalene	60.9	MCIP[d]	77 °K	e
Naphthalene	60.8	Benzene	20 °C	27
1-Chloronaphthalene	59.2	EA[f]	77 °K	g
1-Chloronaphthalene	59.5	Benzene	20 °C	27
1-Bromonaphthalene	59.1	EA	77 °K	g
1-Bromonaphthalene	59.5	Benzene	20 °C	27
Benzil	53.7	MCIP	77 °K	e
Benzil	50.9	Benzene	20 °C	h, i

[a] Triplet energy assignments are based on the position of the 0-0 band. [b] Ether, isopentane, and ethanol, 5:5:2 by volume. [c] E. Clar and M. Zander, *Chem. Ber.*, **89**, 749 (1956). [d] Methylcyclohexane and isopentane, 5:1 by volume. [e] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964). [f] Ether and ethanol, 1:2 by volume. [g] V. Ermolaev and A. Terenin, *J. Chim. Phys.*, **55**, 698 (1958). [h] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960). [i] J. C. Dalton, B.S. Thesis, California Institute of Technology, 1964.

Table VIII. Triplet Excitation Energies of Sensitizers

Sensitizer	E_T,[a] kcal/mole	Solvent	Ref
Triphenylene	66.6	MCIP[b]	32
Thioxanthone	65.5	MCIP	32
Phenanthrene	61.8	EPA[c]	d
2-Acetonaphthone	59.3	MCIP	32
1-Naphthyl phenyl ketone	57.5	MCIP	32
Chrysene	56.6	EPA	35[e]
Fluorenone	53.3	MCIP	32
1,2,5,6-Dibenzanthracene	52.2	EPA	33[d]
1,2,3,4-Dibenzanthracene	50.8	EPA	33[d]
Pyrene	48.2	EPA	33[d]
1,2-Benzanthracene	47.2	EPA	33[d]
9,10-Dimethyl-1,2-benzanthracene	44.3	EPA	36[f]
Anthracene	42.6	EPA	37[g]
3,4-Benzpyrene	41.9[h]	Ethanol	38[i]

[a] Triplet energy assignments are based on the position of the 0-0 band in phosphorescence spectra at 77 °K. [b] Methylcyclohexane and isopentane, 5:1 by volume. [c] Ether, isopentane, and ethanol, 5:5:2 by volume. [d] See footnote c, Table VII. [e] D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949). [f] M. M. Moodie and C. Reid, *Brit. J. Cancer*, **8**, 380 (1954). [g] M. R. Padhye, S. P. McGlynn, and M. Kasha, *J. Chem. Phys.*, **24**, 588 (1956). [h] This phosphorescence spectrum was taken at 93 °K. [i] B. Muel and M. Hubert-Habart, *J. Chim. Phys.*, **55**, 377 (1958).

With some sensitizers, low-temperature phosphorescence has not been reported; consequently, other methods have been employed in making triplet energy assignments. The triplet energy of duroquinone was estimated by assuming it to be identical with the triplet energies of 2,3-dimethyl-1,4-benzoquinone and 2,5-dimethyl-1,4-benzoquinone. Singlet–triplet absorption spectra of these compounds have been obtained in *n*-heptane and have 0-0 bands at 51.6 kcal/mole.[33] Acridine was assigned a triplet energy of 45.3 kcal/mole on the basis of its singlet–triplet absorption spectrum taken with chloroform solvent in the presence of a high oxygen pressure.[34]

The triplet energies of benzanthrone and 3-acetylpyrene were not measured directly. Assignment of triplet energy values of these sensitizers is based upon

(33) A. Kuboyama, *Bull. Chem. Soc. Japan*, **35**, 295 (1962).
(34) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

Figures 1–5, where it appears that triplet energies of 47.0 kcal/mole for benzanthrone and 45.5 kcal/mole for 3-acetylpyrene are in harmony with the different plots. The assumption that sensitizer triplet energy is the controlling factor in rates of energy transfer to the geometric isomers of stilbene and 1,2-diphenylpropene is inherent in these assignments. That these triplet energies are reasonably accurate is demonstrated by the fact that 3-bromobenzanthrone and pyrene have phosphorescence 0-0 bands (77 °K) at 45.7[35] and 48.2 kcal/mole,[36] respectively.

