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Spectral Sensitisation of Photoprocesses in Polymeric Donor-Acceptor Systems

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Processes are considered which involve the spectral sensitisation of polymeric electron donor-electron acceptor (EDA) systems as a result of which an electron is transferred and charged species are formed under the influence of visible light. Problems of the practical utilisation of the phenomenon in the development of light-sensitive recording layers, photovoltaic cells transforming light into electrical energy, and polymeric photoconductors are discussed.
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I. INTRODUCTION

The sensitisation of electron transfer reactions in EDA complexes to radiation at specific wavelengths, particularly in the visible spectral range, has been studied in detail as a fundamental problem of the effect of electromagnetic radiation on organic systems and also in connection with the possible practical applications of this phenomenon. This concerns the employment of organic complexes as photoconductors, as light-sensitive recording layers, and in photovoltaic cells transforming solar energy into electrical energy. The sensitisation is important also in the photochemical oxidation of organic compounds and in the utilisation of solar energy by photochemical methods.

In the present review the concept of "polymeric electron donor–electron acceptor (EDA) complexes" includes not only complexes formed by polymeric components but also complexes which contain low-molecular-weight compounds distributed in a polymer matrix.

Questions concerning the spectral sensitisation of polymer compositions, incorporating donors (D), acceptors (A), and also weak charge-transfer complexes (CTC or D.A) are examined below. The sensitisation is achieved by introducing an additional component—the sensitiser (S), which exhibits optical absorption in the specified wavelength range. The present review does not discuss processes described in detail in existing publications[1-3] and based on the ionic dissociation reaction of polymer CTC ($D.A \xrightarrow{h\nu_{CTC}} D^{\ddagger} + A^{\bar{}}$) as a result of direct photoexcitation. We shall consider reactions involving sensitised electron transfer and reactions due to the sensitised formation of singlet oxygen.

1. The Principal Types of Sensitised Charge-Transfer Reactions

(a) Reactions with Participation of the Sensitiser in Electron Transfer

The sensitiser forms CTC with the donor or acceptor component:

$$^1(D.S)_0 \xrightarrow{h\nu_S, h\nu_{CTC}} {}^1(D^{\ddagger}S^{\bar{}})_1 \rightarrow {}^3(D^{\ddagger}S^{\bar{}})_1 \xrightarrow{^1A_0} {}^{1,3}[D^{\ddagger}...A^{\bar{}}]_0 + {}^1S_0, \quad (I)$$

($^1A_0$; $[D_1^{+} + A_1^{-}]$)

$$^1(S.A)_0 \xrightarrow{h\nu_S, h\nu_{CTC}} {}^1(S^{\ddagger}A^{\bar{}})_1 \rightarrow {}^3(S^{\ddagger}A^{\bar{}})_1 \xrightarrow{^1D_0} {}^{1,3}[D^{\ddagger}...A^{\bar{}}]_0 + {}^1S_0. \quad (II)$$

($^1D_0$)

Here $^{1,3}(D^{+}S^{\bar{}})_0$ and $^{1,3}(S^{+}A^{\bar{}})_1$ are the singlet- or triplet-excited complexes and $^{1,3}[D^{+}...A^{\bar{}}]_0$ is a geminal radical-ion pair in a singlet or triplet state.

The sensitiser forms a collision complex with the donor or acceptor component and also with the complex $^1(D.A)_0$:

$$^1S_0 \xrightarrow{h\nu_S} {}^1S_1 \rightarrow {}^3S_1 \xrightarrow{^1D_0} {}^{1,3}S_1 \cdot {}^1D_0 \rightarrow {}^{1,3}[D^{\ddagger}...S^{\bar{}}]_0 \rightleftarrows D^{\ddagger} + S^{\bar{}}; \quad (III)$$

($^1S_0 \xrightarrow{h\nu_S} {}^1S_1$)

secondary reaction:

$$^{1,3}[D^{\ddagger}...S^{\bar{}}]_0 \text{ (or } S^{\bar{}}) + {}^1A_0 \rightarrow {}^1S_0 + D^{\ddagger} + A^{\bar{}} \rightarrow D_1^{+} + A_1^{-};$$
$$^1S_0 \xrightarrow{h\nu_S} {}^1S_1 \rightarrow {}^3S_1 \xrightarrow{^1A_0} {}^{1,3}S_1 \cdot {}^1A_0 \rightarrow {}^{1,3}[S^{\ddagger}...A^{\bar{}}]_0 \rightleftarrows S^{\ddagger} + A^{\bar{}}; \quad (IV)$$

($^1S_0 \xrightarrow{h\nu_S} {}^1S_1$)

secondary reaction:

$$^{1,3}[S^{\ddagger}...A^{\bar{}}]_0 \text{ (or } S^{\ddagger}) + {}^1D_0 \rightarrow {}^1S_0 + D^{\ddagger} + A^{\bar{}} \rightarrow D_1^{+} + A_1^{-};$$
$$^1S_0 \xrightarrow{h\nu_S} {}^1S_1 \rightarrow {}^3S_1 \xrightarrow{^1(D.A)_0} {}^{1,3}S_1 \cdot {}^1(D.A)_0 - \begin{cases} \rightarrow {}^{1,3}[S^{\ddagger}...DA^{\bar{}}]_0 \rightarrow \\ \rightarrow {}^{1,3}[D^{\ddagger}A...S^{\bar{}}]_0 \end{cases}$$

($^1S_0 \xrightarrow{h\nu_S} {}^1S_1$)

$$\rightarrow {}^1S_0 + (D^{\ddagger} + A^{\bar{}}) \rightarrow D_1^{+} + A_1^{-}. \quad (V)$$

$^{1,3}S_1 \cdot {}^1D_0$, $^{1,3}S_1 \cdot {}^1A_0$, and $^{1,3}S_1 \cdot {}^1(D.A)_0$ are collision complexes.

(b) The Sensitiser Subjected to One-Quantum or Two-Quantum Excitation is the Donor of Triplet Energy

$$^1S_0 \xrightarrow{h\nu_S,\ S_1 - T_1} \begin{cases} {}^3S_1 \\ {}^3S_2 \end{cases} \rightarrow \begin{cases} {}^1(D.A)_0 \ {}^1S_0 + {}^3(D^{\ddagger}A^{\bar{}})_1 \rightarrow D^{\ddagger} + A^{\bar{}} \rightarrow D_1^{+} + A_1^{-}, \\ {}^1D_0 \ {}^1S_0 + {}^3D_1 \xrightarrow{^1A_0} ({}^3D_1 \cdot {}^1A_0), \\ {}^1A_0 \ {}^1S_0 + {}^3A_1 \xrightarrow{^1D_0} ({}^1D_0 \cdot {}^3A_1) \end{cases} \quad (VI)$$

$^1S_0 \xrightarrow{h\nu_S,\ S_1 - T_1} {}^3S_1 \xrightarrow{h\nu_S}$

Processes (I)–(VI) have come to be referred to as autosensitisation when $S \equiv D_1^{+}$ or A_1^{-}.

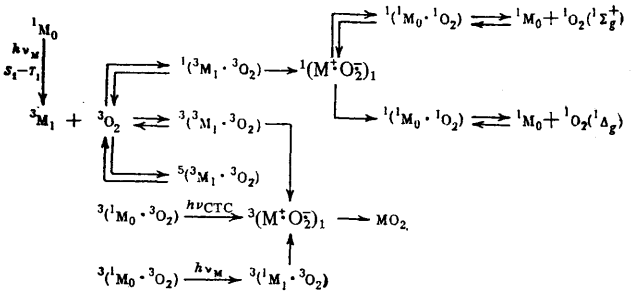
(c) Reactions with Participation of Singlet Oxygen

In the presence of O_2, singlet molecular oxygen is formed in the reaction with the triplet-excited organic molecule ($^3M_1$) ($^1O_2$ can be in the $^1\Sigma_g^{+}$ and $^1\Delta_g$ states). The reactions involving $^1O_2$ are used in information recording processes.

The quantum yield of $^1O_2$ is determined by the relative positions of the $E(^3M_1)$ level and the level of the excited charge-transfer state $E[^{1,3}(M^{+}O_2^{-})_1]$.

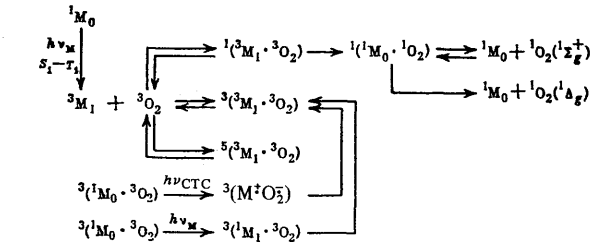
When the $E[^{1,3}M^{+}O_2^{-})_1]$ level lies below $E(^3M_1)$, singlet oxygen is formed via the following reactions:

Scheme 1



When the $E[^{1,3}(M^{+}O_2^{-})_1]$ level lies above $E(^3M_1)$,[4,5] the direct involvement of the $^{1,3}(M^{+}O_2^{-})_1$ states in the process is ruled out:

Scheme 2



Comparison of the reactions via Schemes 1 and 2 shows that in the latter case only one pathway leads to the decomposition of the collision complex $^3M_1.^3O_2$ via the singlet state $^1(^3M_1.^3O_2)$ with formation of singlet oxygen, while in the former case, other conditions being equal, the reaction involving the decomposition via the state $^3(M^{+}O_2^{-})_1$, which does not lead to $^1O_2$, is included. Taking into account the ratios of the populations of levels with different multiplicities, one can postulate that the quantum yield in the formation of singlet oxygen via Scheme 2 will exceed by a factor of 4 the quantum yield in the formation reaction via Scheme 1.

II. PROBLEMS OF THE PRACTICAL UTILISATION OF SENSITISED ELECTRON PHOTOTRANSFER IN EDA COMPLEXES

In the development of recording polymeric donor–acceptor systems for photovoltaic cells sensitive to a given wavelength range, the sensitisers employed are dyes of different classes (cyanine, thiazine, xanthene, etc., dyes), variable valence ions, porphyrins, which are used in silver halide photography[6,7] and in the creation of liquid-phase photochemical systems transforming the energy of solar radiation into electrical or chemical energy.[8–11]

The reduction of acceptors [viologens (V^{2+})] sensitised by ruthenium complexes [including tris(2,2′-bipyridyl)ruthenium(II) or $Ru(bipy)_3^{2+}$], porphyrins, and dyes in the presence of donors of different nature has been successfully investigated in recent years in connection with the search for new systems for the storage of solar energy.[8–12] At the same time, in order to create non-silver (or low-silver) information recording systems, studies have been made of the reduction of acceptors (viologens) in the donor matrix of poly(vinyl alcohol) (PVA) under the conditions of the photoexcitation of additionally introduced sensitisers: riboflavin[13,14] and benzophenone.[15] For this purpose, we can also employ a system comprising V^{2+} and $Ru(bipy)_3^{2+}$ incorporated in a cellophane matrix.[12] A high sensitivity has been obtained in the composition deposited on a triacetate support and comprising PVA as the donor, *NN*′-bis(*p*-cyanophenyl)-4,4′-bipyridyl chloride as the acceptor, and riboflavin as the sensitiser. Excitation of riboflavin by light with $\lambda \cong 360$–440 nm in the PVA donor matrix ensures electron transfer from the matrix to the sensitiser with formation of the reduced form of riboflavin—a semiquinone radical, with a quantum yield of 0.09.[16] In the presence of V^{2+} the subsequent dark electron transfer from this radical to viologen ensures the formation of latent image centres—the radical-cations V^{+}, for the visualisation and enhancement of which a physical development process is employed[14] with formation of a visible image made up of metallic silver:

$$B^{+} + Ag^{+} \rightarrow B^{2+} + Ag^{0};\ Ag^{0} + nAg^{+} + nFe^{II} \rightarrow Ag^{0}Ag_n + nFe^{III}$$

The sensitivity $S_{0,1}$ to monochromatic light with $\nu_{inc} = 436$ nm was determined as the reciprocal of the exposure $H_{0,1}$ (in J cm^{-1}) for which the optical density on the exposed sections exceeds after development by 0.1 the optical density on the unexposed sections (the fog density):[14]

$$S_{0,1} = 1/H_{0,1} = 6.62 \cdot 10^3 \text{ cm}^2 \text{ J}^{-1}$$

Attempts have been made to create liquid-phase photogalvanic cells based on the photochemical reduction of thiazine dyes in the presence of iron(II).[17,18] Different versions of the recording of the effect of light, consisting in the photochemical reduction of thiazine dyes in the presence of donors of different nature and subsequent electron transfer from the reduced form of the dye to the metal cations in solid matrices, have been described by Oster.[19]

The products of the photochemical reduction of thiazine dyes—semiquinone radicals—initiate the polymerisation of vinyl and acrylic monomers.[19–22] A system based on the polymerisation of acrylic monomers initiated by the radical-cations MbH^{+} (Mb^{+} is the dye Methylene Blue) has been used for the phase recording of holograms.[23] The effective photochemical reduction of Mb^{+} was ensured by the presence in the reaction mixture of a donor—toluenesulphonic acid. The holograms were recorded by means of laser radiation with $\lambda = 632.8$ nm, which induces the photoexcitation of the dye Mb^{+}. It has been established[23] that two mechanisms are responsible for the phase recording: the first involves the formation of the relief and the second involves a change in the refractive index of the medium as a result of polymerisation. 4-Nitrophenylacetic acid was introduced into the reaction mixture to fix the light-sensitive layer. The dye Mb^{+} decomposes irreversibly under the conditions of the photoexcitation of the acid by UV radiation. A light sensitivity of ~10^3 cm^2 J^{-1}, a resolution of 1500 mm^{-1}, and a diffraction efficiency of ~45% were attained: the contribution by the change of the refractive index is ~12% and the modulation of the thickness is ~33%.

Gelatine layers containing *N*-vinylcarbazole (VCA and CBr_4, distributed in the matrix in the form of particles whose size ranges from 0.5 to 20 μm, exhibit a high light sensitivity, approaching that of silver halide emulsions ($S_{0,2} = 3 \times 10^6$ cm^2 J^{-1} for the negative process and 3×10^4 cm^2 J^{-1} for the positive process).[24] Depending on the order in which photoexcitation and heat treatment are applied, a positive or negative process is achieved. Under the conditions of the photoexcitation of the sensitiser—the VCA.CBr_4 CTC, the latter undergoes ionic dissociation with formation of the active products VC^{+} and $Br^{-}...\dot{C}Br_3$, which initiate the polymerisation of VCA whose high concentration is due to its disperse

state. A high quantum yield of the polymer is achieved by the subsequent intensification of the image by the alternate heat treatment of the entire layer and its exposure to intense illumination.

