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PHOTOINDUCED E.P.R. SIGNALS IN ORGANIC DYES IN THE CRYSTALLINE STATE

Investigation by the method of electron paramagnetic resonance (e.p.r.) of microcrystalline dye powders showed the absence of noticeable e.p.r. signals in pure dyes (1). At the same time, for crystalline chlorophyll we established the presence of a dark signal and the appearance of an intense e.p.r. signal under illumination with visible light in the presence of H_2O vapor (2)*. In the present study, light-induced e.p.r. signals were detected in a number of triphenylmethane and xanthene dyes.

The e.p.r. spectra were recorded on a radiospectrograph of type RE1301 with high-frequency modulation of the magnetic field, with a sensitivity of $5 \cdot 10^{-12}$ mole for the crystalline free radical diphenylpicrylhydrazyl. A thin-walled quartz ampoule (6 mm in diameter) with a 20–30 mg weighed portion of dye was inserted into the center of a cylindrical resonator with oscillation type H_{01}. The ampoule could be preliminarily evacuated to 10^{-4} mm Hg and filled with gases and vapors of various elasticity directly during the recording of e.p.r. spectra. The samples were illuminated with a 200 W incandescent lamp using a glass light condenser and an aluminized mirror. Portions of the spectrum corresponding to the absorption bands of the dye under study were isolated by glass light filters from a LenZOS set. The illumination at the location of the sample corresponded to $1.4 \cdot 10^{-4}$ W • cm^{-2} (642 mμ) and $5 \cdot 10^{-5}$ W • cm^{-2} (440 mμ) in a band of 30 mμ. Measurements at −183° and −196° were carried out in a special quartz Dewar vessel, the lower finger of which, containing the ampoule, was inserted into the sealed resonator of the radiospectrograph. During the experiments, O_2, obtained by thermal decomposition of $KMnO_4$ and dried by passage through a trap cooled with liquid O_2 (in some cases air dried in this way was used), quinone vapor, or H_2O vapor was admitted into the ampoule. The study used microcrystalline samples of the following dyes: malachite green (NADCDCo**), brilliant green (NADCDCo), patent blue (Agfa), acid bright blue 3 (Agfa), crystal violet (NADCDCo), methyl violet (NADCDCo), fuchsin (NADCDCo), rhodamine B (Agfa), rhodamine 6Zh (Agfa), Bengal rose (NADCDCo), phloxine (NADCDCo), and erythrosine (NADCDCo). In all the dyes investigated, upon illumination with visible light in the absorption band of the dye, an

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

e.p.r. signal arose, consisting of a single symmetric line with $g = 2.003 \pm 0.001$, $\Delta H = 10\text{-}20$ oersteds (Fig. 1). The most intense e.p.r. signal arises upon illumination in vacuum of samples of the following dyes: malachite green, brilliant green, crystal violet, methylo-

violet. The course of the rise of the photoinduced signal and of its decay for crystalline violet is shown in Fig. 2. In vacuum at 20° after illumination the signal decays slowly (half-decay time 45 min.). Dry O_2 (air), quinone vapors, and H_2O exert a suppressing effect on the photoinduced EPR signal both during illumination and after its cessation. Removal of O_2, quinone vapors, or H_2O from the ampoule in the dark at 20° does not restore the EPR signal. For its appearance a new illumination of the specimen is necessary. If illumination is carried out in the presence of O_2, quinone vapors, or H_2O, an analogous EPR signal arises, but of lower intensity, rapidly decreasing in the dark at 20° (Fig. 2). Repeated illumination again causes the appearance of an EPR signal, which again disappears after cessation of illumination. However, repeated prolonged illumination in dry or moist air leads to an irreversible appearance of the EPR signal. The rate of disappearance of the photoinduced EPR signal after cessation of illumination of a dye specimen in vacuum at 20° depends substantially on the temperature of the specimen: with an increase of temperature to 100° the rate increases so much that the EPR signal can no longer be detected after 5 min. This signal arises also

Fig. 1. Photoinduced EPR signal of crystalline violet in vacuum at 20°

during illumination of a dye in vacuum at −196°, but its intensity is insignificant and does not change in the dark at −196°. Rapid thawing to 20° and freezing to −196° slightly decrease the intensity of the EPR signal. The EPR signal disappears rapidly only when the specimen is heated to 100°.

