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Donor-Acceptor Interactions between Non-silver Information Recording Processes

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The use of non-silver layers based on intermolecular charge-transfer complexes (CTC) for the recording of information, the recording of the influence of light, and for microfilming is examined. The processes are based on the ability of the CTC to dissociate following the absorption of light with formation of products whose absorption spectrum is different from that of the initial films incorporating the CTC. General postulates concerning the mechanism of the photodissociation of the CTC are described and the characteristics of the photochemical reactions of specific systems used as light sensitive materials are considered.
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I. INTRODUCTION

Organic systems whose physicochemical properties change under the influence of light have been widely investigated in recent years. Compounds or compositions whose optical properties change as a result of illumination are used to record images[1-4].

Light-sensitive layers based on organic materials are characterised by a high resolving capacity, the possibility in many instances of carrying out repeated recording-deletion cycles, the absence of chemical development and fixing stages, and the development (intensification) of the image on exposure or by simple physical methods (for example, by heat treatment) and hence the possibility of obtaining an image in real time, the elimination of expensive silver from the recording process, and many other valuable properties. At the same time the sensitivity of organic layers is lower by several orders of magnitude than that of silver bromide photographic materials. At the present time all the above factors make such materials promising in copying and special-purpose photography requiring a high resolution. The existing monographs and reviews deal in detail with the mechanisms of the photochromic transformations in organic compounds[1,2,5], the diazo-coupling reaction for diazonium salts in connection with their use in diazo-printing and in the vesicular process[6-10], as well as the physicochemical principles of the electrophotographic process[11,12].

This review discusses the characteristics of the changes under the influence of light in the chemical and optical properties of systems based on charge-transfer complexes (CTC). Two- or multi-component compositions, in which the primary stage of the complex process involving a change in the positions of the optical absorption bands is electron transfer from the donor component of the CTC to the acceptor component, have been examined. The special interest in intermolecular complexes is due to two factors. The first (the presence of an intermolecular bond) rules out the diffusion-dependent limitation of the rate of the photochemical reaction between two molecules. The second (ionisation of the donor component) corresponds to the absorption of a single light quantum, i.e. does not require high-intensity light sources and, depending on the nature of the selected components as well as the properties of the film-forming medium, can occur under the influence of light at wavelengths from 250 to 1500 mm. Systems based on CTC are beginning to find practical applications in the recording of images as a result of their high rate of colour change and the possibility of optical development[13-16] and thermal fixing[17].

The need to obtain materials whose colour changes under the influence of light requires the compounds to have a system of conjugated bonds. In these compounds the delocalised π electrons, characterised by a close proximity of allowed energy levels, are responsible for absorption in the visible and near ultraviolet and infrared regions. The colour of organic molecules is determined by the size of the conjugation system in combination with the presence of electron-donating and electron-accepting groups and their chemical composition[18-20]. The greatest displacement of the optical absorption bands is due to the change in the size of the continuous conjugation regions[18].

The dependence of the position of the optical absorption band on the size of the conjugated bond system was obtained by Kuhn[21-23] for cyanine dyes. It was established that, in symmetrical molecules with equal lengths of single and double bonds, the energy levels are distributed monotonically and correspond to the following relation between the position of the optical absorption maximum and the number of units N in the conjugated chain:

$$\lambda_{max} = \frac{8mcl^2}{h} \cdot \frac{N^2}{N+1}, \qquad (1)$$

where l is the length of a single chain unit. Owing to the difference between the lengths of single and double bonds, the energy spectrum of asymmetric molecules corresponds to an increased distance between the highest occupied and highest unoccupied levels compared with the distances between both highest occupied and lowest unoccupied orbitals. Such distribution of levels is characteristic of many conjugated molecules, which is the reason for the appearance of a spectrum in the long-wavelength region when the molecule is converted into a radical-cation or a radical-anion.

A shift of the absorption spectrum from the visible to the ultraviolet region accompanies the dissociation of the system of conjugated bonds on conversion of thiazine, triphenylmethane, and other dyes into their leuco-forms[18, 24-26, 13-15] and of xanthene dyes into the lactone form[27-31].

Certain specific properties of the CTC, which must be taken into account in selecting the components of the complex, are analysed below. These are the spin state at the dissociative level for complexes of different types as well as the region of maximum light sensitivity under the conditions corresponding to different ways of exciting the system.

II. CONDITIONS GOVERNING THE PHOTODISSOCIATION OF CHARGE-TRANSFER COMPLEXES

Since 1952, when Mulliken surveyed the accumulated data on the donor–acceptor interaction and described the phenomenon for the first time in quantum-chemical terms (in the gas approximation), numerous original papers, reviews, and monographs have been devoted to this field of study[32-39].

According to the ideas developed by Mulliken and Person[33], an intermolecular bond is formed in a system incorporating an electron donor (D) and acceptor (A) as a result of the mixing of the state in which there is only a van der Waals interaction (DA) between D and A and the dative state ($D^{+}-A^{-}$) in which the electron is fully transferred from the donor to the acceptor. The residence time of the system in each state $\tau \simeq h/W_{01} \simeq 10^{-13}-10^{-14}$ s,[40] since the Planck constant $h = 4.2 \times 10^{-15}$ eV s and the integral $W_{01} = \int \varphi(\mathrm{DA}).H.\varphi(D^{+}-A^{-})d\tau = 0.05-0.5$ eV, where $\varphi(\mathrm{DA})$ and $\varphi(D^{+}-A^{-})$ are the wave functions of the non-bonded and dative states respectively. Thus, as a result of the mixing of the states, a dipole $D^{+\delta}A^{-\delta}$ is formed, where δ is the degree of charge transfer. The experimental methods for the measurement of δ have been examined in detail[33,41]. The idea of charge transfer has been introduced by Hausser and Murrel[42] in a quantum-chemical description of the state of dimers comprising identical radical-ions, because the ionisation potential of a radical-ion is close to the electron affinity. In contrast to the dative state of the CTC, in the dimer, owing to the complete identity of the radical-ions, this state corresponds to a jump of two electrons (in a paired state) between radical-ions at a frequency which, as stated above is close to 10^{14} s^{-1} and not to a directional charge transfer from one radical-ion to another.

Fig. 1 presents a generalised energy diagram for donor–acceptor systems of different types. A characteristic feature of the CTC is that, owing to the mixing of the (DA) and ($D^{+}-A^{-}$) states, the energy level of the ground state W_N lies below the positions of its components W_0 and W_1 (section I, Fig. 1). The energy gain is

$$W_N - W_0 = -(W_{01} - W_0S_{01})^2/(W_1 - W_0); \quad (2)$$

for weak CTC, where $W_1 \gg W_0$ (section I*a*, Fig. 1); in the vicinity of $W_0 \simeq W_1$ (section I*b*, Fig. 1) we have

$$W_N - W_0 = -(W_{01} - W_0S_{01})/(1 + S_{01}) \quad (3)$$

if $W_1 \gtrsim W_0$ and

$$W_N - W_1 = -(W_0 - W_1S_{01})/(1 + S_{01}) \quad (4)$$

if $W_0 \gtrsim W_1$, for the "reverse" CTC, where $W_0 \gg W_1$ (section I*c*, Fig. 1), the energy gain is

$$W_N - W_1 = -(W_{01} - W_1S_{01})^2/(W_0 - W_1). \quad (5)$$

For CTC, the overlap integral $S_{01} = \int \varphi(\mathrm{DA}).\varphi(D^{+}-A^{-})d\tau \simeq 0.01-0.1$.[43] The excited energy level W_V in CTC exceeds the components W_1 and W_0 by an amount

$$W_v - W_1 = (W_{01} - W_1S_{01})^2/(W_1 - W_0) \quad (6)$$

or

$$W_v - W_0 = (W_{01} - W_0S_{01})^2/(W_0 - W_1) \quad (7)$$

along sections I*a* and I*c* respectively. We have

$$W_v - W_1 = (W_{01} - W_1S_{01})/(1 - S_{01}) \quad (8)$$

for $W_1 \gtrsim W_0$ (section I*b*) or $W_1 > W_0$ and

$$W_v - W_0 = (W_{01} - W_0S_{01})/(1 - S_{01}) \quad (9)$$

for $W_0 \gtrsim W_1$.

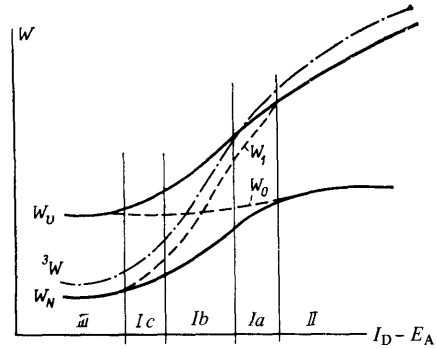


Figure 1. The energy scheme for electronic donor–acceptor complexes. Levels: ground (W_N), excited (W_V), triplet (^3W), non-bonding (W_0)(DA), and dative (W_1)($D^{+}-A^{-}$); I_D is the ionisation potential of the donor and E_A the electron affinity of the acceptor.

In a condensed medium the position of the level W_1 is determined by the relation

$$W_1 = I_D - E_A - Q - P + (C \pm K) \mp V,$$

where Q is the energy of the Coulombic attraction between radical-anions of different signs, P is the polarisation energy of the system, $C + K$ and $C - K$ are the energies of the Coulombic repulsion between unpaired electrons for the singlet and triplet orientations respectively, K is the exchange repulsion energy, and V the contribution of the covalent structure to the dative state. V is large for stable $n\nu$, $\pi\nu$, and $n\sigma$ complexes[35]. Owing to the presence of the contribution of V, the purely ionic triplet level of the dative structure

$$^3W_1 = I_D - E_A - Q - P + C + (V - K) \quad (10)$$

lies above the singlet level

$$^1W_1 = I_D - E_A - Q - P + C - (V - K). \quad (11)$$

for the majority of donor–acceptor systems.

