

**About mechanisms of sensitivity improvement of layers containing amines and CBr<sub>4</sub>**

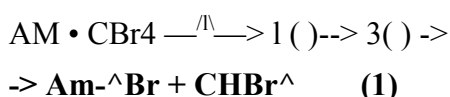
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The investigation in the photoinduced sensitivity enhancement (optical amplification) of photosensitive films containing an amine and CBr<sup>4</sup> has shown that this effect is observed only in the presence of amine radicals (Am<sup>-</sup>). The optical amplification mechanism consists in the energy transfer from the high-excited state of the reaction product (Amp to the amine radical and electron transfer from the excited radical to CBr<sub>4</sub>.

Two-component photosensitive layers containing an amine (Am) and carbon tetrabromide (CBr<sub>4</sub>) as electron donor and acceptor, respectively, are studied today rather comprehensively [1,2]. The absorption spectrum of a composition containing above-mentioned compounds includes, along with absorption bands of initial components, an additional low-intensity band (that of a charge transfer complex, CTC) in 350-400 nm spectral range. UV irradiation of the photosensitive composition (as a layer or a solution) in the absorption region of components or of the additional band causes certain photochemical processes resulting in formation of a product characterized by an absorption band in red spectral range (about 665 nm). Photosensitive layers based on that composition offer a possibility of optical amplification, i.e. of a photosensitivity enhancement due to an uniform exposure of the layer surface by light in the absorption region of the photochemical reaction product.

Photosensitivity of those layers has been shown to be defined by photophysical and photochemical processes where the donor-acceptor complex Am-CBr<sub>4</sub> is involved. The photosensitivity is believed to be due to processes

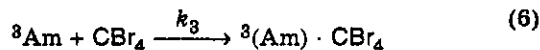
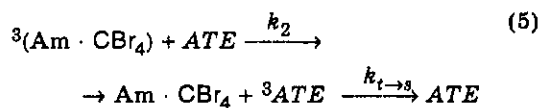
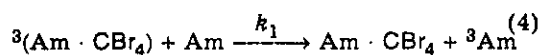
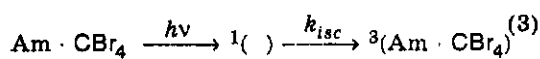


where (Am<sub>1</sub><sup>+</sup>) is a product resulting from the amine oxidation and hydrogen atom transfer (Am - e<sup>-</sup> - H = (Am<sub>1</sub><sup>+</sup>).

Investigation in stages of the reaction (1) has shown that (i) the absorption spectrum in the CTC band region remains unchanged in the course of the phototransformation from the initial product to the final one and (ii) the quantum yield  $\eta$  of the final product formation is related to the initial amine [Am] and the [CBr<sub>4</sub>] concentrations by expressions (2)

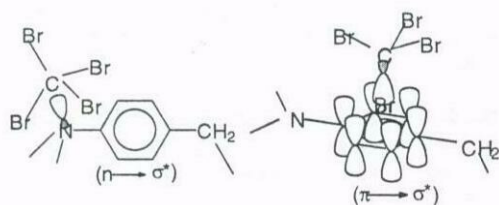
$$\eta \Big|_{[\text{CBr}_4] = \text{const}} = a[\text{Am}];$$
$$\frac{1}{\eta} \Big|_{[\text{Am}] = \text{const}} = b + \frac{c}{[\text{CBr}_4]}. \quad (2)$$

To explain these relationships, the following scheme has been proposed [2] describing the direct amine phototransformation under light absorption by the complex: (3)-(8)



In this scheme, ATE is the acceptor of triplet energy,  $\text{Am} \cdot \text{CBr}_4$  and  ${}^3(\text{Am}) \cdot \text{CBr}_4$  are  $n \rightarrow \sigma^*$  type CTC and a  $\pi \rightarrow \sigma^*$  type exciplex, respectively:

