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Abstract

Full Text

PHYSICAL CHEMISTRY

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ACTIVATION OF THE ELECTRICAL CONDUCTIVITY OF DYES BY HYDRAZINE VAPORS

(Presented by Academician A. N. Terenin, 24 VII 1964)

Oxygen and nitrogen oxide (electron acceptors) suppress the dark conductivity of such electronic organic semiconductors as crystalline methyl violet and methylene blue (1). At the same time, oxygen activates the conductivity of a number of hole semiconductors—magnesium and copper phthalocyanines, chlorophyll, methylchlorophyllide, and hemin (2). Recently, in a series of works (3), the effect of hydrazine vapors (H) on dye layers was studied by a spectrophotometric method; this effect leads to the appearance of characteristic absorption spectra of intermediate and final interaction products: colored ions and quasi-leuco bases. Figure 1 shows the change in the absorption spectrum of fuchsin (curve 1) after its contact with H vapors (curves 2–4). Curve 5 belongs to the quasi-leuco base. The original dye molecules are often obtained from these colorless products with greater or lesser ease; sometimes their contact with air or heating in vacuum is sufficient (curve 6).

It seemed interesting to trace such reversible processes by measuring electrical conductivity and to compare the results with those of spectrophotometric measurements. As far as we know, the effect of H vapors, i.e., of an active donor of electrons and hydrogen, on the electrical conductivity of dyes has not yet been investigated. In addition, such studies, together with investigation of the influence of oxygen, are of interest for clarifying the question of the correlation between the sign of the dye ion or the sign of the dark current carriers, on the one hand, and the nature of the influence of the gases studied, on the other.

In the present work are given the results of studying the influence of H vapors and oxygen on the electrical conductivity of layers of basic and acid dyes of the triphenylmethane and xanthene series (Table 1).

Table 1

Dye and ion sign	Type of semiconductor	Action* N_2H_4	Action* O_2	Activation energy, eV: in vacuum	Activation energy, eV: after N_2H_4	Activation energy, eV: in the presence of O_2	Activation energy, eV: after pumping off O_2
Fuchsin +	Electronic	+	–	1.84	1.45	2.3	2.0
Acid violet –	Hole	+	–	1.78	1.41	2.1	1.78
Water blue –	Electronic	–	–	1.75	2.14	1.75	1.75
Patent blue –	Hole	+	–	1.65	1.28–1.59	2.46	1.52
Aurin (neutral)	Electronic	+	–	2.08	1.95	2.20	2.0
Rhodamine 6G +	Electronic	–	–	2.03	2.25	1.93	2.03
Uranin –	Hole	+		2.23	2.40		
Eosin –	Same	+		2.30	2.54		
Erythrosin –	»	+		2.22	2.38		

* Plus denotes activation; minus denotes suppression.

Among the dyes investigated there are both electron and hole semiconductors. With the exception of water blue, whose layers were obtained from a water-alcohol solution, the salts of the other dyes were precipitated from alcoholic solutions. The apparatus on which the measurements were made has been described previously (^{4}). The currents were measured with an EMU-3 electrometric amplifier equipped with a set of input resistances. The weakest currents that could be measured were of the order of 10^{-14} A.

Since anhydrous H, as an ionizing solvent ($\varepsilon = 52$), is close to water, the appearance in layers of salt-like dyes of electrolytic conductivity is not excluded if capillary condensation occurs at the working vapor pressure.

Fig. 1. Absorption spectral curves: **1**—fuchsin in vacuum; **2-5**—fuchsin in hydrazine vapor at vapor pressures of 0.1, 0.5, 1.0, and 1.5 mm Hg, respectively;

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Indeed, at vapor pressures of 0.5, 0.9, 1.2, and 1.5 mm Hg, the dark current in a fuchsin layer changed by 0, 10, 100, and 1000 divisions, respectively*. At pressures greater than 0.8 mm Hg, a sharp increase in the dark current is observed. To exclude the ionic component of the conductivity, all measurements were carried out under vacuum conditions. Before measurement, the layers were thoroughly degassed in a high vacuum (10^{-5}) at 100°. First, the temperature dependence of the conductivity of a fresh layer was measured in vacuum. The values of ε_m, determined from the slopes of the straight lines

$$\lg \sigma = \lg \sigma_0 - \varepsilon_m \frac{\lg e}{2k} \cdot \frac{1}{T},$$

are given in Table 1. Then, at room temperature, H vapor was admitted onto the layer at various pressures. As a rule, it was not greater than 2 mm Hg. After 1-2 min the vapors were removed, and the layer was treated for an hour in vacuum, first at room temperature and then at 100°. After such treatment, the dark conductivity of the dyes investigated, with the exception of rhodamine and water blue, becomes almost an order of magnitude greater. In Fig. 2, straight line 1 corresponds to a fresh fuchsin layer, and line 2 to the same layer after treatment with Γ vapors at a pressure of 0.8 mm Hg. The electrical conductivity can be increased by another order of magnitude if the dye is entirely converted into the state of the quasi-leuco base and then the dye is thermally regenerated under vacuum conditions (line 3). It should be borne in mind that the quasi-leuco base itself in vacuum does not possess appreciable conductivity. The conductivity increases as the layer is thermally treated and the dye is regenerated.

