to a phase shift δ of about -0.64. If now we consider increasing R values, more and more of the inner nodes must become strongly ellipsoidal; yet if n is large enough, the outermost nodes must be nearly spherical even for very large R values.

A comparison between the cause of the quantum defect δ for penetrating Rydberg AO's and that for H_2^+ MO's is of interest. In both cases, δ arises mainly from departures in the innermost loop or loops from an H-atom-like $(-Z_c e^2/r)$ potential. In the case of the Rydberg AO, its penetration into the core exposes it to a stronger field. This alone would give rise to a δ, because it lowers the energy of the AO even if unchanged in form (first-order effect). However, shrinkage and radial distortion of the inner loops of the AO, especially if the penetration is deep, further increases

δ. Higher members of the Rydberg series, because of orthogonality, approximately recapitulate in their innermost loops the distortions and (with a small weighting factor) the energy changes of their early progenitors, so that δ persists in the energy formula (eq. 1) and phase shifts persist in the asymptotically H-atom-like AO's.

In a similar way for any higher-n H_2^+ MO, the departure of the potential from $-2e^2/r$, mainly in the first progenitor and in the innermost loop or loops of the MO, establishes a δ which then persists in the energy formula and in phase shifts of the outer loops. The two cases are very similar except for the extra degree of freedom in H_2^+ whereby δ varies with R (but is always zero for $R = 0$), and except for the fact that δ in H_2^+ can as well be negative as positive.

Mechanisms of Photochemical Reactions in Solution. XXII.[1] Photochemical *cis–trans* Isomerization

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We report a detailed study of the photochemical isomerization of four pairs of *cis–trans* isomers, the stilbenes, the 1,2-diphenylpropenes, the piperylenes (1,3-pentadienes), and ethyl maleate–ethyl fumarate. Principal emphasis has been placed on isomerization in the presence of photosensitizers although the results have been correlated with those obtained by direct excitation in the case of the stilbenes and diphenylpropenes. The composition of the mixtures in the photostationary states is a complicated, but rational, function of the nature of the photosensitizers. All results can be understood if it is assumed that transfer of triplet excitation may involve excitation of acceptors to nonspectroscopic as well as spectroscopic states. We infer that the stilbene triplet exists in two interconvertible states, one transoid and one twisted. Probably the only stable triplet in the 1,2-diphenylpropene system is a twisted form. Self-quenching of stilbene triplets by ground-state *trans*-stilbene is significant. Sensitizers having low excitation energies function as true "photocatalysts," *i.e.*, in the presence of excited states of the sensitizers the composition of the photostationary mixture approaches that at thermal equilibrium.

Many studies of photochemical *cis–trans* isomerization have been reported and the mechanisms of these processes have been the subject of frequent, lively discussions.[7] Most of the work has involved irradiation with light absorbed directly by the substrate molecules or under conditions such that the primary absorption process is undefinable. Recent work[14–17]

has shown that the reaction can also be effected by irradiation in the presence of suitable photosensitizers. Since the sensitized reaction is in some ways more amenable than the direct process to study in depth, we have investigated several systems in detail. The results not only clarify the specific photochemical process but also give useful information concerning the mechanisms of triplet excitation transfer and the properties of electronically excited states of molecules.

General Theory

We presume the *a priori* hypothesis that most photosensitized reactions involve transfer of electronic excitation from the sensitizer to an acceptor. Transfer of either triplet or singlet excitation can be realized. Triplets are generally much longer-lived than singlets. Consequently triplets are more likely than singlets to live long enough to encounter potential acceptors. All available evidence indicates that triplet transfer requires close contact of the partners in energy exchange. On the other hand, it has been shown[18] that transfer of singlet excitation in solution may occur even when molecules are separated by large distances. However, the requirements for long-range transfer of singlet energy also place stringent restrictions on

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(5) National Science Foundation Undergraduate Research Participant, 1962.

(6) National Science Foundation Undergraduate Research Participant, 1963.

(7) Thorough documentation of the literature is impractical because of its volume. Considerable pertinent discussion has recently been focused on the stilbenes.[8–16] Reference 9 gives a representative treatment.

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(9) S. Malkin and E. Fischer, *J. Phys. Chem.*, **66**, 2482 (1962).

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(17) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Am. Chem. Soc.*, **83**, 2396 (1961); *J. Phys. Chem.*, **66**, 1144 (1962).
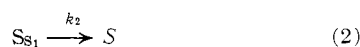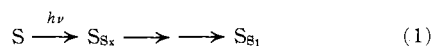
(18) Th. Förster, *Discussions Faraday Soc.*, **27**, 1 (1959).

the relationships between the transitions of donor and acceptor. The transfer must be nearly isoenergetic and the transitions of both donor and acceptor must have fairly strong transition moments. This requires large overlap between the fluorescence spectrum of the donor and the absorption spectrum of the acceptor. In all cases reported in the present study the absorption of sensitizers lies on the long wave length side of the lowest optical transitions of the acceptors. Clearly the conditions for resonance transfer of singlet excitation are not fulfilled. That "good" sensitizers often contain carbonyl groups within their chromophoric units is surely associated with the fact that such compounds usually undergo intersystem crossing from singlets to triplets with high efficiency.[19,20] As has been discussed earlier,[17] the success of sensitized reactions in photochemistry is due in large measure to the fact that the splitting between S_1 and T_1 states varies widely in organic molecules. Therefore, it is feasible to excite a sensitizer using light of a wave length longer than any absorbed by the chemical substrate. Activation of conjugated dienes[17,21-23] by energy transfer from the triplet states of benzophenone and related compounds is a good example.
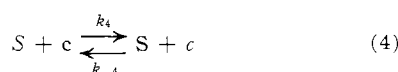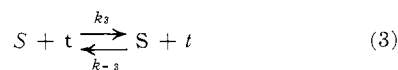
In view of the above considerations, we have formulated only triplet mechanisms for sensitized isomerization. In order to account for the effects of certain low-energy sensitizers we find it necessary to postulate that energy transfer must, in some cases, effect fairly efficient excitation of acceptors by non-Franck–Condon processes.[24] Having introduced this concept, we must also include in any general mechanistic scheme "phantom" triplets which have configurations unlike those of ground-state molecules. The basis for this concept is not new as it has long been recognized that many triplets produced by absorption of light should be able to stabilize themselves by distortion. For example, Mulliken and Roothaan[25] have estimated that the perpendicular form of ethylene triplet should be more stable than the planar form by at least 20 kcal. per mole.

The present discussion requires consideration of a number of steps. In the following mechanism the various steps are classified according to type where italics indicate triplet states (T_1), S,S = sensitizer, t,t = trans substrate, c,c = cis substrate, Q,Q = quencher, and p = phantom triplet.

Excitation

$$S \xrightarrow{h\nu} S_{S_x} \longrightarrow \longrightarrow S_{S_1} \tag{1}$$

$$S_{S_1} \xrightarrow{k_2} S \tag{2}$$

Classical energy transfer

$$S + t \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} S + t \tag{3}$$

$$S + c \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} S + c \tag{4}$$

$$t + Q \xrightarrow{k_5} t + Q \tag{5}$$

$$c + Q \xrightarrow{k_6} c + Q \tag{6}$$

Transfer with nonvertical excitation

$$S + t \xrightarrow{k_7} S + c \tag{7}$$

$$S + c \xrightarrow{k_8} S + t \tag{8}$$

$$S + t \xrightarrow{k_9} S + p \tag{9}$$

$$S + c \xrightarrow{k_{10}} S + p \tag{10}$$

Interconversion of excited states

$$t \underset{k_{-11}}{\overset{k_{11}}{\rightleftarrows}} c \tag{11}$$

$$t \underset{k_{-12}}{\overset{k_{12}}{\rightleftarrows}} p \tag{12}$$

$$c \xrightarrow{k_{13}} p \tag{13}$$

Decay processes

$$t \xrightarrow{k_{14}} t \tag{14}$$

$$t \xrightarrow{k_{15}} c \tag{15}$$

$$c \xrightarrow{k_{16}} c \tag{16}$$

$$c \xrightarrow{k_{17}} t \tag{17}$$

$$p \xrightarrow{k_{18}} t \tag{18}$$

$$p \xrightarrow{k_{19}} c \tag{19}$$

$$t + t \xrightarrow{k_{20}} 2t \tag{20}$$

Other reactions, analogous to some of the above, could be included but are not needed. For example, self-quenching of cis triplets, analogous to reaction 20, might occur but has not yet been observed. Some processes, formulated above as reversible, have thus far been observed in only one direction. Formulation of kinetic expressions for stationary-state relationships and quantum yields including all of the above steps is straightforward. However, the result is unnecessarily complex so only partial laws will be used since in every case some steps are believed to be inoperative.

Most of the steps in the mechanism are well known. Excitation and intersystem crossing are entirely standard.[26] Transfer of triplet excitation is well recognized.[17,27,28] Sandros and Bäckström have shown[28] that the process may be reversible if the excitation energies of donor and acceptor are approximately matched. The energy matching is ordinarily judged by comparison of the phosphorescence or singlet–triplet absorption spectra of the donor and acceptor. There is no such guide to the energetic requirements in nonvertical excitation (vide supra) of flexible molecules. Energy transfer involving flexible molecules may show at least two phenomena not known from the

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(20) G. S. Hammond, A. A. Lamola, and D. O. Cowan, unpublished results.
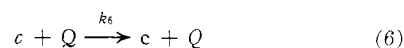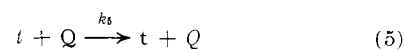(21) G. S. Hammond, N. J. Turro, and A. Fischer, J. Am. Chem. Soc., 83, 4674 (1961).
(22) G. S. Hammond and N. J. Turro, ibid., 84, 2841 (1962).
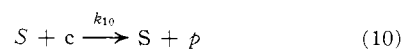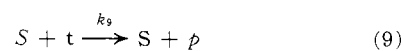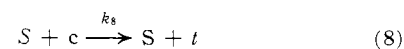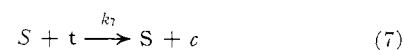(23) G. S. Hammond and R. S. H. Liu, ibid., 85, 477 (1963).
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(28) K. Sandros and H. L. J. Bäckström, Acta Chem. Scand., 16, 958 (1962).

study of relatively rigid, aromatic systems. First, triplets having low excitation energies may function as sensitizers for flexible substrates even though spectroscopic data indicate that energy transfer would be significantly endothermic. Second, the efficient reversibility of energy transfer observed by Sandros and Bäckström[28] may not occur. Maximum efficiency in the transfer of excitation from S to a substrate is observed only if the excitation energy of S is sufficient to promote the substrate to a spectroscopic triplet state. If the spectroscopic triplet is converted by vibrational relaxation to a phantom triplet the latter will possess insufficient excitation energy to promote S to S. Although nonvertical excitation, *e.g.*, reaction 9, should be reversible, the phenomenon may be difficult to observe because of competition of other reactions of p.

Interconversion of excited states may be of importance in many unsaturated, acyclic systems. In the ground states of conjugated polyenes and analogous compounds it is well known that there is a dramatic alternation in the barriers to rotation about alternate bonds. The pattern is well indicated by the Kekulé formulas of the compounds. For example, there is a large barrier to rotation about the 1,2 and 3,4 bonds in butadiene but only a small barrier opposing rotation about the central bond. The situation is drastically altered in the excited states of the molecules. As has been pointed out, the T_1 states of conjugated dienes behave as though they exist in stable *cis–trans* isomeric configurations,[23] indicating development of a substantial barrier to rotation about the central bond. There must also be a decrease in the barriers at the terminal bonds, as is indicated by the mere fact that the piperylenes undergo photoisomerization. It is certainly possible that bonds which are centers of geometrical isomerism in ground states will become free rotators in excited states. In fact, this view seems to have been assumed in many recent discussions of photoisomerization.[12,13,29] That this is not *necessarily* the case has been emphasized by Dyck and McClure in their discussion of the isomerization of the stilbenes.[10,30] Interconversion of triplets should obviously be included as a possible step in any mechanism.

Nonradiative decay processes are probably the least understood of any part of the mechanism. There is increasing suspicion on the part of spectroscopists that nonradiative lifetimes of triplets in solution are ordinarily controlled by quenching by minute, omnipresent traces of impurities.[31,32] The urge to seek such an explanation is supplied in part by theoretical treatments[33,34] which indicate that there should be no large difference between nonradiative decay rates in crystals and glasses at low temperature and in solution at room temperature. In actual fact, decay rates observed in flash experiments with solutions are often much greater than are the rates at low temperatures in nonfluid media. Striking evidence for this phenomenon is provided by the fact that although many substances phosphoresce in glasses or crystals at low temperature, very few show phosphorescence in solution at room temperature. If quenching by tiny amounts of impurities does occur, energy transfer of the classical type must be involved since transfer involving nonvertical transitions is relatively inefficient.

The possibility that *cis–trans* isomerization may be a part of the decay process has often been ignored although Lewis suggested such a mechanism many years ago.[8] The mechanism is feasible if nonradiative decay is a two-step process with the first step being internal conversion[26] (or isoenergetic intersystem crossing[26]) to produce S_0 states in highly excited vibrational levels. The crossover would then be followed by rapid transfer of vibrational excitation to the environment. If the two-step decay mechanism is correct, isomerization might occur rapidly enough to compete with vibrational relaxation. The efficiency of the process would depend upon the relative rates of concentration of the energy on the appropriate internal rotational mode and of the relaxation process.[35] This consideration has a nontrivial implication for studies of mechanistic photochemistry. For example, we have shown that the ratio of *cis* and *trans* isomers produced in the decay processes subsequent to both direct and sensitized excitation is the same for both the stilbenes and diphenylpropenes. One obvious interpretation is that final decay occurs from the same species in both cases, *i.e.*, direct excitation is followed by crossing into the triplet manifold. In this particular instance other observations also indicate that intersystem crossing probably occurs. However, *the identity of the ultimate decay products could arise from a crossing of the paths, not in the triplet system but in the vibrationally-excited S_0 states*.

Reaction 20 is included in the decay scheme in response to demands of experimental data obtained with the stilbenes. Such "self-quenching" reactions have been invoked[36] to account for some features of the kinetics of triplet decay in flash experiments although the step has recently been questioned[32] in one system for which it had been most persistently suggested. That such processes should occur is inherently reasonable. Examples of fluorescence from excited dimers, called "excimers," have recently been reported.[37−39] Formation of excimers having some stability is certainly to be expected since some stabilization should arise from spreading of the excitation over the two molecules. Our general state of ignorance concerning nonradiative decay mechanisms is such that we might expect almost anything for the relative rates of radiationless deactivation of excited monomers and dimers.

(29) G. Zimmerman, L. Chow, and U. Paik, *J. Am. Chem. Soc.*, **80**, 3528 (1958).

(30) Another point of view has also been expressed frequently, although usually informally. This is the belief that the perpendicular configuration, at arbitrarily chosen centers, should be the most stable form of T_1 states of conjugated systems as is the case with ethylene.[25] We can see no *general* justification for this view. In some systems, such as the stilbenes, twisted configurations *may* be stable depending upon details of molecular symmetry and steric interactions between groups attached to the double bond.

(31) G. Jackson and R. Livingston, *J. Chem. Phys.*, **35**, 2182 (1961).

(32) H. Linschitz, C. Steel, and J. A. Bell, *J. Phys. Chem.*, **66**, 2574 (1962).

(33) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962).

(34) M. Gouterman, *ibid.*, **36**, 2846 (1962).

(35) In a molecule such as stilbene, the electronic excitation is probably largely concentrated in the central double bond in the lowest excited electronic states. Intuitively, it seems likely that isoenergetic internal conversion might initially concentrate the vibrational excitation in the same place. Consequently the probability that rotation may occur before vibrational relaxation may be much higher than if the vibrational energy were injected randomly into the molecule. An opposing point of view has been elaborated by Zimmermann.[29]

(36) H. Linschitz and K. Sarkanen, *J. Am. Chem. Soc.*, **80**, 4826 (1958).

