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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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PHOTOCONDUCTOR PROPERTIES OF BILIRUBIN

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At the present time there are known works devoted to the photoconducting properties of pigments of both plant origin (chlorophylls a and b, β-carotene, etc.) and animal origin (hemin, hematoporphyrin, etc.). The structure of the molecules of these pigments is based on the porphyrin skeleton. In close genetic relation to the coloring substances of blood is the bile pigment–bilirubin. In contrast to the molecules of hematoporphyrin and protoporphyrin, the molecule of bilirubin–one of the most important compounds for medicine–represents an open chain between two pyrrole rings, consisting of two identical systems of conjugated double bonds (Fig. 2). The length of each conjugation system is almost half the length of the closed conjugated chain in the protoporphyrin molecule; as a result, the absorption spectrum of bilirubin is shifted considerably toward shorter wavelengths relative to the spectrum of protoporphyrin. For a solution of bilirubin in chloroform, the maximum of the absorption band in the visible region is at 452 mμ (Fig. 2, 1).

This work is devoted to the study of the photoconducting properties of bilirubin. As far as we know, it has not yet been investigated as a semiconductor.

Fig. 1. **1**–temperature dependence of the electrical conductivity of a bilirubin layer in vacuum (circles), **2**–the same in oxygen at an elasticity of 160 mm Hg, **3**–the same after removal of oxygen (crosses), **4**–temperature dependence of photoconductivity in vacuum, **5**–current decay in the coordinates $1/i_\phi$ and t after cessation of illumination of the layer in oxygen

The bilirubin layer was located between platinum electrodes, deposited at a distance of 0.5 mm from one another on the surface of a quartz test tube provided with a ground joint for connection to a high-vacuum installation (10^{-5} mm Hg). The layers were obtained either by deposition of the pigment from a solution in chloroform (thin layers) or by rubbing (thick layers). Thin mirror-like layers with selective reflection had a thickness of several tens of millimicrons, while thick layers had a thickness of several hundreds. Before the start of measurements the layers were carefully degassed in high vacuum. In the course of conditioning, the electrical conductivity of the layer decreased and reached a stationary value. The growth of the resistance of the layer is apparently due mainly to the removal of oxygen. The currents were measured with an EMU-3 direct-current amplifier equipped with a set of input resistances. The highest current sensitivity of the circuit was $1.5 \cdot 10^{-14}$ A. A voltage of up to 500 V was applied to the layer from batteries of dry cells. Illumination was per-

perpendicular to the direction of the applied electric field. Other experimental details are given in papers (^{1}).

Under vacuum conditions, the temperature dependence of the electrical conductivity of dehydrated bilirubin layers (Fig. 1, 1), at voltages for which Ohm' s law is obeyed, follows the law we previously established (^{2}) for organic semiconductors,

$$\sigma = \sigma_0 \exp(-\varepsilon_m/2kT).$$

The activation energy ε_m is 2.35 eV and agrees with the onset of the steep rise of the long-wavelength portion of the optical absorption curve (525 mμ) of the layer (Fig. 2, 2). Consequently, under vacuum conditions a bilirubin layer should be an intrinsic semiconductor. At room temperature the specific conductivity, determined by extrapolating the temperature dependence of the electrical conductivity, has a value of about 10^{-18} $\Omega^{-1} \cdot \mathrm{cm}^{-1}$. It is several orders of magnitude smaller than the specific electrical conductivity of protoporphyrin and hematoporphyrin (^{3}).

Oxygen causes an increase in electrical conductivity that depends on pressure. In contrast to the electrical conductivity of a number of natural pigments studied by us previously, the increased electrical conductivity of bilirubin in the presence of oxygen is established very rapidly in the dark and does not depend on how long the layer remains in oxygen. Ohm' s law is also obeyed in this case for fields up to 10^4 V/cm. In the presence of oxygen at a pressure of 160 mm, the electrical conductivity at 70° is two orders of magnitude greater than in vacuum, and the activation energy is 1.26 eV (Fig. 1, 2). Removal of oxygen leads to the initial values of electrical conductivity and activation energy (Fig. 1, 3).