Fig. 2. Kinetics of the photoinduced EPR signal of crystalline violet at 20°: 1 —in vacuum, 2 —in O_2

An analogous signal, but with an intensity approximately 5 times smaller, arises

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* Continuation of these experiments showed that, in the presence of O_2, the intensity of the light-induced e.p.r. signal in chlorophyll with sorbed H_2O vapor increases significantly.

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Fig. 3 and Fig. 4: kinetic curves of the light-induced EPR signal under illumination and in darkness.

Figure 3: Fig. 3 and Fig. 4: kinetic curves of the light-induced EPR signal under illumination and in darkness.

upon illumination with visible light in vacuum (10^{-4} mm Hg) of fuchsin, rhodamine B, rhodamine 6G, Bengal rose, phloxine, and erythrosine. O_2, quinone vapors, and H_2O exert a suppressing effect on the photoinduced EPR signal of fuchsin, rhodamine B, rhodamine 6G, and erythrosine both during illumination and after its cessation (Fig. 3). On the contrary, in the case of Bengal rose and phloxine, admission into the ampoule with the dye of O_2 or of quinone vapors leads to an increase in the intensity of the photoinduced EPR signal (in comparison with vacuum conditions) during illumination (Fig. 4). H_2O vapors cause a decrease in the photoinduced EPR signal, as for the dyes considered above.

Upon illumination in vacuum of specimens of acid dyes—patent blue and acid bright blue 3—only an insignificant photoinduced EPR signal is observed.

The relaxation curves of the photoinduced EPR signal obtained in this work are very similar to the relaxation curves of photoconductivity measured by Vartanyan for layers of the same dyes deposited from solutions.

dyes (at an illumination comparable to ours) in vacuum and upon exposure of a layer to O_2, quinone vapor, and H_2O (^{3}). According to measurements by I. A. Akimov and E. K. Pushcheiko (^{4}), the dyes listed above belong to two types: in some, the predominant carriers of photocurrent are electrons; in others, electron vacancies (positive holes). Electron-acceptor molecules (O_2, quinone) reduce the photoconductivity of dyes with an electronic type of photocurrent carriers (malachite green, brilliant green, crystal violet, methyl violet, rhodamine). It is precisely in these dyes, according to our observations, that the light-induced EPR signal is suppressed by O_2 and quinone vapor. Conversely, for

Fig. 3. Kinetics of the light-induced EPR signal of fuchsin *(1, 2)* and rhodamine B *(3, 4)*. *1, 3* —in vacuum; *2, 4* —in air

Fig. 4. Kinetics of the light-induced EPR signal of Bengal rose *(1, 2)* and phloxine *(3, 4)*. *1, 3* —in vacuum; *2, 4* —in quinone vapor

those dyes in which holes prove to be the predominant photocurrent carriers (Bengal rose, phloxine), the same gases and vapors increase the photocurrent. In full agreement with this, the light-induced EPR signal is enhanced in them upon sorption of the indicated electron-acceptor molecules.

The parallelism we have established between photoconductivity and the light-induced EPR signal makes it possible to ascribe the latter to unpaired electrons that carry charge in organic semiconductors. According to the views of one of the authors (^{5}), after the initial act of excitation of an individual dye molecule in a weakly bound molecular lattice, an exciton migrates within it to the site of surface or volume charge traps, at which the exciton decays with capture of charge of one sign and liberation of charge of the other sign, which carries the current. Intermolecular charge transfer occurs via the available vacant levels. In the case of capture of a positive hole and preservation of the mobility of the liberated electron, the latter can migrate between vacant electronic levels of the molecules, leading to "relay" charge transfer, i.e., to electronic conductivity known for inorganic semiconductors under conditions of a high concentration of trapping levels.

Electron-acceptor molecules O_2, quinone, and also H_2O create additional deep trapping levels in a semiconductor dye with an electronic type of conductivity and thereby suppress both the conductivity and the light-induced EPR signal. In the case of dyes of the hole type, the photoconductivity, as well as the light-induced EPR signal, increases in the presence of O_2 and quinone vapor. The latter create surface traps for capture of the exciton electron with liberation of its hole, accom-

carrying out a "relay" intermolecular charge transfer between the lowest ground levels of the dye molecules in the lattice (^{5}).

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