The Influence of the Form of Aggregation of Organic Dyes on Their Photosemiconducting and Photoparamagnetic (EPR) Properties

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The Influence of the Form of Aggregation of Organic Dyes on Their Photosemiconducting and Photoparamagnetic (EPR) Properties

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Numerous results on the photosemiconducting properties of dyes have been obtained for layers prepared by various methods: sublimation in vacuum, deposition from solutions, rubbing onto a substrate, and also for the initial polycrystalline powders ([1-6]). For some dyes, the influence of the method of preparation and of the form of aggregation of the dye on its semiconducting properties has been studied ([6-10]).

In one of the preceding works of our laboratory ([11]) it was shown that treatment with solvent vapors of mirror-like layers of dyes of the di- and triphenylmethane class changes both the form of aggregation and the type of conductivity and photoconductivity from electronic to hole. In a subsequent work ([12]) it was shown that this transformation is associated with the transition of the layer from the amorphous state (n-conductivity) to the polycrystalline state (p-conductivity). The present article describes a continuation of the investigation of the influence of the form of aggregation of triphenylmethane dyes (crystal violet, brilliant green, malachite green) and xanthene dyes (rhodamine 6Zh and rhodamine B) on their photosemiconducting and photoparamagnetic properties.

Amorphous and polycrystalline layers of the dyes studied were deposited by the method described in ([11]) onto a glass plate with tin dioxide electrodes (interelectrode distance 1 mm) for the study of photoconductivity, or onto the inner surface of quartz ampoules (diameter 6 mm) in the study of EPR. Before investigation the layers were subjected to prolonged vacuum conditioning at temperatures up to 373° K. Photoconductivity was measured with an EMU-4 dc amplifier with a set of input resistances from 10^6 to 10^9 ohm, to the output of which an S1-19 oscilloscope was connected. The time constant of the instrument did not exceed 0.5 sec. The EPR spectra were recorded on an RE-1301 apparatus. The layers were illuminated with monochromatic light at the maximum of the long-wavelength absorption band of the layer. By the method of capacitor photoemf ([3]), the sign of the photocurrent carriers in layers of rhodamine 6Zh and rhodamine B was determined. For mirror-like layers it proved to be negative. Layers treated in ethanol vapor became scattering, and the type of conductivity changed to positive. In a polarization microscope, individual microcrystallites

Figure 1

Figure 1: Figure 1

are clearly visible in the latter, whereas the mirror-like layers, up to 1000-fold magnification, appeared completely homogeneous. On the basis of analogy with dyes of the triphenylmethane class, it may be assumed that the mirror-like layers of rhodamine 6Zh and rhodamine B are amorphous.

The kinetics of the rise and decay of photoconductivity of the mirror-like layers of the dyes studied is characterized by considerable inertia, and carefully dried oxygen, as an electron acceptor, suppresses the photoconductivity of mirror-like layers in agreement with the data of works (ˆ1). A certain difference for rhodamine B and brilliant green consists in the presence of an initial fast stage as well, whereas in rhodamine 6Zh and malachite green it is immeasurably small.

In contrast to the mirror-like layers (Fig. 1), the scattering (polycrystalline) layers of the dyes studied may be divided into two groups. The first group includes brilliant green, rhodamine B, and rhodamine 6Zh, which possess low inertia of photoconductivity in air and in vacuum (the time of rise and decay of the stationary value of the photocurrent is less than 5 sec). The magnitude of the stationary photoconductivity either

does not change with increasing oxygen pressure, or increases only slightly. The latter is characteristic of Meyer's "oxygen"dyes ([5]) with p-type photoconductivity. The second group includes crystal violet and malachite green. The photoelectric behavior of these dyes in the crystalline and amorphous states is similar (like curves a in Fig. 1). The only difference is an increase in the fraction of the rapid initial stage of the rise of photoconductivity for crystalline layers in comparison with amorphous ones.

In the preceding work it was shown ([13]) that, upon illumination in vacuum (10^{-4} torr) of polycrystalline powders of a number of triphenylmethane and xanthene dyes, intense single e.p.r. signals arise ($H \simeq 10$ Oe, $g = 2.003$). On the basis of comparison with the photosemiconductor properties of the dyes studied, it was suggested that the paramagnetism is connected with the trapping of conduction electrons at trapping levels. Powders of n- and p-type dyes, having slow ($>$ min) and fast ($\leq$ sec) photocurrent relaxation, were investigated ([1]).

Fig. 1. Kinetics of the rise and decay of photoconductivity of an amorphous (a) and polycrystalline (b) layer of brilliant green at different pressures of dry oxygen.
1—$P = 10^{-4}$ torr, 2—$P = 10^{-1}$ torr, 3—$P = 760$ torr

The experiments showed that photoinduced e.p.r. signals (p.i.s. e.p.r.) do not arise in dyes with sharp photocurrent relaxation, but are observed only in n-type dyes with slow photocurrent relaxation. In such dyes there is a high concentration ($\sim 10^{17}$ cm^{-3}) of centers capable of trapping conduction electrons ([6]). The

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

disappearance of the p.i.s. e.p.r. in amorphous layers of the dyes studied in vacuum after cessation of illumination follows the bimolecular hyperbolic law of recombination. Dry oxygen suppresses the photoparamagnetism of amorphous layers. Ethanol vapors change the surface state of the layer, leading to the disappearance of unpaired electrons. In Fig. 2, as an example, relaxation curves of p.i.s. e.p.r. at 300° K in amorphous layers of rhodamine 6Zh are presented.