The CTC triplet state (^3W, Fig. 1) arises after the complete electron transfer from the donor to the acceptor and constitutes none other than a purely ionic triplet configuration of the dative structure[33]. The wave function of the triplet state of the complex (φT) is described by a

combination of the wave functions $\varphi(D^{\cdot})$ and $\varphi(A^{\cdot-})$ corresponding to the distribution of the unpaired electron densities in the radical-cation (D^{+}) and radical-anion ($A^{\cdot-}$):[33]

$$\begin{aligned}\varphi_T(m_s=+1) &= A\{\varphi(D^{+}\uparrow)\varphi(A^{\cdot-}\uparrow)\},\\ \varphi_T(m_s=-1) &= A\{\varphi(D^{+}\downarrow)\varphi(A^{\cdot-}\downarrow)\},\\ \varphi_T(m_s=0) &= (\psi_I-\psi_{II})/(2-S_{01}^2)^{1/2},\end{aligned} \tag{12}$$

where

$$\begin{aligned}\psi_I &= A\{\varphi(D^{+}\uparrow)\cdot\varphi(A^{\cdot-}\downarrow)\} \text{ and}\\ \psi_{II} &= A\{\varphi(D^{+}\downarrow)\cdot\varphi(A^{\cdot-}\uparrow)\}.\end{aligned} \tag{13}$$

The arrows indicate the direction of the spin of the unpaired electron.

In the presence of a contribution by V the ^3W level can lie above W_V for a weak CTC, which in the limit becomes a contact CTC (section II, Fig. 1) with $W_{01}\simeq 0$, $S_{01}\simeq 0$, and $W_V\simeq {}^1W_1$ [Eqn. (6)].[44-46] It shifts to the region $W_N<{}^3W<W_V$ on passing to a stable CTC (section I, Fig. 1) and, as the difference $I_D - E_A$ decreases, it falls to the level $J = {}^3W - {}^1W_1 = 2(V-K)$ on transition to radical-ion salts, for which $W_{01}=0$, $S_{01}=0$, and $W_N={}^1W_1$ [Eqn. (5)].

In $\pi\pi$ complexes the V term is insignificant and the dative structure is largely ionic ($D^{+}A^{\cdot-}$). For such complexes, there is a possibility of a shift of the triplet level to a position below the singlet dative level [Eqns. (10) and (11)].[47,48]

As already mentioned, the dissociation of donor–acceptor complexes into radical-ions is the primary step of the complex process leading to a change in the absorption spectra of film materials. Since dissociation takes place with a greater probability after the light-induced population of the level with the most complete charge separation, it follows that the dissociative levels in weak, contact complexes are both the triplet level ^3W and the excited singlet level W_V, in a stable CTC only the ^3W level is dissociative, while in radical-ion salts both the triplet state and the ground singlet state are dissociative.

The dissociative level can be reached in contact complexes and CTC by the action of light corresponding to the absorption band of the complexes:

$$h\nu = W_v - W_N, \tag{14}$$

and in "reverse" CT by thermal excitation. Dissociation occurs when the dissociative level lies above the level of solvent-separated radical-ions ^2W,[49] i.e. under the condition

$$I_D - E_A - Q - \frac{2(\varepsilon-1)}{2\varepsilon+1}\cdot\frac{\mu^2}{a^3} \gtrless \gtrless I_D - E_A - Q_1 - \frac{2e^2}{r_j}\left(1-\frac{1}{\varepsilon}\right).$$

Here $[2(\epsilon-1)/(2\epsilon+1)](\mu^2/a^3)$ is the polarisation energy of the dipole $\mu = r_{D^{+},A^{\cdot-}}e'$,[37,40] $r_{D^{+},A^{\cdot-}}$ the distance between the donor and acceptor components of the complex, ϵ the dielectric constant of the medium, a the radius of the cavity polarised by the dipole μ, $(e^2/r_j)(1-1/\epsilon)$ the polarisation energy of the radical-ion with radius r_j, and Q_j the energy of the Coulombic attraction between the solvent-separated radical-ions.

The photodissociation process for the dissociative level ^3W is illustrated in Fig. 2. Many non-ordered systems incorporating CTC, liquids and films, are characterised by the presence of radical-ions even under conditions where the difference $^3W - W_N$ [see Eqns. (12), (13), and (2)–(5)] is fairly large and cannot ensure thermal dissociation. According to Stewart and coworkers[50,51], the appearance of radical-ions under dark conditions is associated with the formation of a CTC in an excited triplet state at the instant of formation of the complex on dissolution of an acceptor in a donor liquid. Then $^3W - W_N = \Delta H + \delta$, where $\Delta H = W_0' - W_N$ is the heat of formation of the complex and $\delta = {}^3W - W_0'$ the activation energy for the thermal formation of radical-ions.

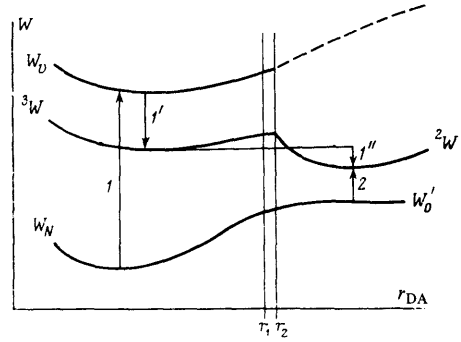


Figure 2. Schematic illustration of the formation of radical-ions in a non-ordered donor–acceptor system: 1),1'), and 1'') photodissociation of the CTC; 2) thermally excited D + A systems; W_0'—the level of separated D and A; ^2W the level of separated D^{+} and $A^{\cdot-}$; $r_{DA}<r_1$—the CTC region; $r_1<r_{DA}<r_2$—exciplexes; $r_{DA}<r_2$—separated D and A or D^{+} and $A^{\cdot-}$.

The above explanation is apparently not the only one possible. As shown in Fig. 2, in a liquid and in films where both CTC and solvent-separated D and A exist simultaneously in equilibrium, one may expect the occurrence of reaction via pathway *2* on thermal excitation:

$$D + A \xrightarrow{\Delta E} D^{+} + A^{\cdot-}$$

without collision of the species. According to the theory developed by Dogonadze and Kuznetsov[52], reaction via pathway *2* takes place without change of the distance between the components and is due to a tunnel electron transfer. This transfer occurs on thermal excitation of the (D + A) system to the position coinciding with the ^2W level and under conditions where, in consequence of fluctuation-induced changes, the orientation of the solvent relative to the A and D molecules coincides with the orientation about the A^{-} and D^{+} ions.

The photodissociation of CTC into radical-ions was first suggested by McGlynn and coworkers[45,46]. The photochemical decomposition of CTC has been examined in the reviews of Sergeev and coworkers[53,54], Nagakura[55], Davidson[37], and in a study by Irie et al.[58] on the use of this phenomenon in photopolymerisation, photosynthesis, and photochemical oxidation.

The elucidation of the nature of the dissociative level is important for finding the conditions under which light-sensitive systems operate. For dissociation via the triplet level in liquid and film systems, oxygen (the quenching agent for triplet energy) greatly reduces the quantum yield of the photodissociation products, which determines the light sensitivity of the system[13,55,59]; the

lack of an effect by molecular oxygen means that dissociation takes place via a singlet state, a characteristic solely of contact complexes[55,59,60-62].

Photodissociation can also occur via the excitation of both the complex and its individual components. In the latter case the electron transfer from the donor to the acceptor is due to the decrease of the difference $I_D - E_A$ owing to the decrease of I_D by $\sim h\nu_D$ on excitation by light corresponding to the absorption band of the donor or an increase of E_A by $h\nu_A$ when the system is acted upon by light corresponding to the absorption band of the acceptor[18,22,63]. The photoexcitation of an individual component is effective when the component of the complex whose colour changes is light-sensitive and the content of the second component, determined by the equilibrium constant

$$K = [DA]/[D][A], \quad (15)$$

ensures that a dominant proportion of the light-sensitive component exists in the form of the complex. The simultaneous presence of the light-sensitive component both as part of the complex and in the free state is responsible for the decrease of the quantum yield of the photodissociation products of the complexes (as a result of the absorption of part of the light quanta by the free molecules).

III. THE LIMITING LIGHT SENSITIVITY OF THE LAYERS IN THE ABSENCE OF IMAGE INTENSIFICATION

The principal characteristics of photolayers are light sensitivity and resolving capacity. Since in organic materials an individual molecule reacts, the resolving capacity of such materials is extremely high and their light sensitivity is low because it is limited by the quantum yield $\Phi \leq 1$. It is possible to estimate the upper limit to light sensitivity on the basis of the decrease of the concentration c of the component undergoing a colour change (or of the entire CTC):

$$-dc/dt = I_{abs}\,\Phi/l, \quad (16)$$

where I_{abs} is the power of the light flux absorbed by the film and l is the film thickness. After substituting $c = D/\epsilon l$ and $I_{abs} = I_0(1 - 10^{-D_1})$ in Eqn. (16), D being the optical density of the component whose colour changes, D_1 the optical density of the layer in the wavelength range of the incident light, ϵ the extinction coefficient, and I_0 the power of the light flux incident on the film, the relation between the incident energy of the light flux $I_0 dt$ (J cm^2) and the change in D assumes the following form:

$$I_0\,dt = \frac{dD}{1-10^{-D_1}}\,\frac{1.196\cdot 10^5}{\varepsilon\Phi\lambda}. \quad (17)$$

Here ϵ is expressed in litre^3 mole^{-1} cm^{-1} for a liquid and in dm^3 mole^{-1} cm^{-1} for films, λ being the wavelength of the incident light in nm. According to a USSR Government Standard (GOST), the light sensitivity of silver bromide layers is determined from the energy of the incident light causing a change in optical density by $\Delta D = 0.2$:

$$S_{0.2} = 10^{-4}/I_0\Delta t K,$$

where K is the coefficient of visibility with a maximum value of 680 at 555 nm.[64] Having adopted $\Phi = 1$, $\epsilon = 10^5$ dm^3 mole^{-1} cm^{-1}, $10^{-D_1} \ll 1$, and a wavelength of incident light $\lambda = 555$ nm identical with that corresponding to the absorption maximum of the compound, we find

$$I_0\Delta t_{0.2} \simeq 0.4\cdot 10^{-3}\ \text{J cm}^{-2},$$

i.e. the limiting attainable light sensitivity corresponds to $S_{0.2} \simeq 4\times 10^{-4}$ GOST units and is lower by several orders of magnitude than for silver bromide films. It is noteworthy that, in order to estimate the light sensitivity of non-silver layers, the value of $I_0\Delta t_1$ corresponding to a change of D by $\Delta D = 1$ was adopted. At the present time $I_0\Delta t_1$ is used mainly when information is recorded by decolorising coloured films, particularly for high optical densities. When a colour was imparted to colourless films, the light sensitivity was estimated in many investigations from $I_0\Delta t_{0.2}$.

