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Photochemical Methods for Recording Information. Primary Photoprocesses

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The principal photographic characteristics of non-silver materials, whose activity is based on photochemical reactions, are presented. The nature of the first stage in the photochemical processes involving the recording of information (the primary photochemical reaction) are analysed and the kinetic approach to the estimation of some of their limiting characteristics is discussed. Materials are classified in terms of the primary photochemical reactions and the threshold of the energetic light sensitivity and the red limit of the region of spectral sensitivity are estimated for each primary reaction.
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I. INTRODUCTION

Among the problems of modern photographic science, the following occupy a central position: the search for highly effective light sensitive materials, the prediction of their properties, and estimation of the limiting values of the principal characteristics of such materials. The properties of individual non-silver chemical materials and processes have been examined in reviews devoted to specific photographic materials: photochromic materials[1-21], materials with physical development[22-30], light-sensitive polymers[31-34], photopolymerisation materials[34-43], diazotype materials[44-52], vesicular materials[52-55], and free-radical materials[56-63]; they are also considered in general reviews[64-78].

In order to solve the problems indicated above, it is necessary to establish a relation between the photographic characteristics of light-sensitive materials and the physicochemical properties of the initial light-sensitive substances.

We shall consider a general approach to the solution of this problem. Fig. 1 presents a scheme for the production of an image when chemical non-silver photographic processes are used. Evidently the production of an

image with the aid of these materials involves several stages. Stage (1) is a photochemical reaction with formation of the primary photoproduct. In individual instances (pathway *A*) the primary product already constitutes a centre for the formation of the image. However, as a rule (pathway *C*) the primary product initiates in stage (2) further dark reactions with formation of a latent image. As a result of stage (3), the latent image is developed (or intensified) and centres of the final image are produced. Sometimes (pathway *B*) the primary photoproduct constitutes the latent image and in this case there is no second stage in the production of the image. The properties of the resulting image are determined by all three stages, so that the determination of a relation between the photographic characteristics of light-sensitive materials and the physicochemical properties of the initial sensitive system is a complex problem and involves the analysis of each stage.

It is in general impossible to carry out a complete analysis of the entire set of processes. This review is devoted to the analysis of the first stage of the production of the image—the primary photochemical reaction. On the basis of this analysis, certain limiting parameters of photographic materials are estimated. The second and third stages in the production of the image (dark reactions and intensification processes) as well as sensitisation problems are not discussed.

If the image formation process has only one stage (pathway *A*, Fig. 1), then the estimates yield the limiting characteristics in the materials. In the presence of other stages (cases *B* and *C*) the estimates constitute the lower limits of the values of these characteristics.

The group of non-silver photographic processes for the recording of information is very large and includes photochemical reactions in non-silver light-sensitive materials based on organic and inorganic compounds, photochemical

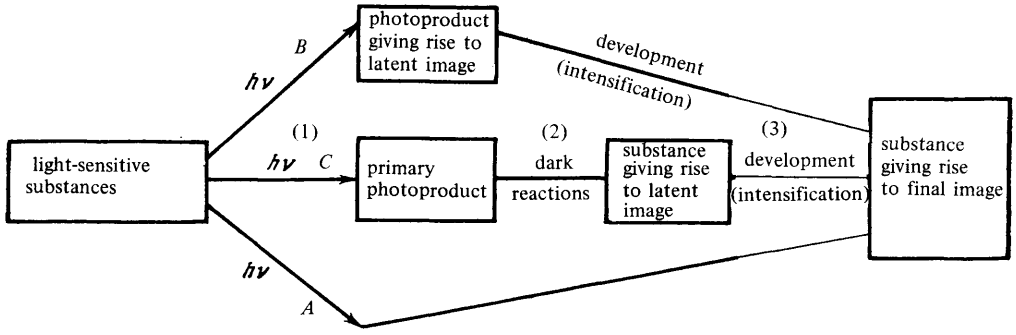


Figure 1. Schematic illustration of the production of the image when chemical non-silver photographic processes are employed.

Table 1. Photographic characteristics of light-sensitive materials whose operation is based on photochemical reactions.

No.	Material	Development (intensification)	$\Delta\lambda$, nm	Q, J cm^{-2}	R, mm^{-1}	No. of rerecording cycles	Type of recording
1	Diazotype (Refs.46,79,80)	Treatment in ammonia vapour	300—500	10^{-1} [46]	1500 [80]	1	Amplitude
2	Vesicular (Refs.81-83)	Thermal	300—500	10^{-2*} [83]	600 [82]	1	Phase
3	Light-sensitive polymers (negative) (Refs. 69,84-86)	Washing in a solvent	250—400	$5\cdot10^{-3}$ [86]	500 [84]	1	Phase relief
4	Light-sensitive polymers (positive) (Refs.69, 87-89)	Ditto	250—480	$3\cdot10^{-1}$ [89]	1400 [88]	1	Phase relief
5	Photochromic (Refs.1-21)	No development stage	250—700	10^{-2} [4,6]	3500 [6]	10^{4} (Ref.4)	Amplitude, phase, phase-amplitude
6	Photopolymerisation (Refs.35-43, 90, 91)	Washing in a solvent	280—700	10^{-3} [91]	1000 [90]	1	Phase relief
7	With physical development (Refs. 22-30, 92, 93)	Physical	300—700	10^{-7} [92]	1200 [93]	1	Amplitude
8	Free-radical (Refs. 56-63)	Optical ($\lambda > 500$)	300—500	$4\cdot10^{-4}$ [57]	5000 [56]	1	"
9	Chromium-treated colloids**	Washing in water	250—580	$2\cdot10^{-3}$ [71, 95]	4000 [96]	1	Phase relief
10	(Refs.71, 94-96)	Thermal	250—400	10^{-4} [97]	1000 [98, 99]	1	"
11	Photodeformation (Refs.97-99)	"	230—260	2 [100]	500 [100]	1	"
12	Photothermopolymerisation (Ref.100) Cyanotype (Refs.75, 101, 103)	No development stage	280—400	—	—	1	Amplitude
13	Luminescent (Refs.104-107)	Optical	150—380	10^{-4} [107]	400 [106]	Several	"
14	Photoenzymographic (Ref.102)	—	—	—	—	—	—

* Calculation based on Fig. 2 [83] for $\Delta D_{project} = 0.3$.

** Dichromated gelatin (Ed. of Translation).

processes in semiconductors, etc. We shall isolate from this large group of processes those which involve photochemical transformations in the molecule, i.e. are unimolecular or bimolecular reactions in the initial organic or inorganic compounds, and shall define them as photochemical processes for the recording of information. In the present review attention is concentrated on organic compounds.

Analysis of the activity of the light-sensitive non-silver materials known hitherto showed that processes in the following fourteen materials can be assigned to the subclass of photochemical processes for the recording of information: diazo-type materials, vesicular materials, light-sensitive polymers (positive and negative), photochromic materials, photopolymerisation materials, materials with physical development, free-radical materials, chromium-treated colloids, photodeformation materials, photothermopolymerisation cyanotype materials, luminescent materials, and photoenzymographic materials; the properties and photographic characteristics of these materials are discussed in the next Section.

