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INTERMOLECULAR ENERGY TRANSFER IN PHOTOCHEMICAL REACTIONS IN SOLUTIONS OF ORGANIC COMPOUNDS†

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1. INTRODUCTION

When a molecule of an organic compound absorbs a quantum of light, it undergoes transition from the ground electronic state to an excited state. The nature of the electronic transitions in the molecule may be explained by means of the somewhat modified Jablonski diagram shown in Fig. 1.[2] For most compounds the ground state of the molecule S_0 is the singlet state, in which the total spin of the orbital electrons (s) is equal to zero, and the multiplicity, denoted by the quantity $2s + 1$, is unity. Electronic transitions from S_0 to excited singlet levels S_1, S_2, etc., without change of spin orientation, are much more probable than transitions with change in multiplicity; generally speaking, the latter are forbidden. According to present interpretations[3], a molecule at a high excited singlet level, S_2, S_3 etc., passes to a lower S_1 level in $\sim 10^{-13}$ s without emission of radiation, where it remains for 10^{-7}–10^{-9} s. The molecule may pass from the S_1 level to the S_0 ground level either without or with the emission of light (fluorescence).

The molecule may also pass from the excited singlet level to a lower triplet level T, for which the resultant spin of the electrons is unity, and the multiplicity is 3.[4,5] A transition from the triplet level to the ground state with a change in multiplicity is forbidden; the molecule therefore remains in the triplet state much longer than in the singlet excited state. A spontaneous transition from the triplet to the ground state may be accompanied by the emission of light (phosphorescence). Compared with fluorescence, phosphorescence is marked by a longer decay period (up to several seconds) and by a displacement towards the long-wave region of the spectrum.

The excited molecules may undergo various unimolecular chemical conversions or enter into chemical reactions with other molecules.

† A previous review dealt with intermolecular energy transfer in the radiolysis of solutions of organic compounds[1].

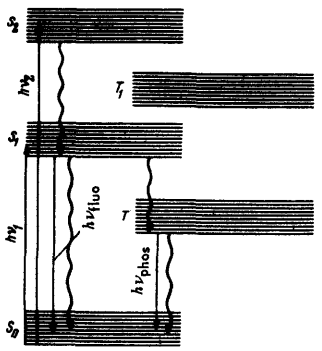


Fig. 1. Scheme of electronic transitions in an organic molecule. The straight arrows correspond to transitions with absorption or radiation of light. The wavy arrows correspond to transitions without radiation.

In multicomponent systems the excited molecules of one component may transfer energy to molecules of another component. The special features of intermolecular energy transfer are largely due to the large number of the excited molecules that take part in it. Energy transfer may occur at singlet levels:

$$A^{S_1} + B^{S_0} \rightarrow A^{S_0} + B^{S_1}.$$

A^{S_1} and B^{S_1} are excited singlet molecules of the energy donor and acceptor, A^{S_0} and B^{S_0} are donor and acceptor molecules at the ground singlet level. This process is called singlet-singlet energy transfer.

If the energy is transferred from the triplet level of the molecule A to the molecule B according to the scheme:

$$A^{T} + B^{S_0} \rightarrow A^{S_0} + B^{T},$$

the process is called energy transfer at triplet levels or triplet-triplet transfer.

The molecules B^{S_1} and B^{T} formed as a result of energy transfer may be deactivated with the emission of luminescent light. This phenomenon is called sensitized fluorescence or sensitized phosphorescence. If the molecules of A are also capable of showing luminescence, quenching of the glow due to the energy of the donor will also be observed.

As a result of energy transfer, chemical conversion of the acceptor may be sensitized or the photochemical reaction of the donor may be inhibited.

It is generally considered that for energy transfer to occur, the level of the excited donor molecule, from which transfer takes place, should be higher than the excited level of the acceptor molecule.

The transfer of energy between singlet levels in solution may occur not only at a direct diffusion approach of the interacting molecules, but also at distances greatly exceeding the kinetic radii of the molecules. In the latter case, the greater the overlap of the fluorescence spectrum of the donor and the absorption spectrum of the acceptor, the greater will be the effectiveness of the transfer. Förster[6] and Galanin and Frank[7] explained the phenomenon of long-range action in singlet-singlet energy transfer in solution by dipole-dipole interactions of the excited donor molecule with the acceptor molecule. These authors

showed that the probability of the "resonance" transfer of energy (W) is determined by the expression:

$$W = \frac{1}{\tau}\left(\frac{R_0}{R}\right)^6,$$

where τ is the lifetime of the excited energy-donor molecules, R is the distance between the interacting molecules, and R_0 is the so-called critical radius of resonance interaction, which is determined by the optical properties of the system, particularly by the oscillator strengths and the area of overlap of the emission spectrum of the donor and the absorption spectrum of the acceptor.

The transfer of energy at triplet levels was first observed by Terenin and Ermolaev[8] in investigating the phosphorescence of a solid solution of naphthalene sensitized with benzaldehyde or benzophenone under the action of light of wavelength 365 nm absorbed by the donor molecules (naphthalene is virtually transparent in this spectral region). The triplet level of naphthalene is lower, and the singlet level higher, than the corresponding levels of benzaldehyde and benzophenone. In this connection the transfer of energy to naphthalene can only take place at the triplet levels.

In liquid solutions, triplet-triplet energy transfer was first discovered by Bäckström and Sandros[9], who studied the quenching of biacetyl phosphorescence by aromatic compounds with triplet levels lower than the triplet level of biacetyl. These workers showed that the rate of energy transfer at triplet levels is close to the value determined by the rate of diffusional encounter of the interacting molecules.

Aromatic compounds containing carbonyl groups are frequently used as energy donors in triplet-triplet transfer[10]. This is because these compounds have high triplet levels and low singlet levels. Moreover, when electronically excited, these compounds show a high probability (frequently close to unity[11,12]) of passing to the triplet state because of the strong spin-orbital interaction in $n \rightarrow \pi^*$ transitions[3].

