KINETIC STUDIES OF ENERGY TRANSFER TO THE GEOMETRIC ISOMERS OF STILBENE AND 1,2-DIPHENYLPROPENE BY KINETIC SPECTROPHOTOMETRY

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ABSTRACT

The rate constants for triplet energy transfer from a series of photosensitizers to the *cis* and *trans* isomers of stilbene and 1, 2-diphenylpropene in benzene solution at room temperature have been measured by kinetic spectrophotometry. A plot of rate constants vs. triplet excitation energies of the sensitizers shows that there is a smooth transition from diffusion controlled to immeasurably small rates. Even when the triplet of the sensitizer is appreciably less energetic than the spectroscopic triplet of the acceptor, energy transfer takes place. In accord with previous work in these laboratories, this observation is interpreted in terms of *non-vertical* excitation in which the acceptor is excited to a triplet having lower energy and different geometry than the spectroscopic triplet. By contrast, dibenzcycloheptenol, selected as an isoenergetic and rigid model for *cis*-stilbene, accepts triplet energy less efficiently than *cis*-stilbene from a sensitizer having less than the spectroscopic triplet energy of these molecules. Evidence that 2, 4, 6-triisopropyl-4'-methoxybenzophenone transfers triplet energy to *cis*- and *trans*-stilbene at a reduced rate because of steric hindrance indicates that factors other than the relative triplet energies of sensitizer and acceptor can be important in the process of energy transfer.

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INTRODUCTION

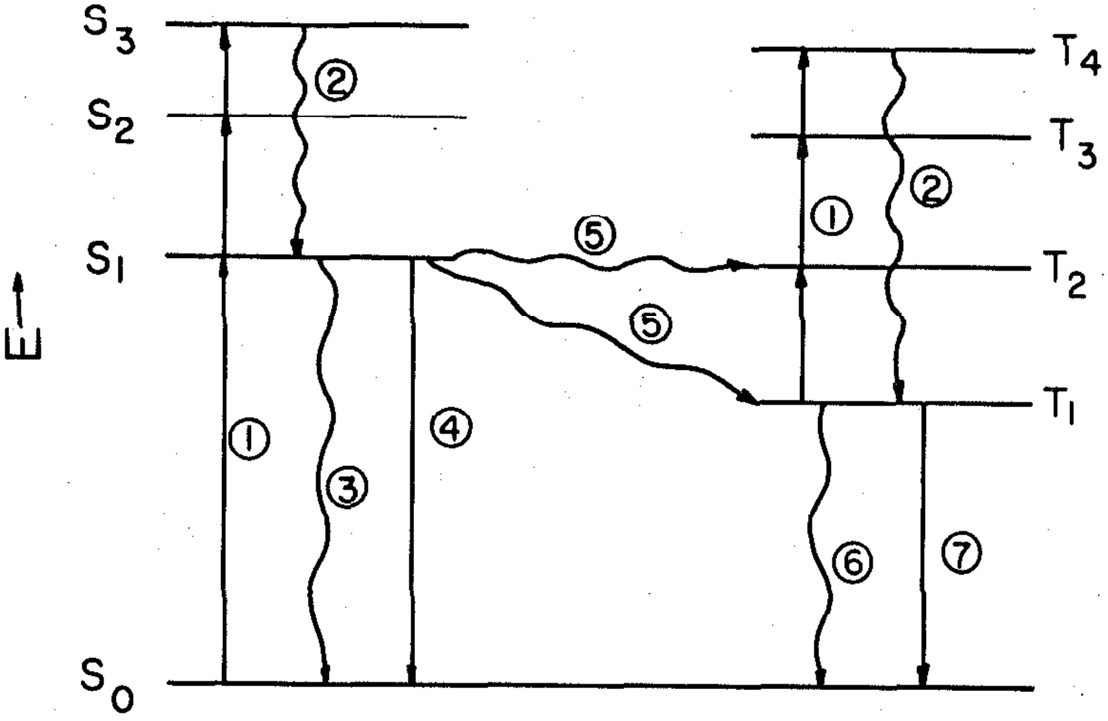
Methods for Direct Study of Triplet States:

The spectroscopist has long applied the term triplet to atoms and molecules having two unpaired electrons with parallel spins. The chemist has been equally familiar with diradicals, or molecules having two distinct unsatisfied valencies. Spectroscopic observations of triplet states originally were confined to atoms and simple molecules whereas complex organic molecules provided the most representative examples of diradicals; only recently have many diradicals been identified as triplets. The observation of triplet states in a wide variety of organic molecules and the determination of the corresponding energy levels have been important advances in the field of molecular spectroscopy. Of primary significance and interest in chemistry has been the development of methods that permit study of the physical stability and chemical reactivity of triplet states.

Present methods for studying triplet states are conveniently discussed in terms of the Jablonski diagram (1) shown in Figure 1. In polyatomic organic molecules, radiative transitions between states of different multiplicity such as singlets and triplets are highly forbidden. Since most molecules have singlet ground states in which all electrons are paired, special methods are required for direct observation and study of triplet states.

Absorption of light by the singlet ground state, depicted by path 1 in Figure 1, produces a molecule in an excited singlet state where electron spins remain paired. As shown by path 2, the molecule relaxes within approximately 10^{-12} sec. to the first

Jablonski Diagram



S_0 is the ground (singlet) state

$S_1, S_2 \ldots, S_n$ are excited singlet states

$T_1, T_2 \ldots, T_n$ are excited triplet states

Straight arrows represent radiative transitions

Wavy arrows represent radiationless transitions.

Figure 1

excited singlet by the process of internal conversion, defined as rapid radiationless combination of electronic states of like multiplicity (2). Fluorescence (path 3), or radiative return to the ground state from the first excited singlet, competes with internal conversion to the ground state (path 4) and typically has a lifetime of 10^{-6} to 10^{-9} sec. This behavior has been summarized in Kasha's rule (2): "The emitting level of a multiplicity is the lowest excited level of that multiplicity." The rationale is that the spacing between excited states is almost always small as is required for effective internal conversion, whereas the spacing between the first excited state and the ground state is large by comparison.

A third process for depopulating the first excited singlet state is intersystem crossing (path 5), defined as internal conversion to the triplet manifold (2). This process involves spin inversion of one electron to produce an excited state in which two unpaired electrons have parallel spins. The triplet state generally has a lower energy than the corresponding singlet because, unlike the singlet, the spacial distribution of unpaired electrons in the triplet state is such as to keep electron-electron repulsion at a minimum (3). The lifetime of the first triplet state is limited by the sum of radiative (path 6) and non-radiative (path 7) decay process to the ground state. The former process, termed phosphorescence, typically has lifetimes from 10^{-4} to more than 10 seconds. The first triplet state has a long lifetime because the highly forbidden nature of the $T_1 \leftarrow S_0$ absorption also applies to the reverse emission.

Although it had been known for half a century that aromatic molecules and dyes phosphoresce, it was not until 1944 that Lewis and Kasha (4) clearly and convincingly interpreted phosphorescence in terms of emission from triplet states. Since this time, extensive work has established the triplet energy levels and radiative lifetimes of a large number of molecules. It is to be noted, however, that phosphorescence is associated almost exclusively with solids and very viscous liquids and is only rarely detected in fluid media.

Two more recently developed methods are now used in the direct observation of triplet states in fluid media. In the first of these, "heavy atom" solvents or environments such as ethyl iodide or high oxygen pressures are employed to enhance the probability of $T_1 \leftarrow S_0$ transitions to the point where they can be detected in triplet-triplet absorption spectra*. By a process called spin-orbital coupling, the heavy atoms induce some mixing between the singlet and triplet states to make the transition less forbidden.

Flash excitation (flash photolysis) techniques have come to be of more use in the study of triplet states. This method utilizes a high intensity burst of light to provide excitation energy for the transition from the ground state to upper singlet states. Triplets are formed after internal conversion and intersystem crossing. Before the molecules decay to the ground state, a second light source is used to detect the triplets by means of their absorption spectra. Absorption from the first excited triplet to higher triplets, path 1 in the triplet manifold in Figure 1, is not forbidden by spin conservation rules and is usually of intensity comparable with

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*For recent results see reference 5.

singlet-singlet absorption spectra. Internal conversion (path 2) in the triplet manifold rapidly returns the molecules to the first triplet state. The time resolution of typical flash apparatus is such that the first triplet is the only excited state with sufficient lifetime to be detected.

Two sub-classifications of flash excitation depend upon the nature of the second light source. If a second flash source is used in conjunction with a spectrograph, the entire triplet-triplet absorption spectrum can be recorded after the first flash. This variation is termed flash spectroscopy. Kinetic spectrophotometry, by contrast, employs a steady-state monitoring source as the second lamp and, with a monochromator to isolate a particular triplet-triplet absorption band, records with a photoelectric detector the change in absorption intensity as a function of time. This latter method is illustrated schematically in Figure 2.

One may question the authority with which absorption spectra are assigned to triplets; other spectra obtained under similar experimental conditions are frequently assigned to sources other than triplets. The triplet assignments are supported by several types of evidence. First, the study of a series of related molecules usually makes possible the identification of spectra which arise from free radicals and other transient products (6). Second, the spectra assigned to triplet states are also observed in rigid solvents where they decay with the same rate as phosphorescence (7); free radicals, if formed at all in rigid solvents, are usually trapped indefinitely (8). More recently, theoretical calculations and absolute measurements of extinction coefficients have provided a third type of evidence. In

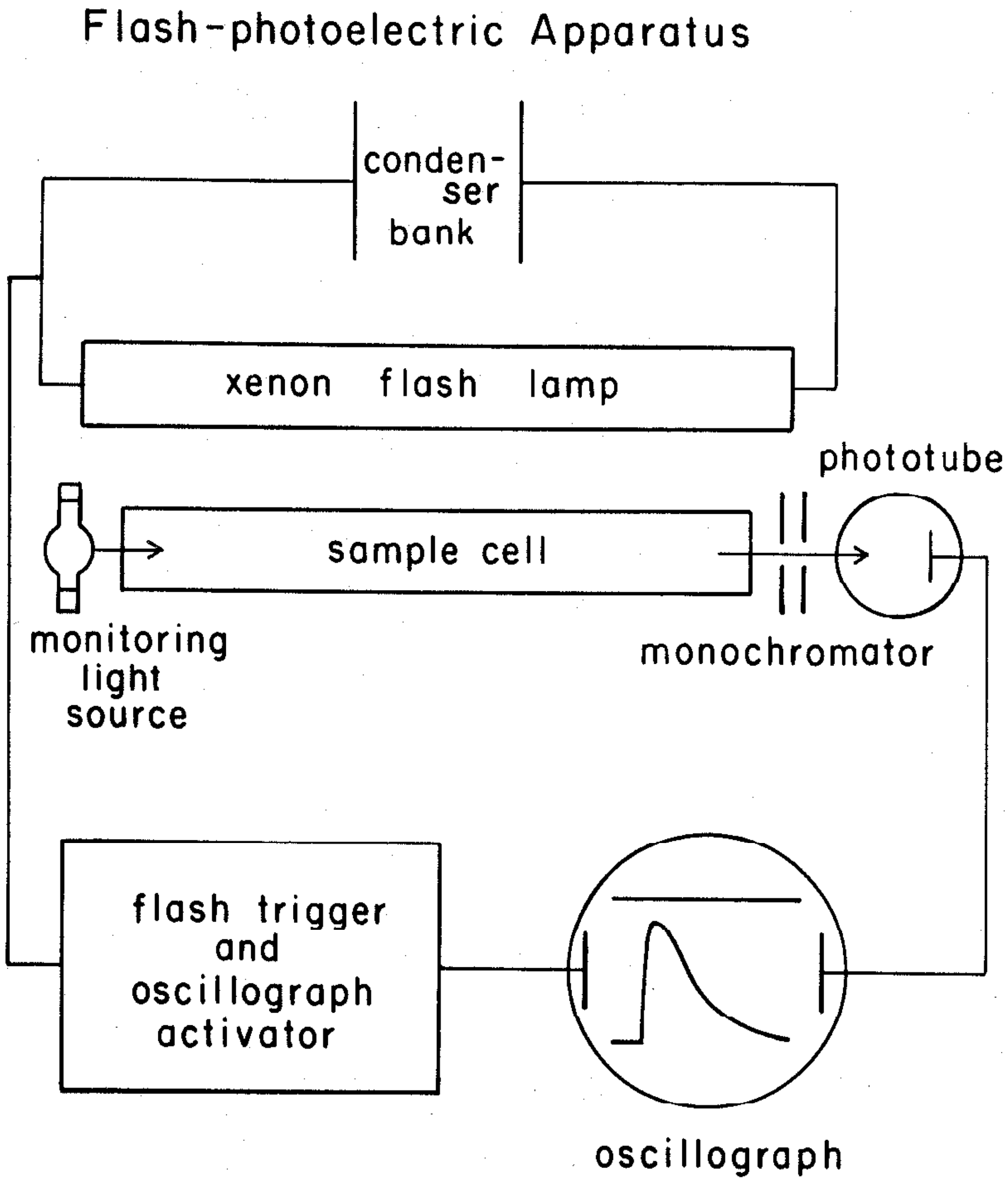
Flash-photoelectric Apparatus
condenser bank
xenon flash lamp
phototube
sample cell
monitoring light source
monochromator
flash trigger and oscillograph activator
oscillograph

Figure 2

some flash experiments, the fraction of molecules converted to the triplet state is sufficiently high to permit measurement of the degree of singlet state depopulation; from this information triplet concentrations and extinction coefficients of triplet-triplet transitions can be determined (7). When these latter values are compared with the results of semi-empirical molecular orbital calculations such as those of Pariser (9), the general picture, although not very precise, leaves little doubt as to the identity of theoretically predicted triplet levels and those measured by flash excitation (7). In many cases, however, comparison of absorption spectra and transient decay kinetics with those of more firmly established examples of triplet transients is the only basis for assignment of transient spectra to triplet states.

The advantages of flash excitation over other methods, both direct and indirect, in the study of triplet states are manifold. To begin with, triplets can be observed in fluid media by flash excitation techniques even though phosphorescence is only rarely detected under such conditions (10). In fact, flash excitation investigations are applicable over wide ranges of physical conditions and in the presence of a variety of chemical reagents. The light intensity available from a flash source is several orders of magnitude greater than from any presently available steady-state lamp (11). Therefore, triplets can be produced in higher concentration and more uniform distribution than would otherwise be possible. Furthermore, it is not necessary that the intersystem crossing efficiency be high. The time required for absorption and return to the ground state within the singlet manifold is very short compared with typical flash duration times so that molecules can be excited repeatedly with a single flash until intersystem crossing is effected. Because of the high fractional yield of triplets, the initial concentration of ground state molecules need not be high.

Many aromatic ketones, heterocycles, and hydrocarbons are amenable to flash excitation investigations of triplet states. Extensive measurements of triplet-triplet absorption spectra together with the corresponding extinction coefficients have been reported by Porter and co-workers (6, 12). In most compounds studied, the triplet-triplet absorption bands can readily be distinguished from the singlet-singlet spectra because the former lie at longer wavelengths. These measurements were made in solution where, in spite of the fact that phosphorescence is rarely observed, triplets are produced in measurable quantity. Kinetic investigations have shown that deactivation processes compete very effectively with phosphorescence to make the overall rate of triplet depopulation in fluid media several orders of magnitude greater than in rigid media. Before the kinetics of triplet decay can be discussed, the concept of energy transfer from the triplet state must be introduced.

Triplet Energy Transfer:

Terenin and Ermolaev (13) were the first to demonstrate unambiguously transfer of electronic energy from donor to acceptor molecules. These authors studied the sensitized phosphorescence of naphthalene and its derivatives (acceptors) with benzophenone and similar molecules as donors in rigid ethanol-ether glasses at -195°C, using light absorbed only by the donors. They detected sensitized acceptor phosphorescence concomitant with quenching of donor phosphorescence and determined rate constants for the transfer process. In all the donor acceptor pairs for which sensitized phosphorescence was observed, the donor triplet levels were higher than the acceptor triplet levels. Furthermore, the first excited singlet level of the acceptor was higher than that of the donor, making transfer involving excited singlet states improbable. The data are consistent with the mechanism depicted in equation 1, where D and A represent donor and acceptor, respectively, and S_0 and T_1 correspond to the electronic states involved.

$$D^{T_1} + A^{S_0} \rightarrow D^{S_0} + A^{T_1} \quad . \qquad (1)$$

These studies by Terenin and Ermolaev (13) also first demonstrated the requirement of close approach of donor and acceptor in triplet energy transfer. The distance between centers of donor and acceptor molecules within which transfer takes place was determined to be 10 - 15 Å for 23 donor-acceptor pairs. This information is consistent with an exchange mechanism requiring overlap of the electron clouds of the participating molecules. This would imply that energy transfer may be possible over distances somewhat larger than those of molecular contact. In fluid solution, however, a molecular encounter (involving repeated collisions) would nevertheless be necessary for the transfer to take place (14).

Porter and Wilkinson (15) employed flash spectroscopy and kinetic spectrophotometry in the investigation of triplet energy transfer in fluid solution. The results, which are listed in Table 1, were much as anticipated. The first 9 pairs of donor and acceptor

TABLE 1

Rate Constants for Energy Transfer in Fluid Solutions

Donor[a]	Acceptor[a]	Solvent	Rate Constant k_Q(M.$^{-1}$sec.$^{-1}$)
phenanthrene	naphthalene	hexane	2.9 ± .7 x 10^6
phenanthrene	naphthalene	ethylene glycol	2.3 ± .8 x 10^6
triphenylene	naphthalene	hexane	1.3 ± .8 x 10^9
phenanthrene	1-bromonaphthalene	hexane	1.5 ± .8 x 10^8
phenanthrene	1-bromonaphthalene	ethylene glycol	1.5 ± .8 x 10^8
phenanthrene	1-iodonaphthalene	hexane	7 ± 2 x 10^9
phenanthrene	1-iodonaphthalene	ethylene glycol	2.1 ± .2 x 10^8
benzophenone	naphthalene	benzene	1.2 x 10^9
biacetyl	1,2-benzonthracene	benzene	3 ± 2 x 10^9
naphthalene	1-iodonaphthalene	ethylene glycol	2.8 ± .3 x 10^8
1-bromonaphthalene	1-iodonaphthalene	ethylene glycol	8 ± 4 x 10^7

Systems showing no quenching for which upper limits were obtained

naphthalene	phenanthrene	hexane	≤ 2 x 10^4
naphthalene	phenanthrene	ethylene glycol	≤ 1 x 10^5
naphthalene	triphenylene	hexane	≤ 5 x 10^4
1-bromonaphthalene	phenanthrene	ethylene glycol	≤ 5 x 10^4
naphthalene	benzophenone	benzene	≤ 1 x 10^4
1,2-benzanthracene	biacetyl	benzene	≤ 5 x 10^4
anthracene	phenanthrene	ethylene glycol	≤ 5 x 10^3
anthracene	naphthalene	hexane	≤ 4 x 10^4
anthracene	1-iodonaphthalene	ethylene glycol	≤ 2 x 10^4

a. Reference to the sources of triplet energies of donors and acceptors is given in reference 14 and the Appendix.

compounds have energy levels such that only the donor molecules absorbed incident light. Both quenching of the donor triplet and formation of the acceptor triplet by energy transfer were observed directly, thus providing proof for the process characterized in equation 1. The only energetically feasible alternative,

$$D^{S_n} + A^{S_0} \rightarrow D^{S_0} + A^{T_1}, \qquad (2)$$

would not lead to quenching of the triplet donor but rather to quenching of the fluorescent state. This process is experimentally excluded by the fact that in all cases where fluorescence was observed the fluorescence yield was unaffected by added quencher. Finally, the "trival process" of light emission and reabsorption can be excluded since, with the exception of biacetyl, the fraction of molecules that decay by a radiative process in fluid solution is negligible (16).

The rate constants listed in Table 1 fall broadly into 3 groups depending upon the relative spacing between donor and acceptor triplet levels. When the triplet level of the donor is 3 or 4 kcal. greater than that of the acceptor, the rate approaches that expected for a reaction determined by the rate of diffusion of reactants together. There is no indication that the quenching efficiency decreases as this separation increases. The rate constant for encounter, k_Q, may be calculated from the following equation of Debye (17)

$$k_Q = \frac{8RT}{3000\eta} \text{ M.}^{-1} \text{ sec.}^{-1}, \qquad (3)$$

where η represents solvent viscosity. At 20°C, the calculated values are 2.0×10^{10}, 1.0×10^{10}, and 3.3×10^{8} for hexane, benzene and ethylene glycol, respectively, and are in fair agreement with the rate constants in Table 1. As the spacing between triplet levels in donor and acceptor molecules decreases, quenching occurs at a rate considerably less than the encounter rate. When the triplet level of the donor is below that of the acceptor, no quenching is observed.

A more detailed study of triplet energy transfer in fluid solution has been carried out by Sandros and Bäckström (14, 18). They measured rates of energy exchange between biacetyl and a variety of acceptors, several of which phosphoresce detectably in benzene solution. The experimental procedure involved exciting biacetyl with a flash source and measuring the decay of biacetyl phosphorescence as a function of added acceptor concentration. Likewise, the decay of acceptor phosphorescence was recorded as a function of biacetyl concentration. Using this technique, Sandros and Bäckström discovered reversible triplet energy transfer between biacetyl and various acceptors. Reversible energy transfer is depicted in equation 4 where k_F and k_R represent the rate constants for the forward and reverse processes, respectively.

$$D^{T_1} + A^{S_0} \underset{k_R}{\overset{k_F}{\rightleftarrows}} D^{S_0} + A^{T_1} \quad . \qquad (4)$$

With reversible energy transfer, of course, the distinction between donor and acceptor is lost. For convenience, however, biacetyl is referred to here as the donor and the other substances as acceptors.

Biacetyl has a measured triplet energy of 56.3 kcal./mole in benzene solution at room temperature (14, 18). Those acceptors with triplet energies less than 49 kcal./mole have practically the same value of k_F. This value is close to the limit set by the rate of diffusion as estimated by the Debye equation (17). As given above, the calculated limiting value in benzene at $20^{\circ}C$ is 1.0×10^{10} M.$^{-1}$ sec.$^{-1}$. For acceptors with triplet levels higher than 49 kcal./mole, the general trend is a lowering of the quenching constant in a smooth progression with increasing triplet state energy. Quenching efficiency is still measurable even when the triplet transition energy of the acceptor is greater than that of the donor. Similar considerations apply to the reverse energy transfer process of equation 4. Diffusion controlled rate constants, k_R, are achieved for those acceptors having a triplet energy 5 kcal./mole above that of biacetyl. The magnitude of the rate constants decreases in a smooth progression with acceptors having lower triplet energies. These results are summarized below in Table 2.

The fact that "endothermic" energy transfer takes place is explained by Sandros and Bäckström (14, 18) in terms of a Boltzmann distribution of vibrational energies in the electronic states involved. The additional energy required by the "endothermic" transfer can be supplied by vibrational energy in the donor triplet and acceptor ground state and vice versa for the reverse reaction. When the triplet energy of the acceptor is higher than that of the donor by a quantity ΔE_T, Sandros (18) has shown that the rate constants k_F and k_R are related by the expression in equation 5, where k is Boltzmann's constant.

$$k_F = k_R \exp(-\Delta E_T/kT) \quad . \tag{5}$$

TABLE 2

Rate Constants for Reversible Energy Transfer with Biacetyl[a.] as Donor

Acceptor	E_T Acceptor[b.] (cm^{-1})	log k_F	log k_R	$\log[k_F \exp(-\Delta E_T/kT)]$	$\log[k_R \exp(-\Delta E_T/kT)]$
Pyrene	16930	9.88	4.23	3.98	-
1, 2 Benzpyrene	18510	9.77	7.69	7.23	-
Fluoranthene	18510	9.72	7.33	7.17	-
2, 2' -Dinaphthyl	19560	9.47	9.13	9.17	-
1, 5-Dinitronaphthalene	19900	9.37	c.	-	-
1, 8-Dinitronaphthalene	20000	9.41	c.	-	-
1-Iodonaphthalene	20500	7.54	c.	-	-
1-Chloronaphthalene	20645	7.46	9.59	-	7.58
1-Bromonaphthalene	20650	7.47	9.53	-	7.51
2-Iodonaphthalene	21040	6.77	c.	-	-
Naphthalene	21180	6.42	9.95	-	6.80

a. The triplet energy of biacetyl is 19700 cm^{-1}.

b. References to the sources of these values are given in reference 18.

c. The reverse rate constant could not be measured in these experiments because the acceptor did not phosphoresce detectably in benzene solution.

When the donor has a higher triplet energy, the expression in equation 6 is valid in the reverse direction.

$$k_R = k_F \exp(-\Delta E_T/kT) \quad . \qquad (6)$$

With a triplet energy difference of zero between donor and acceptor, k_F and k_R are equal to 1/2 the diffusion controlled rate constant. The good agreement between the values predicted by these equations and those measured experimentally is shown in Table 2.

As had been pointed out earlier (13b), the 1-halo naphthalenes are well suited for testing whether the rate constant for triplet energy transfer depends upon the oscillator strength of the $T_1 \leftarrow S_0$ transition in the acceptor. Whereas these substances have approximately the same triplet energies, the oscillator strengths for their $T_1 \leftarrow S_0$ transitions differ markedly. From Ermolaev and Svitashev's (19) measurements, the oscillator strengths for 1-chloro-, 1-bromo-, and 1-iodonaphthalene are in the ratio 1:14:170. Ermolaev and Terenin (13b) found that naphthalene and its 1-halo derivatives were equally effective within experimental error as quenchers of benzophenone phosphorescence. As shown in Table 2, Sandros (18) likewise found the rate of energy transfer from biacetyl to the 1-halo naphthalenes was independent of the above oscillator strengths in the acceptors. It should be noted that Sandros' system was expected to be sensitive to small effects since the acceptors had higher triplet energies than the donor and the rate of energy transfer was less than diffusion controlled by two orders of magnitude.

Kinetics of Triplet State Decay in Fluid Media:

The decay of triplet states of polyatomic molecules in solution conforms to the following empirical equation:

$$-\frac{d[T_1]}{dt} = k_1[T_1] + k_2[T_1]^2 \ . \qquad (7)$$

In this equation k_1 is the sum of all rate constants for first order and pseudo first-order terms in T_1, and k_2 has a similar designation for the second-order terms.

Because primary interest is in the first-order decay terms, only a limited number of second-order rate constants have been reported (20-22) and most of them have been for anthracene triplets. These rate constants, measured in a number of solvents over a 100° range of temperature, are close to those expected of diffusion controlled reactions. The measured values of k_2 are easily reproducible; similar results have been obtained with different samples of solvent and in different laboratories. A probable mechanism for this second-order interaction has been suggested by Robinson and co-workers (23) and also by Parker (24). This process, termed triplet-triplet annihilation, involves energy transfer from one triplet to another to produce an excited singlet in one molecule and the ground state in the other. The excited singlet may then return by conventional means to the ground state.

$$D^{T_1} + D^{T_1} \rightarrow D^{S_n} + D^{S_0} \ . \qquad (8)$$

In contrast to the second-order kinetic terms, widely discordant values have been reported for k_1, depending upon the experimenter and even upon the sample of solvent used by the same experimenter. Exhaustive purification of the system being studied usually reduces the measured value of k_1. Some examples of widely divergent first-order rate constants that have been measured for naphthalene and anthracene triplets are listed in Table 3.

TABLE 3

Measured First-Order Terms in Hexane Solution at Room Temperature

Substance	k_1 (sec^{-1})	Reference
naphthalene (in benzene)	4.1×10^2	18
naphthalene	9.6×10^2	25
naphthalene	2.8×10^3	15
naphthalene	1.2×10^4	20
anthracene	5.6×10^1	26
anthracene	1.3×10^4	20

Livingston and co-workers (25, 27) have presented strong evidence that the rate constant for first-order triplet decay in solution is the sum of two terms. The first of these is independent or practically independent of temperature and viscosity over a wide range and corresponds to the true unimolecular, radiative and non-radiative, disappearance of the triplet state. The second term varies with temperature and viscosity and appears to be the result of bimolecular quenching by adventitious quenchers present in trace amounts. One of the most likely candidates is oxygen, because it is known to be an efficient acceptor of triplet excitation energy (21,28) and is an almost universal impurity. Livingston contends that in viscous or moderately viscous solutions quenching by oxygen or any other quencher should be a process limited by rates of diffusion. Under these circumstances, the first-order rate constants fit the equation

$$k_1 = k_1^{\,o} + k_Q^{\,o} \exp(-\Delta E^{\ddagger}/RT)[Q] , \qquad (9)$$

where $k_1^{\,o}$ is the true unimolecular rate constant. The energy of activation equals

$$\Delta E^{\ddagger} = \Delta E_{\eta} = [RTT'/(T' - T)] \ln(\eta/\eta') , \qquad (10)$$

where η is solvent viscosity. Of course, the rate of quenching cannot increase indefinitely as the viscosity is decreased. At sufficiently high temperatures, quenching must change from a process limited by the frequency of encounters to an ordinary collisional reaction with an activation energy less than that given in equation 10. This explanation is substantiated by reported decreases in activation energies for measured first-order terms as determined from Arrhenius plots (log k_1 vs. $1/T$) (21, 29). Livingston's overall interpretation is believed to be compatible with all published data.

Rate constants for energy transfer to added acceptors can readily be evaluated by measuring the rate of donor triplet decay as a function of acceptor concentration. This quenching process is, of course, subject to the same considerations as adventitious quenching.

Another possible quenching mechanism involves interaction between a triplet and a ground state molecule of the same substance as shown in reaction 11.

$$D^{T_1} + D^{S_0} \rightarrow 2D^{S_0} \ . \qquad (11)$$

This mechanism, termed self-quenching, has been established for chlorophyll (30) and trans-stilbene (31, 32). The magnitude of self-quenching is frequently small and is difficult to distinguish from quenching by impurities added with the solute.

The Photosensitized cis-trans Isomerization of Stilbene and 1, 2-Diphenylpropene:

Transfer of triplet excitation energy has been applied extensively in photochemistry*. In usual practice, a donor molecule transfers energy to an acceptor, which then undergoes reaction in the triplet state. When applied to this process, donor molecules are called photosensitizers or simply sensitizers and the overall process is termed photosensitization. The properties of a good sensitizer are that it be photochemically stable, that it have a smaller splitting than the acceptor between S_1 and T_1 states,

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* See, for example, reference 33 and references therein.

and that it form triplets efficiently (33). The success of sensitized reactions in photochemistry is due in large measure to the fact that the energy gap between S_1 and T_1 states varies widely in organic molecules. It is feasible, therefore, to excite a sensitizer using light of wave length longer than any absorbed by the acceptor and thus effect selective and efficient population of acceptor triplet states.

The study by Hammond and Saltiel (31, 32, 34) of the cis-trans isomerization of stilbene, an application of the method of photosensitization, has been thorough and rewarding. Attempts to detect long-lived triplet state intermediates of stilbene by phosphorescence and flash spectroscopy have been unsuccessful, and study of stilbene triplet states has been accomplished only by means of triplet excitation energy transfer. The behavior of the stilbene isomers in these energy transfer studies has led to certain postulates regarding the nature of triplet excitation transfer processes and the factors that determine their efficiency. Only the highlights of this study are summarized here.