(37) E. D. Förster and Th. Förster, *Z. physik. Chem.* (Frankfurt), **31**, 274 (1962).

(38) C. A. Parker and C. G. Hatchard, *Proc. Chem. Soc.*, 147 (1962).

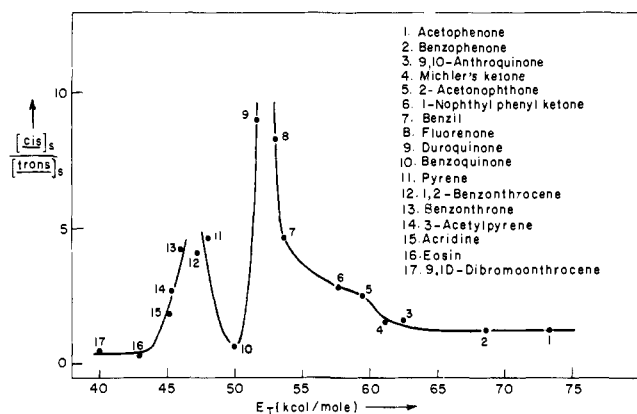(39) B. Stevens and T. Dickinson, *J. Chem. Soc.*, 5492 (1963).

Fig. 1.—Sensitized isomerization of the 1,2-diphenylpropenes.

Results

Two kinds of quantitative measurements have been used to characterize the systems: (1) measurement of quantum yields for the *cis* → *trans* and *trans* → *cis* processes at low conversion and (2) measurement of the composition of the mixtures after photostationary states have been established. Data of the latter type are relatively easy to obtain with high precision, even with sensitizers that are sufficiently inefficient to render measurement of quantum yields imprecise and tedious. The usual criteria for establishment of the accuracy of measurements of thermal equilibria have been applied. The ratio of reactants in the stationary state must become time-independent and the same result must be obtained when the stationary condition is approached from either side. The usual procedure involves irradiation of solutions originally containing pure isomers until no further change occurs. In some instances this procedure did not give satisfactory results; if the sensitized isomerization is of low efficiency, the substrate, the sensitizer, or both may be destroyed in photochemical side reactions. The products of such reactions may themselves be either sensitizers or quenchers so results obtained by long irradiation may be essentially uninterpretable. When this problem is encountered, meaningful results can be obtained from short-time irradiation of mixtures of varying composition. Preliminary experiments with pure, or nearly pure, isomers are used to obtain an approximate value for the stationary state. A series of solutions are then made up having compositions close to and bracketing the suspected stationary mixture. These solutions are then irradiated briefly and the direction of change is noted. If the mixture is very close to the stationary state, the initial rate of change is very slow. The procedure, although time consuming, allows precise estimation of results that are not obtainable by the usual procedure.

Reversibility of energy transfer, reactions 3 and 4, and self-quenching, reaction 20, make the composition of the photostationary mixtures dependent upon the concentrations of substrate and sensitizer. Complete characterization of a system must include documentation of such concentration effects when they exist.

Quantum yield measurements have been made with high precision in some systems. It is relatively easy to obtain good values when using high concentrations of the substrates. Under these circumstances dependence of the value on the rate constants, k_7 and k_8, for

energy transfer disappears since multiple encounters of sensitizer with substrate occur during the lifetime of the excited sensitizer. Results obtained with high concentrations of substrates can be used to calculate triplet decay ratios for the substrates and intersystem crossing ratios for the sensitizers.[20] With care, good results can be obtained with low concentrations of substrates.

General Characteristics of the Kinetics.—The behavior of various sensitizers is believed to be primarily a function of their excitation energies and is discussed in that light. A principal justification for this approach derives from comparison of results with the various substrate pairs. Certain characteristic phenomena are observed with all pairs. However, different sensitizers are involved in the important changes in behavior of the different substrate pairs and the location of the changeover points on plots of stationary-state ratios against sensitizer-excitation energy can be related in a reasonable manner to what is known or estimated about excitation energies of the substrates. For example, groups of "high-energy" sensitizers can be identified for all substrate pairs except maleate–fumarate. All sensitizers having greater than a minimum triplet excitation energy give the same results.[40] This behavior is attributed to the fact that if reactions 3 and 4 are both substantially exothermic, both occur on the first encounter between an excited sensitizer and a substrate molecule. As the energy of the sensitizer is decreased (by changing its structure), various selective phenomena become evident. These include decrease in efficiency of the interaction, reversibility of excitation transfer, and nonvertical excitation of the acceptor. The details are most easily discussed by consideration of the individual *cis–trans* pairs.

1,2-Diphenylpropenes

Photostationary states were established by irradiation of the isomeric 1,2-diphenylpropenes (α-methylstilbenes, **1** and **2**) in the presence of various sensitizers. Results are tabulated in Table I and are shown graphically in Fig. 1. The plot shows the following features

TABLE I

PHOTOSENSITIZED ISOMERIZATION OF 1,2-DIPHENYLPROPENES AT 25–28° IN BENZENE SOLUTION[a]

Sensitizer	$[c]_s/[t]_s$
Acetophenone	1.18
Benzophenone	1.24
Anthraquinone	1.61
Michler's ketone	1.51
2-Acetonaphthone	2.59
1-Naphthyl phenyl ketone	2.81
Benzil	4.56
Fluorenone	8.30
Duroquinone	9.00
Benzanthrone	4.21
Benzoquinone	0.64
Pyrene	4.62
1,2-Benzanthracene	4.07
3-Acetylpyrene	2.77
Eosin	0.20
9,10-Dibromoanthracene	0.50

[a] Concentrations of substrates and sensitizers were both 0.05 M.

(40) The same stationary states are established. Differences in quantum yields arise from variation of the intersystem crossing ratios for the sensitizers.

which were also found in the study of the stilbenes: (1) a "high-energy" region in which the stationary-state ratio $[cis]_s/[trans]_s$ is 1.2–1.3, (2) at least two maxima in the plot of $[cis]_s/[trans]_s$ as a function of sensitizer energy, (3) persistence of the sensitized reaction even with sensitizers having excitation energies well below values that might be reasonably expected to be required for promotion of the olefinic substrates to their spectroscopic triplet states,[41] and (4) the occurrence of limiting behavior with low-energy sensitizers.

$$
\begin{array}{cc}
\underset{H}{\overset{C_6H_5}{>}}C=C\underset{C_6H_5}{\overset{CH_3}{<}} & \underset{H}{\overset{C_6H_5}{>}}C=C\underset{CH_3}{\overset{C_6H_5}{<}} \\
\mathbf{1} & \mathbf{2}
\end{array}
$$
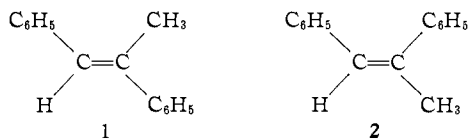
In contrast to the results with the stilbenes, neither variation of the concentration of the sensitizers nor addition of small amounts of azulene effect any measureable change in the stationary-state ratios. The absence of concentration effects shows that reversal of reactions 3 and 4 is unimportant and the lack of an azulene effect shows that triplet quenching, reactions 5 and 6, is also negligible. The two results are complementary since reversible interaction with a sensitizer is just a special case of quenching. Two kinds of explanation could be offered for the failure of substrate triplets to undergo quenching. First, the result might merely indicate that the lifetimes of the triplets are very short, *i.e.*, that some or all of the decay processes, reactions 14–19, are exceptionally rapid in this system. An alternative explanation would invoke rapid relaxation of both *cis* and *trans* triplets to a distorted triplet, p, which is incapable of undergoing efficient quenching. Because of related observations in the stilbene system, we favor the latter explanation. The phantom triplet probably has approximately the perpendicular configuration **3**. However, the only properties that can be considered to be "known" are: (1) that it is more stable than *cis* or *trans* triplets formed by vertical excitation, and (2) return from the phantom triplet to the ground state is a process that is not efficiently coupled with excitation of quenchers in classical energy transfer processes.

$$
\underset{CH_3}{\overset{C_6H_5}{>}}C\text{—}C\underset{C_6H_5}{\overset{H}{<}}
$$
$$
\mathbf{3}
$$
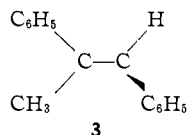
If we assume that p is the only excited species that decays to ground-state molecules, reactions 1–4, 9, 10, 12, 13, 18, and 19 are the minimum number needed to describe the system. If the concentrations of excited species are treated by the steady-state assumption, the dependence of the stationary-state concentration ratios on the various rate constants

is readily obtained. The result is given in eq. 21 in which an s subscript to a concentration term indicates the concentration at the stationary state.

$$
\frac{[c]_s}{[t]_s} = \frac{(k_3 + k_9)k_{19}}{(k_4 + k_{10})k_{18}} \tag{21}
$$

Two factors determine the stationary-state composition, the triplet decay ratio (k_{19}/k_{18}) and a factor dependent on the relative rates of excitation of the isomeric substrates. Reasonable assumptions concerning the way in which the activation rates change as the sensitizer is varied allow useful dissection of eq. 21. We assume that if the excitation energy of the sensitizer is substantially greater than that of the substrates, energy transfer will be predominantly by the classical process and will be diffusion-controlled. Under these conditions the stationary-state ratio is determined only by the triplet decay ratio.

For high-energy sensitizers

$$
k_3 \gg k_9
$$
$$
k_4 \gg k_{10}
$$
$$
k_3 = k_4
$$
$$
\frac{[c]_s}{[t]_s} = \frac{k_{19}}{k_{18}} \tag{22}
$$

The value of k_{19}/k_{18}, obtained from the measurements with high-energy sensitizers, is 1.2. As long as sensitizer molecules do not participate in the decay process, the value of k_{19}/k_{18} should remain constant in any series of measurements made at a constant temperature in a single solvent.[43] The variation in the values of the stationary-state ratios should be understandable in terms of the various excitation processes. The singlet–triplet transition energies of the isomeric substrates will not ordinarily be the same. Different sensitizers will match the transition energies of the two isomers. Studies of quenching of triplets by aromatic molecules indicate that quenching efficiency begins to fall off when the energy of the excited donor is just above the excitation energy of the acceptor.[28] The first change observed as sensitizer energy is decreased (Fig. 1) is enrichment of the systems in the *cis* isomer. This is attributed to a decrease in k_4 so that $k_3 > k_4$ with consequent "pumping" of the system in favor of the *cis* isomer. The effect would be expected in any mechanism involving classical energy transfer as the principal step.

If only classical energy transfer were involved, one would expect monotonic change in the stationary-state ratio until the sensitizer energy fell to a value below the excitation energy of the *trans* substrate. If the two substrate transition energies are separated by several kilocalories per mole, one might expect that the stationary ratios would become immeasurably large with the "endothermicity" of the transfer to the isomer having the higher excitation energy appearing as an activation energy. No modest modification of this point of view can account for the maxima which have now been found in plots of $[cis]_s/[trans]_s$ against sensitizer energy for four systems. Figure 1 shows that

(41) We have been unable to obtain direct evidence concerning the spectroscopic transitions. The spectra of the compounds in ethyl iodide show long wave length absorption but the "tails" are devoid of resolvable structure and permit only crude estimates of the location of band heads. Since the singlet–singlet absorption spectra are similar to those of the stilbenes,[42] with the small shifts expected to arise from steric hindrance introduced by the methyl group, we presume that spectroscopic triplet excitation energies are also similar.

(42) D. J. Cram and F. A. Abd Elhofez, *J. Am. Chem. Soc.*, **74**, 5828 (1952).

(43) Whether or not significant temperature and medium effects on the decay ratios will be found in any system is unknown. There is no indication of temperature sensitivity with the diphenylpropenes (Table I).
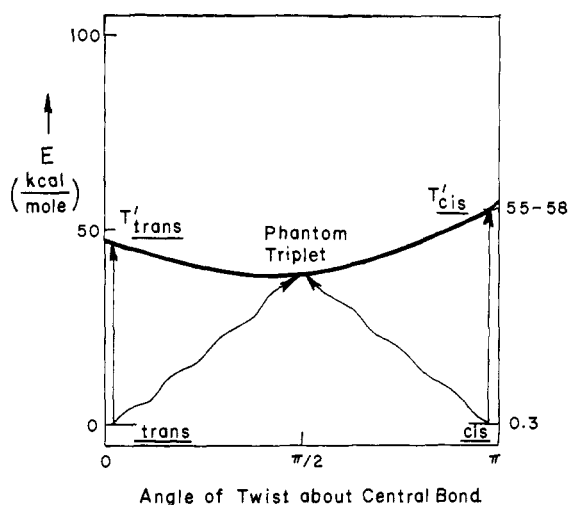
Fig. 2.—Possible potential function for rotation in 1,2-diphenyl-propene triplet state.

there are regions of sensitizer energy in which the *relative* rate of activation of the *cis* isomer is increased by decreasing the energy of the sensitizer. If the efficiency of activation of the *cis* isomer decreases throughout the region there must be regions in which the efficiency of excitation of the *trans* compound falls even more rapidly. The phenomenon *requires* that activation be supplied to the *cis* isomer by some process that does not decrease in efficiency as rapidly as would be expected of classical energy transfer. Although other processes can be conceived, we believe that the most probable is nonclassical energy transfer in which the acceptor is excited with significant change in geometry. Since the previously mentioned absence of quenching effects leads us to suspect that both *cis* and *trans* triplets decay rapidly to the perpendicular configuration, the latter species is a likely end point for nonvertical excitation of either of the isomeric substrates. Figure 2 shows a possible form for the potential function for twisting about the central bond. Shallow minima might also be located close to the perpendicular configurations. Nonvertical transitions are indicated by wavy arrows.

The results obtained with the very low-energy sensitizers, eosin and 9,10-dibromoanthracene, are interesting. With these donors the values of k_3 and k_4 are probably negligible so the stationary-state relationship reduces to eq. 23. The values of the stationary-

$$\frac{[c]_s}{[t]_s} = \frac{k_9 k_{19}}{k_{10} k_{18}} = 0.20\text{-}0.25 \qquad (23)$$

state ratios are rather close to those obtained in thermal equilibration experiments[44] ($[cis]/[trans] = 0.27$ at 139°). Consequently the excited states of the sensitizers appear to function as true catalysts for the isomerization reaction. In terms of the proposed mechanism, the decay ratio, k_{19}/k_{18}, is close to unity, and the observed result indicates that the excitation ratio, k_9/k_{10}, reflects fairly accurately the difference in ground-state energies of the isomeric substrates. The *cis* isomer is a more effective energy acceptor because the energy required to promote it to p is slightly less than is needed to promote the *trans* compound to the same intermediate.[45]

(44) A. Zwierzok and H. Pines, *J. Org. Chem.*, **27**, 4084 (1962).

The interesting details of the curve in Fig. 1 are worthy of speculation since the same features are observed in the study of the stilbenes. There is an inflection around 58, maxima close to 52 and 48, and a minimum at 50 kcal. We suggest a tentative interpretation of these features. First, if the spectroscopic transition energy of the *cis* isomer occurs at about 58 kcal., activation by sensitizers having lower energies may occur with relatively constant efficiencies reflecting the fact that the nonclassical process, reaction 10, is substantially exothermic over a considerable further range of sensitizer energies. The subsequent maxima would then reflect maxima in the rates of energy transfer to the *trans* compound. The maxima may arise from fluctuations reflecting Franck–Condon maxima in the singlet–triplet absorption spectrum of the compound. The separation between the two maxima is about 1400 cm.$^{-1}$, a reasonable value to be expected from a vibronic progression based upon the frequency for stretching a weak carbon–carbon double bond. Such a progression, with a separation of approximately 1500 cm.$^{-1}$, is found in the singlet–triplet absorption spectrum of *trans*-stilbene.[10] While results of the present study are not extensive enough to be definitive, they do suggest that the efficiency of energy exchange between donor and acceptor pairs may be sensitive to vibronic factors if their excitation energies are close to the resonance condition.