The most reliable results on triplet-triplet energy transfer in liquid solutions have been obtained by Porter and Wilkinson[13] by the method of flash photolysis. Essentially, this method consists in producing a high concentration of intermediate particles — radicals or triplet molecules — in solution by means of short-duration light impulses of high intensity; the optical absorption of these particles is determined by means of a "sounding" beam. Flash photolysis may be used to determine both the absorption spectrum of the intermediate particles and the change in their concentration with time.

Using this method, Porter and Wilkinson were able to follow the change in the rate of disappearance of the triplet states of a number of aromatic compounds (energy donors) in the presence of acceptor additives. In some instances they were also able to observe triplet acceptor molecules that arose as a result of energy transfer. The absolute rates of triplet-triplet energy transfer were determined and were found to be close to the diffusion rates, in agreement with the results of Bäckström and Sandros[9].

At present, the mechanism of energy transfer at triplet levels is not quite clear. Terenin and Ermolaev[14,15] consider that the transfer proceeds by an exchange-resonance mechanism[16]. This mechanism requires overlapping of the electronic shells of the interacting molecules, which is in agreement with the diffusion mechanism of energy transfer in solutions.

At low acceptor concentrations, the intermolecular energy transfer competes with the spontaneous deactivation of the excited donor molecules. If the energy transfer is regarded as a bimolecular process, the dependence of the quantum yield on the acceptor concentration can be expressed by simple equations. For the quantum yield (γ) of sensitized processes (luminescence or chemical decomposition) the equation has the form:

$$\frac{\gamma}{\gamma_{\lim}} = \frac{k_{AB}\tau[B]}{1 + k_{AB}\tau[B]}, \quad (1)$$

where $\gamma_{\lim}$ is the limiting quantum yield of the sensitized process at sufficiently high concentrations of B, when there is no spontaneous deactivation of the excited molecules of A; k_{AB} is the rate constant for energy transfer; and τ is the lifetime of excited molecules of A.

If the acceptor is a quencher, the quantum yield for luminescence or chemical decomposition of the donor is determined by the Stern–Volmer equation:

$$\frac{\gamma}{\gamma_0} = \frac{1}{1 + k_{AB}\tau[B]}, \quad (2)$$

where γ_0 is the quantum yield in the absence of quencher.

Although these equations have been derived from the simplest kinetic considerations and are semiempirical, in many instances they are nevertheless in good agreement with experimental results. The product $k_{AB}\tau$, which is determined from the dependence of the quantum yield on the concentration of B, is a measure of the effectiveness of the transfer of excitation energy.

The information presented in this section is sufficient for an understanding of the material on specific photochemical reactions discussed below. Detailed analyses of the problem of intermolecular energy transfer during luminescence may be found in a number of publications[10,17-22].

In the present review, problems of energy migration in biologically important systems[19-23] are not considered, nor are papers on the migration of energy in photochemical reactions in the gas phase and in solid and vitreous media.

The data in a number of papers considered in the review do not allow an unambiguous conclusion to be drawn as to the mechanism of energy transfer; for this reason, it would obviously not be expedient to classify the material on the basis of transfer mechanism. It is arranged according to the type of chemical reaction accompanying the energy transfer.

2. SENSITIZED PHOTODECOMPOSITION

a. Halogeno-Substituted Hydrocarbons

One of the first papers on sensitized photolysis of organic compounds was that of West and Paul[24], published in 1932; they studied the photolysis of solutions of ethyl iodide in hexane and benzene under the action of light of wavelength 254–280 nm (maximum radiation in 261 nm region). Unlike hexane, benzene is not transparent in the 261 nm region, and a considerable portion of the light is absorbed by the solvent in benzene solutions. In particular, with a solution of concentration 0.03 M, benzene absorbs 180 times as much light as ethyl iodide. However, the quantum yield for the photodecomposition of ethyl iodide in such a solution is virtually the same as that for

the photolysis of a 0.03 M solution in hexane, in which light is only absorbed by the ethyl iodide. To explain these results, the authors suggested that excited benzene molecules may transfer energy to ethyl iodide molecules, which decompose into free radicals.

Later, West and Fitelson[25] showed that the sensitized decomposition of ethyl iodide may also occur in such solvents as methyl iodide, hydrogen sulphide, and chlorobenzene, the first two solvents themselves decomposing under the action of light. The transfer of energy to ethyl iodide appears to compete with the decomposition of excited molecules of these solvents.

To explain the mechanism of energy transfer in these reactions, West and Miller[26] compared the kinetics of the naphthalene-sensitized photodecomposition of ethyl iodide in hexane with the kinetics of the quenching of naphthalene fluorescence.

The rate of decomposition of ethyl iodide under the action of light of wavelength 313 nm, which only excites naphthalene, is proportional to the amount of light absorbed. The additivity of the spectral changes that occur when solutions of naphthalene and ethyl iodide are mixed clearly indicates that there is no appreciable complex formation in the unexcited state. Thus, the decomposition of ethyl iodide is the result of transfer of excitation energy. With an ethyl iodide concentration of less than 0.01 M, the quantum yield of the decomposition obeys Eqn. (1); $\gamma_{313m} = 0.3$ agrees with the quantum yield for the decomposition that occurs when light acts directly on ethyl iodide, that is, all the light energy absorbed by naphthalene is transferred to the ethyl iodide. Under these conditions $k_{AB}\tau \simeq 10^3$ litre mole^{-1}.

The quenching of naphthalene fluorescence by ethyl iodide follows the Stern–Volmer law. However, here $k_{AB}\tau = 180$ litre mole^{-1}. The authors explain the difference in the effectiveness of energy transfer obtained from data on fluorescence and data on photolysis on the assumption that the photodecomposition of ethyl iodide is brought about by the transfer of energy, not only from the fluorescing level of the naphthalene molecule, but also from the excited level from which the molecule does not fluoresce. This is probably a triplet level, although the authors themselves put forward no suggestions as to its nature. This is due to the fact that the paper by West and Miller appeared before Terenin[4], and then Lewis and Kasha[5], developed an interpretation of the triplet excitation levels and their roles in photochemical reactions.

Ethyl iodide weakly absorbs light of wavelength 313 nm; for this reason, only ethyl iodide molecules at high vibrational levels absorb light of this wavelength and pass to the excited electronic state, which here is a repulsive state.