An important consideration is the relative energy levels of the ground state and lowest excited states of cis- and trans-stilbene, as shown in Figure 3. The singlet excitation energies refer to the 0' - 0 bands in the absorption and fluorescence spectra of trans-stilbene and in the absorption spectrum of cis-stilbene (35). Since all attempts to detect phosphorescence from stilbene have failed, the assignments of triplet energy values are based upon absorption spectra taken in ethyl iodide solvent (35) and in an environment of high oxygen pressure (36). The difference in the ground state energies of the two isomers is estimated from the respective heats of hydrogenation (37).

Lowest Electronic States of the Stilbene Isomers

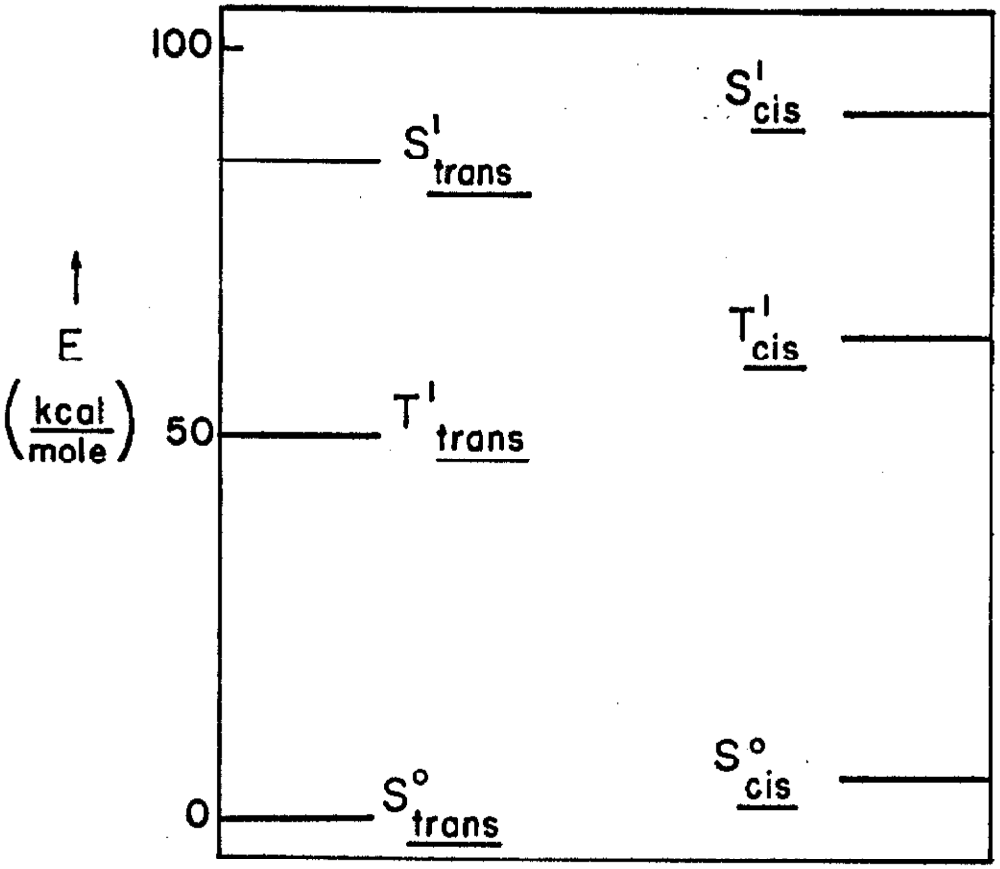


Figure 3

In the study by Hammond and Saltiel (31, 32, 34), solutions containing cis- or trans-stilbene and an appropriate sensitizer were irradiated under conditions such that virtually all incident light was absorbed by the sensitizer. The only energetically feasible process was transfer of triplet energy from sensitizer to stilbene. Regardless of the initial isomeric composition, stilbene isomerization could be effected to a photostationary state characteristic of each particular sensitizer. A photostationary state is defined as the isomeric composition achieved when the rate of conversion from cis- to trans-stilbene is equal to the rate of the reverse process. Results are consistent with the following mechanism, where S represents the sensitizer, t the trans isomer, c the cis isomer, and the superscripts refer to the electronic states involved.

$$S^{S_0} \xrightarrow{h\nu} S^{S_1} \rightarrow S^{T_1} \tag{12}$$

$$S^{T_1} + t^{S_0} \underset{k_{-13}}{\overset{k_{13}}{\rightleftarrows}} S^{S_0} + t^{T_1} \tag{13}$$

$$S^{T_1} + c^{S_0} \xrightarrow{k_{14}} S^{S_0} + c^{T_1} \tag{14}$$

$$S^{T_1} + c^{S_0} \xrightarrow{k_{15}} S^{S_0} + t^{T_1} \tag{15}$$

$$c^{T_1} \xrightarrow{k_{16}} t^{T_1} \tag{16}$$

$${}_{t}T_1 \xrightarrow{k_{17}} {}_{t}S_0 \tag{17}$$

$${}_{t}T_1 \xrightarrow{k_{18}} {}_{c}S_0 \ . \tag{18}$$

As illustrated in Figure 4, the stilbene photostationary states have been correlated with the triplet excitation energies of the various sensitizers (31, 32). The structure of the curve in Figure 4 has been attributed entirely to variation in the rates of excitation transfer. The mechanism given above predicts the following relationship at the photostationary state.

$$\frac{[c]_s}{[t]_s} = \left(\frac{k_{13}}{k_{14} + k_{15}}\right)\left(\frac{k_{18}}{k_{17} + k_{-13}[S]}\right) \ . \tag{19}$$

When the reverse transfer between *trans*-stilbene and the sensitizer is negligible, equation 19 reduces to equation 20.

$$\frac{[c]_s}{[t]_s} = \left(\frac{k_{13}}{k_{14} + k_{15}}\right)\left(\frac{k_{18}}{k_{17}}\right) \ . \tag{20}$$

Since the triplet energies of *cis*- and *trans*-stilbene are 57 and 50 kcal./mole, respectively, it was expected that sensitizers with triplet energy greater than 62 kcal./mole would not differentiate between the two isomers and would transfer to both at a diffusion controlled rate (31, 32, 34a). This appears to be in accord with Figure 4 where all "high-energy" sensitizers are shown to yield

Photosensitized Isomerization of the Stilbenes

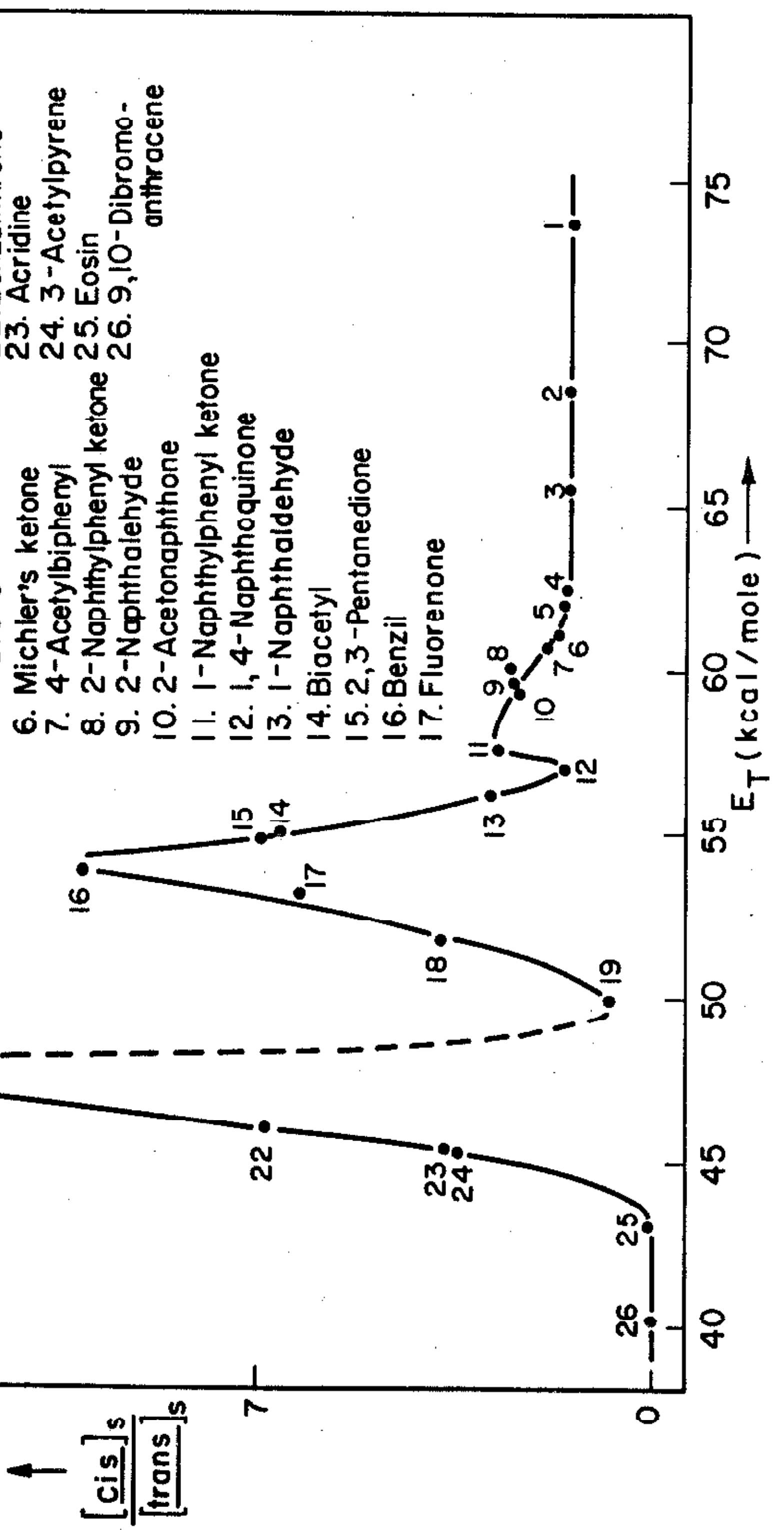


Figure 4

the same photostationary state. In the "high-energy" region, the photostationary compositions were believed to be determined by the relative rates of decay from the intermediate (equations 17 and 18).

The general rise over the region 62-54 kcal./mole on the horizontal axis was assigned to a decrease in the magnitude of k_{14} while k_{13} remains constant (31, 32, 34bc). In order to account for the maximum and minimum near 58 and 57 kcal./mole, respectively, it was proposed that, although the efficiency of energy transfer to cis-stilbene drops when the excitation energy of the sensitizer falls below 62 kcal./mole, it again achieves the diffusion controlled rate when donor and acceptor are in resonance (exactly matched in triplet energy). With sensitizers having excitation energies less than 54 kcal./mole, it was believed that reaction 13 is not sufficiently exothermic to be diffusion controlled and its rate must decrease. The maximum at 48 kcal./mole was again believed to reflect a perfectly coupled transfer, this time between sensitizer and trans-stilbene. This interpretation, however, requires that the reported triplet energy value of trans-stilbene (35, 36) be in error by 2 kcal./mole.

In order to account for the decrease and minimum in Figure 4 between 54 and 48 kcal./mole as well as the decrease below 48 kcal./mole, it was postulated that the rate of transfer to cis-stilbene must again become efficient with respect to the rate of transfer to trans-stilbene. Since the cis isomer has a triplet energy at least 7 kcal./mole higher in energy than the trans isomer, it hardly seemed possible that, in the "low-energy" region, classical transfer to cis-stilbene (equation 14) could effectively compete with classical transfer to trans-stilbene (equation 13). A new step, in which cis-stilbene is converted directly to the trans triplet in the process of energy transfer (equation 15), was introduced to explain the observed behavior. This type of process, named non-vertical energy transfer, is not in accord with the Franck-Condon principle because it requires a change in the geometry of the acceptor in the process of energy transfer. Examples of non-vertical energy transfer are not confined to the study of the photosensitized isomerization of stilbene, but have been demonstrated in other systems where the acceptor has a low-lying triplet of different configuration than the ground state (38).

The existence of trans-stilbene triplets in solution was demonstrated by including azulene in the reaction mixture (31, 32,35b). The low energy of the azulene triplet (39) limits its involvement in the reaction scheme to equation 21. Inclusion of this step in the

$$t^{T_1} + \text{azulene}^{S_0} \rightarrow t^{S_0} + \text{azulene}^{T_1} \qquad (21)$$

mechanism leads to the prediction that the [trans]/[cis] ratios at the photostationary state be linearly dependent upon the concentration of azulene. This prediction was substantiated experimentally for sensitizers over the triplet energy range of 45-68 kcal./mole. By assuming that reaction 21 is diffusion controlled, it was possible to estimate the effective lifetime of stilbene triplets to be of the order of 10^{-8} sec. The fact that cis triplets failed to show either reversible energy transfer with appropriate sensitizers or an azulene effect requires rapid isomerization of the cis triplet to the trans configuration as in reaction 16.

It also was observed that measurements of stilbene photostationary states and quantum yields for the conversion of trans- to cis-stilbene are a function of trans-stilbene concentration (31, 32). This dependence is in accord with the process of self-quenching of trans triplets as given in equation 22.

$$t^{T_1} + t^{S_0} \rightarrow 2t^{S_0} \quad . \qquad (22)$$

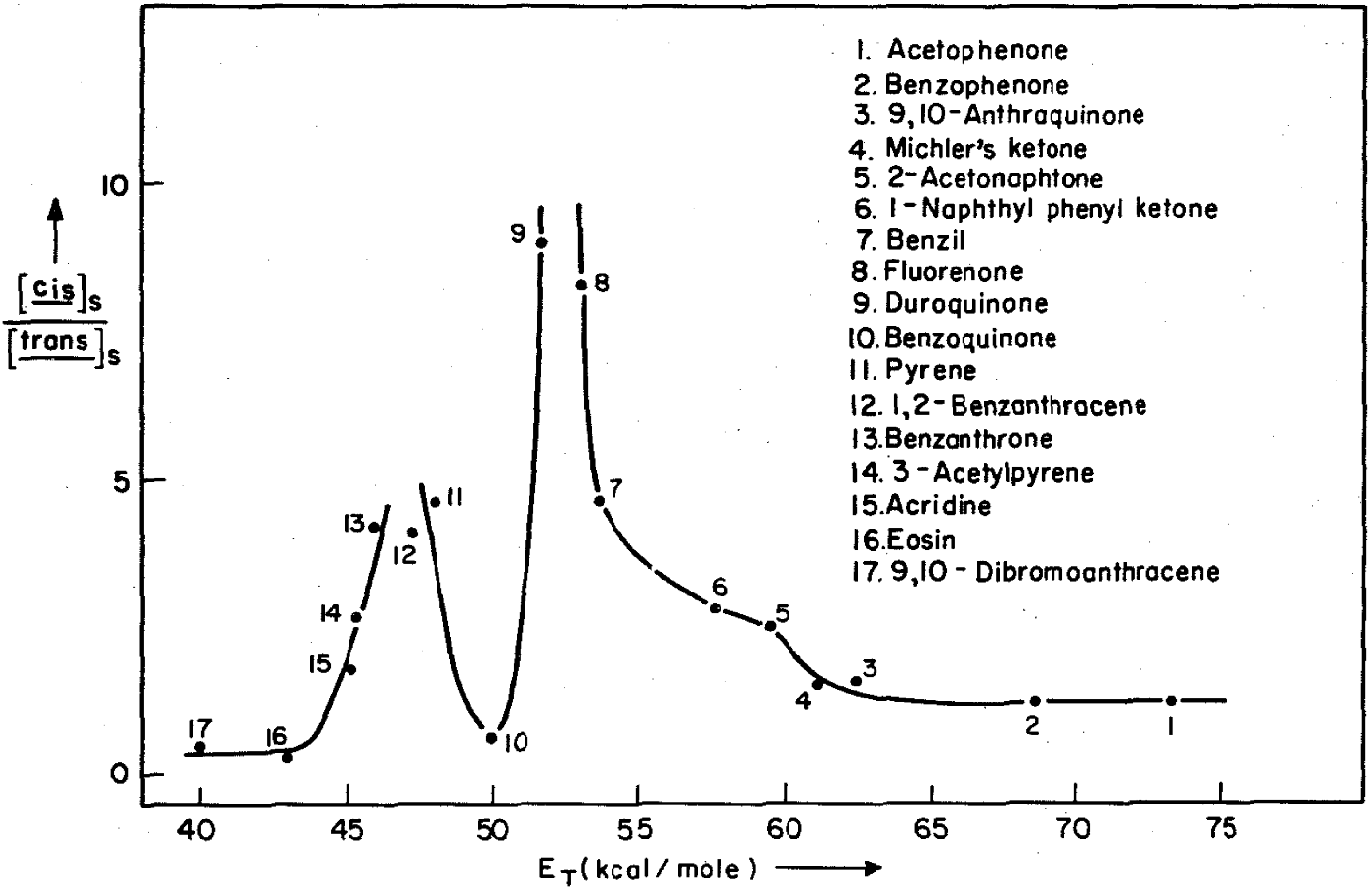
By comparison with the quenching of trans triplets by azulene, which is taken to be a diffusion controlled process, self-quenching of trans triplets was found to be less efficient by two orders of magnitude.

There is an important variation of the proposed mechanism that is equally consistent with presently available data (32, 33, 35). This variation includes in the mechanistic scheme a stilbene triplet with geometry intermediate between the cis and trans configurations. This phantom triplet state may well be formed initially upon non-vertical excitation of cis-stilbene. Inclusion of the phantom triplet in the reaction scheme requires that it be in dynamic equilibrium with the trans-triplet or that it participate in the reverse transfer with sensitizer. This last condition is demanded by the facts that reaction 13 is reversible for sensitizers of triplet energy less than 52 kcal./mole and that the [trans]/[cis] ratios at the photostationary state are linearly dependent upon sensitizer concentration as required by equation 19.

Another process investigated by Hammond and co-workers(32), although less completely than in the case of stilbene, was the photosensitized isomerization of 1, 2-diphenylpropene. In the ground state the cis isomer has 0.3 kcal./mole more energy than the trans isomer (40). Unfortunately, all attempts to measure triplet energies of the diphenylpropene isomers by either phosphorescence or absorption spectroscopy have been unsuccessful. Assignment of these triplet energies was based upon interpretation of Figure 5, a plot of photostationary compositions vs. sensitizer triplet energies that is quite similar in appearance to the corresponding stilbene plot of Figure 4. Presumably, the plot shows no minimum corresponding to resonance energy transfer between cis-1, 2-diphenylpropene and sensitizer because no sensitizer of appropriate energy was used. That there is an inflection near 58 kcal./mole made it appear that the cis isomer has a triplet energy approximating this value. The maximum near 48 kcal./mole was believed to represent resonance transfer to trans-1, 2-diphenylpropene. This interpretation, of course, requires that the trans isomers of stilbene and 1, 2-diphenylpropene have nearly the same triplet energies.

The basic mechanism of equations 12-18 was also believed to apply to the photosensitized isomerization of 1, 2-diphenylpropene. The only important difference between this system and stilbene is the absence of an azulene effect, self-quenching, and reverse energy transfer from trans triplets to sensitizer. This has prompted the conclusion that the configuration of the least energetic 1, 2-diphenylpropene triplet is neither cisoid nor transoid.

The information about the stilbene and 1, 2-diphenylpropene systems that has been gained from studies of the photosensitized isomerization of these substances is an application of chemical spectroscopy, a term coined in these laboratories. Chemical spectroscopy is defined as the use of energy transfer as a tool in determining the electronic structure and geometry of molecules in



Photosensitized Isomerization of the 1, 2-Diphenylpropenes

Figure 5

electronically excited states, in elucidating deactivation paths for excited molecules, and in resolving details of energy transfer processes. The coupling of optical and chemical spectroscopy can thus lead to detailed information concerning both spectroscopic and non-spectroscopic molecular electronic states and interconversions between them.

Subject of the Experimental Investigation:

The subject of the investigation presented here is the direct measurement by means of flash kinetic spectrophotometry of the rates of triplet energy transfer from selected photosensitizers to the individual isomers of stilbene and 1, 2-diphenylpropene. The basic reasons for this study are to measure the efficiency of non-vertical energy transfer and to test the credibility of the proposal that the efficiency of energy exchange between donor and acceptor pairs is sensitive to vibronic factors when their excitation energies are close to the resonance condition. The only other really systematic studies of rates of triplet energy transfer, those of Sandros and Bäckström (14, 18) differ in two important aspects from that presented here. First, there was no indication that the investigations of Sandros and Bäckström were complicated by non-vertical energy transfer. Second, both donor and acceptor had triplets with measurable lifetimes and the energy transfer process was reversible. With the stilbene and 1, 2-diphenylpropene systems, only trans-stilbene among the 4 isomers appears to have a triplet state sufficiently long-lived to undergo reverse energy transfer.

EXPERIMENTAL

Materials:

In those cases where two or more samples of the same substance are listed, numbers are used to facilitate later reference.

Substrates:

cis-Stilbene was prepared and purified by Dr. K. R. Kopecky. Dr. J. Saltiel has shown by vapor phase chromatography that it contains less than 1% trans-stilbene.

(1) trans-Stilbene (Matheson, Coleman, and Bell, Scintillation Grade) was recrystallized under nitrogen at dry ice temperatures first from methanol and then from ether. It was shown by vapor phase chromatography to contain less than 0.70% cis-stilbene.

(2) trans-Stilbene (Matheson, Coleman, and Bell, Scintillation Grade) was sublimed under vacuum by Dr. J. Saltiel. It was shown by vapor phase chromatography to contain less than 0.64% cis-stilbene.

(3) trans-Stilbene (Matheson, Coleman, and Bell, Scintillation Grade) was recrystallized from ethanol and sublimed under vacuum by Dr. J. Saltiel. It was then zone refined in a sealed tube under a partial atmosphere of nitrogen. It was shown by vapor phase chromatography to contain less than 0.32% cis-stilbene.

(4) trans-Stilbene (Hinton, Zone Refined) was used as received. It was stated that the starting material was Eastman, White Label. It was shown by vapor phase chromatography to contain less than 0.09% cis-stilbene.

cis-1,2-Diphenylpropene, supplied by Dr. D. J. Cram and Mr. D. H. Hunter, was used as received.

trans-1, 2-Diphenylpropene, supplied by Dr. D. J. Cram and Mr. D. H. Hunter, was used as received. Dr. A. A. Lamola has shown by vapor phase chromatography that it contains 0.35% of the cis isomer.

5H-Dibenzo(a, d)cyclohepten-5-ol (Dibenzcycloheptenol, Aldrich, Research Grade) was recrystallized several times from petroleum ether (60-70^{0} b. p. range).

Solvents:

(1) Benzene (Mallinckrodt, Analytical Reagent) was extracted with concentrated sulfuric acid until the acid layer no longer became colored, and then neutralized, dried, and distilled.

(2) Benzene (Phillips, Research Grade) was specified to be 99.93% pure and was used as received.

(3) Benzene (Mallinckrodt, Analytical Reagent) was purified by a procedure recommended by Dr. R. Steinmetz (41). Chloranil was dissolved in benzene to the extent of 2 g. /1. The solution was contained in a well surrounding a quartz Hanovia immersion reactor with a 450 watt Hanovia medium pressure mercury lamp. The solution was irradiated for at least one week. A brown substance that deposited on the walls of the reactor was removed daily and the supply of chloranil was replenished at the same time. The solution was passed through an alumina chromatography column to remove all colored substances and finally distilled from phosphorous pentoxide. Analysis of this benzene by vapor phase chromatography showed fewer impurities than the other samples listed here.

Tetrahydrofuran (Matheson, Coleman, and Bell) was refluxed over sodium for two days and then distilled. The distillate was then refluxed over a mixture of lithium aluminum hydride and sodium and finally distilled under nitrogen atmosphere onto small chunks of sodium.

Sensitizers:

2-Acetonaphthone (Matheson, Coleman, and Bell) was recrystallized several times from petroleum ether (60-70° b. p. range) and zone refined in a sealed tube under a partial atmosphere of nitrogen.

3-Acetylpyrene was prepared by Dr. H. P. Waits and purified by Dr. J. Saltiel. Purification procedures included chromatography, treatment with Norite, recrystallization from n-heptane, and short path distillation.

Acridine (Eastman, Practical Grade) was chromatographed by Dr. J. Saltiel on Rosite, a 3:1 mixture of Celite and Norite.

Anthracene (Matheson, Coleman, and Bell, Fluorescent Grade) was used as received.

1, 2-Benzanthracene (Eastman, White Label) was chromatographed on Rosite, recrystallized from ethanol, and chromatographed on alumina. This purification was carried out by Dr. J. Saltiel.

Benzanthrone (Calbiochem, Practical Grade) was chromatographed on alumina and recrystallized from methanol by Dr. J. Saltiel.

Benzil (Matheson, Coleman, and Bell) was recrystallized from a mixture of methanol and water and zone refined in a sealed tube under a partial atmosphere of nitrogen.

1, 12-Benzperylene (K and K) was used as received.

3,4-Benzpyrene (Eastman, White Label) was recrystallized from a mixture of benzene and methanol by Mr. G. F. Vesley.

Camphorquinone (Aldrich, Research Grade) was used as received.

Chrysene (Matheson, Coleman, and Bell) was recrystallized from benzene and sublimed under vacuum by Dr. J. R. Fox.

1,2,3,4-Dibenzanthracene (Aldrich, Research Grade) was used as received.

1,2,5,6-Dibenzanthracene (Eastman, White Label) was obtained from Dr. H. P. Waits following purification by recrystallization from acetic acid and sublimation under vacuum.

9,10-Dibromoanthracene was prepared by Dr. K. R. Kopecky and recrystallized from carbon tetrachloride by Dr. F. G. Moses.

9,10-Dimethyl-1,2-benzanthracene (Eastman, White Label) was used as received.

Duroquinone (Calbiochem, Reagent Grade) was used as received.

Fluoranthene (Matheson, Coleman, and Bell) was obtained from Dr. D. H. Valentine following purification that included treatment with Norite, recrystallization from ethanol, and sublimation under vacuum.

Fluorenone (Matheson, Coleman, and Bell) was subjected to extensive purification. Those steps performed by Dr. J. Saltiel include preparation of the phenyl hydrazone derivative, which was then chromatographed on alumina and recrystallized from a mixture of ethanol and water, regeneration of fluorenone, recrystallization from n-heptane and ligroin (85-100^{o} b. p. range), and vacuum sublimation. The fluorenone was then zone refined in a sealed tube under a partial atmosphere of nitrogen.

Naphthalene (Matheson, Coleman, and Bell) was recrystallized under nitrogen at dry ice temperatures from methanol. It was zone refined in a sealed tube under a partial atmosphere of nitrogen.

Naphthalene-d_8 (Merck) was used as received.

1-Naphthyl phenyl ketone (K and K) was obtained from Dr. A. J. Fry after recrystallization from n-heptane.

Phenanthrene (Matheson, Coleman, and Bell) was treated with maleic anhydride to remove anthracene and then recrystallized from ethanol. The purification was performed by Dr. W. M. Hardham.

(1) Triphenylene (Aldrich, Research Grade) was used as received.

(2) Triphenylene (Hinton, Zone Refined) was used as received.

Thioxanthone (Aldrich, Research Grade) was obtained from Dr. D. H. Valentine after treatment with Norite, recrystallization from methanol, and vacuum sublimation.

2, 4, 6-Triisopropyl-4'-methoxybenzophenone, supplied by the organic research stockroom of the University of Illinois,* was used as received.

2, 4, 6-Trimethyl-4'-methoxybenzophenone, supplied by the organic research stockroom of the University of Illinois,* was used as received.

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* Dr. R. C. Fuson, Dr. S. Smith, and unspecified research students are gratefully acknowledged for donation of this compound.

Solutes in Filter Solutions:

trans-Stilbene (Matheson, Coleman, and Bell, Scintillation Grade) was used as received.

Carbazole (Matheson, Coleman, and Bell) was used as received.

1, 4-Diphenyl-1, 3-Butadiene (Eastman, White Label) was used as received. A comparison of its absorption spectrum with those of the three geometric isomers of this substance (42) indicates that it is primarily the trans-trans isomer.

Bases:

Triethylamine (Matheson, Coleman, and Bell) was twice distilled prior to use.

1, 4-Diazabicyclo-(2, 2, 2)-octane (K and K) was used as received.

Pyridine (Matheson, Coleman, and Bell) was used as received.

Apparatus and Procedures:

Unless otherwise specified, solutions were prepared with benzene solvent and kinetic measurements were made at room temperature using the apparatus and procedures described here.

Solutions were contained in cylindrical pyrex cells measuring 21 cm. in length and 15 mm. in outer diameter with flat windows fused on the ends. Many cells also included an outer jacket with a 6 mm. path length for filter solutions. The cells extended on sidearms from round-bottom bulbs where solutions were contained during the degassing procedure. Connections to the vacuum line were made with standard taper joints. Between the joints and the constrictions for vacuum sealing were traps to prevent contamination of the cells with stopcock grease. The cells were cleaned with soap solution and rinsed repeatedly with distilled water prior to each usage.

The vacuum system employed in degassing solutions had a Welch Model 1402-B forepump and a Consolidated Vacuum Corporation Model PMC-115A oil diffusion pump. Cold traps cooled with liquid nitrogen were on each side of the diffusion pump. Pressure readings were made with a Consolidated Vacuum Corporation Model PHG-09 Philips gage. The ultimate pressure with forepump alone approached 10^{-4} mm. whereas 10^{-6} to 10^{-7} mm. was reached with both pumps in operation. Dow-Corning high vacuum silicone grease was used on all joints and stopcocks.

The degassing procedure involved freezing the solutions to liquid nitrogen temperatures, opening the space above the frozen solutions to the vacuum system, and thawing the solutions to re-establish equilibrium between liquid and vapor phases. This freeze-pump-thaw cycle was repeated 5 times before sealing the cells.

The flash-photoelectric apparatus used in these experiments is depicted schematically in Figure 2. A more complete presentation of the circuitry, construction, and operation of flash apparatus is given elsewhere (11).

The energy for flash discharge was provided by a Shapiro and Edwards Model 118 flash lamp pulser. Energy output was variable between 8 and 800 joules by choice of capacitance (1/8 to 4 μF in discrete levels) and voltage (12 to 20 kV). Two flash lamps were connected in series to the output terminal of the flash lamp pulser. Xenon flash lamps type FX-1 and FX-45 from Edgerton, Germeshausen, and Grier were satisfactory for this purpose. Flash excitation energies of 100 to 200 joules were adequate for most experiments; higher energy discharges usually proved unnecessary and led to more rapid deterioration of the lamps. Return to 1/3 peak flash intensity occurred within 15 to 20 μ sec. although the flash output had a perceptible tail for 100 μ sec. or more. The resolution time of the apparatus was such that it was difficult to detect an intermediate with a lifetime much less than 10 μ sec. A transient lifetime greater than 20 μ sec. was desirable for kinetic measurements.