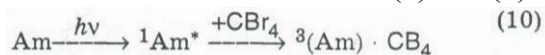
$$\eta = k_1 k_3 [\text{CBr}_4] [\text{Am}] \times \left( (k_3 [\text{CBr}_4] + k_4 [\text{ATE}]) (k_1 [\text{Am}] + K_2 [\text{ATE}]) \right)^{-1}, \quad (9)$$



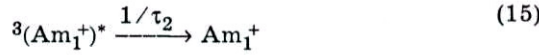
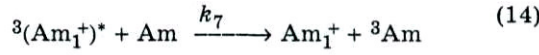
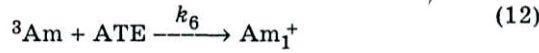
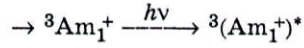
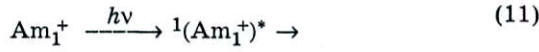
From (4)-(8), the relationship follows (9) that meets the condition (2) if  $k_2[\text{ATE}] > k_1[\text{Am}]$ .

Consideration of the  $n \rightarrow \sigma^*$  type CTC structure shows that the n-molecular orbital (n-MO) localized on nitrogen atom interacts at once with three  $\sigma^*$  MOs of  $\text{CBr}_4$  molecule. Such an interaction results in that an electron turns out to be delocalized over all three  $\sigma^*$  MOs in the CTC excited state. Due to that delocalization, the system becomes stabilized, so there is no dissociation of  $\text{CBr}_4$  that occurs obligatorily in the course of the molecule reduction. Instead, the triplet excitation of CTC is transferred to amine molecule in accordance with the reaction (4). The amine molecule excited into  ${}^3\pi\pi^*$  state may form an exciplex of  $\pi \rightarrow \sigma^*$  type with the mobile  $\text{CBr}_4$  molecule (reaction (6)). It is seen from the exciplex geometry that electron transfer occurs therein from the amine  $\pi$ -MO to  $\text{CBr}_4$   $\sigma^*$ -MO localized on one of C-Br bonds. This is sufficient for the complex dissociation under formation of final products according to (8). The reaction (8) could be expected to run in several stages but those are not identified in [1.2].

Besides of above-mentioned reactions, one due to immediate amine excitation may also run: (10) and further in accordance with (7) and (8)



In the optical amplification process of such a material, the reaction product ( $\text{Am}_1^+$ ) acts as sensitized of the reaction (1). It has been noted [2] that there is no amplification effect in the presence of molecular oxygen. Hence it was concluded that the main sensitization mechanism is based on the triplet excitation energy transfer from  ${}^3(\text{Am}_1^+)$  to Am [1] according to scheme: (11)-(16) and further in accordance with (6)-(8)



In this case, the  $(\text{Am}_1^+)$  accumulation kinetics is described as (17)

$$\frac{d[\text{Am}_1^+]}{dt} = k_3 k_7 \varepsilon_1 \varepsilon_2 [\text{CBr}_4] [\text{Am}] [\text{Am}_1^+] I_0^2 \times \\ \times \left[ (k_3 [\text{CBr}_4] + k_4 [\text{ATE}] + 1/\tau_3) (1/\tau_2 + \right. \\ \left. + k_7 [\text{Am}]) (1/\tau_1 + k_6 [\text{ATE}] + \varepsilon_2 I_0) \right]^{-1} \quad (17)$$

If the  ${}^3(\text{Am}_1^+)$  quenching efficiency by oxygen is high, a square dependence of the product accumulation rate on the light intensity is obtained. While it is linear in the case  $\varepsilon_2 I_0 \gg 1/\tau_1 + k_6 [\text{ATE}]$ . It is just those dependences that were observed in experiments.