Thus systems with $\Phi \leq 1$ can be used successfully in microfilming, where the resolving capacity of the layer is of decisive importance. The problem of obtaining layers with a high light sensitivity requires image intensification analogous to development in silver bromide photography and leading in its turn to a decrease of the resolving capacity, because a grain and not a molecule is now the light-sensitive element.

IV. LIGHT SENSITIVE CHARGE-TRANSFER COMPLEXES BASED ON ORGANIC SYSTEMS

Light-sensitive compositions, consisting of cyanine dyes[65] and their bases[66,67], leucoxanthenes, leucoanthraquinone, leucodiarylmethanes[66,68], amines[67,69,70], leucotriphenylmethane and styryl dyes[13-16,71,72] (as the donor component which undergoes a colour change), and the A–C–X$_3$ acceptors[13-16,65-72] (where A = H, Cl, Br, or I, and X = Cl, Br, or I) or $Cl_2BrCCBrCl_2$, as well as sulphur-containing acceptors of the type ArSh and ArS_2Ar or sulphophenyl halides[66], are being widely used nowadays and are being introduced into industry. In addition to the above substances, the compositions include also a free radical inhibitor and a polymeric binder. The light sensitive composition is deposited on either a paper or a polymeric support. It is noteworthy that the Horizons Co. Inc. in the USA alone took out more than 250 patents for light-sensitive compositions of this type.

Photochemical reactions in solid layers have been investigated in greatest detail using leucotriphenylmethane dyes[13-16] (DyeH) in combination with CBr_4, for example, leuco-Crystal Violet with added inhibitor of $CBr_2^{\cdot\cdot}$ (triphenylantimony) and a polystyrene binder. It has been shown[13-16] that, in contrast to DyeH and CBr_4, which absorb in the region below 370 nm, compositions with these substances give rise to an additional spectrum up to 450 nm, which imparts a yellow colour to the entire film. The additional absorption indicates the formation of a CTC (we shall designate it by DyeH.CBr_4). The photodissociation of the CTC on illumination by light corresponding to its absorption band [Eqns. (14)] takes place only in the absence of O_2 and therefore proceeds via the population of the triplet level ^3W in accordance with reaction

$$\begin{gathered}\text{DyeH}\cdot CBr_4 \xrightarrow{h\nu_1} (\text{DyeH}\cdot CBr_4)^* \rightarrow {}^3(\text{DyeH}^+ + CBr_4^{\cdot-}),\\ {}^3(\text{DyeH}^+ CBr_4^{\cdot-}) \rightarrow \text{DyeH}^+ + CBr_4^{\cdot-}.\end{gathered} \quad (18)$$

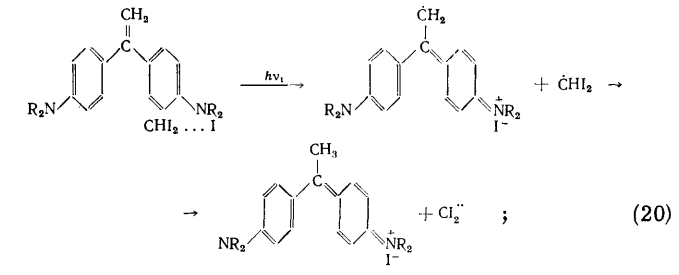
The dye responsible for the image (Dye$^+$), which absorbs in the visible region (λ_2, max = 600 nm, $\epsilon = 1.2\times 10^5$ dm^3 mole^{-1} cm^{-1}), arises via the reaction

$$\text{DyeH}^+ + CBr_4^{\cdot-} \rightarrow \text{Dye}^+Br^- + HBr + CBr_2^{\cdot\cdot}. \quad (19)$$

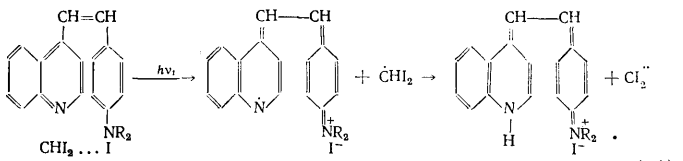
The $CBr_2^{\cdot\cdot}$ radicals which fog the film interact with the added inhibitor, restoring the transparency of the film.

The quantum yield at this stage, under the conditions of continuous circulation of gaseous nitrogen, is $\Phi = 0.1$ and corresponds to $I_0\Delta t_{0.2} = 10^{-2}$ J cm^{-2}.

The formation of an image in layers incorporating a CTC based on CHI_3 and vinylidene or substituted styryl components is due to an analogous set of reactions[71]. The absorption spectra of these compounds are displaced under illumination to a lesser extent than in the transition DyeH → Dye$^+$, since it does not entail an increase in the size of the continuous conjugation system [*Nl* in Eqn. (1)] and is due solely to the formation of electron-accepting groups via the following respective reactions:



(20)



(21)

The initial CTC absorb in these systems in the region of 488 nm and the resulting dyes absorb at λ_{max} = 620 and 580 nm respectively.

The problem of the optical development of the exposed film is also discussed in the studies quoted above[13-16,71]. The latent image arising as a result of brief exposure to radiation with $\lambda_1 < 450$ or 488 nm may be developed via reactions (18)–(21) by light corresponding to the absorption band of the dye. The dye molecules are then used as sensitisers. The effect is absent in the presence of O_2, which indicates energy transfer via triplet levels. The formation of a grain consisting of dye molecules during development takes place via the mechanism[13]

$$\mathrm{Dye}^+ \xrightarrow{h\nu_2} {}^1\mathrm{Dye}^{+\bullet},$$

$$^1\mathrm{DyeH}^{+\bullet} \rightarrow {}^3\mathrm{Dye}^+,$$

$$^3\mathrm{Dye}^+ + (\mathrm{DyeH}\cdot\mathrm{CBr}_4) \rightarrow \mathrm{Dye}^{\cdot+} + {}^3(\mathrm{DyeH}^+\cdot\mathrm{CBr}_4^{\cdot-}).$$

and then in accordance with reactions (18) and (19). Owing to the absence of inclusions of dye molecules at the unexposed sites, the film remains yellow after development due to the presence of the CTC. In contrast to the process discussed above, another mechanism, consisting in the thermal dissociation of the complex as a result of the liberation in a microvolume of the energy absorbed by the dye Dye$^+$ inclusions, has been suggested[14-16]. This conclusion is based on the fact that layers containing DyeH become coloured also on heating. The image is fixed by keeping the film at a temperature of ~140°C, which ensures the decomposition of the halogen-containing component and hence the decomposition of the CTC. The yellow colour then disappears and the unexposed sites become clear. It has been shown[13] that the image can be intensified in this way by a factor of ~1400, with an increase of the effective quantum yield to ~140 and of $I_0\Delta t_{0.2}$ to 7×10^{-6} J cm^{-2}. This corresponds to $S_{0.2}$ = 0.03 GOST units. In the best specimens $S_{0.2}$ reaches 0.1 (Fotland and Fichter[72]) and is close to the light sensitivity of silver halide films with a high resolution.

Polymeric films incorporating CTC comprising an amine (Am) (dibenzylaniline)[70,73,74] and CBr_4 are not coloured on heating to 250°C. Analysis of the influence of triplet energy acceptors on photochemical reactions[73] has established that the complex Am.CBr_4 (λ_{max} = 365 nm) does not dissociate on photoexcitation and, after an intercombination conversion, transfers to the triplet levels the energy absorbed by the Am molecules not involved in the CTC. At high concentrations of the added components, the latter form the exciplex ^{3}(Am).CBr_4, which dissociates via the mechanism

$$^3(\mathrm{Am})\cdot\mathrm{CBr}_4 \rightarrow (\mathrm{Am}^{+\bullet}\cdot\mathrm{Br}^- + \dot{\mathrm{C}}\mathrm{Br}_3) \rightarrow \mathrm{Am}_1^+\cdot\mathrm{Br}^- + \mathrm{HBr} + \ddot{\mathrm{C}}\mathrm{Br}_2 \quad (22)$$

with formation of Am_1^+ (C_6H_5–CH=$\overset{+}{N}$(–C_6H_5)–CH_2–C_6H_5), which absorbs in the visible region with λ_{max} = 665 nm. The optical intensification of the image in this system takes place via a two-quantum mechanism[74] in accordance with the relation (for Am ≫ Am_1^+)

$$\lg\frac{10^D-1}{10^{D_0}-1} = \frac{al_0^2}{bl_0+c[A_1]}\cdot\frac{[Am]}{d[A_2]+f[Am]+g}\cdot\frac{[CBr_4]}{k+h[CBr_4]}\cdot(t-t_0), \quad (23)$$

where D and D_0 are the optical densities at 665 nm at times t and t_0, a, b, c, d, f, g, h, and k are constant coefficients, A_1 and A_2 are oxygen or other acceptors of the triplet energy of singly and doubly excited Am_1^+ species respectively, and I_0 is the intensity of the light acting in the region of λ = 665 nm.

Optical intensification made it possible to increase the effective quantum yield from ~0.14 to ~14 and the light sensitivity at 365 nm from 1.4×10^{-2} to 1.4×10^{-4} J cm^{-2}. In contrast to layers based on leucodyes, amine-containing films are more stable and do not lose their light sensitivity for a long time. In the fixation of films by heating, a stable dye is synthesised simultaneously from Am_1^+ and other components of the layer.

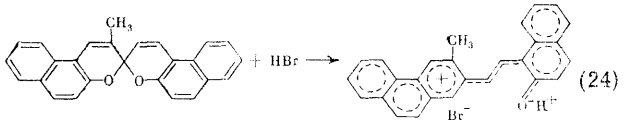
In a photoreproduction process, amines such as *N*,*N*′-diphenylenediamine, *N*,*N*′-diphenyl-*p*-phenylenediamine, and others are used in combination with CBr_4 [75] or CHI_3.[76] These systems are also sensitive to ultraviolet light and the appearance of a colour in them is associated with the formation of stable radical-cations.