The flash lamps, cylindrical in shape, were positioned on each side of a sample cell inside a cylindrical bakelite housing. Magnesium oxide, which reflects visible and near-ultraviolet light with more than 98% efficiency (43), coated the inner surfaces of the housing. The monitoring source was a PEK 75 watt mercury-xenon lamp type 1621 and was powered by storage batteries. This lamp was mounted on an optical bench in series with a collimating lens, the flash lamp and sample cell housing, a light baffle, and focusing lens. The light beam from the monitoring source passed through the sample cell and was focused on the entrance slit of a Jarrell-Ash 500 mm. Ebert spectrometer. The output from a Sylvania 931-A photomultiplier tube, mounted on the exit slit of the spectrometer, was fed into a cathode-follower amplifier and then into a Tektronix 531 wide-band oscilloscope. Oscillographs of changes in light intensity as a function of time were photographed with a DuMont Model 302 oscillograph record camera that was mounted directly on the oscilloscope screen. Photographs were taken with Polaroid Type 46-L transparency film. A Rutherford

Model A-4 time delay generator, included with the flash lamp pulser, could be used to trigger the oscilloscope sweep prior to the flash lamp discharge.

Even though the assembly included a light baffle, stray light from the flash source sometimes was a problem with short lived intermediates. In this respect, it was advantageous, whenever practical, to monitor the experimental solution at the wave length of a mercury resonance line. At these wave lengths the emission from the monitoring source was considerably more intense so that the signal to stray light ratio was greater. Stray light was rarely a problem with transients having lifetimes longer than 100 μ sec.

A typical oscillograph is reproduced in Figure 6. Light intensity reaching the photoelectric detector is plotted on the vertical axis and time is on the horizontal axis. The lower line is the kinetic tracing and the upper is the reference line that corresponds to zero light intensity. The oscilloscope was triggered prior to the flash to provide a reference in the absence of transients. The dip in both lines is stray light interference from the flash source and photographs were taken so that the photoelectric detector saw the same quantity twice. The arbitrary zero time in the decay was chosen at a level where stray light no longer significantly interferes with the shape of the curve.

The oscillograph transparencies were enlarged with a slide projector and the images were traced and measured. The parameters recorded in each case were x_0 and a series of x_t points with the corresponding units of time. An explanation of the kinetic analysis follows in the next section.

Filter solutions were employed whenever absorption characteristics of sensitizers permitted in order to inhibit direct absorption

Typical Oscillograph of Triplet State Decay in Solution

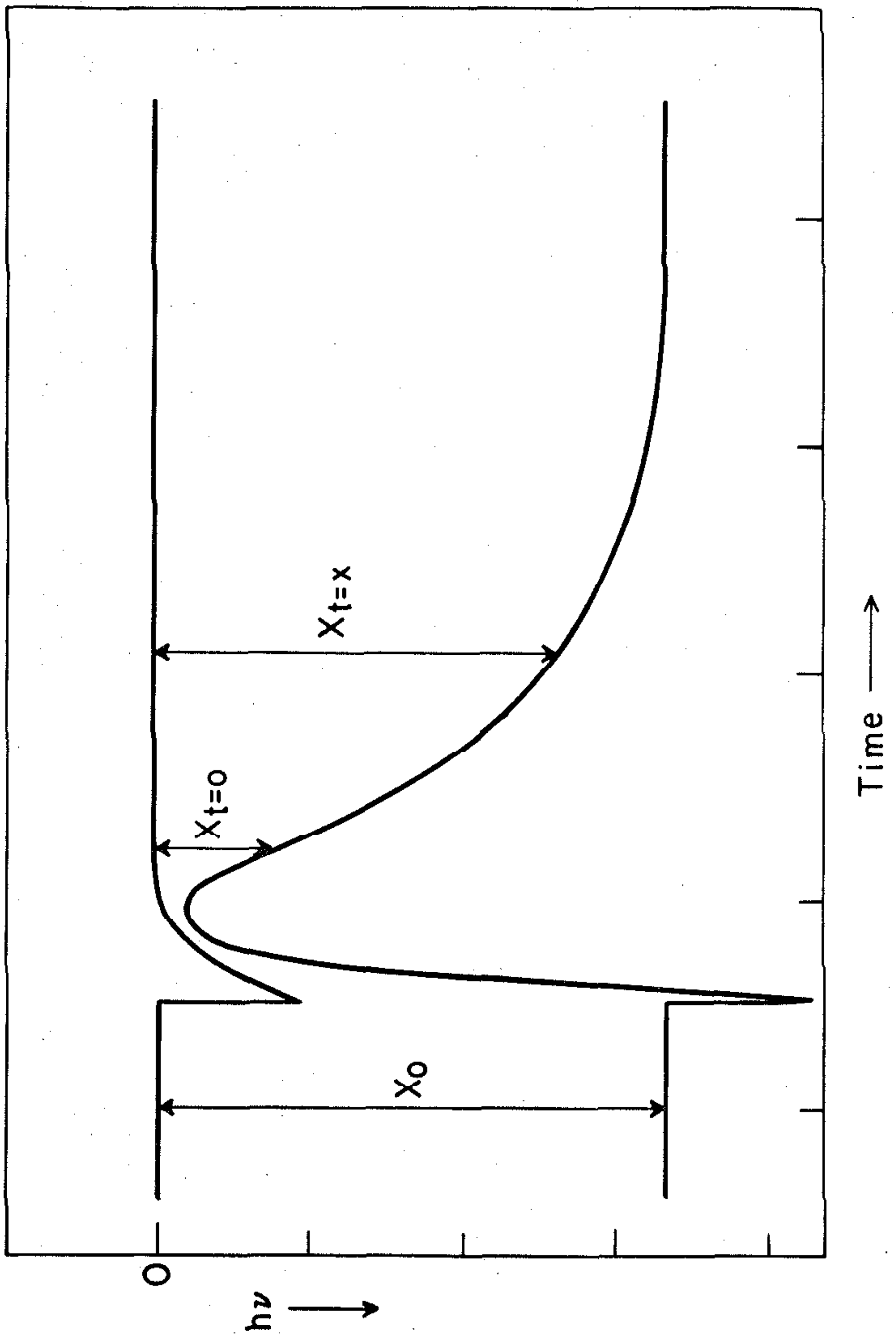

Figure 6

of flash light by acceptor molecules. In addition, a Corning 3060 glass color filter, mounted on the optical bench, effected a similar barrier to light from the monitoring lamp. Two of the filter solution solutes, trans-stilbene and trans-trans-1, 4-diphenyl-1, 3-butadiene, isomerize on absorption of light to give the respective geometric isomers. Since this isomerization leads to reduced light absorption in the near ultraviolet, the filter solutions could be used only a limited number of times. Table 4 lists the filter solutions and the wave length below which 1 cm. of solution absorbs more than 99% of the light. To facilitate later reference, the solutions are numbered.

TABLE 4

Filter Solutions

Solution Number	Solute	Solvent	Concentration (M)	Wave length below which A ≥ 2 for 1 cm. of solution (mμ)
1	t-stilbene	benzene	1.4×10^{-4}	330
2	t-stilbene	benzene	2.1×10^{-3}	338
3	1,4-diphenyl-1,3-butadiene	benzene	1.2×10^{-4}	361
4	carbazole	ethanol	1.9×10^{-3}	342

For purposes of comparison, the extinction coefficients at 360 mμ of the isomeric stilbenes and 1, 2-diphenylpropenes are listed in Table 2. At shorter wave lengths in the near ultraviolet, trans-stilbene has stronger absorption than any of the three other substances (44). The extinction coefficients of *trans*-stilbene at arbitrarily chosen wave lengths in this region are listed in Table 6.

TABLE 5

Extinction Coefficients at 360 mμ of Stilbene and 1, 2-Diphenyl-Propene Isomers in Benzene Solution

Substance	ε
trans-stilbene	0.3
cis-stilbene	2
trans-1, 2-diphenylpropene	~ 0
cis-1, 2-diphenylpropene	1

TABLE 6

Extinction Coefficients of *trans*-Stilbene in Benzene Solution

Wave length (m μ)	ε
355	2
350	9
345	4.4×10
340	3.0×10^{2}
335	2.9×10^{3}
330	1.1×10^{4}

All solutions were prepared originally with pure isomers of the acceptors. With repeated flashing, isomerization took place until the photostationary state was reached. Whenever practical, kinetic measurements were made twice, first with pure isomers and then again at the photostationary state. The concentrations of acceptors frequently were such that it would have been impractical to reach the photostationary state with repeated flashing. These solutions were irradiated with the monitoring lamp for several hours to reach photostationary conditions. In order to check the isomeric distribution after repeated flashing or irradiation, the cells were opened and the solutions were concentrated under a stream of nitrogen to the point where measurement by vapor phase chromatography was possible. A Loenco Model 70 B dual flame gas chromatograph was employed for this purpose. A 5-6 ft. by 0. 25 in. column was packed with Apiezon L on Chromosorb W and operated at 230^{o}C. The gas chromatograph did not effect isomerization of stilbene or 1, 2-diphenylpropene and gave a 1:1 response to the respective isomers of these substances.

Analysis of Triplet Decay Data:

The method developed by Linschitz and Sarkanen (30) for kinetic analysis of triplet decay data is adopted here.

The basic requirement of this method is that the response of the photoelectric detector vary linearly with respect to incident light intensity. Since this was shown to be true over the range of operation of the photoelectric detector, the ratio x_o/x_t of measured distances in Figure 6 is proportional to the ratio I_o/I_t of light intensities. The former ratio may then be substituted in the equation for Beer's law.

$$\log(I_o/I_t) = \log(x_o/x_t) = \epsilon^* c^* \ell = A_t \quad . \tag{23}$$

In this expression ϵ^* is the extinction coefficient of triplet-triplet absorption, c^* is the concentration of triplets, ℓ is the path length of the solution, and A_t is the absorbance at a particular time.

When the decay is first-order with respect to triplet concentration, the following equation is applicable, where k_f represents the sum of all first-order and pseudo first-order rate constants.

$$-(dc^*/dt) = k_f c^* \quad . \tag{24}$$

Integration and substitution lead to an equation in terms of absorbance.

$$\ln c_1^* - \ln c_2^* = k_f(t_2 - t_1) \tag{25}$$

$$\ln c_1^* - \ln c_2^* = \ln \epsilon^* c_1^* \ell - \ln \epsilon^* c_2^* \ell \tag{26}$$

$$\ln A_1 - \ln A_2 = k_f(t_2 - t_1) \tag{27}$$

A plot of $\ln A_t$ versus time has a slope equal to $-k_f$.

When the decay is second-order with respect to triplet concentration, integration and substitution are utilized again in the following derivation. Here k_s represents the sum of all second-order and pseudo second-order rate constants.

$$-(dc^*/dt) = k_s(c^*)^2 \tag{28}$$

$$(1/c_1^*) - (1/c_2^*) = k_s(t_2 - t_1) \tag{29}$$

$$(1/A_1) - (1/A_2) = (k_s/\varepsilon^*\ell)(t_2 - t_1) \tag{30}$$

In this case, a plot of $1/A_t$ versus time has a slope equal to $-(k_s/\varepsilon^*\ell)$. The second-order rate contribution is determined in terms of the extinction coefficient.

In the more general case, triplet decay includes both first- and second-order contributions.

$$-(dc^*/dt) = k_f c^* + k_s (c^*)^2 \tag{31}$$

Substitution of $(A_t/\varepsilon^*\ell)$ for c^* gives this equation.

$$-\frac{dA_t}{dt} = k_f A_t + \frac{k_s}{\varepsilon^*\ell}\,(A_t)^2 \;. \tag{32}$$

For purposes of later reference, k_f is represented by α and $(k_s/\varepsilon^*\ell)$ by β.

$$-\frac{1}{A_t}\left(\frac{dA_t}{dt}\right) = \alpha + \beta A_t \;. \tag{33}$$

A plot of $-\frac{1}{A_t}\left(\frac{dA_t}{dt}\right)$ versus A_t has intercept α and slope β. In practice, this operation has been performed by computer analysis* because of the considerable time required in the manual determination of α and β.

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* The computer program was written by Dr. K. W. Jacob of the California Institute of Technology Computing Center and the analysis has been performed with an IBM 7090 computer.

RESULTS AND DISCUSSION

General Considerations in the Experimental Investigation of Triplet State Decay in Solution:

Early experiments were directed toward gaining an understanding of the process of triplet state decay in solution and the optimum conditions for its study.

The mechanism for triplet state decay proposed by Linschitz and co-workers (22, 30) has been adopted here and, as will be demonstrated, is consistent with all experimental observations. In the following equations, sensitizer (donor) is represented by S, added quencher (acceptor) by Q, and triplet states are denoted by asterisks.

$$S^* \xrightarrow{k_1} S \qquad (34)$$

$$S^* + S^* \xrightarrow{k_2} S^* + S \qquad (35)$$

$$S^* + S \xrightarrow{k_3} 2S \qquad (36)$$

$$S^* + Q \xrightarrow{k_Q} S + Q^* \;. \qquad (37)$$

Equation 34 denotes the sum of radiative and non-radiative unimolecular decay, equation 35 triplet-triplet annihilation, equation 36 self-quenching, and equation 37 transfer of triplet excitation energy to an added quencher (non-reversible). The rate of sensitizer triplet decay as a function of time is given by the following equation:

$$-\frac{d[S^*]}{dt} = k_1[S^*] + k_2[S^*]^2 + k_3[S^*][S] + k_Q[S^*][Q] \ . \quad (38)$$

The triplet concentration $[S^*]$ is conveniently replaced by $A_t/\epsilon^*\ell$ in accord with Beer's law, where A_t is the absorbance of the triplets in solution, ϵ^* is the extinction coefficient of triplet-triplet absorption, and ℓ is the path length of the experimental cell. Also, $[S_o]$ is substituted for the sum of $[S^*]$ and $[S]$.

$$-\frac{dA_t}{dt} = (k_1 + k_Q[Q] + k_3[S_o])(A_t) + \frac{1}{\epsilon^*\ell}(k_2 - k_3)(A_t)^2 \ . \quad (39)$$

The sum of the coefficients, $k_1 + k_Q[Q] + k_3[S_o]$, is represented by α and the difference of the coefficients, $\frac{1}{\epsilon^*\ell}(k_2 - k_3)$, by β to give an expression identical with equation 33 of the previous section.

$$-\frac{dA_t}{dt} = \alpha A_t + \beta (A_t)^2 \ . \quad (40)$$

With any particular sensitizer, the term α is expected to be dependent upon the concentration of sensitizer as well as added quencher, whereas β, by contrast, is expected to be dependent only upon the choice of wave length for analysis.

The kinetic scheme was tested by measuring α and β values by flash kinetic spectrophotometry for a number of selected sensitizers. Results listed in Table 7, as an example, demonstrate the concentration dependence of α and the wave length dependence of β for fluorenone triplets in benzene solution.

TABLE 7

Decay of Fluorenone Triplets in Benzene Solution[a] at Room Temperature

Fluorenone Concentration (M.)	Analysis Wave Length (Å)	α (10^{-3} x sec.$^{-1}$)	β (10^{-4} x sec.$^{-1}$)
4.0×10^{-5}	6600	3.9	18
4.0×10^{-5}	6200	3.4	18
4.0×10^{-5}	5800	5.3	17
4.0×10^{-5}	5400	6.3	25
4.0×10^{-5}	5100	5.2	19
4.0×10^{-5}	4800	4.0	9.5
4.0×10^{-5}	4600	3.6	5.3
4.0×10^{-5}	4465	4.5	5.0
4.0×10^{-5}	4400	3.1	4.7
4.0×10^{-5}	4300	4.6	4.4
4.0×10^{-5}	4200	4.6	4.9
4.0×10^{-5}	4100	4.8	4.9
4.0×10^{-5}	4050	4.1	5.7
1.0×10^{-3}	5800	10	15
1.0×10^{-3}	4800	6.4	8.7
1.0×10^{-3}	4465	8.1	4.4
1.0×10^{-3}	4400	7.1	3.5

Fluorenone Concentration (M.)	Average α (10^{-3} x sec.$^{-1}$)	k_3 (10^{-6} x M.$^{-1}$sec.$^{-1}$)
4.0×10^{-5}	4.5 ± 0.9	{3.5 ± 2.6}
1.0×10^{-3}	7.9 ± 1.6	

[a] Benzene sample #1 was used.

As is readily evident from Table 7, precision in the measurement of α and β values is no better than ± 25%. It is advantageous, however, to confine measurement of α terms to that spectral region where triplet-triplet absorption intensity is strongest. In the case of fluorenone triplets, an absorption maximum occurs in the region 4200-4400Å.

Transfer of triplet excitation energy was tested by measuring the rate at which azulene quenches anthracene triplets. This reaction had been shown previously by Ware (45) to occur at a diffusion controlled rate in hexane solution. Azulene itself shows no triplet-triplet absorption and appears to have a triplet sufficiently low in energy so that the reverse transfer from azulene triplets to sensitizer is negligible. As shown in Table 8, added quencher increased the value of the α terms whereas the β terms remained the same within experimental error. The quenching constant is close to that expected of a diffusion controlled reaction in benzene.

TABLE 8

Quenching of Anthracene Triplets by Azulene in Benzene Solution[a]

Anthracene Concentration (M.)	Azulene Concentration (M.)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	k_Q (M.$^{-1}$sec.$^{-1}$)
4.0×10^{-5}	-	$1.0 \pm .1 \times 10^{3}$	$7 \pm 1 \times 10^{3}$	$7.5 \pm .5 \times 10^{9}$
4.0×10^{-5}	2.0×10^{-6}	$1.6 \pm .1 \times 10^{4}$	$9 \pm 3 \times 10^{3}$	

a. Benzene sample #1 was used.

Some experiments were run to test Livingston's hypothesis that the measured values of k_1 in fluid solution are limited largely by the presence of adventitious quenchers (25, 27). Since oxygen is believed to be the most likely quenching impurity, special methods for removal of oxygen were employed in addition to the standard degassing procedure. With 2-acetonaphthone in benzene, nitrogen was bubbled through the solution prior to freezing and the standard freeze-pump-thaw procedure was interrupted several times with bulb to bulb distillations under vacuum in order to pass the entire solution through the vapor phase. The effect, as shown in Table 9, was to reduce the measured values of α.

TABLE 9

Decay of 2-Acetonaphthone Triplets in Benzene Solution[a]

2-Acetonaphthone Concentration (M.)	Degassing Procedure	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)
2.0×10^{-5}	Standard	4300	$1.2 \pm .2 \times 10^{3}$	$2.7 \pm .1 \times 10^{4}$
2.0×10^{-5}	Special	4300	$7.7 \pm 1.8 \times 10^{2}$	$2.7 \pm .2 \times 10^{4}$

a. Benzene sample #3 was used.

In another experiment, the kinetics of decay of naphthalene triplets in tetrahydrofuran were measured after an elaborate degassing procedure that involved using the naphthalene anion as an oxygen scavenger. A sodium mirror was deposited under vacuum in a degassing bulb connected to a sample cell. Tetrahydrofuran, which had been refluxed over sodium and distilled from lithium aluminum hydride under a stream of nitrogen, was collected along with zone refined naphthalene in the degassing bulb under vacuum at liquid nitrogen temperatures and the cell was sealed. Upon thawing, the solution became dark green in color because of formation of naphthalene anions, known to be highly reactive with oxygen (46), and the solution was flushed throughout the cell in order to bring it into contact with all glass surfaces. With the solution contained in the degassing bulb, the solvent was repeatedly distilled into the cell compartment and poured back to the bulb in order to return all colored material to the bulb. After a final distillation into the cell, kinetic measurements were made and the cell was opened in order to determine the concentration of naphthalene. As shown in Table 10, measurement of triplet decay was made at 3 wave lengths corresponding to triplet-triplet absorption maxima in naphthalene as reported by Porter and Windsor (7c). Absorption at 4150 Å is strongest and the α value at this wave length, because of poor precision in the measurements at 3915 Å and 3720 Å, is taken to be most representative of this experiment.

The possibility of self-quenching of naphthalene triplets at sensitizer concentrations comparable to that used in the previous experiment was investigated. The same source of naphthalene was used, but the solvent was benzene. As summarized in Table 11, there is an increase in the α terms as the naphthalene concentration is raised. Although self-quenching cannot be readily distinguished from the possibility that small quantities of quenching impurities are added with naphthalene, the measured effect is real and correction should be applied.

TABLE 10

Decay of Naphthalene Triplets in Tetrahydrofuran Following Special Deoxygenation Procedure

Naphthalene Concentration (M.)	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)
1.5×10^{-3}	4150	$8.3 \pm 1.0 \times 10^{2}$	$1.5 \pm .1 \times 10^{4}$
1.5×10^{-3}	3915	$9.5 \pm 4.0 \times 10^{2}$	$3.1 \pm .2 \times 10^{4}$
1.5×10^{-3}	3720	$2.1 \pm 1.0 \times 10^{3}$	$7.5 \pm .8 \times 10^{4}$

TABLE 11

Self-Quenching of Naphthalene Triplets in Benzene[a]

Naphthalene Concentration (M.)	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	k_3 (M.$^{-1}$sec.$^{-1}$)
5.0×10^{-4}	4150	$3.2 \pm .5 \times 10^{3}$	$3.0 \pm .2 \times 10^{4}$	$3.6 \pm 2.6 \times 10^{5}$
5.0×10^{-3}	4150	$4.8 \pm .7 \times 10^{3}$	$3.7 \pm .4 \times 10^{4}$	

a. Benzene sample #1 was used.

In Table 12 are listed first-order rate constants for the decay of naphthalene triplets in solvents of comparable viscosity. These rate constants include values from experiments described here as well as representative examples from the literature. The corrected k_1 value from the experiment with tetrahydrofuran solvent compares favorably with the other listed values and is within experimental error of 3.8×10^{-1} sec.$^{-1}$, the rate constant for radiative decay of naphthalene triplets in rigid media (47). This result is, of course, in agreement with Livingston's hypothesis. It should be noted, however, that when measuring small first-order rate constants for triplet decay in fluid media, precision will inevitably be poor when the decay is predominated by second-order contributions.

Included in Table 12 is the k_1 value for perdeuteronaphthalene. The radiative lifetime of this compound in rigid media is approximately 8 times longer than that of naphthalene (48). In benzene solution, however, these two substances have nearly the same first-order decay constants as would be expected if triplet lifetimes in solution are limited by adventitious quenchers.

A problem that may arise in application of kinetic spectrophotometry is that concentration gradients of triplets may form on flashing solutions where the sensitizer absorbs a large fraction of the light. It is reasonable to expect that the yield of triplets be higher near the surface than at the center of the cell. It was suspected that this may have taken place with naphthalene at concentrations of 5×10^{-4} M. and higher. To check whether this phenomenon might affect the measurement of rate constants, benzene solutions of naphthalene and benzophenone were prepared in cells equipped with filter jackets. The jackets were filled with a 0.2 M. solution of naphthalene in benzene in order to keep the naphthalene

TABLE 12

Decay of Naphthalene Triplets in Various Solvents

Naphthalene Concentration (M.)	Solvent	Analysis Wave Length (Å)	k_1 (10^2 x sec.$^{-1}$)	β (10^4 x sec.$^{-1}$)	Reference
1.5×10^{-3}	tetrahydrofuran	4150	2.9 ± 4.9	$1.5 \pm .1$	this work
4.0×10^{-5}	benzene (#3)	4150	22 ± 2	$4.2 \pm .3$	this work
$(C_{10}D_8) 4.0 \times 10^{-5}$	benzene (#3)	4150	30 ± 7	$3.4 \pm .7$	this work
a.	benzene	b.	4.1	a.	18
a.	hexane	a.	9.6[c.]	a.	25
a.	hexane	a.	1.2×10^2	a.	20
a.	hexane	a.	28	a.	15

a. This value was not reported.

b. Kinetic analysis was performed by phosphorescence spectroscopy.

c. Extrapolated from measurements made at 15°C and lower.

in the cells from absorbing light directly. Benzophenone, which absorbs light weakly at wave lengths longer than naphthalene and also has high intersystem crossing efficiency, was used to sensitize the formation of naphthalene triplets to give what was believed to be a more uniform distribution than was achieved on direct absorption of light by naphthalene. Experimental results are summarized in Table 13.

Comparison of the kinetic terms in Tables 11 and 13 makes it appear that a non-uniform distribution of naphthalene triplets resulted in α values that were too large. In both cases the β values and self-quenching constants are the same within experimental error. If it can be assumed that the concentration gradient problem also applies to the naphthalene solution in tetrahydrofuran, a correction would further reduce the measured value of k_1 for that solution.

Another apparent example of concentration gradients in the solution decay of triplets is provided by 5H-dibenzo(a, d)cyclohepten-5-ol(dibenzcycloheptenol). With this substance, in contrast to what may have been expected from the above results with naphthalene, the measured α values increased with more uniform triplet distributions effected by higher flash intensities as shown in Table 14. From these preliminary investigations, it would appear that the kinetic effects of triplet concentration gradients depend largely on the absorption spectrum of the sensitizer involved.

Rates of triplet state decay have been measured for a large number of sensitizers in benzene solution and results are summarized in Table 15. The triplet state lifetimes for most sensitizers investigated are of the order of 50 - 500 μsec., well within the time resolution limits of the flash-photoelectric apparatus. Solutions were scanned at several wave lengths to determine where triplet-

TABLE 13

Decay of Naphthalene Triplets Formed by Energy Transfer from Benzophenone[a.]

Benzophenone Concentration (M.)	Naphthalene Concentration (M.)	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	k_3 (M.$^{-1}$sec.$^{-1}$)
4.0×10^{-5}	5.0×10^{-4}	4150	$1.3 \pm .4 \times 10^{3}$	$3.8 \pm .6 \times 10^{4}$	$4.2 \pm 3.3 \times 10^{5}$
4.0×10^{-5}	5.0×10^{-3}	4150	$3.2 \pm 1.1 \times 10^{3}$	$2.7 \pm .6 \times 10^{4}$	

a. The solvent was benzene sample #1.

TABLE 14

Dibenzcycloheptenol Triplet Decay as a Function of Flash Energy[a]

Analysis Wave Length (Å)	Flash Energy (joules)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	Number of Determinations
4358	128	$4.6 \pm 1.5 \times 10^2$	$1.5 \pm .1 \times 10^4$	3
4358	361	1.6×10^3	1.5×10^4	1
4358	722	$2.0 \pm .1 \times 10^3$	$1.5 \pm .2 \times 10^4$	2

a. The same solution, 3.8×10^{-5}M. dibenzcycloheptenol in benzene sample #3, was used in these determinations.

triplet absorption was strongest. In order to circumvent possible difficulties from production of non-uniform triplet state distributions in experimental cells, high flash intensities and dilute solutions of sensitizer were used whenever practical. A number of sensitizer solutions listed in Table 15 were used for reference when measuring rates of energy transfer to stilbene and 1,2-diphenylpropene. Filter solutions were employed to make certain that the sensitizer absorbed the same quantity of light both in the absence and presence of added quencher. Scrutiny of the data, however, makes it appear unlikely that the filter solutions had any effect on the measured rate constants. There was in some cases significant variation in α and β values among different solutions of the same sensitizer. Although there may be a more subtle cause, this variation is believed due to differences in solvent purity and/or extent of oxygen removal. It is

TABLE 15

Kinetics of Sensitizer Triplet Decay in Benzene Solution

Sensitizer Concentration (M.)	Triplet Energy[a] (kcal./mole)	Benzene Quality[b]	α (sec.$^{-1}$)	β (sec.$^{-1}$)	Number of Determinations	Analysis Wave Length (Å)	Filter Solution
triphenylene	66.6						
(#1) 4.0×10^{-5}		#3-B	1.7×10^3	4.1×10^4	3	4280	-
(#1) 4.0×10^{-5}		#3-F	$1.6 \pm .3 \times 10^3$	$4.4 \pm .2 \times 10^4$	3	4358	-
(#2) 4.0×10^{-5}		#3-P	$1.9 \pm .2 \times 10^3$	$3.3 \pm .1 \times 10^4$	3	4358	-
thioxanthone	65.5						
6.0×10^{-5}		#3-L	$1.3 \pm .1 \times 10^4$	$3.1 \pm .1 \times 10^4$	3	5770	#2
6.0×10^{-5}		#3-P	$1.1 \pm .1 \times 10^4$	$3.6 \pm .1 \times 10^4$	3	5770	#2
phenanthrene	61.8						
4.0×10^{-5}		#3-B	$3.8 \pm .4 \times 10^3$	$3.4 \pm .1 \times 10^4$	3	4810	-
6.0×10^{-5}		#3-M	$9.0 \pm .3 \times 10^3$	$4.1 \pm .2 \times 10^4$	3	4810	-
naphthalene	60.9						
4.0×10^{-5}		#3-D	$2.2 \pm .2 \times 10^3$	$4.2 \pm .3 \times 10^4$	2	4150	-
naphthalene-d_8	60.9						
4.0×10^{-5}		#3-D	$3.0 \pm .7 \times 10^3$	$3.4 \pm .7 \times 10^4$	2	4150	-

TABLE 15 (cont'd)

Sensitizer Concentration (M.)	Triplet Energy^a (kcal./mole)	Benzene Quality^b	α (sec.$^{-1}$)	β sec.$^{-1}$)	Number of Determinations	Analysis Wave Length (Å)	Filter Solution
2-acetonaphthone	59.3						
2.0×10^{-5}		#3-B	$1.2 \pm .2 \times 10^3$	$2.7 \pm .1 \times 10^4$	3	4300	-
4.0×10^{-5}		#2	$3.0 \pm .2 \times 10^3$	$3.1 \pm .1 \times 10^4$	3	4300	-
4.0×10^{-5}		#3-D	$1.7 \pm .2 \times 10^3$	$3.1 \pm .1 \times 10^4$	3	4358	-
4.0×10^{-5}		#3-G	$3.3 \pm .2 \times 10^3$	$2.9 \pm .2 \times 10^4$	3	4358	-
1-naphthyl phenyl ketone							
4.0×10^{-5}	57.5	#2	$2.0 \pm .3 \times 10^3$	$5.8 \pm .7 \times 10^4$	3	4300	-
4.0×10^{-5}		#3-D	$1.1 \pm .5 \times 10^3$	$6.2 \pm .2 \times 10^4$	3	4358	-
4.0×10^{-5}		#3-F	$1.6 \pm .2 \times 10^3$	$6.1 \pm .2 \times 10^4$	3	4358	-
4.0×10^{-5}		#3-H	$1.1 \pm .1 \times 10^3$	$6.4 \pm .1 \times 10^4$	3	4358	-
1.0×10^{-4}		#3-K	$1.8 \pm .3 \times 10^3$	$4.8 \pm .6 \times 10^4$	3	4358	#2
1.0×10^{-4}		#3-K	$1.6 \pm .2 \times 10^3$	$5.2 \pm .2 \times 10^4$	3	4358	-
4.0×10^{-5}		#3-O	$2.2 \pm .6 \times 10^3$	$4.2 \pm .2 \times 10^4$	3	4358	-
chrysene	56.6						
4.0×10^{-5}		#3-K	$2.0 \pm .3 \times 10^3$	$1.5 \pm .1 \times 10^4$	3	5770	-
3.9×10^{-5}		#3-Q	$2.7 \pm .1 \times 10^3$	$1.6 \pm .1 \times 10^4$	3	5790	-
3.9×10^{-5}		#3-Q	$3.6 \pm .2 \times 10^3$	$1.6 \pm .1 \times 10^4$	3	5790	-
fluorenone	53.3						
4.0×10^{-5}		#2	$4.1 \pm .3 \times 10^3$	$6.5 \pm .3 \times 10^4$	3	4400	-
4.0×10^{-5}		#3-F	$3.1 \pm .1 \times 10^3$	$3.8 \pm .1 \times 10^4$	3	4358	-
4.0×10^{-5}		#3-G	$3.0 \pm .4 \times 10^3$	$3.9 \pm .1 \times 10^4$	3	4358	-
2.0×10^{-4}		#3-H	$6.3 \pm .3 \times 10^3$	$3.4 \pm .2 \times 10^4$	3	4358	-