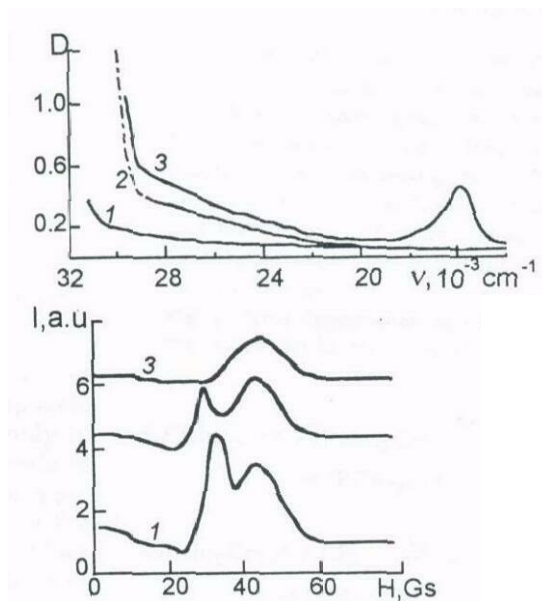
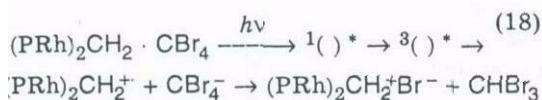


Fig.1. Absorption spectra of poly-[4,4'-bis(aminophenyl)methane] (1),  $(\text{RPh})_2\text{CH}_2^* \text{CBr}_4$  complex (2) in a layer and of the same layer after irradiation (3).

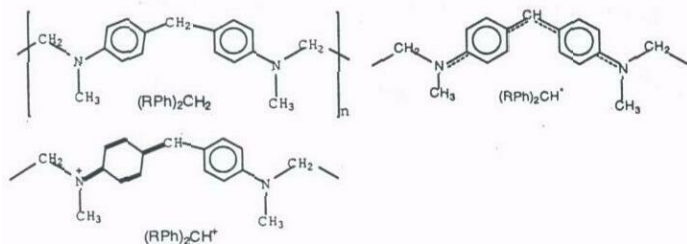
Fig.2. EPR spectra of photosensitive layers at 77 K irradiated by light with  $\lambda = 365 \text{ nm}$  (1) and heated for 1 min at 140 K (2) and 200 K (3).

To refine further photosensitivity mechanisms of layers containing an amine and  $\text{CBr}_4$ , we have studied polymer layers with macromolecules consisting of 4,4'-bis-(aminophenyl)methane units  $\{(\text{RPh})_2\text{CH}_2, \text{R is amine}\}$ . Carbon tetrabromide was introduced into polymer layers in the course of preparation. Such layers are described in [3] where it has been shown that under X-ray irradiation, radicals of diamine fragments are formed providing an enhanced layer conductivity.

The reaction (1) can be written for such layers as



with notations



The system under consideration is distinct essentially from those described before in that amine and  $\text{CBr}_4$  concentrations are rather high (about  $4 \text{ mol/dm}^3$  and  $0.21 \text{ mol/dm}^3$ , respectively). These values are much larger than the equilibrium oxygen concentration in the polymer layer (about  $10^{-3} \text{ mol/dm}^3$ ). Therefore, oxygen influence on photochemical processes could be expected to be reduced to minimum in many cases.

The absorption spectrum of  $(\text{RPh})_2\text{CH}_2\text{CBr}_4$  complex contains an additional broad band in  $27000 \text{ cm}^{-1}$  region ( $\lambda = 370 \text{ nm}$ ) (Fig.1) related to electron transfer from amine to  $\text{CBr}_4$ . The reaction product,  $(\text{RPh})_2\text{CH}^+$ , is characterized in turn by absorption in  $\lambda = 630 \text{ nm}$  region. At this stage, the material photosensitivity attains  $S = 10^2 \text{ cm}^2/\text{J}$ .

It has been shown in our work that the last transformation in the reaction (1) occurs via formation of  $(\text{RPh})_2\text{CH}$  and  $\text{CBr}_3$  radicals. Therewith, the former radical is detectable in the photosensitive layer at room temperature while the latter, only at low one (77 K) (Fig.2).