II. PHOTOGRAPHIC CHARACTERISTICS OF NON-SILVER MATERIALS WHOSE ACTIVITY IS BASED ON PHOTOCHEMICAL REACTIONS

Table 1 presents the main characteristics of fourteen types of the above materials: the method of development of the latent image, the region of spectral sensitivity, the maximum values of energetic sensitivity and resolving power, the number of rerecording cycles, and the types of recording. Table 1 shows that different methods are used to develop and fix the image in non-silver light-sensitive materials of the type under consideration: treatment with a gas, "wet" development (treatment in an appropriate solution), thermal, and optical. The range of spectral sensitivity ($\Delta\lambda$) of the materials is 200–700 nm.

The energetic light sensitivity of a photographic material Q is defined as the minimum amount of energy (in J cm^{-2}) giving rise to a definite photographic effect) i.e. the change in the optical density of the image ΔD (for example $\Delta D = 1$ is adopted for materials Nos. 5 and 8, and $\Delta D = 0.2$ is adopted for material No. 7) or in the depth of the relief (0.1 and 0.2 μm for materials Nos. 10 and 11 respectively). The energetic light sensitivities of the materials listed in Table 1 are in the range 10^{-1}–10^{-7} J cm^{-2}. The resolving power R = 400–5000 mm^{-1} is more than enough for the majority of technical applications of the given materials. The number of rerecording cycles is 1 to 10^4; the materials permit amplitude, phase, and phase-amplitude recording.

The problems of the application of the materials are not considered in this review; they are dealt with in other reviews and monographs[3,4,15,32,36,73]. It is noteworthy that only the resolving power of these materials satisfies all the practical requirements. In terms of important characteristics such as the region of spectral sensitivity and energetic light sensitivity, these materials are greatly inferior to silver halide materials and can replace the latter only in a limited number of instances.

III. GENERAL SCHEME FOR THE KINETIC ANALYSIS OF THE PHOTOCHEMICAL STAGE IN THE RECORDING OF INFORMATION. PRINCIPAL APPROXIMATIONS

We shall consider a general scheme for the kinetic analysis of the photochemical stage in the recording of information. Since the efficiency of the photochemical process is determined by the quantum yield, it is necessary to establish how the principal photographic parameters of the light-sensitive material are related to the quantum yield, namely the energetic light sensitivity Q and the red limit of the region of spectral sensitivity λ_{lim}. Having analysed subsequently the dependence of the quantum yield of the photochemical reaction on the properties of the initial light sensitive system, we can relate Q and λ_{lim} to the initial parameters of the substance and hence can estimate the limiting values of these parameters.

The primary photochemical reaction can be unimolecular or bimolecular. The unimolecular reaction can be represented in the following form:

$$A^0 \xrightarrow{h\nu} A^*,$$
$$A^* \xrightarrow{k} B \text{ (product)},$$
$$A^* \xrightarrow{k_d} A^0,$$

where A^0 is the initial substance in the ground electronic state and A* is the initial substance in the excited state. The quantum yield in the formation of the photoproduct is

$$q_B = k/(k + k_d), \quad (1)$$

i.e. is determined by the ratio of the rate constants for the photochemical reaction (k) and for the deactivation of the excited state (k_d).

A bimolecular photochemical reaction can be regarded in the most general form as a process involving a random approach of the reacting molecules to a distance necessary for the occurrence of the reaction (this event will be called an "encounter") and the chemical reaction proper. At the instant of the "encounter" the molecules are surrounded by a cage of solvent molecules. Diffusion-controlled processes are usually understood as those whose rate is controlled by the frequency of "encounters". The mechanism of a bimolecular reaction can be represented as follows:

$$A^0 \xrightarrow{h\nu} A^*,$$
$$A^* + C \underset{k_r}{\overset{k_{diff}}{\rightleftharpoons}} [A^* \ldots C],$$
$$[A^* \ldots C] \xrightarrow{k} B \text{ (product)},$$
$$A^* \xrightarrow{k_d} A^0,$$
$$[A^* \ldots C] \xrightarrow{k_d} A^0 + C,$$

where k_{diff} is the rate constant for the enclosure of the reactants in the solvent cage and k_r the rate constant for the emergence from the cage. The quantum yield in the formation of the photoproduct is

$$q_B = \frac{k_{diff}[C]}{k_{diff}[C] + k_d} \cdot \theta_1, \quad (2)$$

where θ_1 is the probability of the reaction in the cage.

Thus the dependence of the quantum yield of the product of the primary photochemical process on the properties of the initial light-sensitive system is determined by its dependence on a number of constants. The rate constant for the photochemical reaction k is in the general case a function of the symmetry and energy $\epsilon_{S(T)}$ of the electronic state, the distribution of electron density in the excited

state, and the properties of the medium in which the reaction takes place (viscosity, temperature, etc.). For each specific photochemical reaction, different parameters among those enumerated can assume the main role, and the exact calculation from the constants for photochemical reactions is at present impossible.

According to this scheme, the rate constant k_d characterises the rate of radiative and non-radiative deactivation of the excited state. It is determined both by the properties of the reacting molecule (symmetry, spin–orbit interaction, vibronic interaction, etc.) and the properties of the matrix (temperature, viscosity, concentration of excitation quenching agents, etc.). However, if we confine ourselves to the case of viscous solutions, which are of main interest in the practical application of light sensitive materials, then many factors become insignificant and it is possible to obtain an answer to the main question—how k_d changes on passing from one compound to another. It is then assumed *a priori* that there is a possibility of synthesising compounds absorbing light and having an energetically predetermined reactive state. Theory[108] and experiment[109] showed that, for conjugated organic molecules with $\epsilon_{S(T)} < 20\,000$ cm^{-1} (in the estimation of the red limit of the region of spectral sensitivity this energy range is of interest), the constant k_d is determined by a non-radiative process, i.e. $k_d = k_{nr}$, where k_{nr} is the rate constant for the non-radiative deactivation of the excited state. For different compounds belonging to a single class, the constant k_{nr} is fully determined by the energy of the excited state $\epsilon_{S(T)}$ and the dependence of its values on $\epsilon_{S(T)}$ is exponential. The empirical dependence of the rate constant k^T_{nr} on the energy of the triplet state ϵ_T of aromatic compounds is described by the formula

$$k^T_{nr} = {}^0k^T_{nr} \exp(-\varepsilon_T/\varepsilon_0), \qquad (3)$$

where ${}^0k^T_{nr}$ and ϵ_0 are constants within a single class of compounds and their numerical values (${}^0k^T_{nr} = 10^{7.5}$ s^{-1} and $\epsilon_0 = 1000$ cm^{-1}) have been calculated[109]. According to the theory, the above relation breaks down for $\epsilon_T \leqslant \epsilon_{vib}$.

We shall now proceed to the specific estimation of the long-wavelength limit of the region of spectral sensitivity. The region of spectral sensitivity of the material is determined by the dependence of the quantum yield in the primary photoprocess q on the frequency of the incident light, since the remaining stages in the production of the image as a rule take place in the dark. It should be noted that, only when a vibrationally unexcited singlet (or triplet) state is involved in the photochemical reaction, does the spectral sensitivity coincide with the absorption spectrum of the light-sensitive substance[110]; in many instances these spectral curves may not coincide[111]. In order to determine the red limit of the region of spectral sensitivity of materials, it is necessary to estimate the minimum energy of photons ϵ^{lim} which cause an excitation of the photochemical reaction such that the latter has an adequate quantum yield, for example $q = 10^{-1}$. This choice is arbitrary, but, for $q < 10^{-1}$, the overall light sensitivity of the material becomes low (for an insignificant or zero intensification coefficient), and the region where the material can be used is restricted.