However, in the presence of naphthalene and with ethyl iodide concentrations greater than 0.01 M, all the energy of light of wavelength 313 nm absorbed by naphthalene is transferred by ethyl iodide molecules. Evidently, ethyl iodide molecules in the lower vibrational levels can receive energy quanta from naphthalene molecules of a size such that they would remain virtually unabsorbed under the direct action of light. The explanation of this effect given by West and Miller is illustrated schematically in Fig. 2. Curve *1* is the potential curve of ethyl iodide in the ground state; the shape of the curve should not change appreciably in collisions between unexcited molecules of naphthalene (N) and ethyl iodide (Et–I), since there is little interaction between these; *2* is the repulsion curve of ethyl iodide. The energy of the configuration formed when a molecule of

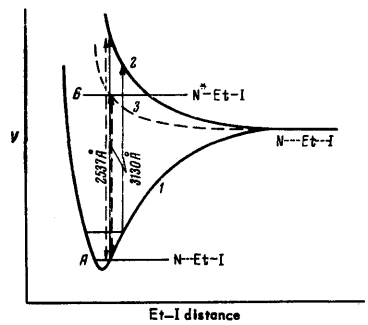


Fig. 2. Mechanism of photosensitized decomposition of ethyl iodide.

ethyl iodide collides with an excited naphthalene molecule (curve *3*) will be less than the energy of (EtI)*, if there is appreciable interaction between the excited naphthalene molecules (N*) and ethyl iodide. Accordingly, the sensitized decomposition of ethyl iodide requires less energy than that required under the direct action of light.

Wilkinson[27] studied the sensitized photodecomposition of solutions of 1-iodonaphthalene in the presence of various sensitizers under the action of light of wavelength 365 nm, for which iodonaphthalene is virtually transparent. The photodecomposition of iodonaphthalene occurs in the presence of additives (acetophenone, benzophenone, anthraquinone, 2-acetonaphthone), the triplet level of which lies above the corresponding naphthalene level, and it does not occur when the triplet level of the additive (anthracene) is lower than that of iodonaphthalene. The reaction probably proceeds by the transfer of energy between the triplet levels.

Kallmann-Oster and Kallmann[28], who studied the concentration dependence of free radical yields in the photolysis and radiolysis of carbon tetrachloride solutions in benzene, concluded that the sensitized photodecomposition of carbon tetrachloride is the result of transfer of energy from benzene to CCl_4‡. The rate of formation of free radicals was determined with the aid of the free-radical acceptor 1,1-diphenyl-2-picrylhydrazyl (DPPH). The concentrations of DPPH and CCl_4 were such that the direct action of light ($\lambda = 254$ nm) on these compounds could be neglected. The rate of formation of free radicals in photolysis reaches a limiting value at CCl_4 concentrations of about 10^{-2} M, and it decreases in the presence of additions of the organic luminophores, fluoranthene, *p*-terphenyl, and phenylbiphenylyloxadiazole. The authors consider that energy transfer occurs at low excited singlet levels. Van Dusen and Hamill[29], who studied the photolysis ($\lambda = 254$ nm) of mixtures of benzene with carbon tetrachloride, ethyl iodide, chloroform, and other chlorides over a wide concentration range, consider that sensitized photodecomposition of chlorides is associated with transfer of energy from benzene at the triplet levels.

Semeluk and Unger[30], who studied the benzene-sensitized photodecomposition of chloroform in the gas phase,

‡ We have already discussed in detail the problem of energy transfer in the radiolysis of solutions containing CCl_4 and other halogeno-substituted hydrocarbons[1]. See also Van Dusen and Hamill[29].

also consider that decomposition of chloroform is due to triplet-triplet energy transfer from benzene to chloroform.

When the sensitizing additive itself undergoes chemical change, it is difficult to decide whether the photochemical reaction is due to the transfer of energy from this additive and subsequent reaction of acceptor decomposition products with the additive, or to the immediate entry of excited additive molecules into photochemical reaction with the other compound. Thus, Bowen and Rohatgi[31] found that when light acts on anthracene (A) dissolved in carbon tetrachloride, recombination products of $^{\cdot}ACl_4$ and $^{\cdot}CCl_3$ radicals are formed. They consider that the latter radicals are formed by abstraction of a Cl$^{\cdot}$ atom from CCl_4 by excited anthracene.

To find the nature of the excited anthracene molecules which react with carbon tetrachloride, Kusuhara and Hardwick[32] compared the rate of this reaction for anthracene under the direct action of light with that for anthracene excited by energy transfer from coronene. It was first shown by flash photolysis that energy is transferred from coronene to anthracene at triplet levels. The relative concentrations of triplet molecules produced by direct action and as a result of energy transfer were also evaluated. Comparison showed that the rates of the direct and sensitized reactions are proportional to the concentrations of triplet anthracene molecules. Bagdasar'yan[33,34] observed an increase in the rate of initiation of photopolymerization of various vinyl monomers (styrene, α-methylstyrene, allyl acetate, isoprene, chloroprene) in the presence of CCl_4; he considers this to be due to the removal of Cl$^{\cdot}$ atoms from CCl_4 by excited monomer molecules. Robb and coworkers obtained analogous results in a study of the photochemical telomerization of styrene and methyl methacrylate with CCl_3Br.[35,36]

b. Some Other Readily Decomposable Compounds

Organic peroxides, hydroperoxides, azo- and diazo--compounds, disulphides, and some other compounds are readily decomposed in solution under the action of light, and some are also decomposed by heating; for this reason, they are frequently used as sources of free radicals in the initiation of chemical reactions[37,38]. Because of the readiness with which these compounds are decomposed when electronically excited, they may be used as very sensitive acceptors in sensitized reactions.

Luner and Szwarc irradiated dilute benzene solutions of acetyl peroxide with light of wavelength 254 nm, which is absorbed virtually by benzene alone, and they observed sensitized decomposition of the peroxide[39]. Sensitized decomposition of the peroxide also occurs in iso-octane in the presence of anthracene or naphthacene under the action of light of wavelength 265 nm, which is absorbed by these hydrocarbons.