TABLE 15 cont'd

Sensitizer Concentration (M.)	Triplet Energy[a] (kcal./mole)	Benzene Quality[b]	c (sec.$^{-1}$)	β (sec.$^{-1}$)	Number of Determinations	Analysis Wave Length (Å)	Filter Solution
fluorenone (cont'd)	53.3						
2.0×10^{-4}		#3-Q	$1.5 \pm .3 \times 10^{3}$	$3.6 \pm .2 \times 10^{4}$	6	4358	#3
fluoranthene	52.9						
4.0×10^{-5}		#3-K	3.6×10^{3}	3.3×10^{4}	1	4045	-
1, 2, 5, 6-dibenzanthracene							
4.0×10^{-5}	52.2	#3-D	$8.2 \pm .2 \times 10^{2}$	$1.9 \pm .1 \times 10^{4}$	3	5460	-
4.0×10^{-5}		#3-J	$7.3 \pm 1.5 \times 10^{2}$	$1.6 \pm .1 \times 10^{4}$	3	5460	-
4.0×10^{-5}		#3-O	$7.3 \pm 1.4 \times 10^{2}$	$1.2 \pm .1 \times 10^{4}$	3	5460	#3
4.0×10^{-5}		#3-O	$8.2 \pm .8 \times 10^{2}$	$1.3 \pm .1 \times 10^{4}$	3	5460	#3
4.0×10^{-5}		#3-Q	$6.3 \pm 1.3 \times 10^{2}$	$1.2 \pm .1 \times 10^{4}$	3	5790	#3
4.0×10^{-5}		#3-Q	$5.9 \pm 1.0 \times 10^{2}$	$1.2 \pm .1 \times 10^{4}$	4	5790	#3
duroquinone	51.6						
1.0×10^{-4}		#3-F	$1.9 \pm .2 \times 10^{4}$	$3.9 \pm .2 \times 10^{4}$	3	4358	-
benzil	50.9						
4.0×10^{-5}		#3-H	$2.4 \pm .1 \times 10^{4}$	$1.5 \pm .2 \times 10^{4}$	3	4865	-
1.0×10^{-3}		#3-H	$1.7 \pm .1 \times 10^{4}$	$2.1 \pm .1 \times 10^{4}$	3	4865	#3
1.0×10^{-4}		#3-N	$1.7 \pm .1 \times 10^{4}$	$1.0 \pm 1.0 \times 10^{4}$	3	4865	#2
2.5×10^{-4}		#3-P	$1.8 \pm .1 \times 10^{4}$	$1.2 \pm .1 \times 10^{4}$	3	4865	#3

TABLE 15 cont'd

Sensitizer Concentration (M.)	Triplet Energy[a] (kcal./mole)	Benzene Quality[b]	α (sec.$^{-1}$)	β (sec.$^{-1}$)	Number of Determi-nations	Analysis Wave Length (Å)	Filter Solution
1, 2, 3, 4-dibenzanthracene							
4.0×10^{-5}	50.8	#3-J	1.6×10^{3}	1.9×10^{4}	1	4358	-
1.0×10^{-4}		#3-N	$1.2 \pm .2 \times 10^{3}$	$1.9 \pm .1 \times 10^{4}$	3	4358	#3
1.0×10^{-4}		#3-N	$1.1 \pm .4 \times 10^{3}$	$1.8 \pm .1 \times 10^{4}$	3	4358	#2
1.0×10^{-4}		#3-O	$7.8 \pm 1.3 \times 10^{2}$	$1.7 \pm .1 \times 10^{4}$	3	4358	#2
camphorquinone	50.0						
4.0×10^{-4}		#3-G	3.0×10^{3}	4.7×10^{4}	1	3130	-
pyrene	48.2						
4.0×10^{-5}		#2	$4.7 \pm .5 \times 10^{3}$	$2.9 \pm .8 \times 10^{4}$	3	4160	-
4.0×10^{-5}		#1	$1.4 \pm .4 \times 10^{3}$	$1.5 \pm .2 \times 10^{4}$	3	4160	-
4.0×10^{-5}		#3-D	$1.5 \pm .3 \times 10^{3}$	$1.5 \pm .1 \times 10^{4}$	3	4160	-
4.0×10^{-5}		#3-G	$1.4 \pm .4 \times 10^{3}$	$1.8 \pm .1 \times 10^{4}$	3	4160	-
4.0×10^{-5}		#3-H	$6.5 \pm 2.5 \times 10^{3}$	$1.7 \pm .2 \times 10^{4}$	3	4160	-
5.0×10^{-4}		#3-N	$3.2 \pm .4 \times 10^{2}$	$1.4 \pm .1 \times 10^{4}$	3	4045	#3
5.0×10^{-4}		#3-N	$1.2 \pm .2 \times 10^{3}$	$2.6 \pm .1 \times 10^{4}$	3	4045	#2
1, 2-benzanthracene							
4.0×10^{-5}	47.2	#1	$9.7 \pm 1.2 \times 10^{2}$	$1.4 \pm .1 \times 10^{4}$	3	4850	-
4.0×10^{-5}		#3-H	$2.2 \pm .3 \times 10^{2}$	1.3×10^{4}	3	4850	-
4.0×10^{-5}		#3-N	$3.5 \pm 1.8 \times 10^{2}$	$1.1 \pm .1 \times 10^{4}$	3	4850	#3

TABLE 15 cont'd

Sensitizer Concentration (M.)	Triplet Energy[a] (kcal./mole)	Benzene Quality[b]	α (sec.$^{-1}$)	β (sec.$^{-1}$)	Number of Determinations	Analysis Wave Length (Å)	Filter Solution
benzanthrone	47.0						
4.0×10^{-5}		#1	$4.5 \pm .2 \times 10^{3}$	$3.4 \pm .1 \times 10^{4}$	3	4493	-
4.0×10^{-5}		#3-A	$7.3 \pm 2.9 \times 10^{2}$	$4.3 \pm .1 \times 10^{4}$	3	4358	-
4.0×10^{-5}		#3-E	$1.1 \pm .2 \times 10^{3}$	$3.4 \pm .2 \times 10^{4}$	3	4500	-
1, 12-benzperylene	46.2						
4.0×10^{-5}		#3-L	4.9×10^{2}	8.5×10^{3}	1	4681	-
3-acetyl pyrene	45.5						
4.0×10^{-5}		#1	$8.9 \pm .8 \times 10^{2}$	1.9×10^{4}	3	4358	-
4.0×10^{-5}		#3-G	$6.9 \pm .1 \times 10^{2}$	$1.9 \pm .1 \times 10^{4}$	3	4358	-
5.0×10^{-4}		#3-J	$8.0 \pm .5 \times 10^{2}$	$1.7 \pm .1 \times 10^{4}$	3	4358	#3
acridine	45.3						
4.0×10^{-5}		#3-E	$1.9 \pm .1 \times 10^{3}$	$1.1 \pm .1 \times 10^{4}$	3	4358	-
4.0×10^{-5}		#3-F	$2.5 \pm .1 \times 10^{3}$	1.2×10^{4}	3	4358	-
4.0×10^{-5}		#3-G	$2.3 \pm .2 \times 10^{3}$	$1.2 \pm .1 \times 10^{4}$	3	4358	-
9, 10-dimethyl-1, 2-benzanthracene							
4.0×10^{-5}	44.3	#3-E	$9.1 \pm 1.4 \times 10^{2}$	$1.3 \pm .1 \times 10^{4}$	3	4680	-
4.0×10^{-5}		#3-M	$6.2 \pm .9 \times 10^{2}$	1.3×10^{4}	3	4681	#3
4.0×10^{-5}		#3-Q	$4.2 \pm .6 \times 10^{2}$	1.2×10^{4}	3	4678	#3

TABLE 15 cont'd

Sensitizer Concentration (M.)	Triplet Energy[a] (kcal./mole)	Benzene Quality[b]	α (sec.$^{-1}$)	β (sec.$^{-1}$)	Number of Determinations	Analysis Wave Length (Å)	Filter Solution
anthracene	42.6						
4.0×10^{-5}		#1	$1.0 \pm .1 \times 10^3$	$6.9 \pm .7 \times 10^3$	5	4240	-
4.0×10^{-5}		#1	$3.0 \pm .4 \times 10^2$	$9.7 \pm .4 \times 10^3$	3	4358	-
4.0×10^{-5}		#3-K	$5.6 \pm .6 \times 10^2$	$8.9 \pm .3 \times 10^3$	3	4358	-
4.0×10^{-5}		#3-M	$2.7 \pm .2 \times 10^3$	$9.8 \pm 1.3 \times 10^3$	3	4358	#3
4.0×10^{-5}		#3-P	$1.5 \pm .2 \times 10^3$	$8.4 \pm .6 \times 10^3$	3	4358	#3
4.0×10^{-5}		#3-Q	$6.7 \pm .7 \times 10^2$	$8.1 \pm .3 \times 10^3$	3	4358	#3
3, 4-benzpyrene	41.9						
4.0×10^{-5}		#3-L	$1.2 \pm .1 \times 10^3$	$8.7 \pm .5 \times 10^3$	3	4681	-
4.0×10^{-5}		#3-M	$7.2 \pm .7 \times 10^2$	$9.3 \pm .2 \times 10^3$	3	4681	#3
9, 10-dibromoanthracene							
4.0×10^{-5}	40.2	#3-S	$3.4 \pm .1 \times 10^4$	$7.6 \pm 3.2 \times 10^3$	3	4358	-
4.0×10^{-5}		#3-M	$3.1 \pm .1 \times 10^4$	$2.9 \pm 1.0 \times 10^4$	3	4358	-

a. Reference to the sources of sensitizer triplet energies is given in the Appendix.

b. Letters refer to different preparations of benzene sample #3.

deemed advisable, when measuring quenching constants, to include with each experiment a sensitizer reference that has been prepared with the same sample of solvent and degassed simultaneously with the cell containing sensitizer and added quencher.

Figure 7 is a plot of the unimolecular rate constants from Table 15 against triplet state energies of the sensitizers involved. The ordinate is plotted on a logarithm scale for convenience. For a particular sensitizer, a circle denotes the average value and a straight line includes the range of all measured values. The fact that rate constants for different sensitizers vary by as much as two orders of magnitude may, at first, appear to present evidence against Livingston's hypothesis (25, 27). Substances such as 9, 10-dibromoanthracene, however, have radiative lifetimes so short that they are not affected by small quantities of quencher in solution (12). It is believed that the same argument may apply to thioxanthone, duroquinone, benzil and possibly fluorenone, fluoranthene, camphorquinone, and acridine, although radiative lifetimes for these substances have not been reported. With the exception of phenanthrene, the remaining sensitizers can be divided into two classes. Those with triplet energy greater than 56 kcal./mole have rate constants that cluster about 2×10^3 sec.$^{-1}$. Below 56 kcal./mole, there is a gradual decrease in measured rate constants to values below 1×10^3 sec.$^{-1}$. There are, of course, some variations in this pattern that may have been caused by differences in solvent purity and/or extent of oxygen removal from one experiment to another. The gradual decrease below 56 kcal./mole may indicate that there was some quencher present in the solvent with a triplet energy in the range 50-55 kcal./mole. Perhaps the most disturbing feature of Table 15 and Figure 7 in terms of Livingston's hypothesis is the

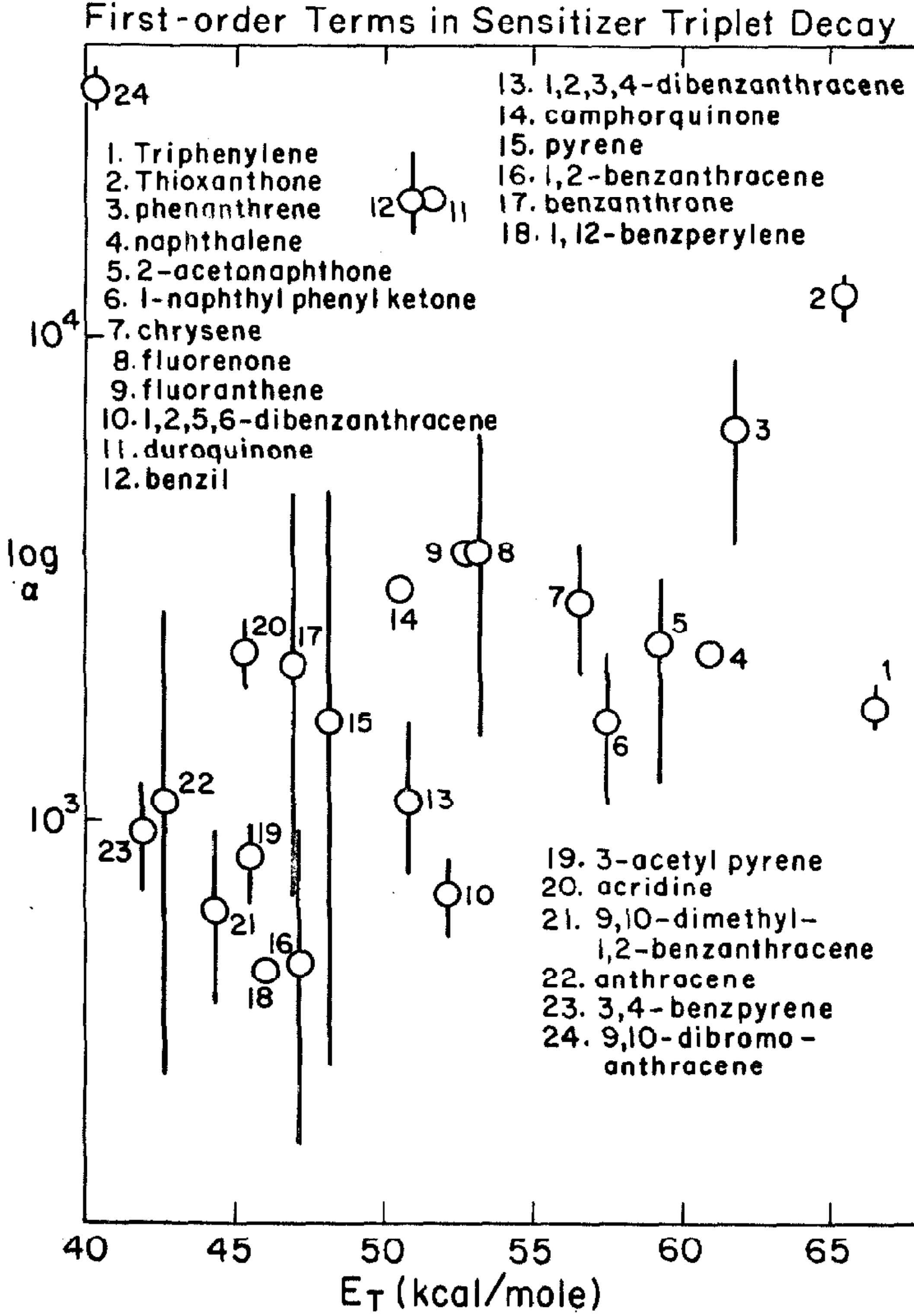
First-order Terms in Sensitizer Triplet Decay
log α
10^4
10^3
40
45
50
55
60
65
E_T (kcal/mole)
1. Triphenylene
2. Thioxanthone
3. phenanthrene
4. naphthalene
5. 2-acetonaphthone
6. 1-naphthyl phenyl ketone
7. chrysene
8. fluorenone
9. fluoranthene
10. 1,2,5,6-dibenzanthracene
11. duroquinone
12. benzil
13. 1,2,3,4-dibenzanthracene
14. camphorquinone
15. pyrene
16. 1,2-benzanthracene
17. benzanthrone
18. 1,12-benzperylene
19. 3-acetyl pyrene
20. acridine
21. 9,10-dimethyl-1,2-benzanthracene
22. anthracene
23. 3,4-benzpyrene
24. 9,10-dibromo-anthracene
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

Figure 7

unexpectedly high value of k_1 for phenanthrene, which is known to have a radiative lifetime of 3.3 sec. (47). However, only two independent measurements of this rate constant were made and the possibility that the measured values were limited by impurities in either phenanthrene or the solvent cannot be dismissed. One may conclude, therefore, that there is no compelling evidence against Livingston's hypothesis.

In order to evaluate rate constants for the process of triplet-triplet annihilation, one must know, in addition to measured values of β, the extinction coefficient of triplet-triplet absorption and the path length of the cell. Self quenching constants, k_3, are usually several orders of magnitude smaller than k_2 and can be ignored. Although triplet absorbance can readily be measured after flashing, extinction coefficients cannot be evaluated without knowing the concentration of molecules in the triplet state. Porter and Windsor (7c) have estimated extinction coefficients in triplet-triplet absorption by assigning the observed decrease in singlet-singlet absorption intensity to conversion to the triplet state. In those cases where Porter and Windsor reported ϵ^* values for sensitizers whose β values were measured here, rate constants for triplet-triplet annihilation have been calculated and are listed in Table 16. These values all appear to be within experimental error of the expected diffusion controlled rate constant.

TABLE 16

Rate Constants for Triplet-Triplet Annihilation in Benzene

Sensitizer	β^a (sec.$^{-1}$)	$(\epsilon*)^b$	Wave Length (Å)	k_2 (M.$^{-1}$sec.$^{-1}$)
triphenylene	4.1×10^4	4.1×10^3	4280	3.5×10^9
naphthalene	4.2×10^4	1.0×10^4	4150	8.8×10^9
chrysene	1.5×10^4	8.8×10^3	5700	2.8×10^9
1, 2, 5, 6-dibenzanthracene	1.5×10^4	6.3×10^4	5460	2.0×10^{10}
1, 2-benzanthracene	1.2×10^4	2.3×10^4	4850	5.8×10^9
anthracene	6.9×10^3	7.2×10^4	4240	1.0×10^{10}

a. The average of the values from Table 15 is given here.

b. The values of $\epsilon*$ are from reference 7c.

Rate Constants for Triplet Energy Transfer to the Stilbenes and 1, 2-Diphenylpropenes:

The first step in the investigation of triplet energy transfer to stilbene was to check the possibility of viewing stilbene triplets directly. No transient absorption over the spectral region 3420-5790 Å could be detected with the flash-photoelectric apparatus after subjecting benzene solutions of trans-stilbene (1×10^{-2}M. and 2×10^{-4}M.) to intense flashes of light. In similar experiments with cis-stilbene, a transient with absorption in the region 4200-4900 Å and a lifetime greater than 5 sec. formed on flashing. The transient absorption intensity, detected with a cis-stilbene concentration of 2×10^{-4}M., was weak and increased only slightly with higher flash intensities and higher stilbene concentrations. The lifetime and absorption spectrum of this transient match those of dihydrophenanthrene, which has been shown to form from the first excited singlet state of cis-stilbene (31, 32). The fact that reversion of dihydrophenanthrene to cis-stilbene is known to be a photochemical reaction would be expected to keep the concentration of dihydrophenanthrene at a low level and could account for the observed weak absorption intensity.

With fluorenone as sensitizer, benzene solutions of cis- and trans-stilbene, respectively, were prepared and, using the technique of flash kinetic spectrophotometry, the spectral region between 4150 and 6000 Å was scanned for transient absorption. Filter solutions were employed to prevent direct absorption of light by stilbene. In both cases, the concentration of stilbene (1×10^{-2}M.) was sufficient to quench completely all detectable triplet-triplet absorption in fluorenone. Porter (49), using flash spectroscopy, also was unable to view absorption of stilbene triplets in fluid solution. The fact that no absorption was observed is consistent with the short stilbene triplet lifetimes suggested by the studies of Hammond and Saltiel (31, 32, 34).

It is of considerable advantage to these studies that triplet-triplet absorption in stilbene cannot be detected with the experimental techniques used here. For example, when measuring the rate of triplet energy transfer from sensitizer to stilbene, the decay of sensitizer triplet-triplet absorption cannot be distorted by simultaneous absorption in stilbene. If stilbene triplets are indeed very short-lived, then the effective concentration of ground state stilbene will remain constant during the process of energy transfer and there will be little complication from reversible energy transfer.

Since direct absorption of light by stilbene leads to isomerization exclusive of energy transfer (31, 32), filter solutions were employed whenever practical to effect necessary spectral barriers. The use of filter solutions also prevents formation of dihydrophenanthrene, which absorbs in the same region as many sensitizer triplets and may itself be a quencher. As described in the experimental section, the absorption spectrum of 1, 4-diphenyl-1, 3-butadiene is such that this substance is effective in filtering light absorbed by the stilbene isomers. Less effective in the same role is trans-stilbene. Absorption spectra of the sensitizers vary considerably and it was not always practical or possible to get sufficient light into the sensitizer when using filter solutions. These exceptions are noted subsequently.

Listed in Table 17 are the rate constants that have been measured by flash kinetic spectrophotometry for the process of triplet energy transfer from 18 different photosensitizers to the

TABLE 17

Rate Constants for Triplet Energy Transfer from Photosensitizers to cis- and trans-Stilbene

Sensitizer and Triplet Energy[a] (kcal/mole) Concentration (M.)		Stilbene Concentration[b] (M.)	Initial % cis	Filter Solution	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	(k_Q)cis ($M^{-1}sec^{-1}$)	(k_Q)trans ($M^{-1}sec^{-1}$)	Basis of Calculation[c]
triphenylene	66.6									
4.0×10^{-5}		-	-	-	4358	$1.6 \pm .3 \times 10^{3}$	$4.4 \pm .2 \times 10^{4}$	-	-	-
4.0×10^{-5}		8.6×10^{-6}	100	-	4358	$5.9 \pm .1 \times 10^{4}$	d.	6.6×10^{9}	6.6×10^{9}	PSS
4.0×10^{-5}		5.0×10^{-6}	0	-	4358	$4.0 \pm .2 \times 10^{4}$	d.	7.6×10^{9}	7.6×10^{9}	PSS
thioxanthone	65.5									
6.0×10^{-5}		-	-	#2	5770	$1.3 \pm .1 \times 10^{4}$	$3.1 \pm .1 \times 10^{4}$	-	-	-
6.0×10^{-5}		5.4×10^{-6}	100	#2	5770	$3.9 \pm .1 \times 10^{4}$	$2.1 \pm .5 \times 10^{4}$	4.8×10^{9}	4.8×10^{9}	PSS
6.0×10^{-5}		5.0×10^{-6}	0	#2	5770	$3.9 \pm .2 \times 10^{4}$	$1.5 \pm .7 \times 10^{4}$	5.2×10^{9}	5.2×10^{9}	PSS
phenanthrene	61.8									
6.0×10^{-5}		-	-	-	4810	$9.0 \pm .3 \times 10^{3}$	$4.1 \pm .2 \times 10^{4}$	-	-	-
6.0×10^{-5}		5.4×10^{-6}	100	-	4810	$3.2 \pm .1 \times 10^{4}$	$5.0 \pm .8 \times 10^{4}$	4.0×10^{9}	4.9×10^{9}	PSS
6.0×10^{-5}		5.0×10^{-6}	0	-	4810	$2.8 \pm .1 \times 10^{4}$	$4.9 \pm .4 \times 10^{4}$	3.6×10^{9}	4.3×10^{9}	PSS
2-acetonaphthone	59.3									
4.0×10^{-5}		-	-	-	4358	$3.3 \pm .2 \times 10^{3}$	$2.9 \pm .2 \times 10^{4}$	-	-	-
4.0×10^{-5}		8.6×10^{-6}	100	-	4358	$3.5 \pm .2 \times 10^{4}$	$1.4 \pm .9 \times 10^{4}$	3.3×10^{9}	4.7×10^{9}	PSS
4.0×10^{-5}		5.0×10^{-6}	0	-	4358	$2.3 \pm .1 \times 10^{4}$	$1.9 \pm .4 \times 10^{4}$	3.5×10^{9}	5.1×10^{9}	PSS
1-naphthyl phenyl ketone	57.5									
4.0×10^{-5}		-	-	-	4358	$1.1 \pm .1 \times 10^{3}$	$6.4 \pm .1 \times 10^{4}$	-	-	-
4.0×10^{-5}		8.6×10^{-6}	100	-	4358	$2.7 \pm .2 \times 10^{4}$	$3.3 \pm 1.1 \times 10^{4}$	2.5×10^{9}	4.3×10^{9}	PSS
4.0×10^{-5}		5.0×10^{-6}	0	0	4358	$1.7 \pm .1 \times 10^{4}$	$4.2 \pm .4 \times 10^{4}$	2.7×10^{9}	4.6×10^{9}	PSS
1.0×10^{-4}		-	-	#2	4358	$1.8 \pm .3 \times 10^{3}$	$4.8 \pm .6 \times 10^{4}$	-	-	-
1.0×10^{-4}		1.1×10^{-5}	100	#2	4358	$3.6 \pm .3 \times 10^{4}$	d.	2.6×10^{9}	4.4×10^{9}	PSS
1.0×10^{-4}		1.0×10^{-5}	0	#2	4358	5.4×10^{4}	d.	-	5.2×10^{9}	PI
1.0×10^{-4}		-	-	-	4358	$1.6 \pm .2 \times 10^{3}$	$5.2 \pm .2 \times 10^{4}$	-	-	-
1.0×10^{-4}		1.1×10^{-5}	100	-	4358	$3.2 \pm .2 \times 10^{4}$	$2.6 \pm .7 \times 10^{4}$	2.3×10^{9}	3.9×10^{9}	PSS
1.0×10^{-4}		1.0×10^{-5}	0	-	4358	$3.0 \pm .2 \times 10^{4}$	$3.2 \pm .7 \times 10^{4}$	2.4×10^{9}	4.0×10^{9}	PSS

TABLE 17 cont'd

Sensitizer and Triplet Energy[a] (kcal/mole) Concentration (M.)	Stilbene Concentration[b] (M.)	Initial % cis	Filter Solution	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	(k_Q)cis ($M^{-1}sec^{-1}$)	(k_Q)trans ($M^{-1}sec^{-1}$)	Basis of Calculation[c]
chrysene 56.6									
4.0×10^{-5}	-	-	-	5770	$2.0 \pm .3 \times 10^3$	$1.5 \pm .1 \times 10^4$	-	-	-
4.0×10^{-5}	1.1×10^{-5}	100	#2	5770	$3.5 \pm .2 \times 10^4$	d	2.4×10^9	4.9×10^9	PSS
4.0×10^{-5}	1.0×10^{-5}	0	#2	5770	$5.8 \pm .1 \times 10^4$	d	-	5.6×10^9	PI
4.0×10^{-5}	1.1×10^{-5}	100	-	5770	$3.6 \pm .3 \times 10^4$	d	2.5×10^9	5.0×10^9	PSS
4.0×10^{-5}	1.0×10^{-5}	0	-	5770	$3.4 \pm .2 \times 10^4$	$2.3 \pm 1.3 \times 10^4$	2.6×10^9	5.1×10^9	PSS
fluorenone 53.3									
4.0×10^{-5}	-	-	-	4358	$3.0 \pm .4 \times 10^3$	$3.9 \pm .1 \times 10^4$	-	-	-
4.0×10^{-5}	2.2×10^{-5}	100	-	4358	$2.9 \pm .2 \times 10^4$	$3.3 \pm .8 \times 10^4$	8.7×10^8	3.3×10^9	PSS
4.0×10^{-5}	1.0×10^{-5}	0	-	4358	$1.7 \pm .1 \times 10^4$	$3.5 \pm .3 \times 10^4$	1.0×10^9	3.8×10^9	PSS
2.0×10^{-4}	-	-	#3	4358	$6.3 \pm .3 \times 10^3$	$3.4 \pm .2 \times 10^4$	-	-	-
2.0×10^{-4}	2.2×10^{-5}	100	#3	4358	$3.4 \pm .3 \times 10^4$	$1.4 \pm .7 \times 10^4$	9.3×10^8	3.6×10^9	-
2.0×10^{-4}	1.0×10^{-5}	0	#3	4358	$1.9 \pm .1 \times 10^4$	$2.4 \pm .7 \times 10^4$	9.3×10^8	3.6×10^9	-
1,2,5,6-dibenzanthracene 52.2									
4.0×10^{-5}	-	-	-	5460	$7.3 \pm 1.5 \times 10^2$	$1.6 \pm .1 \times 10^4$	-	-	-
4.0×10^{-5}	2.7×10^{-5}	100	#3	5460	$3.3 \pm .3 \times 10^4$	$1.9 \pm 1.5 \times 10^4$	8.4×10^8	3.5×10^9	PSS
4.0×10^{-5}	1.5×10^{-5}	0	#3	5460	$2.1 \pm .2 \times 10^4$	$1.3 \pm .7 \times 10^4$	9.4×10^8	3.9×10^9	PSS
4.0×10^{-5}	-	-	#3	5460	$8.2 \pm .8 \times 10^2$	$1.3 \pm .1 \times 10^4$	-	-	-
4.0×10^{-5}	2.7×10^{-5}	100	#3	5460	$2.6 \pm .1 \times 10^4$	$1.1 \pm .1 \times 10^4$	9.3×10^8	-	PI
4.0×10^{-5}	1.0×10^{-5}	0	#3	5460	3.3×10^4	2.5×10^3	-	3.2×10^9	PI
4.0×10^{-5}	2.7×10^{-5}	100	#3	5460	$3.3 \pm .4 \times 10^4$	d	8.4×10^8	3.5×10^9	PSS
4.0×10^{-5}	1.0×10^{-5}	0	#3	5460	$1.2 \pm .1 \times 10^4$	$1.6 \pm .2 \times 10^4$	7.8×10^8	3.3×10^9	PSS
benzil 50.9									
1.0×10^{-3}	-	-	#3	4865	$1.7 \pm .1 \times 10^4$	$2.1 \pm .5 \times 10^4$	-	-	-
1.0×10^{-3}	4.3×10^{-5}	100	#3	4865	$3.5 \pm .1 \times 10^4$	d	2.8×10^8	2.0×10^9	PSS
1.0×10^{-3}	5.0×10^{-5}	0	#3	4865	$3.9 \pm .3 \times 10^4$	$1.1 \pm .1 \times 10^4$	2.9×10^8	2.1×10^9	PSS
1.0×10^{-4}	-	-	#2	4865	$1.7 \pm .1 \times 10^4$	$1.0 \pm 1.0 \times 10^4$	-	-	-
1.0×10^{-4}	5.4×10^{-5}	100	#2	4865	3.1×10^4	9.2×10^3	5.7×10^8	-	PI
1.0×10^{-4}	5.0×10^{-5}	0	#2	4865	8.7×10^4	d	-	1.7×10^9	PI
1.0×10^{-4}	5.4×10^{-5}	100	#2	4865	$3.7 \pm .5 \times 10^4$	d	2.5×10^8	1.8×10^9	PSS
1.0×10^{-4}	5.0×10^{-5}	0	#2	4865	$3.6 \pm .3 \times 10^4$	d	2.5×10^8	1.8×10^9	PSS

