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1963

SovietRxiv

Abstract

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ACTIVATION ENERGY OF THE DARK CONDUCTIVITY AND PHOTOCONDUCTIVITY OF CHLOROPHYLL *a*

(Presented by Academician A. N. Terenin, 20 X 1962)

If the spectral dependence of the nonlinearity index of a photoconductor, n, is taken into account, then under vacuum conditions (10^{-5} mm Hg) the spectral curve of the photocurrent in a thin ($\sim 0.01\,\mu$) layer of chlorophyll a in the region 460–800 mμ coincides with the absorption spectrum of the layer measured in vacuum(1). For thick ($\sim$ 0.1-0.5$\,\mu$) layers the photocurrent curve has a more complicated form, but, as analysis shows, it too is genetically related to the absorption spectrum. Owing to this, for a thick layer one can reconstruct a photocurrent curve coinciding with the spectral absorption curve. This fact makes it possible to judge the nature of the photoconductivity from the action spectrum of layers that are not very thin, which is convenient, since the photocurrent increases with increasing layer thickness. The spectral photocurrent curves calculated by the formula $S_\lambda = i_{\phi\lambda}^{1/n}/L_\lambda^n$ for the thinnest layers make it possible to determine the optical activation energy of photoconductivity $\mathcal{E}_{\lambda_{1/2}}$. Such a determination of $\mathcal{E}_{\lambda_{1/2}}$ is equivalent to determining the energy from the absorption spectrum. It was of interest to compare it with the optical activation energy $\mathcal{E}_\phi$, obtained by the method of photoelectric slopes, and with the thermal activation energy of electrical conductivity $\varepsilon_T(\sigma - \sigma_0 \exp(-\varepsilon_T/2kT))$.

The energy ε_T for chlorophyll was first determined for chlorophyll a + b (Heil) in the interval 40-90°. For vacuum conditions a value of 2 eV was found(2). Soon afterward there appeared the work of Arnold and Sherwood(3) on the electrical conductivity of dried chloroplasts. Measurements were carried out in the interval from room temperature to 140°, and for ε_T a value of 2.1 eV was found. Recently, Rosenberg and Camiscoli(4) measured ε_T for crystalline chlorophylls a and b and obtained 1.12 and 1.44 eV, respectively.

In the present work, amorphous layers of pure chlorophyll a were obtained by deposition from a concentrated solution of the pigment in chloroform. The investigation was carried out both in high vacuum and in an oxygen atmosphere. The temperature of the layer during conditioning and during measurements did not rise above 70°. The light source was an incandescent lamp with a tungsten ribbon (SI-16), calibrated by brightness temperatures for 656 mμ. Other details of the experiments are given in article(1).

Fig. 1

Figure 1: Fig. 1

To determine $\mathcal{E}_\phi$, we measured in vacuum the photocurrents arising in the layer when it was illuminated by radiation from the SI-16 lamp, as a function of the temperature of the filament (“black body”). Measurements were made every 100° in the interval 1200-2200°. Since the strength of the photocurrent changed by almost two orders of magnitude in this case, it was necessary to determine n_T for each temperature. It turned out that when the filament temperature was changed from 2200 to 1600°, n_T slowly increased from 0.72 to 0.76; while when it was changed from 1600 to 1200°, n_T rapidly increased from 0.76 to 1.01 (Fig. 1, 1).

For the internal photoeffect, Ya. Tauc (^5) showed that, in the first approximation, the photocurrent i_ϕ arising upon irradiation of a semiconductor by the full radiation of a black body is related to the black-body temperature T by the relation $i_\phi = AT\exp(-\mathcal{E}_\phi/kT)$. If one takes into account the dependence of n_τ on the illumination level and plots a graph in the coordinates $\lg(i_\phi^{1/n_\tau}/T)$ and $1/T$, a straight line is obtained (Figs. 1, 2), whose slope gives $\mathcal{E}_\phi = 1.91$ eV. This value is 0.13 eV greater than the value $\mathcal{E}_{\lambda_{1/2}}$ (^1). Rosenstein (^6), having obtained Tauc’ s formula for a more general case, established that the cause of such a discrepancy may be distortions introduced into the value of the photocurrent when a tungsten ribbon, calibrated according to brightness temperatures, is used as the black body. The resulting systematic error in determining $\mathcal{E}_\phi$ can be compensated by increasing the exponent of T in the pre-exponential factor. As our measurements ($^{7-}$12) showed, the best agreement with experiment can be achieved if T^2 is introduced into the pre-exponential multiplier instead of T. From the slope of straight line 3 (Fig. 1), plotted in the coordinates $\lg(i_\phi^{1/n_\tau}/T^2)$ and $1/T$, it follows that $\mathcal{E}_\phi = 1.77$ eV and coincides with $\mathcal{E}_{\lambda_{1/2}} = 1.78$ eV (^1).