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* The vapor pressure was set by the temperature of liquid H. For temperatures below 0°, the vapor pressures of H have not been determined. To estimate their order of magnitude, we were guided by the results of extrapolation, giving 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} mm Hg for temperatures of −85, −72, −56, −37, and 12.5°, respectively.

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Fig. 2. Temperature dependence of dark conductivity. 1 –fuchsin in vacuum before admission of Γ vapors, $\varepsilon_m = 1.84$ eV; 2 –the same layer in vacuum after removal of Γ vapors at a pressure of 0.8 mm Hg, $\varepsilon_m = 1.57$ eV; 3 –the same layer in vacuum after complete decolorization and subsequent regeneration of the dye, $\varepsilon_m = 1.45$ eV; 4 –in oxygen; 5 –in oxygen after treatment of the layer with Γ vapors.

For the triphenylmethane dyes considered, activation of dark conductivity by Γ vapors is accompanied by a decrease in ε_m (Table 1). For patent blue, ε_m falls to 1.28 eV. If, however, this layer is heated to 150°, a more complete regeneration of the dye occurs, and ε_m increases and reaches 1.59 eV, differing from the value of ε_m for a fresh layer by only 0.06 eV. Earlier [3] it was shown spectrophotometrically that patent blue and aurin belong to dyes in which the processes of bleaching and regeneration are the most reversible. Fuchsin and acid violet also can readily be regenerated from the corresponding quasi-leuco bases, but, as is seen from Fig. 1, for fuchsin (curve 6), and also for acid violet [3], some irreversible change also takes place, causing increased absorption in the region of 360 mμ. The resistance of these dyes continues to decrease even when the layer is heated to 150°. The conductivity of water blue, unlike the dark conductivity of the other triphenylmethane dyes investigated, is suppressed by Γ vapors, with ε_m becoming greater than under vacuum conditions. Measurement of the corresponding spectra showed that, in the layer of water blue, along with reversible processes, irreversible processes also occurred. Calculations showed that the change in conductivity is associated with a change not only in ε_m, but also in the pre-exponential factor. In those cases where the substance undergoes substantial changes, the influence of the pre-exponential factor can be very large, and therefore the nature of the influence of Γ vapors on dark conductivity will be determined by changes not only in ε_m, but also in the pre-exponential factor.

In contrast to Γ vapors, oxygen suppresses the dark conductivity of almost all the triphenylmethane dyes investigated, and the suppression is basically reversible and does not depend either on the sign of the dye ion or on the nature of the current carrier. In the presence of oxygen, ε_m is greater than under vacuum conditions. Pumping off the oxygen and conditioning the layers in vacuum in most cases

cases brings ε_m to values characteristic of layers before the admission of oxygen. Oxygen has a very weak suppressing effect on the conductivity of water blue in the temperature range from 50 to 100°. In the presence of oxygen, and also after its removal, ε_m is almost unchanged. Meanwhile, in the region from 20 to 50° the plot of the dependence of $\lg \sigma$ on $1/T$ is slightly curved toward a smaller slope, apparently owing to the appearance of impurity conduction. We encountered an analogous phenomenon in studying the effect of oxygen on the dark conductivity of acidic xanthene dyes (^{5}).

vapors activate the dark conductivity of uranine, eosin, and erythrosin, while ε_m increases. If the bond of with the dye is weak, as, for example, in the case of eosin, then after prolonged conditioning of the layer at 100° under continuous pumping the value of ε_m is close to the value before the admission of vapors. The conductivity of rhodamine is suppressed both by vapors and by oxygen, but the influence of these gases on ε_m is opposite (Table 1). Evidently, also in the case of rhodamine, the change in the pre-exponential factor substantially affects the conductivity. After the oxygen is pumped out, ε_m returns to the value before admission of oxygen.

It should be noted that the values of ε_m given in Table 1, which refer to layers in oxygen or in vacuum after removal of vapors, may fluctuate within certain limits depending on the layer thickness, the pressure of oxygen and of vapors, the duration of the dye' s stay in the atmosphere of the foreign gas, the conditioning temperature, etc. The numbers given in Table 1 show only the direction in which ε_m changes in one gas or another. If the strength of the bond between the dye and the foreign gas is small, it may happen that, during prolonged treatment of the layer in vacuum, after some decrease in ε_m, it will begin to grow. What is important here is that oxygen and vapors act on the dark conductivity of most of the dyes studied in opposite directions, independently of the sign of the dye ion and of the nature of the charge carrier.

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