The region of spectral sensitivity of the films has been extended to ~540 nm when the bases of cyanine dyes began to be used in conjunction with CBr_4 [66,67] and to 700 nm when cationic cyanine dyes were used[65]. The presence of CTC of CBr_4 and cyanine dyes or their bases has been merely postulated[65,67]. These systems are used without image intensification. Compositions consisting of cationic cyanine dyes and anionic aryl borates $(BR_1R_2R_3R_4)^-$, where R_{1-4} are aryl-substituted groups which are effectively decolorised on photoexcitation of the dye, have also been proposed for use in reproduction using visible light. Lifanov et al.[77] and Chibisov[78] established that, on photoexcitation of cyanine dyes, there is an effective electron transfer to the dye with formation of a radical-anion if the system contains simultaneously a donor (ascorbic acid, diphenylamine, hydroquinone, etc.), but in the presence of acceptors the products are radical-cations.

The photographic process involving A–C–X_3 is referred to by convention as a free radical process. It is noteworthy that in all systems free-radical reactions take place under the conditions of the photoexcitation of the halogenomethane (<300 nm) as a result of its dissociation, for example into CBr_3 and Br$^\cdot$, and the occurrence of subsequent reactions with participation of these radicals[69]. When the reactions are initiated by the photoexcitation of

the CTC or the donor under these conditions, the primary stage is electron transfer from the donor to the halogenomethane. This transition has been demonstrated by flash photolysis[18,79] using also the aromatic amine–CCl_4 liquid system. The nature of the subsequent reactions is determined by that of the donor. In contrast to the compositions examined above, these reactions take place with participation of the $\dot{C}Br_3$ radical also in the liquid phase via a chain mechanism when donors such as diphenylamine[69] and polyvinylcarbazole (PVCA) are used[80]. When illuminated films containing PVCA and halogenomethane complexes are placed in a solvent, the effective quantum yield of the PVCA photochemical oxidation product increases from 5×10^{-2} to approximately unity as a result of the decrease of the rigidity of the matrix and the establishment of conditions for the occurrence of free-radical reactions[80].

Smets et al.[81] proposed a complex light-sensitive system incorporating the CTC of polyvinylcarbazole and CBr_4 as well as di-β-naphthospiropyran. The well known[2,5] displacement of the absorption spectra of spiropyrans from the ultraviolet to the visible region under dark conditions when the pH changes as a result of the occurrence of the reaction


(24)

is used in this system. The enhancement of the acid properties of the films is due to the photodissociation of the CTC on exposure to light corresponding to its absorption band [Eqn.(14)] at $\lambda_1 = 405$ nm: $PVCA.CBr_4 \xrightarrow{h\nu_1} (PVCA.CBr_4)^*$ and then

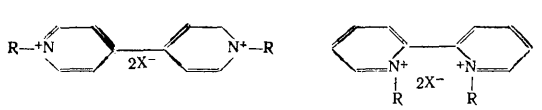
$$(PVCA\cdot CBr_4)^* \rightarrow PVCA^{\ddagger} + HBr + \dot{C}Br_3. \qquad (25)$$

The quantum yield of the products of reaction (25) is close to 0.23 and is independent of the CBr_4 content. The authors demonstrated the possibility of the optical manifestation of the latent image produced on exposure by employing as sensitiser di-β-naphthopyrylium bromide (DNP), formed by reaction (24) and absorbing in the range $\lambda_2 = 600$–700 nm. Since the rate of development increased in proportion to the CBr_4 concentration, the authors postulated the formation of CTC between DNP and CBr_4 and their participation in the development reaction:

$$DNP\cdot CBr_4 \xrightarrow{h\nu_2} (DNP\cdot CBr_4)^*,$$
$$(DNP\cdot CBr_4)^* + PVCA\,CBr_4 \rightarrow DNP\cdot CBr_4 + (PVCA\cdot CBr_4)^*,$$

this being followed by reaction (25). The HBr formed by reaction (25) ensures the appearance of an additional amount of coloured DNP by reaction (24). It was also established that the $\dot{C}Br_3$ radicals are inserted in the chain and that, together with $PVCA^{\ddagger}$, they ensure the cross-linking of the polymer in the exposed regions. In this system there is a possibility of the appearance of an image as a result of the dissolution of the non-cross-linked PVCA.

Systems based on bipyridylium salts with acceptor properties, such as 2,2′-bipyridylium ($2,2'\text{-}BP^{2+}2X^-$) and 4,4′-bipyridylium ($4,4'\text{-}BP^{2+}X^-$) also acquire a colour on ultraviolet irradiation:



They exist either in low-molecular-weight[82–85] or polymeric forms[86]. The optical absorption spectra of the above dications lie in the range 200–300 nm. Photoexcitation of the salt in the presence of a donor component such as the film-forming poly(vinyl alcohol)(PVA) [82–85] leads to the formation of the radical-cations $BP^{\ddagger}$ via the mechanism (in relation to the $4,4'\text{-}BP^{2+}$–PVA system):

$$BP^{2+} \xrightarrow{h\nu_1} (BP^{2+})^* \xrightarrow{RCH_2OH} BP^{\ddagger} + H^+ + R\dot{C}HOH,$$
$$BP^{2+} + R\dot{C}HOH \rightarrow RCHO + H^+. \qquad (26)$$

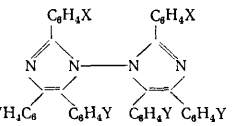
It has been established for aqueous solutions of BP^{2+} [87] that the photochemical reduction is irreversible only in the presence of primary and secondary alcohols, owing to the possible elimination of a proton in the α-position relative to the alcoholic group and the formation of the corresponding carbinol. The finding that the alcohols quench the fluorescence of $2,2'\text{-}BP^{2+}$ salts served as a basis for the conclusion that the electron-accepting state is the excited singlet state of the salt. It has been shown for the liquid phase[88–90] that $4,4'\text{-}BP^{2+}$ forms CTC with benzilate and oxalate anions, which absorb in the region of $\lambda_{max} =$ 370 nm and dissociate on photoexcitation with formation of $BP^{\ddagger}$. In a solid-phase system with $4,4'\text{-}BP^{2+}X^-$ and PVA the quantum yield of the formation of the radical-cations depends on the nature of X^-. The values of $I_0\Delta t_{0.2}$, characterising the sensitivity of the films to light with $\lambda_1 =$ 270 nm, and the quantum yields Φ are listed below as a function of the anion in bipyridylium salts:

Anion	Br^-	SO_4^{2-}	NO_3^-	Cl^-
Φ	0.015	0.028	0.045	0.047
$I_0\cdot\Delta t_{0.2}\cdot10^3$, J cm^{-2}	200	130	82	80.6

The radical-cations $BP^{\ddagger}$ transfer their charge to oxygen when the latter is introduced. However, the solubility of oxygen in PVA films is so low that the image obtained persisted throughout the period of the observation (1 year). It has been suggested in a patent[85] that cationic dyes be introduced into a chloride–4,4′-bipyridylium–PVA composition. Heat treatment of this system after the photochemical reduction of the salt ensures the transfer of an electron from the radical-cation $BP^{\ddagger}$ to the dye and the decolorisation of the latter as a result of the formation of the leuco-form. Such electron transfer ensures an increase of photosensitivity within the limits of one order of magnitude owing to the increase of the extinction coefficient of the films from $(1.2\text{–}2.4)\times10^4$ dm^3 mole^{-1} cm^{-1} for $BP^{\ddagger}$ to $(0.8\text{–}1.2)\times10^5$ dm^3 mole^{-1} cm^{-1} on passing to the dye.

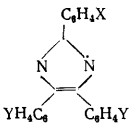
A composition of benzoyl-leuco-Methylene Blue as the donor and an aromatic nitro-compound as a photosensitive acceptor has also been proposed[91] as a system sensitive to ultraviolet light. Illumination of the system in a polymeric polyester binder for 2 s with light from a 20 W lamp and subsequent heat treatment at 120°C for 5 s ensure the conversion of most of the leuco-form into the dye.

The du Pont de Nemours Co. (USA) developed a "dyelux" process[91–94], where the colour change is associated with the interaction of two basic components. Hexa-arylbisimidazoles having the structure


(27)

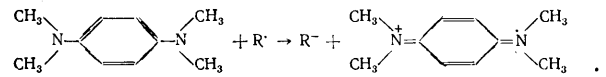
are used as the light sensitive component in this process. The component whose colour changes consists of amines[92,93] and leucodyes DyeH (see, for example, Ref. 94).

Under the influence of light with $\lambda_1 \simeq 250-360$ nm, the dimers (27) undergo homolytic dissociation with formation of the triarylimidazolyl radicals R$^{\cdot}$:[95]



(28)

These radicals absorb in the visible region (530–620 nm), but are characterised by a lower extinction coefficient [$\epsilon \simeq (1.3 - 8.1) \times 10^3$ litre mole^{-1} cm^{-1} in solution]. A detailed study of the nature of the reactions occurring in solution[1,2,96-100] showed that the radicals (28) oxidise amines in the dark[92,93,96] as well as leuco-dyes[94,96-100]. When amines are used, the appearance of the colour is due to the formation of radical-cations, for example by the following reaction in the case of tetramethyl-*p*-phenylenediamine[93,95]:



The resulting radical-cation has absorption maxima at 575 and 625 nm and the extinction coefficient in the film is $\epsilon \simeq 10^5$ dm^3 mole^{-1} cm^{-1}.