Krongauz and Bagdasar'yan[40], and later Vasil'ev and Krongauz[41,42], made a detailed study of the solvent-sensitized radiolysis and photolysis of benzoyl peroxide in benzene and in toluene. Luminophore additives (anthracene, phenanthrene, *p*-terphenyl, etc.) reduce the yield in the sensitized decomposition of benzoyl peroxide. At the same time, benzoyl peroxide quenches the solvent-sensitized fluorescence of these luminophores. They suggested that the same excited states of the solvent molecules participate in the transfer of energy both to the peroxide and to the luminophore, and they obtained concordant values of the constants for energy transfer from the solvent to the additives; these values were calculated from data on the sensitized fluorescence of the luminophores and the sensitized decomposition of peroxide in three-component solutions (solvent–benzoyl peroxide–luminophore). In sensitized fluorescence, the energy transfer occurs at singlet excitation levels. Thus, the decomposition of benzoyl peroxide also appears to be due to singlet-singlet energy transfer. Subsequently, an attempt was made to give a more detailed elucidation of the mechanism of energy transfer in these systems[43-45]. It was shown that energy transfer occurs at a distance exceeding the kinetic radii of the molecules, but the effectiveness of the transfer largely depends on the rate of diffusion of the molecules in the solution.

The sensitized photodecomposition of benzoyl peroxide resulting from the transfer of energy from the luminophores to the peroxide has also been studied. This process leads to quenching of the luminophore phosphorescence, which also indicates singlet-singlet energy transfer. However, here the rate constant for the transfer is much lower than with sensitization by a solvent and it is in satisfactory agreement with the hypothesis that energy is transferred by diffusion approach of the molecules to a distance equal to the kinetic radii.

Kardash and Krongauz[46] compared the kinetics of the naphthalene-sensitized photodecomposition of propionyl peroxide in benzene under the action of light of wavelength 313 nm (which is absorbed only by naphthalene) with the kinetics of the photolysis of solutions of naphthylpropionyl peroxide; they showed that naphthylpropionyl peroxide decomposes by a bimolecular mechanism. With peroxide concentrations less than 5×10^{-3} M, the quantum yield tends to zero. In the low-concentration region, the concentration dependence of the quantum yield for the photodecomposition of naphthylpropionyl peroxide is similar to the same dependence for a 2:1 mixture of naphthalene and propionyl peroxide. It appears that excited molecules of naphthylpropionyl peroxide can transfer energy directly to the peroxide groups of other molecules.

Überreiter and Bruns[47] studied the fluorenone-sensitized photodecomposition of tetralin hydroperoxide in chlorobenzene under the action of light of wavelength greater than 365 nm. At concentrations less than 5×10^{-3} M, the rate of decomposition of tetralin hydroperoxide is proportional to the hydroperoxide concentration. The sensitized decomposition of the hydroperoxide is due to energy transfer between triplet levels; the formation of hydrogen bonds between the donor and acceptor plays an important part in this transfer. The authors consider that this is confirmed by the failure of fluorenone to sensitize the photodecomposition of benzoyl peroxide, with which it does not form hydrogen bonds. The rate of hydroperoxide photodecomposition depends linearly on the square root of the fluorenone concentration; this appears to be related to the mutual deactivation of two triplet fluorenone molecules.

In a study of the so-called "delayed fluorescence" of a number of aromatic luminophores in solution, Parker and Hatchard observed similar interaction between two triplet molecules with the formation of excited and unexcited singlet molecules[48]:

$$A^T + A^T \longrightarrow A^{S_1} + A^{S_0}.$$

The benzophenone-sensitized photodecomposition of diazomethane into methylene and nitrogen is an interesting example of a reaction resulting from energy transfer at

triplet levels. When light acts directly on diazomethane[49,50] dissolved in cyclohexene, or when diazomethane is decomposed by heat, a mixture of norcarane and methylcyclohexenes is formed, as a result of the reaction of cyclohexene with methylene, which appears to occur in the singlet state. In the photodecomposition of diazomethane sensitized by benzophenone (as noted above, on photoexcitation benzophenone passes virtually completely into the triplet state), norcarane is mainly formed. This appears to be related to the triplet state of the methylene in this case. Methylene formed by the direct photolysis of diazomethane in octane reacts with *cis*- or *trans*-but-2-ene to give the corresponding *cis*- or *trans*-dimethylcyclopropane. At the same time, when diazomethane undergoes sensitized photodecomposition, a mixture of *cis*- and *trans*-dimethylcyclopropane is always formed. The intermediate formed by the addition of the triplet methylene to butene can probably undergo internal rotation before cyclization.

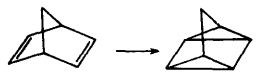
Hammond and coworkers have shown that, with the use of energy transfer at triplet levels, it is possible to induce sensitized photodecomposition of ethyl pyruvate into acetaldehyde and carbon monoxide with a much higher quantum yield than that obtained in the direct photolysis of this α-keto-ester[51]. They used benzophenone as an energy donor. The energy transfer is evidently very effective in this instance, since small additions of ethyl pyruvate (0.05 M) completely suppress the photoreduction of benzophenone to benzohydrol, which proceeds through the triplet state of benzophenone (see Section 6). β-Acetonaphthone, the triplet level of which (59 kcal mole^{-1} [52]) is considerably lower than the triplet level of ethyl pyruvate, does not sensitize the photodecomposition of this compound.

Berman and coworkers[53] have studied the ketone-sensitized photochemical decarbonylation of aldehydes, such as ethylenehexanal, heptanal, octanal, etc. Benzophenone, acetophenone, their chloro- and methoxy-derivatives, and 2-octanone, which have excitation triplet levels of about 70–75 kcal mole^{-1}, sensitize the photodecomposition, but acetophenone is ineffective, as with ethyl pyruvate. 2-Ethylenehexanal inhibits the photoreduction of benzophenone in propan-2-ol. The ratio of the rate constant for the transfer of energy from benzophenone to the aldehyde to the rate constant for the photoreduction is 70. It is interesting that for the inhibition by naphthalene of the photoreduction of benzophenone by alcohol this ratio is $\sim 3 \times 10^3$.[54]

3. SENSITIZED INTRAMOLECULAR REARRANGEMENTS

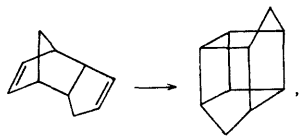
The first investigation of sensitized chemical reactions in solution was described in a paper published in 1931 by Weigert and Pruckner[55]. This dealt with the conversion of *o*-nitrobenzaldehyde into *o*-nitrobenzoic acid, photosensitized by acetone. When light of wavelength 313 nm acts on 0.05–2% solutions of *o*-nitrobenzaldehyde, the quantum yield for the rearrangement of aldehyde to acid (~ 0.5) is almost independent of concentration, although in a 2% solution the aldehyde absorbs three times as much light as acetone, but at 0.05% concentration, acetone accounts for 90% of all the light absorbed by the solution. Evidently all the energy absorbed by the acetone is transferred to the aldehyde.