The minimum energy of photons required for the occurrence of a unimolecular photochemical reaction ϵ^{lim}_T can be obtained from Eqn. (1) after substituting in the latter the values of k and k_{nr} as a function of the energy of the reactive state ϵ_T (in the given case the triplet state) and after solving the equation for ϵ_T when $q = 10^{-1}$. In the most general case it is probably possible to assume that, on passing from one molecule to another within a given class, the rate constant for the photoprocess is zero when the energies of the electronic state ϵ_T are smaller than the energies expended on the primary photochemical reaction $\epsilon_{(I)}$ [i.e. $k = 0$ for $\epsilon_T < \epsilon_{(I)}$] and, when $\epsilon_T > \epsilon_{(I)}$, k increases with increase of ϵ_T [i.e. $k = f(\epsilon_T)$ when $\epsilon_T > \epsilon_{(I)}$]. Unfortunately it is as a rule not known how k depends on ϵ_T. If the dependence of the rate constant k_{nr} for a non-radiative transition on the energy of the excited state ϵ_T is described by Eqn. (3), then, when account is taken of the foregoing considerations, Eqn. (1) yields the following minimum energy of the reactive triplet state:

$$\varepsilon^b_T = \varepsilon_0 \ln({}^0k^T_{nr}/9k). \qquad (4)$$

In order that the above expression should have a physical significance, the following boundary condition must hold: the energy of the absorbed photon must be greater than or equal to the energy $\epsilon_{(I)}$ required for the occurrence of the primary photochemical reaction $\epsilon^b_T \geqslant \epsilon_{(I)}$. Consequently the red limit of the region of spectral sensitivity in photochemical processes involving the recording of information is determined by two restrictions—energetic and kinetic. If the limits of the estimate based on energetic conditions are known, it is possible to claim *a priori* that allowance for kinetic limitations can lead to a hypsochromic shift of the red limit of the region of spectral sensitivity.

For a bimolecular reaction, the minimum energy of photons required to ensure the occurrence of the reaction can be obtained analogously from Eqn. (2) having substituted in the latter k_d and θ_1 as functions of the energy of the reactive state ϵ_T.

When the reaction proceeds via a singlet molecular state, the approach to the determination of the limiting characteristics remains the same with the sole difference that ${}^0k^T_{nr}$ in Eqn. (4) is replaced by the rate constant ${}^0k^S_{nr}$, the numerical value of which is determined by the ratio ${}^0k^S_{nr}/{}^0k^T_{nr} \simeq 10^6$.[112]

In those cases where the image is determined by the absorption of light by the final products of the overall reaction (photochemical or chemical) the energetic sensitivity of light can be estimated from a formula analogous to that quoted by Jackson[18]:

$$Q = 96DE/qN\varepsilon, \qquad (5)$$

where ϵ is the molar extinction coefficient of the substance (litre mole^{-1} cm^{-1}) which gives rise to the final image, E the energy of the photon in eV, D the optical density of the image ($D_0 = 0$), and N the coefficient of the intensification of the primary action of light. The maximum value of N is determined by the ratio of the reactivities of the initial substance and the photoproduct in relation to the reaction involving the intensification of the primary image.

Thus Eqn. (5) shows that the light sensitivity is determined mainly by the product qN. Evidently, for low quantum yields in the primary photoprocess q but an effective intensification process (i.e. a high value of N), the material can exhibit a high light sensitivity.

If it is assumed that the quantum yield in all primary reactions is unity, the final product has an extinction coefficient $\epsilon = 10^5$ litre mole^{-1} cm^{-1} (this is virtually the limiting value for molecular systems), and the primary image intensification stage is absent, then the limiting energetic light sensitivity of the material, calculated by Eqn. (5) for $\lambda = 400$ nm, is $Q^{400}_{D=1} = 3 \times 10^{-3}$ J cm^{-2}.

In order to estimate the red limit of the region of spectral sensitivity in specific systems by the scheme described above, it is necessary to establish beforehand the type of primary photochemical reactions in the light-sensitive materials employed and to classify these materials in terms of such reactions.

IV. CLASSIFICATION OF LIGHT-SENSITIVE MATERIALS IN TERMS OF PRIMARY PHOTOCHEMICAL REACTIONS

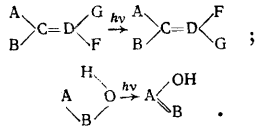
The materials will be classified and their characteristics within each group will be compared†. For this purpose, the primary photochemical reactions of the light sensitive materials listed in Table 1 were analysed. It was found that four primary photochemical reactions are characteristic of materials in this group.

I. Photoaddition:

$$A + B \xrightarrow{h\nu} AB .$$

Here and henceforth A and B are radicals, ions, or molecules. This group includes light-sensitive polymers (negative materials) and photochromic, photodeformation, and luminescent materials.

II. Photorearrangement:



Photochromic materials and materials with physical development belong to this group.

III. Phototransfer of an electron:

$$A + B \xrightarrow{h\nu} A^+ + B^- .$$

The third group includes cyanotype materials, chromium-treated colloids, materials with physical development, and photopolymerisation, photochromic, and free-radical materials.

IV. Photodissociation:

$$AB \xrightarrow{h\nu} A + B .$$

The fourth group includes diazotype and vesicular materials, light-sensitive polymers (negative or positive), and photodeformation, photochromic, photopolymerisation, and photothermopolymerisation materials with physical development.

All four possible elementary photochemical reactions employ only photochromic materials in the production of an image. This is natural, since a property common to all photochemical reactions (reversibility) is used in photochromic materials. In materials with physical development three elementary photochemical reactions are employed: photorearrangement, phototransfer of an electron, and photodissociation. The activity of photopolymerisation materials is based on two elementary photoprocesses: electron transfer and dissociation. Materials of this type cannot be synthesised on the basis of photoaddition and photoisomerisation reactions. Indeed two types of photopolymerisation are known: ionic and radical. In order to initiate polymerisation, it is necessary to generate (by irradiation with light) radicals or ions, which cannot be obtained in photoaddition and photoisomerisation reactions.

Table 2 presents the principal characteristics of materials for each elementary photochemical reaction occurring in them. Evidently materials involving different primary reactions have significantly different energetic light sensitivities, in particular materials with minimum sensitivity have been obtained on the basis of the photoaddition reaction. The observed difference is associated with the fact that the photoprocesses enumerated can generate primary products with the same or different reactivities. Because of this, in some cases there is a possibility of processes involving the intensification of the primary image, while in others there is no such possibility. It will be shown below that the type of primary photochemical reaction determines to a large extent also the red limit of the region of spectral sensitivity of materials.

Table 2.