TABLE 17 cont'd

Sensitizer and Triplet Energy[a] (kcal/mole) Concentration (M.)		Stilbene Concentration[b] (M.)	Initial % cis	Filter Solution	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	(k_Q)cis ($M^{-1}sec^{-1}$)	(k_Q)trans ($M^{-1}sec^{-1}$)	Basis of Calculation[c]
1,2,3,4-dibenzanthracene										
1.0×10^{-4}	50.8	-	-	#3	4358	$1.2 \pm .2 \times 10^{3}$	$1.9 \pm .1 \times 10^{4}$	-	-	-
1.0×10^{-4}		5.4×10^{-5}	100	#3	4358	2.3×10^{4}	2.5×10^{4}	4.1×10^{8}	-	PI
1.0×10^{-4}		-	-	#2	4358	$1.1 \pm .4 \times 10^{3}$	$1.8 \pm .1 \times 10^{4}$	-	-	-
1.0×10^{-4}		1.5×10^{-5}	0	#2	4358	2.9×10^{4}	2.5×10^{4}	-	1.9×10^{9}	PI
1.0×10^{-4}		5.4×10^{-5}	100	#2	4358	$3.1 \pm .1 \times 10^{4}$	$1.6 \pm .3 \times 10^{4}$	3.8×10^{8}	2.4×10^{9}	PSS
1.0×10^{-4}		1.5×10^{-5}	0	#2	4358	$1.0 \pm .1 \times 10^{4}$	$1.7 \pm .1 \times 10^{4}$	4.1×10^{8}	2.6×10^{9}	PSS
pyrene	48.2									
4.0×10^{-5}		-	-	-	4160	$6.5 \pm 2.5 \times 10^{2}$	$1.7 \pm .2 \times 10^{4}$	-	-	-
4.0×10^{-5}		8.6×10^{-5}	100	#1	4160	$7.5 \pm .1 \times 10^{3}$	$1.7 \pm .2 \times 10^{4}$	7.9×10^{7}	-	PI
4.0×10^{-5}		5.0×10^{-5}	100	#1	4160	$1.0 \pm .1 \times 10^{4}$	$3.0 \pm .8 \times 10^{4}$	6.9×10^{7}	8.1×10^{8}	PSS
4.0×10^{-5}		8.6×10^{-5}	0	#1	4160	$8.0 \pm .2 \times 10^{3}$	$1.7 \pm .3 \times 10^{4}$	9.5×10^{7}	1.1×10^{9}	PSS
5.0×10^{-4}		-	-	#3	4160	$3.2 \pm .4 \times 10^{2}$	$1.4 \pm .1 \times 10^{4}$	-	-	-
5.0×10^{-4}		1.1×10^{-4}	100	#3	4160	5.0×10^{3}	1.2×10^{4}	4.3×10^{7}	-	PI
5.0×10^{-4}		-	-	#2	4045	$1.2 \pm .2 \times 10^{3}$	$2.6 \pm .1 \times 10^{4}$	-	-	-
5.0×10^{-4}		2.5×10^{-5}	0	#2	4045	2.8×10^{4}	d	-	1.1×10^{9}	PI
5.0×10^{-4}		1.1×10^{-4}	100	#2	4045	$7.4 \pm .5 \times 10^{3}$	$3.2 \pm .4 \times 10^{4}$	3.7×10^{7}	4.3×10^{8}	PSS
5.0×10^{-4}		2.5×10^{-5}	0	#2	4045	$3.6 \pm .2 \times 10^{3}$	$3.2 \pm .1 \times 10^{4}$	6.2×10^{7}	7.4×10^{8}	PSS
1,2-benzanthracene										
4.0×10^{-5}	47.2	-	-	-	4850	$2.2 \pm .3 \times 10^{2}$	1.3×10^{4}	-	-	-
4.0×10^{-5}		8.6×10^{-5}	100	#2	4850	$6.5 \pm .4 \times 10^{3}$	$1.2 \pm .1 \times 10^{4}$	7.3×10^{7}	-	PI
4.0×10^{-5}		8.6×10^{-5}	100	#2	4850	$7.6 \pm .1 \times 10^{3}$	$1.1 \pm .1 \times 10^{4}$	5.9×10^{7}	3.3×10^{8}	PSS
4.0×10^{-5}		5.0×10^{-5}	0	#2	4850	$5.1 \pm .1 \times 10^{3}$	$1.0 \pm .1 \times 10^{4}$	6.7×10^{7}	3.8×10^{8}	PSS
4.0×10^{-5}		-	-	#3	4850	$3.5 \pm 1.8 \times 10^{2}$	$1.1 \pm .1 \times 10^{4}$	-	-	-
4.0×10^{-5}		1.1×10^{-4}	100	#3	4850	6.5×10^{3}	$1.0 \pm .1 \times 10^{4}$	5.5×10^{7}	-	PI
4.0×10^{-5}		5.0×10^{-4}	0	#3	4850	2.2×10^{4}	1.3×10	-	4.2×10^{8}	PI
4.0×10^{-5}		1.1×10^{-5}	100	#3	4850	9.2×10^{3}	$1.1 \pm .1 \times 10^{4}$	5.5×10^{7}	3.1×10^{8}	PSS
4.0×10^{-5}		5.0×10^{-5}	0	#3	4850	$4.7 \pm .2 \times 10^{3}$	$1.1 \pm .1 \times 10^{4}$	5.9×10^{7}	3.3×10^{8}	PSS

TABLE 17 cont'd

Sensitizer and Triplet Energy[a] (kcal/mole) Concentration (M.)	Stilbene Concentration[b] (M.)	Initial % cis	Filter Solution	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	(k_Q)cis ($M^{-1}sec^{-1}$)	(k_Q)trans ($M^{-1}sec^{-1}$)	Basis of Calculation[c]
benzanthrone 47.0									
4.0×10^{-5}	-	-	-	4358	$7.3 \pm 2.9 \times 10^{2}$	$4.3 \pm .1 \times 10^{4}$	-	-	-
4.0×10^{-5}	2.2×10^{-4}	100	#2	4358	1.3×10^{4}	$3.8 \pm .1 \times 10^{4}$	5.5×10^{7}	-	PI
4.0×10^{-5}	1.5×10^{-4}	0	#2	4358	2.7×10^{4}	2.1×10^{4}	-	1.7×10^{8}	PI
4.0×10^{-5}	2.2×10^{-4}	100	#2	4358	$1.9 \pm .1 \times 10^{4}$	$2.8 \pm .3 \times 10^{4}$	5.8×10^{7}	2.4×10^{8}	PSS
4.0×10^{-5}	1.5×10^{-4}	0	#2	4358	$1.6 \pm .1 \times 10^{4}$	$2.9 \pm .3 \times 10^{4}$	7.1×10^{7}	3.0×10^{8}	PSS
3-acetyl pyrene 45.5									
4.0×10^{-5}	-	-	-	4358	$6.9 \pm .1 \times 10^{2}$	$1.9 \pm .1 \times 10^{4}$	-	-	-
4.0×10^{-5}	6.1×10^{-3}	100	#1	4358	$2.6 \pm .1 \times 10^{4}$	$3.4 \pm .8 \times 10^{4}$	4.3×10^{6}	-	PI
4.0×10^{-5}	3.0×10^{-3}	0	#1	4358	$3.9 \pm .3 \times 10^{4}$	$3.1 \pm 2.0 \times 10^{4}$	-	1.3×10^{7}	PI
5.0×10^{-4}	-	-	#3	4358	$8.0 \pm .5 \times 10^{2}$	$1.7 \pm .1 \times 10^{4}$	-	-	-
5.0×10^{-4}	3.0×10^{-3}	0	#3	4358	$4.3 \pm .5 \times 10^{4}$	$3.4 \pm 2.5 \times 10^{4}$	-	1.4×10^{7}	PI
5.0×10^{-3}	-	-	#3	4358	$9.9 \pm 3.6 \times 10^{2}$	$1.7 \pm .3 \times 10^{4}$	-	-	
5.0×10^{-3}	3.0×10^{-3}	0	#3	4358	$4.2 \pm .2 \times 10^{4}$	$2.2 \pm 1.3 \times 10^{4}$	-	1.4×10^{7}	PI
acridine 45.3									
4.0×10^{-5}	-	-	-	4358	$2.5 \pm .1 \times 10^{3}$	1.2×10^{4}	-	-	-
4.0×10^{-5}	5.9×10^{-3}	100	#1	4358	1.7×10^{4}	$4.1 \pm .3 \times 10^{4}$	2.5×10^{6}	-	PI
4.0×10^{-5}	3.0×10^{-3}	0	#1	4358	$2.0 \pm .1 \times 10^{4}$	$3.0 \pm .4 \times 10^{4}$	-	5.8×10^{6}	PI
9,10-dimethyl-1,2-benzanthracene 44.3									
4.0×10^{-5}	-	-	#3	4681	$6.2 \pm .9 \times 10^{2}$	1.3×10^{4}	-	-	-
4.0×10^{-5}	9.4×10^{-3}	100	#3	4681	$8.7 \pm .4 \times 10^{3}$	$1.4 \pm .2 \times 10^{4}$	8.6×10^{5}	-	PI
4.0×10^{-5}	8.0×10^{-3}	0	#3	4681	$1.4 \pm .1 \times 10^{4}$	$2.2 \pm .2 \times 10^{4}$	-	1.6×10^{6}	PI

TABLE 17 cont'd

Sensitizer and Triplet Energy[a] (kcal/mole) Concentration (M.)	Stilbene Concentration[b] (M.)	Initial % cis	Filter Solution	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	(k_Q)cis ($M^{-1}sec^{-1}$)	(k_Q)trans ($M^{-1}sec^{-1}$)	Basis of Calculation[c]
anthracene 42.6									
4.0×10^{-5}	-	-	#3	4358	$2.7 \pm .2 \times 10^{3}$	$9.8 \pm 1.3 \times 10^{3}$	-	-	-
4.0×10^{-5}	2.1×10^{-2}	100	#3	4358	$4.3 \pm .1 \times 10^{3}$	$9.6 \pm .3 \times 10^{3}$	7.6×10^{4}	-	PI
4.0×10^{-5}	4.0×10^{-2}	0	#3	4358	$6.6 \pm .4 \times 10^{3}$	$9.9 \pm 1.1 \times 10^{3}$	-	9.7×10^{4}	PI
4.0×10^{-5}	-	-	#3	4358	$1.5 \pm .2 \times 10^{3}$	$8.4 \pm .6 \times 10^{3}$	-	-	-
4.0×10^{-5}	4.0×10^{-2}	0	#3	4358	$6.3 \pm .1 \times 10^{3}$	$7.7 \pm .5 \times 10^{3}$	-	1.2×10^{5}	PI
4.0×10^{-5}	4.0×10^{-2} e	0	#3	4358	$5.4 \pm .2 \times 10^{3}$	$8.7 \pm .6 \times 10^{3}$	-	9.8×10^{4}	PI
4.0×10^{-5}	4.0×10^{-2} f	0	#3	4358	$5.8 \pm .3 \times 10^{3}$	$8.6 \pm .8 \times 10^{3}$	-	1.1×10^{5}	PI
4.0×10^{-5}	3.2×10^{-2} g	0	#3	4358	$4.9 \pm .2 \times 10^{3}$	$7.8 \pm .3 \times 10^{3}$	-	1.1×10^{5}	PI
3,4-benzpyrene 41.9									
4.0×10^{-5}	-	-	#3	4681	$7.2 \pm .7 \times 10^{2}$	$9.3 \pm .2 \times 10^{3}$	-	-	-
4.0×10^{-5}	3.9×10^{-2}	100	#3	4681	$4.1 \pm .2 \times 10^{3}$	$9.6 \pm .7 \times 10^{3}$	8.7×10^{4}	-	PI
4.0×10^{-5}	4.0×10^{-2}	0	#3	4681	$3.7 \pm .2 \times 10^{3}$	$9.1 \pm .1 \times 10^{3}$	-	7.5×10^{4}	PI

a. Reference to the source of triplet energy values listed here is given in the Appendix.

b. Except where indicated otherwise, the trans-stilbene used was sample #1.

c. The symbol PSS is used to denote that in evaluating the quenching constants it was assumed that the photostationary state had been reached. If it was assumed that no isomerization had taken place, then the symbol PI (pure isomer) is used.

d. The measured β value is either negative or shows very poor precision.

e. This was trans-stilbene sample #4.

f. This was trans-stilbene sample #2.

g. This was trans-stilbene sample #3.

cis and trans isomers of stilbene. With each experiment, the rate of decay of sensitizer in the absence of added quencher was measured for reference purposes. Quenching constants were then evaluated from the increase in α terms as a function of added quencher concentration. The values of k_Q are in many cases more precise than any of the other parameters derived from the kinetics, since quenching can be made the dominant decay process. The effect of added stilbene isomers on the triplet lifetime of 1, 2, 5, 6-dibenzanthracene is illustrated by the oscillographs reproduced in Figure 8. The results from runs based upon a particular sensitizer reference solution are grouped together in Table 17. Many rate constants were measured independently more than once. Values of β are included for purposes of comparison because they are expected to remain independent of added quencher. In some instances, however, large α terms dominated triplet decay and rendered measurement of β terms very imprecise. At the concentrations of sensitizer used here, reverse energy transfer from trans-stilbene triplets to sensitizer is expected to be negligible (31, 32).

With sensitizers having triplet excitation energies greater than 53 kcal./mole, the stilbene concentrations used were so dilute that it was questionable whether isomeric purity in stilbene persisted after only one flash. These solutions were subjected to repeated flashing in order to reach photostationary conditions prior to kinetic measurements. The same rate of quenching was achieved in solutions prepared initially from either pure cis- or pure trans-stilbene, thus indicating that a common state had been reached. In order to check the actual isomeric composition of stilbene, many of these solutions were concentrated by a factor of 100 or more under a stream of nitrogen and analyzed by vapor phase chroma-

Quenching of 1,2,5,6-Dibenzanthracene Triplets
by *cis* and *trans*-Stilbene

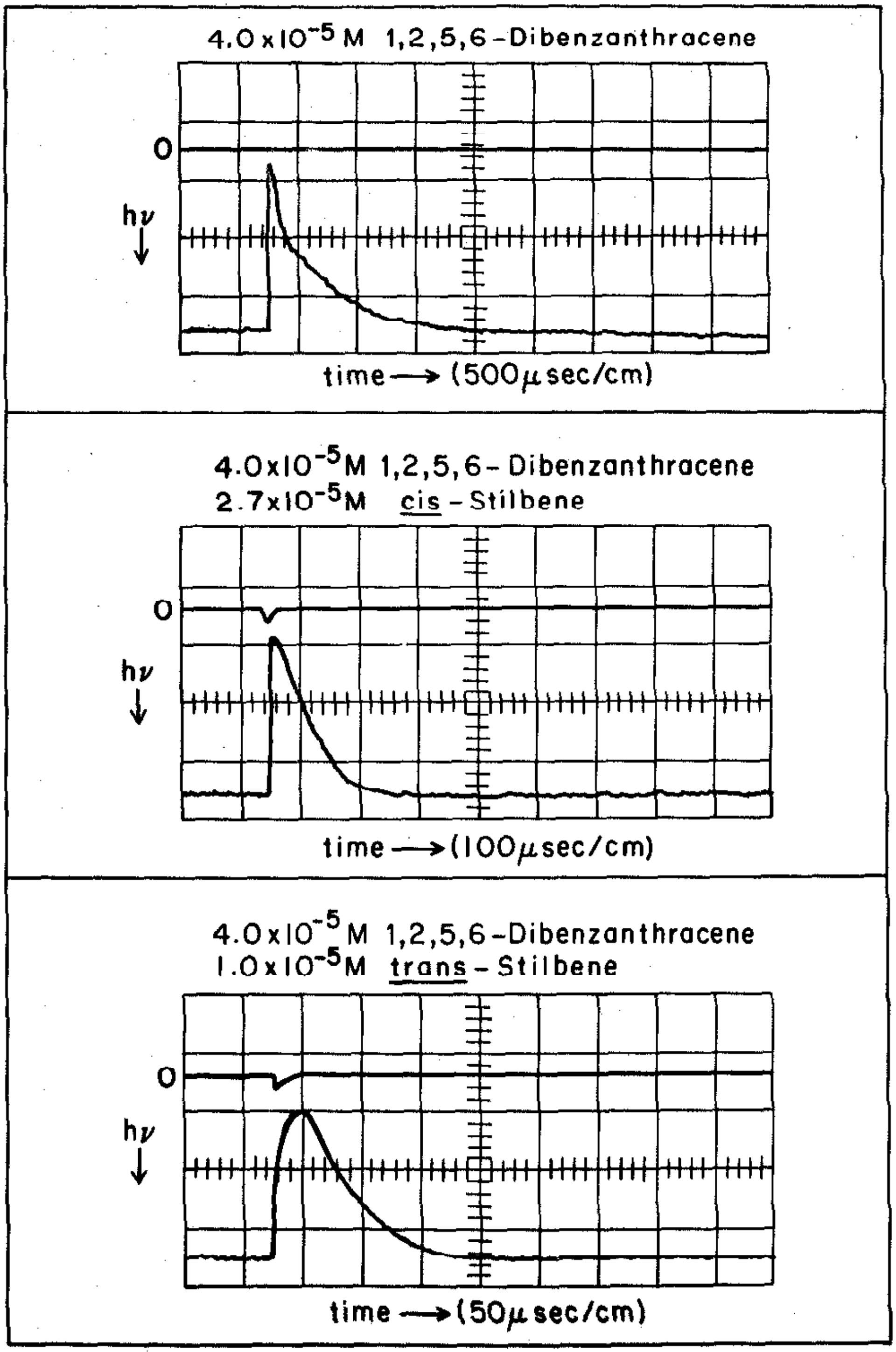

Figure 8

tography. As shown below in Table 18, there is fair agreement between the results of these analyses and previously measured photostationary state values.

With sensitizers having triplet energies greater than 62 kcal./mole, Hammond and Saltiel (34a) reported the photostationary ratio of cis- to trans-stilbene to be 1.5 in solutions 0.05M in stilbene. In this "high-energy" region, it was proposed that sensitizers did not differentiate between the stilbene isomers in the process of energy transfer and that the cis rich mixture resulted from the mode of decay of stilbene triplets. It was later found that this photostationary ratio was 1.6 in more dilute solutions of stilbene ($<10^{-3}$M) where self-quenching of stilbene triplets made no important contribution (31, 32). In more recent studies, Valentine (51) has found that among different classes of "high-energy" sensitizers there is a variation of about 6 per cent in the isomeric composition of stilbene at the photostationary state. It is believed that this variation is caused by small changes in the rates of energy transfer to the individual stilbene isomers rather than by sensitizer effects upon the decay of stilbene triplets. In subsequent discussion, the value of the decay ratio is taken to be 1.6, although it is recognized that this number may be somewhat in error.

In order to make use of the quenching rates measured at the photostationary state, it is necessary to assume the mechanism given in equations 12-18. If excitation of cis- or trans-stilbene leads to a common triplet intermediate, then the composition of the photostationary state is determined by the relative rates of energy transfer to the two isomers as well as by the decay ratio of the stilbene triplets. If, as discussed in the previous paragraph, this latter value is known, the rates of quenching at the photostationary

TABLE 18

Comparison of Photostationary State Measurements for Stilbene

Sensitizer	Triplet Energy (kcal./mole)[a]	Photostationary State[b.] (% cis)	Predicted Photostationary State from k_Q's[c.] (% cis)	VPC Analysis After Flashing (% cis)
triphenylene	66.6	d.	-	73
thioxanthone	65.5	60	-	e.
phenanthrene	61.8	65	-	72[f.]
2-acetonaphthone	59.3	70	-	76[f.]
1-naphthyl phenyl ketone	57.5	73	-	73
chrysene	56.6	76	-	77
fluorenone	53.3	86	-	84
1,2,5,6-dibenzanthracene	52.2	88	85	87
benzil	50.9	91	83	e.
1,2,3,4-dibenzanthracene	50.8	-	88	91
pyrene	48.2	93	97	95
1,2-benzanthracene	47.2	93	92	90

TABLE 18 cont'd

Sensitizer	Triplet Energy (kcal. /mole)[a]	Photostationary State[b] (% cis)	Predicted Photostationary State from k_Q's[c] (% cis)	VPC Analysis After Flashing (% cis)
benzanthrone	47.0	87	83	-
3-acetyl pyrene	45.5	76	83	-
acridine	45.3	79	79	-
9, 10-dimethyl-1, 2-benzanthracene	44.3	-	76	-
anthracene	42.6	-	69	-
3, 4-benzpyrene	41.9	-	57	-

a. Reference to the source of triplet energies listed here is given in the Appendix.

b. The numbers in this column are from references 31, 32, 34, and 51.

c. These photostationary state values were evaluated by assuming that decay from a common stilbene triplet leads to a cis : trans ratio of 1.6.

d. See text for explanation.

e. Side products interfered with VPC analysis.

f. Some side products were observed but did not interfere with VPC analysis.

state can be partitioned into rates of energy transfer to the individual stilbene isomers. In the following scheme, which applies only at the photostationary state, $k_Q[Q]$ represents the total rate of quenching. Equation 41 is the reciprocal of equation 20.

$$\frac{[t]_s}{[c]_s} = \left(\frac{k_{14} + k_{15}}{k_{13}}\right)\left(\frac{k_{17}}{k_{18}}\right) = \frac{1}{1.6}\left(\frac{k_{14} + k_{15}}{k_{13}}\right) \tag{41}$$

$$k_Q[Q] = k_{13}[t] + (k_{14} + k_{15})[c] \tag{42}$$

$$k_{13} = \frac{k_Q[Q]}{2.6[t]} = (k_Q)\,\text{trans} \tag{43}$$

$$(k_{14} + k_{15}) = \frac{k_Q[Q]}{1.6[c]} = (k_Q)\,\text{cis}\ . \tag{44}$$

When using those sensitizers having triplet energies between 47 and 53 kcal./mole, it was possible to measure quenching constants with pure stilbene isomers and again at the photostationary state. The agreement between the two sets of numbers shown in Table 17 provides considerable support for the mechanism of equations 12-18. Higher concentrations of stilbene were required with sensitizers of triplet energy below 47 kcal./mole and, since it was not attempted to bring these solutions to photostationary conditions, quenching constants were measured individually only.

The relationship in equation 41 can also be applied to the evaluation of photostationary state values from the individual quenching constants. Of course, this operation is meaningful only with those constants measured with pure stilbene isomers. Included in Table 18 is a comparison of these predicted photostationary states with those measured by Hammond and Saltiel (31, 32, 34). The agreement, which is good when considering the precision involved in measuring quenching constants, provides additional support for the mechanism.

Some problems arose with individual sensitizers. Thioxanthone was the only sensitizer with triplet energy higher than 58 kcal./mole with which filter solutions could be effectively employed. Triphenylene, phenanthrene, and 2-acetonaphthone have absorption spectra such that it was difficult or impossible, using filtered light, to get sufficient triplet populations in solutions of these molecules. With stilbene concentrations of 2.5×10^{-5}M. and less, however, absorption of light by stilbene did not appear to cause any difficulties. Stilbene quenching constants with 1-naphthyl phenyl ketone, chrysene, and fluorenone were measured with and without filter solutions and both sets of rate constants were identical within experimental error. In no experiment was absorption from dihydrophenanthrene observed even though most sensitizers were monitored at a wave length where this substance absorbs. Also, if dihydrophenanthrene were present, it apparently had no detectable effect on the rate of quenching.

Triphenylene presents a special problem. Not only can one not use filter solutions with this sensitizer, but photostationary states measured with triphenylene were richer in trans-stilbene than was expected. For example, Coyne and Valentine (52) found that a solution 0.05 M in both triphenylene and stilbene gave a photostationary state value of 46 ± 1% cis-stilbene after irradiation with a medium pressure mercury arc lamp and a pyrex filter. By comparison, other "high-energy" sensitizers gave photostationary state values of approximately

60% cis-stilbene. The facts that stilbene absorbed a large quantity of the incident light and that trans-stilbene has larger extinction coefficients than cis-stilbene were expected to lead to a photostationary state containing more than 60% cis-stilbene. Solutions 4 x 10^{-5}M. in triphenylene and 1 x 10^{-5}M. or less in stilbene were used in measuring rate constants for energy transfer and, after repeated flashing with xenon flash lamps, gave apparent photostationary state values of 73 ± 4% cis-stilbene. Because of the different lamps and different reagent concentrations used in the two experiments, it is difficult to relate these two numerical results. In lieu of additional information about energy transfer from triphenylene to stilbene, the only reasonable interpretation of the quenching data seemed to be to assume that triphenylene transfers triplet energy equally well to cis- and trans-stilbene.

After concentration of the solutions used in these investigations, analysis by vapor phase chromatography often showed traces of materials other than solvent and reagents. It was established that several substances were in benzene initially, although it was necessary to concentrate them in benzene under a stream of nitrogen before they could be detected. Extensive formation of side products was detected in solutions with phenanthrene as sensitizer and some side products were also found in the presence of thioxanthone, 2-acetonaphthone, and benzil. In the solutions with thioxanthone and benzil, some of the by-products were not readily separated from trans-stilbene. No side products were observed with these 4 sensitizers in previous photostationary state determinations (31, 32, 51). Although there is no obvious reason why, it is possible that these by-products arrived either by concentration of the solutions or, because of the relatively high incident light intensities in the flash experiments, by interaction between transients.

Eosin and 9, 10-dibromoanthracene were used previously as "low energy" sensitizers with stilbene and were found to effect conversion to 99. 8% trans isomer at the photostationary state (31, 32). Measurement of quenching constants with these sensitizers was not practical because the combination of short sensitizer triplet lifetimes and rather inefficient energy transfer would have required unreasonably high concentrations of stilbene. Anthracene and 3, 4-benzpyrene, which have triplet energies comparable to those of eosin and 9, 10-dibromoanthracene, were selected for measurement of energy transfer to stilbene because of "long" triplet lifetimes in solution. It was quite surprising when it was discovered that the quenching constants with anthracene and 3, 4-benzpyrene predict photostationary state compositions of 69 and 57% cis-stilbene, respectively. At first it was suspected that impurities in trans-stilbene may have effected the unexpectedly high quenching constants with trans-stilbene. This process now seems unlikely because, within experimental error, the same effective quenching constant was measured with anthracene and 4 samples of trans-stilbene purified independently of each other by different means. Another possibility is that anthracene and 3, 4-benzpyrene triplets were quenched by trans-stilbene in a manner that did not effect isomerization of the latter. On the other hand, eosin and 9, 10-dibromoanthracene are distinguished from other sensitizers in the study of the photosensitized isomerization of stilbene in that they have bromine substituents. More recently, Valentine (51) used p-bromobenzophenone as a sensitizer and found a photostationary composition of 95% trans-stilbene despite the fact that this sensitizer has a triplet energy of 68. 4 kcal. /mole (53) in the "high energy" region. It is now surmised that these bromine substituted sensitizers effect stilbene isomerization principally by a process that may involve catalysis by hydrobromic acid or bromine atoms instead of triplet energy transfer. As a first step in resolving this problem, photostationary state measurements should be made with anthracene and 3, 4-benzpyrene.

Figure 9 is a plot of the average rate constant values for each sensitizer in Table 17 against the sensitizer triplet energies. The logarithmic scale is used on the ordinate for convenience. Because of the distributions of the two sets of points, it seemed appropriate to draw smooth curves through them. The deviations with triphenylene, phenanthrene, and benzil may be caused by the difficulties with these sensitizers that are discussed above.

With sensitizers having triplet energies more than 3-5 kcal./mole above the triplet energies of the individual stilbene isomers, the rates of energy transfer occur at what is believed to be a diffusion controlled rate. The actual rate constants are in the range 3-8 x 10^9M.$^{-1}$sec.$^{-1}$ and are in good agreement with those measured by Sandros and Bäckström (14, 18) and also by Porter and Wilkinson (15) for reactions presumed to be diffusion controlled in benzene. Since the encounter rates from bulk diffusion coefficients in benzene solution at 20°C are calculated to be 1 x 10^{10}M.$^{-1}$sec.$^{-1}$ or slightly greater (17, 54), it may be that energy transfer to stilbene from the "high energy" sensitizers does not actually occur on every encounter. Noyes (55), however, after finding a similar discrepancy in rates of recombination of iodine atoms, concluded that the model for calculation may be in error. He reasoned that the bulk diffusion constant might not be a valid measure of the diffusion rate of a solute molecule in the vicinity of another solute molecule.