In some instances sensitized reactions proceed with a higher quantum yield than the same reactions under the direct action of light. Thus, Hammond and coworkers[56] showed that the photochemical rearrangement of norbornadiene to quadricyclene:



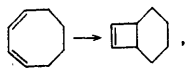
gives a much higher quantum yield when sensitized by such compounds as acetone, acetophenone, and benzophenone than the same reaction under the direct action of light[57].

Schenck and Steinmetz[58] showed that endodicyclopentadiene isomerizes to pentacyclo[5,2,1,$0^{2,6}$,$0^{3,9}$,$0^{4,8}$]-decane:



in the presence of acetone with a greater yield than that obtained under the direct action of light.

The photochemical isomerization of 1,3-cyclo-octadiene to Δ^7-bicyclo[4,2,0]octene[59]



can also be sensitized in the presence of benzophenone[60].

In all the intramolecular rearrangement reactions enumerated above ketones were used as sensitizers; as mentioned above, the probability of ketones passing into the triplet state when subjected to photoexcitation is very high. The rearrangements also appear to proceed through the triplet state. This may explain the higher quantum yields in the sensitized reactions, which, in contrast to the unsensitized reactions, appear to be a consequence of triplet-triplet energy transfer.

4. SENSITIZED *cis–trans* ISOMERIZATION

cis–trans isomerization relative to the ethylenic bond usually proceeds readily under the action of light[61]. Lewis and coworkers were the first to make a detailed study of photochemical isomerization; they studied the photoisomerization of stilbene in liquid and solid solutions[62]. Because of the stability of both its isomers, the substantial differences in their optical properties, and the high quantum yield in the *cis–trans* conversion, stilbene has also been frequently used in later investigations into the reaction mechanism of direct and sensitized isomerization. Lewis and coworkers compared data on absorption and fluorescence spectra and on quantum yields of the isomerization and concluded that when light is absorbed each isomer passes into its excited electronic level. Transition to the other isomeric form occurs by degradation of the electronic excitation to vibrational excitation, the energy of which is sufficient for rotation of groups in the molecule.

In subsequent papers[63–65], this picture was given concrete expression in accordance with Mulliken's ideas[66,67] on the excited state of ethylene and its derivatives. When the ethylene molecule is excited, the parallel position of the π-orbitals of the C=C bond ceases to be the position most favoured energetically and the orbitals are twisted through an angle of 90°. The triplet state then becomes

more stable than the singlet state. According to Dyck and McClure[63], because of conjugation of the ethylene bond with the phenyl rings in stilbene, a strictly perpendicular position of the π-orbitals in the excited state is not necessarily the most favourable position[63]. However, in the triplet state there must be much less restriction to rotation of groups about the ethylenic bond. A curious feature of the photoisomerization of *trans*-stilbene is the low activation energy of ~ 2 kcal mole^{-1}.[68,69] Stegemeyer suggests that a potential barrier separates the triplet states of *trans*- and *cis*-stilbene[68]. However, a number of other workers consider that this barrier exists in the transition of *trans*--stilbene from the first excited singlet state to the triplet state[63,69,70].

Investigation of the sensitized isomerization of stilbene has confirmed the view that *cis–trans* isomerization proceeds through the triplet state[71,72]. Hammond and coworkers[71] used acetophenone, benzophenone, and anthraquinone as additives in sensitizing the isomerization of stilbene in solution; the triplet levels of these compounds are higher than the triplet level of *cis*- and *trans*-stilbene[71]. In the sensitized reaction, the ratio of the concentration of the *cis*-isomer to that of the *trans*-isomer in a state of photo--equilibrium was found to be $[cis]_{equil}/[trans]_{equil} \simeq 1.5$. For direct isomerization under the action of light, $[cis]_{equil}/[trans]_{equil} \simeq 11$. The ratio of the absorption coefficient of the *trans*-isomer to that of the *cis*-isomer in the 313 nm region is 7.2. These workers consider that if the absorption coefficients were identical, triplet molecules of *cis*- and *trans*-stilbene would be formed at the same rate. In the photoequilibrium state, the ratio $[cis]_{equil}/[trans]_{equil}$ for the direct action of light would then be $11/7.2 \simeq 1.5$, that is, the same value as in sensitized isomerization. In the authors' opinion, this indicates that isomerization proceeds through the triplet state. Malkin and Fischer[69] determined the product of the rate constant for energy transfer from benzophenone to *trans*-stilbene and the lifetime of the benzophenone triplet molecules as $k_{AB}\tau = 2 \times 10^3$ litre mole^{-1}. Assuming that k_{AB} is determined by the diffusion rate (in methylcyclohexane $k_{AB} \simeq 3 \times 10^9$ litre mole^{-1} s^{-1}), they obtained $\tau \simeq 5 \times 10^{-7}$ s. These workers also showed that *trans*-stilbene passes from the triplet state to the lower singlet level of the *trans*- or *cis*--form with about the same probability.

Hammond and coworkers obtained results of particular interest on the sensitized photoisomerization of stilbene, pent-2-ene, 1,2-dichloroethylene, 1,2-diphenylpropene, piperylene, and ethyl maleate–ethyl fumarate in the presence of energy-donor additives with triplet levels lower than the triplet levels of the acceptors[73–76]. The authors explain the occurrence of reaction in this instance by the possibility of "non-vertical" energy transfer to the triplet levels of the energy acceptors which correspond to the already "twisted" position of the groups in the molecule relative to the double bond. Here it is assumed that the triplet level of such a twisted molecule is lower than the triplet level to which the molecule passes when the position of the atoms is unchanged in accordance with the Franck–Condon principle (vertical transitions).

