PHYSICS

1960

SovietRxiv

Abstract

Full Text

PHYSICS

A. T. VARTANYAN and L. D. ROZENSHTEIN

ON THE PARTICIPATION OF THE SINGLET EXCITED STATE IN THE ELECTRICAL CONDUCTIVITY OF A NUMBER OF ORGANIC SEMICONDUCTORS

(Presented by Academician A. N. Terenin on 20 XI 1959)

In works by one of the authors ([1],[2]) it was shown that the temperature dependence of the electrical conductivity of layers of a large number of dyes deposited from alcoholic solution follows the exponential law $\sigma = \sigma_0 \exp(-\varepsilon_m/2kT)$. The values found for the thermal activation energies ε_m were compared with the spectral absorption curves of solid layers obtained by the same method. For a number of dyes (erythrosin, phloxine, trypaflavine, pinacyanol, and others) the values of ε_m corresponded to the beginning of the steep rise of the long-wavelength absorption band of the layer; for some dyes, however, no such agreement was observed. For example, for crystalline violet the beginning of the steep rise of the absorption band lies in the region of 700 mμ, whereas for ε_m a value of 0.74 eV was found, which corresponds to 1670 mμ. Such dyes also included Capri blue, phenosafranine, thionine, phthalocyanines, and others. It was assumed that, for these compounds, the conductivity of layers deposited from solutions was impurity conductivity; possibly it was due to the presence in the layer of water or oxygen molecules that could not be removed even by prolonged conditioning in vacuum at high temperature. But, as was shown later, for phthalocyanines ε_m agrees well with the absorption spectra if the layers are obtained by sublimation under high-vacuum conditions ([3]). Subsequently, such agreement was also found for sublimed layers of indigo ([4]). This made it possible to hope that for other dyes studied in ([2]) the same correspondence could be found if sublimation were used to obtain the layers.

The absorption spectra of solid layers of most dyes obtained by rapid deposition from alcoholic solutions or by sublimation reproduce, in their main features, the spectra of solutions ([5],[6]). Since in the spectrum of the solid dye layer no new absorption bands characteristic of the solid state appear, it must be assumed that the absorbing centers in the layer remain molecules. The mutual perturbation of identical molecules manifests itself only in broadening of the spectrum, shifts, and redistribution of the heights of the maxima. The lifetime of the nonequilibrium electron on the excited singlet level is of the order of 10^{-9}

Fig. 1. Spectral absorption curves of solid layers. The numbers by the curves correspond to Table 1.

Figure 1: Fig. 1. Spectral absorption curves of solid layers. The numbers by the curves correspond to Table 1.

sec. The proximity of identical molecules, leading to concentration deactivation of the excited molecule, reduces this time still further, which, in particular, is manifested in the well-known concentration quenching of fluorescence ([7]). On the basis of these experimental facts, A. N. Terenin put forward a new point of view on the nature of the photoconductivity of dyes ([8]), according to which the internal photoelectric effect in dye crystals occurs with the participation of electrons located on the triplet level. Absorption of a light quantum in the intrinsic band of the dye transfers the molecular center of the lattice to the singlet excited level, from which some of the electrons can pass to the lower triplet level.

conduction band. A direct optical transition to this level from the ground singlet is forbidden. Experimental work confirms this point of view ([^9]).

The task of the present work was to determine which electrons—those in the singlet excited level or those in the triplet level—are responsible for the dark electrical conductivity of organic semiconductors; in other words, whether the activation energy of dark conductivity corresponds to the height of the triplet or singlet excited state. The correspondence observed in works ([2-4]) between ε_m and the long-wavelength falloff region of the spectral absorption curve of a solid layer, i.e., the region corresponding to the singlet excited level of the dye molecules, did not yet justify an unambiguous conclusion as to which of the two possible levels is responsible for electrical conductivity. Indeed, the triplet state appears in phosphorescence, whereas dyes in the solid state do not phosphoresce. Transferring data for the phosphorescence of solutions to the solid state is not legitimate, since, generally speaking, the height of the triplet level can change upon transition to another aggregate state. In addition, as is known from measurements on solutions, the distance between the triplet and excited singlet energy levels of dye molecules is comparatively small. Therefore, the choice of objects for the present investigation was determined, on the one hand, by the requirement that these substances possess phosphorescence in the solid state, which would make it possible to estimate the height of the triplet level of the substance in precisely the aggregate state in which electrical conductivity is studied, and, on the other hand, that the distance between the triplet and excited singlet levels be, as far as possible, much greater than the error of measurement of ε_m, which in our experiments was ~ 0.13 eV.

Fig. 1. Spectral absorption curves of solid layers. The numbers by the curves correspond to Table 1.