With reference to the horizontal axis of Figure 9, the efficiency of energy transfer to each stilbene isomer begins to drop

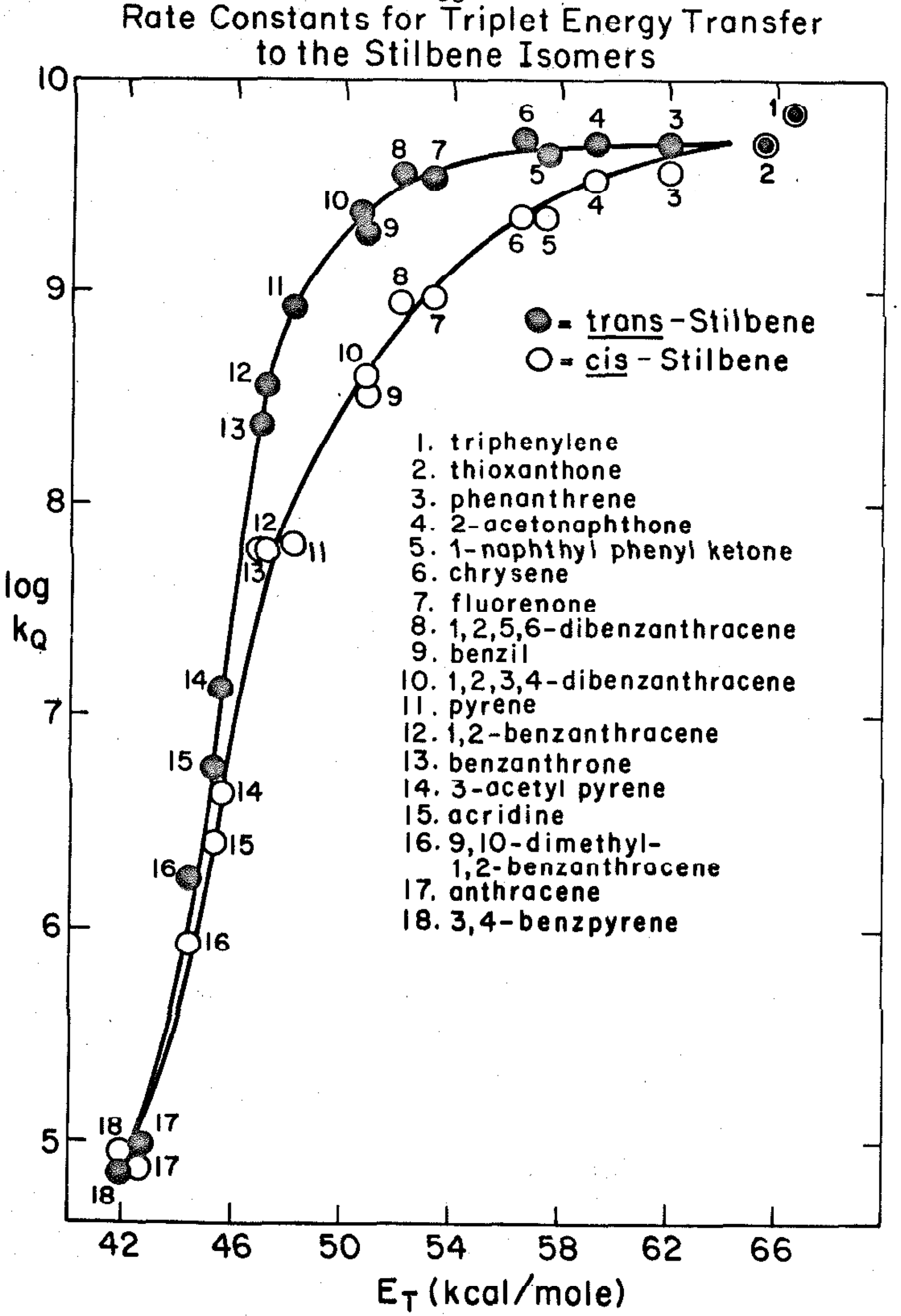
Rate Constants for Triplet Energy Transfer
to the Stilbene Isomers
log
k_Q
10
9
8
7
6
5
42
46
50
54
58
62
66
E_T (kcal/mole)
● = trans-Stilbene
○ = cis-Stilbene
1. triphenylene
2. thioxanthone
3. phenanthrene
4. 2-acetonaphthone
5. 1-naphthyl phenyl ketone
6. chrysene
7. fluorenone
8. 1,2,5,6-dibenzanthracene
9. benzil
10. 1,2,3,4-dibenzanthracene
11. pyrene
12. 1,2-benzanthracene
13. benzanthrone
14. 3-acetyl pyrene
15. acridine
16. 9,10-dimethyl-1,2-benzanthracene
17. anthracene
18. 3,4-benzpyrene
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

Figure 9

approximately 3-5 kcal./mole above the triplet energies of the respective isomers. This drop continues in smooth progression down to the lowest energy sensitizer employed. There is a marked difference in the relative rates of decrease with the two isomers. A separation between the rates of transfer to cis- and trans-stilbene begins at 62 kcal./mole on the abscisa, reaches a maximum near 48 kcal./mole, and vanishes again at 42 kcal./mole. That triplet energy transfer to cis-stilbene can effectively compete with transfer to trans-stilbene in the "low energy" region despite the requirement of an extra 7 kcal./mole excitation energy seems to demand the hypotheses of non-vertical excitation of cis-stilbene. Since the ground state of cis-stilbene lies 6 kcal./mole higher than that of trans-stilbene (37), excitation of the cis isomer to the transoid or phantom triplet should be exothermic with sensitizers of triplet energy greater than 44 kcal./mole. The rate of non-vertical energy transfer to cis-stilbene is obviously less than diffusion controlled, but is considerably greater than what would have been expected for classical energy transfer from sensitizers having energies less than 57 kcal./mole.

A comparison of the trans-stilbene curve of Figure 9 with a similar plot of Sandros' data for energy transfer from a number of sensitizers to biacetyl (18) is given in Figure 10. Except for a shift of several kcal./mole along the horizontal axis and a small difference in the "high energy" region, the two curves are almost superimposable. The corresponding curve for cis-stilbene, by contrast, has a lesser slope in the region below its spectroscopic triplet state. There has been no indication of non-vertical excitation in Sandros' system and, from this comparison, it would also not appear to make a significant contribution to the excitation of trans-stilbene. This

A Comparison of Rate Constants for Triplet Energy Transfer to Biacetyl and trans-Stilbene

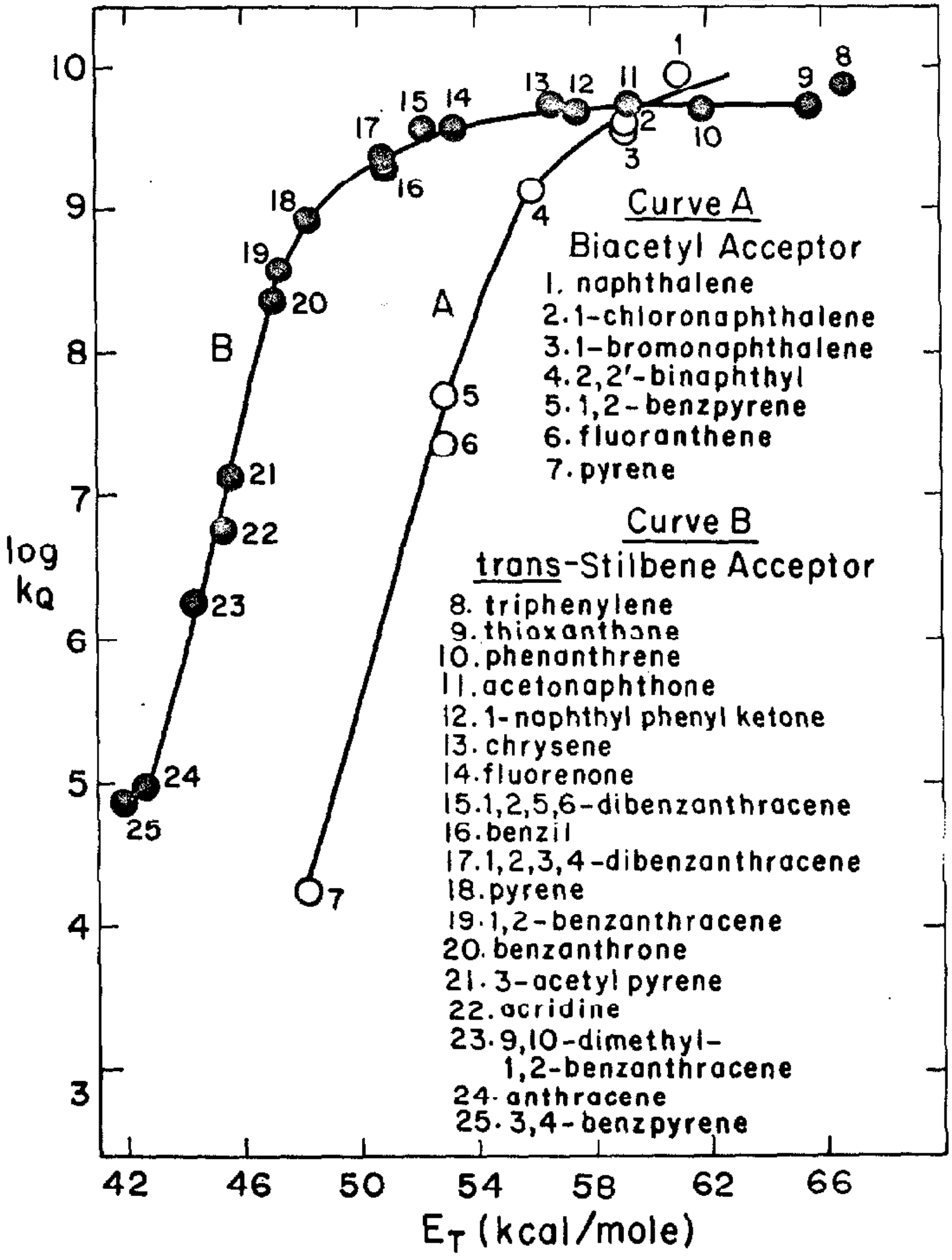

Figure 10

conclusion is compatible with nearly isoenergetic transoid and phantom triplets in stilbene. Because there was extensive reversible energy transfer in Sandros' system but not in the experiments with trans-stilbene described here, it may be surmised that rate constants for energy transfer are independent of contributions to the reverse process.

One of the more striking features of Figure 9 is the lack of structure in the two curves. This behavior was, of course, expected by analogy with the work of Sandros and Bäckström (14, 18), but leaves unexplained the structure in Figure 4, whose appearance had led to the hypothesis that the efficiency of energy exchange between sensitizer and acceptor is sensitive to vibronic factors when their excitation energies are close to the resonance condition (31, 32). The untenability of this interpretation is now demonstrated by the results of the kinetic investigations presented here as well as other recent data by Valentine (51) and Howell (56).

Because of a maximum in Figure 4 associated with pyrene and 1, 2-benzanthracene, it was proposed that energy transfer from these two sensitizers to trans-stilbene was diffusion controlled (31,32). As is readily evident from Table 17 and Figure 9, however, the rates of energy transfer from these two sensitizers to trans-stilbene are less than diffusion controlled by a factor of 10. There would no longer appear to be any justification for assuming that the trans triplet has an energy of 48 kcal. /mole rather than the previously measured value of 50 kcal. /mole.

It now appears that much of the structure in Figure 4 was the result of several unfortunate choices of sensitizer combined with a fortuitous set of circumstances. The point for pyrene was plotted incorrectly and, as is explained in the Appendix, the triplet energy value of benzil in Figure 4 is believed to be in error. Scrutiny of the plot in question reveals that the minima are determined by quinone sensitizers. Additional hydrocarbon sensitizers near the quinones in triplet energy gave photostationary state measurements very different from those of the quinones (51, 56). Both 1, 4-naphthoquinone and p-benzoquinone were shown to form ground-state charge-transfer complexes with stilbene (31, 32), and it is conjectured that this may have influenced the nature of the triplet energy transfer. Unfortunately, measurement of rates of energy transfer with these two quinone sensitizers was not possible because they showed no detectable triplet-triplet absorption. As expected from the appearance of Figure 9, a new plot of photostationary compositions vs. sensitizer triplet energies in Figure 11 has but one large maximum, although there are numerous individual deviations from the curve. Figure 11 includes presently known values for measured and predicted photostationary states with the exception of those corresponding to 1, 4-naphthoquinone, p-benzoquinone, and bromine-containing sensitizers.

The measurement of rates of triplet energy transfer from a variety of photosensitizers to cis- and trans-1, 2-diphenylpropene also has been accomplished and the results are summarized in Table 19. This study was similar in many respects to that with stilbene.

With sensitizers having triplet excitation energies greater than 53 kcal. /mole, measurement of rates of energy transfer to diphenylpropene was performed only with mixtures having photostationary compositions. In the range of sensitizer energies between 48 and 53 kcal. /mole, quenching constants were measured with pure isomers and again at the photostationary state. Those solutions with sensitizers of triplet energy below 48 kcal. /mole were not brought to the photostationary state.

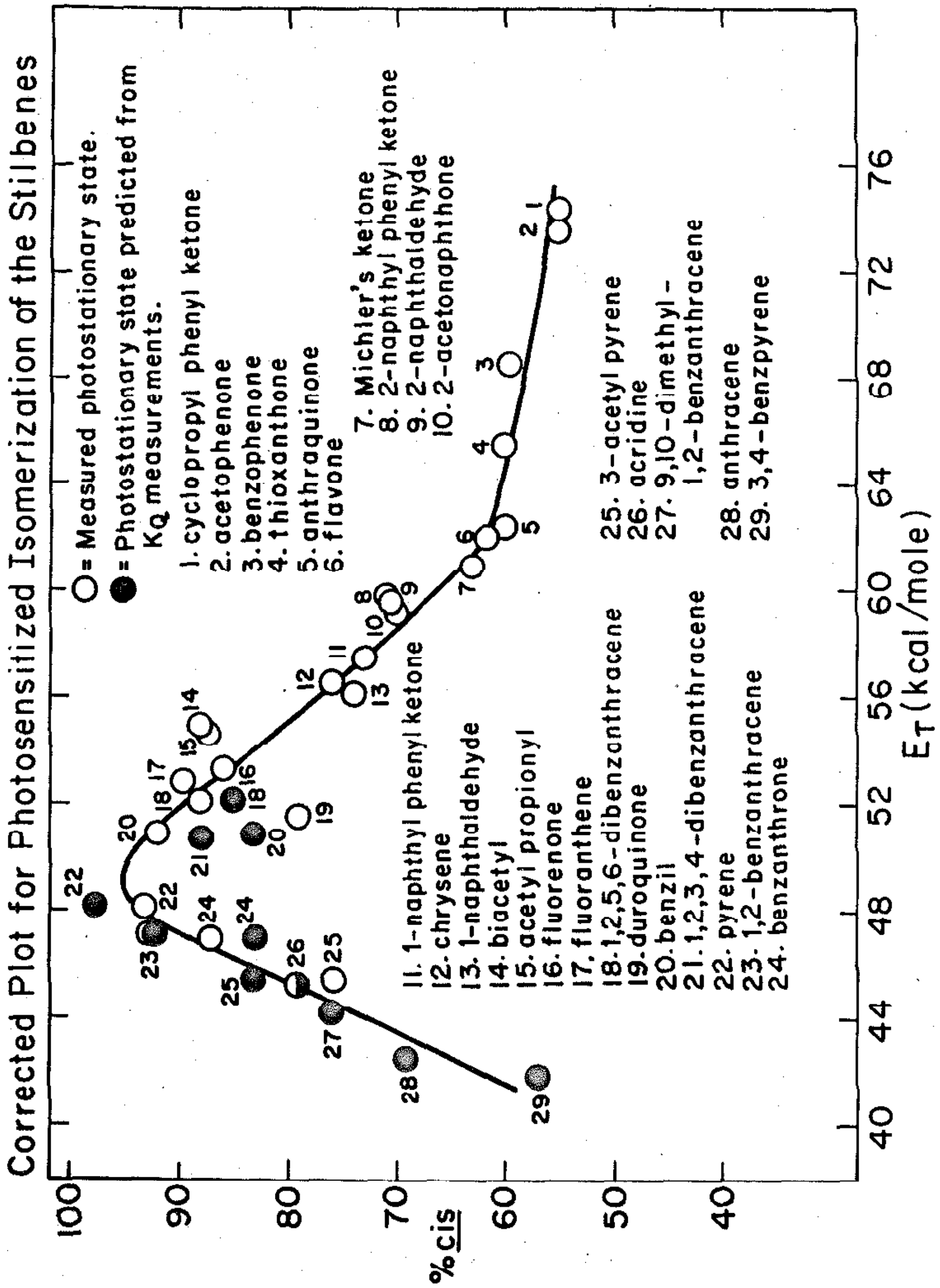
Corrected Plot for Photosensitized Isomerization of the Stilbenes
○ = Measured photostationary state.
● = Photostationary state predicted from K_Q measurements.
1. cyclopropyl phenyl ketone
2. acetophenone
3. benzophenone
4. thioxanthone
5. anthraquinone
6. flavone
7. Michler's ketone
8. 2-naphthyl phenyl ketone
9. 2-naphthaldehyde
10. 2-acetonaphthone
11. 1-naphthyl phenyl ketone
12. chrysene
13. 1-naphthaldehyde
14. biacetyl
15. acetyl propionyl
16. fluorenone
17. fluoranthene
18. 1,2,5,6-dibenzanthracene
19. duroquinone
20. benzil
21. 1,2,3,4-dibenzanthracene
22. pyrene
23. 1,2-benzanthracene
24. benzanthrone
25. 3-acetyl pyrene
26. acridine
27. 9,10-dimethyl-1,2-benzanthracene
28. anthracene
29. 3,4-benzpyrene
% cis
100
90
80
70
60
50
40
E_T (kcal/mole)
40
44
48
52
56
60
64
68
72
76
1
2
3
4
5
6
7
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Figure 11

TABLE 19

Rate Constants for Triplet Energy Transfer from Photosensitizers to cis- and trans-1, 2-Diphenylpropene

Sensitizer and Triplet Energy[a] (kcal/mole) Concentration (M.)	Diphenylpropene Concentration (M.)	Initial % cis	Filter Solution	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	(k_Q)cis (M^{-1}sec^{-1})	(k_Q)trans (M^{-1}sec^{-1})	Basis of Calculation[b]
triphenylene 66.6									
4.0×10^{-5}	-	-	-	4280	$7.4 \pm .8 \times 10^{3}$	$5.2 \pm .6 \times 10^{4}$	-	-	-
4.0×10^{-5}	1.0×10^{-5}	100	-	4280	$4.7 \pm .3 \times 10^{4}$	$8.5 \pm 3.4 \times 10^{4}$	4.0×10^{9}	4.0×10^{9}	PSS
4.0×10^{-5}	5.0×10^{-6}	0	-	4280	$3.1 \pm .5 \times 10^{4}$	$4.8 \pm 2.6 \times 10^{4}$	4.8×10^{9}	4.8×10^{9}	PSS
4.0×10^{-5}	-	-	-	4358	$1.9 \pm .2 \times 10^{3}$	$3.3 \pm .1 \times 10^{4}$	-	-	-
4.0×10^{-5}	5.1×10^{-6}	100	-	4358	$3.0 \pm .1 \times 10^{4}$	$2.1 \pm .4 \times 10^{4}$	5.5×10^{9}	5.5×10^{9}	PSS
4.0×10^{-5}	5.1×10^{-6}	0	-	4358	$3.0 \pm .1 \times 10^{4}$	$2.0 \pm .2 \times 10^{4}$	5.5×10^{9}	5.5×10^{9}	PSS
thioxanthone 65.5									
6.0×10^{-5}	-	-	#2	5770	$1.1 \pm .1 \times 10^{4}$	$3.6 \pm .1 \times 10^{4}$	-	-	-
6.0×10^{-5}	5.1×10^{-6}	0	#2	5770	$3.4 \pm .2 \times 10^{4}$	$2.3 \pm .3 \times 10^{9}$	4.5×10^{9}	4.5×10^{9}	PSS
2-acetonaphthone 59.3									
2.0×10^{-5}	-	-	-	4300	$1.2 \pm .2 \times 10^{3}$	$2.7 \pm .1 \times 10^{4}$	-	-	-
4.0×10^{-5}	1.2×10^{-5}	100	#1	4300	$2.2 \pm .4 \times 10^{4}$	c.	1.3×10^{9}	2.8×10^{9}	PSS
4.0×10^{-5}	6.0×10^{-6}	0	#1	4300	$1.1 \pm .2 \times 10^{4}$	c.	1.3×10^{9}	2.7×10^{9}	PSS
4.0×10^{-5}	-	-	-	4300	$3.0 \pm .2 \times 10^{3}$	$3.1 \pm .1 \times 10^{4}$	-	-	-
4.0×10^{-5}	1.0×10^{-5}	100	#1	4300	$1.9 \pm .1 \times 10^{4}$	$3.5 \pm 1.1 \times 10^{4}$	1.2×10^{9}	2.6×10^{9}	PSS
4.0×10^{-5}	5.0×10^{-6}	0	#1	4300	$9.4 \pm 1.0 \times 10^{3}$	$3.9 \pm .8 \times 10^{4}$	9.7×10^{8}	2.1×10^{9}	PSS
1-naphthyl phenyl ketone 57.5									
4.0×10^{-5}	-	-	-	4358	$1.1 \pm .5 \times 10^{3}$	$6.2 \pm .2 \times 10^{4}$	-	-	-
4.0×10^{-5}	2.5×10^{-5}	100	#1	4358	$2.1 \pm .3 \times 10^{4}$	$6.6 \pm 2.8 \times 10^{4}$	5.9×10^{8}	1.4×10^{9}	PSS
4.0×10^{-5}	1.0×10^{-5}	0	#1	4358	$1.4 \pm .3 \times 10^{4}$	$3.4 \pm 1.5 \times 10^{4}$	9.6×10^{8}	2.3×10^{9}	PSS
4.0×10^{-5}	-	-	-	4358	$1.6 \pm .2 \times 10^{3}$	$6.1 \pm .2 \times 10^{4}$	-	-	-
4.0×10^{-5}	2.5×10^{-5}	100	-	4358	$2.4 \pm .2 \times 10^{4}$	$6.5 \pm .5 \times 10^{4}$	6.5×10^{8}	1.5×10^{9}	PSS
4.0×10^{-5}	1.0×10^{-5}	0	-	4358	1.4×10^{4}	$4.4 \pm 2.2 \times 10^{4}$	8.9×10^{8}	2.1×10^{9}	PSS

TABLE 19 cont'd

Sensitizer and Triplet Energy[a] (kcal/mole) Concentration (M.)		Diphenylpropene Concentration (M.)	Initial % cis	Filter Solution	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	(k_Q)cis ($M^{-1}sec^{-1}$)	($M^{-1}sec^{-1}$)	Basis of Calculation[b].
1-naphthyl phenyl ketone (cont'd)										
4.0×10^{-5}	57.5	-	-	-	4358	$2.2 \pm .6 \times 10^3$	$4.2 \pm .2 \times 10^4$	-	-	-
4.0×10^{-5}		2.6×10^{-5}	100	-	4358	2.1×10^4	3.9×10^4	7.3×10^8	-	PI
4.0×10^{-5}		2.6×10^{-5}	100	-	4358	$2.8 \pm .2 \times 10^4$	$3.0 \pm .3 \times 10^4$	7.4×10^8	1.9×10^9	PSS
4.0×10^{-5}		1.0×10^{-5}	0	-	4358	$1.5 \pm .1 \times 10^4$	$3.8 \pm .2 \times 10^4$	9.6×10^8	2.3×10^9	PSS
fluorenone	53.3									
4.0×10^{-5}		-	-	-	4400	$4.1 \pm .3 \times 10^3$	$6.5 \pm .3 \times 10^4$	-	-	-
4.0×10^{-5}		2.5×10^{-5}	100	#1	4400	$1.4 \pm .1 \times 10^4$	$6.4 \pm .7 \times 10^4$	2.5×10^8	1.7×10^9	PSS
4.0×10^{-5}		1.0×10^{-5}	0	#1	4400	$9.2 \pm .4 \times 10^3$	$7.0 \pm .4 \times 10^4$	3.1×10^8	2.1×10^9	PSS
4.0×10^{-5}		-	-	-	4358	$3.1 \pm .1 \times 10^3$	$3.8 \pm .1 \times 10^4$	-	-	-
4.0×10^{-5}		2.5×10^{-5}	100	#1	4358	$1.0 \pm .1 \times 10^4$	$3.7 \pm .7 \times 10^4$	1.7×10^8	1.2×10^9	PSS
4.0×10^{-5}		1.0×10^{-5}	0	#1	4358	$6.3 \pm .6 \times 10^3$	$3.1 \pm .3 \times 10^4$	2.0×10^8	1.4×10^9	PSS
2.0×10^{-4}		-	-	#3	4358	$1.5 \pm .3 \times 10^3$	$3.6 \pm .2 \times 10^4$	-	-	-
2.0×10^{-4}		2.6×10^{-5}	100	#3	4358	$3.4 \pm .1 \times 10^3$	2.7×10^4	2.7×10^8	-	PI
2.0×10^{-4}		2.6×10^{-5}	100	#3	4358	$11.5 \pm .4 \times 10^3$	$3.6 \pm .1 \times 10^4$	2.4×10^8	1.6×10^9	PSS
1,2,5,6-dibenzanthracene	52.2									
4.0×10^{-5}		-	-	-	5460	$3.2 \pm .2 \times 10^2$	$1.9 \pm .1 \times 10^4$	-	-	-
4.0×10^{-5}		5.0×10^{-5}	100	#2	5460	1.3×10^4	$1.5 \pm .1 \times 10^4$	1.5×10^8	7.8×10^8	PSS
4.0×10^{-5}		2.5×10^{-5}	0	#2	5460	$7.0 \pm .1 \times 10^3$	$1.6 \pm .1 \times 10^4$	1.6×10^8	8.3×10^8	PSS
4.0×10^{-5}		-	-	#3	5460	$7.3 \pm 1.4 \times 10^2$	$1.2 \pm .1 \times 10^4$	-	-	-
4.0×10^{-5}		5.1×10^{-5}	100	#3	5460	3.1×10^3	1.2×10^4	1.5×10^8	-	PI
4.0×10^{-5}		2.5×10^{-5}	0	#3	5460	1.9×10^4	1.2×10^4	-	7.3×10^8	PI
4.0×10^{-5}		5.1×10^{-5}	100	#3	5460	$1.2 \pm .1 \times 10^4$	$1.2 \pm .1 \times 10^4$	1.3×10^8	7.0×10^8	PSS
4.0×10^{-5}		2.5×10^{-5}	0	#3	5460	$7.1 \pm .3 \times 10^4$	$1.2 \pm .1 \times 10^4$	1.6×10^8	8.2×10^8	PSS
duroquinone	51.6									
1.0×10^{-4}		-	-	-	4358	$1.9 \pm .2 \times 10^4$	$3.9 \pm .2 \times 10^4$	-	-	-
1.0×10^{-4}		1.0×10^{-4}	100	-	4358	$3.6 \pm .7 \times 10^4$	c.	1.0×10^8	7.7×10^8	PSS
1.0×10^{-4}		1.0×10^{-4}	0	-	4358	$3.5 \pm .3 \times 10^4$	$5.7 \pm 2.7 \times 10^4$	9.7×10^7	7.3×10^8	PSS

TABLE 19 cont'd

Sensitizer and Triplet Energy^{a}(kcal/mole)									
Concentration (M.)		Diphenylpropene Concentration (M.)	Initial % cis	Filter Solution	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	(k_Q)cis ($M^{-1}sec^{-1}$)	(k_Q)trans ($M^{-1}sec^{-1}$)	Basis of Calculation$^{b.}$
benzil	50.9									
2.5×10^{-4}		-	-	#3	4865	$1.8 \pm .1 \times 10^{4}$	$1.2 \pm .1 \times 10^{4}$	-	-	-
2.5×10^{-4}		1.0×10^{-4}	100	#3	4865	2.4×10^{4}	6.5×10^{3}	5.8×10^{7}	-	PI
2.5×10^{-4}		5.1×10^{-5}	0	#3	4865	2.8×10^{4}	5.2×10^{3}	-	2.0×10^{8}	PI
2.5×10^{-4}		1.0×10^{-4}	100	#3	4865	$2.7 \pm .1 \times 10^{4}$	$7.6 \pm 3.9 \times 10^{3}$	5.9×10^{7}	2.2×10^{8}	PSS
2.5×10^{-4}		5.1×10^{-5}	0	#3	4865	$2.2 \pm .1 \times 10^{4}$	$1.3 \pm .1 \times 10^{4}$	5.0×10^{7}	1.9×10^{8}	PSS
1, 2, 3, 4-dibenzanthracene										
1.0×10^{-4}	50.8	-	-	#2	4358	$7.8 \pm 1.3 \times 10^{2}$	$1.7 \pm .1 \times 10^{4}$	-	-	-
1.0×10^{-4}		1.5×10^{-4}	100	#2	4358	9.4×10^{3}	1.7×10^{4}	5.6×10^{7}	-	PI
1.0×10^{-4}		5.1×10^{-5}	0	#2	4358	1.7×10^{4}	2.2×10^{4}	-	3.2×10^{8}	PI
1.0×10^{-4}		1.5×10^{-4}	100	#2	4358	$1.3 \pm .1 \times 10^{4}$	$1.8 \pm .1 \times 10^{4}$	4.8×10^{7}	3.2×10^{8}	PSS
1.0×10^{-4}		5.1×10^{-5}	0	#2	4358	$4.8 \pm .4 \times 10^{4}$	$2.0 \pm .2 \times 10^{4}$	4.9×10^{7}	3.2×10^{8}	PSS
pyrene	48.2									
4.0×10^{-5}		-	-	-	4160	$1.4 \pm .4 \times 10^{3}$	$1.5 \pm .2 \times 10^{4}$	-	-	-
4.0×10^{-5}		1.0×10^{-3}	100	#1	4160	8.4×10^{3}	2.0×10^{3}	7.0×10^{6}	-	PI
4.0×10^{-5}		5.0×10^{-4}	0	#1	4160	1.9×10^{4}	c.	-	3.8×10^{7}	PI
4.0×10^{-5}		1.0×10^{-3}	100	#1	4160	$1.3 \pm .1 \times 10^{4}$	c.	8.0×10^{6}	3.0×10^{7}	PSS
4.0×10^{-5}		1.0×10^{-3}	100	#2	4160	$1.8 \pm .2 \times 10^{4}$	c.	1.1×10^{7}	4.3×10^{7}	PSS
4.0×10^{-5}		5.0×10^{-4}	0	#1	4160	$1.2 \pm .1 \times 10^{4}$	$1.5 \pm .5 \times 10^{4}$	1.5×10^{7}	5.6×10^{7}	PSS
4.0×10^{-5}		5.0×10^{-4}	0	#2	4160	$10.5 \pm .6 \times 10^{3}$	$6.4 \pm 3.3 \times 10^{3}$	1.2×10^{7}	4.6×10^{7}	PSS
4.0×10^{-5}		-	-	-	4160	$1.5 \pm .3 \times 10^{3}$	$1.5 \pm .1 \times 10^{4}$	-	-	-
4.0×10^{-5}		1.0×10^{-3}	100	#2	4160	1.1×10^{4}	9.9×10^{3}	9.2×10^{6}	-	PI
4.0×10^{-5}		5.0×10^{-4}	0	#1	4160	$1.5 \pm .1 \times 10^{4}$	$1.5 \pm 1.1 \times 10^{4}$	-	2.8×10^{7}	PI
1, 2-benzanthracene										
4.0×10^{-5}	47.2	-	-	-	4850	$9.7 \pm 1.2 \times 10^{2}$	$1.4 \pm .1 \times 10^{4}$	-	-	-
4.0×10^{-5}		3.0×10^{-3}	100	#2	4850	$2.1 \pm .1 \times 10^{4}$	$1.4 \pm .3 \times 10^{4}$	6.6×10^{6}	-	PI
4.0×10^{-5}		1.0×10^{-3}	0	#2	4850	$1.8 \pm .1 \times 10^{4}$	$1.6 \pm .4 \times 10^{4}$	-	1.7×10^{7}	PI