Quantum Yields.—Quantum yields for isomerization of the diphenylpropenes in the presence of benzophenone were measured and are summarized in Table II.

TABLE II

QUANTUM YIELDS FOR ISOMERIZATION OF THE 1,2-DIPHENYLPROPENES SENSITIZED BY BENZOPHENONE

Starting material	Φ
trans	0.54
cis	0.44

If the mechanism described is correct, eq. 24 should relate the quantum yields and the stationary state ratios *for the high-energy sensitizer*.

$$\frac{[c]_s}{[t]_s} = \frac{\Phi_{t \to c}}{\Phi_{c \to t}} \qquad (24)$$

The ratio of the quantum yields is 1.23, in good agreement with the experimental value of $[c]_s/[t]_s$. The sum of $\Phi_{t \to c}$ and $\Phi_{c \to t}$ is 0.98. Since the measurements were made with relatively high concentrations of the substrates, sensitizer triplets should have no opportunity to decay before encountering acceptor molecules; consequently 0.98 should be the fraction of excited benzophenone molecules that undergo intersystem crossing to triplets. The value is in excellent agreement with those obtained in the study of other systems.[20]

Direct Excitation.—Isomerization by direct excitation was compared with the sensitized process by irradiation of solutions of the isomeric olefins until stationary states were established. The value of $[c]_s/$

(45) The behavior of 9,10-dibromoanthracene and eosin could be rationalized if any other highly energetic, common intermediate were formed by interaction of the excited sensitizer with the two substrates. For example, the biradical mechanism suggested by Schenck[46] might also be used to rationalize the results if it is presumed that formation of a bond from substrate to sensitizer involves little or no activation energy.

(46) G. O. Schenck and R. Steinmetz, *Bull. soc. chim. Belges*, **71**, 781 (1962).

[t]$_s$ of 2.64 was obtained in experiments starting with either isomer. A filter system was used to isolate the 3130 Å. band from the source. If decay from the same state is involved in the sensitized and unsensitized experiments, the stationary states should be related to those obtained with high-energy sensitizers by eq. 25.

$$\frac{[c]_s}{[t]_s} = \frac{\epsilon_t k_{19}}{\epsilon_c k_{18}} \qquad (25)$$

Using the extinction coefficients for the two isomers at 3130 Å. and the value of 1.2 for k_{19}/k_{18}, a predicted value of 2.74 is calculated for $[c]_s/[t]_s$. Agreement with the measured value is excellent. The result conveys the very strong implication that *direct isomerization involves crossing into the triplet system before the final geometry is fixed.* As was pointed out in the General Theory section, the result is also consistent with the view that isomerization, in both direct and sensitized experiments, occurs as the excited molecules cascade through vibrationally excited levels of the S_0 system.

Stilbenes

Data for the stilbenes are more extensive and somewhat more precise than those for the 1,2-diphenylpropenes. Many important aspects of the results are similar but the stilbenes show additional effects which are both instructive and, at times, confusing. Excitation of either *cis-* or *trans*-stilbene leads to production of a long-lived[47] excited state which can be quenched to the ground state of *trans*-stilbene by interaction with a number of other species including unexcited sensitizer molecules, azulene, and even *trans*-stilbene. The results can be explained either by the assumption that two triplets, t and p, are in dynamic equilibrium or that a single triplet, t, is present. To accommodate the latter hypothesis one must assume that in quenching reactions t is selectively deactivated to t but that in spontaneous decay large amounts of c are also formed. Although the latter assumption is compatible with the decay mechanism involving internal conversion to a highly vibrationally excited S_0 state, some aspects of the dynamic behavior seem a little more reasonable if the model involving two triplets is used. This view also permits easy correlation of the results with those obtained with the diphenylpropenes. All available evidence indicates that the lifetime of triplets having cisoid configurations is very short. The results will be discussed in terms of a mechanism including reactions 1–4 and 13 occurring in the forward direction only; reactions 5, 9, 10, and 12 occurring in both directions; and the decay processes 14, 15, and 18–20. The reverse of reaction 11, conversion of c to t, is omitted only because the process is also the sum of (13) and the dynamic equilibrium (12). Omission of the step does not imply that direct conversion of c to t cannot occur. The mechanism implies that the potential function for rotation about the central bond is of the form shown in Fig. 3.

Since in some cases the composition of the stationary states depends upon the concentration of the sensitizer, the data are not easily presented as were those for the
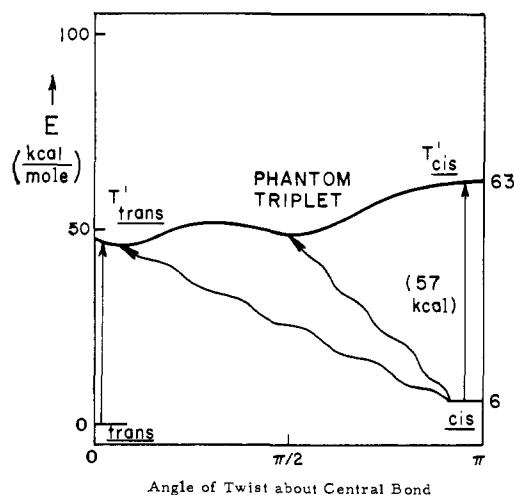

Fig. 3.—Potential function for rotation in stilbene triplet states.

diphenylpropenes. The values obtained in all stationary-state measurements made at 28° are tabulated in Table III.[48] Figure 4 shows the results obtained by

Fig. 4.—Photosensitized isomerization of the stilbenes.

extrapolation to infinite dilution with respect to sensitizer concentration. The solid points are extrapolated, open circles indicate sensitizers that give no concentration dependence. No correction has been made for the small variation of stationary states with stilbene concentration that was discovered during the latter part of the study. The correction would only introduce small changes and would not change the shape of the curve in any way.

The curve in Fig. 4 shows all of the features shown by the data for the diphenylpropenes. There is a clear-cut minimum at 57 kcal. that probably corresponds to the inflection near the same point in Fig. 1. In the case of the stilbenes, interpretation of the data can be supplemented by consideration of the known singlet–triplet absorption spectra of the two isomers[49] (measured by the oxygen perturbation method). The spectrum of *cis*-stilbene shows no vibronic structure but the long wave length edge is close to 5000 Å. (57 kcal. per mole). Assignment of the vibrationless c → c transition at this point accounts for the general upward trend of the curve with sensitizers having excitation energies less than 62 kcal.; the value of k_4 falls in this region and the principal mechanism for excitation of the *cis* isomer ceases to be reaction 4 and be-

(47) The observation concerning lifetime is not yet based upon direct measurement but derives from the fact that the excited molecule survives long enough to interact with solutes present in low concentration.

(48) A. Schönberg, A. Mustafa, and M. Z. Barakat, *Nature*, **160**, 401 (1947).

(49) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

TABLE III

STATIONARY STATES OF THE STILBENES WITH DIFFERENT SENSITIZERS[a]

Sensitizer concn., mole/l.	Total stilbene concn., mole/l.	Initial % cis	Filter system[b]	Method of analysis[b]	% cis at photostationary state
Acetophenone					
0.050	0.050	0	1	1	59.3 ± 1.0
0.0102	0.051	100	1	1	59.1 ± 0.5
Benzophenone					
0.050	0.050	0	1	1	59.6 ± 0.4
0.050	0.050	100	1	1	59.6 ± 0.8
Thioxanthone					
0.050	0.050	0	4	3	61.5 ± 0.2
0.050	0.050	100	4	3	58.9 ± 0.5
Flavone					
0.050	0.050	0	3	2	61.7 ± 0.1
0.050	0.051	100	3	2	61.3 ± 0.6
Michler's ketone					
0.050	0.050	0	3	2	63.2 ± 0.3
0.050	0.050	100	3	2	62.8 ± 0.2
4-Acetylbiphenyl					
0.050	0.050	0	4	3	64.6 ± 0.2
0.050	0.050	100	4	3	65.2
2-Acetylfluorene[c]					
0.050	0.050	0	4	3	65.4 ± 0.1
0.050	0.050	100	4	3	66.1 ± 0.3
9,10-Anthraquinone					
0.013	0.025	0	1	1	60.5 ± 0.6
0.008	0.020	0	1	1	60.0 ± 1.2
0.008	0.020	100	1	1	59.7 ± 0.3
2-Naphthaldehyde					
0.050	0.050	0	3	2	69.7 ± 0.3
0.050	0.051	100	3	2	71.3 ± 0.3
2-Naphthyl phenyl ketone					
0.050	0.050	0	3	2	71.1 ± 0.7
0.050	0.053	100	3	2	71.4 ± 0.4
2-Acetonaphthone					
0.080	0.050	0	3	2	70.2 ± 0.1
0.080	0.050	100	3	2	70.4 ± 0.1
0.050	0.051	100	1	1	69.2 ± 0.3
0.050	0.050	0	3	2	70.8 ± 0.5
0.050	0.050	100	3	2	70.0 ± 0.6
0.050	0.020	0	3	2	68.9 ± 0.5
0.050	0.020	100	3	2	69.1 ± 0.4
0.010	0.050	0	3	2	71.1 ± 1.6
0.010	0.050	100	3	2	70.7 ± 1.1
1-Naphthyl phenyl ketone					
0.050	0.050	0	3	2	73.4 ± 0.1
0.050	0.052	100	3	2	73.4 ± 0.9
1-Naphthaldehyde					
0.050	0.050	100	1	1	74.0 ± 1.0
β-Naphthil					
0.050-1[c]	0.050	0	2	2	85.2 ± 0.7
0.050-1[c]	0.051	100	2	2	84.7 ± 0.4
0.020-2	0.050	0	2	2	84.2 ± 0.5
0.020-2	0.050	100	2	2	83.9 ± 0.8
α-Naphthil					
0.015	0.050	0	2	2	87.2 ± 0.5
0.015	0.051	100	2	2	87.2 ± 0.6

Sensitizer concn., mole/l.	Total stilbene concn., mole/l.	Initial % cis	Filter system[b]	Method of analysis[b]	% cis at photostationary state
Fluorenone[d]					
0.080	0.050	0	2	2	86.1 ± 1.0
0.080	0.050	100	2	2	86.0 ± 0.2
0.050	0.050	0	1	1	86.2 ± 0.4
0.050[c]	0.055	100	1	1, 2	85.4 ± 0.4
0.027	0.050	0	2	2	86.5 ± 0.4
0.027	0.050	100	2	2	86.4 ± 0.5
0.013	0.050	0	2	2	86.7 ± 0.5
0.013	0.050	100	2	2	85.6 ± 0.4
0.050	0.100	100	4	3	86.4 ± 0.1
0.050	0.050	0	4	3	85.8 ± 0.5
0.050	0.050	100	4	3	86.9 ± 0.1
0.050	0.040	0	4	3	85.7 ± 0.4
0.050	0.040	100	4	3	84.7 ± 0.1
0.050	0.030	0	4	3	86.5 ± 0.3
0.050	0.030	100	4	3	86.2 ± 0.3
0.050	0.020	0	4	3	86.3 ± 0.6
0.050	0.020	100	4	3	85.7 ± 0.3
0.050	0.010	0	4	3	87.6 ± 0.1
Benzil (n-heptane)					
0.020	0.020	0	2	1	94.7 ± 0.2
0.010	0.020	0	2	1	95.2 ± 0.7
0.006	0.020	0	2	1	94.5 ± 0.4
0.001	0.020	0	2	1	93.5 ± 1.0
Benzil (EPA, diethyl ether–isopentane–ethanol, 5:5:2 by volume)					
0.050	0.050	0	2	1	93.2 ± 0.4
Benzil					
0.050	0.050	0	2	1	90.8 ± 1.0
0.050	0.050	0	4	3	92.0 ± 0.5
0.050	0.050	100	4	3	92.7 ± 0.5
Benzil (acetonitrile)					
0.050	0.050	0	4	3	92.0
0.050	0.050	100	4	3	92.7
2,3-Pentanedione					
0.051	0.050	0	2	1	87.4 ± 0.6
2,3-Pentanedione (EPA)					
0.051	0.050	0	2	1	91.5 ± 1.0
Biacetyl					
0.201	0.050	0	1	1	86.8 ± 0.4
0.050	0.050	0	4	3	88.0 ± 0.5
0.050	0.050	100	4	3	89.0 ± 0.5
Biacetyl (acetonitrile)					
0.050	0.050	0	4	3	89.9
0.050	0.050	100	4	3	89.7
1,4-Naphthoquinone[e]					
0.050	0.050	40	2	2	59.2 ± 0.5
0.050	0.050	80	2	2	60.9 ± 0.3
Duroquinone					
0.080	0.050	0	4	4	65.8 ± 0.8
0.080	0.050	100	4	4	65.1 ± 0.2
0.050	0.050	0	2	2	71.4 ± 0.2
0.050	0.050	100	2	2	71.0 ± 0.5
0.050	0.050	0	4	4	71.7 ± 0.1
0.050	0.050	100	4	4	72.8 ± 0.4
0.020	0.050	0	4	4	75.2 ± 0.8
0.020	0.050	100	4	4	74.2 ± 0.4

TABLE III (*Continued*)

Pyrene

Sensitizer concn., mole/l.	Total stilbene concn., mole/l.	Initial % cis	Filter system[b]	Method of analysis[b]	% cis at photostationary state
0.050	0.050	80	1	3	91.5 ± 0.2
0.050	0.050	100	1	3	91.5 ± 0.2
0.020	0.050	80	1	3	90.8 ± 0.3
0.020	0.050	100	1	3	91.3 ± 0.1
0.010	0.050	80	1	3	87.5 ± 0.1
0.010	0.050	100	1	3	88.2 ± 0.2

1,2-Benzanthracene[f]

Sensitizer concn., mole/l.	Total stilbene concn., mole/l.	Initial % cis	Filter system	Method of analysis	% cis at photostationary state
0.050	0.050	40	4	3	80.4 ± 0.3
0.050	0.050	80	4	3	79.8 ± 0.1
0.020	0.050	40	4	3	87.6 ± 0.2
0.020	0.050	80	4	3	88.2 ± 0.2
0.010	0.050	40	4	3	90.7 ± 0.1
0.010	0.050	80	4	3	90.3 ± 0.1

Benzanthrone

Sensitizer concn., mole/l.	Total stilbene concn., mole/l.	Initial % cis	Filter system	Method of analysis	% cis at photostationary state
0.051	0.050	0	2	2	42.1 ± 0.9
0.050	0.051	100	2	2	40.9 ± 1.0
0.020	0.050	20	2	2	62.2 ± 0.5
0.020	0.050	60	2	2	60.9 ± 0.4
0.015	0.050	0	2	2	66.8 ± 0.8
0.015	0.050	100	2	2	65.9 ± 0.8
0.010	0.050	20	2	2	72.0 ± 0.5
0.010	0.050	60	2	2	70.6 ± 0.2

Acridine

Sensitizer concn., mole/l.	Total stilbene concn., mole/l.	Initial % cis	Filter system	Method of analysis	% cis at photostationary state
0.050	0.050	40	4	3	38.5 ± 0.2
0.050	0.050	80	4	3	38.2 ± 0.1
0.020	0.050	40	4	3	55.4 ± 0.1
0.020	0.050	80	4	3	55.4 ± 0.1
0.010	0.050	40	4	3	64.8 ± 0.3
0.010	0.050	80	4	3	64.9 ± 0.5

3-Acetylpyrene

Sensitizer concn., mole/l.	Total stilbene concn., mole/l.	Initial % cis	Filter system	Method of analysis	% cis at photostationary state
0.080	0.050	0	3	2	29.2 ± 0.5
0.080	0.050	100	3	2	29.3 ± 0.0
0.050	0.050	0	3	2	39.8 ± 0.7
0.050	0.053	100	3	2	39.6 ± 0.3
0.020	0.050	0	3	2	55.0 ± 0.1
0.020	0.050	100	3	2	55.2 ± 0.1
0.010	0.050	0	3	2	65.0 ± 0.9
0.010	0.050	100	3	2	64.1 ± 0.6