Parameters of materials	Type of reaction			
	I	II	III	IV
R, mm^{-1}	200—3000	2000	400—5000	50—5000
q	10^{-1}—1	10^{-1}—1	10^{-1}—1	10^{-1}—1
N	1	$\geqslant 1$	$\geqslant 1$	$\geqslant 1$
Q, J cm^{-2}	10^{-1}—10^{-2}	10^{-1}—$5\cdot10^{-4}$	10^{-1}—10^{-7}	10^{-1}—10^{-4}

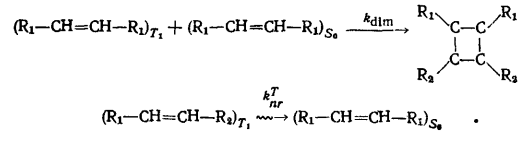
V. RELATION BETWEEN THE RED LIMIT OF THE SPECTRAL SENSITIVITY OF MATERIALS AND THE KINETIC AND SPECTROSCOPIC CONSTANTS OF LIGHT-SENSITIVE SUBSTANCES

We shall consider in succession the primary photochemical reactions enumerated above, which occur in the recording of an image on light-sensitive materials.

1. Photoaddition

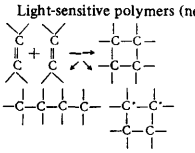
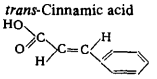
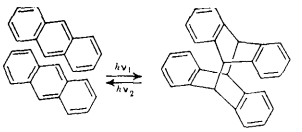
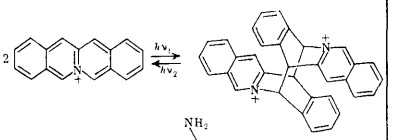
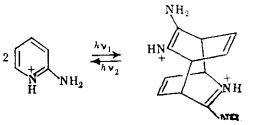
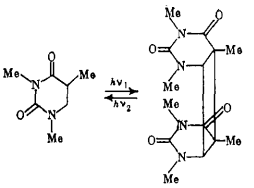
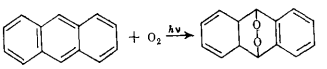
Table 3 presents the principal properties of specific light-sensitive materials in which the primary photochemical reaction is photoaddition. We shall consider photoaddition to an ethylenic double bond, which takes place, for example, in negative photoresistors based on cinnamates and constitutes a model photoaddition reaction. The transition from the primary photochemical reaction to the final parameters of the material will be discussed in relation to this reaction.

Dimerisation involving an ethylenic double bond is a bimolecular reaction in which an excited molecule is added to an unexcited molecule with formation of a cyclobutane ring. Experiments on the sensitisation of this reaction by the triplet–triplet energy transfer showed that it can proceed via an excited triplet state[123–125]. The kinetic scheme for the photodimerisation process can be formulated as follows:



† The classification of inorganic light-sensitive materials in terms of primary photoprocesses has been described[74, 75] without the analysis of the limiting characteristics.

Table 3. Photoaddition.

Light-sensitive substance	Primary photochemical reaction	Type of reaction	Region of spectral sensitivity $\Delta\lambda$, nm*	Refs.
	Light-sensitive polymers (negative)			
Cinnamic acid derivatives $R_1-C(=O)-(CH=CH)_x-C_6H_4-R_2$ R_1 — polymer chain; $=1, 2\ldots$ $x = 1,2,\ldots$		Photodimerisation involving an olefinic double bond	275**	31, 33, 69, 85, 113—115
	Photochromic materials			
trans-Cinnamic acid 	ditto	ditto	$\lambda<300$, $\lambda_2>300$	116—117
Anthracene		Photodimerisation of aromatic hydrocarbons	$\lambda_1=380$, $\lambda_2=280$	118—120
Acridizinium and benzacridizinium salts		Photodimerisation of aromatic heterocycles	$\lambda_1=500$, $\lambda_2=360$	118
2-Aminopyridine				
		ditto	$\lambda_1=310$, $\lambda_2=240$	118
1,3-Dimethylthymine		»	$\lambda_1=\sim278$, $\lambda_2=\sim240$	118
	Photodeformation materials			
Rosin	Replacement of two conjugated double bonds by single bonds		λ u.v.	118, 119
Abietic acid	Photosensitised oxygen transfer		λ u.v.	98, 99
	Luminescent materials			
Anthracene		Photoaddition of oxygen	λ u.v.	104—107

* λ_1 represents the region of spectral sensitivity of the initial substance and λ_2 the region of spectral sensitivity for the reverse reaction.

** The values of λ_{max} are quoted.

There are no energetic restrictions in the dimerisation reaction, since it proceeds after each "suitable" collision of excited and unexcited molecules. It is probably possible to consider two cases of dimerisation: dimerisation controlled by diffusion and addition of molecules "prepared" beforehand in a cage of matrix molecules. The first instance occurs in reactions in liquid and gas phases and also in a solid–gas system. The second obtains in reactions of molecules in solid solutions and polymers.

The second case is characteristic of the majority of light-sensitive materials, whose activity is based on the photoaddition reaction. Only in photodeformation (abietic acid) and luminescent materials is the addition reaction diffusion-controlled. When the reacting molecules have been enclosed in cages beforehand and the bimolecular reaction proceeds after the collision of species in the cage, the quantum yield can be formulated thus:

$$q=\frac{k_{col}}{k_{col}+k_{nr}}\theta_2,$$

where k_{col} is the rate constant for the collision process in the cage and θ_2 is the probability of reaction on collision. If it is assumed that $\theta_2 = 1$ for the photoaddition reaction in the cage, then the overall quantum yield of

the reaction is equal to the probability of the collision of excited and unexcited molecules in the cage, whereupon $k_{dim} = k_{col}$. The constant k_{col} is determined by the mobility of the reacting molecules, i.e. ultimately by the size and shape of the cage and the dimensions of the reacting molecules, as well as the energy of the intermolecular additive-matrix interaction. In the general case, for a reaction in the cage, it is given by the formula

$$k_{col} = k^0_{col} \exp(-E/RT), \quad (6)$$

where k^0_{col} is the frequency of collisions of two molecules and E is the activation energy for the collision of molecules in the cage. The red limit of the region of spectral sensitivity of materials operating on the basis of the photoaddition reactions can be obtained in this case from Eqn. (4) after substituting in the latter $k = k_{col}$ from Eqn. (6).

For numerical estimates of values of ϵ^{lim}_T, it is necessary to know the specific values of the rate constants and activation energies E. The recombination in a radical pair incorporated in a matrix is a model addition reaction for molecules in a cage. The recombination process itself, like the addition reaction, proceeds without activation energy and the observed activation energy E is due to kinetic causes—it is the activation energy for the mutual approach of molecules. The rate constant for the recombination of radicals of the type $\dot{N}\!\!<^{Ph}_{Ph}$ has been found[126] ($k^0_{rec} = 10^{8.5}$ s^{-1}, E = 7000 cal mole^{-1}).

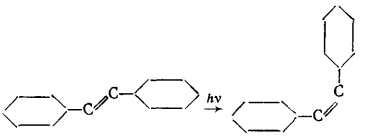
The same value of the rate constant, i.e. $k_{dim} = k_{rec}$, can probably be adopted for the addition reactions of compounds in which R_1 and R_2 are substituents such as phenyl rings. For compounds where more rigid matrices are used as the substituents, the dimerisation rate constant k_{dim} may be much smaller, mainly as a consequence of the increased activation energy for the collision process. If it is assumed that $k^0_{dim} = 10^9$ s^{-1} and E = 7 kcal mole^{-1} for all dimerisation reactions in solid solutions, then we have ϵ^{lim}_T = 6000 cm^{-1} from Eqn. (4).

