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Abstract

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PHYSICS

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PHOTOCONDUCTOR PROPERTIES OF METHYL CHLOROPHYLLIDE a

(Presented by Academician A. N. Terenin, 30 V 1963)

The photoconductivity of methyl chlorophyllide a was observed by A. N. Terenin and E. K. Putseiko (^1) and by Nelson (^2). Recently we (^3, ^4) investigated the photosemiconductor properties of chlorophyll a.* Chlorophyllides differ from chlorophylls in the absence of the phytol chain. It is of interest to determine to what extent this fact affects their photosemiconductor properties. In addition, as far as we know, the dark conductivity of methyl chlorophyllide a has not yet been investigated by anyone.

We investigated amorphous layers obtained by deposition of the pigment dissolved in chloroform.** A detailed description of the experimental part is given in article (^3). The investigations were carried out both in vacuum and in an oxygen atmosphere. In the experiments on measuring the dark current, the layer thickness was about $0.2\,\mu$. As the air was pumped out and the layer was conditioned in vacuum at 70°, the conductivity decreased and after several hours stabilized; in this process the resistance of the layer increased by more than two orders of magnitude. At room temperature the layers had a resistance greater than 10^{16} ohms, which corresponds to a specific resistance of the order of 10^3 ohm · cm, close to the specific resistance of some phthalocyanines (^5). The specific resistance of chlorophyll a is an order of magnitude greater ($\sim 10^{14}$ ohm · cm). Ohm' s law is obeyed up to fields of 10^4 V/cm.

The temperature dependence of the dark current obeys the law $i_\tau = a\exp(-\varepsilon_\tau/2kT)$ (^{6}-8). From Fig. 1, 1 it follows that, under vacuum conditions, $\varepsilon_\tau = 1.71$ eV. This value agrees with the absorption spectrum of the pigment layer (Fig. 2, 1) and is only 0.03 eV smaller than the value of ε_τ found by us for chlorophyll a (^4). The closeness of the ε_τ values of the two related pigments was to be expected, since their spectra also differ only slightly (^3). This serves as an argument in favor of our idea that, for intrinsic organic semiconductors, ε_τ correlates more or less with the absorption spectrum. For

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Fig. 1

Figure 1: Fig. 1

methyl chlorophyllide that had been exposed to air for a long time, ε_τ is smaller (1.4-1.6).

In the presence of oxygen (30 mm Hg), the dark current increases in accordance with its hole nature (ˆ1), while ε_τ falls to 1.2 eV. Such behavior of methyl chlorophyllide is similar to the behavior of chlorophyll a (ˆ4), hemin and hematin (ˆ9), and a number of metal phthalocyanine complexes ($^{5\text{-}}$7). It should be noted, however, that in the case of chlorophyll a the sensitivity of ε_τ to oxygen is smaller. Indeed, after a two-day exposure of the layer to oxygen at a pressure of 245 mm, ε_τ decreases by only 0.1 eV. With respect to oxygen, methyl chlorophyllide is closer to phthalocyanines than to chlorophyll. This is probably due to the absence of the phytol chain in chlorophyllide. The increase in conductivity depends on the pressure and duration of the action of oxygen. Pumping out oxygen leads to an increase in resistance and ε_τ to the values in vacuum (Fig. 1, 3). Consequently, in the dark oxygen is weakly bound to methyl chlorophyllide.

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* The literature on the photoelectric properties of chlorophyll a is given in (ˆ3).

** The pigment was isolated at the Botanical Institute of the Academy of Sciences of the USSR. I express my deep gratitude to I. A. Popova, who kindly provided us with the pure preparation.

If the pigment is fresh and the layer has been well aged in vacuum, then the time required to establish the steady photocurrent is no greater than the time constant of the input circuit of the amplifier ($<$ 4 sec). After the light is switched off, the current falls by 98% in the same time. Nelson considers the most distinctive feature of methyl chlorophyllide to be the presence of two time constants both in the rise of the photocurrent (less than 1 sec and about 15 min) and in the fall of the current after illumination is stopped. In Nelson' s experiments the fast component reached values less than half of the steady photocurrent. We observed such behavior of the photocurrent in insufficiently completely degassed layers, as well as in layers in oxygen.

In vacuum the photoconductivity as the temperature of the layer is varied follows the law $\sigma_\phi = \sigma_0 \exp(-\varepsilon_\phi/kT)$ (10^{-12}). At room temperature, illumination of the layer produced a photocurrent whose magnitude was more than two orders of magnitude greater than the dark current. For the interval $0 \div 70°$ (Fig. 1, 4), $\varepsilon_\phi = 0.23$ eV, and for the interval $-27 \div 0°$ $\varepsilon_\phi = 0.15$ eV (Fig. 1, 5). The value 0.15 eV coincides with ε_ϕ of chlorophyll a (4) and corresponds to the energy difference between the maxima of the long-wavelength absorption bands and of the action spectrum of the photocurrent of a thin layer.

Fig. 1. **1** –temperature dependence of dark conductivity in vacuum; **2** –

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Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

the same in oxygen (30 mm Hg); **3** –the same in vacuum after removal of oxygen; **4**, **5** –temperature dependence of the photocurrent ($\lambda = 680$ mμ); **6** –"photoelectric straight line."