Sensitised donor–acceptor systems based on diazonium salts [*p*-aminobenzenediazonium sulphate and salts having the general formula $p\text{-}X\text{–}C_6H_4\text{–}\overset{+}{N}\equiv N\ BF_4^-$, where X = $(C_2H_5)_2N$, CH_3O, Br, CH_3COO, or NO_2] as acceptors[16,25–33] have been proposed for the recording of information. The donors employed are toluenesulphonic acid, sodium toluene-*p*-sulphonate, diphenylamine, 1,4-diazobicyclo[2.2.2]octane,[25–28] hypophosphorous acid, ascorbic acid, and the polymeric PVA matrix [combined with poly(ethylene glycol) as plasticiser].[16, 29–33]

The sensitisers are dyes (thiazine, acridine, and xanthene dyes), riboflavin,[16,25–33] and variable-valence ions.[33] The essential components are also phenols and an acid stabiliser. In these systems the recording of information is due to the decomposition of the acceptors (diazonium salts) as a result of electron transfer, initially from the donor to the photoexcited sensitiser and then from the reduced sensitiser to the acceptor.

The image appears on treatment of the exposed layer with ammonia, which transforms the phenol RC_6H_4OH into phenoxide ions ($RC_6H_4O^-$). The latter, which have more pronounced electron-donating properties than RC_6H_4OH, enter into the dark azo-coupling reaction with the acceptor preserved in the unexposed sections—the diazonium salts. This leads to the formation of the azo-dye and the colouring of the unexposed sections:

$$ArN_2^+ + RC_6H_4O^- \rightarrow Ar\text{—}N{=}N\text{—}RC_6H_3OH$$

The products of the photochemical decomposition of the diazonium salts do not react with phenoxide ions.

Depending on the polarity of the medium, the diazonium salts decompose via either ionic (heterolytic decomposition in polar matrices) or radical (homolytic decomposition in nonpolar matrices) mechanisms:

$$p\text{-}X\text{—}C_6H_4\text{—}N_2^+ + e \rightarrow p\text{-}X\text{—}C_6H_4^{\cdot} + N_2$$

As a result of the interaction of the aryl radicals formed in the homolytic decomposition with H-donors (RH), new electron-donating free radicals R$^{\cdot}$, inducing the additional decomposition of the diazonium salt, are formed.[16,27] The formation of free radicals is used to initiate the polymerisation of the acrylamide introduced additionally into the layer.[28] The photoexcitation of Mb^+ by light with $\lambda = 665$ nm in a system containing *p*-aminobenzenediazonium sulphate as the acceptor, sodium toluene-*p*-sulphonate as the donor, Mb^+ as the sensitiser, and also acrylamide results in the formation of polyacrylamide (molecular weight $M = 7 \times 10^6$) with a quantum yield $\phi = 1.3 \times 10^4$. As noted above, the photosensitive dye Mb^+ initiates the polymerisation of monomeric acrylamide derivatives even in the absence of a diazonium salt. For example, the transformation of acrylamide into the polymer ($M = 9 \times 10^5$) has been found to occur[28] with a quantum yield of 1.7×10^3.

Layers based on polyvinylcarbazole (PVCA) and polyepoxypropylcarbazole (PEPC) as donors with acceptors of different nature, after the additional introduction of sensitising dyes, acquire a photosensitivity over a wide spectral range, including the absorption band of the dye. Rhodamine 6G, coumarin 6,[34] eosin,[35] as well as cyanine dyes with electron-accepting properties,[36] whose ground level lies below the upper limit of the valence band of PVCA are effective spectral sensitisers for PVCA. The effects of the sensitised photoconductivity in these systems have been discussed in detail.[1–3]

It is noteworthy that injection and chemical sensitisations are widely used for PVCA layers. Injection sensitisation at the PVCA/selenium boundary arises when aromatic molecules are introduced and is due to the formation on the interface of CTC between selenium and the aromatic molecule,[37] which equalise the "ceilings" of the valence bands of selenium and PVCA and ensure the transfer to PVCA of the holes† photogenerated in selenium.

Chemical sensitisation is ensured by the introduction of additives such as trichloroacetic acid[38] and diazonium salts[39–43] in a system consisting of a donor (PVCA) and a spectral sensitiser or acceptor (*o*-dinitrobenzene, trinitrofluorenone). The introduction of such additives increases the photoconductivity of the system almost by an order of magnitude and leads to the appearance of a "memory effect" consisting in an increase by 3–4 orders of magnitude (up to 24 h) of the time during which the photocurrent decreases after the illumination has been switched off. The effects are associated with the interaction of the radical-anions ($A^{\cdot-}$ or $S^{\cdot-}$), formed in the phototransfer of electrons, with the additive introduced (for example, $A^{\cdot-} + H^+ \rightarrow HA^{\cdot}$), which lowers the rate constants for the bulk-phase recombination of the electron–hole pairs. The "memory effect" is used in the recording of information under electrophotographic conditions. A simplified scheme for the electrophotographic process on PVCA layers consists in the following steps: the layers are negatively charged uniformly with the aid of a corona discharge. After exposure, free holes, recombining with the surface negative charge, are generated in the section of the layer acted upon by light. This results in the formation of potential relief on the surface, which reproduces the distribution of illumination during exposure. The development is carried out with the aid of charged dye species.[1,44,Ch.2] The time required for this process, from exposure to development, is determined by the "retention" time of the charge on the surface, which generally speaking is short (not more than several minutes). The "memory effect" makes it possible to simplify significantly this process and to expose the uncharged surface of the film, i.e. to separate the charging and exposure stages in time and as regards apparatus. The retention of increased electroconductivity on the exposed section permits the visualisation of the image by charging the surface along time after exposure.

In photovoltaic cells and in information recording processes, it is possible to use systems which are a combination of thin metal layers and organic semiconductors. Layers of pure PVCA or PVCA containing disperse ZnO,[45] deposited on a metallic layer, are used for the electrophotographic process. In order to sensitise these systems with respect to visible light, a dye is introduced at the metal/organic layer interface. By employing dyes of different nature (sensitisers for either ZnO or PVCA), it has been established[45] that the primary stage is the photochemical oxidation of the sensitiser dye with electron transfer from the photoexcited dye to ZnO, while the secondary stage is the electron transfer from PVCA to the oxidiser sensitiser. As a result of this process, a pair of charged species is generated, which can recombine or move apart into space, contributing to the photoconductivity of the layer.

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†Here and henceforth we shall speak of *p*-type (holes) and *n*-type (electrons) charge carriers in those cases where there is a possibility of the movement of electrons via the $M\ldots M^{+}\ldots M$ and $M\ldots M^{\cdot-}\ldots M$ systems, where M is a neutral molecule and M^+ and $M^{\cdot-}$ are radical-cation and radical-anion respectively.

The use of organic layers in photovoltaic cells for the transformation of solar energy into electrical energy is of special interest. The Schottky barrier, arising in the organic layer when it comes into contact with the metal, is usually employed for this purpose. Since the organic semiconductors usually exhibit *p*-type conductivity, a necessary condition for the formation of the Schottky barrier is $\Phi_m < \Phi_{sc}$ (Φ_m and Φ_{sc} are the electron work functions for the metal and semiconductor respectively). In this case, the organic metallic layers are charged positively and negatively respectively on contact, the height of the Schottky barrier does not exceed the difference $V_0 = \Phi_{sc} - \Phi_m$, and the electric field in the barrier region is $E_d = 2V_0/d$ (d is the width of the barrier).

The advantages of systems based on the Schottky barrier are the low cost of the necessary components and the ease of divising a technology for the preparation of the cells. Among the numerous studies devoted to this problem, we shall be interested in communications about the preparation of organic layers based on phthalocyanine without a metal (Phtc) dispersed in a polymer matrix.[46-48] Maximum efficiencies for organic systems (several per cent) have been attained on such layers sensitised by dyes. In principle, the mechanism of the generation of charge carriers in these systems is the same as in organic layers with a homogeneous distribution of the dye and semiconductor in the polymer. However, there are also specific features associated with the fact that the dye is distributed at the disperse Phtc/metal interface. In this case the redox processes in the solid-phase system proceed with electron transfer across the interface. Furthermore, for Phtc it is possible to employ the ideas of the band model of solids. Compared with the sputtered Phtc layers, polymer layers with dispersed Phtc particles make it possible to obtain cells with much higher efficiencies.[48] The main element of the photovoltaic cell is a thin (~1 μm) layer of the polymer (PVA, PVCA, polycarbonate) in which the particles of polycrystalline Phtc, with linear dimensions of several hundreds of ångstroms, are linearly distributed. This layer is deposited on a conducting support forming an ohmic contact with the latter (this requires the fulfillment of the condition $\Phi_{sup} > \Phi_{Phtc}$). A transparent layer of SnO_2 on glass or quartz and also metals (Au, Ag, Cu, Pt), are used as the conducting supports. A semitransparent layer of metal with a low electron work function is sputtered onto the free surface of the organic layer. The most stable characteristics of the cells have been obtained with indium ($\Phi_{In} = 4.0$ eV, $\Phi_{Phtc} = 5.1$ eV). When the cell is illuminated from the side of the metallic layer (for the maximum effectiveness, it is important that all the light is absorbed in the region of the barrier), electron–hole pairs are generated, are separated in the field E_d, the electron passes to the metal, and the positive charge passes into the bulk phase of the semiconductor. If the cell is in a closed electric circuit, then a short circuit current I_{sc} arises in the circuit on illumination. When the circuit is broken, a potential difference is generated in the metallic and SnO_2 layers—the open-circuit photo-e.m.f. (V_{oc}) which cannot exceed V_0. When a load resistance R is included in the external circuit, its value determines V and I generated when the cell is illuminated and the useful work is then VI.

The photo-e.m.f. and the photocurrent at which the useful work is a maximum are designated by V_{max} and I_{max}. In order to estimate the efficiency of the cell, the so called filling factor F is introduced:[34]

$$F = \frac{I_{max} V_{max}}{I_{sc} V_0}$$

I_{sc}, V_0, and F can be calculated from the voltage–current characteristic of the cell on illumination.

The efficiency of the photovoltaic cell can be calculated relative to the intensity of the light incident on the cell L_0:

$$\eta = \frac{I_{sc} V_0 F}{L_0} \cdot 100\% \qquad (1)$$

or relative to the intensity of the light which has passed through the metallic electrode L_T:

$$\eta' = \frac{I_{sc} V_0 F}{L_T} \cdot 100\% \qquad (2)$$

The efficiency η characterises the efficiency of the cell as a whole and η' characterises the efficiency of the transformation of the energy at the barrier.

The quantum efficiency of the photogeneration of charge carriers can be obtained from I_{sc}:[34]

$$\varphi = 1.24 I_{sc}/L_T \lambda_{inc}, \qquad (3)$$

where I_{sc} is expressed in A cm^{-2} and L_T in W cm^{-2}; λ_{inc} (nm) is the wavelength of the incident radiation.

The photocurrent spectrum is correlated with the absorption spectrum of Phtc, which indicates the independence of ϕ of λ_{inc} ($\phi = 0.27$ and $F = 0.33$). For monochromic radiation, $\lambda_{inc} = 670$ nm, $L_T = 6$ μW cm^{-2}, $I_{sc} = 1.4 \times 10^{-6}$ A cm^{-2}, $V_0 = 0.86$ V, $\eta' = 6.5\%$, and $\eta = 2\%$. However, for radiation having the same spectral composition as sunlight, $L_T =$ 1 mW cm^{-2} (0.01 of the intensity of solar radiation) and $\eta' =$ 0.5%. With increase of L_T to 10 mW cm^{-2}, η' falls to 0.07%. The most readily understood pathways leading to an increase of η' are associated with the increase of I_{sc} owing to the increase of ϕ and the more effective absorption of sunlight, since the optical absorption by Phtc in the green part of the spectrum, where the maximum energy of solar radiation is concentrated, exhibits a break. The increase of ϕ on excitation by light corresponding to the absorption band Phtc can be achieved as a result of the chemical sensitisation of the system, for example, by introducing an acceptor which forms a CTC with Phtc. By selecting dyes having an absorption maximum in the green gap in the absorption by Phtc, it is possible to achieve the spectral sensitisation of the layer, which should ultimately also lead to an increase of ϕ and I_{sc}. The mechanisms of sensitisation have been discussed in two communications[34,35] and will be described in Section III.

Layers for the recording of information based on CTC between donors [aromatic amines (Am)] and acceptors (carbon tetrabromide (CBr_4) or bis(tribromomethyl) sulphone ($CBr_3SO_2CBr_3$)], which are sensitive to light in the wavelength range below 500 nm, have been sensitised with respect to visible light by the introduction of cyanine dyes;[3, Ch. 5; 44, Ch. 6; 49,50]. As in the silver halide process, the spectral sensitisation of these non-silver photographic systems is due to electron phototransfer reactions.