On photoexcitation of the system, the triplet state is formed from the singlet state as a result of the $S-T$ transformation. Since ϵ_{S-T} = 2000–3000 cm^{-1} for molecules with low-lying triplet states, the red limit for the photochemical reaction involving the triplet state is defined as follows: $\nu^{lim} = \epsilon^{lim}_T + \epsilon_{ST}$ = 8000 cm^{-1}, so that λ_{lim} = 1250 nm.

The dependence of the limiting energies of the triplet and singlet state ϵ_T and ϵ_S on the activation energy E for different constants k^0_{col}, $^0k^T_{nr}$, and $^0k^S_{nr}$ is illustrated in Fig. 2.

2. Photorearrangement

Table 4 lists the light-sensitive materials employing the photorearrangement reaction. The most thoroughly investigated case is that of *trans–cis* isomerisation, namely the *trans–cis* isomerisation relative to ethylenic bonds. Examples of such compounds are provided by aryl derivatives of ethylene and thioindigo dyes. The characteristics of the isomerisation of arylethylenes are in broad outline typical of the isomerisation of other classes of compounds. We shall consider the *trans–cis* isomerisation process in relation to the stilbene molecule. For stilbene and arylethylenes, it has been shown that the *trans–cis* isomerisation can proceed via both triplet[131,132] and singlet[133–135] excited states. The general process mechanism can be represented as follows:



$$trans\text{-form}^{S(T)} \xrightarrow{k^{S(T)}_{tc}} cis\text{-form}^{S_0},$$
$$trans\text{-form}^{S(T)} \xrightarrow{k_{nr}} trans\text{-form}^{S_0}, \quad (7)$$

where k_{tc} is the rate constant for the *trans–cis* isomerisation.

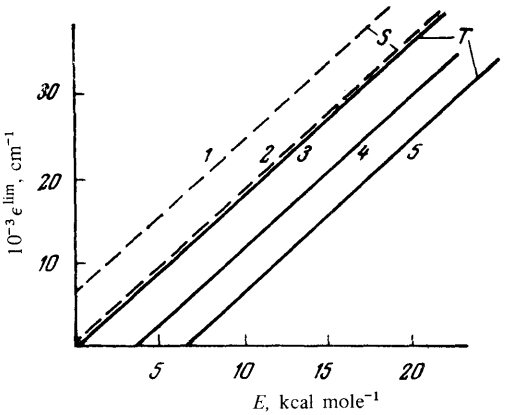


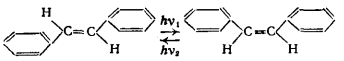
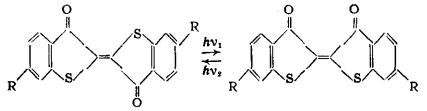
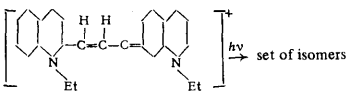
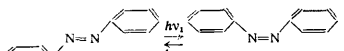
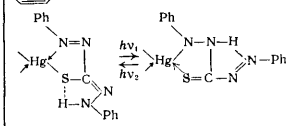
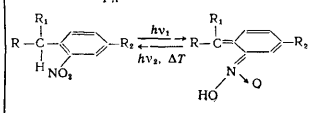
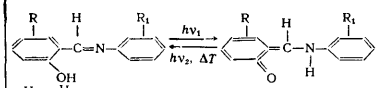
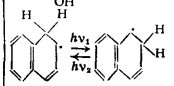
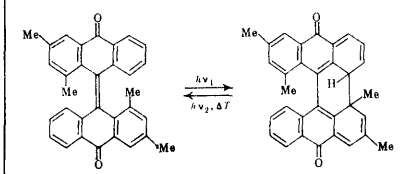
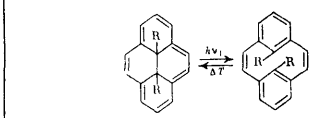
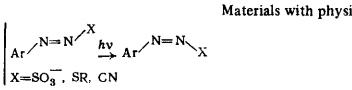
Figure 2. Dependence of the limiting energies ϵ^{lim} of the triplet and singlet states of the molecules on the activation energies; k^0_{col} (s^{-1}): 1), 4), and 5) 10^9; 2) and 3) 10^{12}; $^0k^S_{nr}$ (s^{-1}): 1) and 2) 10^{13}; $^0k^T_{nr}$ (s^{-1}): 3) and 4) $10^{7.5}$; 5) 10^{10}.

Scheme (7) shows that a molecule in the excited state can be either converted into the *cis*-form, which corresponds to the rotation of one fragment relative to the connecting bond, or it can relax to the ground state. For arylethylenes in the triplet state, rotation about the central bond (without taking into account the interaction with the medium) is virtually free from an energy barrier (its height amounts to several kcal)[136,137] and the rotation frequency of the fragment is close to the rotation frequency of the molecule as a whole. It can be assumed that, for identical matrices, the rate constant for the isomerisation of electronically excited molecules is the same as the frequency of the thermal rotation of a molecule of similar size, i.e. it can be formulated as follows:

$$k_{tc} = k^0_{tc} \exp(-E_{rot}/RT), \quad (8)$$

where E_{rot} is the activation energy for rotation determined by the interaction of the molecule with the matrix.

Table 4. Photorearrangement.

Light-sensitive substance	Primary photochemical reaction	Type of reaction	Region of spectral sensitivity, Δλ, nm*	References
	Photochromic materials			
Substituted ethylenes		*trans-cis* isomerisation	$\lambda_1=295$, $\lambda_2=280$	2, 9, 11, 12, 14, 16
Indigoid compounds		Ditto	$\lambda_1=510$, $\lambda_2=450$	2–4, 9, 127
Cyanine dyes		» »	565, 610 **	2
Azo-compounds		» »	$\lambda_1=319$, $\lambda_2=324$	2, 11, 14
Metal dithizonates		Tautomerism with hydrogen transfer	$\lambda_1=490$, $\lambda_2=600$	2, 4, 128, 129
Nitrobenzyl derivatives		Ditto	$\lambda_1=\lambda_{u.v.}$ $\lambda_2=600$	2, 14
Anils		» »	$\lambda_1=\lambda_{u.v.}$ $\lambda_2=500$	2, 4, 9, 16
Radicals formed by adhesion of hydrogen to aromatic hydrocarbons		» »	$\lambda_1=335$, $\lambda_2=385$*	130
2,4,2',4'-Tetramethyl-bianthrone		Valence tautomerism	$\lambda_1=\lambda_{u.v.}$ $\lambda_2=650$	2, 11, 16
Derivatives of trans-15,16-dialkyldihydropyrene		Ditto	$\lambda_1=600$	2
Aromatic hydrocarbons		*T-T* absorption	$\lambda_1=\lambda_{u.v.}$ $\lambda_2=\lambda_{visible}$	2
	Materials with physical development			
Benzenediazosulphides Benzenediazosulphonates Benzenediazocyanides		*trans-cis*-isomerisation	<450	24, 29

* λ_1 represents the region of spectral sensitivity of the initial substance and λ_2 the region of spectral sensitivity for the reverse reaction.

