Reports of the Academy of Sciences of the USSR

1962

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1962. Volume 143, No. 6

PHYSICS

A. T. Vartanyan

SEMICONDUCTING PROPERTIES OF BLOOD PIGMENTS

(Presented by Academician A. N. Terenin on 17 XI 1961)

A new class of semiconductor materials—organic semiconductors—includes not only relatively simple compounds of the type of polynuclear aromatic hydrocarbons, but also the most complex organic formations—polymers and proteins. Along with many organic substances, in particular dyes, we investigated several pigments important in biological respects—chlorophyll, hematin, hemin, and hematoporphyrin. It was shown that under vacuum conditions the electrical conductivity of layers of these pigments, as of other organic semiconductors, changes with temperature according to the law $\sigma = \sigma_0 \exp(-\varepsilon_\tau/2kT)$. For the thermal activation energy ε_τ of hematin and hematoporphyrin layers, values of 1.83 eV (([1]), line 6) and 2.08 eV (([1]), line 13), respectively, were obtained*. In the present communication we give the results of a detailed study of the temperature dependence of electrical conductivity, as well as the results of an investigation of the photoconductivity of blood pigments.

For these studies a quartz vessel in the form of a test tube ("finger") was used, on the outer surface of which platinum electrodes 3 cm high were deposited, with a gap between them of about 0.5 mm. After deposition of the layer, the quartz finger was inserted into a jacket connected to a high-vacuum apparatus, and the layer was carefully degassed. Hemin and hematin were usually degassed at 140°. Hematoporphyrin was degassed at temperatures not exceeding 100°. As is known, hematin decomposes at 200°. Studies of electrical conductivity showed that a change in hematin can be detected at 150–160°.

The currents were measured with an EMU-3 direct-current amplifier equipped with a set of input resistances. The largest resistance was 6.8 GΩ; with this, the sensitivity of the measuring circuit was $1.5 \cdot 10^{-14}$ A. Before the currents were measured, the layers were kept for a long time in the dark. The direction of illumination was perpendicular to the direction of the electric field. To obtain monochromatic light, an ISP-17A mirror monochromator with glass optics was used. To determine the optical activation energy of photoconductivity, we used an incandescent lamp with a tungsten ribbon (SI-16), calibrated by brightness temperatures for 656 mμ. The intensity of the light incident on the layer was varied with the aid of blackened metallic meshes.

In fields with strengths up to 10,000 V/cm the dark current obeys Ohm' s law. Figure 1 gives the temperature dependence of the electrical conductivity σ in the coordinates $\lg\sigma$ and $1/T$. In the temperature intervals investigated, the exponential law for the temperature dependence of conductivity is well fulfilled. The values of the thermal activation energy ε_τ, determined from the slopes of the straight lines

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

are given in Table 1. They are in good agreement with the absorption spectra of the layers investigated compounds (2). As can be seen from Table 1, the wavelengths corresponding to ε_t belong to portions of the absorption curves corresponding to the energies of a singlet-singlet transition.

Under vacuum conditions, the resistance of carefully dehydrated layers of hemin and hematin could not be measured at room temperature. It was determined by extrapolating the straight lines $\lg\sigma = f(1/T)$ to 20°. Table 1 also gives the values of the specific resistances at 20°. The resistance of the layers depends on the method of their preparation and on the degree of their dehydration; therefore the values of ρ_{sp} given here provide only the order of magnitude.

Table 1

Compound	ρ_{sp} at 20°, cm · cm	Temperature interval, °C	ε_t, eV	Wavelength region of the decline in the absorption curve of the layer, mμ
Hematin	10^{15}	52–155	2.03 (609 mμ)	480–640
Hemin	10^{14}	35–140	1.85 (667 mμ)	650–700
Hematoporphyrin	10^{12}	35–100	2.07 (597 mμ)	565–620

Since hematoporphyrin in vacuum at temperatures above 105° passes into protoporphyrin with the loss of two water molecules, a thin layer of hematoporphyrin

---

* In Table 1 of paper (1), for hematoporphyrin the data relating to hematin were erroneously repeated. From the slope of line 13 in the figure of paper (1), it follows that for hematoporphyrin $\varepsilon_\tau = 2.08$ eV.

was heated in vacuum for 15 min at 135°, and then the temperature dependence of the electrical conductivity was measured. In Fig. 1 this dependence is shown by straight line 4. For the compound formed, $\varepsilon_t = 1.83$ eV, which also agrees with the absorption spectrum of the protoporphyrin layer (^{2}). The value 1.83 eV, apparently, may be taken as the thermal activation energy of the electrical conductivity of protoporphyrin. Unfortunately, we did not have protoporphyrin in a quantity sufficient for a direct measurement of the temperature dependence of the electrical conductivity.