Experimental Section

Materials. *cis*-Stilbene was prepared and purified by Dr. K. R. Kopecky. Vapor phase chromatography showed that the sample contained less than 1% *trans*-stilbene. Four different samples of *trans*-stilbene were used. Sample 1 (Matheson Coleman and Bell, Scintillation Grade) was recrystallized under nitrogen at Dry Ice temperatures, first from methanol and then from ether. It was shown by vapor chromatography to contain less than 0.70% of the *cis* isomer. Sample 2 (Matheson Coleman and Bell, Scintillation Grade) was sublimed under vacuum by Dr. J. Saltiel. Vapor chromatography indicated that the sample contained less than 0.64% of the *cis* isomer. Sample 3, from the same commercial supply, was recrystallized from ethanol and sublimed under vacuum. It was then zone refined in a sealed tube under nitrogen. Vapor chromatography indicated that the sample contained less than 0.32% *cis*-stilbene. Sample 4 (Hinton Co., zone refined) was used as received. It was stated that the starting material was Eastman, White Label Grade. Vapor chromatography showed that the sample contained less than 0.09% *cis*-stilbene. Both *cis*- and *trans*-1,2-diphenylpropene, generously supplied by Professor D. J. Cram and Dr. D. H. Hunter, were used as received. *Sensitizers* were the purest samples available from commercial suppliers and further purification was usually carried out by recrystallizations, column chromatography, vacuum sublimation, zone refining, or various combinations of these procedures.[37] Benzene (Mallinckrodt, Analytical Reagent) was purified by a procedure recommended by Dr. R. Steinmetz. Chloranil was dissolved in benzene to the extent of 2 g/l. The solution was placed in a well surrounding the quartz probe of a Hanovia immersion reactor (450-w, medium-pressure, mercury lamp). The solution was irradiated for at least a week, the brown deposits on the walls of the reactor were removed daily, and the supply of chloranil was also replenished daily. The solution was then passed over a column of active alumina and distilled from phosphorus pentoxide. The purified solvent was compared with samples purified by conventional acid washing and with a Phillips Research Grade sample specified to be 99.93% pure. Vapor chromatography indicated that the sample, purified as described, contained the fewest impurities. In preliminary flash studies of various sensitizers, it was inevitably found that the smallest values of first-order decay constants were obtained with benzene purified by irradiation with chloranil. All of the data reported in Tables III–VI were obtained using benzene purified in the manner described. Data shown in Table I and II were obtained using a sample of benzene purified by extensive acid washing followed by drying and distillation.

Procedures. The flash apparatus consisted of two xenon flash lamps (Edgerton, Germeshausen, and Grier, Model FX-45) positioned on either side of a sample cell holder inside a cylindrical, Bakelite housing. Magnesium oxide, which is reported to reflect visible and near-ultraviolet light with at least 98% efficiency,[38] coated the inner surfaces of the housing. The energy of the discharge was supplied by a Shapiro and Edwards Model 118 flash lamp pulser. The energy output was variable between 8 and 800 joules by choice of capacitance ($^1/_8$ to 4 μF in discrete levels) and voltage (12 to 20 kv). The flash returns to $^1/_3$ peak intensity within

(35) D. N. Shigorin, N. A. Shcheglova, and N. S. Dokunikhin, *Dokl. Akad. Nauk SSSR*, **137**, 1416 (1961); *Proc. Acad. Sci. USSR, Phys. Chem. Sect. (English Transl.)*, **137**, 371 (1961).
(36) See footnote f, Table VII.
(37) W. G. Herkstroeter, Ph.D. Thesis, California Institute of Technology, 1965.
(38) G. W. Robinson in "Molecular Physics (Methods of Experimental Physics)," Vol. III, D. Williams, Ed., Academic Press Inc., New York, N. Y., 1962, p 155.

15–20 μsec although a noticeable "tail" persists for as long as 100 μsec. The monitoring source was a PEK 75-w, mercury–xenon lamp, Type 1621, powered by storage batteries. This lamp was mounted on an optical bench in series with a collimating lens, the flash chamber, a focusing lens, and a Jarrell-Ash 500-mm Ebert spectrometer. The analyzing beam, after passing through the sample cell, was focused on the extrance slit of the spectrometer. Light intensity was measured by means of a Sylvania 931-A photomultiplier tube located at the exit slit of the spectrometer. The output from the phototube was fed into a cathode-follower amplifier and then into a Tektronix 531, wide-band oscilloscope. Oscillographs were photographed with a DuMont, Model 302, oscillograph-record camera. A Rutherford, Model A-4, time-delay generator was used to trigger the oscilloscope sweep prior to the discharge of the flash lamps and thus provided a reference for light intensity reaching the detector in the absence of triplet–triplet absorption. Circuitry for similar apparatus has been described in detail by Porter.[11]

The cylindrical Pyrex sample cells were 21 cm in length and had a 15-mm o.d.; flat Pyrex windows were fused to the ends. Many cells were also equipped with outer jackets for filter solutions. The annulus of the filter sleeve was 6 mm. The cells were connected by side arms to bulbs where solutions were placed during the degassing procedure. The cells were cleaned with soap solutions and rinsed repeatedly with distilled water prior to use.