1,4-Benzoquinone

Sensitizer concn., mole/l.	Total stilbene concn., mole/l.	Initial % cis	Filter system	Method of analysis	% cis at photostationary state
0.080	0.050	0	2	2	19.6 ± 0.8
0.080	0.054	65	2	2	17.8 ± 0.7
0.050	0.050	0	2	2	20.6 ± 0.9
0.050	0.051	69	2	2	20.4 ± 1.7
0.030	0.050	10	2	2	22.6 ± 0.8
0.030	0.050	40	2	2	22.6 ± 0.5
0.020	0.050	20	2	2	29.7 ± 0.6
0.020	0.050	50	2	2	30.5 ± 1.0
0.010	0.050	30	2	2 }	35.0 ± 1.0[g]
0.010	0.050	50	2	2 }	
0.005	0.050	40	2	2 }	39.3 ± 0.3[g]
0.005	0.050	60	2	2 }	
0.030	0.050	10	2	2	24.2 ± 0.7

Eosin[c] (benzene–diethyl ether, 1:1 by volume)

Sensitizer concn., mole/l.	Total stilbene concn., mole/l.	Initial % cis	Filter system	Method of analysis	% cis at photostationary state
<0.050 (satd.)	0.050	0	4	3	0.2 ± 0.1
<0.050 (satd.)	0.050	100	4	3	0.2 ± 0.1

9,10-Dibromoanthracene

Sensitizer concn., mole/l.	Total stilbene concn., mole/l.	Initial % cis	Filter system	Method of analysis	% cis at photostationary state
0.010	0.050	0	4	3	0.2 ± 0.0
0.010	0.050	100	4	3	0.2 ± 0.0

[a] Unless otherwise indicated, the solvent was benzene and the irradiations were carried out at 28°. The errors represent average deviations for several determinations. [b] The filter systems as well as the methods of analysis are described in the Experimental section. [c] These irradiations were carried out at ~13°. [d] Fluorenone interfered slightly with analysis 3 of the stilbenes. [e] The photostationary state for 1,4-naphthoquinone was further established by irradiating for short time periods samples of two solutions whose initial compositions were 60 and 70% *cis*-stilbene. The results showed that the stationary state is 60.6 ± 0.3% *cis*-stilbene. [f] A white photoproduct precipitated from solution. Since this is probably 1,2-benzanthracene dimer,[48] the initial concentration of the sensitizer should be taken as upper limits. [g] This value was obtained by extrapolation.

comes 8. The minimum that seems to appear at 57 kcal. may represent exact matching of the vertical transition energy of *cis*-stilbene by that of the sensitizer (1,4-naphthoquinone). The subsequent maxima and minima are again tentatively attributed to fluctuations in the efficiency of classical energy transfer to *trans*-stilbene as the sensitizer energy is varied through the resonance condition with the lower vibronic components of the $S_0 \rightarrow T_1$ transition. The spectrum of the *trans* compound does show well developed vibrational structure with a principal separation of ~1500 cm.$^{-1}$. The first maximum has been assigned at 5770 Å. or 50.8 kcal. per mole (oxygen method[49]) and 5620 Å. or 49.5 kcal. per mole (spectrum in ethyl iodide[9]). If this band is really the 0–0 component of the transition, we are hard pressed to account for the occurrence of a maximum in the "chemical spectrum" at about 47 kcal. We suggest that the band head is actually at about 6100 Å. and that the feature at ~5700 Å. is really the 0–1 component. We recognize that without this speculative assumption we would be forced either to abandon our general approach or devise some explanation for the occurrence of wide fluctuations in the efficiencies of the nonvertical excitation processes, reactions 7–10.[50]

The very low-energy sensitizers, eosin and 9,10-dibromoanthracene, both effect establishment of photostationary states that are almost pure *trans*-stilbene. Conversion of *cis*- to *trans*-stilbene was immediately observed. Since the ground state of *trans*-stilbene is stable, even with respect to the *cis* isomer, by 6 kcal. per mole,[51] the result shows that thermodynamic equilibrium is approached in the presence of the low-energy sensitizers, as was observed with the diphenylpropenes.

Concentration Effects.—Table III includes data for sensitizers which give concentration-dependent stationary states and also shows evidence that no such dependence appears with sensitizers, *e.g.*, 2-acetonaphthone and fluorenone, having excitation energies above 53 kcal. The effect is attributed to reversibility of energy transfer involving *trans*-stilbene, *i.e.*, reaction 3 proceeds in both directions. Introduction of this step in the mechanism, while temporarily ignoring reaction 20, gives the relationship of eq. 26 and 27.

We again assume that the natural decay ratio, B, can be determined by measurements with high-energy

(50) The fact that there are actually two potential nonvertical transitions of *cis*-stilbene, reactions 8 and 10, would supply the necessary number of parameters to sustain such a discussion.

(51) R. B. Williams. *J. Am. Chem. Soc.*, **64**, 1395 (1942).

$$\frac{[c]_s}{[t]_s} = \frac{k_4 + k_{10}}{k_3 + k_9} \frac{k_{15} + k_{19}K_{12}}{k_{14} + k_{18}K_{12} + k_{-3}[S]} \quad (26)$$

$$\frac{[t]_s}{[c]_s} = A\left(B + \frac{k_{-3}[S]}{k_{15} + k_{19}K_{12}}\right) \quad (27)$$

$$A = \frac{k_3 + k_9}{k_4 + k_{10}} = \text{the excitation ratio}$$

$$B = \frac{k_{14} + k_{18}K_{12}}{k_{15} + k_{19}K_{12}} = \text{the natural decay ratio}$$

$$K_{12} = \frac{k_{12}}{k_{-12}} = \frac{[p]}{[t]}$$

sensitizers for which $A \cong 1$ and k_{-3} is too small to be detected. The value of B obtained from stationary-state measurements in the presence of 9,10-anthraquinone, benzophenone, and acetophenone is 0.66 at 28° with the total concentration of stilbenes equal to 0.05 M. The value for the benzophenone (0.05 M) sensitized isomerization is 0.63 with the sum of the substrate concentrations 10^{-3} M at 28° and the value decreases as the temperature is raised.[52]
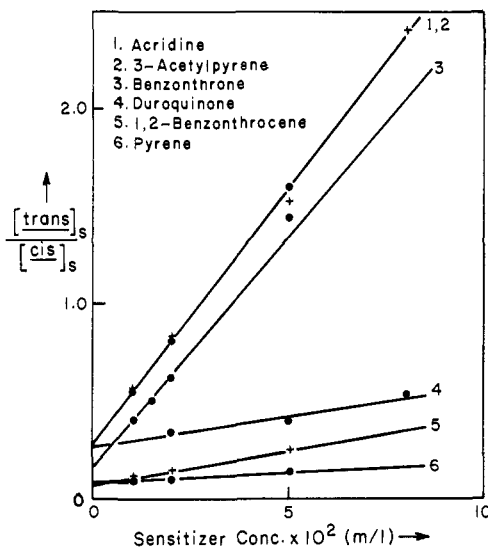
Fig. 5.—Sensitizer concentration effect on stilbene isomerization.

Figure 5 shows plots of $[t]_s/[c]_s$ against $[S]$. The approximations to linear relationships are adequate. The intercepts at $[S] = 0$ are the values of AB that are plotted in Fig. 4. The slopes are equal to $Ak_{-3}/(k_{15} + k_{19}K_{12})$. Since B has been evaluated independently, the values of A characteristic of each sensitizer can be calculated as can the values of $k_{-3}/(k_{15} + k_{19}K_{12})$. These derived data are gathered in Table IV.

The data for benzoquinone are complicated by the fact that spectrophotometric measurements show that ground-state complexes between sensitizer and substrate are formed; the consequences of direct excitation of such a complex are unknown so the value of the slope is, at present, meaningless in this case.[53] In

(52) Since B depends on $[t]_s$, eq. 26 and 27 are obviously incomplete. Study of the variation of stationary-state ratios with sensitizer concentration and with added azulene was carried out with fixed total substrate concentration before the small dependence of the ratio on substrate concentration was studied. Consequently, data are presented without explicit inclusion of the self-quenching effect as a matter of convenience.

(53) The value of A obtained by extrapolation to infinite dilution is still valid since both reversibility of energy transfer and ground-state com-
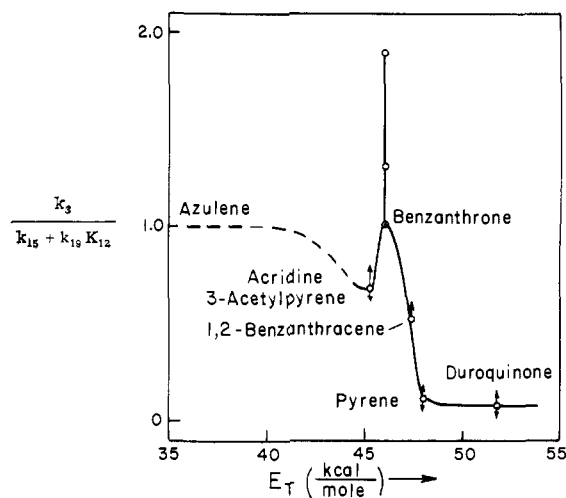

Fig. 6.—Relative rates of quenching of *trans* triplet.

the other cases it is interesting to seek for possible correlations of structure with reactivity. Figure 6 shows a plot of $k_{-3}/(k_{15} + k_{19}K_{12})$ against the excitation energies of the sensitizers. By way of comparison, the value of $k_5/(k_{15} + k_{19}K_{12})$ obtained in the study of azulene quenching (*vide infra*) is $1.3 \times 10^{+2}$ sec.$^{-1}$ l. mole^{-1}. The structure of the curve in Fig. 6 is reminiscent of Fig. 1 and 4. The maximum value of the rate constant for quenching of t by a sensitizer is encountered with benzanthrone which, within experimental error, has the same reactivity as azulene.

TABLE IV

EXCITATION RATIOS AND RATE CONSTANTS FOR REVERSIBLE ENERGY TRANSFER

Sensitizer	A	$k_{-3}/(k_{15} + k_{19}K_{12})$, 10^{-2} l. mole^{-1}
Duroquinone	0.405	0.10
Benzoquinone	2.03	0.37
Pyrene	0.120	0.14
1,2-Benzanthracene	0.104	0.52
Benzanthrone	0.224	1.7
Acridine	0.420	0.87
3-Acetylpyrene	0.438	0.88

Since we would expect azulene to quench at the diffusion-controlled rate, we infer that benzanthrone accepts energy on every collision with t. Since a maximum in the efficiency of the reverse process occurs with a sensitizer having an excitation energy of 46 kcal., we infer that a perfectly-coupled transition appears at this point. The lowest maximum in Fig. 4 was at 47 kcal. The fact that the two maxima do not quite coincide[54] indicates that there is a small loss of energy from t between the time that it is produced and the time that it returns energy to an acceptor. This corresponds to the small red shifts in band heads that are often found when emission spectra are compared carefully with absorption spectra measured under

plexing disappear in very dilute solution. No evidence for formation of a ground-state complex was found by examination of the absorption spectra of solutions containing benzanthrone (0.025 M) and *trans*-stilbene (0, 0.13, 0.050, or 0.062 M). The fact that change of either stilbene or sensitizer concentration does not affect the stationary composition of the stilbenes when 2-acetonaphthone, benzil, or fluorenone are used as sensitizers (Table I) implies that ground-state complexes are not involved in these three cases.

(54) Note that the conclusion does not depend upon exact assignments of energies; both pyrene and 1,2-benzanthracene appear to be more reactive than benzanthrone as donors. Experimentally, the maxima involve compounds, rather than energies, so there is no doubt as to the noncoincidence of the maxima in Fig. 4 and 6.

identical circumstances.[55] It is for this reason that *t* has been assigned a shallow potential minimum slightly displaced from the planar configuration in Fig. 3. The procedure is schematic and may be entirely incorrect since coordinates other than torsion about the central bond might be involved in the 1-kcal. relaxation process.

Effects of Azulene.—Explanations other than that which we prefer could be offered to account for variation in the stationary states as the concentrations of sensitizers are changed. Reversible energy transfer is only a special example of quenching of *t* and, if the mechanism is correct, other compounds having low-lying triplet states should show the same behavior. A number of likely test candidates, such as anthracene, were eliminated because they absorb the useful exciting light strongly. However, azulene, which has at least one very low-lying triplet state,[56] has a convenient window in its absorption spectrum in the 4200 Å. region. Furthermore, it has been shown that azulene quenches both benzophenone[57] and anthracene[58] at diffusion-controlled rates. Addition of small amounts of azulene to any of the reaction mixtures does change the photostationary states; in all cases the final mixtures become richer in *trans*-stilbene. Inclusion of reaction 5 in the mechanism changes eq. 27 to 28.

$$\frac{[t]_s}{[c]_s} = A\left(B + \frac{k_{-3}[S] + k_5[Q]}{k_{15} + k_{19}K_{12}}\right) \quad (28)$$

Figure 7 shows plots of $[t]_s/[c]_s$ against azulene concentration and Table V summarizes the values of $k_5/(k_{15} + k_{19}K_{12})$ extracted from the data with the usual assumption that B is constant. Within experimental

TABLE V

RELATIVE RATE OF QUENCHING OF *t* BY AZULENE

Sensitizer	E_T, kcal./mole	$k_5/(k_{15} + k_{19}K_{12})$, 10^{-2} l./mole
Benzophenone	68.7	1.2 ± 0.1
9,10-Anthraquinone	62.4	1.4 ± 0.2
Benzil	53.7	1.2 ± 0.5
Fluorenone	53.0	1.4 ± 0.2
Benzanthrone	~46	1.3 ± 0.5

error, the same result is obtained with all sensitizers. Apparently azulene produces *trans*-stilbene by quenching the same species in all experiments. The result seems to exclude all mechanisms involving decay from complex species in which sensitizer molecules are bound to substrates. It is also clear that energy transfer from the sensitizers to either *cis*- or *trans*-stilbene must lead to the ultimate production of the same species in all cases. This is the most direct available evidence for two important features of the mechanism; (1) the rapid decay of *c*, believed to be produced by transfer of triplet excitation from high-energy sensitizers to *cis*-stilbene, and (2) the production of an electronically-excited substrate species by interaction of low-energy sensitizers with *cis*-stilbene. The latter conclusion follows from the fact that the species quenched by azulene must live long enough to find
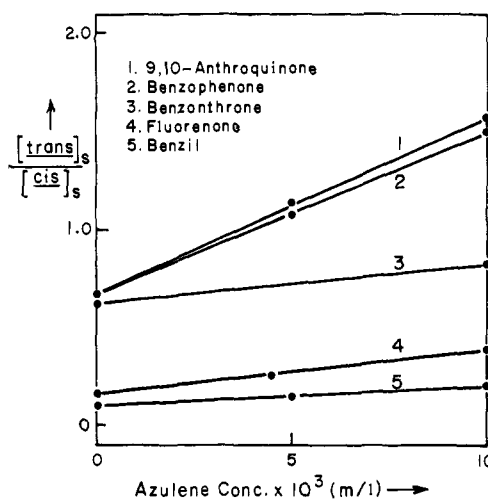

Fig. 7.—Azulene concentration effect on stilbene isomerization.

quencher molecules present in low concentration in solution. If the low-energy sensitizers were to deliver energy to *cis*-stilbene as vibrational excitation, the acceptor molecules would undergo vibrational relaxation before leaving their original site in the solution.