** The values of λ_{max} are quoted.

Thus in making the estimate we assume that the activation energy for an electronically excited molecule is determined, regardless of the energy of the excited states, by the activation energy for the rotation of the molecules in the given matrix. On the assumption that the reaction rate constant $k = k_{tc}^{S(T)}$ is independent of the energy of the excited state $\epsilon_{S(T)}$, the red limit of the region of spectral sensitivity can be estimated from Eqn. (4) after substituting in the latter the numerical values of the reaction rate constant.

There are no data for the parameters of the rotation of aromatic molecules (benzene, naphthalene, etc.) in polymeric matrices. On the other hand, there is much information about the pre-exponential factors and activation energies for the rotation of iminoxy-radicals in

various polymers. For the estimates, we shall assume that the characteristics of the rotational motion of iminoxy-radicals simulate the corresponding parameters for the simplest aromatic compounds. This assumption is probably valid, since the dimensions of the radicals and the compounds which they simulate (for example, arylethylenes and the simplest thioindigo dyes) are approximately the same, and in both cases there is no specific additive–matrix interaction. Having assumed for the *trans–cis* isomerisation in the polymer the activation energy and pre-exponential factor obtained for the rotation of the iminoxy-radical in polystyrene (E_{rot} = 18.2 kcal mole^{-1} and $k^0_{tc} = 4\times10^{18}$ s^{-1} [138]), we can calculate from Eqn. (4), for k_{tc} derived from Eqn. (8), the quantity ϵ^{lim}_T = 3000 cm^{-1} at 300 K. This result is comparable to ϵ_{vib}.

The red limit for a photochemical reaction involving the triplet state with the direct excitation of the molecule to the singlet state and subsequent $S-T$ transition to the triplet state is determined as follows: $\nu lim = \epsilon^{lim}_T + \epsilon_{ST}$ = 5000 cm^{-1}; λ_{lim} = 2000 nm.

It is most probable that the red limit of the region of the spectral sensitivity obtained is too high. The main cause of this is the assumption of the absence of an internal barrier to rotation. For polymethine dyes, the activation energy increases several fold with decrease of the energy of triplet levels[139]. Allowance for this factor leads to a hypsochromic shift of the red limit.

3. Phototransfer of an Electron

Materials whose activity is based on the phototransfer of an electron are listed in Table 5. In the general form the phototransfer of an electron can be represented schematically as follows[148]:

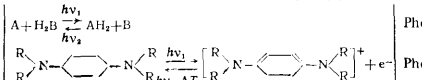
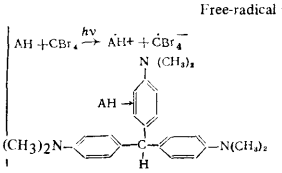
$$A^{S(T)} + H_2Y \xrightarrow{k_e} A^{\cdot}e^- + H_2Y^{\cdot+},$$
$$A^{S(T)} \xrightarrow{k^{S(T)}_{nr}} A^0,$$

where k_e is the rate constant for electron transfer.

As in photoaddition, the process consists of two stages—the mutual approach to a distance R_0 and subsequent electron transfer over this distance. It has now been established that phototransfer of an electron is a tunnel process and to a first approximation its rate constant varies exponentially with the distance. However, for the estimates in the present review, one can assume that, when $r \leq R_0$, the rate constant for electron transfer is large (the estimate yields $k_e = 10^{14}$ s^{-1} for $r < R_0$ [149]) and the probability of electron transfer over such distances $\theta_1 \simeq 1$, because the constants for the deactivation of the singlet ($k^S_{nr} = 10^{13}$ s^{-1}) and triplet ($k^T_{nr} = 10^{7.5}$ s^{-1}) states (see above) are smaller than the rate constant for electron transfer indicated above.

Thus the overall quantum yield in the phototransfer of an electron is determined by the probability of the mutual approach of the donor and acceptor to the transfer distance

Table 5. Electron phototransfer.

Light-sensitive substance	Primary photochemical reaction	Type of reaction	Region of spectral sensitivity Δλ, nm*	References
	Cyanotype materials			
Iron oxalate	$2Fe^{3+} + C_2O_4^{2-} \xrightarrow{h\nu} 2Fe^{2+} + 2CO_2$	Photochemical reduction	$\lambda_{u.v.}$	75, 101, 103
	Chromium-treated colloids			
Chromium-treated gelatin	Cr^{6+} + colloid $\xrightarrow{h\nu}$ Cr^{3+} + oxidised cross-linked colloid	Oxidation-reduction reaction	<580	71, 94–96
	Materials with physical development			
Fe^{3+} salts of organic acids + Pd, Pt, Rh, Ag, Au, Hg, and Cu salts	$Fe_2(C_2O_4)_3 \xrightarrow{h\nu} 2Fe(C_2O_4) + 2CO_2$ $2Fe^{2+} + Pd^{2+} \rightarrow 2Fe^{3+} + Pd^0$	Photochemical reduction	<400	24, 140, 141
Anthraquinone-2,7-disulphonate	$AQ + BH_2 \xrightarrow{h\nu} AQH(AQH_2) + BH(B)$	Ditto	$\lambda_{u.v.}$	24, 142–144
Methylene Blue	$D + BH_2 \xrightarrow{h\nu} DH(RH_2) + BH(B)$	»	$\lambda_{visible}$	24
	Photopolymerisation materials			
Dyes: Bengal Rose, Eosin, etc.	$A + RH \xrightarrow{h\nu} AH^{\cdot} + R^{\cdot}$	Photochemical reduction	$\lambda_{visible}$	76, 90, 145, 146
Peroxides + Fe^{3+}	$Fe^{3+} \xrightarrow{h\nu} Fe^{2+}$; $Fe^{2+} + H_2O_2 \rightarrow HO^{\cdot} + OH^- + Fe^{3+}$	Photochemical oxidation	$\lambda_{u.v.}$	76
	Photochromic materials			
Dyes: Thiazine, Oxazine	$A + H_2B \underset{h\nu_2}{\overset{h\nu_1}{\rightleftarrows}} AH_2 + B$	Photochemical reduction	$\lambda_1 = \lambda_{visible}$	2
p-Phenylenediamine derivatives		Photochemical oxidation	$\lambda_1 = \lambda_{u.v.}$ $\lambda_2 = \lambda_{visible}$	147
	Free-radical materials			
Leucoform of dyes (triphenylmethane, cyanine)		Photochemical oxidation	300–500	56–63

*λ_1 represents the region of spectral sensitivity of the initial substance and λ_2 the region of spectral sensitivity for the reverse reaction.

and can be calculated from Eqn. (2), where $c = H_2Y$ and $\theta_1 = 1$.

Two cases are possible in this reaction.

1. The distance between the donor and acceptor is small ($r \leq 5$) and the mutual approach stage is not required for the occurrence of the reactions; the process involves solely electron transfer. In this case there are no kinetic limitations, i.e. the first multiplier in Eqn. (2) is unity and the red limit of the region of spectral sensitivity is determined solely by energetic limitations: $\epsilon^{\lim}_{S(T)} = \epsilon(I)$.