By plotting $[cis]_{equil}/[trans]_{equil}$ for the isomerizing acceptors against the energy of the triplet level of the sensitizers (E_T), Hammond and coworkers obtained peculiar "spectra"[76]. Fig. 3 shows an example of such a spectrum for stilbene. To interpret this spectrum, the authors put forward a scheme for the arrangement of the triplet levels of stilbene (Fig. 4). All the sensitizers with triplet

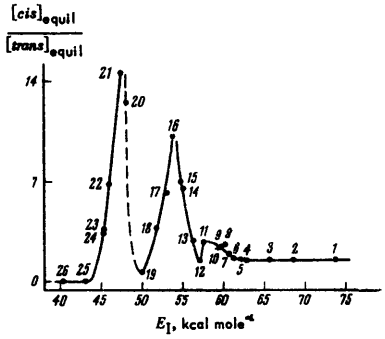


Fig. 3. Sensitized photoiosomerization of stilbene. Dependence of $[cis]_{equil}/[trans]_{equil}$ on the position of the triplet level of sensitizers:
1) acetophenone; 2) benzophenone; 3) thioxanthone; 4) anthraquinone; 5) flavone; 6) Michler's ketone; 7) 4-acetylbiphenyl; 8) 2-naphthyl phenyl ketone; 9) naphthalene-2-carbaldehyde; 10) 2-acetonaphthone; 11) 1-naphthyl phenyl ketone; 12) 1,4-naphthoquinone; 13) 1-naphthalene-1-carbaldehyde; 14) biacetyl; 15) penta-2,3-dione; 16) benzyl; 17) fluorenone; 18) duroquinone; 19) benzoquinone; 2) pyrene; 21) 1,2-benzanthracene; 22) benzanthrone; 23) acridine; 24) 3-acetylpyrene; 25) eosin; 26) 9,10-dibromoanthracene.

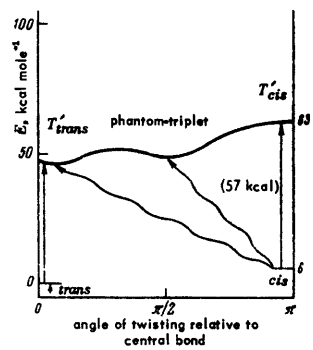


Fig. 4. Potential energy of rotation of stilbene in triplet state.

levels higher than the triplet levels of both stilbene isomers, that is, higher than 63 kcal mole^{-1}, probably give rise to vertical transitions to the triplet levels of both isomers. The ratio $[cis]_{equil}/[trans]_{equil}$ is then ~ 1.5. As the triplet levels of the sensitizers are reduced, the rate of energy transfer to *cis*-stilbene, the triplet level of which is higher than the corresponding level of *trans*-stilbene, apparently decreases faster than the rate of energy transfer to *trans*-stilbene. This leads to an increase in the ratio $[cis]_{equil}/[trans]_{equil}$.

However, at the 57 kcal mole^{-1} point (sensitizer: 1,4--naphthaquinone) corresponding to the O–O transition of *cis*-stilbene from the unexcited singlet state to the triplet state, a distinct minimum is observed (exact resonance). The second maximum (benzyl) corresponds to passage through the resonance condition for the vertical transition of *trans*-stilbene to the triplet level. The subsequent

minimum and maximum are due to non-vertical transitions to the corresponding triplet levels of twisted molecules. Finally, eosin and dibromoanthracene, in which E_T is less than 45 kcal mole^{-1}, can produce non-vertical transition and isomerization of *cis*-stilbene only, since the unexcited singlet level of the latter is 6 kcal mole^{-1} higher than in *trans*-stilbene. Similar spectra are also obtained for other acceptors that undergo isomerization.

Krongauz used the sensitized *trans–cis* isomerization of stilbene to study the triplet molecules of benzene in the liquid phase[77]. When dilute solutions of *trans*-stilbene in benzene are irradiated by light of wavelength 254 nm, which is absorbed almost entirely by the benzene alone, the stilbene is isomerized. In the concentration range studied (10^{-5} to 10^{-3} M), stilbene does not change the luminescence of benzene, that is, it does not deactivate the singlet excited benzene molecules. Energy transfer appears to take place between triplet levels. The lifetime of triplet benzene molecules ($\sim 10^{-6}$ s) and the lower limit of their quantum yield (0.1) were evaluated.

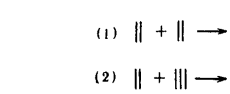
An important feature of this sensitization reaction is that the quantum yield for the isomerization of *trans*-stilbene is inversely proportional to the square root of the intensity of light absorption. This dependence is explained by the fact that the incident light is absorbed in a thin layer of solvent (half the light of wavelength 254 nm is absorbed by a benzene layer about 2.7×10^{-3} cm thick). The transfer of energy from benzene to stilbene also occurs in this layer, which leads to high stationary concentrations of triplet molecules in the thin layer and promotes the possible bimolecular deactivation of these molecules. By analogy with delayed fluorescence, it may be supposed that, when two triplet molecules of *trans*-stilbene interact, excited and unexcited singlet molecules are formed. On the basis of this explanation, the lifetime of *trans*-stilbene in the triplet state was found to be about 10^{-3} s.

Krongauz later used the sensitized isomerization of stilbene as a method of investigating triplet molecules in a liquid with the object of demonstrating the participation of triplet monomer molecules in the initiation of the photopolymerization of methyl methacrylate[78]. Bagdasar'yan suggested this mechanism for the photoinitiation of the polymerization of vinyl monomers[79]. When light of wavelength 254–265 nm acts on dilute solutions of *trans*-stilbene in methyl methacrylate, solvent-sensitized isomerization of the stilbene occurs. At the same time *trans*-stilbene inhibits the photopolymerization of methyl methacrylate, but has no effect on polymerization initiated by material initiators. Since the isomerization of stilbene is caused by energy transfer at triplet levels, it has been concluded that triplet monomer molecules participate in the initiation of photopolymerization.