Fig. 2 presents the second derivative of the EPR spectrum at 77 K (curve 1) in the  $\text{DH} = 80 \text{ Gs}$  range. The broad band is related to  $(\text{RPh})_2\text{CH}$  radical, the narrow one to  $\text{CHBr}_3$ . Both radicals were shown to be essentially stable at 77 K. The vanishing of  $\text{CBr}_3$  and reduction in  $(\text{RPh})_2\text{CH}$  concentration at temperature elevation (Fig.2, curves 2 and 3) are associated with increasing mobility of  $\text{CBr}_3$  and recombination of radicals.

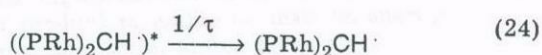
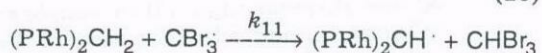
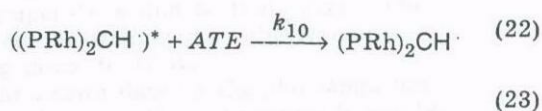
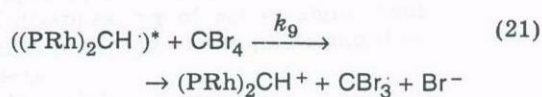
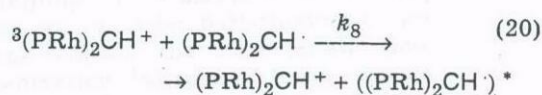
$(\text{RPh})_2\text{CH}$  radicals, in turn, exhibit an instability at room temperature (Fig.3). The kinetics of the radical concentration drop at room temperature includes two components, a fast ( $x = 0.5 \text{ h}$ ) and a slow one (several days) (Fig.4).

Study of the material photosensitivity enhancement effect has shown that it decreases as the layer is stored in darkness at room temperature and vanishes completely in 2 h after exposure, i.e. it exists only in the presence of active  $(\text{RPh})_2\text{CH}$  radicals in amounts corresponding to the first component of their concentration drop. While the concentration of the reaction product  $(\text{RPh})_2\text{CH}^+$  remains constant. This fact evidences no sensitization occurs due to the triplet excitation energy transfer from the reaction product to the photosensitive complex or to amine.

The photoamplification rate measured immediately after the photosensitive layer exposure increases in parallel with the initial  $(\text{RPh})_2\text{CH}^+$  concentration. The kinetics of the  $(\text{RPh})_2\text{CH}^+$  concentration increase at the photoamplification includes the stage of some discoloration (due likely to the photooxidation by oxygen) and the second one, viz. the amplification itself. The first stage becomes appreciable at longer storage time when the contribution of the second one decreases substantially.

The  $(\text{RPh})_2\text{CH}^+$  accumulation kinetics in our experiments on photoamplification of freshly exposed layers corresponded to linear time dependence of  $(\text{RPh})_2\text{CH}^+$  concentration within a wide range of visible light exposure duration. If the main photoamplification mechanism would be the excitation energy transfer to the initial amine, a nonlinear  $(\text{RPh})_2\text{CH}^+$  concentration increase would be expected.

Taking into account existing experimental data, the sensitization of the recording material can be described by the following scheme:



According to this scheme, when one light quantum is absorbed by the sensitizer, one molecule of the final product is formed (reaction (21)) and one amine molecule is consumed (reaction (23)). It should be born in mind that the reaction (12) may run in several paths, including one that results in formation of new products not absorbing in red spectral range. Kinetics of concentration decrease of initial amine units according to (19)- (25) has been shown to be described by the following equation:

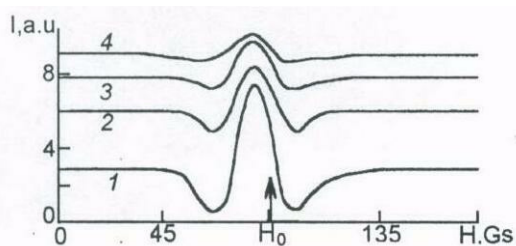


Fig. 3. EPR spectrum (2nd derivative) of photosensitive layers at 293 K irradiated by light with  $\lambda = 365$  nm (1) and then stored in dark for 12 min (2), 22 min (3) and 1 h (4). The arrow shows  $H_0$  value ( $g = 2000$ ).