Fig. 1. **1** –dependence of the nonlinearity exponent n on the temperature of the ribbon of the incandescent lamp (illumination level); **2** –photoelectric straight line calculated by the formula $i_\phi^{1/n_\tau}/T = A(\exp -\mathcal{E}_\phi/kT)$; **3** –the same, calculated by the formula $i_\phi^{1/n_\tau}/T^2 = A\exp(-\mathcal{E}_\phi/kT)$

The value ε_τ, determined from the temperature dependence of the electrical conductivity $\sigma = \sigma_0\exp(-\varepsilon_\tau/2kT)$ of an amorphous layer of chlorophyll a, is equal to 1.74 eV (Fig. 2, 1). This value is 0.62 eV greater than for crystalline chlorophyll a (^4). We again measured ε_τ for pure chlorophyll a + b, obtained at the Botanical Institute of the Academy of Sciences of the USSR, and obtained for the interval 35-65° a value of 1.77 eV, close to ε_τ of chlorophyll a. As for a number of dyes and pigments, in particular for chlorophyll analogs–phthalocyanines (^7) and blood pigments (^12)–the values ε_τ, $\mathcal{E}_{\lambda_{1/2}}$, and $\mathcal{E}_\phi$ for chlorophyll a almost coincide. Apparently, in layers of chlorophyll a, electrical conductivity is also realized with participation of the singlet excited state.

In the presence of oxygen, the dark current in a layer of chlorophyll a, in accordance with its hole nature of conductivity (⌒13), increases, while the activation energy decreases. After the layer has remained in oxygen (145 mm Hg) for two days, $\varepsilon_\tau = 1.63$ eV, and the conductivity is correspondingly greater by approximately a factor of 10 (Fig. 2, 2). Since in an oxygen atmosphere ε_τ is smaller than in vacuum, it is possible that the value 1.12 eV obtained by Rosenberg and Camiscoli (⌒4) is partly due to insufficiently complete removal of oxygen from the crystals, as the authors themselves indicate.

The increase in the photoconductivity of organic semiconductors with increasing temperature according to the law $\sigma_\phi = \sigma_0 \exp(-\varepsilon_\phi/kT)$ was first shown in our laboratory more than 20 years ago ($^{14\text{-}}$16). Since then this law has been confirmed by many authors for a large number of organic

photoconductors. We measured the temperature dependence of the photocurrent in chlorophyll **a** layers under vacuum conditions and at illuminances that ensured an increase in the photocurrent at 20° by more than two orders of magnitude. Straight line 3 in Fig. 2 was obtained upon illumination of the layer with light of λ695 mμ. The points on it correspond to measurements under constant illumination and heating of the layer, and the crosses to short-term illumination at the moment of measurement and cooling of the layer ($66 \div -28^\circ$). The energy $\varepsilon_\phi = 0.15$ eV. It is equal to the energy difference between the maxima of the spectral photocurrent curve (673, 624 and 580 mμ), which pertains to a very thin pigment layer (^{1}). ε_ϕ of chlorophyll **a**, as of many other organic photoconductors, is on average an order of magnitude smaller than ε_τ. Note that, as the photocurrent weakens as a result of cooling of the layer, the nonlinearity exponent increases from 0.8 to 1.0 (Fig. 2, 4).