The value of ε_t given here for hematin (2.03 eV), although somewhat greater than the value obtained by us earlier (^{1}), and the value 1.74 eV obtained by Cardew and Eley (^{3}), is nevertheless considerably smaller than the activation energy of the electrical conductivity of hemoglobin in the solid state under vacuum conditions, equal to 2.66 eV (^{4}). Evidently, the electrical conductivity of hemoglobin is determined mainly by its protein part, since for globin $\varepsilon_t \approx 3$ eV (^{3}, ^{5}).

Oxygen slightly suppresses the electrical conductivity of a hematoporphyrin layer. In the presence of oxygen at a pressure of 215 mm Hg, the electrical conductivity decreases by approximately a factor of 1.5, and the activation energy increases from 2.07 to 2.1 eV (Fig. 1, straight line 5). Such behavior of hematoporphyrin is similar to the behavior of metal-free phthalocyanine in an oxygen atmosphere (^{6}, ^{7}). The hematoporphyrin molecule, like the metal-free phthalocyanine molecule, does not contain a metal atom.

It was shown by us (^{3}) that the electrical conductivity of a number of metallic phthalocyanine complexes increases strongly when oxygen is admitted. In contrast to hematoporphyrin, the electrical conductivity of layers of hematin and hemin, which contain iron atoms, also increases sharply in the presence of oxygen. At room temperature the increase in conductivity of a hemin layer in the dark is observed over many hours. Raising the temperature of the layer accelerates the increase in conductivity. Straight line 6 in Fig. 1 was obtained after the hemin layer (straight line 2) had been kept for one hour in oxygen at a pressure of 470 mm at 100°. Along with a significant increase in electrical conductivity, a decrease in the activation energy to 1.4 eV is observed. After the layer has been kept for one hour in oxygen at 130°, the energy falls to 1.3 eV. If the oxygen is removed and the layer is trained for 1 hour at 130° under vacuum conditions, then the energy increases to the initial value of 1.87 eV.

We investigated iron phthalocyanine, which among the metallic phthalocyanine complexes is the closest analogue of hemin and hematin. Under vacuum conditions the activation energy of the electrical conductivity of iron phthalocyanine is 1.6 eV. When oxygen is admitted, the electrical conduct-

conductivity increases, while ε_τ drops sharply to 0.8—0.9 eV in the presence of oxygen at a pressure of 90 mm.

The behavior of hematin in oxygen is very interesting. At temperatures above 110°, despite the presence of oxygen, no effect is observed at a pressure of 500

Fig. 1. Temperature dependence of the electrical conductivity of layers of compounds: 1 —hematin in vacuum, 2 —hemin in vacuum, 3 —hematoporphyrin in vacuum, 4 — “protoporphyrin,” 5 —hematoporphyrin in oxygen (215 mm), 6 —hemin in oxygen (470 mm), 7 —hematin in oxygen (500 mm)

Figure 1: Fig. 1. Temperature dependence of the electrical conductivity of layers of compounds: 1 —hematin in vacuum, 2 —hemin in vacuum, 3 —hematoporphyrin in vacuum, 4 — “protoporphyrin,” 5 —hematoporphyrin in oxygen (215 mm), 6 —hemin in oxygen (470 mm), 7 —hematin in oxygen (500 mm)

mm.

When the temperature is changed from 144 to 110°, the decrease in electrical conductivity in the presence of oxygen is the same as in vacuum (Fig. 1, straight lines 1 and 7). For this temperature interval $\varepsilon_\tau = 2.03$ eV. However, at temperatures below 110° an increase in the dark current is observed owing to adsorption of oxygen, which increases as the layer is cooled. At temperatures below 4°, the increase in conductivity caused by oxygen adsorption proves stronger than its decrease owing to cooling of the layer. Evidently, at high temperatures hematin in oxygen is an intrinsic semiconductor, while at low temperatures it is an impurity semiconductor. We observed an analogous effect in studying the temperature dependence of the dark conductivity of layers of acidic xanthene dyes (uranin, eosin, erythrosin, phloxine, and Bengal rose) in the presence of oxygen (8). The reversible interaction of hematin with oxygen, which depends strongly on temperature, is of interest in connection with the process of respiration.

Fig. 1. Temperature dependence of the electrical conductivity of layers of compounds: 1 —hematin in vacuum, 2 —hemin in vacuum, 3 —hematoporphyrin in vacuum, 4 — “protoporphyrin,” 5 —hematoporphyrin in oxygen (215 mm), 6 —hemin in oxygen (470 mm), 7 —hematin in oxygen (500 mm).