In this connection, benzophenone, anthranilic and phenylanthranilic acids, and

three compounds of the phthalimide class were selected for investigation: 3-acetylamino-*N*-methylphthalimide, 3-acetylamino-*N*-phenylphthalimide, and 3-benzoylamino-*N*-methylphthalimide*. In addition, the electrical conductivity of fluorescein was investigated, as well as that of some of the dyes for which the discrepancy indicated above had previously been observed. Sufficiently thick ($\sim 50\,\mu$) and dense layers were obtained by sublimation of the substance under high-vacuum conditions ($\sim 10^{-5}$ mm). The layers were sublimed onto the surface of a quartz vessel, on which platinum elec-

* The authors are deeply grateful to V. V. Zelinskii and I. I. Reznikova, who kindly provided the phthalimides they had synthesized, of a high degree of purity.

electrodes 30 mm long with a gap between them of 0.4 mm. A battery of dry cells at 560 V served as the voltage source. Currents (down to 10^{-14} A) were measured with an EMU-3 electrometric amplifier, equipped with a switch for input resistances from 68 ohms to 1 megohm. The magnitude of the voltage was chosen so as to ensure strict fulfillment of Ohm' s law. The current flowing through the layer did not depend on the direction of the field. Since anthranilic and phenylanthranilic acids and phthalimides, when heated in vacuum to 50—60°C, begin to sublime at an appreciable rate, their study was carried out in an atmosphere of spectrally pure helium at a pressure of about 1 atm. The electrical conductivity of the remaining substances was measured in vacuum. To measure the absorption spectra, the layers were deposited on a quartz plate fastened to a rotating disk. This made it possible to obtain uniform layers. Unfortunately, for the phthalimides it was not possible to obtain sufficiently transparent layers. The absorption spectra of solid layers measured by us on SF-4 are presented in Fig. 1. The spectral regions corresponding to the long-wavelength falloff of the first absorption bands are given in Table 1. The spectra of solid layers of substances 1–7 were measured for the first time. The data for dyes 8–11 were taken from work ([6]).

The results of measurements of the temperature dependence of electrical conductivity are presented in Fig. 2.

Fig. 2. Temperature dependence of the electrical conductivity of solid layers. The numbers next to the curves correspond to Table 1.

ε_m, determined from the slope of the straight lines $\lg\sigma = \lg\sigma_0 - (\varepsilon_m \lg e/2k)\cdot\frac{1}{T}$, are given in Table 1. As is evident from consideration of the table,

Table 1

No.	Compound	Long-wavelength falloff region of the absorption spectrum of a solid layer, mμ	ε_m, eV	λ, corresponding to ε_m, mμ	Energy corresponding to the long-wavelength boundary of the phosphorescence band of the solid layer, eV
1	Benzophenone	330—400	3.34	370	2.8 ([10])
2	Anthranilic acid	340—400	3.38	366	2.8
3	Phenylanthranilic acid	375—430	3.30	375	2.7
4	3-acetylamino-*N*-methylphthalimide	350—390	3.46	375	2.9
5	3-acetylamino-*N*-phenylphthalimide	340—400	3.50	353	2.7
6	3-benzoylamino-*N*-methylphthalimide	360—410	2.28	377	2.8
7	Fluorescein	490—530	2.44	506	
8	Thionine	650—700	1.83	675	
9	Crystal violet	630—710	1.78	694	
10	Phenosafranin	570—620	2.08	595	
11	Capri blue	700—760	1.67	740	

The wavelengths corresponding to the thermal activation energies ε_m are in good agreement with the regions of the long-wavelength falloffs of the absorption curves. For compounds 1—6, which phosphoresce in the solid state at low temperatures, the energy values corresponding to the short-wavelength boundary of the phosphorescence band of the solid layer are also given.* These energies are much smaller than ε_m and cannot be connected with the observed electrical conductivity. The results obtained make it possible to accept that, for the

organic semiconductors we have studied, electrical conductivity occurs via the singlet excited level. It is important to note that this conclusion also applies to thionine, crystal violet, phenosafranine, and Capri blue, for which very low values of ε_m had previously been obtained. As was already noted above, the mutual perturbation of identical molecules when they are packed into a solid layer is usually manifested spectrally in a bathochromic shift and broadening of the long-wavelength absorption band of the layer relative to the band of the solution ([5,6]). The correspondence of ε_m to the singlet excited state of the molecules of organic semiconductors compels one to suppose that this comparatively small perturbation is apparently sufficient for the formation, within this state, of a certain delocalized zone, through which dark conductivity is effected.

Received
30 X 1959

CITED LITERATURE

[1] A. T. Vartanyan, *ZhFKh*, **22**, 769 (1948).
[2] A. T. Vartanyan, *Izv. AN SSSR, ser. fiz.*, **20**, 1541 (1956).
[3] A. T. Vartanyan, I. A. Karpovich, *DAN*, **111**, 561 (1956); *ZhFKh*, **32**, 178 (1958).
[4] A. T. Vartanyan, L. D. Rozenshtein, *DAN*, **124**, 295 (1959).
[5] A. T. Vartanyan, *ZhTF*, **20**, 847 (1950).
[6] A. T. Vartanyan, *ZhFKh*, **30**, 1028 (1956).
[7] V. L. Levshin, *Photoluminescence of Liquid and Solid Substances*, Moscow–Leningrad, 1951, p. 173.
[8] A. N. Terenin, *Radio Engineering and Electronics*, **1**, 1127 (1956).
[9] B. Rosenberg, *J. Chem. Phys.*, **29**, 1108 (1958).
[10] V. L. Ermolaev, Dissertation, Moscow, 1958.

---

* The authors express their sincere gratitude to V. L. Ermolaev for kindly providing the apparatus for measuring the phosphorescence spectra, and also for valuable advice.

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