Non-silver photographic systems based on CTC between donors of different nature [the leuco-form of Crystal Violet,[51] PVCA,[52] 1,1-bis(*p*-dimethylaminophenyl)ethylene and *p*-diethylaminostyrylquinoline,[53] and benzyldiphenylamine and dibenzylaniline;[3, Ch. 5; 44, Ch. 6] and acceptors (CBr_4 and CHI_3) exhibit a high light sensitivity ($S_{02} \cong 10^5$ cm^2 J^{-1} [3,13,51-58]) by virtue of the possibility of the optical intensification of the latent image, first established by Fotland.[51] The possibility of the optical intensification of the latent image is due to the fact that the coloured product formed as a result of the photodissociation of the CTC (in the final form[13,51-53,55-57] or intermediate form[3, Ch. 5; 44, Ch. 6; 50,58]) is a sensitiser (autosensitiser) of a CTC-based composition for light in the region of the intrinsic absorption. The idea has been

developed[51-53] that the mechanism of the optical intensification is due to the transfer of triplet energy from the photoexcited coloured product to the nearest CTC. A two-quantum mechanism of this process in the system based on the CTC between benzylamines and CBr_4 has been established.[58]

III. REACTIONS WITH PARTICIPATION OF THE SENSITISER IN ELECTRON TRANSFER

1. Energy Relations

In estimating the efficiency of electron transfer, the relative positions of the energy levels of the interacting components are compared. Together with energy characteristics such as the ionisation potential of the molecule I_M (I_D for the donor) or the electron affinity of the molecule E_M (E_A for the acceptor) in the condensed phase one uses the equilibrium oxidation-reduction potentials. The relation between these quantities is given by Eqns.(4) and (4a) for the ionisation potential and (5) and (5a) for the electron affinity

$$I_M^p = I_M^{liq} + (E_M^+ - P_M^+), \quad (4)$$

$$I_M^{liq} = I_M^{gas} - E_M^+ = E_0 + eE_{1/2}(M/M^+), \quad (4a)$$

$$E_M^p = E_M^{liq} - (E_M^- - P_M^-), \quad (5)$$

$$E_M^{liq} = E_M^{gas} + E_M^- = E_0 + eE_{1/2}(M^-/M). \quad (5a)$$

Here the superscripts p, liq, and gas denote the values of I_M and E_M in the polymer and in the liquids and gas phases respectively, E_M^+ or $E_M^- = (e^2/2r^\pm)(1 - 1/\kappa)$ is the change in the real solvation energy in the liquid phase in the transition from the molecule to the radical-cation or radical-anion respectively, κ the dielectric constant of the liquid in which the potentials $E_{1/2}^{ox, red}$ have been measured,

$$P_M^+ \text{ or } P_M^- = \frac{e^2}{2r^\pm}\left(1 - \frac{1}{\kappa_p}\right) \quad (6)$$

the change in the polarisation energy of the polymer in the transition from the molecule to the radical-cation or radical-anion respectively, κ_p the dielectric constant of the polymer layer, $r^\pm$ the radius of the radical-cation or radical-anion respectively, $E_{1/2}^{ox} \equiv E_{1/2}(M/M^+)$ the equilibrium potential of the oxidation of the molecule via the redox reaction

$$M \rightleftarrows M^+ + e(S \rightleftarrows S^+ + e,\ D \rightleftarrows D^+ + e), \quad (VII)$$

$E_{1/2}^{red} \equiv E_{1/2}(M^-/M)$ the equilibrium potential of its reduction via the redox reaction

$$M^- \rightleftarrows M + e(S^- \rightleftarrows S + e,\ A^- \rightleftarrows A + e), \quad (VIII)$$

and E_0 the position of the level of the reference electrode relative to which the equilibrium oxidation-reduction potentials $E_{1/2}(M/M^+)$ and $E_{1/2}(M^-/M)$ measured in the liquid phase are reckoned. According to Gurevich and co-workers,[59-61] $E_0 = \Phi + e\Delta\Phi$—reckoned from the vacuum energy of the electron in the Fermi level of the reference electrode at the equilibrium electrode potential—is determined as the electron work function (for the ejection of the electron into the gas phase) of the material of the reference electrode (Φ) with allowance for $\Delta\Phi$, where $\Delta\Phi$ is the surface potential jump due to the interaction of the reference electrode with the oriented solvent molecule; $\Delta\Phi$ depends on the nature of the reference electrode and the solvent.[59,60] Using $\Phi = 4.5$ eV and $e\Delta\Phi = -0.07$ eV for the platinum reference electrode in 1 *N* aqueous acid solution (normal hydrogen electrode: n.h.e), $E_0 = 4.43$ eV (n.h.e) was obtained.[60,61] This corresponds to $E_0 = 4.67$ eV (saturated calomel reference electrode: sat.c.e) and $E_0 = 4.62$ eV [silver chloride reference electrode in the 1:1 (vol.%) methanol: water mixture: Ag/AgCl].[62]

It has been noted[59] that the potential $\Delta\Phi$ is known only for some metal–solution combinations. Apparently for this reason E_0 is frequently identified with Φ. For example, E_0 has been estimated in a review,[8], p.199 as $\Phi = 4.5$–4.7 eV (n.h.e.).

It follows from the analysis of literature data that $\Delta\Phi' = 0.53$ V, i.e. the potential of the reaction at the reference electrode

$$e\ (\text{in Hg}) + HgCl_{surf} \rightleftarrows Hg^0 + Cl^-.$$

and not $E_0 = 5.07$ eV (sat.c.e.),[63,64] obtained on the basis of the idea that $E_0 = \Phi + e\Delta\Phi'$ in which $\Phi = 4.54$ eV was adopted, has been used in investigations in recent years.

The energy E_0 of the saturated calomel electrode has been calculated[65] from the measured redox potentials in aromatic hydrocarbons (AH). E_0 was obtained by adding together Eqns.(4a) and (5a) for the same molecule:

$$E_0 = \frac{I_{AH}^{gas} + E_{AH}^{gas}}{2} - \frac{e[E_{1/2}(AH/AH^+) + E_{1/2}(AH^-/AH)]}{2} + (E_{AH}^- - E_{AH}^+).$$

According to experimental data, we have

$$(I_{AH}^{gas} + E_{AH}^{gas})/2 = 4.34 \text{ eV};$$

$$\frac{e[E_{1/2}(AH/AH^+) + E_{1/2}(AH^-/AH)]}{2} = -0.31 \text{ eV (sat.c.e.)};$$

$$E_{AH}^+ = E_{AH}^- = 1.94 \text{ eV}.$$

Thus $E_0 = 4.65$ eV (sat.c.e.). According to experimental estimates for aromatic hydrocarbons,[65,66,67] arylazonaphthols,[68] and cyanine dyes,[69] $E_M^- \cong E_M^+ \cong 1.8$–$2.0$ eV in media with $\kappa > 10$ [when $(1 - 1/\kappa) \cong 1$].

Comparison of the values of I_M^{gas} measured by different methods and $E_{1/2}(M/M^+)$ yielded the relation

$$I_M^{gas} = E_0' + eE_{1/2}(M/M^+) \quad (4b)$$

in which $E_0' = E_0 + E_M^+ = 4.65 + 1.94 = 6.59$ eV (sat.c.e.),[65] $E_0' = 6.5$ eV (sat.c.e.),[70,71] and $E_0' = 4.5 + 1.94 = 6.44$ eV (n.h.e.) [66] have been quoted for aromatic hydrocarbons in acetonitrile and $E_0' = 4.51 + 1.84 = 6.35$ eV (Ag/AgCl) for cyanine dyes in water (pH 10).[69,72,73]

Comparison of the values of E_A^{gas} measured by the magnetron method with the equilibrium potentials $E_{1/2}(A^-/A)$ for strong acceptors (mainly those containing cyano-groups) yielded the relation[74]

$$E_A^{gas} = E_1'' + eE_{1/2}(A^-/A), \text{ eV}, \quad (5b)$$

in which $E_0'' = E_0 - E^- = 2.7$ eV was obtained for solutions in acetonitrile. Similar values of E_0'' have been obtained for cyanine[69] and thiazine[75] dyes. It follows from the comparison of Eqns.(4b) and (5b) that $(E_M^+ + E_M^-) = (E_0' - E_0'') = 3.89$–$3.8$ eV for the radical-ions derived from large molecules with conjugated bonds and that the real formation energy is $E_M^\pm \cong E_M^- \cong 1.95$–$1.9$ eV.

The polarisation energy in the solid medium P_M^+ or P_M^- is determined by comparing I_M^{gas} with the threshold value for photoelectron emission.

The photoelectron emission from organic solids (including polymers) has been analysed in monographs.[76,77] By comparing I_M^{gas} [78] with the threshold values of the photoelectron emission from compounds of different classes,[77] it is possible to estimate $P_M^\pm \cong 1.5$–1.9 eV from Eqns.(4) and (4a). For molecules at an interface, $P_M^\pm$ differs from the value characteristic of the molecules within the solid phase.[47,7] At the interface between phases having the dielectric constants κ_1 and κ_2, the energy $P^\pm = (e^2/2r^\pm)(1 - 1/\kappa')$, where

$\kappa' = (\kappa_1 + \kappa_2)/2$; at the air–solid interface, $\kappa' = (1 + \kappa_{solid})/2$.[36] For PVCA molecules, the polarisation energy of the radical-cation has been determined as the difference $P^+ = I^{gas}_{PVCA} - I^{layer}_{PVCA} = 1.5$ eV [79] on the assumption that $I^{gas}_{PVCA} = I^{gas}_{IPC} = 7.6$ eV, where IPC = *N*-isopropylcarbazole. The value $I^{layer}_{PVCA} = 6.1$ eV has been obtained[79] by comparing the electron work function for metals *in vacuo* and the threshold energy of the light quanta ensuring the photoemission of holes from metals, sputtered onto a PVCA layer, into this polymer layer. The polarisation energies ~1.2 to 2.04 eV and 1.8 eV for aromatic hydrocarbons in polystyrene and poly(methyl methacrylate) respectively have been published in a monograph.[80] These values represent the differences between the threshold values for two-quantum ionisation of molecules in the gas phase and in the polymer matrix.

Taking into account the scatter of the values of E_0, $E^{\pm}_M$, and $P^{\pm}_M$ quoted in the above study, one can propose the following expressions relating the ionisation potentials of the molecule in the polymer matrix I^p_M and the electron affinity E^p_M to the equilibrium redox potentials.

$$I^p_M = E_0 + 1.9\left(\frac{1}{\kappa_p} - \frac{1}{\varkappa}\right) + eE_{1/2}(M/M^+), \text{ eV}, \quad (7)$$

$$E^p_M = E_0 - 1.9\left(\frac{1}{\kappa_p} - \frac{1}{\varkappa}\right) + eE_{1/2}(M^-/M), \text{ eV}, \quad (8)$$

where $E_0 = 4.6$ eV (sat.c.e.), 4.55 eV (Ag/AgCl in 1:1 (vol.%) $CH_3OH : H_2O$ mixture, and 4.36 (n.h.e.). The following notation has been adopted below:

$$\Delta G^+_p = \Delta G^-_p = 1.9\left(\frac{1}{\kappa_p} - \frac{1}{\varkappa}\right)$$

$$eE'_{1/2}(M/M^+) = eE_{1/2}(M/M^+) + \Delta G^+_p, \; eE'_{1/2}(M^-/M) = eE_{1/2}(M^-/M) - \Delta G^-_p. \quad (9)$$

2. Relative Positions of the Levels in the Electron Phototransfer Process

The quantum-mechanical theory of the elementary electron transfer step has been examined in detail in a monograph.[81,82] The relation between the rate constant for the quenching of the photoexcitation of molecules via electron transfer and the free energy of activation for this process in liquid media has been discussed.[83–89] In the present review attention is concentrated on the analysis of the energy characteristics of the components involved in the redox reactions and the relations between them as factors determining the direction and mechanism of the redox processes in these systems. In the development of photochemically active polymeric media on the basis of EDA complexes, the components D and A, forming either weak CTC or contact complexes corresponding to the complete electron transfer from D to A in the excited state, are employed. The use of CTC with a low-lying level and involving complete charge transfer would lead to the dark accumulation of electron transfer products.

We shall consider initially reactions with participation of the complexes D.S or S.A [compounds (I) and (II)]. Under the conditions of the formation of electron donor–electron acceptor complexes between S and D or A, there is a possibility of the processes illustrated in Fig.1. In the case of the CTC $^1(D.S)_0$, these processes can be represented by process (I) (Fig.1a):

$$^1(D^{+\delta}.S^{-\delta})_0 \xrightarrow{h\nu_S} (^1D_0.{}^1S_1);$$
$$^1(D^{+\delta}.S^{-\delta})_0 \xrightarrow{h\nu_{CTC}} {}^1(D^{1-\delta}.S^{-1+\delta})_1 - {}^3(D^+S^-)_1.$$

Here δ is the degree of charge transfer in the ground state of the complex and $^1(D^{1-\delta}.S^{-1+\delta})_1$ the lowest excited singlet state of the CTC. For contact complexes, $\delta = 0$ and $^1(D^{1-\delta}.S^{-1+\delta})_1 \equiv {}^1(D^{\pm}S^{\mp})_1$.

Next follows the formation of the collision complex with A (with the constant k_{12}) and electron transfer (k_{23}):

$$^1(D^{1-\delta}.S^{-1+\delta})_1 + {}^1A_0 \overset{k_{12}}{\rightleftarrows} {}^1(D^{1-\delta}.S^{-1+\delta}.A_0)_1 \xrightarrow{k_{23}} {}^{1,3}[D^+...A^-]_0 + {}^1S_0.(IX)$$
$$^3(D^+S^-)_1 + {}^1A_0 \overset{k_{12}}{\rightleftarrows} {}^3(D^+S^-.{}^1A_0)_1$$
$$(^1D_0 + {}^1A_0) \quad D^+ + A^- \quad (D^+_1 + A^-_1)$$

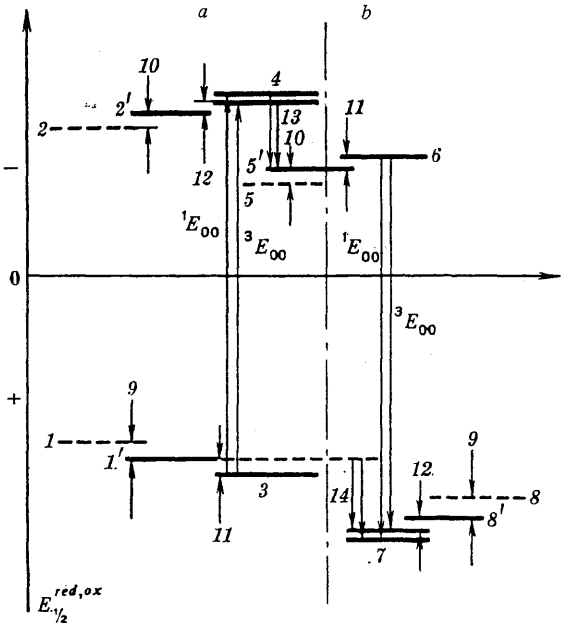


Figure 1. Schematic illustration of the relative positions of the oxidation-reduction potentials of the donor (D), the acceptor (A), and the complexes D.S (*a*) and S.A (*b*) in the ground and excited states; S = sensitiser; continuous line—polymer matrix; dashed line—liquid phase: *1*) and *1'*) $E_{1/2}(^1D_0/D^+)$, $E'_{1/2}(^1D_0/D^+)$; *2*) and *2'*) $E_{1/2}(S^-/{}^1S_0)$, $E'_{1/2}(S^-/{}^1S_0)$; *3*) $E_{1/2}[^1(D.S)_0/(D^+S)]$; *4*) $E_{1/2}[^{1,3}(D^+S^-)/.(D^+S)$; *5*) and *5'*) $E_{1/2}(A^-/{}^1A_0)$, $E'_{1/2}(A^-/{}^1A_0)$; *6*) $E_{1/2}.[(SA^-)/{}^1(S.A)_0$; *7*) $E_{1/2}[(SA^-)^{1,3}(S^+A^-)_1]$; *8*) and *8'*) $E_{1/2}.(^1S_0/S^+)$, $E'_{1/2}(^1S_0/S^+)$; *9*) ΔG^+_p; *10*) ΔG^-_p; *11*) X; *12*) ΔG^p_{CTC}; *13*) ΔG_{23} (IX); *14*) ΔG_{23} (X).