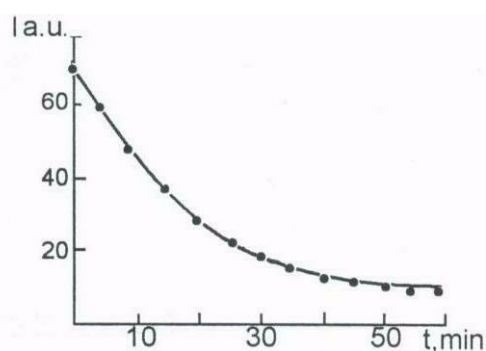


Fig.4. Time dependence of  $(\text{RPh})_2\text{CH}\cdot$  radical concentration in the layer stored at 293 K.

$$\frac{-d[AM]}{dt} = k_8 k_9 k_{11} \varepsilon_1 [CBr_4] [Am] [Am\cdot] [Am_1^+] I_0 \times \\ \times \left[ (k_{11}[Am] + k_{12}[Q]) (1/\tau_4 + k_{10}[ATE] + k_9[CBr_4]) \times \right. \\ \left. \times (1/\tau_1 + k_6[ATE] + k_8[Am\cdot]) \right]^{-1} \quad (26)$$

$$[Am_1^+] = [Am_1^+]_0 \exp(A_0 C_0 t) \quad (27)$$

Hence it follows that no amplification takes place at  $[Am\cdot]=0$ .

At low  $[Am_1^+]$  and  $[Am\cdot]$  concentrations, the solution of (26) has the form (27) where  $A_0$  is a coefficient in (26) independent of  $[Am_1^+]$ ,  $C_0$  is the initial amine concentration in the layer. Since  $A_0$  is small, the solution (27) is displayed by a straight line within a wide time range, in agreement with experiments.

The fact of two-quantum photosensibility amplification noted in literature evidences that the energy transfer described by reaction (20) occurs in fact from the highly-excited state  $\{^3(RPh)_2CH^+\}^*$ . This sensitization mechanism is in agreement with the value of excitation energy for  $(RPh)_2CH\cdot$  radical [4]; meanwhile,  $E(S_0 \rightarrow T_2) > E(S_0 \rightarrow S_1)$  for  $Am_1^+$  [5]. In this case,

$$\frac{-d[AM]}{dt} = k_8 k_9 k_{11} \varepsilon_1 \varepsilon_2 [CBr_4] [Am] [Am\cdot] [Am_1^+] I_0^2 \times \\ \times \left[ (k_{11}[Am] + k_{12}[Q]) (1/\tau_4 + k_{10}[ATE] + k_9[CBr_4]) \times \right. \\ \left. \times (1/\tau_1 + k_6[ATE] + \varepsilon_2 I_0) (1/\tau_2 + k_8[Am\cdot]) \right]^{-1} \quad (28)$$

that is agreed with the photoamplification rate dependence on the light intensity described by (17). In (28),  $\varepsilon^*$  is the extinction coefficient for triplet-triplet absorption of  $Am_1^+$ .

Thus, taking photosensitive layers containing poly-bis(aminophenyl)methane and  $CBr_4$  as examples, we have shown in this work that:

(1) the photoamplification effect in layers containing donor-acceptor amine: $CBr_4$  complexes occurs under participation of active amine radicals; the characteristic time for concentration decrease of these radicals in the layer at room temperature is about 30 min; disappearing of active amine radicals results in fading of the photoamplification effect;

(2)  $CBr_3\cdot$  radicals disappear rapidly at room temperature due to their high mobility but can be stabilized by the temperature lowering down to 77 K;

(3) the known data on the photoamplification dependence on the light intensity can be explained in terms of the energy transfer from the highly-excited state of the stable reaction product to amine radical; no energy transfer to the initial amine takes place.