TABLE 19 cont'd

Sensitizer and Triplet Energy^a(kcal/mole) Concentration (M.)	Diphenylpropene Concentration (M.)	Initial % cis	Filter Solution	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	(k_Q)cis ($M^{-1}sec^{-1}$)	(k_Q)trans ($M^{-1}sec^{-1}$)	Basis of Calculation^b.
benzanthrone 47.0									
4.0×10^{-5}	-	-	-	4493	$4.5 \pm .2 \times 10^3$	$3.4 \pm .1 \times 10^4$	-	-	-
4.0×10^{-5}	1.0×10^{-3}	100	#2	4493	$6.9 \pm .5 \times 10^3$	$2.9 \pm .3 \times 10^4$	2.4×10^6	-	PI
4.0×10^{-5}	5.0×10^{-4}	0	#2	4493	$10.0 \pm .2 \times 10^3$	$3.3 \pm .1 \times 10^4$	-	1.1×10^7	PI
4.0×10^{-5}	-	-	-	4358	$1.1 \pm .2 \times 10^3$	$3.4 \pm .2 \times 10^4$	-	-	-
4.0×10^{-5}	1.0×10^{-3}	100	#2	4358	$7.3 \pm .2 \times 10^3$	$3.3 \pm .1 \times 10^4$	6.2×10^6	-	PI
4.0×10^{-5}	5.0×10^{-4}	0	#2	4358	$6.0 \pm .1 \times 10^3$	$3.1 \pm .2 \times 10^4$	-	9.8×10^6	PI
3-acetyl pyrene 45.5									
4.0×10^{-5}	-	-	-	4358	$8.9 \pm .2 \times 10^2$	1.9×10^4	-	-	-
4.0×10^{-5}	6.0×10^{-3}	100	#2	4358	$4.8 \pm .2 \times 10^3$	$1.7 \pm .1 \times 10^4$	6.5×10^5	-	PI
4.0×10^{-5}	3.0×10^{-3}	0	#2	4358	$5.0 \pm .2 \times 10^3$	$1.9 \pm .1 \times 10^4$	-	1.4×10^6	PI
acridine 45.3									
4.0×10^{-5}	-	-	-	4358	$1.9 \pm .1 \times 10^3$	$1.1 \pm .1 \times 10^4$	-	-	-
4.0×10^{-5}	6.0×10^{-3}	100	#2	4358	$6.0 \pm .3 \times 10^3$	$1.6 \pm .2 \times 10^4$	6.8×10^5	-	PI
4.0×10^{-5}	3.0×10^{-3}	0	#2	4358	$3.8 \pm .2 \times 10^3$	$1.1 \pm .1 \times 10^4$	-	6.3×10^5	PI
4.0×10^{-5}	-	-	-	4358	$2.3 \pm .2 \times 10^3$	$1.2 \pm .1 \times 10^4$	-	-	-
4.0×10^{-5}	6.0×10^{-3}	100	#1	4358	$6.1 \pm .1 \times 10^3$	1.4×10^4	6.3×10^5	-	PI
4.0×10^{-5}	3.0×10^{-3}	0	#1	4358	$4.3 \pm .3 \times 10^3$	$1.3 \pm .2 \times 10^4$	-	6.7×10^5	PI
9, 10-dimethyl-1, 2-benzanthracene 44.3									
4.0×10^{-5}	-	-	-	4680	$9.1 \pm 1.4 \times 10^2$	$1.3 \pm .1 \times 10^4$	-	-	-
4.0×10^{-5}	1.2×10^{-2}	100	#1	4680	$2.3 \pm .1 \times 10^3$	$1.4 \pm .1 \times 10^4$	1.2×10^5	-	PI
4.0×10^{-5}	8.0×10^{-3}	0	#1	4680	$2.2 \pm .3 \times 10^3$	$1.4 \pm .1 \times 10^4$	-	1.6×10^5	PI
4.0×10^{-5}	-	-	#3	4678	$4.2 \pm .6 \times 10^2$	1.2×10^4	-	-	-
4.0×10^{-5}	1.2×10^{-2}	100	#3	4678	$1.7 \pm .1 \times 10^3$	$1.2 \pm .1 \times 10^4$	1.0×10^5		PI
4.0×10^{-5}	8.0×10^{-3}	0	#3	4678	$2.2 \pm .1 \times 10^3$	1.1×10^4		2.2×10^5	PI

TABLE 19 cont'd

Sensitizer and Triplet Energy[a] (kcal/mole) Concentration (M.)	Diphenylpropene Concentration (M.)	Initial % cis	Filter Solution	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)	(k_Q)cis ($M^{-1}sec^{-1}$)	(k_Q)trans ($M^{-1}sec^{-1}$)	Basis of Calculation[b]
anthracene 42.6									
4.0×10^{-5}	-	-	-	4358	$3.0 \pm .4 \times 10^{2}$	$9.7 \pm .4 \times 10^{3}$	-	-	-
4.0×10^{-5}	3.0×10^{-2}	100	#2	4358	$2.0 \pm .1 \times 10^{3}$	$9.3 \pm .1 \times 10^{3}$	5.7×10^{4}	-	PI
4.0×10^{-5}	3.2×10^{-2}	0	#2	4358	$1.3 \pm .1 \times 10^{3}$	$9.3 \pm .7 \times 10^{3}$	-	3.0×10^{3}	PI
4.0×10^{-5}	-	-	#3	4358	$6.7 \pm .7 \times 10^{2}$	$8.1 \pm .3 \times 10^{3}$	-	-	-
4.0×10^{-5}	3.0×10^{-2}	100	#3	4358	$1.5 \pm .1 \times 10^{3}$	$8.0 \pm .4 \times 10^{3}$	2.6×10^{4}	-	PI
4.0×10^{-5}	3.0×10^{-2}	0	#3	4358	$1.5 \pm .1 \times 10^{3}$	$7.8 \pm .3 \times 10^{3}$	-	2.8×10^{4}	PI

a. Reference to the source of triplet energies listed here is given in the Appendix.

b. The symbol PSS is used to denote that in evaluating the quenching constants it was assumed that the photostationary state had been reached. If it was assumed that no isomerization had taken place, then the symbol PI (pure isomer) is used.

c. The measured β value is either negative or shows very poor precision.

As discussed below, the same basic mechanism for photosensitized isomerization applies to the stilbene and 1, 2-diphenylpropene systems. Complications involving self-quenching and small variations in "high energy" photostationary compositions have not been detected in the latter system. The triplet intermediate of diphenylpropene is believed to give a cis to trans ratio of 1.2 in the process of decay to the ground state. Included in Table 20 are the diphenylpropene photostationary states predicted from the individually measured quenching constants. Once again, the mechanism of photosensitized isomerization is substantiated by the agreement between the measured and predicted photostationary compositions.

Filter solutions to prevent direct absorption of light by diphenylpropene were not employed with triphenylene and duroquinone. Quenching constants with 1-naphthyl phenyl ketone were measured both with and without filter solutions and, within experimental error, there was no difference between the two sets of numbers. In no experiment was any absorption observed other than triplet-triplet absorption of the sensitizer, nor was there any indication that quenchers were produced upon direct absorption of light by diphenylpropene.

Many solutions believed to be at the photostationary state were analyzed by vapor phase chromatography after concentration under a stream of nitrogen, and the results are summarized in Table 20. For those solutions with triphenylene, thioxanthone, and duroquinone as sensitizers, the analysis showed some side product formation. One such product in the benzil solution interfered with analysis for trans-1, 2-diphenylpropene and a correction had to be applied.

TABLE 20

Comparison of Photostationary State Measurements for 1, 2-Diphenylpropene

Sensitizer	Triplet Energy (kcal. /mole)[a]	Photostationary State[b] (% cis)	Predicted Photostationary State from k_Q's[c] (% cis)	VPC Analysis After Flashing (% cis)
triphenylene	66.6	d.	-	d.
thioxanthone	65.5	-	-	55[e]
2-acetonaphthone	59.3	72	-	52
1-naphthyl phenyl ketone	57.5	74	-	74
fluorenone	53.3	89	-	87
1, 2, 5, 6-dibenzanthracene	52.2	86	87	82
duroquinone	51.6	90	-	84[e]
benzil	50.9	82	81	84[f]
1, 2, 3, 4-dibenzanthracene	50.8	89	88	90
pyrene	48.2	82	83	73
1, 2-benzanthracene	47.2	80	76	-
benzanthrone	47.0	81	76	-
3-acetyl pyrene	45.5	74	72	-
acridine	45.3	65	55	-

TABLE 20 cont'd

Sensitizer	Triplet Energy (kcal. /mole)[a]	Photostationary State[b] (% cis)	Predicted Photostationary State from k_Q's[c] (% cis)	VPC Analysis After Flashing (% cis)
9, 10-dimethyl-1, 2-benzanthracene	44. 3	-	67	-
anthracene	42. 6	-	48	-

a. Reference to the source of triplet energies listed here is given in the Appendix.

b. The numbers in this column are from references 32 and 53.

c. These photostationary state values were evaluated by assuming that decay from a common triplet state leads to a cis : trans ratio of 1. 2.

d. See text for explanation.

e. Some side products were observed but did not interfere with VPC analysis.

f. Side products interfered with VPC analysis.

Triphenylene also presents special problems with the diphenylpropene system. In photostationary state determinations with this sensitizer, Coyne (53) has found a concentration dependence such that a solution .05 M. in both triphenylene and diphenylpropene gave 40% cis isomer, whereas a solution .05 M. in triphenylene and .001 M. in diphenylpropene gave a cis isomer content of 67%. These values were obtained under conditions where triphenylene absorbed most of the light. Analysis of 3 separate solutions from the flash experiments gave presumed photostationary values of 6, 35, and 59% cis. Although it is recognized that this assumption may be incorrect, the only reasonable interpretation of kinetic results seemed to be that triphenylene transfers triplet energy with equal facility to cis- and trans-1, 2-diphenylpropene.

The photostationary values with the two bromine containing sensitizers, eosin and 9, 10-dibromoanthracene, differ significantly from that predicted by the quenching constants measured with anthracene. Again, it is surmised that with the former two sensitizers the measured photostationary states may have been strongly influenced by the presence of hydrobromic acid or bromine atoms.

In Figure 12 is a plot of the average rate constant values for each sensitizer in Table 19 against the sensitizer triplet energies. Although Figures 9 and 12 are similar in appearance, the set of curves in the latter is shifted to higher energies along the horizontal axis by several kcal./mole. Hammond and co-workers (32) had proposed that the trans isomers of stilbene and 1, 2-diphenylpropene have approximately the same triplet energies (48 kcal./mole) because interpretation of Figures 4 and 5 called for diffusion controlled resonance transfer between the sensitizers pyrene and 1, 2-benzanthracene and the two trans isomers. The inconsistency of this

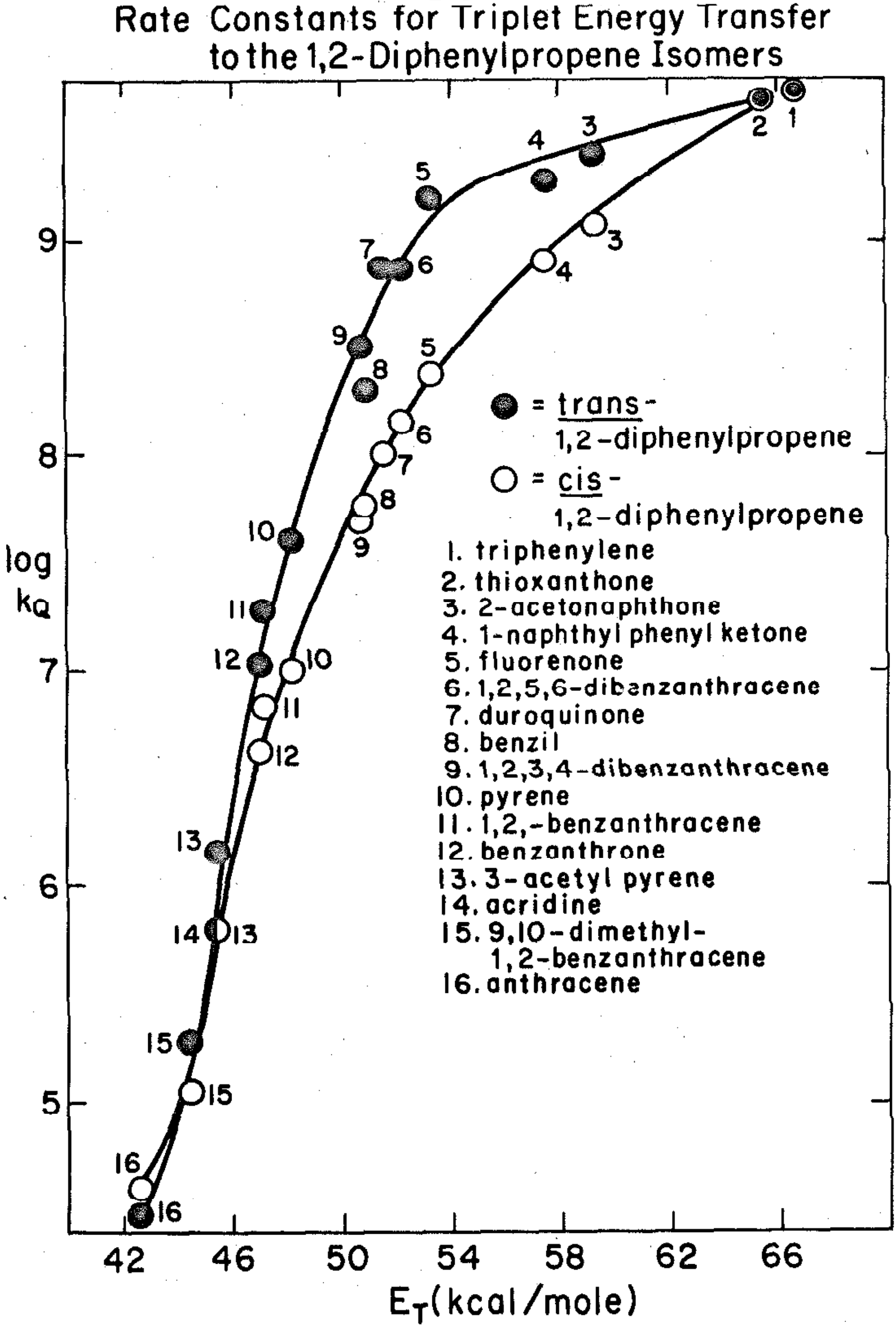

Rate Constants for Triplet Energy Transfer to the 1,2-Diphenylpropene Isomers
log kQ
9
8
7
6
5
42
46
50
54
58
62
66
E_T(kcal/mole)
● = trans-1,2-diphenylpropene
○ = cis-1,2-diphenylpropene
1. triphenylene
2. thioxanthone
3. 2-acetonaphthone
4. 1-naphthyl phenyl ketone
5. fluorenone
6. 1,2,5,6-dibenzanthracene
7. duroquinone
8. benzil
9. 1,2,3,4-dibenzanthracene
10. pyrene
11. 1,2,-benzanthracene
12. benzanthrone
13. 3-acetyl pyrene
14. acridine
15. 9,10-dimethyl-1,2-benzanthracene
16. anthracene
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

Figure 12

interpretation with trans-stilbene is discussed above. That it is also untenable with trans-1, 2-diphenylpropene is demonstrated by rates of energy transfer from pyrene and 1, 2-benzanthracene that are less than diffusion controlled by two orders of magnitude. Application of Sandros' (18) suggestion that the rate constant for energy transfer is 1/2 that of a diffusion controlled rate when donor and acceptor have identical triplet energies leads to a predicted triplet energy of 53-55 kcal. /mole for trans-1, 2-diphenylpropene. This value is consistent with a trans-stilbene triplet energy of 50 kcal. /mole because of the shift in position of several kcal. /mole between the curves of Figures 9 and 12. By similar considerations, the triplet energy of cis-1, 2-diphenylpropene is predicted to lie between 59 and 62 kcal. /mole.

Unless there is a large error in the assigned energy value of the spectroscopic triplet states, non-vertical excitation of cis- and trans-1, 2-diphenylpropene is required because isomerization is effected with sensitizers of triplet energy between 42 and 48 kcal. /mole. Since the ground state of the cis isomer is only 0. 3 kcal. /mole higher than that of trans-1, 2-diphenylpropene (40), excitation of both isomers to a phantom triplet of energy less than either spectroscopic triplet would seem energetically feasible. Such a triplet, if short-lived, would be consistent with the earlier observation of no reversible energy transfer, self-quenching, nor quenching by azulene in the diphenylpropene system (32). By comparison of rate constants for energy transfer to stilbene and diphenylpropene, one might expect the diphenylpropene phantom triplet to have an energy of 44-46 kcal. /mole.

With reference to Figures 9 and 12, the slope of the curve for trans-stilbene is greatest in the regions below the spectroscopic triplet states of each substrate. The lesser slopes of the curves for cis-stilbene and cis- and trans-1, 2-diphenylpropene is believed to be due to the requirement for non-vertical excitation of these substances. That each of the latter 3 curves is unique probably indicates a different contribution of non-vertical excitation in each case.

The role of the diphenylpropene triplet in the isomerization of the parent substrate requires a modification of the mechanism of equations 12-18. The only real change is that the phantom triplet rather than the transoid triplet is taken to be the common intermediate, and this in no way alters the basic kinetic scheme. The phantom triplet replaces the transoid triplet in equations 15-18, the reverse transfer in equation 13 is eliminated, and equations 13a and 16a are added, where p represents the phantom triplet.

$$ {}_{s}T_1 + {}_{t}S_0 \xrightarrow{k_{13a}} {}_{s}S_0 + {}_{p}T_1 \tag{13a} $$

$$ {}_{t}T_1 \xrightarrow{k_{16a}} {}_{p}T_1 \; . \tag{16a} $$

The expression relating the photostationary ratio of cis and trans diphenylpropene differs in only one small detail from equation 20.

$$ \frac{[c]_s}{[t]_s} = \left(\frac{k_{13} + k_{13a}}{k_{14} + k_{15}}\right) \left(\frac{k_{18}}{k_{17}}\right). \tag{45} $$

The quenching constants, (k_Q)cis and (k_Q)trans, are given by $k_{14} + k_{15}$ and $k_{13} + k_{13a}$, respectively.

The "high energy" region of the two curves in Figure 12 is not well defined because there are only two points above 60 kcal./mole, and the corresponding sensitizers, triphenylene and thioxanthone, are subject to special considerations. The fact that neither curve reaches a point of zero slope may be due to the arbitrary way in which the curves were drawn or to lack of data in the "high energy" region. Unfortunately, there seems to be a dearth of sensitizers with triplet energies greater than 60 kcal./mole which also have absorption characteristics and triplet lifetimes desirable in these experiments.

The minimum in Figure 5 is defined by the p-benzoquinone point alone. Benzoquinone is now believed to give photostationary compositions with diphenylpropene and stilbene that are incompatible with energy transfer alone. In recent experiments, Coyne (53) has measured diphenylpropene photostationary states with sensitizers near benzoquinone in triplet energy and obtained values very different from that reported for the quinone sensitizer. In Figure 13 is plotted, with the exception of the points for benzoquinone, eosin, and 9, 10-dibromoanthracene, all measured and predicted photostationary values as a function of triplet energy. Although there are individual variations, the trend in Figure 13 is to one large maximum near 52 kcal./mole.

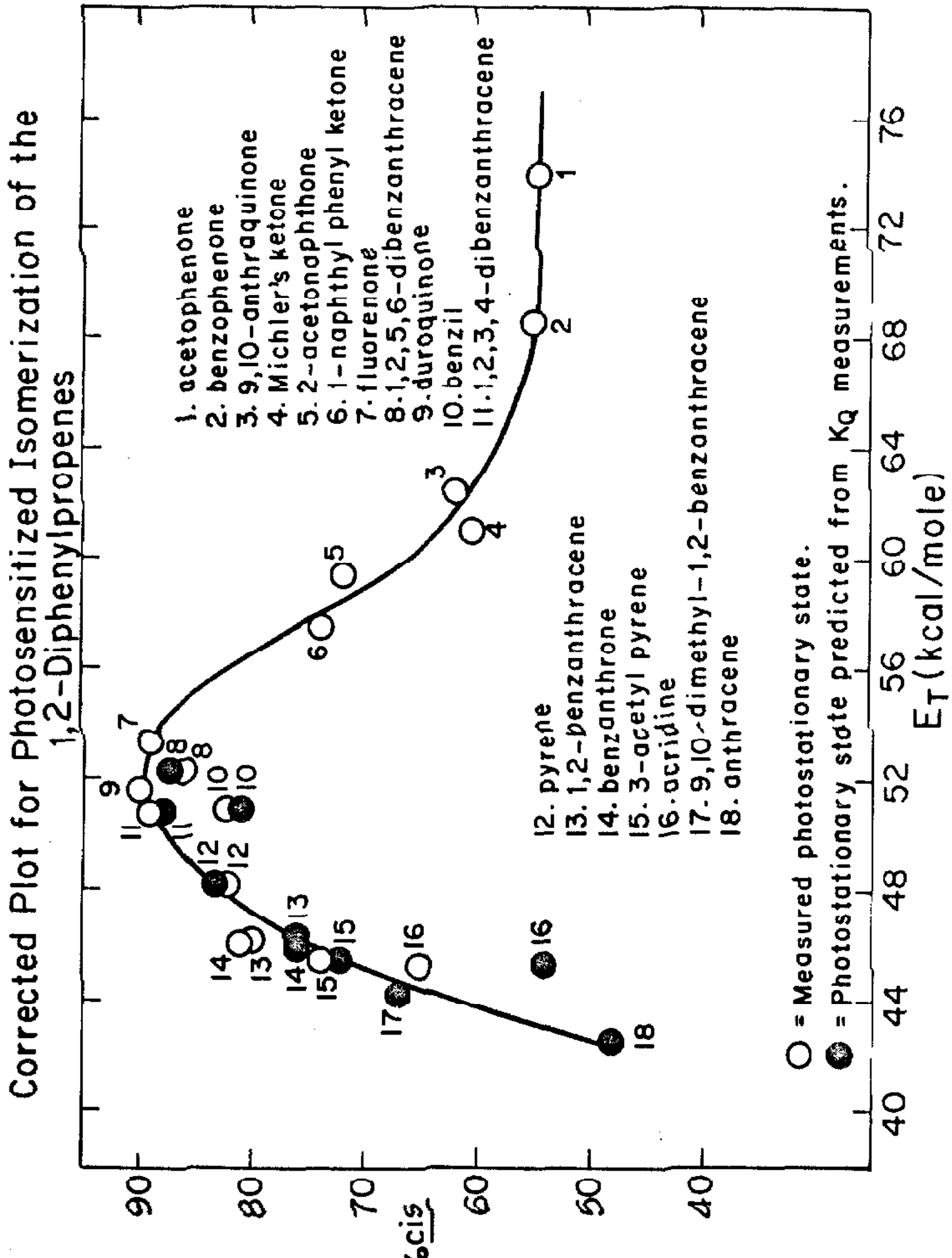
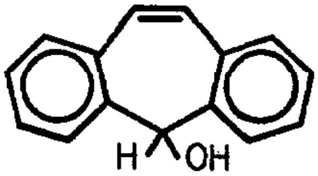

Corrected Plot for Photosensitized Isomerization of the 1,2-Diphenylpropenes
1. acetophenone
2. benzophenone
3. 9,10-anthraquinone
4. Michler's ketone
5. 2-acetonaphthone
6. 1-naphthyl phenyl ketone
7. fluorenone
8. 1,2,5,6-dibenzanthracene
9. duroquinone
10. benzil
11. 1,2,3,4-dibenzanthracene
12. pyrene
13. 1,2-benzanthracene
14. benzanthrone
15. 3-acetyl pyrene
16. acridine
17. 9,10-dimethyl-1,2-benzanthracene
18. anthracene
○ = Measured photostationary state.
● = Photostationary state predicted from K_Q measurements.
%cis
90
80
70
60
50
40
E_T (kcal/mole)
40
44
48
52
56
60
64
68
72
76

Figure 13

Dibenzcycloheptenol as a Rigid Model for cis-Stilbene:

Non-vertical excitation of cis-stilbene is believed to involve rotation about the central bond in proceeding from the cisoid ground state to the transoid or phantom triplet. In a rigid molecule, such rotation would be energetically unfavorable. One way of testing the present interpretation of non-vertical excitation is to compare the rates at which cis-stilbene and dibenzcycloheptenol (5H-dibenzo-(a, d)-cyclohepten-5-ol), selected as a rigid model for cis-stilbene, accept triplet energy from different sensitizers. In the "low energy" region, the rate constants for energy transfer to cis-stilbene are expected to be much larger.

A structural formula for dibenzcycloheptenol is shown below. The ultraviolet absorption spectra of cis-stilbene and its rigid



counterpart in cyclohexane solution closely resemble each other with maxima at 2800 and 2840 Å, respectively; differences in the absorption intensities of the two substances are summarized briefly in Table 21. Although cis-stilbene and dibenzcycloheptenol may well be expected to have nearly equal vertical excitation energies, assignment of the energy of the dibenzcycloheptenol triplet has not been accomplished, because this substance did not phosphoresce (53). After flash excitation of dibenzcycloheptenol in benzene solution, triplet-triplet absorption was observed with a maximum near 4358 Å. The first-order rate constant in the triplet decay of dibenzcycloheptenol is 2.0×10^{-3} sec.$^{-1}$. No triplet-triplet absorption was

TABLE 21

Extinction Coefficients in the Absorption Spectra of cis-Stilbene and Dibenzcycloheptenol[a]

	Extinction Coefficients			
Wave Length (Å)	3200	3000	2800	2475
cis-Stilbene	1.9×10^3	7.2×10^3	1.1×10^4	6.0×10^3
Dibenzcycloheptenol	7.4×10^2	1.0×10^4	1.5×10^4	3.9×10^3

a. Absorption spectra were recorded with cyclohexane solvent.

observed with cis-stilbene, presumably because of rapid deactivation of cisoid triplets proceeding through transoid or phantom triplets to the ground state.

The rate constants for energy transfer from several sensitizers to dibenzcycloheptenol were measured for purposes of comparison with those measured with cis-stilbene. With quenchers having triplet lifetimes as long as that of dibenzcycloheptenol, kinetic measurements of triplet energy transfer are complicated by triplet-triplet absorption in the quencher, depletion of the supply of quencher ground state molecules, and reverse energy transfer from quencher to sensitizer. The first problem was circumvented by selection of sensitizers having strong triplet-triplet absorption in a spectral region where the dibenzcycloheptenol triplet does not absorb. The sensitizers chosen, thioxanthone, chrysene, and 1, 2, 5, 6-dibenzanthracene, have triplet energies of 65.5, 56.6, and 52.2 kcal./mole, respectively, as compared with the cis-stilbene triplet energy of 57 kcal./mole. Kinetic measurements with these sensitizers were monitored at 5790 Å.

A kinetic scheme for reversible energy transfer is given in equations 46-52, where S and Q represent sensitizer and quencher, respectively. The principle difference between this mechanism and that of Sandros (18) is the inclusion of second-order triplet-triplet annihilation.

$$S^* \xrightarrow{k_{1S}} S \tag{46}$$

$$Q^* \xrightarrow{k_{1Q}} Q \tag{47}$$

$$S^* + Q \underset{k_R}{\overset{k_F}{\rightleftharpoons}} S + Q^* \tag{48}$$

$$S^* + S^* \xrightarrow{k_{2S}} S^* + S \tag{49}$$

$$Q^* + Q^* \xrightarrow{k_{2Q}} Q^* + Q \tag{50}$$

$$S^* + Q^* \xrightarrow{k_{2SQ}} S^* + Q \tag{51}$$

$$S^* + Q^* \xrightarrow{k_{2QS}} S + Q^* \quad . \tag{52}$$

The decay of [S*] and [Q*] with respect to time is given by equations 53 and 54, respectively.

$$-\frac{d[S^*]}{dt} = k_{1S}[S^*] + k_F[S^*][Q] - k_R[S][Q^*] + k_{2S}[S^*]^2 + k_{2QS}[S^*][Q^*] \tag{53}$$

$$-\frac{d[Q^*]}{dt} = k_{1Q}[Q^*] + k_R[Q^*][S] - k_F[Q][S^*] + k_{2Q}[Q^*]^2 + k_{2SQ}[Q^*][S^*] \quad . \tag{54}$$

Solution of equation 53 or 54 can be greatly facilitated by steady-state assumptions for $[Q^*]$ or $[S^*]$, respectively. One of the requirements in applying the steady-state assumption for a particular substance is that its concentration change slowly with respect to the increment being measured. Obviously, it would be totally unreasonable to make this assumption for a triplet whose decay is being monitored. Sandros and Bäckström (14) have pointed out that the steady-state assumption for $[Q^*]$ is a good approximation when the rate constant k_{1Q} is much greater than k_{1S}. The same logic would apply to $[S^*]$ when the magnitude of the rate constants is reversed. For purposes of simplicity, second-order terms are not included in the steady-state approximation of equations 55 and 56.

$$[S^*] = \frac{k_R[Q^*][S]}{k_F[Q] + k_{1S}} \tag{55}$$

$$[Q^*] = \frac{k_F[S^*][Q]}{k_R[S] + k_{1Q}} \tag{56}$$

Substitution of the steady-state expression for $[S^*]$ into equation 54 gives an equation that can be resolved into first- and second-order terms for $[Q^*]$.

$$-\frac{d[Q^*]}{dt} = \left(k_{1Q} + k_R[S] - \frac{k_F k_R[Q][S]}{k_F[Q] + k_{1S}}\right)[Q^*] + \left(k_{2Q} + \frac{k_{2SQ}k_R[S]}{k_F[Q] + k_{1S}}\right)[Q^*]^2 \quad . \tag{57}$$

In accord with equations 38-40, the terms α and β have new meaning when applied to equation 57.

$$\alpha = k_{1Q} + \frac{k_{1S}k_R[S]}{k_F[Q] + k_{1S}} \tag{58}$$

$$\beta = \frac{1}{\epsilon^* l}\left(k_{2Q} + \frac{k_{2SQ}k_R[S]}{k_F[Q] + k_{1S}}\right) \quad . \tag{59}$$

Thioxanthone, a "high-energy" sensitizer with respect to cis-stilbene, is also expected to transfer triplet energy to dibenzcycloheptenol at near the diffusion controlled rate. Under such conditions the reverse transfer from quencher to sensitizer should be negligible. In flash experiments with thioxanthone and dibenzcycloheptenol, filter solutions were employed so that only the former absorbed light initially. Since the dibenzcycloheptenol triplet has a longer lifetime than that of thioxanthone, the concentration of ground state dibenzcycloheptenol did not remain effectively constant during the process of energy transfer from thioxanthone. In addition to kinetic measurements at 5790 Å, the solution was monitored at 4358 Å where triplets of both substances absorb. Dibenzcycloheptenol, however, has the longer-lived triplet and its presence was readily detected. The quenching constant, k_F, in Table 22 is only a lower

TABLE 22

Quenching of Thioxanthone Triplets by Dibenzcycloheptenol[a]

Thioxanthone Concentration (M.)	Dibenzcyclo-heptenol Concentration (M.)	Filter Solution	α (sec.$^{-1}$)	β (sec.$^{-1}$)	k_F (M.$^{-1}$sec.$^{-1}$)
6.0×10^{-5}	-	#2	$1.1 \pm .1 \times 10^{4}$	$3.6 \pm .1 \times 10^{4}$	-
6.0×10^{-5}	1.9×10^{-5}	#2	$5.3 \pm .3 \times 10^{4}$	$4.7 \pm 1.6 \times 10^{4}$	$\geq 2.2 \times 10^{9}$

a. The solvent was benzene sample #3.

limit to the actual rate constant for triplet energy transfer from thioxanthone to dibenzcycloheptenol.