When the leuco-form of the dye is used, the colour is associated with the formation of the dye itself[94] by the reaction[96-100]

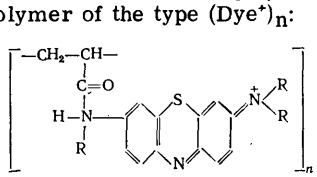
$$\mathrm{DyeH} + 2\mathrm{R}^{\cdot} \rightarrow \mathrm{Dye}^{+} + \mathrm{RH} + \mathrm{R}^{-}.$$

In order to rule out the acquisition of a colour by the unexposed regions of the film under the influence of ultraviolet light after the recording of the image, it has been suggested that a third component be used[94]—1,6- or 1,8-pyrenequinone or 9,10-anthraquinone—in combination with a polymeric donor matrix. As a result of the interaction with the matrix in an excited state (under the influence of light with $\lambda_2 = 380-500$ nm), the quinones (O=Ar=O) are converted into hydroquinones (HO–Ar–OH), which react with the dimers under dark conditions:

$$\mathrm{HO—Ar—OH} + \mathrm{R—R} \rightarrow \mathrm{O{=}Ar{—}O{+}\ 2RH}.$$

ensuring the transformation of the dimer R–R (27) into the lophine form (RH), which is insensitive to the action of light with $\lambda > 250$ nm. The "dyelux" process does not provide for image intensification and can be used in the formation of duplicates in microfilming. Its sensitivity is $I_0 \Delta t_{0.2} = 2 \times 10^{-3}$ J cm^{-2}.

In order to obtain non-silver layers sensitive in the red part of the spectrum, Oster and coworkers[101-103] investigated the photochemical reduction of thiazine dyes, which have an optical absorption maximum at 590–665 nm, to the leuco-form, which absorbs in the ultraviolet when present in PVA films and in hydroxylated glasses—fructose, glucose, etc. In order to obtain films whose colour changes under the influence of red light, Kamogawa[104,105] synthesised a polymer of the type (Dye^{+})$_n$:



(29)

The reduction of Methylene Blue (a thiazine dye) MB^{+} ($\lambda_{max} = 665$ nm) to the leuco-form MBH ($\lambda_{max} \simeq 260$ nm) in layers deposited on a support, under dark conditions on contact with gaseous H_2S as a donor, has been studied by Vartanyan[106,107], who suggested[106] that the photodecolorisation of MB^{+} in gelatine films observed by Lazarev (1912) is associated with the photochemical reduction of the dye to MBH. Oster et al.[101] showed that the rate of decrease of the optical density of the dye in hydroxylated films and glasses is accelerated after the introduction of electron-donating components such as ascorbic acid, phenylhydrazine, allylthiourea, $SnCl_2$, ethylenediaminetetra-acetic acid, etc., increasing linearly with increase of the ratio $(T/\eta)^{1/2}$, where T is the temperature and η the viscosity of the medium. This relation served as a basis for the conclusion that the decolorisation process is controlled by the diffusion of the components. It has been suggested that, in the absence of donors, the unexcited dye molecules serve as a reductant to a greater extent than the medium.

Kamogawa[104,105] investigated the photodecolorisation of polymeric dyes introduced into a PVA or cellulose matrix together with Fe^{2+} as the donor and enzymes. As expected from the consideration of the phenomenon in the liquid phase[108-111], the added Fe^{2+} ions do not ensure the complete decolorisation of the film, since the Fe^{3+} ions formed in the course of the reduction of the dye are a powerful oxidant and induce the reverse reaction in the dark. Enzymes increase the rate of the photochemical reduction of the polymeric dye, but the addition of water constitutes the most effective means of accelerating the photochemical decolorisation process. An estimate based on the experimental data presented in the relevant paper shows that the transmittance at $\lambda = 600$ nm increases from 4 to 94% as a result of the absorption of the light energy $I_0 \Delta t = 1-4$ J cm^{-2}.

The finding that the rate of photochemical reduction is controlled by diffusion and therefore proceeds slowly in the solid phase apparently limited the number of studies whose aim was to employ the photodecolorisation of thiazine dyes in photography. In contrast to solid layers, numerous studies have been devoted to the photochemical reduction of thiazine dyes in the liquid phase. When aqueous and alcoholic solutions are used, the nature of the decrease of the concentration of the dye following its photoexcitation confirms[112-116] the hypothesis but forward for the solid phase that the colourless leuco-form is produced as a result of the interaction of the excited dye molecule with a donor and, in its absence, with an unexcited dye molecule. A slow decomposition of the functional groups as a result of the interaction of the excited dye with the solvent has also been observed in alcoholic solutions. In aqueous and alcoholic solutions Dye^{+} and D do not exist as a complex but interact on collision, as shown by the increase of the quantum yield with increasing donor concentration in accordance with the relation

$$1/\Phi = a + b/[\mathrm{D}]. \qquad (30)$$

Arvan and coworkers[24,117-120] demonstrated the formation of a σ-complex (quasi-leuco-form) between Dye^{+} and the leuco-form of a dye of a different class and also between Dye^{+} and the solvent (pyridine) under the influence of light corresponding to the Dye^{+} absorption band. It was shown[120] that pyridine or an electron-donating additive add to the central nitrogen atom of the dye, which ensures its decolorisation. The increase almost by an order of magnitude of the rate of reduction of MB^{+} by hydrogenated aromatic hydrocarbons under dark conditions after the introduction of amines has been explained[121] by the primary formation of a σ-complex and its subsequent reaction with the hydrocarbons, terminating in the formation of MBH, the initial amine, and an aromatic molecule. In contrast

to PVA films, when poly(vinyl chloride) (PVC) was used as the film-forming material, the independence of the quantum yield of the products of the decolorisation of MB^+, in the presence of tribenzylamine (TBA) as the donor, of the MB^+ and TBA concentrations[122,123] was demonstrated for [TBA] > 0.1 mole dm^{-3}. The yield Φ was calculated from experimental data by the formula

$$\lg(10^{D_0}-1)-\lg(10^{D}-1)=\Phi\frac{\varepsilon\lambda I_0}{1.196\times10^6}\cdot\Delta t, \qquad (31)$$

obtained by integrating Eqn. (17) for $D = D_1$ and amounted to $\Phi = 0.08$. Here D_0 and D are respectively the optical densities (at $\lambda_{max} = 665$ nm) of the initial film and the film illuminated during the period Δt with monochromatic light ($\lambda = 652$ nm) having an intensity I_0.

The independence of Φ of [TBA] and $[MB^+]$ indicates the presence of associated species comprising MB^+ and TBA, for example of the type of weak σ-complexes. The following set of reactions then take place:

$$(MB^+ \ldots TBA) \xrightarrow{h\nu_1} (MB^{+*} \ldots TBA),$$

$$(MB^{+*} \ldots TBA) \xrightarrow{k_1} (MB^+ \ldots TBA),$$

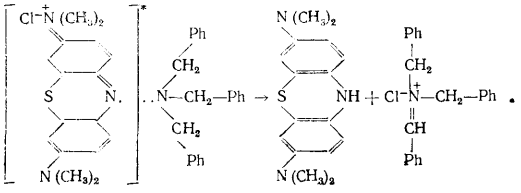
$$(MB^{+*} \ldots TBA) \xrightarrow{k_2} MBH + A_1^+,$$

and Φ is determined by the relation

$$\Phi = \frac{[MBH]}{[MB^{+*} \ldots TBA]} = \frac{k_2}{k_2+k_1},$$

which differs from Eqn. (30) for photochemical reduction on collision between the component molecules.

Since the rate of photodecolorisation of coloured PVC films on photoexcitation of MB^+ in the absence of a donor was the same as that measured in the presence of triphenylamine (TPA) but increased by a factor of 130 on passing to TBA and since the radicals MB· arose in the presence of TPA at higher concentration than after the addition of TBA, it was concluded that TBA ensures the reduction of MB^+ to MBH by transferring not only an electron but also a hydrogen atom to the dye via the reaction



At low TBA concentrations, corresponding to an appreciable fraction of MB^+ in a non-associated state according to Eqn. (15), the relation $\lg(10^D - 1) = f(\Delta t)$ gives rise to two sections corresponding to the photochemical reduction of the dye molecules in both associated and free states. The separation of these contributions at different TBA concentrations made it possible to determine $K \simeq 10$ dm^3 $mole^{-1}$ [Eqn. (15)]. In the system considered the light sensitivity in the region of $\lambda \simeq 600$–700 nm corresponds to a decrease of the optical density by $\Delta D = 1$ as a result of the effect of the incident light having an energy $I_0\Delta t_{1.0} = 33\times10^{-3}$ J cm^{-2}.[122,123] This quantity exceeds approximately by two orders of magnitude the light sensitivity of PVA films coloured by MB^+ and is due to the presence of associated species, which rule out diffusion-dependent limitation of the rate of the photochemical reaction.

Japanese investigators[1,31] suggested that dye layers vacuum sputtered onto a support at 60–70°C be used in reproduction (they designated these dyes by the abbreviation TED–Thermally Evaporated Dyes). The process is based on the ability of certain dyes to dimerise as a result of photoexcitation[18]. Since the dimers absorb light in the region displaced by several tens of nm towards shorter wavelengths compared with the absorption of the monomer, the image remains coloured and is difficult to distinguish from the unexposed regions. The image is developed by treating the layer with a non-polar solvent and heating. In the former case the dye is removed from the unexposed regions but remains in the exposed regions owing to the decrease of solubility as a result of the formation of dimers. In the case of xanthene dyes such as rhodamine B and its derivatives, the greater thermal stability of the dimers compared with the monomers is used. In order to develop the exposed regions, which have a higher content of dimers, use was made[31] of the ability of these dyes to undergo an irreversible conversion into the lactone form as a result of heating to 70–140°C, which has been thoroughly investigated[24,27,30]. After heating, the coloured layer remains on the exposed regions, but the unexposed regions become colourless, since, in contrast to the cationic dye which absorbs in the region of 550 nm, the absorption spectrum of the lactone form is in the ultraviolet. The light sensitivity of the layers is low (~0.3 J cm^{-2}), but the layers consist of only one component and are distinguished by a high resolving capacity.

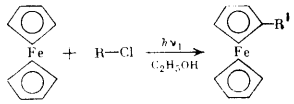
V. LIGHT SENSITIVE CHARGE-TRANSFER COMPLEXES BASED ON ORGANOMETALLIC COMPOUNDS

There exists yet another class of compounds which undergo further chemical reactions involving charge-transfer states and are extremely promising for the formation of image recording systems. These are organometallic compounds and in the first place ferrocene and its derivatives.