The free energy ΔG_{23} (IX) of the electron transfer stage of reaction (IX) represents the difference between the redox potentials (Fig.1a):

$$\Delta G_{23}(IX) = eE'_{1/2}[^{1,3}(D^+S^-)_1/(D^+S)] - eE'_{1/2}(A^-/{}^1A_0) \quad (10)$$

In this formula $E'_{1/2}[^{1/3}(D^+S^-)_1/(D^+S)]$ is the potential, adjusted to the polymer matrix, for the oxidation of the excited complex in the redox reaction

$$^{1,3}(D^+S^-)_1 \rightleftarrows (D^+S) + e$$
$$[\text{or } {}^1(D^{1-\delta}.S^{-1+\delta})_1 \rightleftarrows (D^+S) + e],$$

which can be calculated from the relation

$$eE'_{1/2}[^{1,3}(D^{+}S^{-})_1/(D^{+}S)] = eE'_{1/2}[^1(D.S)_0/(D^{+}S)] - {}^{1,3}E_{00}, \quad (11)$$

where $^{1,3}E_{00}$ is the distance from the ground to the excited singlet or triplet level of the complex:

$$eE'_{1/2}[^1(D.S)_0/(D^{+}S)] = eE_{1/2}(^1D_0/D^{+}) + X + \Delta G_p^{+} \quad (11a)$$

—the equilibrium potential, adjusted to the polymer matrix, for the oxidation of the complex in the ground state by the reaction

$$^1(D.S)_0 \rightleftarrows (D^{+}S) + e.$$

In Eqn.(11a), X is the formation energy of the complex; for contact complexes, the term $X = 0$ and for CTC we have

$$X = \frac{\{W_{01} - eS_{01}[E'_{1/2}(^1D_0/D^{+}) + E_0]\}^2}{e[E'_{1/2}(^1D_0/D^{+}) - E'_{1/2}(S^{-}/^1S_0)] + (P_D^{+} + P_S^{-}) - (Q^{gas} + P)},$$

where $W_{01} = \int \phi_1(D,S)H\phi_2(D^{+}S^{-})d\tau$ is the energy of the interaction of uncoupled states $[\phi_1(D,S)]$ and states corresponding to the total charge transfer between the components $[\phi_2(D^{+}S^{-})]$; $W_{01} = 0$ for contact complexes and $W_{01} \cong 0.05$ to 0.5 eV for CTC; $S_{01} = \int \phi_1(D,S)\phi_2(D^{+}S^{-})d\tau$ the overlap integral of the wavefunctions of these states; $S_{01} = 0$ for contact complexes and $S_{01} = 0.01$–0.1 for CTC. $Q^{gas} = e^2/2r$ is the energy of the Coulombic attraction of the radical-ions in the state $^{1,3}(D^{+}S^{-})_1$ in the gas phase.

$$P = 2\mu^2\left(\frac{\kappa_p - 1}{2\kappa_p + 1}\right)/a^3 \quad (12)$$

P is the energy of the polarisation of the polymeric medium by the dipole $^{1,3}(D^{+}S^{-})_1$ including the rapid electronic and also the atomic and slow orientational components. $\mu = er_{D^{+}S^{-}} \cong 2er$ is the dipole moment, $a(\cong 2r)$ the radius of the cavity of the polarising dipole, and $r = r^{+} = r^{-}$ the radius of the radical-cation or radical-anion. Hence

$$Q^{gas} + P = 1.9\left(\frac{4\kappa_p - 1}{2\kappa_p + 1}\right).$$

In reaction (IX) the lifetime of the polar states $^1(D^{1-\delta}.\ .S^{-1+\delta}.A)_1$ is $>10^{-12}$ s when the formation of the collision complex between the excited complex and the molecule A is a result solely of the increase of the size of the complex on its photoexcitation. During this period, only the electronic polarisation of the medium is established (whence $\kappa_p = n^2$, n being the refractive index). At the same time, under the conditions of the segmental mobility of the polymer unit, collision with a molecule can occur after the relaxation of the excited complex to a state of equilibrium ($^{1,3}E_{00}$) corresponding to the polarisation energy P and hence corresponding to equilibrium in relation to the redox potential of the excited complex:

$$^{1,3}E_{00} = I_D^{gas} - E_S^{gas} + X - (Q^{gas} + P) + {}^{1,3}Q_e =$$
$$e[E'_{1/2}(^1D_0/D^{+}) - E'_{1/2}(S^{-}/^1S_0)] + X + \Delta G_{CTC}^{P} + {}^{1,3}Q_e, \quad (13)$$

$$\Delta G_{CTC}^{P} = (P_D^{+} + P_S^{-}) - (Q^{gas} + P), \quad (14)$$

where $^1Q_e = X + {}^1Q'_e$, $^1Q'_e = J_{12} + K_{12}$, and $^3Q_e = J_{12} - K_{12}$ are the interelectron repulsion energies in the singlet-excited and triplet-excited complex. J_{12} and K_{12} are the Coulombic and exchange energies respectively.[90]

According to Eqns.(11), (11a), and (13),

$$eE'_{1/2}[^{1,3}(D^{+}S^{-})_1/(D^{+}S)] = eE_{1/2}(S^{-}/^1S_0) - \Delta G_{CTC}^{P} - \Delta G_P^{-} - {}^{1,3}Q_e. \quad (15)$$

Thus we obtain from Eqns.(10) and (15) (Fig.1*a*):

$$\Delta G_{23}(IX) = e[E_{1/2}(S^{-}/^1S_0) - E_{1/2}(A^{-}/^1A_0)] - \Delta G_{CTC}^{P} - {}^{1,3}Q_e. \quad (10a)$$

When a CTC of the type $^1(S.A)_0$ participates in the electron transfer, photoprocesses (X), analogous to (IX), proceed in accordance with Scheme (II) (with replacement of D by S and of S by A). The free energy of electron phototransfer is (Fig.1b)

$$\Delta G_{23}(X) = e\{E'_{1/2}(^1D_0/D^{+}) - E'_{1/2}[(SA^{-})/^{1,3}(S^{+}A^{-})_1]\}, \quad (16)$$

where

$$E'_{1/2}[(SA^{-})/^{1,3}(S^{+}A^{-})_1] = eE'_{1/2}[(SA^{-})/^1(SA)_0] + {}^{1,3}E_{00};$$
$$eE'_{1/2}[(SA^{-})/^1S.A_0)] = eE'_{1/2}(A^{-}/^1A_0) - X;$$
$$^{1,3}E_{00} = e[E'_{1/2}(^1S_0/S^{+}) - E'_{1/2}(A^{-}/^1A_0)] + \Delta G_{CTC}^{P} + X + {}^{1,3}Q_e.$$

After substitutions, Eqn.(16) becomes

$$\Delta G_{23}(X) = e[E_{1/2}(^1D_0/D^{+}) - E_{1/2}(^1S_0/S^{+})] - \Delta G_{CTC}^{P} - {}^{1,3}Q_e.$$

We shall now proceed to the consideration of reactions (III) to (V) of the photoexcited sensitiser. The electron phototransfer reactions involving a sensitiser which does not form complexes with D or A components in the ground state are considered below. Spectral sensitisation is in this case caused by the formation of the collision complex between the photoexcited sensitiser and the D and A components of the system. It is shown below that the direction of the charge transfer process (the type of primary reaction) is determined by the relative positions of the levels of the photoexcited sensitiser and the equilibrium redox potential of the components of the EDA system.

We shall now examine the primary oxidation of the donor and the reduction of the excited sensitiser [reactions (III) to (V)]:

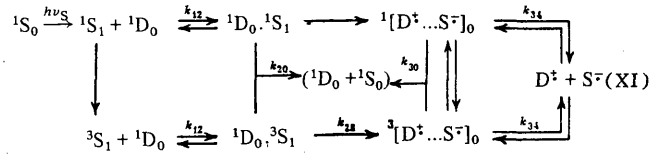


Fig.2*a* shows that reaction (XI) in stage 23 is determined by the shift of the reduction potential of the sensitiser in the excited state in the positive direction up to the value (in the polymer composition)

$$eE'_{1/2}(S^{-}/^{1,3}S_1) = eE_{1/2}(S^{-}/^1S_0) - \Delta G_P^{-} + {}^{1,3}E_{00} \text{ (or } {}^{1,3}E). \quad (17)$$

The potential defined by Eqn.(17) corresponds to equilibrium if the electron transfer reaction takes place after the transitions of $^{1,3}S_1$ to the lowest excited singlet or triplet level ($^{1,3}E_{00}$).

The free energy of electron transfer (stage 23) in reaction (XI) is

$$\Delta G_{23}(XI) = e[E_{1/2}(^1D_0/D^{+}) - E_{1/2}(S^{-}/^1S_0)] + 2\Delta G_P^{+} - \frac{e^2}{R\kappa} - {}^{1,3}E_{00}, \quad (18)$$

where R is the distance between D^{+} and S^{-} in the geminal pair. It has been suggested that, in contrast to the excited CTC, for example $^{1,3}(D^{+}S^{-})_1$, polarising the medium as a single dipole [see Eqn.(12)], the geminal pair $^{1,3}[D^{+}...S^{-}]_0$ corresponds to the Coulombic attraction ($e^2/R\kappa$) of the radical-ions having their own solvation shells.

The free energy of the secondary reaction

$$S^{-} + {}^1A_0 \rightleftarrows {}^1S_0 + A^{-} \quad (XII)$$

is defined as the difference between the following equilibrium redox potentials:

$$\Delta G_{sec}(XII) = e[E_{1/2}(S^{-}/^1S_0) - E_{1/2}(A^{-}/^1A_0)]. \quad (19)$$

In the primary reduction of the acceptor as a result of the oxidation of the photoexcited sensitiser [reaction (IV)], processes (XIII) and (XIV) (Fig.2*b*), analogous to processes (XI) and (XIX) (with the replacement of D by S and of S by A), take place.

The free energy of electron transfer via reaction (XIII) is (Fig. 2*b*)

$$\Delta G_{23}(\text{XIII}) = e[E_{1/2}(^1S_0/S^+) - E_{1/2}(A^-/^1A_0)] + 2\Delta G_p^{\ddagger} - \frac{e^2}{R\kappa} - {}^{1,3}E_{00}, \quad (20)$$

while that of electron transfer via reaction (XIV) is given by

$$\Delta G_{sec}(\text{XIV}) = e[E_{1/2}(^1D_0/D^+) - E_{1/2}(^1S_0/S^+)]. \quad (21)$$

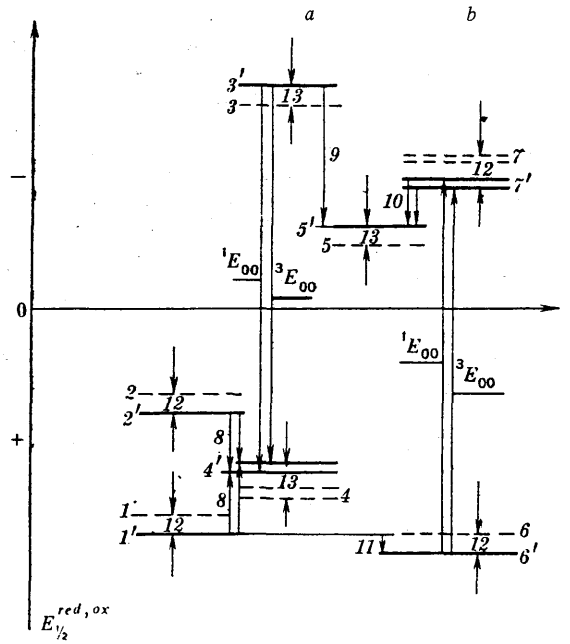


Figure 2. Schematic illustration of the relative positions of the oxidation-reduction potentials in the primary donor oxidation (*a*) and acceptor reduction (*b*) reactions; D and D′ = donors of different nature: *1*) and *1′*) $E_{1/2}(^1D_0/D^+)$, $E'_{1/2}(^1D_0/D^+)$; *2*) and *2′*) $E_{1/2}(^1D)'_0/(D')^+$, $E'_{1/2}[^1(D')_0/(D')^+]$; *3*) and *3′*) $E_{1/2}(S^-/^1S_0)$, $E'_{1/2}(S^-/^1S_0)$; *4*) and *4′*) $E_{1/2}$. $(S^-/^{1,3}S_1)$, $E'_{1/2}(S^-/^{1,3}S_1)$; *5*) and *5′*) $E_{1/2}(A^-/^1A_0)$, $E'_{1/2}$. $(A^-/^1A_0)$; *6*) and *6′*) $E_{1/2}(^1S_0/S^+)$, $E'_{1/2}(^1S_0/S^+)$; *7*) and *7′*) $E_{1/2}(^{1,3}S_1/S^+)$, $E'_{1/2}(^{1,3}S_1/S^+)$; *8*) ΔG_{23} (XI); *9*) ΔG_{sec} (XII); *10*) ΔG_{23} (XIII); *11*) ΔG_{sec} (XIV); *12*) ΔG_p^+; *13*) ΔG_p^-.