Chrysene is a sensitizer whose triplet is nearly isoenergetic with that of cis-stilbene. In studies of energy exchange between chrysene and dibenzcycloheptenol, mutual triplet quenching was observed. A series of solutions was prepared containing the same concentration of chrysene (3.9×10^{-5}M.) and different concentrations of dibenzcycloheptenol (up to 1.1×10^{-3}M.). The rate of decay of chrysene triplets very noticeably increased with added dibenzcycloheptenol. The kinetics of the process did not appear consistent with a steady-state approximation for [Q*]. The analysis into first- and second-order terms was not independent of the choice of zero time in the decay curves. However, at dibenzcycloheptenol concentrations of 1.9×10^{-4}M. and 1.1×10^{-3}M., the rate of decay of chrysene triplets was so rapid that decay of dibenzcycloheptenol triplets could be monitored at 4358 Å essentially free of any contributions from triplet-triplet absorption in chrysene. The decay of dibenzcycloheptenol triplets under these conditions could be resolved into first-and second-order terms that were independent of the point of zero time. These results are summarized in Table 23.

TABLE 23

Reversible Energy Exchange Between Triplets of Chrysene and Dibenzcycloheptenol[a, b]

Dibenz-cycloheptenol Concentration (M.)	Chrysene Concentration (M.)	Analysis Wave Length (Å)	α (sec.$^{-1}$)	β (sec.$^{-1}$)
-	3.9×10^{-5}	5790	$3.6 \pm .2 \times 10^{3}$	$1.6 \pm .1 \times 10^{4}$
3.8×10^{-5}	-	4358	$2.0 \pm .1 \times 10^{3}$	$1.5 \pm .2 \times 10^{4}$
1.9×10^{-4}	3.9×10^{-5}	4358	$2.7 \pm .2 \times 10^{3}$[c]	$1.7 \pm .2 \times 10^{4}$[c]
1.1×10^{-3}	3.9×10^{-5}	4358	$2.0 \pm .2 \times 10^{3}$[c]	$1.6 \pm .2 \times 10^{4}$[c]

a. Benzene sample #3 was used.

b. No filter solutions were employed.

c. Analysis of kinetics of decay of dibenzcycloheptenol triplets.

Whether the steady-state approximation applies to [S*] (chrysene triplets) in the experiments corresponding to the last two entries in Table 23 is questionable, because k_{1S} is only slightly larger than k_{1Q}. The validity of equation 57 is, nevertheless, assumed in the following analysis for k_F and k_R. Two simultaneous linear equations in k_F and k_R were derived from the numbers of Table 23 applied to equation 58. It was found that k_R is slightly larger than k_F, but the range of possible values is between $5 \times 10^6 M.^{-1} sec.^{-1}$ and $1 \times 10^{10} M.^{-1} sec.^{-1}$. Greater precision in the numbers of Table 23 is required for a more precise evaluation of k_F and k_R. Sandros (18) has pointed out, however, that the forward and reverse rate constants for energy exchange between isoenergetic triplets are equal and 1/2 those of diffusion controlled reactions. This situation apparently applies to energy transfer from chrysene to cis-stilbene ($k_Q = 2.5 \times 10^9 M.^{-1} sec.^{-1}$); that it should also apply to the chrysene-dibenzcycloheptenol pair is reasonable.

With 1, 2, 5, 6-dibenzanthracene, a sensitizer believed to have 4-5 kcal./mole less triplet energy than both cis-stilbene and dibenzcycloheptenol, the efficiency of energy transfer to dibenzcycloheptenol appeared to be considerably less than with thioxanthone and chrysene. In this system, however, the reverse transfer from dibenzcycloheptenol to sensitizer is expected to predominate. Added dibenzcycloheptenol had only a small effect on the rate of decay of dibenzanthracene triplets as shown in Table 24.

TABLE 24

Quenching of 1, 2, 5, 6-Dibenzanthracene Triplets by Dibenzcycloheptenol[a]

Dibenz-anthracene Concentration (M.)	Dibenz-cycloheptenol Concentration (M.)	Filter Solution	α (sec.$^{-1}$)	β (sec.$^{-1}$)
4.0×10^{-5}	-	#3	$5.9 \pm 1.0 \times 10^2$	$1.2 \pm .1 \times 10^4$
4.0×10^{-5}	3.8×10^{-5}	#3	$4.6 \pm .8 \times 10^2$	$1.2 \pm .1 \times 10^4$
4.0×10^{-5}	9.1×10^{-4}	#3	$9.3 \pm .9 \times 10^2$	$1.2 \pm .1 \times 10^4$

a. Benzene sample #3 was used.

The small negative effect with an added dibenzcycloheptenol concentration of 3.8 x 10^{-5}M. is disturbing, but probably is within experimental error of zero or a small positive effect. At a dibenzcycloheptenol concentration of 9.1 x 10^{-4}M., the quenching constant, k_F, was evaluated as 3.7 x 10^5M.$^{-1}$sec.$^{-1}$ without considering the reverse transfer process. It is recognized that correction for this effect would raise the above value perhaps by as much as an order of magnitude or more*; present data is too limited for application of this correction. The average of the rate constant values in Table 17 for energy transfer from 1,2,5,6-dibenzanthracene to cis-stilbene is 8.6 x 10^8M.$^{-1}$sec.$^{-1}$. This number is almost certainly greater than the rate constant for energy transfer from dibenzanthracene to dibenzcycloheptenol; the difference is believed due to the contribution of non-vertical excitation in cis-stilbene.

In view of the lack of quantitative data relating to the reversible exchange of triplet energy between sensitizer and quencher, a discussion of certain limiting cases of reversible energy transfer seems to be in order. If $k_{1Q} >> k_{1S}$, then contributions to the reverse transfer process are negligible. This behavior is typical of energy transfer from photosensitizers to the geometric isomers of stilbene and 1,2-diphenylpropene.

When $k_{1S} >> k_{1Q}$, then the principal contribution of added quencher to the decay of sensitizer triplets will be second-order triplet-triplet annihilation (equations 50-52).

When k_{1Q} and k_{1S} are of the same order of magnitude, the effects of reversible transfer are largely a function of the energy spacing between sensitizer and quencher triplets. If the sensitizer

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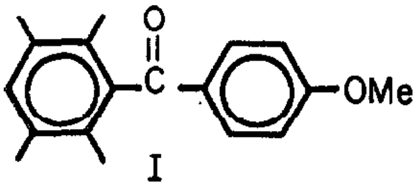
* See references 14 and 18 for a comparison of quenching constants uncorrected and corrected for reversible energy transfer.

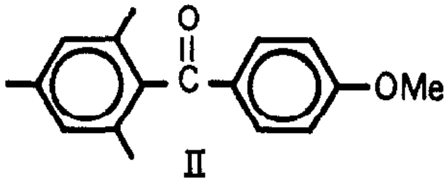
has the higher triplet energy, then the forward transfer process is expected to be dominant. A quencher with a triplet energy higher than that of the sensitizer should give a good deal of excitation back to the sensitizer. If the sensitizer and quencher triplets are nearly isoenergetic, then, according to Sandros (18), the rate constants for forward and reverse transfer are equal to 1/2 the diffusion controlled rate. When this condition applies, the concentration of triplet molecules of both species, immediately following flash excitation, should be sufficiently high to facilitate a rapid exchange of energy (equilibrium) between sensitizer and quencher. Both triplet species should then be expected to decay at a rate controlled by the larger of k_{1S} and k_{1Q}.

Steric Hindrance in Triplet Energy Transfer to Stilbene:

A series of substituted benzophenones with alkyl substituents providing steric hindrance about the carbonyl group, has been employed by Jones (57) as photosensitizers to effect stilbene isomerization in benzene solution. Structural formulas of these ketones are shown below. Since the triplet energies of these substances are



I



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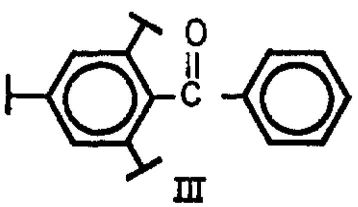

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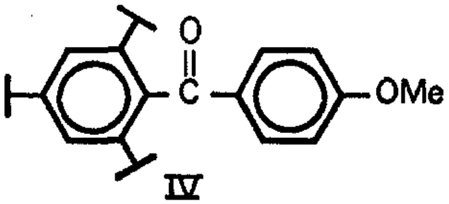


IV

all greater than 68 kcal./mole, one would expect, on the basis of triplet energies alone, identical rates of energy transfer to both stilbene isomers. Photostationary state measurements indicate that this is true with sensitizers having methyl substituents (I, II), but that 2, 4, 6-triisopropylbenzophenone (III) and 2, 4, 6-triisopropyl-4'-methoxy-benzophenone (IV) differentiate by transferring triplet energy less efficiently to cis-stilbene. Results are summarized in Table 25.

TABLE 25

Photosensitized Isomerization of Stilbene in Benzene Solution[a] with Sterically Hindered Benzophenones

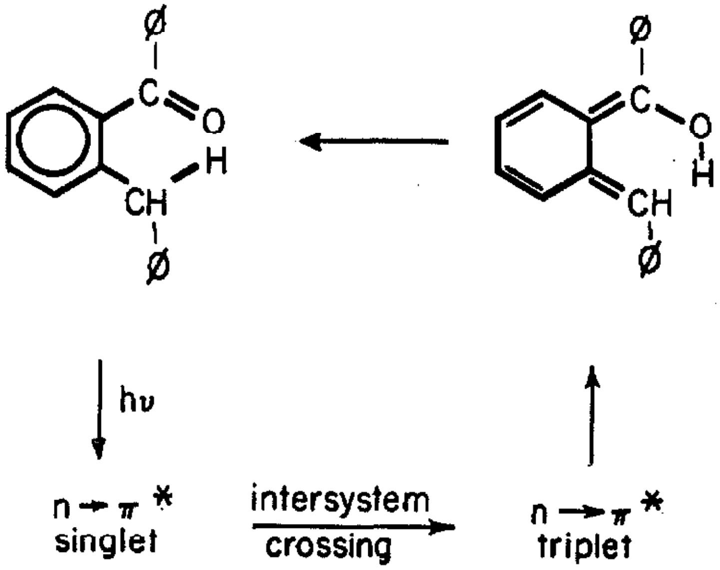
	Sensitizer	Triplet Energy[b] (kcal./mole.)	Expected Ratio[c] $\frac{[cis]}{[trans]}$	Observed Ratio $\frac{[cis]}{[trans]}$
(I)	2, 3, 5, 6-tetramethyl-4'-methoxybenzophenone	70. 2	1. 47	1. 45 ± . 02
(II)	2, 4, 6-trimethyl-4'-methoxybenzophenone	68. 4	1. 47	1. 47 ± . 03
(III)	2, 4, 6-triisopropyl-benzophenone	68. 7	1. 47	1. 92 ± . 02
(IV)	2, 4, 6-triisopropyl-4'-methoxybenzophenone	69. 9	1. 47	1. 93 ± . 04

a. Concentrations of substrates and sensitizers were both 0. 05 M.

b. Triplet energy values are from reference 53.

c. This ratio was achieved with solutions 0. 05 M in both stilbene and benzophenone.

Benzophenones with alkyl substituents in an *ortho* position are known to form enols on irraadiation (58) and all evidence indicates that this is a triplet state reaction. As an example, Zwicker, Grossweiner, and Yang (59) studied the intramolecular photoreduction of *o*-benzylbenzophenone by flash spectroscopy. They observed two transients, the substrate triplet and the photoenol, and found that the rate of decay of the former was identical with the rate of appearance of the latter. This mechanistic scheme is given in equation 60.

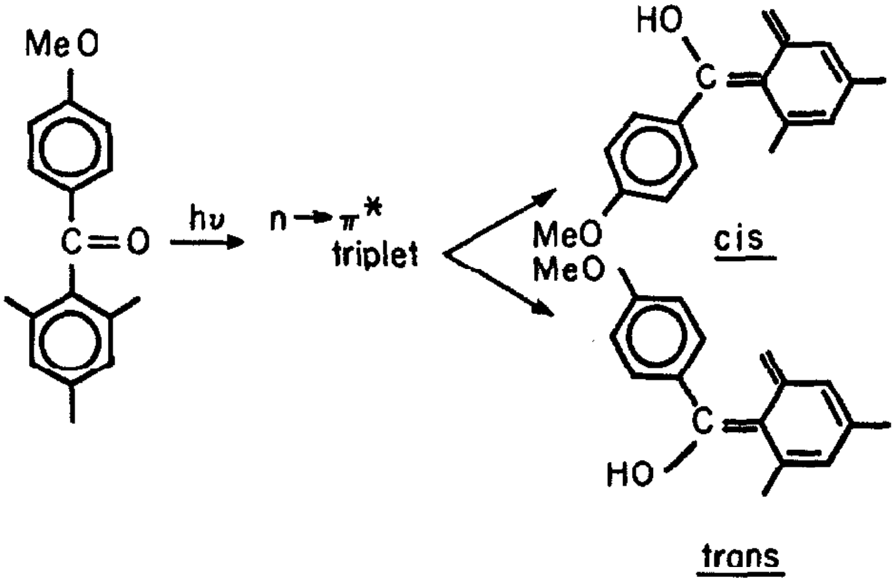


(60)

Beckett and Porter (60) conducted flash photolytic investigations with 2-methyl- and 2-ethylbenzophenone. On flashing, these two substances, each gave unstable photoproducts identified as photoenols with absorption in the region 3400-4400 Å. The yellow color gradually disappeared over several hours and could be regenerated with an additional flash. It would appear that a six-membered ring transition state is essential for this tautomerization to take place because it was not observed with 2-t-butylbenzophenone.

The investigation of steric hindrance to energy transfer with ortho substituted benzophenones is, of course, complicated by the possibility of photoenol formation. It was not clear whether the results with the isopropyl substituted benzophenones as listed in Table 25 could be interpreted in terms of steric hindrance to energy transfer or whether the corresponding photoenols functioned as lower energy and, therefore more selective, sensitizers.

The technique of kinetic spectrophotometry was utilized to help resolve this problem. The sensitizers 2, 4, 6-trimethyl-4'-methoxybenzophenone and 2, 4, 6-triisopropyl-4'-methoxybenzophenone were selected for these investigations. On flashing these substances in benzene solution, they both formed transients with absorption maxima near 4000 Å and the color in the solutions persisted for approximately 30 minutes. In addition, there was weak absorption in the same spectral region from a second set of transients with lifetimes close to 100 msec. The former pair of transients exhibited behavior similar to that of the photoenols Beckett and Porter (60) observed with 2-methyl- and 2-ethylbenzophenone. There was no precedent for the latter pair of transients, because their lifetimes were much too long to be compatible with triplet states. However, stereoisomeric modifications of the photoenols are possible as shown by equation 61.



(61)

In the cisoid modifications, the hydroxy hydrogens are more favorably situated for return to the starting position, so that these species would be expected to have a shorter lifetime than the *trans* isomers. The long- and intermediate-lived transients are tentatively assigned to the transoid and cisoid modifications, respectively, of the photoenols. At longer wave lengths where the photoenols did not absorb (5460 and 5790 Å), a transient with a lifetime of approximately 50 μsec. was observed in the 2,4,6-trimethyl-4'-methoxybenzophenone solution, whereas nothing could be detected in the isopropyl-substituted benzophenone solution. This transient was believed to be a triplet, but it was uncertain whether it was the ketone or enol triplet. There was, however, no increase in enol absorption coincident with decrease in triplet absorption.

Several experiments were run in order to check the validity of the assignment of transients to photoenols. Organic bases were added to the solutions for the purpose of catalyzing the reverse tautomerization from enol to ketone. It should be noted that the decay kinetics of the long-lived transients, because of the time resolution limit of the flash-photoelectric apparatus, could be measured only during the first 45 sec. With either pyridine in concentration of 0. 5 M or triethylamine in concentration of 2×10^{-5}M., there was no detectable effect upon the phototransients of 2, 4, 6-triisopropyl-4'-methoxybenzophenone. At a triethylamine concentration of 2×10^{-3}M., the lifetime of the longest-lived transient was reduced to the order of 20 sec. At higher base concentrations it appeared that complications set in. For example, the enol lifetime was approximately 4 sec. with triethylamine concentrations of 0. 14 M and 0. 72 M. Moreover, in these solutions a new transient with absorption at 4045 Å slowly appeared approximately 5 sec. after the flash. With the methyl-substituted benzophenone, an enol lifetime of 8 sec. was reached at triethylamine concentrations greater than 0. 1 M. as well as at diazabicyclooctane concentrations greater than 1×10^{-3}M, but no new transient was observed. Although the nature of the mechanism is not understood, enhancement of the rate of reversion of the long-lived transients to the respective parent molecules was effected by organic bases, and is consistent with the assignment of the structures of the long-lived transients to photoenols.

The fact that both 2, 4, 6-triisopropyl-4'-methoxybenzophenone and 2, 4, 6-trimethyl-4'-methoxybenzophenone form photoenols combined with the expectation of nearly identical triplet energies for the respective enols makes it appear unlikely that enol triplets effected the isomerization of stilbene observed by Jones (57). If ketone triplets sensitized this isomerization and if, by analogy with the results of Zwicker, Grossweiner, and Yang (59), triplet intermediates preceded enol formation, then addition of quenchers of lower triplet energy would be expected to reduce enol yields. Testing this possibility involves comparing initial absorption intensities of the photoenols in the presence and absence of triplet quenchers. It is important that the sensitizer absorb the same quantity of light in all runs that are to be compared. Error is introduced by variations in the optical properties of different cells as well as by fluctuations in the output intensity of the flash lamps.

Both piperylene and oxygen are known acceptors of triplet energy from sensitizers having triplet excitation energies comparable to those of the isopropyl- and methyl-substituted benzophenones (21, 28, 32). Addition of 0.9 M piperylene to a solution of 2,4,6-triisopropyl-4'-methoxybenzophenone completely quenched all transient formation and exposure of a solution of the same ketone to the atmosphere reduced transient formation by 2/3. With piperylene, the possibility of singlet energy transfer can be ruled out on energetic grounds.

Stilbene was also employed as a quencher of enol formation. Filter solutions were required in order to prevent internal filtering of light absorbed by the ketones. Because the absorption spectra of the filter solutions overlap extensively with those of the hindered ketones, there was a considerable decrease in the quantity of light absorbed by the ketones and, even with high flash intensities, the yield of photoenol was small. Experimental results are summarized in Table 26 where, for convenience, the isopropyl- and methyl-substituted benzophenones are abbreviated isopropyl and methyl,

TABLE 26

Quenching of Photoenol Formation by Stilbene

Sensitizer	Sensitizer Concentration (M.)	Quencher	Quencher Concentration (M.)	Filter Solution	Initial Absorbance	$\frac{\Delta A}{[Q]}$ (M.$^{-1}$)
isopropyl	2.0×10^{-4}	-	-	#2	3.1×10^{-1}	-
isopropyl	2.0×10^{-4}	cis	5.7×10^{-4}	#2	2.9×10^{-1}	32
isopropyl	2.0×10^{-4}	trans	5.0×10^{-4}	#2	2.7×10^{-1}	83
isopropyl	2.0×10^{-4}	-	-	#4	2.7×10^{-1}	-
isopropyl	2.0×10^{-4}	trans	3.0×10^{-3}	#4	1.3×10^{-1}	48
isopropyl	1.9×10^{-4}	-	-	#3	2.1×10^{-2}	-
isopropyl	1.9×10^{-4}	cis	1.9×10^{-3}	#3	1.1×10^{-2}	5.3
isopropyl	1.9×10^{-4}	trans	2.0×10^{-3}	#3	9.8×10^{-3}	5.8
isopropyl	1.9×10^{-4}	-	-	#3	3.8×10^{-2}	-
isopropyl	1.9×10^{-4}	cis	1.9×10^{-3}	#3	2.2×10^{-2}	8.5
isopropyl	1.9×10^{-4}	trans	2.0×10^{-3}	#3	2.1×10^{-2}	8.5
isopropyl	1.9×10^{-4}	-	-	#3	3.5×10^{-2}	-
isopropyl	1.9×10^{-4}	cis	1.9×10^{-3}	#3	2.2×10^{-2}	6.9
isopropyl	1.9×10^{-4}	trans	2.0×10^{-3}	#3	2.1×10^{-2}	7.0
isopropyl	1.9×10^{-4}	-	-	#3	4.8×10^{-2}	-
isopropyl	1.9×10^{-4}	cis	1.9×10^{-3}	#3	2.5×10^{-2}	12
isopropyl	1.9×10^{-4}	trans	2.0×10^{-3}	#3	2.3×10^{-2}	12
isopropyl	1.9×10^{-4}	-	-	#3	8.0×10^{-2}	-
isopropyl	1.9×10^{-4}	cis	2.9×10^{-3}	#3	3.5×10^{-2}	16
isopropyl	1.9×10^{-4}	trans	3.0×10^{-3}	#3	2.7×10^{-2}	18
isopropyl	1.9×10^{-4}	-	-	#3	8.8×10^{-2}	-
isopropyl	1.9×10^{-4}	cis	2.9×10^{-3}	#3	3.7×10^{-2}	18
isopropyl	1.9×10^{-4}	trans	3.0×10^{-3}	#3	3.2×10^{-2}	18
isopropyl	1.9×10^{-4}	-	-	#3	8.3×10^{-2}	-
isopropyl	1.9×10^{-4}	cis	2.9×10^{-3}	#3	3.5×10^{-2}	17
isopropyl	1.9×10^{-4}	trans	3.0×10^{-3}	#3	3.1×10^{-2}	17

TABLE 26 (cont.)

Sensitizer	Sensitizer Concentration (M.)	Quencher	Quencher Concentration (M.)	Filter Solution	Initial Absorbance	$\frac{\Delta A}{[Q]}$ ($M.^{-1}$)
isopropyl	1.9×10^{-4}	-	-	#3	7.8×10^{-2}	-
isopropyl	1.9×10^{-4}	cis	2.9×10^{-3}	#3	3.0×10^{-2}	17
methyl	2.0×10^{-4}	-	-	#4	3.1×10^{-1}	-
methyl	2.0×10^{-4}	cis	1.2×10^{-4}	#4	1.0×10^{-1}	1.7×10^{3}
methyl	2.0×10^{-4}	trans	1.0×10^{-4}	#4	1.1×10^{-1}	2.0×10^{3}
methyl	2.0×10^{-4}	-	-	#4	2.1×10^{-1}	-
methyl	2.0×10^{-4}	cis	1.2×10^{-4}	#4	9.1×10^{-2}	1.0×10^{3}
methyl	2.0×10^{-4}	trans	1.0×10^{-4}	#4	9.5×10^{-2}	1.1×10^{3}
methyl	2.0×10^{-4}	-	-	#4	2.0×10^{-1}	
methyl	2.0×10^{-4}	trans	1.0×10^{-4}	#4	7.6×10^{-2}	1.3×10^{3}
methyl	2.0×10^{-4}	-	-	#4	2.0×10^{-1}	
methyl	2.0×10^{-4}	trans	1.0×10^{-4}	#4	7.5×10^{-2}	1.3×10^{3}
methyl	2.0×10^{-4}	-	-	#4	1.5×10^{-1}	-
methyl	2.0×10^{-4}	cis	1.1×10^{-4}	#4	6.9×10^{-2}	7.7×10^{2}
methyl	2.0×10^{-4}	trans	1.0×10^{-4}	#4	6.6×10^{-2}	9.7×10^{2}

respectively, and the stilbene isomers are listed simply as cis and trans. For data grouped together in Table 26 experimental conditions were kept as nearly constant as possible. The last column is the decrease in initial absorbance intensity with added quencher divided by quencher concentration, and is believed to provide some measure of the efficiency with which stilbene reduces enol formation.

All solutions were monitored at 4045 Å and initial absorbance measurements include the long- and intermediate-lived transients. Added stilbene had no apparent effect upon the lifetimes of these transients, but only upon the quantity formed. The same was true of the short-lived transient of the methyl substituted benzophenone whose absorption was observed at 5460 and 5790 Å. The first-order term in the decay of this transient was 1.5 ± .5 x 10^4 sec.$^{-1}$ in the presence and absence of stilbene. These results are consistent with assignment of the short-lived transient to the photoenol triplet of 2,4,6-trimethyl-4'-methoxybenzophenone, if it is assumed that this triplet has energy less than 48 kcal./mole.

Perusal of Table 26 reveals that stilbene is effective in inhibiting enol formation with both 2,4,6-triisopropyl-4'-methoxybenzophenone and 2,4,6-trimethyl-4'-methoxybenzophenone, although the efficiency with the former is less by a factor of approximately 50 than with the latter. Unfortunately, the poor precision of these values does not permit meaningful comparison of the inhibiting efficiencies of each stilbene isomer with the individual ketones. The number 50 should be corrected for the fact that the expected enolization rates of the two ketones differ. Walling and Gibian (61), for example, have shown that in benzene solution, benzophenone triplets abstract hydrogen from cumene 3.4 times more readily than from toluene. Application of this number to the differential factor in question reduces it in value to approximately 15.

Since the methyl-substituted benzophenone gave a stilbene photostationary state expected of a high energy photosensitizer, it seems reasonable to assume that the rates of energy transfer to the individual stilbene isomers are diffusion controlled. The rates of energy transfer from the isopropyl-substituted benzophenone should then be less by a factor of 15. It appears that, because the triplet excitation energy in 2,4,6-triisopropyl-4'-methoxybenzophenone is localized largely in the carbonyl group, the adjacent isopropyl substituents sterically hinder energy transfer to cis- and trans-stilbene. The photostationary state measurements by Jones (57) indicate that the steric effect is somewhat greater with the cisoid isomer.

APPENDIX

Triplet State Energies of Sensitizers:

The sources of triplet energies used throughout the text deserve some comment. Since all experiments but one were run at room temperature with benzene solvent, it would be desirable to base triplet energy assignments on phosphorescence spectra taken under the same conditions. Only a limited number of sensitizers are known to phosphoresce in degassed benzene solution. Sandros (18) has observed phosphorescence from naphthalene and 2, 2'-binaphthyl in benzene solution at 20°C and reports 0'-0 bands at 60. 8 and 56. 1 kcal. /mole, respectively. The energy values from phosphorescence in rigid media at 77°K are 60. 9 kcal. /mole for naphthalene (33) and 55. 9 kcal. /mole for 2, 2'-binaphthyl (62). Because of the good agreement between these two pairs of numbers, it appears that, at least for aromatic hydrocarbons or molecules with $\pi \rightarrow \pi^*$ lowest triplet states, triplet energy assignments from low temperature phosphorescence spectra are good approximations to triplet energies in benzene solution. It is questionable whether the same can be said for molecules with $n \rightarrow \pi^*$ lowest triplet states. Benzil, for example, has phosphorescence 0'-0 bands at 53. 7 kcal. / mole in a rigid hydrocarbon glass at 77°K (33) and 50. 9 kcal. /mole in benzene solution at room temperature (63).

Low temperature phosphorescence spectra are usually measured in glass-forming solvents. Common among these are EPA (ether, isopentane, and ethanol, 5:5:2 by volume), mixtures of ethanol and ether, and several hydrocarbon solvents made up of methylcyclohexane, isopentane, 3-methylpentane, and 2, 2, 4-trimethylpentane in various proportions. It has been pointed out that spectral shifts due to solvent effects depend upon the type of transition involved*. Phosphorescence from carbonyl compounds where the transition is $n \leftarrow \pi^*$ shows a large hypsochromic shift in polar, hydrogen-bonding solvents compared to non-polar solvents. The position of the $0'-0$ band in benzophenone, for example, is 69.2 kcal./mole in EPA and 68.5 kcal./mole in a hydrocarbon solvent (33). Phosphorescence due to $\pi \leftarrow \pi^*$ transitions such as those occurring in aromatic hydrocarbons is, to a first approximation, independent of solvent polarity. Naphthalene has a triplet energy of 60.9 kcal./mole in both EPA (47) and hydrocarbon solvents (33). The energy assignments for those sensitizers with $n \leftarrow \pi^*$ lowest triplets are based upon phosphorescence in non-polar hydrocarbon solvents, whereas phosphorescence spectra of aromatic hydrocarbons in either hydrocarbon or ethanol-containing solvents are considered reliable. Listed in Table 27 are the sensitizer triplet energies used in evaluating the experimental results of the previous section along with the corresponding sources of reference and type of solvent employed. Of these sensitizers, only camphorquinone and possibly thioxanthone are believed to have $n \rightarrow \pi^*$ lowest triplet states.

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* For a discussion of solvent effects on electronic transitions of organic molecules, see reference 64.

TABLE 27

Triplet State Energies of Sensitizers

Sensitizer	Triplet Energy[a] (kcal./mole)	Solvent[b]	Reference
triphenylene	66.6	HC	33
thioxanthone	65.5	HC	33
phenanthrene	61.8	EPA	62
naphthalene	60.9	HC	33
2-acetonaphthone	59.3	HC	33
1-naphthyl phenyl ketone	57.5	HC	33
chrysene	56.6	EPA	47
fluorenone	53.3	HC	33
fluoranthene	52.9	EPA	62
1, 2, 5, 6-dibenzanthracene	52.2	EPA	62
1, 2, 3, 4-dibenzanthracene	50.8	EPA	62
Camphorquinone	50.6	HC	65
pyrene	48.2	EPA	62
1, 2-benzanthracene	47.2	EPA	62
1, 12-benzperylene	46.2	EPA	62
9, 10-dimethyl-1, 2-benzanthracene	44.3	EPA	66
anthracene	42.6	EPA	67
3, 4-benzpyrene	41.9[c]	ethanol	68

a. Triplet energy assignments are based on the position of the 0'-0 band in phosphorescence spectra at 77°K.

b. The symbol HC refers to a glass-forming hydrocarbon solvent.

c. This phosphorescence spectrum was taken at 93°K.

With some sensitizers, low temperature phosphorescence has not been reported; consequently, other methods have been employed in making triplet energy assignments. The triplet energy of duroquinone was estimated by assuming it to be identical with the triplet state energies of 2, 3-dimethyl-1, 4-benzoquinone and 2, 5-dimethyl-1, 4-benzoquinone. Singlet-triplet absorption spectra of these compounds have been obtained in n-heptane and have 0'-0 bands at 51. 6 kcal. /mole (69). Acridine was assigned a triplet energy of 45. 3 kcal. /mole on the basis of its singlet-triplet absorption spectrum taken with chloroform solvent in the presence of a high oxygen pressure (36). The corresponding energy for 9, 10-dibromoanthracene (40. 2 kcal. /mole) was obtained from its singlet-triplet absorption spectrum in carbon disulfide (67).

The triplet energies of benzanthrone and 3-acetyl pyrene were not measured directly. Assignment of triplet energy values for these sensitizers is based upon Figures 9-13, where it appears that triplet energies of 47. 0 kcal. /mole for benzanthrone and 45. 5 kcal. /mole for 3-acetyl pyrene are in harmony with the different plots. The assumption that sensitizer triplet energy is the controlling factor in rates of energy transfer to the geometric isomers of stilbene and 1, 2-diphenylpropene is inherent in these assignments. That these triplet energies are reasonably accurate is demonstrated by the fact that 3-bromobenzanthrone and pyrene have phosphorescence 0'-0 bands (77°K) at 45. 7 (70) and 48. 2 kcal. /mole (62), respectively.

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