For one layer we give the values of the electrical conductivity σ_p and activation energy ε_m at various oxygen pressures p.

p, mm Hg	0	1.5	4	10	60	200	400	500
$\sigma_p \cdot 10^{16}$, Ω^{-1}, 100°	6	30	45	60	111	180	243	269
ε_m, eV	2.35	1.55	1.45	1.39	1.27	1.26	1.25	1.25

In the pressure interval from 1.5 to 500 mm, the relation between p and $\Delta\sigma = \sigma_p - \sigma_0$ is well described by the well-known Freundlich formula $\Delta\sigma = ap^m$, where $m \approx 0.5$. The action of oxygen is evidently due mainly to adsorption. At $p < 1$ mm the law governing the change in resistance will evidently be different. It is also clear from the data presented that the activation energy falls sharply even at low oxygen pressures; moreover, as the pressure increases it approaches the value 1.25 eV, characteristic of a bilirubin layer with impurity conductivity.

Since the electrical conductivity of protoporphyrin increases, while that of hematoporphyrin decreases in the presence of oxygen, one may suppose that oxygen is localized at the double bonds of the vinyl groups of the bilirubin molecule.

In vacuum, under monochromatic illumination in the absorption band, the resistance of the layer decreases by several orders of magnitude. The photocurrent is almost inertia-free and, in fields with strengths up to 10^4 V/cm, follows Ohm' s law. For well-dehydrated layers, the dependence of the photocurrent i_ϕ on the light intensity L, when the latter is varied within one order of magnitude, is described by the relation $i_\phi = aL^n$, where n (the nonlinearity exponent), depending on the illumination level, may vary within the range 0.9-1.0 ([8]). At low illumination levels $n = 1$.

The temperature dependence of the photoconductivity follows the law we previously established for organic dyes,

$$\sigma_\phi = \sigma_0' \exp(-\varepsilon_\phi/kT)$$

([4,5]). As for many organic photoconductors, ε_ϕ for bilirubin is almost an order of magnitude smaller than ε_m and is equal to 0.25 eV (Fig. 1, 4). It characterizes the depth of the trap levels.

The spectral distribution of the photosensitivity of bilirubin, defined as the photocurrent referred to a unit of incident energy with allowance for the nonlinearity exponent, as for a number of dyes ([5]), and also natur-

pigments [^1][^6], depends on the thickness of the layer. In Fig. 2, curves 3 and 5 respectively refer to the thin and thick layers of bilirubin. The correlation of

Fig. 2

Figure 2: Fig. 2

curve 3 and the anticorrelation of curve 5 with the corresponding absorption curves (2 and 4) are obvious. The optical activation energy of the photoconductivity, determined from curve 3 by the $\lambda_{1/2}$ method ($\mathcal{E}_{\lambda 1/2}$), is 2.4 eV. The same energy, determined by the method [^1][^7] of "photoelectric straight lines," taking into account the nonlinearity index $\mathcal{E}_{\phi}$, is 2.36 eV.

Fig. 2. Spectral curves of optical absorption (1, 2, 4) and of photoelectric sensitivity $i_{\phi}^{1/n_{\lambda}}/L_{\lambda}$ (3, 5):
1 –solution of bilirubin in chloroform, 2 –layer obtained by precipitation of the pigment from a solution in chloroform (measurements in vacuum and in air), 3 –thin layer, 4, 5 –thick layer, obtained by rubbing.

The results obtained give grounds to assert that, under vacuum conditions, a well-trained layer of bilirubin is an intrinsic photoconductor.

In the presence of oxygen, not only the dark current but also the photocurrent increases, and the latter becomes highly inertial. We observed analogous behavior of the photocurrent in some acid xanthene dyes [^8], phthalocyanines [^9], chlorophyll [^1][^6], and hemin [^3]. The increase in photocurrent depends on the oxygen pressure. At a pressure of 160 mm, the stationary value of the current, reached at the given illumination intensity after 8 min, exceeds by a factor of 35 the stationary value of the photocurrent under vacuum conditions. After illumination is stopped, the current falls to 99% of the stationary value in approximately 1 h. If the fall of the current during the first 15 sec is excluded, then the fall over this entire time obeys the relation we established

earlier [10] hyperbolic law: $1/i_t = 1/i_0 + kt$ (Figs. 1, 5), where t is the time elapsed from the moment the light was switched off, i_0 is the initial photocurrent in the stationary state, i_t is the current strength t sec after illumination was stopped, and k is a constant. It follows from this that the disappearance of current carriers proceeds according to the bimolecular scheme $di/dt = -\gamma i^2$.

The totality of the results obtained indicates that the photosemiconductor properties of bilirubin layers have much in common with the properties of other natural pigments possessing a porphyrin skeleton.

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