Fig. 2. **1** –optical absorption spectrum; **2** –action spectrum of the photocurrent in a thin layer; **3** –the same in a thick layer.

of the pigment (676, 628, 580, 540 mμ), i.e., it corresponds to the magnitude of the vibrational quantum.

Recently we showed (^{3}) that, in order to obtain an undistorted spectral curve of the photocurrent, it is necessary to take into account the spectral dependence of the nonlinearity exponent n, since the photocurrents at the edges and at the maximum of the action spectrum may differ by 2–3 orders of magnitude. Earlier, an increase of n with decreasing illumination level was shown (^{7}). Curve 2 in Fig. 2 is the photoelectric sensitivity of a thin layer of methyl chlorophyllide a, calculated from the formula $S_\lambda = i_{\phi\lambda}^{1/n_\lambda}/L_\lambda$, where L_λ is the intensity of the incident monochromatic light and n_λ is the nonlinearity exponent for the given wavelength. In the layer to which curve 2 refers, n varied from 0.65 to 1. The curve reproduces rather well the spectral absorption curve obtained by us for a layer in vacuum (Fig. 2,1), the photocurrent maxima being located at the same wavelengths as the maxima of the absorption bands of the layer. The somewhat smaller height of the maximum of the band at 435 mμ (curve 2) can probably be explained if recombination at the surface of the photoconductor is taken into account (^{13}).

Fig. 3. 1 –growth of the photocurrent during illumination of the layer in oxygen (100 mm Hg); 2 –decay of the current in coordinates i_ϕ and t after the illumination is stopped; 3 –the same in coordinates $1/i_\phi$ and t.

If the layer is thick (Fig. 2,3), then strong absorption bands (676, 628, 435 mμ) correspond to photocurrent minima (anticorrelation), while weak absorption bands correspond to clearly expressed photocurrent maxima (correlation at 580, 540, and 500 mμ). Consequently, in the case of thick layers as well, there is a similarity between the photocurrent action spectrum and the absorption spectrum, which serves as an argument in favor of the intrinsic nature of the photoconductivity. At the same time, it is clear that there can be no question of any shift of the 676 mμ band toward longer wavelengths (on curve 3 the maximum is at 685 mμ). To determine the optical activation energy of photoconductivity one can also use the absorption spectrum, but for this it is necessary to be certain that the photocurrent action spectrum is similar to the absorption spectrum; for this, in many cases, photocurrents must be measured in very thin layers. From curve 2 of Fig. 2 it follows that the optical activation energy of the photoconductivity of methyl chlorophyllide a, determined by the $\lambda'_{1/2}$ method, is equal to 1.75 eV and agrees with the value $\varepsilon_\tau = 1.71$ eV and with the value given below for the optical activation energy determined by the "photoelectric straight-line" method ($\mathcal{E}_\phi$).

To determine $\mathcal{E}_\phi$, photocurrents arising in the layer under illumination by the full radiation of an SI-16 lamp were measured in vacuum as a function of the temperature of the filament ("black body"). When the filament temperature was varied from 1200 to 2200° C, the photocurrent changed by more than two orders of magnitude. Therefore the nonlinearity coefficient n_T was determined by us for each measured point. It turned out that n_T varied from 1.16 to 0.9. From the slope of the straight line 6 in Fig. 1, plotted in coordinates $\lg(i_{\phi T}^{1/n_T}/T^2)$ and $1/T$ (4), it follows that $\mathcal{E}_\phi = 1.70$ eV.

For methyl chlorophyllide a, the values of all activation energies are somewhat lower than the corresponding values for chlorophyll a. This is consistent with the fact that the absorption spectrum of chlorophyllide is slightly (~ 0.1 eV) shifted relative to the spectrum of chlorophyll toward longer wavelengths. Consequently, the presence or absence of the phytol chain has no substantial effect on the values of the activation energies.

In the presence of oxygen, not only the dark current but also the photocurrent increases, and the latter becomes very inertial. A stationary state of the photocurrent can be reached only tens of minutes after the onset of illumination (Fig. 3, 1). The decay of the current in the dark lasts several hours (Fig. 3, 2). With respect to oxygen, the photocurrent in layers of methyl chlorophyllide behaves similarly to the photocurrent in layers of chlorophyll (4), phthalocyanines (5), and also eosin, erythrosin, phloxine, and Bengal rose (7,14). The hyperbolic law of current decay in the dark established by us (11,14,4),

$$1/i_t = 1/i_0 + kt,$$

which indicates a bimolecular scheme for the disappearance of charge carriers,

$$di/dt = -\gamma i^2,$$

is also valid for methyl chlorophyllide. As can be seen from Fig. 3, 3, the current drop obeys this law 15 sec after illumination is discontinued. This is explained by the fact that during the first 5 sec after the light is switched off the current falls by almost 50% of the stationary value. The same current jump is observed at the beginning of illumination. Such abrupt changes are characteristic of a pigment in vacuum. The magnitude of the change in current during the first 5 sec is close to the value of the photocurrent observed before oxygen was admitted. Illumination of the layer in the presence of oxygen is accompanied not only by a photoelectric but also by a "photochemical" process associated with the interaction of oxygen with the pigment during illumination.

The results obtained indicate that the photosemiconducting properties of amorphous layers of methyl chlorophyllide a and chlorophyll a almost coincide, and, consequently, the presence of the phytol chain in chlorophyll a is scarcely reflected in its photoelectric properties.

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