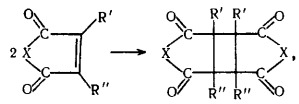
5. SENSITIZED DIMERIZATION AND POLYMERIZATION OF UNSATURATED COMPOUNDS

Bäckström and Sandros[9] studied the triplet-triplet transfer of energy from biacetyl to anthracene and found that, in addition to the quenching of the biacetyl fluorescene, a dimer of anthracene was formed.

Schenck and Steinmetz used sensitized dimerization for the synthesis of a large number of cyclobutane and cyclobutene derivatives[60,80,81]. The formation of cyclodimers by the interaction of two identical, or different, molecules containing C=C or C≡C bonds may be represented by the following scheme:



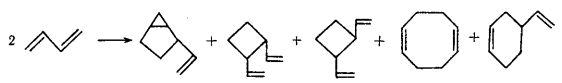
Various aldehydes, ketones, quinones, quinoid dyes, etc. have been used as sensitizers. The sensitization method has been used for the cyclodimerization of indene, coumarin, butadiene, etc., and also for reactions of the following type:



where R = H, CH_3; X = O, NH, N–C_6H_5, or N–C_6H_{11}. Many of these reactions do not occur under the direct action of light. Examples of sensitized reactions in which two different molecules interact include numerous reactions of the anhydrides of maleic and dimethylmaleic acids with benzene, thiophen, cyclohexene, chloro-derivatives of ethylene, furan, butyne, etc. Many of these reactions are recommended for preparative purposes.

After an examination of the mechanism of sensitization, Schenck and Steinmetz were inclined to favour the hypothesis that in many instances there is no transfer of energy but that intermediate biradical addition products are formed[60,82].

In dimerization reactions that occur under the direct action of light, a whole range of isomeric products is generally formed. On the other hand, sensitized reactions usually give a considerably lower number of isomers. For example, five different isomers are formed in the direct photodimerization of butadiene,



but in the sensitized reaction only the last three isomers are formed[56]. The ratios of the amounts of isomers formed depend on the nature of the sensitizer. In the cyclodimerization of isoprene, the distribution of dimerization products also depends on the nature of the sensitizer[83].

In the case of butadiene and isoprene, the ratio of the amounts of dimerization products is determined by the position of the triplet level of the sensitizer; the corresponding relationships form characteristic spectra with a minimum in the region $E_T \simeq 50$ kcal mole^{-1}.[108] The concept of sensitization of non-vertical transitions has been used in the interpretation of these spectra, and it has also been applied to sensitized *cis–trans* isomerizations. Hammond and coworkers[108] have put forward a number of objections to the view of Schenck and Steinmetz that sensitized dimerization proceeds through a stage in which intermediate biradical addition products are formed.

Norrish and coworkers have studied the sensitized photopolymerization of styrene[84,85]. The aromatic hydrocarbons anthracene, pyrene, and chrysene were used as sensitizers that absorb active light. It was shown by the flash photolysis method that additions of styrene (0.3–1.5 M) deactivate the triplet states of anthracene in solution. It was concluded that triplet molecules of anthracene

initiate the photopolymerization of styrene. The results of Norrish and coworkers do not lead unequivocally to this conclusion, since styrene can also effectively deactivate molecules in the singlet excited state[86].

The photoinitiation of polymerization of vinyl monomers by excited molecules of dye additives has been investigated[87-90]. Some workers consider that initiation is preceded by transfer of energy from the additive to the monomer[87]; others consider that polymerization is initiated by triplet molecules of the additive itself[85,88,90]. Solution of the problem is further complicated, because some additives enter into copolymerization or chain-transfer reactions with polymer radicals[78,85].

We are not, of course, here concerned with those reactions in which additive molecules are converted, as a result of decomposition or some other chemical reaction, into radicals that initiate polymerization. We shall only mention the example of sensitized decomposition of a radical initiator of polymerization which has been investigated by Überreiter and Sorge[87]. These workers carried out the photopolymerization of styrene in the simultaneoues presence of the two additives, Neutral Red and benzoyl peroxide, and they found that the dye (as an energy donor) sensitizes decomposition of the peroxide and thus accelerates photopolymerization.

6. OXIDATION–REDUCTION REACTIONS

The intermolecular transfer of energy has been used to elucidate the nature of excited states that participate in various photochemical oxidation–reduction reactions of organic compounds. The photochemical reactions of alcohols with quinones is an important example of these[91].

The photoreduction of benzophenone by alcohols, which was first carried out by Ciamician and Silber[92], proceeds with a high quantum yield and is used as a method for the preparation of benzopinacol. The process appears to occur according to the following scheme[93]:

$$(C_6H_5)_2CO + h\nu \longrightarrow (C_6H_5)_2CO^*,$$
$$(C_6H_5)_2CO^* + R_2CHOH \rightarrow (C_6H_5)_2\dot{C}OH + R\dot{C}OH,$$
$$R_2\dot{C}OH + (C_6H_5)_2CO \rightarrow R_2CO + (C_6H_5)_2\dot{C}OH,$$
$$2\,(C_6H_5)_2\dot{C}OH \rightarrow (C_6H_5)_2{-}\underset{\displaystyle OH}{\overset{|}{C}}{-}\underset{\displaystyle OH}{\overset{|}{C}}{-}(C_6H_5)_2.$$

States corresponding to $n \rightarrow \pi^*$ transitions appear to be the active excited states of carbonyl-containing compounds in these reactions[94].

Hammond and coworkers[12,95] found that the product of the rate constant for the interaction of excited benzophenone molecules with benzohydrol in benzene solution and the lifetime of the excited benzophenone molecules, $k_\gamma\tau$, is about 20 litre mole^{-1}. Assuming that the maximal value of k_γ is about 2×10^9 litre mole^{-1} s^{-1} (if the process is determined by the diffusion rate) these workers obtained a minimum value of 10^{-8} s for τ. In their opinion, the lifetime of the excited benzophenone molecules in the excited singlet state does not exceed 10^{-10} s, and they therefore concluded that triplet molecules take part in the reaction. The introduction of paramagnetic additives, such as oxygen and iron dipivaloylmethide, reduces the rate of reduction of benzophenone; this rate decrease is connected with the deactivation of the triplet state of benzophenone by these compounds. The more precise values of $k_\gamma = 5 \times 10^6$ litre mole^{-1} s^{-1} and $\tau = 4 \times 10^{-6}$ s have been derived from kinetic results on the quenching of benzophenone triplet molecules by oxygen and the iron chelate.