The dominant direction of the primary reaction is determined by the difference between free energies ΔG_{23}(XI) to ΔG_{23}(XIII) and the ratio of the equilibrium concentrations is given by the expression

$$\frac{{}^{1,3}[D^+S^-]_1}{{}^{1,3}[S^+A^-]_1} = \exp\left[\frac{\Delta G_{23}(\text{XI}) - \Delta G_{23}(\text{XIII})}{kT}\right]$$

The collision of $^{1,3}S_1$ (energy $^{1,3}E_{00}$) with the complex $^1(D.A)_0$ entails two possible reaction pathways (*a* or *b*):

$$^{1,3}S_1 + {}^1(D.A)_0 \rightarrow {}^{1,3}S_1.{}^1(D.A)_0 \xrightarrow{a} {}^{1,3}[D^+A...S^-]_0,$$

$$\downarrow b \qquad\qquad \downarrow$$

$$^{1,3}[S^+...DA^-]_0 \rightarrow {}^{1,3}[D^+...A^-]_0 \rightarrow D^+ + A^-;$$

$$\rightarrow D_1^+ + A_1^-,$$

$$\rightarrow {}^1(D.A)_0,$$

for which

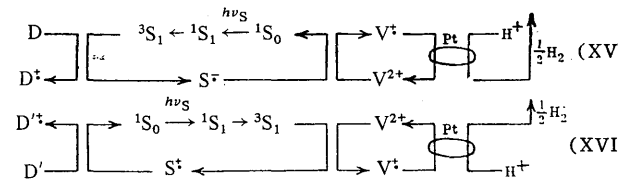
$$\Delta G(a) = e[E_{1/2}(^1D_0/D^+) - E_{1/2}(S^-/^1S_0)] + 2\Delta G_p^{\ddagger} + X + {}^{1,3}E_{00},$$

$$\Delta G(b) = e[E_{1/2}(^1S_0/S^+) - E_{1/2}(A^-/^1A_0)] + 2\Delta G_p^{\ddagger} + X - {}^{1,3}E_{00}.$$

The dominant pathway is determined by the difference $\Delta G(a) - \Delta G(b)$:

$$\frac{{}^{1,3}[D^+A...S^-]_0}{{}^{1,3}[S^+...DA^-]_0} = \exp\left[\Delta G(a) - \Delta G(b)\right]/kT.$$

Liquid-phase systems incorporating donors of different nature (D and D′), sensitisers comprising low-molecular-weight and high-molecular-weight derivatives $Ru(bipy)_3^{2+}$, xanthene dyes, and porphyrins, and acceptors comprising the viologens (V^{2+}) in the presence of dispersed platinum have been investigated in detail[8-11,71,91-96] in connection with the development of converters of solar radiation into the chemical energy of the evolution of molecular hydrogen. The set of reactions can be represented by two schemes:



In reactions (XV) and (XVI) the free energy of formation of H_2 is

$$\Delta G(H_2) = e[E_{1/2}(V^+/V^{2+}) - E_{1/2}(0.5H_2/H^+)]$$

where $E_{1/2}(0.5H_2/H^+) = -0.059\text{pH}$ V (n.h.e.) is the equilibrium potential of the reduction of H^+ to $0.5H_2$ in the reaction $0.5H_2 \rightleftharpoons H^+ + e$ on the platinum surface.

A high quantum yield of H_2 [$\phi(0.5H_2) = 0.25$] has been attained in a composition where S was a complex system comprising a mixture of three xanthene dyes with different regions of optical absorption which transmit the absorbed solar energy to the "aerial"—anthracene-9-carboxylic acid. The "aerial" in the excited triplet state participates in electron transfer from the donor [ethylenediaminetetraacetic acid (EDTA)] to the acceptor—methylviologen.[96]

Fig. 2 shows that the position of the ground energy level of the sensitiser, for example, the ruthenium complex $Ru(bipy)_3^{2+}$, is characterised by two redox potentials:[71]

$$eE_{1/2}\{Ru(bipy)_3^{1+}/^3[Ru(bipy)_3^{2+}]_1\} =$$
$$= eE_{1/2}\{Ru(bipy)_3^{1+}/^1[Ru(bipy)_3^{2+}]_0\} + {}^3E_{00} = 0.84 \text{ eV} \quad (22)$$
$$({}^3E_{00} = 2.1 \text{ eV})$$
$$eE_{1/2}\{^1[Ru(bipy)_3^{2+}]_0/Ru(bipy)_3^{3+}\} = 1.27 \text{ eV (n.h.e.)}.$$

which determine the free energies of electron transfer in the interaction with the donor. The first value characterises the free energy, defined by Eqn. (18), of electron transfer from D to the lowest level of the triplet-excited sensitiser [reaction (XV)] and the second corresponds to the free energy, defined by Eqn. (21), of the secondary reaction (XVI) involving electron transfer from D′ to the oxidised sensitiser.

The position of the excited energy level of the sensitiser is characterised analogously by the redox potentials[71]

$$eE_{1/2}\{^3[Ru(bipy)_3^{2+}]_1/Ru(bipy)_3^{3+}\} =$$
$$= eE_{1/2}\{^1[Ru(bipy)_3^{2+}]_0/Ru(bipy)_3^{3+}\} - {}^3E_{00} = -0.83 \text{ eV};$$
$$eE_{1/2}\{Ru(bipy)_3^{1+}/^1[Ru(bipy)_3^{2+}]_0\} = -1.26 \text{ eV (n.h.e.)}.$$

which determines the free energies, defined by Eqns. (20) and (19), of electron transfer to the acceptor respectively from the excited ruthenium complex in the primary reaction (XVI)

and from the reduced sensitiser in the secondary reaction tion (XV). Reaction (XV) predominates when donors with a low value of $E_{1/2}(^1D_0/D^+)$ [0.16–0.64 V (n.h.e.)] are used, such as tetramethyl-*p*-phenylenediamine, diphenyl-*p*-phenylenediamine, tetramethylbenzidine, and tetrapyrenediamine, in combination with $Ru(bipy)_3^{2+}$ and methylviologen (MV^{2+}) as the acceptor: $E_{1/2}(MV^{+\cdot}/MV^{2+}) = -0.44$ V (n.h.e). Reaction (XVI) proceeds in the presence of donors such as triethanolamine (TEOA) and EDTA, whose equilibrium oxidation potentials are $E_{1/2}[(^1D')_0/(D')^{+\cdot}] = 0.82$ and 0.9 V (n.h.e.) respectively and are almost identical with or more positive than the potential defined by Eqn.(22).

The positions of the energy levels of the sensitised dyes (azine, thiazine, and xanthene dyes) and donors (EDTA and TEOA) depend on the acid–base properties of the medium.[76, 97–100] For example, the thiazine dyes (Dy^+), thionine (TH^+) and Mb^+, widely used in non-silver information recording processes, have an equilibrium reduction potential in their protonated form which is more positive than in the non-protonated form by the amount

$$E_{1/2}(DyH^{+\cdot}/{}^1(DyH^{2+})_0 - E_{1/2}(Dy^{\cdot}/{}^1(Dy^+)_0 =$$
$$2.303\frac{kT}{e}(pK_s - pK_a),\ (2.303\frac{kT}{e} = 0.059,\ V,\ \text{at } 293\ K),$$

where K_S and K_a are the equilibrium constants of the reactions

$$DyH^+ \overset{K_s}{\rightleftarrows} Dy + H^+ \text{ and } DyH^{2+} \overset{K_a}{\rightleftarrows} Dy^+ + H^+.$$

The quantities pK_S and pK_a are 10.4 and −0.4 for thionine and 9 and 0 respectively for Methylene Blue. The equilibrium potentials of the reduction of the triplet-excited dyes are more positive in the protonated form than in the non-protonated form by the amount

$$E_{1/2}(DyH^{+\cdot}/{}^3(DyH^{2+})_1] - E_{1/2}[Dy^{\cdot}/{}^3(Dy^+)_1] = 0.059\ (pK_s - pK_t),$$

where K_t is the equilibrium constant of the reaction

$$^3(DyH^{2+})_1 \overset{K_t}{\rightleftarrows} {}^3(Dy^+)_1 + H^+,$$

amounting to 7.0 and 7.2 respectively for TH^+ and Mb^+.

The decrease (shift in the positive direction) of the energy levels of the triplet-excited dyes on protonation increases the free energy (rate constant) for electron transfer from the donor to the photoexcited dye.

3. Methods of Limiting the Reverse Reactions

The suppression of the reverse reactions is one of the central problems for the practical realisation of electron transfer processes in systems incorporating CTC. In photoconducting systems, the suppression of the reverse reactions (recombination in geminal pairs) increases the quantum efficiency of the generation of free charge carriers. This can be achieved by applying strong electric fields or, for example, in the case of PVCA, by increasing the initial distance separating the charges in the geminal pair by increasing the energy of the excited quanta.[1,3]

In non-silver light-sensitive systems based on CTC, halogen-containing compounds (CBr_4, $CBr_3SO_2CBr_3$) are used as acceptors. The reverse reaction is quenched as a result of the dissociation of the acceptor on electron capture ($CBr_4 + e \to Br^- \ldots \dot{C}Br_3$; $CBr_3SO_2CBr_3 + e \to Br^- \ldots \dot{C}Br_2SO_2.\ .CBr_3$, etc.). In sensitised systems based on viologens as acceptors one uses donors and conditions where the radical-cationic forms, formed as a result of the electron transfer reactions, are deprotonated [$DH^+ \to D^{\cdot} + H^+$ ($PVA^{+\cdot}$,[3,101] $TEOA^{+\cdot}$,[102,103] $EDTA^{+\cdot}$ [104,105])]. In contrast to DH^+, the radicals $D^{\cdot}$ [$-CH-\dot{C}OH-$(PVA$^{\cdot}$), $(CH_2OHCH_2)_2\dot{N}CH_2CHOH$ or $(CH_2.\ .OHCH_2)_2\dot{N}CHCH_2OH$ (TEOA$^{\cdot}$), $R_2N-(CH_2)_2-(R)N-\dot{C}HCOO^-H^+$ with $R \equiv CH_2COO^-H^+$ (EDTA$^{\cdot}$)] are strong donors and effect additional electron transfer to the acceptor under dark conditions, accompanied by the irreversible formation of the carbonyl groups $-CH_2-\overset{O}{\overset{\|}{C}}-$ in PVA [3,101] and also of unstable imino-forms $\overset{+}{\underset{}{\gtrless}}N=CH-CH_2OH$ or $-\overset{+}{\underset{R}{N}}=CHCOO^-H^+$ in TEOA [102] or EDTA,[105] which undergo subsequent irreversible decomposition. Thus in systems of this kind not only are the reverse reactions suppressed but the quantum yield of the reduced viologen is also doubled. In polymer systems the doubling of $\phi(V^{+\cdot})$ is attained by the conversion of low-molecular-weight acceptors into polymeric forms with a high local concentration of viologen units, such as polypentamethyleneviologen, polydecamethyleneviologen, or poly-*p*-xylyleneviologen.[3,101,106]

According to Ohsako et al.[107], the polymer based on polystyrene with viologen substituents in the phenyl group [PV^{2+}: $E_{1/2}(PV^{+\cdot}/PV^{2+}) = -0.135$ V (n.h.e.)] does not enter into a redox interaction either with the excited or the oxidised complex $Ru(bipy)_3^{2+}$ apparently due to steric hindrance. Electron phototransfer takes place after the additional introduction into the system of electron transferring agents (ET), for example, dipropyl-4,4′–dipyridylsulphonate [$E_{1/2}(ET^{-\cdot}/ET) = -0.68$ V (n.h.e.)]. The charge transfer

$$^3[Ru(bipy)_3^{2+}]_1 + ET \to Ru(bipy)_3^{3+} + ET^{-\cdot},$$

which takes place after electron phototransfer via the reaction

$$ET^{-\cdot} + PV^{2+} \to ET + PV^{+\cdot},$$

effectively competes with the reverse reaction

$$ET^{-\cdot} + Ru(bipy)_3^{3+} \to ET + Ru(bipy)_3^{2+},$$

ensuring a PV^+ lifetime of ~1.2 s and a ~50-fold increase of $\phi(PV^{+\cdot})$ compared with $\phi(ET^{-\cdot}) = 0.12 \times 10^{-2}$ in the absence of PV^{2+}.

In order to separate the reaction products in liquid media, use is made of micellar solutions, two-layer membranes,[9,10] and the components at the interface in the field of a negatively charged dispersed SiO_2.[108,109]

4. Oxidation-Reduction Potentials and Optical Transition Energies

The relation between the redox potentials, the electronic transition energies, and the positions of the highest occupied (ε_1) and lowest unoccupied (ε_2) orbitals, calculated by quantum-chemical methods (mainly the Hückel molecular orbital method: HMO) has been discussed in monographs[6,110,111] and in a large number of original and new communications in relation to polyenes and aromatic hydrocarbons,[110–113] heterocyclic compounds,[68,112,114] and dyes of different classes (palmitic, thiazine, oxazine, acridine, and xanthene dyes, aza-pigments, etc).[6,7,69,72,73,112,115,116] It has been demonstrated in monographs[110,111] in relation to a large number of polyenes and aromatic hydrocarbons that, for compounds of the same class, there is a linear relation between the experimental $E_{1/2}^{ox}$ (or I_M), $E_{1/2}^{red}$ (or E_M), and the values of m_1 and m_2, characterising the coefficients of the orbitals and calculated by the HMO method:

$$\varepsilon_1 = \alpha + \beta_0 m_1,\quad \varepsilon_2 = \alpha - \beta_0 m_2$$

where α and β_0 are the Coulombic and resonance integrals.

The following linear relations have been established:

$$E_{1/2}(M/M^{\pm}) = \beta_1 m_1 + c$$

or [see Eqn.(4b)]

$$I_M = \beta_1 m_1 + c_1,$$

and also

$$E_{1/2}(M^{\mp}/M) = -\beta_2 m_2 + c_2$$

or [see Eqn.(5b)]

$$E_M = -\beta_2 m_2 + c_2,$$

where $c - c_3$ are constants.

The following correlation has been derived:[6,7,72,73,115,116]

$$h\nu_{max,exp} = \beta_3(m_1 - m_2).$$

A linear relation has been proposed for aromatic hydrocarbons:[112]

$$^3E_{00} = \beta_4(m_1 - m_2)$$

where $\beta_1 - \beta_4$ are correlation parameters relating the experimental and calculated quantities.