The average value of $k_5/(k_{15} + k_{19}K_{12})$ is 1.3 × 10² l. mole⁻¹. By analogy to the quenching of anthracene[58] and benzophenone[57] by azulene we would reasonably expect the value of k_5 to be at least close to that for a diffusion-controlled process. A conservative lower limit estimate would be 10⁹ l. mole⁻¹ sec.⁻¹. This places a lower limit of 7.7 × 10⁶ sec.⁻¹ on $k_{15} + k_{19}K_{12}$, the sum of the rate factors for natural decay process producing the *cis* ground state. Since B is 0.66, the sum of all of the rate factors for natural decay is at least 1.3 × 10⁷, that is, the effective triplet lifetime is 7.7 × 10⁻⁸ sec. or shorter. In reiteration of the qualitative argument given above, this time constant is much too long to be compatible with any relaxation process other than decay of an electronically-excited state. On the other hand, the lifetime is considerably shorter than any yet reported for triplets studied in flash experiments. The result is revealing, rather than surprising. All triplets for which decay rates have been reported phosphoresce at low temperature whereas the stilbene triplets do not. Furthermore, the fact that triplet decay times fall outside the range of those observed in studies of decay of transients in flash experiments is not surprising. The time characteristics of most flash lamps are such as to render decay times of the order of microseconds immeasurably rapid.[59] It is very likely that decay from *p* is an unusually rapid process. If the phantom triplet is distorted by twisting about the central bond, it may be very close, both in energy and configuration, to a point on the potential energy curve for the ground singlet state. Intersystem crossing at such a point would be expected to be very fast.[60]

Temperature Effects.—A preliminary study has been made on the effects of variation of temperature. Only sensitizers having activation energies of 53 kcal. per mole (fluorenone) or above have been studied and in

(55) E. Lippert, *Z. Elektrochem.*, **61**, 962 (1957).

(56) R. Pariser, *J. Chem. Phys.*, **25**, 1112 (1956).

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

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

(59) W. G. Herkstroeter has investigated this behavior of sensitizers in flash experiments in these laboratories. If a solution containing fluorenone and an excess of *trans*-stilbene is flashed, no trace of the characteristic triplet-triplet absorption spectrum of fluorenone can be seen and no new spectra are observed.

(60) W. J. Potts, Jr., *J. Chem. Phys.*, **23**, 65 (1955).

TABLE VI

TEMPERATURE EFFECTS ON SENSITIZED STILBENE ISOMERIZATION

Sensitizer	Temp., °C.	[t]$_s$/[c]$_s$	Ratio[a]
Benzophenone	28	0.69	
Benzophenone	59	0.58	1.16
4-Acetylbiphenyl	28	0.54	
4-Acetylbiphenyl	59	0.46	1.17
2-Acetylfluorene	31	0.52	
2-Acetylfluorene	59	0.46	1.13
β-Naphthyl phenyl ketone	31	0.37	
β-Naphthyl phenyl ketone	59	0.32	1.16
Fluorenone	28	0.16	
Fluorenone	59	0.11	1.45

[a] Ratio of the value of [t]$_s$/[c]$_s$ at higher temperature to that at lower temperature.

each case only high temperature (59°) has been employed. The data of Table VI show that there is a small effect in all cases. In every instance the stationary states become richer in the *cis* isomer at the higher temperature. The result is contrary to our expectations since we had anticipated that reaction 4, vertical excitation of the *cis* isomer, would show up as an activated process. This would have increased the value of A in eq. 27 making the mixtures *trans*-rich at high temperatures. The observed effect in the case of benzophenone, a high-energy sensitizer, shows that some activated step must be involved in the decay process since, in this case, A is believed to be the ratio of two diffusion-controlled rate constants. With the exception of fluorenone, the effects observed in the presence of other sensitizers are within experimental error of that observed with benzophenone. This indicates that A remains temperature-independent even when the phasing-out of reaction 4 has been well started; consequently we must infer that nonvertical excitations, reactions 8 and 10, become the dominant modes of transfer to *cis*-stilbene even with sensitizers lying in the 60 kcal. per mole energy region. Since nonclassical energy transfer is believed to be over-all exothermic in these cases, an activation energy is not necessary although we would not have been surprised to find one because of the superficial similarity between the reactions and ordinary thermal reactions.[61] *The result seems to be a striking confirmation of our inference that excitation of cis-stilbene by energy transfer need not go through known spectroscopic states of the acceptor.*

The effect with fluorenone seems to be different by an amount lying outside experimental error. Tentatively, we associate the extra large increase in [t]$_s$ with the fact that fluorenone lies to the left of the first maximum in Fig. 5. If the temperature dependence of B is considered to be known from the results obtained with the other sensitizers, we can estimate that A increases by about a factor of 1.25 when the temperature is raised from 28 to 59°. This indicates that a small activation energy must be involved in the reactions that activate the *trans* isomer. The decrease from the maximum at 54 kcal. has been interpreted as due to a decrease in the value of k_3. Consistent

(61) For example, we believe that in order for *cis*-stilbene to accept energy from a low-energy sensitizer the substrate must twist about the central bond. This might have been viewed as a modification of the thermal isomerization reaction with large assistance from the excited sensitizer. The data indicate that the analogy to the thermal process is probably a poor one. Of course, some activation energy in transfer to the *cis* isomer might be compensated by early development of activation in classical transfer to the *trans* isomer. At the most the effect must be small.

TABLE VII

QUANTUM YIELDS FOR THE PHOTOSENSITIZED ISOMERIZATIONS OF *cis*- AND *trans*-STILBENES

Sensitizer	Sensitizer concn.,[a] mole l.$^{-1}$	Stilbene concn., mole l.$^{-1}$	$\Phi_{t \to c}$	$\Phi_{c \to t}$
Benzophenone	0.1	0.05	0.42 ± 0.01[b]	
			0.41[b]	
	0.05		0.45	
			0.45	
			0.45	
			0.45	
			0.43[c]	
			0.44[c]	
		0.025	0.45	
			0.45	
		0.001	0.48	
			0.49	
	0.05	0.10		0.37 ± 0.01
				0.37
		0.05		0.38
				0.41
		0.001		0.39
				0.41
Acetophenone	1.0	0.05	0.41	
			0.40	
				0.39
				0.39
Fluorenone	0.05	0.10	0.41	
			0.41	
				0.24
				0.24
Michler's ketone	0.10	0.05	0.43 ± 0.01	
			0.43	
4-Methylbenzophenone	0.05		0.43	
			0.43	

[a] The solvent was benzene unless otherwise noted.   [b] Benzophenone used in these runs was not zone refined.   [c] The solvent was cyclohexane.

with this view is the postulate that k_3 increases as the temperature increases; *i.e.*, at higher temperatures fluorenone behaves more like benzil as a sensitizer. The effect that had been expected with the *cis* isomer has, in fact, appeared first with the *trans* compound! A corollary to this hypothesis is the conclusion that there is no readily-available path for excitation of *trans*-stilbene to a state lying lower than the spectroscopic triplet; p must lie at least as high as t on the energy scale.

The temperature dependence of B may provide a further clue as to the relative energy contents of p and t. If k_{14}, k_{15}, k_{18}, and k_{19} are assumed to be independent of temperature, the results indicate that K_{12} increases with increasing temperature.[62] This would imply that p has a higher enthalpy content than t, as is indicated in Fig. 3.

Clearly, much more extensive and accurate data are needed for proper elucidation of temperature effects. Interesting results may be expected with sensitizers having excitation energies below 50 kcal. per mole.

Quantum Yields.—Still another unanticipated phenomenon developed when quantum yields were measured. A fit to eq. 24 was expected. However, as is shown by the data in Table VII, the ratio of the quantum yields with benzophenone as a sensitizer is not equal to the ratio of the concentrations of the isomers at the stationary state. The quantum yields predict

(62) Assuming that decay of p forms more *cis*-stilbene than does decay of t.

that the stationary states should be richer in the *trans* isomer than is actually the case. Furthermore, the value of $\Phi_{t \to c} + \Phi_{c \to t}$ is consistently less than the sum of the quantum yields obtained with the 1,2-diphenylpropenes as substrates.

Four of the ketones studied, benzophenone, acetophenone, Michler's ketone, and 4-methylbenzophenone, are high-energy sensitizers which we would expect to be quenched by the stilbenes in diffusion-controlled processes; consequently, we do not expect inefficiency in the delivery of energy from the sensitizer to substrates when the latter are present in concentrations as high as 0.05 M. The four sensitizers give very similar results for $\Phi_{t \to c}$ and, in the two cases in which measurements were made, for $\Phi_{c \to t}$. Although the data in Table VII may indicate a small dependence of quantum yield of the concentration of sensitizer, we believe that the inefficiency revealed in the over-all process is largely independent of any action of the sensitizers.[63] Comparison of the data for stationary-state compositions and quantum yields serves further to localize the source of inefficiency. The quantum yield for the *cis* → *trans* process is 0.39 ± 0.02 with both acetophenone and benzophenone. These results and the stationary-state ratio (1.60) characteristic of high-energy sensitizers and very dilute stilbene solutions predict (by eq. 24) that $\Phi_{t \to c}$ should be 0.62 ± 0.02. If this were the case, the sum of the two quantum yields would, within experimental error, be equal to 1.00, our preferred figure for the efficiency of intersystem crossing of the ketones.[20] The actual results imply that there is some source of inefficiency in the *trans* → *cis* process. Variation in the concentration of *trans*-stilbene reveals the source of at least part of the difficulty. As the concentration of substrate is decreased, the value of $\Phi_{t \to c}$ increases. Two explanations can be offered to account for the result: either *trans*-stilbene itself is a quencher or the samples used contained an impurity that acts as a quencher. The latter explanation seems unlikely because the *trans*-stilbene was carefully purified and showed no impurities other than a trace of *cis*-stilbene by v.p.c. analysis. Furthermore, the same values for the stationary-state ratios were obtained starting with either *cis*- or *trans*-stilbene; different values would have been obtained if a quenching impurity had been introduced along with one isomer.[64] Consequently we invoke self-quenching by *trans*-stilbene, reaction 20, as at least a partial explanation of the results. The effect of this process would be to make the value of $\Phi_{t \to c}$ time dependent in experiments in which pure isomers are used originally; $\Phi_{t \to c}$ and $\Phi_{c \to t}$ should both be higher at the stationary state than they are when measured using initial rates of isomerization of pure isomers.

Inclusion of reaction 20 modifies the form of the stationary-state relationship from eq. 27 to eq. 29

$$\frac{[t]_s}{[c]_s} = A\left(B + \frac{k_{20}[t]_s}{k_{15} + k_{19}K_{12}} + \frac{k_3[S]}{k_{15} + k_{19}K_{12}}\right) \quad (29)$$

The equation predicts that the stationary-state com-

(63) Small variations in the quantum yields could be attributed to variations in the efficiencies of intersystem crossing of the sensitizers. However, the yields of triplets are believed to be greater than 0.9 in all cases.[20]

(64) We cannot rigorously exclude the possibility that samples of *trans*-stilbene originally contained a quencher that was destroyed by the time the photostationary condition was established.

position should depend on the value of $[t]_s$ and should, therefore, change as the total substrate concentration changes. The data in Table VIII show that there is a change in the expected direction. Comparison of our value with 0.001 M stilbenes with that obtained by Fischer[16b] with 0.0001 M solutions indicates that a limiting value has been attained. The limited data available indicate a tentative value of 2.3 l. mole^{-1} for $k_{20}/(k_{15} + k_{19}K_{12})$. That the rate constant for self-quenching should be about two orders of magnitude (2.3/130) smaller than that for quenching by azulene is reasonable.

TABLE VIII

EFFECT OF STILBENE CONCENTRATION ON THE PHOTOSTATIONARY STATE MIXTURES OF STILBENES USING BENZOPHENONE AS THE SENSITIZER

Concentration of stilbene	*cis/trans*
0.1	1.49–1.50
0.05	1.50
0.001	1.59
0.0001[a]	1.60

[a] Value determined by Fischer.[16b]

Although the trends are in qualitative agreement with the mechanism presented, quantitative correlations are not yet satisfactory. For example, the data in Table VIII indicate that the value of AB is 0.63. This should be the value of the ratio $\Phi_{c \to t}/\Phi_{t \to c}$ in the absence of self-quenching. Under such circumstances the sum of the quantum yields should be equal to the intersystem-crossing efficiency, believed to be unity for benzophenone.[20] Use of these numbers gives values for $\Phi_{t \to c}$ and $\Phi_{c \to t}$ of 0.61 and 0.39, respectively, at the stationary state in infinitely dilute solution. The predicted dependence of $\Phi_{t \to c}$ on $[t]$ is given by eq. 30

$$\frac{1}{\Phi_{t \to c}} = \frac{k_{14} + k_{18}K_{12} + k_{20}[t]}{k_{15} + k_{19}K_{12}} =$$

$$\left(\frac{1}{\Phi_{t \to c}}\right)_{[t] \to 0} + \frac{k_{20}[t]}{k_{15} + k_{19}K_{12}} \quad (30)$$

Using the value of 0.45 for $\Phi_{t \to c}$ with 0.05 M *trans*-stilbene and the value of the self-quenching constant obtained from stationary-state measurements, the value of 0.48 is calculated for $\Phi_{t \to c}$ at infinite dilution with respect to *trans*-stilbene. This is in good agreement with the values reported in Table VII but is in disagreement with the value of 0.58 estimated from the stationary-state ratio at infinite dilution. Although the source of the discrepancy cannot be pinpointed at this time, the measured values of $\Phi_{t \to c}$ change more with changing substrate concentration than would be anticipated on the basis of the changes in the stationary-state ratios. Although the estimates have been made with the minimum number of data, the discrepancy lies outside the range of probable error in the measurements. We regard self-quenching as an established factor but believe that some other process must also contribute to inefficiency in the over-all excitation process.

Behavior of the Naphthils.—The systematic variation in the stationary-state composition with the excitation energies of sensitizers is impressive and suggests that measurements made with two or three substrates

should serve as a basis for assignment of excitation energies of sensitizers. Irregularities in the relationships can always be attributed to development of more structure in curves such as that in Fig. 4 or to fundamental inadequacies in a general theory that is still in its infancy. However, in two cases, consideration of apparent anomalies has led to discovery of interesting new spectroscopic phenomena. The stationary states established in the presence of two α-diketones, α- and β-naphthil, did not seem to correlate well with triplet excitation energies estimated from phosphorescence spectra. Data are shown in Table IX. As has been reported elsewhere,[65] closer examination of the spectra clearly indicates that there are two emitting species of the α-diketones, believed to be stereoisomeric triplet states. The values of $[c]_s/[t]_s$ are in both cases intermediate between the values expected on the basis of the two different spectroscopic transition energies. Consequently, we believe that the results indicate that at room temperature excitation of the diketones produces, in each case, two isomeric triplets that can transfer energy to the stilbenes with efficiencies determined by their individual excitation energies.

TABLE IX

BEHAVIOR OF α- AND β-NAPHTHIL IN PHOSPHORESCENCE AND AS PHOTOSENSITIZERS

Sensitizer	$[c]_s/[t]_s$	Hydrocarbon glass E_T, kcal./mole[a]
$(\alpha\text{-}C_{10}H_7CO)_2$	6.81	55.3, 53.4
$(\beta\text{-}C_{10}H_7CO)_2$	5.45	58.2, 53.8

[a] See ref. 66.

Solvent Effects.—Both fluorescence and phosphorescence spectra of many carbonyl compounds show rather large solvent effects. In polar solvents the emission is found at shorter wave lengths than in nonpolar solvents.[55,66] Similar shifts are also observed in absorption spectra[67] and attributed to the fact that the normal polarity of the carbonyl group is either reversed or greatly diminished in an n $\rightarrow$ π^* transition. Since the behavior of photosensitizers in the isomerization reaction is a sensitive function of the excitation energy of the donor triplet, we were interested to see whether or not solvent effects would also appear in the sensitized reaction. Biacetyl and benzil seemed appropriate test cases since their transition energies place them in a region where high sensitivity is observed in Fig. 4. Furthermore, phosphorescence from both compounds can be observed in liquid solution at room temperature. Table X shows the observed results. The emission spectra at room temperature do not show resolvable fine structure, hence only positions of the maxima are reported. Since the entire spectrum is shifted, we presume that shifts in the maxima reflect reasonably accurately shifts in the vibrationless transitions. Since benzil is at a maximum in Fig. 4, one cannot predict accurately the direction of shift to be expected from an increase in excitation energy of $\sim$0.5 kcal. Certainly a large effect *might* have been found whereas the actual change is small. Biacetyl is located on the first steep slope of Fig. 4 so an increase in the excitation energy would have been expected to make the

photostationary mixture more *trans*-rich, i.e., the behavior should be more like that of a high-energy sensitizer. The data indicate a small shift in the opposite direction. Consequently we conclude that solvent effects on spectra are not reflected in the behavior of the compounds as sensitizers. This might mean that solvent molecules normally associated with the carbonyl group must be removed before the excitation can be delivered to an acceptor.