The fundamental studies carried out during the last ten years showed that the photochemistry of organometallic compounds has its characteristic features and many phenomena have still not been fully explained even for the simplest systems. Photochemical reactions involving the decomposition of many ferrocene derivatives were first observed by Nesmeyanov and coworkers[124–126]. A number of reviews have been devoted to the chemistry of metallocenes and transition metal carbonyls[127–129]. The mechanisms of photochemical reactions have been considered mainly in relation to solutions and it is very difficult to use these results for reactions in solid matrices, particularly since the solvent effects for organometallic compounds are very considerable. The use of organometallic compounds in recording systems is based on photochemical reactions in the solid state and, with a rare exception[130], the chemistry of photochemical processes has not been established at all reliably in most instances.

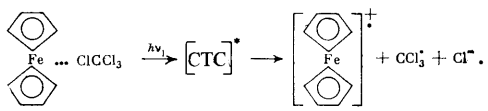
Systems where the photochemical reactions proceed with precipitation of charge-transfer complexes are of interest for the present review. These are the most promising for use in recording systems. Brand and Snedden[131] observed a dissociative charge-transfer band in the absorption spectra of ferrocene solutions in carbon tetrachloride. When these solutions are irradiated with ultraviolet light, ferricenium tetrachloroferrate(III) is formed quantitatively. In the presence of compounds containing mobile hydrogen, the ferricinium salt is transformed into ferrocene[132]. The formation of ferricinium

tetrachloroferrate(III) was also observed[133] in the photolysis of ferrocene in hexachlorocyclopentadiene. In solutions of organic halogeno-derivatives in ethanol photochemical substitution of ferrocene takes place[134]. It is thus possible to introduce ethoxycarbonyl, formyl, ethoxymethyl, benzyl, and allyl groups into the ferrocene molecule under the influence of ultraviolet light[135] via the general mechanism

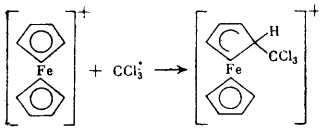


R = CCl_3, $CHCl_2$, or CH_2Cl;
R' = $CO_2C_2H_5$, CHO, or $CH_2OC_2H_5$.

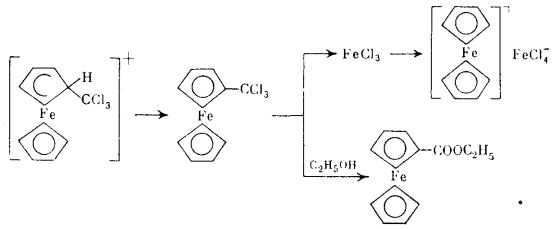
The ultraviolet absorption spectrum of ferrocene in ethanol has a band with λ_{max} = 440 nm, which has been attributed to a $d \rightarrow d^*$ transition and a band with λ_{max} = 325 nm assigned to $3d \rightarrow$ MO*, MO $\rightarrow$ MO*, or symmetry-prohibited $\pi \rightarrow \pi^*$ transitions. The absorption at wavelengths below 300 nm is apparently due to a $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition[136]. An absorption with a maximum at 307 nm, associated with charge-transfer, is manifested in ferrocene solutions in carbon tetrachloride. When other halogen-containing organic solvents are used, such as chloroform, dichloromethane, allyl bromide, benzyl chloride, trichloromethylbenzene, and *p*-nitrobenzyl chloride, λ_{max} for the charge-transfer band is located in the region between 300 and 380 nm, while for chlorides such as n-butyl chloride, allyl chloride, and a number of others, a charge-transfer band was not observed in the presence of ferrocene. Accordingly the yield of substitution products in the latter case is much lower than in systems forming CTC. The mechanism of the substitution reaction has been investigated in detail[137]. The dependence of the quantum yield of the photosubstitution reaction (and of the decomposition of ferrocene) on the wavelength shows that it is zero in the region of the $d \rightarrow d^*$ transition, while excited states with charge transfer lead to the effective formation of substitution products. Excitation by light at shorter wavelengths stimulates such reactions as a result of the decomposition of ferrocene molecules by the chlorine atoms generated by the direct photochemical decomposition of the halogenohydrocarbons. Measurements by flash photolysis[137] suggested a mechanism of the formation of coloured products: the first stage of the photochemical reaction is believed[131] to consist of the excitation and decomposition of the CTC:



According to Beckwith and Leydon[138], the ferricinium cation is extremely reactive towards free radicals, in contrast to ferrocene itself:



The subsequent stages were determined less reliably. On pulsed illumination, $FeCl_3$ is formed in an overall process which obeys first-order kinetics and has a rate constant of $\sim(1.6 \pm 0.5) \times 10^5$ s with subsequent formation of ferricinium tetrachloroferrate(III) and, in the presence of ethanol, of ferrocenecarboxylic acid:

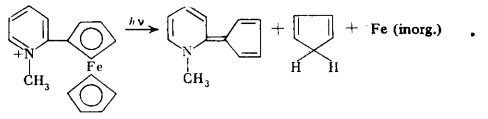


In contrast to normal ferricinium ions, ferricinium tetrachloroferrate(III) does not interact with trichloromethyl radicals. It has been suggested that the formation of ferricinium tetrachloroferrate(III) in ferrocene solutions in CCl_4 be used in ^{60}Co γ-radiation dosimeters[139], because the concentration of the ferricinium salt formed is proportional to the absorbed dose.

The formation of CTC between ferrocene and halogenohydrocarbons is used in recording layers. On formation of the CTC in the solid state, the acceptor interacts with the pentadienyl ring and not with the metal[134]. The exact mechanism of the photochemical processes in such solid systems has not been investigated, but there is no doubt that its main stages have much in common with reactions in solution. Compositions containing ferrocene or its derivatives and photolytic halogenohydrocarbons are characterised by a spectral sensitivity which embraces the visible region, in contrast to many other organic systems which are sensitive only in the ultraviolet region. In a system incorporating ferrocene and CBr_4 a complex having the composition $Fc.3CBr_4$ with λ_{max} = 388 nm is formed[143]. The absorption band of the complex extends into the visible region up to ~600 nm. The bathochromic shift of the CTC absorption band when CCl_4 is replaced by CBr_4 is associated with the increase of the electron affinity (0.15 and 1.17 eV respectively). The formation of the CTC and its absorption spectrum fully determine the light sensitivity of the recording layers and its spectral range[143].

Compositions based on ferrocene or its derivatives and halogenohydrocarbons are used in the manufacture of reproducing materials with an increased sensitivity in the visible light. These layers can be effectively stored in the dark, are fixed on heating, are readily activated, and do not require a chemical treatment[140]. Other ways of employing light-sensitive layers containing CTC have also been proposed. Thus layers based on vinylferrocene copolymers with halogenohydrocarbons become electrically conducting in the exposed regions. The subsequent employment of electrophotographic stages makes it possible to obtain a large number of copies from a single exposed layer. Layers with CTC comprising vinylferrocene copolymers with nitrogen-containing heterocyclic compounds and halogenohydrocarbons have now been obtained; after their exposure and treatment with methanol, a coloured image is produced[141].

The latter process can also be regarded as a photochemical reaction of the ammonium forms of nitrogen-containing ferrocenes[142], which was first observed in relation to α-ferrocenylpyridinium methiodide:



The above discussion shows that definite achievements have been made in the use of charge-transfer states for the formation of light-sensitive layers with a wide variety of photographic characteristics. Interactions with charge transfer are universal—it is difficult to point to a system in which they do not occur and in which they do not contribute to photochemical processes, but their detection involves difficulties in many instances. The formation on photoexcitation of radical-cations and radical-anions changes the spectroscopic characteristics in the visible region under the influence of infrared and ultraviolet radiation, which makes it possible to obtain contrasting layers. One may also note that, among other organic systems, only layers based on the use of charge-transfer states approach the sensitivity of silver bromide layers. This is associated with the possibility of using physical developers and of intensifying the latent image by the action of light corresponding to the absorption band of the coloured photochemical reaction products. These layers also possess special properties—sensitivity within narrow spectral regions of the visible, infrared, and ultraviolet, the possibility of multicoloured recording, as well as the recording of holograms.

The mechanism of the photochemical reactions of CTC has been studied mainly in solution. The application of the results to solid layers is open to serious objections, particularly in systems sensitive to the characteristics of the medium. The study of the photochemistry of charge-transfer states in solid multicomponent systems forming CTC is therefore important for the development of light-sensitive layers.