The relations between the positions of the energy levels and the calculated values for dyes have been subjected to a detailed analysis[68,69] on the basis of correlations:[114]

$$^1E_{00} = \beta_5(m_1 - m_2) - J_{12} + 2K_{12} \quad (23)$$

$$^3E_{00} = \beta_5(m_1 - m_2) - J_{12} \quad (24)$$

$$e[E_{1/2}(^1M_0/M^{\pm}) - E_{1/2}(M^{\mp}/^1M_0)] = \beta_5(m_1 - m_2). \quad (25)$$

According to Eqns.(23)–(25), the difference between the redox potentials defined by Eqn.(25) can be regarded as the experimental distance between the half-filled orbitals ε_1 and ε_2 in the absence of electron-electron interaction. The occurrence of electronic interaction under the conditions of the photoexcitation of the molecule ($-J_{12} + 2K_{12}$ for the excited singlet state and $-J_{12}$ for the excited triplet state) should entail the appearance of the following relations:

$$^1E_{00} = e[E_{1/2}(^1M_0/M^{\pm}) - E_{1/2}(M^{\mp}/^1M_0)] - J_{12} + 2K_{12}, \quad (26)$$

$$^3E_{00} = e[E_{1/2}(^1M_0/M^{\pm}) - E_{1/2}(M^{\mp}/^1M_0)] - J_{12}. \quad (27)$$

In related series, such as those of aromatic compounds, monoaza-compounds, and poly-*N*-heterocyclic compounds, an increase in molecular size leads simultaneously to a decrease of both J_{12} and of the polarisation energy $P^{\pm}$.[110] The experimental relations[68,112]

$$J_{12} = a + be[E_{1/2}(M/M^{\pm}) - E_{1/2}(M^{\mp}/M)], \quad (28)$$

$$^3E_{00} = (1-b)e[E_{1/2}(M/M^{\pm}) - E_{1/2}(M^{\mp}/M)] - a. \quad (29)$$

are linked to these changes. Table 1 presents the experimental constants $-J_{12} + 2K_{12}$, $1 - b$, and a in Eqns.(26) and (29) for a series of related compounds. Deviations from the common relations (26) and (29) are characteristic of molecules with either complex substituting groups or with variable conformations, which requires allowance for additional intramolecular interactions between non-neighbouring atoms.[110,111] It has been suggested[117] that the optical absorption energy of cyanine dyes be related to the redox-potentials by means of the formula [1 : 1 (vol.%) water–methanol mixture]:

$$h\nu_{max} = 0.87e[E_{1/2}(S/S^{\pm}) - E_{1/2}(S^{\mp}/S)], \text{ eV}.$$

The relation (in aqueous methanolic solutions)

$$^1E_{00} = e[E_{1/2}(^1S_0/S^{\pm}) - E_{1/2}(S^{\mp}/^1S_0)] + 0.37, \text{ eV}, \quad (30)$$

or

$$^1E_{00} = I_S^{gas} - E_S^{gas} - 3.28, \text{ eV}, \quad (31)$$

has been obtained[69] for 100 sensitising dyes (mainly cyanine dyes—90 compounds, and also xanthene and thiazine dyes, and individual representatives of the groups of acridine, oxazine, and alloxazine dyes), which have been investigated in detail in connection with their use in the silver halide and non-silver photographic processes and in the development of photovoltaic cells. According to literature data, the splitting $S_1 - T_1$ is $2K_{12} \approx 0.27$ eV for cyanine dyes,[90] ~0.32 eV, for acryidine dyes,[118] and ~0.31 eV for xanthene dyes.[118] We find from Eqns.(26) and (30) that the interelectron repulsion energy is small: $-J_{12} = +0.37 - 2K_{12} = 0.37 - (0.27–0.32) = +0.1–0.05$ eV. Thus, for sensitising dyes, we have

$$^3E_{00} = e[E_{1/2}(^1S_0/S^{\pm}) - E_{1/2}(S^{\mp}/^1S_0)] + (\leqslant 0.1), \text{ eV}; \quad (32)$$

for this series of compounds, we have the coefficients $b \approx 0$ and $a \approx -0.1$ eV in Eqn.(29) (Table 1).

Table 1. The coefficients $-J_{12} + 2K_{12}$, $1 - b$, and a in Eqns.(26) and (29) for a series of related compounds (aqueous and methanol solutions).[112]

Coefficient	Aromatic hydrocarbons	Mono-*N*-heterocyclic compounds ($n \to \pi^*$ transition)	Poly-*N*-heterocyclic compounds ($\pi \to \pi^*$ transition)	Dyes*
$-J_{12}+2K_{12}$	—	—	0.3	0.37**
$(1-b)$	0.82	0.88	0.9	1.0**
a	0.52	0.54	0.687	−0.1***

*Cyanine, acridine, thiazine, oxazine, xanthene, etc. dyes (100 compounds in all).[69]

**Data of Loutfy and Sharp.[69]

***Calculated by the authors of the review.

Table 2. Electrochemical and spectral characteristics of the additives and the energy characteristics of the photovoltaic cells based on Phtc.[34]

Additive	$E_{1/2}^{red}$	$E_{1/2}^{ox}$	Absorption		Φ	η' %
	volts (sat.c.e.)		λ_{max}, nm	ϵ_{max}, $dm^3\ mol^{-1}cm^{-1}$		
TMF*	−0.42	1.5	370	$1\cdot10^4$	0.93	1.58
Coumarin 6	−1.50	1.16	480	$1\cdot10^5$	0.84	1.54
Rubrene	−1.55	0.86	525	$1.2\cdot10^5$	0.76	1.44
Rhodamine 6G	−0.84	1.30	545	$1.2\cdot10^5$	0.40	1.00
Perylene	−1.72	1.06	440	$3.4\cdot10^4$	0.33	0.48
Phtc without additives	−1.24	0.90	—	—	0.27	0.50
DPBF**	−1.98	0.73	420	$1\cdot10^4$	0.14	0.27
BPEA***	−1.40	1.22	470	$3.4\cdot10^4$	0.04	0.06
Safranine	—	0.5	—	—	0.02	0.02

*Trinitrofluorenone. **1,4-Diphenyl-2,3-benzofuran. ***9,10-Bi(phenylethynyl)anthracene.

5. The Mechanisms of the Spectral Sensitisation of the Photoelectric Sensitivity in Photovoltaic Cells

In the study of the processes in photovoltaic cells based on Phtc dispersed in a polymer matrix,[34,46–48] the positions of the levels of the additives adsorbed on the surfaces of the Phtc particles were estimated from electrochemical data, which, together with spectral and energy characteristics, are listed in Table 2. Polycarbonate was used as the polymer matrix in the photovoltaic cell. The quantity ϕ was

determined from Eqn.(3) for $\lambda = 620$ nm and $L_T = 0.1$ mW cm^{-2}. The efficiency η' [see Eqn.(2)] was measured with exposure to sunlight; $L_T = 1$ mW cm^{-2}.

In a layer without additives, the charge carriers are generated at the Schottky barrier in accordance with the scheme in Fig. 3*a*. The electron-hole pair formed in the region of the Schottky barrier dissociates in the barrier electric field, the electron passing to the metal and the hole drifting into the bulk of the Phtc. If the added substance S has an oxidation potential satisfying the condition $E_{1/2}.(^1S_0/S^+) < E_{1/2}(^1Phtc_0/Phtc^+)$, then it captures a hole and functions as a densensitiser (Fig. 3*b*):

$$S + Phtc^+(hole) \rightarrow S^+ + Phtc.$$

The hole does not then escape into the bulk phase but is trapped by the additive molecule, which sharply increases the probability of its recombination with an electron and leads to a decrease of the photocurrent compared with the initial layer. Among the additives listed in Table 2, safranine and DPBF satisfy this condition. The densensitising effect of BPEA may be determined by the tendency of this substance to aggregate with formation of insulating layers on the Phtc grains, which diminish I_{SC}.

In a solid, the absorption of light by Phtc particles leads to the formation of the exciton state $^1Phtc_1$, which diffuses to the Phtc/S interface and forms an exciplex with a molecule of the additive, which can decompose into charged species, the process intensifying in an electric field (E_d):

$$^1Phtc_1 + {}^1S_0 \rightarrow {}^1(Phtc.S)_1 \rightarrow {}^1(Phtc^+S^-)_1 \xrightarrow{E_d} Phtc^+ + S^-.$$

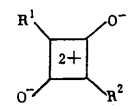
The free holes $Phtc^+$ escape into the bulk of the phthalocyanine particle and the reduced molecule of the additive gives up an electron to the metal (Fig. 3*c*). This chemical sensitisation process constitutes an additional channel to the formation of free separated charge carriers and to the increase of J_{SC}.

In spectral sensitisation (Fig. 3*d*), the additive molecule absorbs light. For effective spectral sensitisation, it is essential that the excited additive molecule should accept an electron from Phtc. The relation between the electrochemical and spectral parameters of the additive is given[34] by Eqn.(26) on the assumption that $-J_{12} + 2K_{12} \cong 0$, i.e. that the reduction potential of the excited additive molecule is equal to the oxidation potential of the molecule in the ground state. According to Table 2, almost all additives in their excited states, with the exception of DPBF and safranine, are capable of injecting holes into (of capturing electrons in) the bulk of the semiconductor Phtc and thus of effecting spectral sensitisation. In reality, spectral sensitisation was a maximum for coumarin 6 or rhodamine 6G and was weaker for rubrene and perylene, while DPBF, BPEA, and safranine did not influence the photosensitivity of Phtc. The agreement between experiment and the mechanism considered, involving charge transfer, does not rule out the contribution to the spectral sensitisation by processes involving the transfer of excitation energy from the additive to Phtc.

The study[119] of the photovoltaic effect in the cells

Al/the dye I dispersed in the polymer/SnO_2 – Sb

showed that I_{SC} is smaller by four orders of magnitude than in the cells based on sensitised Phtc. Here the dye I has the structure



R^1 and R^2 are radicals derived from anilines, indoles, azulenes, indolizines, and methines.

6. Spectral Sensitisation of Non-silver CTC-based Photographic Systems by Cyanine Dyes

Cyanine dyes, which have a large extinction coefficient, a small $S_1 - T_1$ splitting, and hence a short lifetime in the excited singlet state, enter into photochemical reactions in the excited triplet state.[85,87,90]

Table 3 presents the characteristics of cyanine dyes, which, as mentioned above (Section II), have been investigated as sensitisers of non-silver photographic polymeric layers based on the CTC of benzyldiphenylamine (Am) as the donor and acceptors (A = CBr_4 or $CBr_3SO_2CBr_3$). These polymeric layers are sensitive to light at wavelengths $\lambda \leq 500$ nm as a consequence of the optical absorption of A and Am in the region up to ~320 nm and of the CTC in the range 320–500 nm. The coloured product (Am_1^+), which is assumed to have the structure

$$(C_6H_5)_2\overset{+}{N}{=}CH{-}C_6H_5 \qquad \text{(XVII)}$$

is formed under the influence of light.

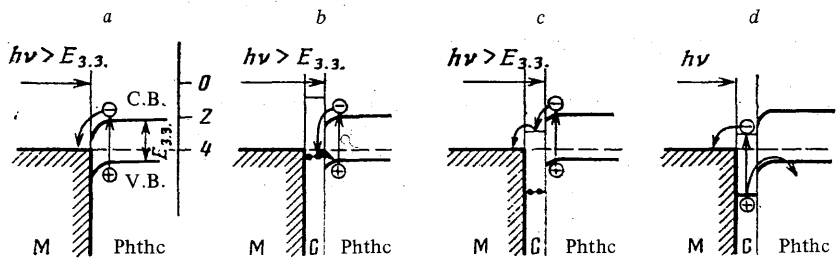


Figure 3. Schematic illustration of the generation of charge carriers (holes) at the Schottky barrier in the M/Phtc (dispersed in polycarbonate) photovoltaic cell; *a*) no additives; *b*) desensitisation by added safranine and DPBF; *c*) chemical sensitisation by added TNF and coumarin 6; d) spectral sensitisation by added rhodamine 6G, coumarin 6, etc.; M = metallic semitransparent layer; C.B. = conductivity band; V.B. = valence band; $E_{f.g.}$ = width of the forbidden gap of Phtc.[34]

When cyanine dyes are introduced, processes of three types take place:

(1) Dyes with $E_{1/2}(^1S_0/S^{\cdot+}) < 0.5$ V (sat.c.e.) are decolorised in the dark on contact with acceptors.

(2) Dyes having $E^{ox}_{1/2}$ in the range $0.5 < E^{ox}_{1/2} < 0.9$ V (sat.c.e) are decolorised as a result of photoexcitation on contact with A (Fig. 4*a*), the efficiency of the process increasing with decrease of $E_{1/2}(^1S_0/S^{\cdot+})$. Such dyes are weak spectral sensitisers of compositions incorporating the complexes Am.A. It has been established[3, Ch.5; 49,50] that the quantum yield of the decolorisation of dyes increases linearly with acceptor concentration: $\phi_{dec} = a[A]$, where A = CBr_4 or $CBr_3SO_2CBr_3$.

Table 3. The structural formulae of the dyes, the potentials $E^{ox}_{1/2}$ and $E^{red}_{1/2}$ (sat.c.e.) measured in acetonitrile[49] and in the 1 : 1 (vol.%) C_2H_5OH–H_2O mixture at pH 10–12,[72,73] and the values of λ_{max} in a CPVC film.[49]

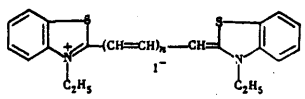
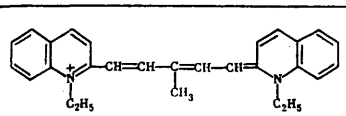
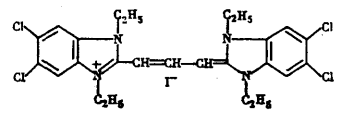
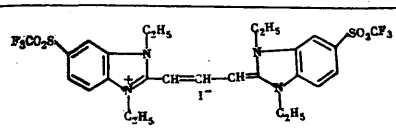
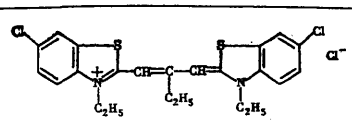
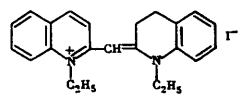
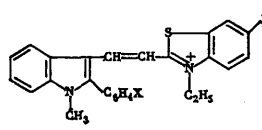
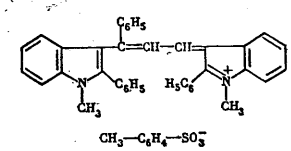
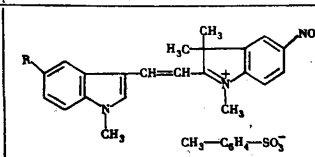
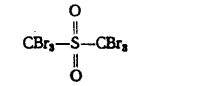
No.	Dye (S)	$E_{1/2}(S/S^{\cdot+})$, V	$E_{1/2}(S^{\cdot-}/S)$, V	λ_{max}, nm	Refs.
1	 $n = 5$	0.03	—0.6	1020	[49]
2	$n = 4$	—	—0.7	—	[72]
		0.12	—0.68	874	[49]
3			—0.8		[72, 73]
	$n = 3$	0.26	—0.8	762	[49, 72, 73]
4	$n = 2$	0.48	—0.93	656	[49, 72]
5	$n = 1$	0.71	—1.1	560	[6, 72]
6		—	—	740	[49]
7		0.55	—1.62	522	[49]
8		0.73	—1.42	531	[49]
9		0.90	—0.94	571	[49]
10		0.99	—1.03	—	[6]
		0.9	—1.15	531	[49]
11	 X=H	0.90	—0.65	535	[49]
12	X=CH_3	0.93	—0.58	535	[49]
13	X=Br	1.18	—0.42	538	[49]

Table 3 (contd.).