TABLE X

SOLVENT EFFECT ON EMISSION SPECTRA OF SENSITIZERS AND ON THEIR ACTION IN STILBENE ISOMERIZATION

Sensitizer	Solvent	Fluorescence maximum, Å.	Phosphorescence maximum,[a] Å	% cis-stilbene at stationary state
Biacetyl	Benzene	4705	5200	88.5
Bacetyl	Acetonitrile	4635	5145	89.8
Benzil	Benzene	5035	5610	92.9
Benzil	Acetonitrile	5020	5510	92.4
Benzil	n-Heptane	..	5325[b]	94.5
Benzil	EPA	..	4690[b]	93.2
2,3-Pentanedione	Benzene	..	..	87.4
2,3-Pentanedione	n-Heptane	..	5230[b]	91.1
2,3-Pentanedione	EPA	..	4950[b]	91.5

[a] Unless it is otherwise indicated, the emission spectra were recorded at room temperature, and the maximum wave lengths indicated probably do not represent 0–0 bands. [b] These values are estimations of the 0–0 band from the phosphorescence spectrum at 77°K. in the appropriate solvent.[66]

Unsensitized Isomerization.—Discussions of isomerization of the stilbenes by light absorbed directly by the substrates have been numerous and extensive. Unfortunately, most of the data that formed the basis for all but the most recent discussions were untrustworthy. For example, examination of the familiar work of Smakula[68] indicates that the quantum yields were calculated incorrectly. A more subtle source of uncertainty has recently been clarified by definition of the conditions leading to photochemical formation of phenanthrene from cis-stilbene.[69-71] Quantum yields measured without careful exclusion of oxygen are likely to be in error. Measurements of photostationary states are less likely to be in error since dissolved oxygen may be consumed at an early stage in the experiments so that stationary-state ratios are characteristic of oxygen-free conditions. One interesting feature of the unsensitized reaction is a significant dependence of the quantum yields on temperature at low temperature. Similar results have been observed in studies of isomerization of aromatic azo compounds.[9] Recent discussions show a consensus in the opinion that triplet states play a crucial role in isomerization. There is, however, divergence of opinion as to the appropriate place where activated processes should be introduced. Schulte-Frohlinde, et al.,[13] and Dyck and McClure[10] favor the view that there is a small activation energy involved in intersystem crossing, at least in the *trans* system. Malkin and Fischer[9] and Stegemeyer[12] have supported the view that there is a small barrier to interconversion of isomeric triplet

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(69) F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, J. Am. Chem. Soc., **84**, 4361 (1962).

(70) W. M. Moore, D. D. Morgan, and F. R. Stermitz, ibid., **85**, 829 (1963).

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states, although Fischer has since revised his views.[16b] The only argument that seems to be convincing to us is the demonstration by Dyck and McClure that the quantum yield of fluorescence from *trans*-stilbene is temperature-dependent. Clearly, fluorescence competes with some activated process. On the other hand, the variation of $\Phi_{t \to c}$ with temperature is very similar in stilbene and *p*-bromostilbene, despite the fact that the latter compound shows very little fluorescence at any temperature. Apparently there may be two, rather than one, activated processes.[72]

If the unsensitized reaction at room temperature involved quantitative intersystem crossing followed by decay from *t* and *p*, the photostationary states should be given by eq. 31. As is shown by the data in Table XI, there is excellent agreement between

$$\frac{[c]_s}{[t]_s} = \left(\frac{\epsilon_t}{\epsilon_c}\right)\left(\frac{k_{15} + K_{12}k_{19}}{k_{14} + K_{12}k_{18}}\right) \qquad (31)$$

calculated and measured photostationary states. Only data for dilute solutions are appropriate for comparison since the photostationary states vary with varying concentration of the substrates. The vary small quantum yield for formation of dihydrophenanthrene has been neglected in the calculation.

TABLE XI

PHOTOSTATIONARY STATES ESTABLISHED BY IRRADIATION OF
STILBENE SOLUTIONS WITH 3130 Å. LIGHT

Stilbene concn., mole l.$^{-1}$	Solvent, ϵ_t/ϵ_c		% *cis* at stationary state Obsd.	% *cis* at stationary state Calcd.^{a}
1×10^{-5}	*n*-Hexane	7.2^b	93.0^c	92.0
	Isohexane		93.0^d	92.0
1.6×10^{-3}	Benzene	5.83	89.7	90.3

^{a} Calculated from eq. 31. ^{b} Value measured in isooctane, ref. 8. ^{c} Ref. 12. ^{d} Ref. 9.

The data indicate very strongly that the natural decay ratio is the same in sensitized and unsensitized reactions. This is certainly consistent with the view that decay from triplets is involved in both cases. However, the similarity of results might also be expected if decay involved production of a high vibrational level of the S_0 state from either excited singlets or triplets, although it would be difficult to account for the effects of temperature variation on this basis. We sought more direct evidence for the implication of triplets in the unsensitized reaction. Photostationary states were established by irradiation of solutions containing stilbenes and varying amounts of azulene with 3130 Å. light. As is shown by the data in Table XII, addition of azulene makes the stationary mixtures become more *trans*-rich, as was the case in the sensitized reaction.

(72) Comparison of the arguments of Stegemeyer and Schulte-Frohlinde illustrates the all-too-common state of affairs. Both consider the feasibility of assigning the activation energy to a process that is competitive with fluorescence of the excited singlet state of *trans*-stilbene. Stegemeyer concluded that the activated process could not possibly be fast enough to compete with fluorescence whereas Schulte-Frohlinde concluded that the observed barrier was much too low to prevent destruction at a rate that would completely prevent fluorescence. The method used by the former to estimate the frequency factor for the rate process seems invalid to us. Schulte-Frohlinde makes no explicit mention of the frequency factors but apparently considers his argument valid only for adiabatic processes, such as *trans–cis* isomerization, since he later assigned the activation energy to intersystem crossing. Such presumptions seem tenable to us but are by no means definitive.
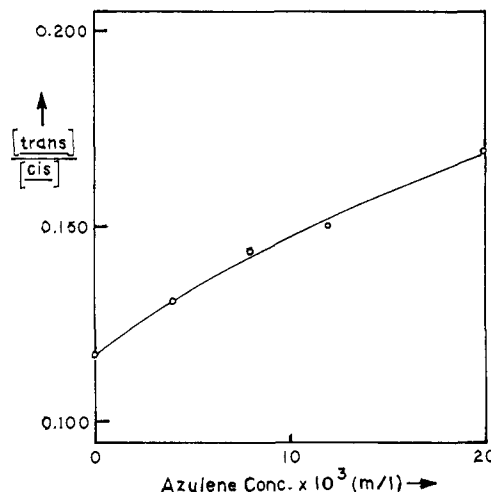

Fig. 8.—Effect of azulene on unsensitized isomerization of stilbene.

Quantitative examination of the data shows that the effect of azulene is not as large as would be predicted by eq. 32

$$\frac{[t]_s}{[c]_s} = \left(\frac{\epsilon_c}{\epsilon_t}\right)\left(B + \frac{k_5[Az]}{k_{15} + k_{19}K_{12}}\right) \qquad (32)$$

The data are plotted in Fig. 8. The relationship is not linear and the value of $k_5/(k_{15} + k_{19}K_{12})$ estimated from the initial slope is 30, as compared with the value of 130 obtained from study of sensitized reactions. The difference is much too large to be attributed to experimental error so eq. 32 must be incomplete or entirely incorrect. Two possibilities have been considered: (1) quenching of *trans*-stilbene singlets by azulene, and (2) quenching by products of side reactions. The singlet-quenching mechanism has not been ruled out but is made unlikely by the fact that

TABLE XII

EFFECT OF AZULENE IN UNSENSITIZED ISOMERIZATION^a

Azulene concn. × 10⁴, mole l.$^{-1}$	% *cis*-stilbene at stationary state
None	89.5
4.0	88.4
8.0	87.5
12.0	87.0
20.0	85.5

^{a} All experiments in benzene solution with total stilbene concentration 1.60 × 10^{-3} *M*.

addition of 1.6–2.4 × 10^{-3} *M* tris[dibenzoylmethanato]-iron(III) has no influence on the photostationary state for the unsensitized reactions. The iron chelate has been found to be an exceptionally active acceptor of singlet excitation with other donors having spectroscopic characteristics similar to those of *trans*-stilbene.[73] Although the rules governing transfer of singlet excitation are by no means clear, the result suggests that the lifetime of the S_1 state of *trans*-stilbene is too short at room temperature to allow appreciable quenching by a solute present in the concentrations involved in the experiments with azulene.

The second possibility seems very probable. Moore, Morgan, and Stermitz[70] have shown that an orange-colored intermediate is built up during irradiation of *cis*-stilbene in oxygen-free solutions. The compound

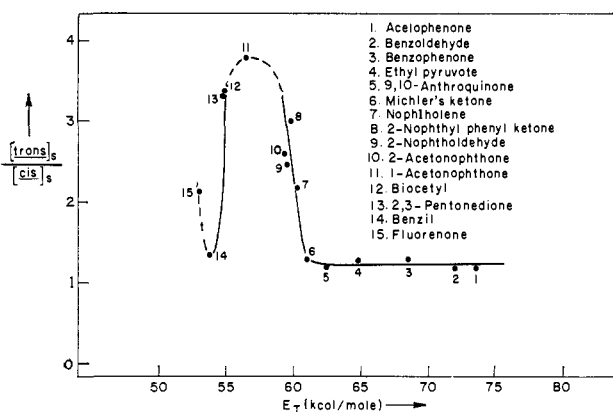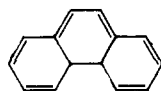(73) R. P. Foss and D. O. Cowan, unpublished studies in this laboratory.

Fig. 9.—Sensitized isomerization of the piperylenes.

is converted to phenanthrene by oxygen and slowly reverts to *cis*-stilbene in the dark and in the absence of oxygen. The following dihydrophenanthrene structure has been assigned to the intermediate:

We have also observed the rise of absorption at 4500 Å. in unsensitized experiments; there is no evidence for formation of a long-lived transient in experiments with sensitizers. Examination of solutions to which azulene was added reveals that the 4500 Å. absorption is more intense than in solutions containing no azulene. Furthermore, the decay of the long wave length absorption in the dark is not first order and is initially more rapid than in experiments without azulene. The data suggest that more than one metastable intermediate is formed and that all such intermediates are involved in the photochemistry.[74] We tentatively suggest that competitive quenching by the intermediates is responsible for attenuation of the azulene effect in unsensitized experiments. We must point out that it is not easy to devise schemes which both predict the observed effect and maintain the same decay ratio in sensitized and unsensitized reactions.

Piperylenes

Sensitized isomerization of the piperylenes has already been discussed in some detail.[17] The stationary-state ratios reported in Table XIII and Fig. 9 include data for low-energy sensitizers that were not studied previously. Improvement of the vapor chromatographic analysis has also led to modification of the numbers reported earlier.

Documentation of the behavior of low-energy sensitizers is less complete than with the stilbenes and diphenylpropenes but is sufficient to show that the response of the piperylenes to variation of the excitation energy of the sensitizers is as observed with the other substrates. There is a well defined "high-energy" region, and at least one maximum and one minimum in the curve.

The first change occurs as the sensitizer energy approaches and then drops below 60 kcal. per mole. Since stationary states become *trans*-rich as the energy of the sensitizers is decreased, we infer that *trans*-

(74) The rate of thermal reversion of Moore's intermediate to *cis*-stilbene is so slow that it would become the principal species in solution if it were not destroyed photochemically.

Sensitizer	Initial % *cis*	% *trans* at stationary state
Acetophenone	0	55
	100	53
Benzaldehyde	0	55
	100	53
Benzophenone	0	57
	100	56
Ethyl pyruvate	0	58
	100	54
9,10-Anthraquinone	0	57
	100	57
Michler's ketone	0	56
	100	56
Naphthalene	0	69
	100	68
2-Naphthyl phenyl ketone	0	76
	100	74
2-Naphthaldehyde	0	72
	100	71
2-Acetonaphthone	0	72
	100	72
1-Acetonaphthone	0	79
	100	79
Biacetyl	0	77
	100	77
2,3-Pentanedione	0	77
	100	76
Benzil	0	58
	100	56
Fluorenone	0	69
	100	67

[a] Samples in benzene solution and irradiated for 5–10 hr.

piperylene must have a transition with an excitation energy of about 59 kcal. per mole and that the lowest-lying vertical transition of the *cis* isomer must involve a slightly lower transition energy. The singlet–triplet absorption spectra of the piperylenes have now been measured by the oxygen perturbation technique[75] and the results are in striking agreement with the implications of the chemical data. The *trans* isomer has a 0–0 band at 58.8 kcal. and that of the *cis* isomer is at 56.9 kcal.

A principal reason for our not having explored the behavior of low-energy sensitizers more completely is the realization that the system will become very complicated in the low-energy region. From the study of photosensitized dimerization of butadiene and isoprene we have deduced that excitation of *s-cis* forms of open-chain dienes is an important mechanism for accepting energy from low-energy sensitizers.[22] The same should be true of the piperylenes so four vertical transitions and a variety of nonvertical transitions should play roles in energy transfer to the dienes. If an attempt is made to unscramble the behavior of this system, the first effort should involve preliminary sorting based upon expected differences in chemical behavior of triplets having fixed *cis* and *trans* configurations about the central bond of the diene system. Such a study is now in progress with 3-ethylidenecyclohexene.

Preliminary measurements were made with varying concentrations of sensitizers. As would be expected, benzophenone shows no concentration effect. Small effects were found with fluorenone and 2-acetonaph-

(75) R. E. Kellog, Du Pont Radiation Physics Laboratory, private communication.

Table XIV

Quantum Yields in Isomerization of Piperylenes by High-Energy Sensitizers

Sensitizer	Exciting light, Å.	$\Phi_c \to {}_t$	$\Phi_t \to {}_c$	$\Phi_c \to {}_t/$ $\Phi_t \to {}_c$
Benzophenone	3660	0.55 ± 0.01	0.44 ± 0.01	1.25
Thioxanthone	3130	...	...	1.24
Anthraquinone	3130	...	...	1.22
Michler's ketone	3130	0.55 ± 0.01	0.43 ± 0.01	1.23
			Av.	1.24^a

^{a} The value of $[t]_s/[c]_s$ for high-energy sensitizers is 1.22 $\pm$ 0.05.

thone. The magnitude of the effects is not large enough to modify the general shape of the curve drawn in Fig. 9 and the results are not sufficiently precise to warrant a detailed report at this time. Measurements made in various solvents (ethanol, pentane, chlorobenzene, benzene, and acetonitrile) show virtually no change of the stationary-state ratios.

Quantum Yields.—The behavior of high-energy sensitizers with the piperylenes should be relatively uncomplicated if energy transfer is diffusion-controlled with only vertical excitation of the acceptor species. Despite the fact that the natural decay ratio may be determined by decay from more than one species, a relationship such as that of eq. 24 should exist between quantum yields and the photostationary ratios. The data in Table XIV show that this expectation is realized.

Ethyl Maleate–Ethyl Fumarate

No emission spectra have been observed from either ethyl maleate or ethyl fumarate. Absorption spectra of 1.2 M solutions of the esters in ethyl iodide have been measured in 10-cm. cells. Both solutions were yellow but the spectra showed only long, structureless "tails." Since the absorption of ethyl fumarate extends farther into the visible than that of ethyl maleate, the former probably has the lower triplet excitation energy. Rough estimates of the onset of absorption suggest that the singlet–triplet excitation of the maleate lies between 72 and 77 kcal. per mole and that of the fumarate between 61 and 67 kcal. per mole.