2. The reaction is controlled by diffusion and its quantum yield is determined by the probability of encounters. This case corresponds to low concentrations of the acceptor or a low rate constant k_{diff} for the diffusion of the donor to the acceptor. In this case the stage involving the mutual approach of the donor and acceptor is rate-limiting. The red limit of the region of spectral sensitivity is determined from Eqn. (4), which in this case assumes the following form:

$$\epsilon^{\lim}_T = \varepsilon_0 \ln (k^T_{nr}/9k_{dif}[H_2Y]) \quad . \tag{9}$$

Fig. 3 presents the dependence of $\epsilon^{\lim}_T$ on $[H_2Y]$ plotted on the basis of Eqn. (9). It is noteworthy that the dependence has a physical significance only for $\epsilon^{\lim}_T > \epsilon(I)$. The necessary energetic limitation of the electron phototransfer reaction $\epsilon(I)$ is determined (without taking into account the interaction with the medium)[150] from the condition:

$$\varepsilon(I) = I_{H_2Y} - Q_A - W_e, \tag{10}$$

where W_e is the energy of the Coulombic interaction of the charges in the ion pair (the dissociation energy of the ion pair), Q_A is the electron affinity of the electron acceptor, and I_{H_2Y} is the ionisation potential of the electron donor.

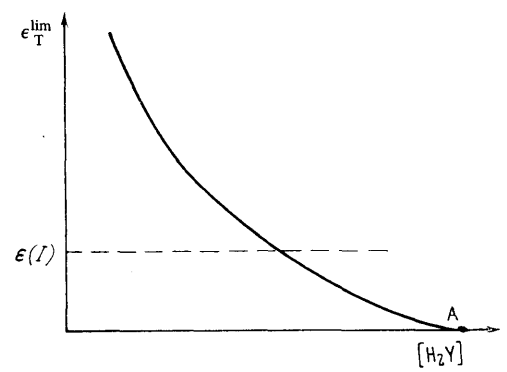


Figure 3. Dependence of $\epsilon^{\lim}_T$ on the concentration of the electron donor H_2Y. $[H_2Y] = k^T_{nr}/9k_{dif}$ at point A.

Since experimental relations between k^T_{nr} and ϵ_T were used in the given study for conjugated hydrocarbons, in the estimates it is useful to employ as the electron acceptor (excited molecule) a substance in the class of conjugated hydrocarbons for which $Q_A = 0$–1.0 eV.[151]

For the zinc oxide ($I_{ZnO} = 6.6$ eV) [152]–conjugated hydrocarbon donor–acceptor pair, the estimate of the minimum value of $\epsilon(I)$ based on Eqn. (10) for $W_e = 3 - 4$ eV yields $\epsilon(I) = 1.6$ eV and correspondingly $\lambda(I) = 770$ nm.

4. Photodissociation

Table 6 presents data whose employment is based on the photodissociation reaction. This elementary reaction embraces the largest number of light sensitive materials. It has been established that the photodissociation of organic compounds can proceed via several mechanisms[162].

Dissociation into a continuum. In this case the molecule is excited directly to the repulsive state. The molecule excited from the ground to a non-bonding state decomposes during the period of one vibration, which is approximately 10^{-13} s. This mechanism of the decomposition reaction is characteristic of simple molecules (Fig. 4*a*).

Thermal or quasi-equilibrium dissociation. The molecule is excited to a bonding state, which lies above the bond dissociation energy Fig. 4*b*). After the electronic energy has been transformed into the vibrational energy of the entire molecule, the latter is concentrated in a single bond and causes its rupture. As a rule this is the weakest bond.

Non-adiabatic dissociation. In this case the electron energy is concentrated in one specific vibration (or in several vibrations). As a rule, this is the most anharmonic vibration. For example, in hydrocarbon molecules, the most anharmonic vibration is that of the C–H bond.

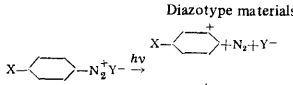
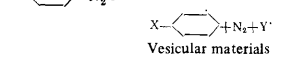
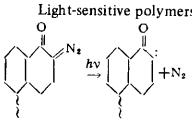
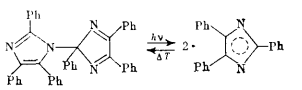
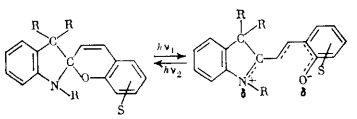
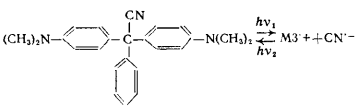
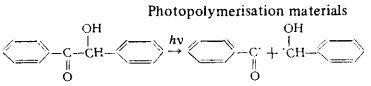
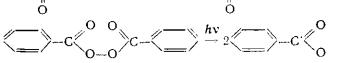
Predissociation. This dissociation mechanism obtains in complex organic molecules. The molecule is excited to a higher bonding state, i.e. the electronic excitation is delocalised over the entire molecule (Fig. 4*c*). This high bonding state intersects the repulsive state associated with any one bond and the interaction of the states leads to a transition of the molecule from a bonding to a repulsive state. This is followed by the dissociation of the given bond as a result of the concentration of the electron energy in the latter.

Dissociation involving a multistage intramolecular process. In complex molecules containing several chromophoric groups the dissociation process can consist of several intramolecular stages. In the first stage intramolecular charge transfer takes place, which results in the weakening or dissociation of one of the bonds. The next stage involves the decomposition of the unstable form into molecular fragments.

In order to determine the red limit of the region of spectral sensitivity of materials whose employment is based on the photodissociation reaction, it is necessary to examine the energetic and kinetic limitations in this reaction.

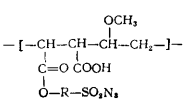
From the energetic point of view the minimum energy of the absorption of a photon, giving rise to photochemical activity, is limited by the dissociation energy of the weakest bond and in thermal dissociation of light-sensitive substances is directly equal to the energy of the weakest bond (Fig. 4*b*)[163]: $h\nu^{\lim}(I) = D_{A-B} = 30$ kcal mole^{-1} = 1.3 eV, so that $\lambda_{\lim}(I) = 1000$ nm. On the other hand, if the predissociation mechanism operates, the minimum energy of the photon must be about 1.5 times greater than the energy of the bond undergoing dissociation (Fig. 4*c*).

Table 6. Photodissociation.