No.	Dye (S)	$E_{1/2}(S/S^{\cdot+})$, V	$E_{1/2}(S^{\cdot-}/S)$, V	λ_{max}, nm	Refs.
14		1.0	—0.5	630	[120]
15	 R=H	1.1	—0.55	530	[120]
16	R=NO_2	1.35	—0.65	540	[49]
17	$(C_6H_5)_2N{-}CH_2{-}C_6H_5$	0.98	—	296**	[49]
18	CBr_4	—	—0.7*	240**	[49]
19		—	—0.6*	238** (shoulder at 265)	[50]

Remarks. *Calculated by Eqn.(5b) from $E_A(CBr_4)$ = 2.0 eV and $E_A(CBr_3SO_2CBr_3)$ = 2.1 eV.[50] **Measured in ethanol.

The type of decolorisation of group 1 and 2 dyes described justifies the conclusion[3, Ch.5; 49,50] that the decolorisation is determined by electron-donating properties.

(3) Dyes with $E_{1/2}(^1S_0/S^{\cdot+}) > 0.9$–$1.0$ V (sat.c.e.), i.e. with $E_{1/2}(^1S_0/S^{\cdot+}) > E_{1/2}(^1Am_0/Am^{\cdot+})$ (Table 3) are not decolorised on photoexcitation in the presence of A or simultaneously Am and A. These dyes are effective spectral sensitisers of the polymer composition based on Am.A.

The efficiency of the formation of $Am^{\cdot+}_1$ increases with decrease of the concentration of agents quenching the triplet excitation (for example, O_2), which confirms the idea that triplet-excited dye molecules participate in the sensitisation process.

The oxidation-reduction mechanism of spectral sensitisation has been established by EPR. The first step in the sensitisation process is electron transfer from the amine to the photoexcited sensitiser (Fig. 2*a*):

$$^1Am_0 + {}^3S_1 \rightarrow Am^{\cdot+} + S^{\cdot-}. \qquad \text{(XVIII)}$$

The appearance of the EPR spectrum of the radical-cations $Am^{\cdot+}$ (a quartet with intensity ratios of 1 : 2 : 2 : 1) at the instant of the excitation S in the absence of the acceptor component from the layer corresponds to this stage.[120] Further reactions are as follows:

$$S^{\cdot-} + CBr_4 \rightarrow {}^1S_0 + Br^-...CBr_3, \qquad \text{(XIX)}$$

$$Am^{\cdot+} + Br^-...CBr_3 \rightarrow Am^+_1Br^- + CHBr_3. \qquad \text{(XX)}$$

The absence of the EPR spectrum under the conditions of the photoexcitation of S in the presence of only A in the layer and the simultaneous formation of $Am^{\cdot+}$ and radicals formed from $A^{\cdot-}$ as a result of the abstraction of the bromide ion on photoexcitation of S in the presence of Am and A correspond to these stages.[120]

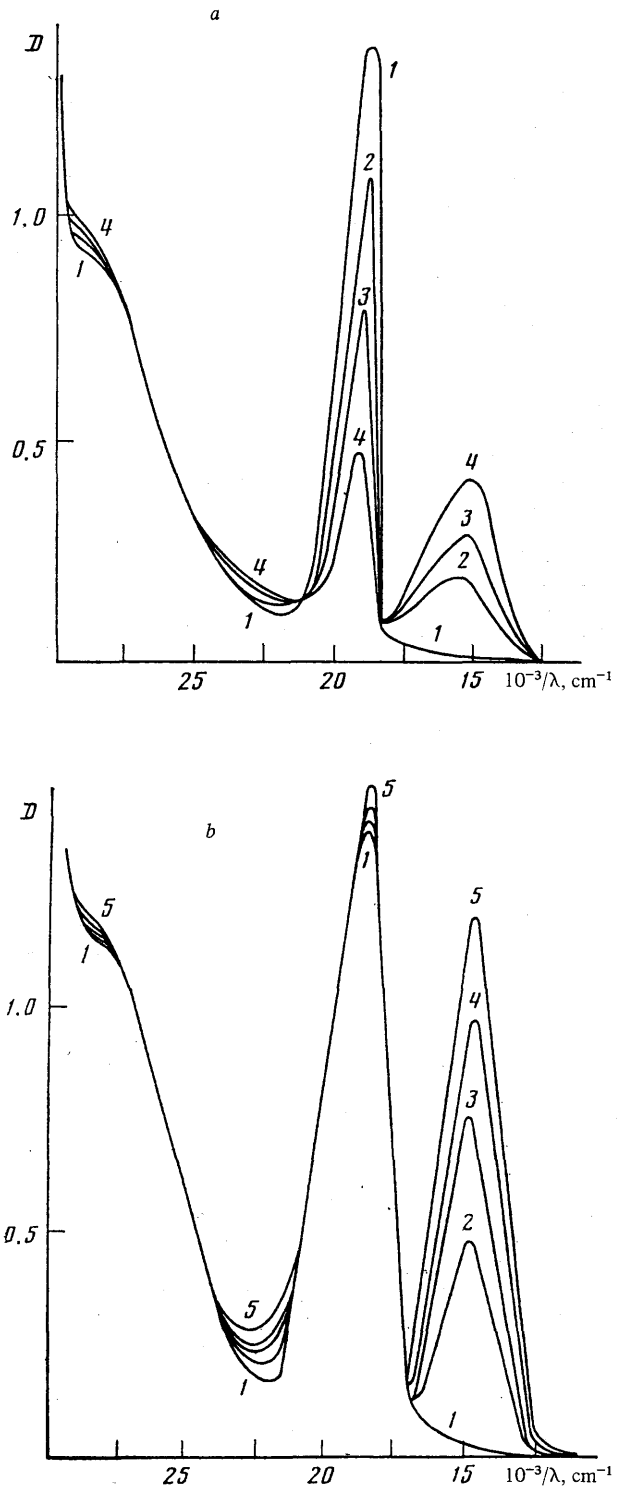


Figure 4. Variation of the optical spectra under the conditions of the photoexcitation of the dye (λ = 531–533 nm, $L_0 = 10^{-3}$ W cm^{-2}) in a composition containing benzyldiphenylamine (0.8 mol dm^{-3}) and CBr_4 (2.3 mol dm^{-3}); [S] = 0.03 ml dm^{-3}; *a*) dye No.7 (Table 3); illumination time (s): *1*) 0 (initial spectrum); *2*) 120; *3*) 240; *4*) 360; *b*) dye No.16 (Table 3); illumination time (s): *1*) 0 (initial spectrum); *2*) 15; *3*) 30; *4*) 45; *5*) 60.[49]

The quantum yield in the formation of the coloured product Am_1^+ via the reactions (XVIII)–(XX) initially increases with increasing concentrations of Am and A:

$$\varphi_{sens} = 0.12[Am][CBr_4]. \quad (33)$$

Then, after the attainment of the values [Am] = 1 and [A] = 1 mol dm^{-3}, it assumes the constant value ϕ_{sens} = 0.12.

In conformity with the above scheme (Fig. 2*a*), the cyanine dye participates in reaction (XVIII) at the oxidation-reduction potential $E'_{1/2}(S^-/{}^3S_1)$, defined by Eqn.(17), while in the secondary reaction (XIX) the reduced sensitiser interacts with the acceptor at the equilibrium potential $E'_{1/2}(S^-/{}^1S_0)$. The cyanine dyes listed in Table 3 belong to the group for which $^3E_{00}$ is related to $E_{1/2}^{ox,\ red}$ by Eqn.(32). Since the value of $^3E_{00}$ are unknown for many dyes (Table 3), Eqns.(17) and (32) were used to calculate $E'_{1/2}(S^-/{}^3S_1)$:

$$eE'_{1/2}(S^-/{}^3S_1) = eE'_{1/2}({}^1S_0/S^+) + (\leqslant 0.1) + \Delta G_p^+.$$

The free energy of electron transfer from the Am molecule to $^3S_1$ via reaction (XVIII) is (Fig. 2*a*)

$$\Delta G(\text{XVIII}) = e[E'_{1/2}({}^1Am_0/Am^+) - E'_{1/2}(S^-/{}^3S_1)] =$$
$$e[E_{1/2}({}^1Am_0/Am^+) - E_{1/2}({}^1S_0/S^+)] - (\leqslant 0.1), \text{ eV}.$$

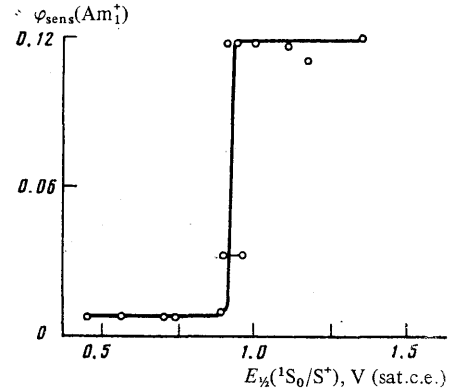


Figure 5. Dependence of the quantum yield ϕ_{sens} for the formation of Am_1^+ on $E_{1/2}({}^1S_0/S^+)$; concentrations of the components (in CPVC): [S] = 10^{-3}, [Am] = 0.8, [CBr_4] = 1.2 mol dm^{-3}.[3], Ch.5; [120]

Fig. 5 illustrates the dependence of ϕ_{sens} on $E_{1/2}({}^1S_0/S^+)$ (Table 3). With increase of $E_{1/2}({}^1S_0/S^+)$, there is a tenfold increase of ϕ_{sens} in the region of $E_{1/2}({}^1S_0/S^+) = E_{1/2}$. $({}^1Am_0/Am^+)$ = 0.98 V (Table 3).

Thus the rate of the process is determined by reaction (XVIII) in the formation of Am_1^+ [reactions (XVIII)–(XX)] sensitised by cyanine dyes. The secondary reaction (XIX) does not influence appreciably the quantum yield in the formation of Am_1^+.

The coloured product Am_1^+ is unstable and, as a result of the interaction with CBr_4 and amine molecules, is transformed on heating, with an activation energy of 0.9 eV, into a dye resistant to light and heat[55] and is tentatively assigned to the triphenylmethane series. It has been established[55] that this dye is a sensitiser (autosensitiser) with respect to light active in the region of intrinsic absorption. The mechanism

of the autosensitisation apparently consists in the involvement of the photoexcited dye in electron transfer from the donor to the acceptor [reactions (XVIII)–(XX)].[120]

IV. SENSITISATION VIA ENERGY TRANSFER

1. The Role of the CTC as the Triplet Energy Donor

The sensitisation via a mechanism of type (VI) (Section I) has been postulated in a polymer composition based on a CTC between benzylamines (benzyldiphenylamine, dibenzylaniline) and CBr_4.[3,54,57,121,122] According to the existing ideas about the formation of complexes by aromatic amines,[123] their interaction with CBr_4 entails the formation of complexes of at least two types: a complex of the n,σ-type between the nitrogen atom and the acceptor, responsible for the long-wavelength optical absorption (in the range 330–500 nm) of the polymer composition based on Am.CBr_4, and the complex of the π,σ-type, which is formed by the aromatic rings of the donor (possibly the excited donor) and the acceptor.

Under the conditions of the photoexcitation of the n,σ-type complex, the quantum yield $\phi(Am_1^+) = 0.12–0.16$ and is independent of [Am] and [CBr_4] [for an optical density $D(Am_1^+) < 1$]. The introduction of a triplet energy acceptor (TEA), namely 1-naphthol, lowers $\phi(Am_1^+)$ and leads to the appearance of the relations[124]

$$\varphi(Am_1^+) = b[Am] \text{ and } 1/\varphi[Am_1^+] = b_1 + b_2/[CBr_4]. \qquad (34)$$

The appearance of such relations cannot be accounted for on the basis of the idea that a coloured product is formed as a result of the photodissociation of the n,σ-type complex itself, since in this case $\phi(Am_1^+)$ could not correspond to Eqn.(34) and should decrease with increase in the TEA concentration. The reactions leading to the cyclisation of amines, methylphenylamine and diphenylamine (the methylcarbazole and carbazole formation reactions), occurring as a result of triplet energy transfer to amines from triplet energy donors (propiophenone, acetophenone, benzaldehyde, etc.) photoexcited by light with $\lambda = 365$ nm, are well known.[125] It has been established that the effective triplet energy donors for these amines are compounds whose triplet level lies above the position of this level in the amines by 0.06 eV. In the diphenylamine (A), methyldiphenylamine (B), and benzyldiphenylamine series, the optical absorption maxima are at 282, 292, and 296 nm. The positions of the triplet levels in the liquid phase correspond to $^3E_{00} = 3.14$ and 3.05 eV for (A) and (B) respectively.[125] It is to be expected that the triplet level in the benzyldiphenylamine molecule is similar to that in compound (B) or is somewhat reduced relative to the latter.

In the light-sensitive system based on Am.CBr_4, the influence of TEA can be readily explained by the occurrence of competing reactions on the basis of the idea that, under the conditions of excitation by light with $\lambda = 365$ nm, the complex of the n,σ-type does not dissociate itself but serves as a triplet energy donor for benzyldiphenylamine molecules; the coloured product Am_1^+ is formed as a result of the dissociation of the complex of the π,σ-type:

$$A\cdot CBr_4(n,\sigma) \xrightarrow{h\nu_{CTC}:S_1-T_1} {}^3(Am.CBr_4)_1 \begin{cases} \xrightarrow{Am} {}^3Am_1 + Am.CBr_4 \\ \xrightarrow{TEA} Am.CBr_4 + {}^3TEA_1 \rightarrow {}^1TEA_0; \end{cases} \qquad (XXI)$$

$$^3Am_1 + CBr_4 \rightarrow {}^3Am_1.CBr_4(\pi,\sigma) \rightarrow [Am^+Br^-...\dot{C}Br_3] \rightarrow Am_1^+Br^- + CHBr_3.$$

2. Desensitisation

On photoexcitation by light with $\lambda_{inc} = 742 \pm 3$ nm in a composition containing Am and CBr_4, the cyanine dye (Table 3, No.6) is decolorised in accordance with $\phi_{dec} = 0.0052[CBr_4]$ and also sensitises the given composition with respect to red light, ensuring the formation of Am_1^+ and with $\phi_{sens} = 0.0014$ for [Am] = [CBr_4] = 1 mol dm^{-3}.[122] The same dye is an effective quenching agent for the photoexcitation of the n,σ-complex Am.CBr_4. On photoexcitation of the complex Am.CBr_4 by light with $\lambda_{inc} = 365$ nm, this dye is decolorised with the quantum yield $\phi'_{dec} = 0.15$ for [Am] = [CBr_4] = 1 mol dm^{-3}.[122] There is no decolorisation under the influence of near UV radiation if the composition contains either no donor or no acceptor component (i.e. the CTC Am.CBr_4 is absent). The value of ϕ'_{dec} exceeds by a factor of ~30 that of ϕ_{dec} obtained under the conditions of the photoexcitation of the dye itself. This difference can be due to the fact that by accepting the triplet energy of the CTC, the dye can pass to a second triplet state in which the decolorisation is more effective than in the first.