Upon illumination of layers of the pigments studied, as well as of iron phthalocyanine, under vacuum conditions, an inertialess increase in conductivity is observed. For blood pigments, the study of photoconductivity cannot have the primary importance that it has for chlorophyll in connection with the problem of photosynthesis. Nevertheless, these investigations are necessary, first, for confirming the results obtained for the dark current, and, second, for the study of organic semiconductors in general.

Photocurrents are observed at room temperature. In fields with strength up to 10000 V/cm, the photocurrent obeys Ohm' s law. The dependence of the photocurrent i_ϕ on the illumination intensity L, when the latter is varied within two orders of magnitude, can be described by the relation $i_\phi = aL^n$, where n for well-degassed layers is close to 1. As the temperature of the layer is raised, the strength of the photocurrent increases. For hematoporphyrin and hemin in the interval from 5 to 80°, the dependence $i_\phi = i_0 \exp(-\varepsilon_\phi/kT)$ is satisfied. The-

Fig. 2

Figure 2: Fig. 2

mic activation energy of the photocurrent ε_ϕ is equal, for hematoporphyrin and hemin, to 0.2 and 0.18 eV, respectively. For hematin the temperature dependence could be measured in the interval from −30 to 135°. The graph plotted in the coordinates $\lg i_\phi$ and $1/T$ is curved. A similar curvature was observed by us for phthalocyanines (^{7}). The exponential dependence of the photocurrent on the reciprocal temperature with an activation energy of 0.1 eV holds in the interval from −30 to 30°.

Fig. 2. Spectral curves of the photoelectric sensitivity (1) and optical absorption of layers in vacuum (2): *a*—hematoporphyrin, *b*—hemin

Since the pigments studied absorb very strongly in the region 350–450 mμ, layers whose thickness was of the order of 0.1 μ were used to measure the spectral dependence of the photocurrent. Figure 2 gives, for hematoporphyrin (*a*) and hemin (*b*), the spectral dependences of the photocurrent calculated per unit of incident energy. The positions of the photocurrent maxima in general coincide rather well with the maxima of the absorption spectrum. It should be noted, however, that there is a certain decrease in sensitivity in the region of the absorption maxima. Apparently, the layers were not sufficiently thin. For the thinnest layers of hematin it has not yet been possible to obtain a good curve of the spectral dependence of the photocurrent, and therefore we do not present it. From the spectral photocurrent curves shown in Fig. 2 it is difficult to determine the optical activation energy of the photocurrent E_ϕ by the $\lambda_{1/2}$ method. It was determined by the method of "photoelectric straight lines." For hematin, hemin, and hematoporphyrin, the values obtained were, respectively, 2.05, 1.87, and 2.03 eV, in good agreement with ε_{g}. However, for hematin, at lamp-filament temperatures below 1700°, an energy of 1.6 eV was obtained.

In the presence of oxygen at pressures of several hundred millimeters of mercury, the photocurrent in hematoporphyrin and hemin layers increases tens of times, but, unfortunately, becomes inertial. If the oxygen is removed, the initial properties of the layer are restored. Under the same conditions the photocurrent in a hematin layer increases only severalfold, while the inertia still remains small. Evidently, under illumination the interaction of hematin with oxygen remains weak. Further experiments will show to what extent the features of hematin are inherent in the pigment itself and are not due to some impurity.

The totality of the results obtained leads to the conclusion that, under vacuum conditions, the blood pigments studied are intrinsic semiconductors.

Received
10 XI 1961

CITED LITERATURE

1. A. T. Vartanyan, *Izv. AN SSSR, ser. fiz.*, **20**, 1541 (1956).
2. A. T. Vartanyan, Reports at the XIV Conference on Spectroscopy, Gorky, 1961 (in press).
3. M. H. Cardew, D. D. Eley, *Farad. Soc. Discuss.*, **27**, 115 (1959).
4. D. D. Eley, D. I. Spivey, *Trans. Farad. Soc.*, **56**, 1432 (1960).
5. M. G. Evans, J. Gergely, *J. Biochim. et biophys. acta*, **3**, 188 (1949).
6. A. T. Vartanyan, *ZhFKh*, **22**, 769 (1948).
7. A. T. Vartanyan, A. I. Karapov, *ZhFKh*, **32**, 78 (1958).
8. A. T. Vartanyan, L. D. Rozenshtein, *Fiz. tverd. tela*, **3**, 713 (1961).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.