Fig. 2. 1 –temperature dependence of the dark conductivity in vacuum; 2 –the same in oxygen (245 mm Hg); 3 –temperature dependence of the photoconductivity in vacuum; 4 –dependence of the nonlinearity exponent n on the temperature of the layer

Fig. 3. 1 –growth of the photocurrent during illumination of the layer in oxygen (245 mm Hg); 2 –decay of the photocurrent after cessation of illumination in coordinates i_ϕ and t; 3 –the same in coordinates $1/i_\phi$ and t

In paper (^{1}) it was noted that, in the presence of oxygen, the inertia of the photocurrent in a chlorophyll **a** layer increases. From Fig. 3, 1 it is seen that 3 min after the beginning of illumination of the layer in oxygen (245 mm Hg), the photocurrent is still far from its stationary value. The decay of the photocurrent in the dark lasts several tens of minutes (Fig. 3, 2). We had long ago shown (^{15,17}) that in layers of organic dyes the decay of the photocurrent after cessation of illumination follows, in vacuum, the hyperbolic law $1/i_t = 1/i_0 + kt$, where t is the time elapsed from the moment the light was switched off, i_0 is the initial photocurrent intensity, i_t is the photocurrent intensity at time t, and k is a constant. Later this regularity was confirmed by Nelson ([18]). The same law was established by us jointly with I. A. Karpovich ([19]) for the later stages of photocurrent decay in phthalocyanine layers containing oxygen. The hyperbolic law was also established for early (up to 0.01 sec) stages of photocurrent decay in layers of phthalocyanine ([20,21]), chlorophyll **a** + **b**, and pigments of the green leaf ([22]). As is seen from Fig. 3, 3,

15 sec after the illumination of the chlorophyll *a* layer is stopped, the decrease of the photocurrent over at least 30 min also follows the hyperbolic law corresponding to the bimolecular scheme of decrease in the number of charge carriers $di/dt = -\gamma i^2$.

Received
16 X 1962

CITED LITERATURE

1. A. T. Vartanyan, DAN, **149**, No. 3 (1963).
2. A. T. Vartanyan, Izv. AN SSSR, ser. fiz., **20**, 1541 (1956).
3. W. Arnold, N. Sherwood, Proc. Nat. Acad. Sci. USA, **43**, 105 (1957).
4. V. Rosenberg, J. F. Camiscoli, J. Chem. Phys., **35**, 982 (1961).
5. Ya. Tauts, Czechoslovak Phys. J., **4**, 236 (1954).
6. L. D. Rosenstein, Author' s abstract of dissertation, LGU, 1961.
7. A. T. Vartanyan, I. A. Karpovich, DAN, **111**, 561 (1956); ZhFKh, **32**, 274 (1958).
8. A. T. Vartanyan, I. A. Karpovich, DAN, **113**, 1020 (1957).
9. A. T. Vartanyan, I. A. Karpovich, ZhFKh, **32**, 543 (1958).
10. A. T. Vartanyan, *Materials of the V All-Union Conference on Luminescence*, Tartu, 1957, p. 159.
11. A. T. Vartanyan, L. D. Rosenstein, DAN, **124**, 595 (1959).
12. A. T. Vartanyan, DAN, **143**, 1317 (1962).
13. E. K. Pucheiko, A. N. Terenin, DAN, **136**, 1223 (1961).
14. A. T. Vartanyan, A. N. Terenin, J. Phys. USSR, **4**, 173 (1941).

15. A. T. Vartanyan, ZhFKh, **20**, 1065 (1946).

16. A. T. Vartanyan, ZhFKh, **24**, 1361 (1950).

17. A. T. Vartanyan, *Collection Dedicated to the Memory of Acad. P. P. Lazarev*, Publishing House of the Academy of Sciences of the USSR, 1956, p. 30.

18. R. C. Nelson, J. Chem. Phys., **19**, 798 (1951); **20**, 1327 (1952); **22**, 885, 890, 892 (1954).

19. A. T. Vartanyan, I. A. Karpovich, DAN, **111**, 561 (1956); ZhFKh, **32**, 178 (1958).

20. E. K. Pucheiko, DAN, **132**, 1299 (1960).

21. G. Tollin, D. R. Kearns, M. Calvin, J. Chem. Phys., **32**, 1013 (1960).

22. E. K. Pucheiko, DAN, **138**, 1381 (1961).

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