An effective quenching agent for the excited state of the complex Am.CBr_4 is the coloured product Am_1^+. As Am_1^+ accumulates on photoexcitation of the CTC, in the quantum yield in the formation of the coloured product Am_1^+ is given by the following expression when its optical density $D(Am_1^+) \cong 1$ has been reached:

$$\varphi = \frac{0.12k[Am]}{k[Am] + k_1[Am_1^+]} \cong \frac{0.12k[Am]}{k_1[Am_1^+]}.$$

This relation can be accounted for by the competition between Am and Am_1^+ [analogously to the behaviour of TEA in reaction (XXI)] for the capture of the energy of the complex $^3(Am.CBr_4)_1$ (of the n,σ-type). This desensitisation process determines the photographic characteristics of the light-sensitive polymer layers based on the CTC Am.CBr_4.[126]

3. The Sensitisation Effect Associated with the Polymeric State of the CTC

The polymer matrix exerts a sensitising influence in the region of visible light (400–600 nm) on the light-sensitive composition based on the complex Am.CBr_4. Indeed, it has been shown on the basis of the complex between benzyldiphenylamine and CBr_4 [127] that the optical spectrum of the complex Am.CBr_4 (of the n,σ-type) in the polymer matrix [chlorinated poly(vinyl chloride)—CP VC or polystyrene (PS)] and in the liquid (hexane) has the Gaussian form

$$D(\nu) = D(28,2)\exp[-(\Delta\nu_1)^2/\sigma^2] \qquad (35)$$

where $D(28.2)$ is the optical density at the absorption maximum at $\nu_{max} = 28.2 \times 10^3$ cm^{-1}, $\Delta\nu_1 = 28.2 - \nu_1$, and $\nu_1 = 10^{-3}\nu$ cm^{-1}.

The hexane $\sigma^2 = 7.0$; in polymer layers σ^2 is independent of the nature of the polymer and amounts to 13.5 in PS and 14.5 in CPVC. Thus, in the liquid phase, the optical spectrum of the complex Am.CBr_4 is approximately twice as narrow as in the polymer and does not extend outside the limit of the UV region (the long-wavelength edge corresponds to 400 nm). In the polymer matrix the optical spectrum of the complex extends to 500–600 nm. Apparently this effect occurs because, under the conditions of a limited free volume in the polymer, conformations of the amine in the CTC Am.CBr_4, of the type which do not obtain under equilibrium conditions in the liquid, are "frozen". Data have been published,[127] according to which the light sensitivity in the region of the absorption of the complex Am.CBr_4 has the following spectral

in mind that $E_{1/2}(O_2^-/O_2) = -0.82$ V (sat.c.e.) in acetonitrile:[144]

$$E[^{1,3}(M^+O_2^-)_1] = e[E_{1/2}(M/M^+) + 0.82] + \Delta G^p_{CTC} + {}^{1,3}Q_e.$$

According to generally accepted ideas concerning the nature of molecular complexes,[145] the wavefunction of the excited oxygen complex $^3(M.O_2)_1$ consists of the set of contributions of the following individual states:

$$\varphi^3(M\cdot O_2)_1 = \alpha_1\varphi_1^3(M^+O_2^-)_1 + \alpha_2\varphi_2^3(^3M_1\cdot{}^3O_2) + \alpha_3\varphi_3^3(^1M_1\cdot{}^3O_2) \quad (37)$$

The wavefunction of the singlet-excited complex $^1(M.O_2)_1$ is given by the set of the following contributions:

$$\varphi^1(M\cdot O_2)_1 = \alpha_1'\varphi_1^1(^1M_0\cdot{}^1O_2) + \alpha_2'\varphi_2^1(M^+O_2^-)_1 + \alpha_3'\varphi_3^1(^3M_1\cdot{}^3O_2) \quad (38)$$

We shall now consider Scheme 1 (Scheme I) when $E(^3M_1) > E[^3M^+O^-)_1]$ (Fig. 6*a*). In this case the energetically lowest triplet state is the state with complete charge transfer $^3(M^+O_2^-)_1$, which makes the main contribution to the configuration $^3(M.O_2)_1$ [it will be shown below that $\alpha_1 \cong 1$ in Eqn.(37)]. The contribution of other states, determined by the multipliers $(\alpha_2/\alpha_1)^2$ and $(\alpha_3/\alpha_1)^2$, is associated with the relative positions of the energy levels $\Delta E_1 = E(^3M_1) - E[^3(M^+O_2^-)_1]$, because $\alpha_2/\alpha_1 = \beta/\Delta E_1$ and $\Delta E_2 = E(^1M_1) - E[^3(M^+O_2^-)_1]$, since $\alpha_3/\alpha_1 = \beta/\Delta E_2$. Here

$$\beta = \int \varphi_3^3(^3M_1\cdot{}^3O_2) H \varphi_1^3(M^+O_2^-)_1 \, d\tau \simeq 0.01\text{—}0.1\ \text{eV}$$

is the potential energy of the transferred charge distributed in the electrostatic field of the radical-cation M^+.[145] The collision complex $^3(^3M_1.{}^3O_2)$ or the state $^3(^1M_1.{}^3O_2)$ is transformed into $^3(M.O_2)_1$ via the complex formation mechanism (37) with a rate constant $k = \beta/h \cong 2 \times 10^{12}$–$2 \times 10^{13}$ s^{-1} ($h = 4.2 \times 10^{-15}$ eV s). It is possible to estimate that the contribution to $\phi^3_3(M.O_2)_1$ by the states $^3(M^+O_2^-)_1$ is $\geqslant 96\%$ and that by the states $^3(^3M_1.{}^3O_2)$ and $^3(^1M_1.{}^3O_2)$ is $\leqslant 4\%$ when $\Delta E_1 \geq 0.5$ eV. Hence it follows that the formation of the triplet collision complex $^3(^3M_1.{}^3O_2)$ determines the primary electron transfer in the oxidation reaction of the organic compound.

The energetically lowest configuration among the states which contribute to $^1(M.O_2)_1$ [Eqn.(38)] is the collision complex $^1(^1M_0.{}^1O_2)$. The excited complex in the singlet state $^1(^3M_1.{}^3O_2)$, formed on collision of $^3M_1$ and $^3O_2$, is initially transformed, with a rate constant $\beta/h \cong 10^{13}$ s^{-1}, into the configuration with total charge transfer $^1(M^+O^-)_1$, which is transformed in its turn into the state $^1(^1M_0.{}^1O_2)$ with a rate constant $\beta_1/h \cong 10^{11}$ s^{-1}, where

$$\beta_1 = \int \varphi_3^1(M^+O_2^-)_1 H \varphi_1^1(^1M_0\cdot{}^1O_2)\, d\tau \simeq 10^{-2}\ \text{eV}$$

is the energy of the dipole $M^+O_2^-$ in the potential field of the neutral $^1O_2$ molecule. The dissociation of the states $^1(^1M_0.{}^1O_2 : {}^1\Delta_g)$ and $^1(^1M_0.{}^1O_2 : {}^1\Sigma_g^+)$ leads to the formation of $^1O_2$ in the forms $^1\Delta_g$ and $^1\Sigma_g^+$. Taking into account the statistical weights of the states with different multiplicities, formed on collision of $^3M_1$ and $^3O_2$ (see Section I), it is to be expected that in the case considered (Scheme 1) 75% of the total number of the triplet-excited molecules $^3M_1$, constituting the state $^3(M^+O_2^-)_1$ [see Eqn.(37)], quench the energy in processes involving electron transfer from $^3M_1$ to $^3O_2$, while 25% of the $^3M_1$ participate in the formation of $^1(^3M_1.{}^3O_2)$ [see Eqn.(38)] and lead to the appearance of $^1O_2$. Hence it follows that the compounds satisfying the inequality $E(^3M_1) > E[^{1,3}(M^+O_2^-)_1]$ are weak sensitisers of the formation of $^1O_2$ and may be oxidised via the mechanism involving electron transfer to oxygen.

We shall consider Scheme 2 (Section I) (see Fig. 2*b*) when $E(^3M_1) < E[^{1,3}(M^+O_2^-)_1]$ and the main contribution to the overall configuration of the triplet-excited state [Eqn.(37)]

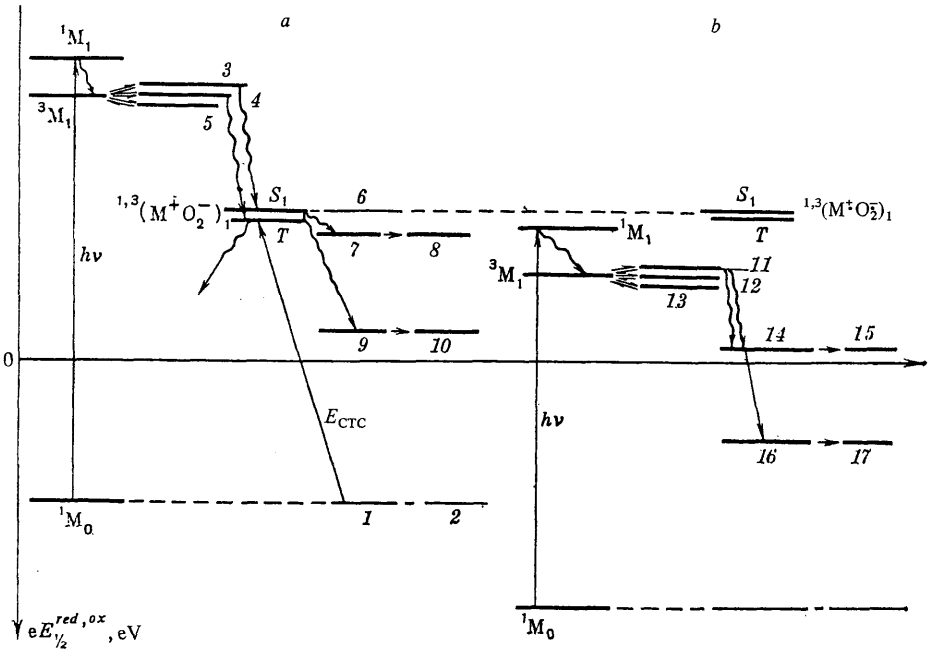


Figure 6. Schematic illustration of the photoprocess with participation of O_2: *a*) $E(^3M_1) > E[^{1,3}(M^+O_2^-)_1]$; *b*) $E(^3M_1) < E[^{1,3}(M^+O_2^-)_1]$; the molecules M are of different nature and the levels are reckoned from $E(^1M_0) = E_{1/2}(^1M_0/M^+)$; the states corresponding to the positions of the levels: *1*) $^3(^1M_0.{}^3O_2)$; *2*) $^3\Sigma_g^-$; *3*) and *11*) $^1(^3M_1.{}^3O_2)$; *4*) and *12*) $^3(^3M_1.{}^3O_2)$; *5*) and *13*) $^5(^3M_1.{}^3O_2)$, S_1—$^1(M^+O_2^-)$, T—$^3(M^+O_2^-)$; *6*) $E_{1/2}(O_2^-/O_2)$; *7*), *9*), *14*), and *16*) $^1(^1M_0.{}^1O_2)$; *8*) and *15*) $^1\Sigma_g^+$; *10*) and *17*) $^1\Delta g$.[3], Ch.7.

comes from the state $^3(^3M_1.^3O_2)$. The contribution of the state $^3(M^+O_2^-)_1$ in Eqn.(37) is determined by the ratio (α_1'/α_2'), where $\alpha_1'/\alpha_2' = \beta_2/\Delta E_3$, $\Delta E_3 = E[^3(M^+O_2^-)_1] - E(^3M_1)$, and

$$\beta_2 = \int \varphi_1^3(M^+O_1^-)_1 \, H\varphi_2 \cdot {}^3(^3M_1 \cdot {}^3O_2)\,d\tau = 10^{-2} \text{ eV}$$ [145]

is the energy of the dipole $M^+O_2^-$ in the potential field of the neutral molecule $^3O_2$.[145] Hence $(\alpha_1'/\alpha_2')^2 < 2\%$ for $\Delta E_3 > 0.5$ eV and the charge transfer state $^3(M^+O_2^-)_1$ does not participate directly in the photochemical oxidation process. In this case, which has been considered in detail,[146-148] the efficiency of the transformation of the energy of the triplet-excited molecules into the energy of singlet oxygen reaches 100%.

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The above discussion of the charge transfer reactions with participation of CTC in polymer matrices confirms the validity of the initial postulate that the energy relations of the process are determined mainly by dielectric parameters of the polymer matrix, which functions as a binder for the photoactive components and it is immaterial whether the latter are monomeric or polymeric compounds. This should apparently be manifested in the kinetic characteristics of the process. However, kinetic studies of this kind have so far been clearly insufficient.

One can also conclude that the oxidation-reduction potentials measured in liquid solutions by electrochemical methods and adjusted with respect to the polymer matrix can be usefully employed for the analysis of charge transfer processes in polymers instead of the gas-phase values of the ionisation potential and the electron affinity. Firstly, this is consistent with the essential physicochemical nature of the processes considered and, secondly, it makes it possible to employ the numerous data on the oxidation-reduction potentials of a large number of organic compounds.

It also follows from the above analysis that measurements of the energies of the optical transitions of the donor–acceptor systems in the polymer matrices are necessary, since their comparison with the energies of the analogous transitions in liquid media, where oxidation-reduction potentials are measured, makes it possible to obtain directly the ionisation energies and electron affinities of the molecules in polymer matrices without using the polarisation energies in polymers and in solutions, which are difficult to fix.

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