Light-sensitive substance	Primary photochemical reaction	Type of reaction	Region of spectral sensitivity Δλ, nm*	References
	Diazotype materials			
Diazonium Salts		Heterolytic decomposition	300—500	44—46,153,154
		Homolytic decomposition		
	Vesicular materials			
Diazonium salts	Ditto	Ditto	Ditto	81
Diazo-compounds	$RC{=}N^{-}{=}N^{+} \xrightarrow{h\nu} R\ddot{C}{+}N_2$	Homolytic decomposition into a molecule and a biradical	<500	44,46,49
Aromatic and heterocyclic azides	$R{-}N{=}N{=}N \xrightarrow{h\nu} R{-}\ddot{N}{+}N_2$	Ditto	250—400	155
	Light-sensitive polymers (negative)			
Bisazides	$N{-}R{-}N_3 \xrightarrow{2h\nu} 2N_2{+}\ddot{N}{-}R{-}\ddot{N}$	»	250—400	156—159
Arylsulphonylazide group	$SO_2N_3 \xrightarrow{h\nu} SO_2\ddot{N}{+}N_2$ ***	»	240—290	86
Azide polymers		»	300**	160
	Light-sensitive polymers (positive)			
Naphthoquinone diazides		»	420**	87—89
	Photodeformation materials			
Azides	$R{-}N{=}N{=}N \xrightarrow{h\nu} R{-}\ddot{N}{+}N_2$	»	250—400	161
Triazenes	$R_1{-}N{=}N{-}NH{-}R_2 \xrightarrow{h\nu} R_1{+}N_2{+}\dot{N}H{-}R_2$	»	285—400	97
	Photochromic materials			
Bi-imidazolyls		Homolytic decomposition into two radicals	$\lambda_1=365$, $\lambda_2=351,574$	2,4
β-Tetrachlorooxodihydronaphthalene		»	$\lambda_1=\lambda_{u.v.}$, $\lambda_2=550$	2
Spiropyrans		Heterolytic decomposition into two ions	$\lambda_1=400$, $\lambda_2=\lambda_{u.v.}$	2,4
Derivatives of triarylmethane dyes			$\lambda_1=313$, $\lambda_2=430\,625$	2
Photodimers: of anthracene, acridizinium and benzacridizinium salts, 2-amino-pyridine, 1,3-dimethylthymine	(see photoaddition)	»		
	Photopolymerisation materials			
Carbonyls		Homolytic decomposition into two radicals	390**	73,76
Peroxides		Homolytic decomposition into two radicals	<320	76
Organic sulphur compounds	$C_4H_9S{-}SC_4H_9 \xrightarrow{h\nu} 2C_4H_9S$	Homolytic decomposition into a molecule and a radical	340**	76
	Photothermopolymerisation materials			
Poly(butyl methacrylate), copolymer of butyl methacrylate and methacrylic acid	Tentative photodissociation of a fragment of polymer chain	Homolytic decomposition into two radicals	—	100
	Materials with physical development			
Diazonium salts	$ArN_2^{+} \xrightarrow{h\nu} Ar^{\cdot}{+}N_2 \xrightarrow[H_2O]{} ArOH + N_2 + H^{+}$	—	380—420	29,52
Leucocyanides of triphenylmethane dyes	$Ar_3C{-}CN \xrightarrow{h\nu} Ar_3C^{+} + \dot{C}N^{-}$		$\lambda_{u.v.}$	24

*λ_1 represents the region of spectral sensitivity of the initial substance and λ_2 the region of spectral sensitivity for the reverse reaction.

**The values of λ_{max} are quoted.

***SO_2N_3 is the light-sensitive group of the polymer 

However, if $k_{diss} \ll k_{nr}$, then the quantum yield in the primary photochemical reaction may be close to zero even when the photon energy exceeds the bond energy. In this case kinetic limitations operate and $\lambda_{lim} < 1000$ nm. It is not possible to obtain a kinetic estimate of the red limit of spectral sensitivity owing to the lack of sufficiently well developed models of the photodissociation of complex molecules. If the photodissociation reaction proceeds by

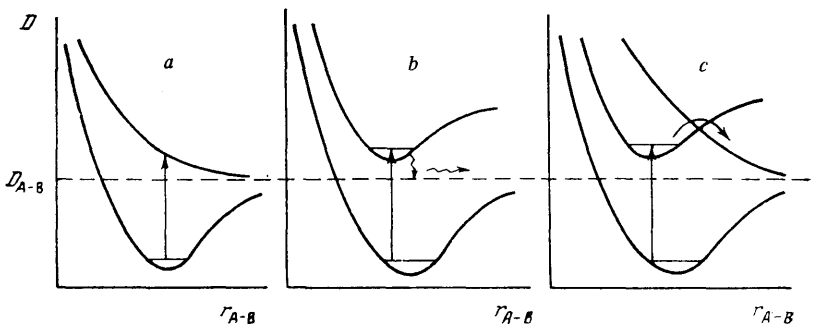


Figure 4. Mechanisms of the photodissociation of molecules: *a*) dissociation into continuum; b) thermal or quasi-equilibrium dissociation; c) predissociation. The arrows indicate the two stages of the process–conversion of electron energy into vibrational energy and bond dissociation.

dissociation into a continuum, then the condition $k_{diss} \gg k_{nr}$ holds and such photochemical reactions will have the energetic red limit calculated above.

VI. CONCLUSION

This review examines the properties of non-silver light-sensitive materials whose activity is based on photochemical reactions, analyses the nature of the primary photochemical reactions employed, and classifies the materials in terms of primary photochemical reactions. The classification shows that the type of primary photochemical reaction determines the nature of the primary photoproduct, i.e. the possibility of subsequent chemical intensification and hence the energetic light sensitivity of the material. The importance of assessing the possibility of intensifying the primary effect follows from the fact that the experimental energetic light sensitivities of such materials do not usually exceed 10^{-1} J cm^{-2}. This difference from the limiting calculated light sensitivity is apparently associated with the fact that the quantum yield of the photochemical reactions of the substances employed $q < 1$ and the extinction coefficient of the photoproduct $\epsilon < 10^5$ litre mole^{-1} cm^{-1}.

Thus the importance of seeking possible intensification processes is evident. Chemical intensification reactions are in principle possible only subject to the condition that the initial substance and the product have different reactivities. We shall consider which photochemical reactions permit further intensification.

According to Table 3, a photoaddition reaction as a rule gives rise to stable products and both the initial substance and the final product have no catalytic activity and cannot initiate oxidation-reduction or polymerisation processes. Consequently the occurrence of a chemical intensification process in such materials is unlikely.

Photorearrangement as a rule results in the formation of stable products. However, cases are known where reaction products are also formed. For example, Jonker and coworkers[24,29] found that the primary action of light may be intensified. They used the ability of the *cis*-benzenediazo-sulphides and -sulphonates, obtained as a result of *trans–cis* isomerisation, to disproportionate mercurous ions with formation of metallic mercury nuclei—centres for physical development. This made it possible to attain a light sensitivity $Q = 5 \times 10^{-4}$ J cm^{-2} for materials with physical development based on the *trans–cis* isomerisation reaction.

The phototransfer of an electron leads to the formation of products, which have reactivities markedly different from those of the starting materials and which are capable of initiating oxidation–reduction reactions, polymerisation, etc. Because of this, materials whose employment is based on electron phototransfer have the highest energetic light sensitivity—up to 10^{-7} J cm^{-2}.

Photodissociation gives rise to radicals, biradicals, or radical-ions, which can initiate polymerisation processes ensuring high values of the coefficient of the intensification of the primary action of light.

The approach proposed in this review, which takes into account both kinetic and energetic limitations in the primary photochemical reaction, has made it possible, in conjunction with several specific models, to estimate the red limit of the region of spectral sensitivity for primary photochemical reactions. However, one should note that the values obtained are only approximate. It is better to regard them as an illustration of the fact that the proposed approach permits a quantitative analysis of the properties of light sensitive materials on the basis of the characteristics of photochemical reactions.

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