REFERENCES

1. R. J. Cox (Editor), "Proceedings of the Symposium on Non-Silver Photographic Processes", Acad. Press, London, 1975.
2. V. A. Barachevskii, G. I. Lashkov, and V. A. Tsekhomskii, "Fotokhromizm i Ego Primenenie" (Photochromism and Its Applications), Izd. Khimiya, Moscow, 1977.
3. [Sic] [This may be a reference to "Applications of Photochromism", Tech. Chem., 1971, **3**, 733 (1971) (Ed. of Translation)].
4. V. I. Sheberstov and A. A. Slutskin, Zhur. Nauch. Prikl. Fotogr. i Kinematogr., **20**, 151 (1975).
5. V. D. Ermakova, V. D. Arsenov, M. I. Cherkashin, and P. P. Kisilitsa, Uspekhi Khim., **46**, 292 (1977) [Russ. Chem. Rev., No. 2 (1977)].
6. A. A. Slutskin and V. I. Sheberstov, "Kopiroval'nye Protsessy i Apparaty Reprografii i Poligrafii" (Copying Processes and Apparatus for Reproduction and Small-Scale Printing), Izd. Kniga, Moscow, 1971.
7. T. A. Yurre, V. V. Shaburov, and A. V. El'tsov, Zhur. Vses. Khim. Obshch. im. Mendeleeva, **19**, 412 (1974).
8. P. Pinot de Moira, J. Photogr. Sci., **22**, 187 (1974).
9. V. I. Sheberstov, V. I. Uspenskii, and M. S. Borodkina, Zhur. Nauch. Prikl. Fotogr. i Kinematogr., **20**, 3 (1975).
10. V. I. Nagornyi and V. I. Sheberstov, Zhur. Nauch. Prikl. Fotogr. i Kinematogr., **11**, 384 (1966).
11. R. M. Schaffert, "Electrophotography", The Focal Press, London, 1976.
12. S. G. Grenishin, "Elektrofotograficheskii Protsess" (The Electrophotographic Process), Izd. Nauka, Moscow, 1970.
13. R. A. Fotland, J. Photogr. Sci., **18**, 88 (1970).
14. V. M. Kozenkov, N. N. Mashtalir, and V. A. Barachevskii, Symposium, "Uspekhi Nauchnoi Fotografii" (Advances in Photographic Science), Izd. Nauka, Moscow, 1978, Vol. 9, p. 142.
15. N. N. Mashtalir, V. A. Barachevskii, V. M. Kozenkov, V. V. Belov, E. A. Kuz'mina, Yu. M. Udachin, N. N. Artamonova, P. P. Kisilitsa, and Yu. V. Shulev, Symposium, "Besserebryanye i Neobychnye Fotograficheskie Protsessy. Tezisy Dokladov II Vsesoyuznoi Konferentsii" (Non-Silver and Unusual Photographic Processes. Abstracts of Reports at the IInd All-Union Conference), Kishinev Gos. Univ., Kishinev, 1975, p. 90.
16. N. N. Mashtalir, E. A. Kuz'mina, and A. A. Pankratov, Symposium, "Besserebryanye i Neobychnye Fotograficheskie Protsessy. Tezisy Dokladov II Vsesoyuznoi Konferentsii" (Non-Silver and Unusual Photographic Processes. Abstracts of Reports at the IInd All-Union Conference), Kishinev Gos. Univ., Kishinev, 1975, p. 93.
17. Brit. Appl. 1 431 435 (1976); Izobr. za Rubezhom, 44, No. 9, 15 (1976).
18. A. N. Terenin, "Fotonika Molekul Krasitelei" (Photonics of Dye Molecules), Izd. Nauka, Leningrad, 1967, Chapter 3.
19. B. I. Stepanov, "Vvedenie v Khimiyu i Tekhnologiyu Organicheskikh Krasitelei" (Introduction to the Chemistry and Technology of Organic Dyes), Izd. Khimiya, Moscow, 1976, Chapter 1.
20. A. Ya. Il'chenko, M. M. Kul'chinskii, L. I. Trushanina, and L. M. Yagupol'skii, Symposium, "Uspekhi Nauchnoi Fotografii" (Advances in Photographic Science), Izd. Nauka, Moscow, 1976, Vol. 17, p. 136.
21. H. Kuhn, J. Chem. Phys., 17, 1198 (1949).
22. V. A. Kargin (Editor), Symposium, "Organicheskie Poluprovodniki" (Organic Semiconductors), Izd. Nauka, Moscow, 1968, Chapter 12.
23. H. G. O. Becker, "Introduction to the Photochemistry of Organic Compounds" (Translated into Russian), Izd. Khimiya, Leningrad, 1976, Chapters 2, 5, and 12.
24. G. A. Korsunovskii and Kh. A. Arvan, Symposium, "Molekulyarnaya Fotonika" (Molecular Photonics), Izd. Nauka, Leningrad, 1970, p. 264.
25. G. A. Korsunovskii, Zhur. Fiz. Khim., **42**, 264 (1968) [Russ. J. Phys. Chem., No. 1 (1968)].
26. A. T. Vartanyan, Zhur. Fiz. Khim., **35**, 2241 (1961) [Russ. J. Phys. Chem., No. 10 (1961)].
27. A. T. Vartanyan, Zhur. Fiz. Khim., **30**, 1028 (1956).
28. A. T. Vartanyan, Zhur. Fiz. Khim., **30**, 424 (1956).
29. A. T. Vartanyan, Zhur. Fiz. Khim., **36**, 1891 (1962) [Russ. J. Phys. Chem., No. 9 (1962)].
30. G. A. Korsunovskii and A. N. Sidorov, Zhur. Fiz. Khim., **42**, 286 (1968) [Russ. J. Phys. Chem., No. 1 (1968)].
31. M. Ikeda and S. Taguchi, J. Photogr. Sci., **23**, 6 (1975).
32. L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1967.
33. R. S. Mulliken and B. J. Person, "Molecular Complexes", Wiley, London, 1969, Chapter 1.
34. R. Foster, "Organic Charge-Transfer Complexes", Acad. Press, London, 1969, Chapters 1, 2, 3, and 10.
35. E. N. Gur'yanova, I. P. Gol'dshtein, and I. P. Romm, "Donorno-Aktseptornaya Svyaz'" (The Donor–Acceptor Bond), Izd. Khimiya, Moscow, 1973, Chapter 3.

36. R. Foster (Editor), "Molecular Complexes", Acad. Press, London, 1973, Vol. 1, Chapters 1 and 6; 1974, Vol. 2, Chapters 3 and 5.
37. R. Foster (Editor), "Molecular Association", Acad. Press, London, 1975, Vol. 1, pp. 1, 151, 216.
38. "Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po Kompleksam s Perenosom Zaryada i Ion-Radikal'nym Solyam" (Abstracts of Reports at the IInd All-Union Conference on Charge-Transfer Complexes and Radical-Ion Salts), Izd. Zinatne, Riga, 1973.
39. "Tezisy Dokladov III Vsesoyuznogo Soveshchaniya po Kompleksam s Perenosom Zaryada i Ion-Radikal'nym Solyam" (Abstracts of Reports at the IIIrd All-Union Conference on Charge-Transfer Complexes and Radical-Ion Salts), Izd. Zinatne, Riga, 1976.
40. S. Yooa, J. Phys. Chem. Soc. Japan, **36**, 1655 (1974).
41. O. Kh. Poleshchuk and Yu. K. Maksyutin, Uspekhi Khim., **45**, 2097 (1976) [Russ. Chem. Rev., No. 12 (1976)].
42. K. Hausser and J. N. Murrel, J. Chem. Phys., **27**, 510 (1957).
43. J. J. Weiss, Phil. Mag., 8, 1169 (1963).
44. S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice Hall, 1969 (Translated into Russian), Izd. Mir, Moscow, 1972, Chapter 1.
45. S. P. McGlynn and J. D. Boggus, J. Amer. Chem. Soc., 80, 5096 (1958).
46. S. P. McGlynn, Chem. Rev., 58, 1113 (1958).
47. L. A. Blyumenfel'd and V. A. Benderskii, "Trudy II Vsesoyuznogo Soveshchaniya po Organicheskim Poluprovodnikam" (Proceedings of the IInd All-Union Conference on Organic Semiconductors), Izd. Zinatne, Riga, 1968, p. 6.
48. L. A. Blyumenfel'd, V. A. Benderskii, and P. A. Stunzhas, Zhur. Strukt. Khim., 7, 868 (1966).
49. Kh. S. Bagdasar'yan, "Dvukhkvantovaya Fotokhimiya" (Two-Quantum Photochemistry), Izd. Nauka, Moscow, 1976, Chapter 1.
50. F. Stewart, M. Eisher, and W. R. Carper, J. Chem. Phys., 44, 2866 (1966).
51. F. Stewart and M. Eisher, Mol. Phys., 12, 173 (1967).
52. R. R. Dogonadze and A. M. Kuznetsov, "Itogi Nauki i Tekhniki, Ser. Fiz. Khimiya" (Advances in Science and Engineering. The Physical Chemistry Series), Moscow, 1973, Vol. 2.
53. G. B. Sergeev, Yu. A. Serguchev, and V. V. Smirnov, Uspekhi Khim., **42**, 1545 (1973) [Russ. Chem. Rev., No. 9 (1973)].
54. G. B. Sergeev and I. A. Leenson, Uspekhi Khim., 41, 1566 (1972) [Russ. Chem. Rev., No. 9 (1972)].
55. S. Nagakura, in "Excited States" (Edited by E. C. Lim), Acad. Press, London, 1975, Vol. 2, p. 216.
56. M. Suzuki, Y. Yamamoto, M. Irie, and K. Hayashi, J. Macromol. Sci.-Chem., A10, 1607 (1976).
57. E. M. Kosower, Symposium, "Novye Problemy Fizicheskoi Organicheskoi Khimii" (New Problems in Physical Organic Chemistry) (Translated into Russian), Izd. Mir, Moscow, 1969, p. 36.
58. M. Irie, H. Masuhara, K. Hayashi, and M. Mataga, J. Phys. Chem., 78, 341 (1974).
59. Y. Ahiba, S. Katsumata, and K. Kimura, Chem. Phys. Letters, 13, 213 (1972).
60. A. D. Grishina and V. D. Ermakova, Vysokomol. Soed., **19A**, 2228 (1977).
61. G. M. Chernov, A. D. Grishina, V. D. Ermakova, and V. D. Arsenov, Vysokomol. Soed., 18A, 2192 (1976).
62. A. D. Grishina, V. D. Ermakova, and G. M. Chernov, "Tezisy III Vsesoyuznogo Soveshchaniya po Fotokhimii" (Abstracts of Reports at the IIIrd All-Union Conference on Photochemistry), Moscow, 1977, p. 158.
63. M. G. Kuz'min, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 19, 362 (1974).
64. A. A. Vol'kenshtein and E. V. Kuvaldin, "Photoelektricheskaya Impul'snaya Fotometriya" (Photoelectric Pulse Photometry), Izd. Mashinostronie, Leningrad, 1975.
65. BRD P. 1 152 608 (1963); Chem. Abs., 61, 3850 (1964).
66. A. C. Hazy, J. E. Shirey, and L. Ramis, Brit. Appl., 1 423 620 (1976); Izobr. za Rubezhom, 44, No. 3 (1976).
67. R. H. Spraque, J. Urbancik, and J. Stewart, Photograf. Sci. and Eng., 9, 133 (1965).
68. R. Fotland, B. P. 180 883 (1970); Chem. Abs., 73, 30 631 (1970).
69. R. H. Spraque, H. L. Fichter, and E. Wainer, Photogr. Sci. and Eng., 5, 98 (1961).
70. A. D. Grishina, Khim. Vys. Energii, 13, 137 (1979).
71. A. C. Hazy and V. P. Petro, Laser Focus, 8, No. 2, 32 (1972).
72. R. A. Fotland and H. L. Fichter, US P. 3 510 300 (1970); Chem. Abs., 76, 40 306 (1972).
73. G. M. Chernov, A. D. Grishina, and A. V. Vannikov, Symposium, "X Koordinatsionnoe Soveshchanie po Organicheskim Poluprovodnikam. Tezisy Dokladov. Kosov, 1979" (The Xth Coordination Conference on Organic Semiconductors. Abstracts of Reports, Kosov, 1979), p. 67.
74. A. D. Grishina and G. M. Chernov, Symposium, "X Koordinatsionnoe Soveshchanie po Organicheskim Poluprovodnikam. Tezisy Dokladov. Kosov, 1979" (The Xth Coordination Conference on Organic Semiconductors. Abstracts of Reports, Kosov, 1979), p. 56.
75. N. Hiroyuki, I. Yoshinobu, and Y. Masatsugu, Japanese P. 75 104 636 (1975); Chem. Abs., 84, 67 894 (1976).
76. R. A. Fotland, V. E. Straughan, and J. Cameron, BRD P. 2 028 419 (1970); Chem. Abs., 74, 70 269 (1971).
77. Yu. I. Lifanov, V. E. Korobov, A. V. Karyakin, and A. K. Chibisov, Khim. Vys. Energii, 9, 265 (1975).
78. A. K. Chibisov, J. Photochem., 6, 199 (1976).
79. O. D. Dmitrievskii, Symposium, "Molekulyarnaya Fotonika" (Molecular Photonics), Izd. Nauka, Leningrad, 1970, p. 144.
80. O. V. Kolninov, V. V. Kolesnikova, and V. K. Milinchuk, "X Koordinatsionnoe Soveshchanie po Organicheskim Poluprovodnikam. Tezisy Dokladov. Kosov, 1979" (The Xth Coordination Conference on Organic Semiconductors. Abstracts of Reports, Kosov, 1979), p. 82.
81. G. J. Smets, J. Thoen, and A. Aerts, J. Polymer Sci. C, 51, 119 (1975).
82. V. F. Ivanov, A. D. Grishina, and B. I. Shapiro, Izv. Akad. Nauk SSSR, Ser. Khim., 1383 (1976).
83. V. F. Ivanov and A. D. Grishina, Akad. Nauk SSSR, Ser. Khim., 1783 (1977).
84. V. F. Ivanov and A. D. Grishina, "Tezisy III Vsesoyuznogo Soveshchaniya po Fotokhimii" (Abstracts of Reports at the IIIrd All-Union Conference on Photochemistry), Moscow, 1977, p. 153.