Stationary states established by irradiation of benzene solutions containing the esters and various sensitizers have been measured and are recorded in Table XV. In all cases the stationary states were approached from both directions.

In Fig. 10 the photostationary state ratios are plotted against the excitation energies of the sensitizers. There is clearly no "high-energy" group of sensitizers as was true with all other substrate pairs for which data are reported in this paper. The first trend is toward *cis*-rich mixtures as the excitation energies of the sensitizers are lowered. *We interpret this trend as indicating that the vertical excitation energy of ethyl maleate lies higher than that of ethyl fumarate.* The structure in the curve between 60 and 69 kcal. is attributed to vibronic structure in the transitions of ethyl fumarate. We would assign the vibrationless transition to the maximum at about 61 kcal. per mole and would place the first member of a principal progression at about 65–67 kcal. The separation between the two maxima, 1400–2100 cm.$^{-1}$, is reasonable for a vibronic progression associated with stretching of a carbon–carbon double bond. In short, the explanation given for the struc-
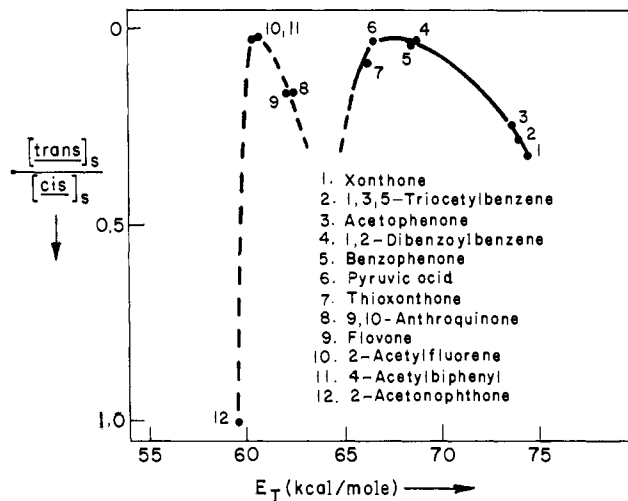

Fig. 10.—Diethyl maleate–diethyl fumarate sensitized isomerization.

ture in the plot for the stilbenes seems to be applicable to the maleate–fumarate system and leads to assignment of the triplet excitation energy of ethyl fumarate as ∼61 kcal. per mole (∼21,400 cm.$^{-1}$). Sensitizers having excitation energies below 59 kcal. per mole do not effect isomerization at appreciable rates. The data indicate as strongly, and for the same reasons, as do those for the stilbenes and diphenylpropenes that energy transfer from low-energy sensitizers must effect nonvertical excitation of ethyl maleate.

Table XV

Photostationary States Produced by Irradiation of Ethyl Maleate and Ethyl Fumarate in the Presence of Various Sensitizers at 28.5 $\pm$ 0.5°

Sensitizer^a	Ethyl maleate, %^{b}
Benzophenone	96.8 ± 0.1
Benzophenone^c	95.3 ± 0.1
Acetophenone	80.3 ± 0.3
Anthraquinone	85.8 ± 1.0
Flavone	86.3 ± 0.2
Xanthone	76.6 ± 0.8
Xanthone^c	75.4 ± 0.6
1,3,5-Triacetylbenzene	78.2 ± 0.1
p-Diacetylbenzene	96.6 ± 0.1
Pyruvic acid	92.0 ± 0.4
4-Acetylbiphenyl	97.4 ± 0.1
o-Dibenzoylbenzene	96.8 ± 0.1
Thioxanthone	95.6 ± 0.4
Thioxanthone^c	96.3 ± 0.3
2-Acetylfluorene	98.1 ± 0.1
2-Acetonaphthone	50.2 ± 0.5
2-Acetonaphthone^c	49.2 ± 0.2
1-Naphthyl phenyl ketone	42.1 ± 1.1

^{a} Sensitizer concentration 0.05 M unless otherwise noted. ^{b} Average deviations for 2–4 measurements are recorded. ^{c} Sensitizer concentration 0.01 M.

Concentration Effects.—Measurements were made using four sensitizers, benzophenone, xanthone, thioxanthone, and 2-acetonaphthone. The former pair might have been expected to show reversible energy transfer with ethyl maleate triplets and the latter two might have been expected to quench ethyl fumarate triplets. In no case was there more than a minor change in the composition of the photostationary mixture. The nonradiative decay times of the planar triplets must be very short. It is not clear whether
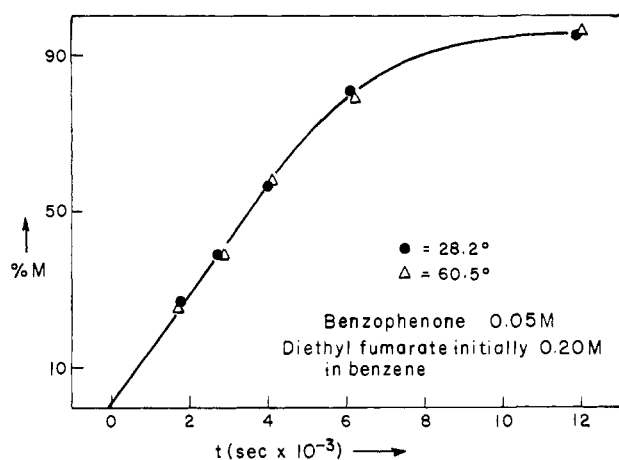
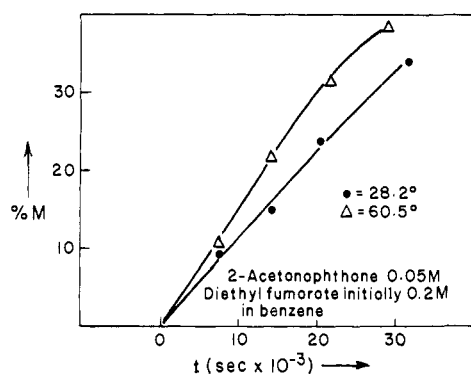Fig. 11.—Temperature effects on the benzophenone sensitized isomerization of diethyl fumarate.

Fig. 12.—Temperature effect on the 2-acetonaphthone sensitized isomerization of diethyl fumarate.

or not the fast decay processes involved distortion to twisted configurations.

Temperature Effects.—Measurements were made at 60.2° with benzophenone and 2-acetonaphthone. In the former case the amount of ethyl maleate present at the stationary state was 95.3 ± 0.1% as compared with 96.8% at 28.5°. Although the change appears small it could be interpreted as indicating that the $[c]_s/[t]_s$ ratio falls from 30.3 to 21.7 as a consequence of the increase in temperature. That the effect is associated with excitation of the *cis* isomer is indicated by measurements of the initial rates of isomerization in both directions at 60.2° and at room temperature. The results are reported graphically in Fig. 11. There is no change in the initial fumarate → maleate conversion rate with temperature and so the effect must be associated with the maleate → fumarate conversion. Precise measurement of the initial rate of the maleate → fumarate reaction is difficult since conversion is less than 5% at the stationary state. We have inferred, from the ethyl iodide absorption spectrum, that the vertical excitation energy of ethyl maleate is probably above 72 kcal. per mole; consequently one might expect that benzophenone (E_T 68.5) would excite the ester by a vertical process having an activation energy of 4–9 kcal. per mole.

With 2-acetonaphthone upon raising the temperature the amount of ethyl maleate is increased from 50.2% to 58.3 ± 0.1%; the stationary state ratio is increased by a factor of 1.4 from 1.01 to 1.40. Measurements of the initial rate of isomerization of ethyl fumarate in the presence of 2-acetonaphthone show that the effect
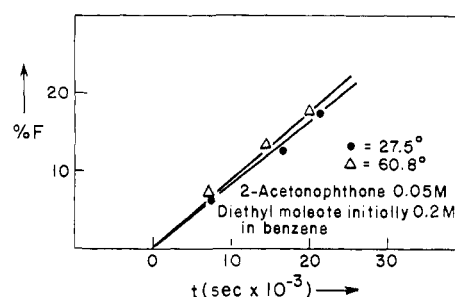

Fig. 13.— Temperature effect on the 2-acetonaphthone sensitized isomerization of diethyl maleate.

of temperature can be entirely assigned to the step involving excitation of ethyl fumarate. As is indicated by Fig. 12 the initial rate of isomerization is increased by a factor of 1.4 at the higher temperature. Assignment of the entire effect of temperature variation to energy transfer to the *trans* isomer is confirmed by measurement of the rate of isomerization of ethyl maleate by 2-acetonaphthone at the two temperatures. The data are plotted in Fig. 13. The measured rate ratio, 1.06, is really not distinguishably different from unity.

We are thus presented with an interesting paradox. Although the vertical excitation energy of ethyl maleate is believed to be higher than that of ethyl fumarate, the only activation energy in the over-all process seems to be associated with excitation of the latter. This can only be understood if the maleate is being converted directly to a low-energy, twisted intermediate. The activation energy in excitation of the fumarate may then be variously interpreted: (1) the fumarate may also be converted directly to the phantom triplet with the activation energy merely arising from the fact that the ground state of the fumarate is more stable by 4.2 kcal. per mole[52] than the ground state of the maleate; (2) fumarate is activated by a mixed process with some of the excitation involving a planar, *trans* triplet which can be reached only if excess activation energy is supplied; and (3) a small activation energy is required to push the triplet over a barrier that separates the planar *trans* triplet from the more stable phantom triplet. If the last view is adopted, it would be necessary to explain the apparent absence of activation energy in excitation of the fumarate by benzophenone. Since benzophenone triplets have more than the minimum excitation energy required to produce fumarate triplets, the latter may be produced with enough vibrational excitation to allow them to cross the barrier before they undergo vibrational deactivation.

The appearance of an activation energy in excitation of ethyl maleate by benzophenone, but not in excitation by 2-acetonaphthone, compels the conclusion that vertical and nonvertical excitation are really discontinuous processes. If this is so, vertical excitation would continue as a slightly activated process in competition with nonvertical excitation with sensitizers having just a little less excitation energy than is required for the vertical process. With sensitizers having still lower excitation energies, the vertical process would disappear completely leaving only the unactivated, nonvertical process which may be relatively inefficient because of probability factors.

Experimental

Materials. Sensitizers.—Acetophenone, biacetyl, and pyruvic acid were Matheson Coleman and Bell reagent grade and were distilled prior to use. Benzophenone, fluorenone, and benzil were Matheson Coleman and Bell reagent grade and were recrystallized prior to use. For some experiments the fluorenone was further purified by an elaborate procedure involving preparation of its phenylhydrazone and purification of the latter by chromatography on alumina and several recrystallizations from aqueous ethanol. The fluorenone was then regenerated by treatment of the pure phenylhydrazone with pyruvic acid. It was recrystallized twice from petroleum ether (b.p. 60–90°), sublimed, and zone refined.[76] The elaborate purification did not alter the behavior of fluorenone in our experiments. Benzophenone was also zone refined prior to use in some experiments. Chloranil was Matheson Coleman and Bell reagent grade and was used without purification. 1,4-Benzoquinone was Matheson Coleman and Bell practical grade. After chromatography on rosite (a 1:3 mixture by weight of carbon black in Celite), the 1,4-benzoquinone was crystallized from the concentrated eluent (benzene) and sublimed prior to use. Pyrene was Matheson Coleman and Bell practical grade. It was dissolved in benzene and chromatographed on rosite. The eluent was concentrated to dryness and the residue was recrystallized from ethanol prior to use. 9,10-Anthraquinone, Eastman Kodak sublimed, was recrystallized from acetic acid before use. 1-Naphthaldehyde and 2,3-pentanedione were Eastman Kodak White Label and were distilled prior to use. 1,4-Naphthoquinone was Eastman Kodak practical grade. It was chromatographed on rosite, recrystallized from benzene, and sublimed before use. 2-Acetonaphthone and phenanthrenequinone were Eastman Kodak White Label and were recrystallized before use. Michler's ketone (4,4'-bisdimethylaminobenzophenone) was Eastman Kodak practical grade and was recrystallized twice from methanol before use. 4-Acetylbiphenyl (Aldrich research grade), thioxanthone (Aldrich research grade), benzanthrone (Cal Biochem. practical grade), and 2-acetylfluorene (Aldrich research grade) were each chromatographed on alumina with benzene as the eluent, treated with carbon black in methanol, and recrystallized from methanol. Acridine was Eastman Kodak practical grade. It was chromatographed on rosite with diethyl ether as the eluent and was recrystallized from petroleum ether. Xanthone was Aldrich research grade and was chromatographed on rosite and on alumina using benzene as the eluent. It was recrystallized from benzene before use. Flavone was Aldrich research grade and was used without purification. 1,2-Benzanthracene was Eastman Kodak White Label and was chromatographed on rosite (benzene as the eluent), recrystallized from ethanol, and finally chromatographed on alumina. White crystals were obtained upon concentration of the benzene eluent and these were used without further purification. Eosin was from a student laboratory preparation and was recrystallized from ethanol before use. 3-Acetylpyrene was obtained crude from Dr. H. P. Waits. It was purified by chromatography on alumina, treated with carbon black, recrystallized from *n*-heptane, and finally short path distilled. 9,10-Dibromoanthracene was obtained from Dr. K. R. Kopecky and was used without purification. β-Naphthoin was prepared by the method of Gomberg and Bachmann[77] and was oxidized to β-naphthil as described by Clarke and Dreger.[78] The crude β-naphthil was chromatographed on alumina, recrystallized twice from *n*-heptane, and rechromatographed on alumina. α-Naphthoin was prepared using the procedure of Gomberg and Van Natta.[79] Oxidation of α-naphthoin and purification of α-naphthil were as described for the β-analogs.

Quenchers.—Azulene was Aldrich research grade and was sublimed twice before use. Tris[dibenzoylmethanato]iron(III) was obtained pure from Dr. R. P. Foss and was used without further purification. Its origin and physical properties have been reported.[80]

Substrates.—Samples of pure *cis*- and *trans*-1,2-diphenylpropene were generously supplied to us by Professor D. J. Cram and Mr. D. H. Hunter and were used without further purification.

cis-Stilbene was prepared and purified by Dr. K. R. Kopecky. It was shown to contain less than 1% *trans*-stilbene (v.p.c. analysis) and was used without further purification. *trans*-Stilbene was Matheson Coleman and Bell scintillation grade and was purified by either recrystallization from ethanol or by sublimation at reduced pressure. For quantum yield measurements *trans*-stilbene was purified by recrystallization, sublimation, and zone refining. This procedure yielded *trans*-stilbene which contained less than 0.1% *cis*-stilbene (v.p.c. analysis). The results obtained were independent of the method of purification of *trans*-stilbene. *trans*-Piperylene was Matheson Coleman and Bell technical grade. It contained *cis*-piperylene and cyclopentene as major impurities. Separation of the *trans* isomer was effected by preparative vapor phase chromatography on either a 6 ft. by ³/₈ in. silver nitrate–ethylene glycol column or a 12 ft. by ³/₈ in. 1,2,3-tris[2-cyanoethoxy]propane column using a Beckman Megachrom. After separation *trans*-piperylene was distilled before use. *cis*-Piperylene was Matheson Coleman and Bell technical grade and contained *trans*-piperylene and cyclopentene as major impurities. The *trans* isomer was eliminated by the method of Craig[81] and separation of *cis*-piperylene from cyclopentene was effected by preparative vapor phase chromatography on a 12 ft. by ³/₈ in. 1,2,3-tris[2-cyanoethoxy]propane column using a Beckman Megachrom. *cis*-Piperylene was distilled before use. Diethyl fumarate and diethyl maleate were Eastman Kodak White Label and were vacuum distilled prior to use.