Moore and Ketchum showed that naphthalene is about as effective in reducing the rate of reaction of benzophenone with benzohydrol as are the paramagnetic additives[96]. Naphthalene affects the photoreduction of benzophenone by propan-2-ol in the same way[54]. Since naphthalene is diamagnetic, and its first excited singlet level is higher than the corresponding level of benzophenone, the inhibiting effect of naphthalene is explained by the transfer of energy from benzophenone to naphthalene at triplet levels (see Section 1).

Later, Hammond and Leermakers showed that 2-acetophenone, piperylene, azulene, cyclo-octatetraene, biacetyl, and a number of other compounds that have triplet levels lower than the triplet level of benzophenone are about as effective as naphthalene in inhibiting the photoreduction of benzophenone[97]. These workers consider that this confirms the hypothesis that the rate of triplet-triplet energy transfer in these systems is controlled by diffusion, that is, energy is transferred in each collision of an excited benzophenone molecule with an acceptor molecule.

Using data on the kinetics of the benzophenone-sensitized phosphorescence of benzene solutions of biacetyl, Bäckström and Sandros[98] found that for benzophenone τ is about 2×10^{-6} s; it was assumed that the rate constant for triplet-triplet energy transfer, which is controlled by diffusion, is 1×10^{10} litre mole^{-1} s^{-1}. When propan-2-ol is used as a solvent, quenching of the phosphorescence occurs, evidently because of a reaction between the benzophenone and the alcohol; the lifetime of triplet benzophenone molecules is then reduced to 5.7×10^{-8} s.

The results obtained by Porter and coworkers by flash photolysis provide a direct proof that the triplet state participates in the reduction of benzophenone to benzpinacol[99,100]; it was shown by this method that the intermediates formed in the photolysis of benzophenone in benzene in the presence of propan-2-ol are ketyl radicals, $(Ph)_2{=}C{-}OH$. When naphthalene is added to the solution, the absorption band corresponding to the ketyl radicals disappears, and a new band characteristic of triplet naphthalene molecules appears[101]; virtually no benzpinacol is then formed. The lifetime of triplet benzophenone molecules in propan-2-ol, calculated from data on the kinetics of benzophenone consumption in the presence of naphthalene, is 6×10^{-8} s, which is in good agreement with the results of Bäckström and Sandros.

As in the reaction with benzophenone, the photochemical reaction between quinones and alcohols leads to the removal of hydrogen atoms from the alcohol and reduction of the quinone[102,103]. The following is a possible reaction scheme[104]:

$$Q + h\nu \rightarrow Q^*,$$
$$Q^* + R_2CHOH \rightarrow Q\dot{H} + R_2\dot{C}OH,$$
$$Q\dot{H} + R_2CHOH \rightarrow QH_2 + R_2\dot{C}OH,$$
$$2Q\dot{H} \rightarrow Q + QH_2,$$
$$2R_2\dot{C}OH \rightarrow R_2CO + R_2CHOH,$$

where Q is the quinone molecule and QH$^\cdot$ is a semiquinone radical.

Obviously, the nature of the active excited state may differ in different quinones.

Bridge and Porter, who used the method of flash photolysis to study the intermediate particles formed in the photoexcitation of duroquinone in various solvents, showed that the disappearance of quinone triplet molecules and the formation of the semiquinone radical are independent processes that proceed at different rates [105]. From this it was concluded that the reduction of duroquinone proceeds through the excited singlet state. At the same time, the photoreduction of anthraquinone by propan-2-ol is greatly retarded in the presence of anthracene or naphthalene and it does not change in the presence of biphenyl [27]. The triplet levels of the first two hydrocarbons are lower, and that of the third is higher, than the corresponding anthraquinone level. For this reason, the inhibiting action of these additives is due to the transfer of energy from the anthraquinone triplet level, which appears to be the photochemically active level in this reaction.

In the presence of oxygen the mechanism of oxidation–reduction reactions may undergo substantial change [21]; oxygen itself then plays the part of the oxidant, and it is sensitized by the components that absorb light. In many instances (see, for example, Karyakin [106]), the reactions proceed through a stage in which intermediate peroxide compounds are formed. It is possible, however, that even here energy transfer from the sensitizer to oxygen is of considerable importance. Thus, Porter and Windsor [107] proposed the following scheme, which includes energy transfer, to explain the photo-oxidation of hydrocarbons by oxygen sensitized by anthracene:

$$A^T + O_2^T \rightarrow A^{S_0} + O_2^S,$$
$$O_2^S + RH \rightarrow R^{\cdot} + HO_2,$$
$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot},$$

where O_2^T is the triplet ground state of oxygen and O_2^S is an excited singlet state.

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The material discussed in this review shows that the phenomenon of intermolecular transfer of excitation energy plays an important part in photochemical reactions of organic compounds in solution. In many instances the redistribution of the primarily absorbed light energy between the components of the solution considerably changes the course of the photochemical reaction. In particular, some reactions that proceed very slowly or not at all under the direct action of light can be induced by energy transfer from sensitized additives.

Sensitization and inhibition effects in photochemical reactions produced by intermolecular energy transfer are frequently used to elucidate the nature of excited states resulting from the action of light. An important advantage of sensitized photochemical reactions is their "cumulativeness", or their capacity to accumulate changes in the acceptor molecules that occur with the transfer of energy. This allows investigation of systems that are difficult to study by the luminescence method because of small quantum yields of the excited molecules under examination.

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OPTICALLY ACTIVE CHELATE COMPOUNDS

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I. INTRODUCTION

The exceptional sensitivity of optical rotation to various types of reaction (structural changes, intermolecular interaction, etc.) and the unique nature of the properties of optically active compounds is leading to the broad extension of