85. M. Tsuneyuki, Japanese P. 7 590 321 (1975); Chem. Abs., 84, 114 178 (1976).
86. M. S. Simon and P. T. Moore, J. Polymer Sci., Polymer Ed., **13**, 1 (1975).
87. A. S. Hopkins, A. Ledwith, and M. F. Stum, Chem. Comm., 494 (1970).
88. A. Ledwith and J. H. Wood, J. Chem. Soc. (C), 1422 (1970).
89. B. G. White, Trans. Faraday Soc., 65, 2000 (1969).
90. N. N. Mel'nikov, E. T. Novikov, and B. A. Khaskin, "Khimiya i Biologicheskaya Aktivnost' Dipiridinov i Ikh Proizvodnykh" {The Chemistry and Biological Activity of Dipyridines [Bipyridyls ?] and Their Derivatives}, Izd. Khimiya, Moscow, 1975.
91. M. Tsuda and A. Ohshima, Japanese P. 7 600 941 (1976); Chem. Abs., 85, 114 845 (1976).
92. L. A. Cescon and R. Dessauer, BP. 1 271 174 (1972); Chem. Abs., 77, 27 439 (1972).
93. L. A. Cescon and R. Dessauer, BRD P. 2 028 124 (1971); Chem. Abs., 76, 119 931 (1972).
94. L. A. Cescon, BRD P. 1 772 534 (1972); Chem. Abs., 77, 27 439 (1972).
95. T. Hayashi, K. Maeda, and M. Takenchi, Bull. Chem. Soc. Japan, **37**, 1717 (1964).
96. R. H. Riem, A. McLachlan, G. R. Coraor, and E. J. Urban, J. Org. Chem., 36, 2272 (1971).
97. L. A. Cescon, G. R. Coraor, R. Dessauer, E. F. Silversmith, and E. J. Urban, J. Org. Chem., **36**, 2262 (1971).
98. L. A. Cescon, G. R. Coraor, R. Dessauer, A. S. Deutsch, H. L. Jackson, A. L. A. McLachlan, K. Marcali, E. M. Potrafke, R. E. Read, E. F. Silversmith, and E. J. Urban, J. Org. Chem., **36**, 2267 (1971).
99. A. McLachlan and R. H. Riem, J. Org. Chem., **36**, 2275 (1971).
100. R. L. Cohen, J. Org. Chem., **31**, 2280 (1971).
101. G. Oster and N. Wotherspoon, J. Chem. Phys., **22**, 157 (1954).
102. G. Oster and N. Wotherspoon, J. Amer. Chem. Soc., 79, 4836 (1957).
103. B. Broyde and G. Oster, J. Amer. Chem. Soc., **81**, 5099 (1959).
104. H. Kamogawa, M. Kato, and Sugiiyma, J. Polymer Sci., **A1**, 2967 (1968).
105. H. Kamogawa, J. Appl. Polymer Sci., **13**, 1883 (1969).
106. A. T. Vartanyan, Zhur. Fiz. Khim., **29**, 1304 (1955).
107. A. T. Vartanyan, Zhur. Fiz. Khim., **29**, 1447 (1955).
108. G. Parker, J. Phys. Chem., **63**, 26 (1959).
109. G. Hatchard and G. Parker, Trans. Faraday Soc., 57, 1093 (1961).
110. R. Hardwick, J. Amer. Chem. Soc., 80, 5667 (1958).
111. R. Hardwick, J. Phys. Chem., **66**, 349 (1962).
112. M. Koizumi, H. Obata, and S. Hayashi, Bull. Chem. Soc. Japan, **37**, 117 (1964).
113. S. Kato, M. Morita, and M. Koizumi, Bull. Chem. Soc. Japan, **37**, 108 (1964).
114. M. Kosui, K. Uchida, and M. Koizumi, Bull. Chem. Soc. Japan, **38**, 1958 (1965).
115. Y. Usui, Bull. Chem. Soc. Japan, **38**, 206 (1965).
116. M. Nemoto, H. Kokobun, and M. Koizumi, Bull. Chem. Soc. Japan, **42**, 2464 (1969).
117. Kh. L. Arvan, Zhur. Fiz. Khim., **40**, 972 (1966) [Russ. J. Phys. Chem., No. 5 (1966)].
118. Kh. L. Arvan, Zhur. Fiz. Khim., **40**, 977 (1966) [Russ. J. Phys. Chem., No. 5 (1966)].
119. Kh. L. Arvan and D. N. Glebovskii, Zhur. Fiz. Khim., **25**, 2822 (1961) [Russ. J. Phys. Chem., No. 12 (1961)].
120. Kh. L. Arvan and V. E. Kholmogorov, Dokl. Akad. Nauk SSSR, **169**, 365 (1966).
121. Y. Iwasawa, M. Soma, T. Onishi, and K. Tamaru, J. Chem. Soc., Faraday Trans. I, 1697 (1972).
122. A. D. Grishina, Symposium, "Sbosoby Zapisi Infromatsii na Besserebryanykh Nositelyakh" (Methods of Recording Information on Non-Silver Carriers), Izd. Vishcha Shkola, Kiev, 1977, No. 8, p. 56.
123. A. D. Grishina, Vysokomol. Soed., **19B**, 411 (1977).
124. A. N. Nesmeyanov, V. A. Sazonova, V. I. Romanenko, N. A. Rodonova, and G. P. Zol'nikova, Dokl. Akad. Nauk SSSR, **155**, 1130 (1964).
125. A. N. Nesmeyanov, Pure App. Chem., **17**, 220 (1968).
126. A. N. Nesmeyanov, V. A. Sazonova, V. I. Romanenko, V. N. Postov, G. P. Zol'nikova, V. A. Blonova, and R. M. Kozlyanova, Dokl. Akad. Nauk SSSR, **173**, 589 (1967).
127. E. Korner von Gustorf and F. W. Grevels, Fortschr. Chem. Forsch., **13**, 366 (1969).
128. V. Balzani and V. Carassiti, "Photochemistry of Co-ordination Compounds", Acad. Press, London, 1970.
129. M. Wrighton, Chem. Rev., **74**, 401 (1974).
130. A. W. Adamson and P. D. Fleischauer (Editors), "Concepts of Inorganic Photochemistry", Wiley, London, 1975, Chapters 6 and 9.
131. J. C. D. Brand and W. Snedden, Trans. Faraday Soc., 53, 894 (1957).
132. E. Korner von Gustorf, H. Koller, M. J. Jun, and G. O. Schenk, Chem. Eng. Tech., **35**, 591 (1963).
133. I. J. Spilners, J. Organometal. Chem., **11**, 381 (1968).
134. Y. Hoshi, T. Akiyama, and A. Sugimori, Tetrahedron Letters, 1485 (1970).
135. T. Akiyama, Y. Hoshi, S. Goto, and A. Sugimori, Bull. Chem. Soc. Japan, **46**, 1851 (1973).
136. D. R. Scott and R. S. Becker, J. Chem. Phys., **35**, 516 (1961).
137. T. Akiyama, A. Sugimori, and H. Hermann, Bull. Chem. Soc. Japan, **46**, 1855 (1973).
138. A. L. J. Beckwith and R. J. Leydon, Tetrahedron Letters, 385 (1963).
139. E. Koermer von Gustorf, H. Köller, M. Jun, and G. O. Schenk, Z. Naturforsch, **19b**, 170 (1964).
140. "NIITEKhIM, Obzornyna Informtsiya, Ser. 'Kremnii-organicheskie Prudukty i Ikh Primenenie'. Primenenie Ferrotsena" (NIITEKhIM. Review Information. 'Organosilicon Products and Their Applications' Series. Applications of Ferrocene), 1976.
141. D. M. Allen, J. Phot. Sci., 24, 61 (1976).
142. A. N. Nesmeyanov, V. A. Sazonova, A. V. Gerasimenko, and N. S. Sazonova, Dokl. Akad. Nauk SSSR, **149**, 1354 (1963).
143. A. N. Nesmeyanov, A. V. Vannikov, V. A. Zver'kov, L. V. Balabanova, G. A. Shvekhgeimer, and N. S. Kochetkova, 240, 121 (1978).

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