Solvents.—For most stationary-state measurements benzene was Mallinckrodt analytical reagent grade and was washed with portions of concentrated sulfuric acid until no further darkening of the sulfuric acid layer was observed. It was then washed with water and finally with a saturated aqueous sodium chloride solution. The benzene was distilled and only a middle fraction (about 75% of total volume) was retained for use. For most quantum yield measurements benzene was Phillips research grade and was used without further purification. The two lots used were specified to be 99.89 and 99.93% pure, respectively, with toluene being the most likely impurity. However, no toluene could be found by v.p.c. analysis under conditions where even 0.1% would be detectable. Methanol was Baker and Adamson reagent grade and was used without further purification. *n*-Heptane was Phillips reagent grade and was distilled prior to use through a 4-ft. spinning band column. Acetonitrile was Matheson Coleman and Bell Spectroquality reagent and was used without purification. Ethyl iodide was Mallinckrodt A.R. grade and was chromatographed on alumina and distilled immediately prior to use.

Actinometry.—Potassium ferrioxalate was prepared using the procedure of Hatchard and Parker.[82] One volume (150 ml.) of a 1.5 F solution of ferric chloride hexahydrate (Baker and Adamson reagent grade, minimum assay 99.5%) in water was added to three volumes (450 ml.) of a 1.5 F aqueous solution of potassium oxalate monohydrate (Baker and Adamson reagent grade, minimum assay 99.0%). The flask containing the solution was wrapped in aluminum foil and refrigerated. Green crystals of potassium ferrioxalate formed. These were recrystallized three times from warm water. The formation, as well as the recrystallization of potassium ferrioxalate, was carried out in a room which was dark except for the red light from an infrared lamp. Other chemicals used in connection with the potassium ferrioxalate actinometry were reagent grade and were used without further purification.

Analytical Procedures. 1,2-Diphenylpropenes.—Mixtures of the 1,2-diphenylpropenes were analyzed by vapor phase chromatography through a column packed with Carbowax 20 M using a Loenco Model 15B vapor phase chromatographer equipped with a thermal conductivity detector. Analysis for the quantum yield experiments was carried out with a Loenco Model 15B chromatograph fitted with a flame ionization detector. A 6–7 ft. by 0.25 in. column packed with Apiezon L on 60–80 mesh firebrick was used for these analyses. Areas of peaks in v.p.c. traces were measured by disk integrators.

Stilbenes.—Four methods of analysis were employed for the determination of [*cis*]/[*trans*] ratios. These will be numbered as indicated in Table III. (1) The first method was ultraviolet spectrophotometric analysis of the mixtures of sensitizer and stilbenes. Extinction coefficients were measured for each sensitizer and the stilbenes. λ-Pipets were used for dilution purposes.

(76) All zone refining mentioned in this paper was carried out by Mr. W. G. Herkstroeter.

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Optical densities were measured for methanol solutions using 1-cm. matched quartz cells and a Beckman DU or a Cary 14 spectrophotometer. The blank solutions were methanol plus the appropriate amount of solvent in the solutions containing the stilbenes. Inclusion of the solvent in the blank was especially critical when irradiation was carried out in benzene. The wave lengths selected for analyses were 263, 276, and 295 mμ. The 263 mμ wave length is an isosbestic point for the stilbenes in methanol and the optical density at that wave length could be used to monitor the total stilbene concentration. (2) To avoid the need for correction for absorption by each sensitizer, the stilbenes were separated from sensitizers by chromatography on alumina. Contents of each reaction tube were poured on a small column (∼10 g. of alumina/3 ml. of reaction mixture) and eluted with 8–15 ml. benzene. After concentration on the steam bath, the stilbene compositions were determined by ultraviolet spectrophotometric analysis. (3) This method involved v.p.c. analysis on 4–7 ft. by 0.25 in. columns packed with 20% Apiezon L on either C-22 Firebrick (42–60 mesh) or on 20 M Chromosorb P (45–60 mesh). The same fractometers were used as were described for the 1,2-diphenylpropenes. (4) In a few cases the sensitizer interfered with the v.p.c. analysis of the stilbenes. It was, therefore, necessary to separate the sensitizer by chromatography on alumina prior to analysis by v.p.c. When the total stilbene concentration was small, some of the benzene was evaporated prior to analysis. This was accomplished by warming the solution on the steam bath under a stream of purified air. Care was taken to avoid evaporation to dryness since, when this happened, fractionation of the mixtures occurred resulting in measurements of *trans/cis* ratios which were too large.

Piperylenes.—Stationary-state mixtures were determined by v.p.c. analysis on a 10 ft. by 0.25 in. column packed with a 60:40 mixture of 25% saturated solution of silver nitrate in ethylene glycol and 25% oxydipropionitrile on C-22 Firebrick. For quantum yield measurements a 20 ft. by 0.25 in. column packed with β,β'-oxydipropionitrile (15% by weight) on Chromosorb (40–80 mesh) was employed. In general the Loenco Model 15B chromatograph equipped with the flame ionization detector was used for quantum yield measurements whereas usually the Loenco Model 15B chromatograph with a thermal conductivity detector was used for measurement of stationary states.

Diethyl Maleate–Diethyl Fumarate.—Analysis was by v.p.c. on a 6 ft. by 0.25 in. column packed with Carbowax 20M (35% by weight) on Chromosorb (40–80 mesh).

Stationary-State Determinations for Sensitized Isomerizations.—In all cases about 3-ml. samples of the solutions containing the desired concentration of substrate and sensitizer in a chosen solvent were added to each of several Pyrex culture tubes (13 × 100 mm.) which had been washed and dried and had been constrictd about 20 mm. from the top. The samples were then degassed with three to four freeze–degas (about 1 μ pressure)-thaw cycles. After degassing the tubes were sealed at the constriction.

Irradiation was carried out in an apparatus known as "the merry-go-round."[83] The tubes were held equidistant from the light source. They fitted snugly into either an inner ring of 18 circular openings, or into an outer ring of 24 openings on a rotating turntable. The tubes and the apparatus were immersed in a thermostated water bath. At the center of the rotating turntable was the inner jacket of a quartz Hanovia immersion reactor. The jacket housed a 450-w. Hanovia medium pressure mercury lamp. Cold water or filter solution was circulated through the jacket during the period of irradiation. Four different filter systems were used to insure that most, or all, of the light incident upon the tubes would be absorbed by the sensitizers rather than by the substrates. (1) The first system was merely a cylindrical Pyrex glass filter. Its absorption spectrum was measured with a Cary 14 spectrophotometer. It was opaque below 2900 Å. and transmitted 47, 75, and 90% of the 3130, 3340, and 3660 Å. mercury lines, respectively, as well as the lines of long wave lengths. (2) The second system consisted of the glass filter described above in addition to a cupric tetraammine sulfate filter solution. This solution was prepared by dissolving cupric sulfate pentahydrate (40 g.) in concentrated ammonia (68 ml.) and diluting to 1 l. with water. It was circulated through the immersion jacket (optical path about 0.7 cm.) by means of a water pump and was passed through a copper coil immersed in an ice–water bath. This system transmitted only the 4045 and

4358 Å. lines of mercury. (3) The third system was identical with system 2 except that the filter solution was 0.50–0.75 F in cupric nitrate hexahydrate. The only important line transmitted by this solution was the 3660 Å. line as well as lines of longer wave lengths. (4) The fourth filter system was a cylindrical uranium glass tube. This transmitted light of wave lengths longer than 3300 Å.

Filter system 1 was used for the piperylene experiments and system 4 was used for the 1,2-diphenylpropene and the diethyl maleate–diethyl fumarate experiments. The filter system employed for individual stilbene experiments is designated in Table III.

Stationary States for Isomerizations Induced by Direct Absorption of Light.—The apparatus described by Moore[84] was used in these experiments. It consisted of a Westinghouse (SAH 800-C) 800-w. short arc, medium pressure, mercury lamp whose light was collected and collimated by mirrors so that a parallel beam of light would pass through a filter holder and cell holder mounted on an optical bench. Four 15-mm. test tubes placed in a Beckman DU ultraviolet spectrophotometer cell holder could fit into the beam. A filter train consisting of a Corning C.S. 7-54 filter (3 mm.) and aqueous filter solutions of nickel chloride (0.455 F, 2.5-cm. path length), potassium dichromate (0.005 F, 2.0-cm. path length), and potassium biphthalate (0.0049 F, 2.0-cm. path length) in quartz cells was used to isolate the 3130 Å. mercury line. The cells in which reaction mixtures were irradiated were 15 × 125 mm. Pyrex test tubes sealed to 12/30 ground glass female joints. They were constricted a short distance below the joint. The degassing and sealing procedure was as described in the previous section, except that the tubes were connected to the vacuum system by means of glass joints rather than rubber stoppers.

The stationary states were approached from both isomers. Analyzes for the [cis]/[trans] ratios were carried out after sufficient time had elapsed to allow the colored transient(s) to disappear. In a few cases the rate of decay of transient was measured spectrophotometrically.

The extinction coefficients of the stilbenes in the 3130 Å. region as well as the extinction coefficients of azulene and tris[dibenzoylmethanato]iron(III) at 3130 Å. in benzene were measured using the Cary 14 spectrophotometer. They are shown in Table XVI. The result of this study was that the possibility that the azulene concentration effect on the unsensitized stilbene isomerization could be due to internal filtering by azulene was eliminated.

TABLE XVI

EXTINCTION COEFFICIENTS OF THE STILBENES AND QUENCHERS IN THE 3130 Å. REGION (BENZENE)

	Wave length, Å.						
	3115	3120	3125	3130	3135	3140	3150
	Extinction coefficient × 10⁻⁴						
trans-Stilbene	2.65	2.64	2.62	2.61	2.58	2.54	2.40
cis-Stilbene	0.502	0.489	0.468	0.448	0.428	0.410	0.375
Azulene				0.18			
Fe(DBM)₃				5.0			

Quantum Yield Determinations.—The optical bench described in the previous section was used. The 3660 Å. mercury line was isolated by Corning filters C.S. 7-37 and C.S. 0-52 placed in series. This line was used for the sensitized isomerization of the 1,2-diphenylpropenes and of the stilbenes. For the piperylene experiments the 3130 Å. filter train described in the previous section was employed.

The sample cells were 15 × 125 mm. Pyrex test tubes sealed to 12/30 ground glass female joints provided with a constriction for sealing and a small trap which prevented contamination of the reaction mixtures by stopcock grease from the vacuum system.

Benzene solutions of either pure *cis* or pure *trans* substrate and sensitizer were degassed and sealed (four freeze–degas–thaw cycles). The concentration of the sensitizer was in all cases sufficiently high to ensure total absorption of the incident radiation. The sample tubes were placed in a Beckman DU cell holder which was in the path of the light beam. At small time intervals, irradiation was interrupted, the contents of the tubes mixed by shaking, and the tubes placed in different positions in the cell holder before resuming irradiation. The tubes were irradiated for equal time intervals in each position of the cell holder. Total periods of irradiation were adjusted so that usually

(83) We are grateful to Mr. F. G. Moses for designing this apparatus which will be described in detail in a forthcoming paper.

(84) W. M. Moore, Ph.D. Thesis, Iowa State University, 1959.

only 2–5% isomer conversion resulted. Poassium ferrioxalate actinometry was employed.[82] Tubes containing solutions of potassium ferrioxalate (0.006 F) in 0.1 N sulfuric acid were irradiated prior to, during, and at the end of each experiment. The production of ferrous ion was determined by measuring the optical density of its complex with 1,10-phenanthroline. The extinction coefficient of the complex at 5100 Å., $(1.132 \pm 0.003) \times 10^4$ 1. mole^{-1} cm.$^{-1}$, was determined by the recommended procedure[82] using a standardized solution of ferrous sulfate. The quantum yield for ferrous ion production at 3660 Å. was taken as 1.21.[82,85]

Excitation Energies.—A detailed study of phosphorescence spectra from sensitizers used in this work will be published shortly.[89] The values of triplet excitation energies (used) refer to 0–0 band maxima in phosphorescence spectra of sensitizer solutions in glasses consisting of methylcyclohexane and isopentane (5:1 by volume) at 77°K. The emission spectra of biacetyl and benzil were also measured at room temperature in various solvents. The phosphoroscopes used in such experiments have been described.[66,90] In some cases phosphorescence could not be detected and the excitation energies refer to 0–0 bands in $S_0 \rightarrow T_1$

absorption spectra measured in ethyl iodide, carbon disulfide, o^r in the presence of high pressures of oxygen. Such values were taken from the literature.[49,91–94]

The triplet-state energy of duroquinone was estimated by assuming it to be identical with the excitation energies of 2,3-dimethyl-1,4-benzoquinone and 2,5-dimethyl-1,4-benzoquinone.[95]

The phosphorescence spectra of 4-acetylbiphenyl and 2-acetylfluorene were recorded and excitation energies of 67.5 and 64.1 kcal./mole were indicated for these two compounds, respectively. These values were not used because the presence of emitting impurities was suspected. In view of the stilbene stationary states established in the presence of these sensitizers and the fact that the 0–0 band of the phosphorescence spectrum of 4-benzoylbiphenyl is reported to be at 60.6 kcal./mole,[96] we tentatively assumed that the 0–0 phosphorescence bands for 4-acetylbiphenyl and 2-acetylfluorene are close to 60.6 kcal./mole.[97]

The 0–0 band of the phosphorescence spectrum of benzanthrone was estimated to lie at about 46.0 kcal./mole.[98]

(85) The higher value (1.7) reported by Lee and Seliger[88] is probably in error. The ferrioxalate actinometer has been checked against uranyl oxalate actinometry[82,87] and against benzophenone–benzhydrol actinometry[88] and in all cases the values of Hatchard and Parker appear to be correct.

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Charge-Transfer Complexes in Solution. I. Spectrophotometric Studies of Aromatic Hydrocarbon–Aromatic Nitro Compounds Dissolved in Carbon Tetrachloride

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Here there is reported an ultraviolet absorption spectral study of the charge-transfer complexes formed between certain methylbenzenes and selected aromatic nitro compounds in carbon tetrachloride at 20 and 45°. Toluene, *m*-xylene, mesitylene, durene, pentamethylbenzene, and hexamethylbenzene were the donors used. Acceptors were nitrobenzene, *m*-dinitrobenzene, *p*-dinitrobenzene, *sym*-trinitrobenzene, and *sym*-trinitrotoluene. The new computer method[2] designed to eliminate ambiguities from the literature was used to process all experimental information. For a given donor, the absorptivity of the complex (a_C) increases as the strength of the acceptor is increased by increasing the number of nitro groups. This fact is predicted by the charge-transfer theory. The relative order of a_C for each donor is nitrobenzene, *m*-dinitrobenzene, *p*-dinitrobenzene, *sym*-trinitrotoluene, and *sym*-trinitrobenzene. This contrasts with the well-known contradictions of Mulliken's charge-transfer hypotheses reported for complexes of a given acceptor with donors of increasing strength. Formation constants, computed with the assumption that only a 1:1 complex is formed, vary with the wave length, and the absorptivities of the complexes vary with the temperature. These facts are explained by the simultaneous formation of isomeric 1:1 and higher order complexes. Average formation constants for each of the twenty-two systems studied at 20 and 45° are given.

Introduction

It has been well established that aromatic nitro compounds are capable of forming complexes of the charge-transfer type as described by Mulliken[3–5] and more recently by Dewar and Lepley.[6] Bier[7] has investigated *sym*-trinitrobenzene complexed with aromatic amines and hydrocarbons in chloroform. Foster and co-workers[8–10] have studied a number of

nitro systems. From these works it has been determined[8] that steric effects play an important role in complex formation. Further, it has been shown that an increase in the number of nitro groups in the acceptor molecule produces an increase in the degree of association as shown by the magnitude of association constants with a number of amines.[10] Thompson and de Maine[2] have studied the effect of solvent on the *sym*-trinitrobenzene–naphthalene system. A change of solvent was found to be able to vary the magnitude of the association constants, K, by a factor of at least five. Also, the solvent has been shown to change the absorptivity of the complex.

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