Fig. 2. Relaxation curves of p.i.s. e.p.r. of a mirror layer of rhodamine 6Zh at 300° K

On amorphous layers of the dyes studied, the temperature dependences of the rates of formation $(dn/dt)_{\text{v}}$ and disappearance $(dn/dt)_{\text{i}}$ of the p.i.s. e.p.r. were studied. The data of Fig. 3 indicate an exponential dependence of $(dn/dt)_{\text{v}}$ and $(dn/dt)_{\text{i}}$ on temperature:

$$(dn/dt)_{\text{v}} \sim \exp(-E'_a/kT), \qquad (dn/dt)_{\text{i}} \sim \exp(-E'_d/kT),$$

where n is the number of unpaired electrons; E_a and E_d are the thermal activation and deactivation energies of the appearance and disappearance of e.p.r., respectively.

Thus, for the appearance of photoinduced unpaired

electrons an additional thermal activation energy $E_a = 0.05$—0.18 eV is required (Table 1). The energy found for deactivation of photoinduced EPR signals, $E_d = 0.3$—0.4 eV, coincides with the thermal activation energy of photoconductivity E_ϕ, obtained from other experiments (Table 1). If, by treatment with ethanol vapor, the amorphous dye layers are converted into polycrystalline ones, illumination of the layers does not cause the appearance of EPR signals. Photoinduced EPR also does not arise after prolonged training of the crystallized dye layer under pumping (10^{-4} torr) at 373°K.

Fig. 3. Temperature dependence of the activation rate (a) and deactivation rate (b) of photoinduced EPR signals in mirror layers of dyes: 1 —crystal violet, 2 —malachite green, 3 —rhodamine B, 4 —rhodamine 6Zh

All the observed effects are strictly reversible: dissolution of the polycrystalline dye layer and repeated deposition of a mirror layer from the resulting solution completely restores its photosemiconducting and photoparamagnetic properties.

The photoinduced EPR detected earlier in the initial dye powders ([13,14]) indicates the presence in the samples, in addition to the crystalline phase, of an amorphous one as well. The data of the present work compel caution in interpreting results obtained on initial dye powders with an undefined form of aggregation.

Table 1

Thermal activation energies E_a and deactivation energies E_d of photoinduced EPR and activation energies E_ϕ of photoconductivity

Dye	E_a, eV	E_d, eV	E_ϕ
Malachite green	0.14	0.42	0.92 ([5])
Crystal violet	0.16	0.36	0.4 ([6])
Crystal violet	0 ([17])	$1/2 \times 0.7$ ([17])	0.3 ([1])
Crystal violet			0.45 ([5])
Rhodamine B	0.05	0.32	0.38–0.42 ([6])
Rhodamine B	0.2 ([17])	$1/2 \times 1.1$ ([17])	0.62 ([5])
Rhodamine 6Zh	0.10	0.38	0.54 ([6])
Rhodamine 6Zh			–

The appearance of photoinduced unpaired electrons in amorphous layers of n-type dyes can be explained by the following scheme (Fig. 4). Upon absorption of a photon, an electron of a dye molecule weakly interacting with neighboring molecules is transferred to the first excited singlet state S^*, which migrates as an exciton through the layer. For decay of the exciton, thermal energy (0.05–0.2 eV) is required; as a result of its absorption, the electron passes to the "conduction" level of the ensemble of dye molecules and migrates to a local center. Photoinduced EPR is associated with capture of electrons at trapping levels; moreover, both the hole (ion-radical of the dye molecule) and the electron captured at the trapping level may possess paramagnetic properties. The trapping level lies below the "conduction" level (by 0.3–0.4 eV) and below the first singlet excited state of the molecule ([1,15]). Direct

transitions from the ground level S and the level S^* to the trapping level and back are unlikely, since they are spatially separated. Trapped electrons can be thermally transferred to the "conduction"level, where they acquire the possibility of recombining with the positive hole that has been left behind. In the presence of an electron-acceptor gas this recombination occurs through the surface levels of the adsorbed gas. The possibility is not excluded of direct recombination of the trapped electron with its vacancy ("hole") under vacuum conditions, bypassing the "conduction" level. However, for this it is necessary to assume migration of the "hole" along the ground level ([16]) to the trapped electron.

Since in dyes with n-type conductivity the mobility of "holes" is small, such recombination is unlikely. At present there are still insufficient experimental data for constructing an energy diagram of the crystalline state of dyes with p-type conductivity, but the following assumption may be made. In p-type dyes, where the mobility of the "hole" is large in comparison with the mobility of the excited electron, under vacuum conditions direct recombination of the trapped photoexcited electron with the "hole" that has approached it is favored, which leads to a decrease in the concentration of trapped electrons. This is manifested in the absence of inertia in the relaxation of the photocurrent of most p-type dyes. We attribute the absence of photoinduced e.p.r. from trapped electrons to the low sensitivity of the method. The scheme proposed on the basis of the experimental facts for the mechanism of appearance of unpaired electrons upon illumination of layers of the dyes considered also explains the mechanism of photoconductivity. This scheme is consistent with Vartanyan' s previously proposed ([1]) explanation of the mechanism of photoconductivity of solid mirror-like dye layers.

Fig. 4. Energy diagram of amorphous layers of dyes with n-type conductivity: S and S^* are the levels of the ground and excited states of the molecule; E_a and E_d are the thermal energies of activation and deactivation of photoinduced e.p.r.

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* The presence of a trapping level for the photoexcited electron in *n*-type dyes is confirmed by the positive temperature coefficient of photoconductivity with a thermal activation energy of the order of 0.2–0.5 eV ([2]).

Note: Figure translations are in progress. See original paper for figures.