Solutions were degassed by attachment to a vacuum manifold equipped with a pumping system capable of evacuation to 10^{-7}–10^{-6} mm. Dow-Corning, high-vacuum, silicone grease was used to lubricate all joints and stopcocks. Samples were frozen to the temperature of liquid nitrogen, evacuated, isolated from the system during a thawing cycle, and then refrozen, and again pumped down. The cells were sealed after five freeze–pump–thaw cycles.

Despite the inclusion of a light baffle in the chamber, stray light from the flash lamps sometimes caused problems in experiments with short-lived triplets. In this respect, it was advantageous to monitor the experimental solution at the wavelength of a principal mercury line whenever this occurred near the maximum of sensitizer triplet-triplet absorption. At these wavelengths, the emission from the monitoring source was considerably more intense, so that the signal to stray light ratio was greater. Stray light was rarely a problem in measurement of transient lifetimes greater than 100 μsec.

The oscillograph transparencies were enlarged with a slide projector and the images were traced and measured. Since the response of the photoelectric detector was linear over the range of light intensities employed, the data for absorbance of the sensitizer triplets were analyzed by the method of Linschitz and Sarkanen.[19] In practice, this operation was performed by an IBM 7090 computer which gave best values for the coefficients of first- and second-order terms.

Whenever the absorption characteristics of the sensitizers were appropriate, filter solutions were used to prevent direct excitation of the olefinic substrates by the excitation flash. Table IX gives the critical characteristics of filter solutions used.

Table IX. Filter Solutions

Solution no.	Solute[a]	Concn, M	Wavelength, A[b]
1	trans-Stilbene	1.4×10^{-4}	3300
2	trans-Stilbene	2.1×10^{-3}	3380
3	trans,trans-1,4-Diphenyl-1,3-butadiene	1.2×10^{-4}	3610

[a] Benzene solutions. [b] Below which A (absorbance) > 2 for 1 cm of solution.

Because the absorbing solutes undergo photoisomerization, absorption by the filter solutions changes with time so each solution was used for only a few flashes. The light from the monitoring source was passed through a Corning 3060 glass color filter, mounted on the optical bench to prevent excitation of the quenchers during the kinetic measurements.

Mechanisms of Photochemical Reactions in Solution. XL.[1] Steric Hindrance to Energy Transfer

William G. Herkstroeter,[2] Lee B. Jones,[3] and George S. Hammond

Contribution No. 3318 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California. Received April 11, 1966

Abstract: Derivatives of benzophenone in which the two ortho positions of one of the aromatic rings are substituted by alkyl groups have been studied as photosensitizers for the cis–trans isomerization of the stilbenes. Compounds in which the substituents are methyl groups show behavior virtually identical with that of the parent compound. However, introduction of two isopropyl groups effects a substantial change. We infer that the bulky substituents decrease the rates of energy transfer and that transfer to the cis isomer is the more sensitive of the two processes to steric hindrance. In the course of the work the appearance of photoenols was observed and studied in detail in two cases. In both systems two enols, believed to be stereoisomers, were produced from a single ketone.

A mechanism of photosensitized reactions that was apparently first suggested by Franck[4] has been shown to be applicable to photosensitized cis–trans isomerization reactions.[5] A key step in the mechanism is transfer of electronic excitation from an excited

(1) Part XXXIX: W. G. Herkstroeter and G. S. Hammond, J. Am. Chem. Soc., 88, 4769 (1966).
(2) National Science Foundation Predoctoral Fellow, 1961-1965.
(3) National Science Foundation Postdoctoral Fellow, 1964.
(4) J. Franck, Z. Physik, 9, 259 (1922); G. Cario and J. Franck, ibid., 11, 161 (1922).
(5) G. S. Hammond, et al., J. Am. Chem. Soc., 86, 3197 (1964).