KINETICS OF THE PHOTOCONDUCTIV-ITY OF CHLOROPHYLL AND PIGMENTS OF THE GREEN LEAF

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KINETICS OF THE PHOTOCONDUCTIVITY OF CHLOROPHYLL AND PIGMENTS OF THE GREEN LEAF

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In the work of Nelson ([1]), who studied the photoconductivity of chlorophyll *a* and methylchlorophyllide *a*, the rise and decay of the photocurrent in time had two different time constants: less than a second and on the order of several minutes. He attributed the two time constants to two different forms of pigment aggregation—colloidal and crystalline.

In the present work, relaxation processes in solid layers of chlorophyll and its analogs were studied at the very initial stages of the rise and decay of the photocurrent. The objects of investigation were crystalline layers of chlorophyll $(a + b)$ and methylchlorophyllide $(a + b)$, isolated at the Botanical Institute of the Academy of Sciences of the USSR. In addition, pigments of green leaves of nettle and jasmine, isolated from an acetone extract, were investigated. Such an extract contains, in addition to chlorophylls *a* and *b*, the principal carotenoids of the leaf (β-carotene, lutein, violaxanthin, and neoxanthin) and the lipoproteid fraction of destroyed chloroplasts. Although in the process of extraction the lipoproteid complex is destroyed, one may expect that the chlorophyll still remains bound to the carotenoids, and its phytol chain to the lipoids.

The layers under investigation were deposited from concentrated solutions of the pigments in chloroform or acetone onto quartz plates bearing on their surface evaporated platinum electrodes in the form of two combs with gaps of 0.1 mm. A voltage of 100–200 V was applied to the photoresistance electrodes. The thickness of the layers varied from 0.01 to 1 μ.

The relaxation of the photoconductivity of chlorophyll layers, as in the case of phthalocyanines ([2]), was investigated by the taumeter method ([3]), which made it possible to observe the entire course of the process of rise and decay of the photocurrent in the time interval from $5 \cdot 10^{-6}$ to 10^{-2} sec. Illumination was produced by visible light, modulated at a frequency of 100 cps, from an SVDSH-120 mercury lamp, isolated by a yellow ZhS-12 light filter (2 mm thick). The illumination intensity ranged from 10^{-3} to 10^{-5} W/cm^2.

1. Investigation of the kinetics of photoconductivity of crystalline layers of chlorophyll $(a+b)$ in air at room temperature showed that the processes of

Fig. 1

Figure 1: Fig. 1

rise and decay of the photocurrent, for all the samples studied, occur over a wide time interval, from several microseconds to seconds and minutes. Fig. 1 presents photographs of oscillograms of the relaxation curves of the rise and decay of the photocurrent in time for samples of crystalline chlorophyll $(a+b)$ in air, in linear (A) and exponential (B) sweeps. During illumination by a rectangular light pulse of duration 10^{-2} sec, the photoconductivity in layers of chlorophyll $(a+b)$ in air does not reach its stationary value. The curves of photocurrent rise are in most cases symmetrical to the decay curves. The fraction of the inertial component is large and amounts to almost 80% of the "maximum" value of the photocurrent. In general form, the character of the rise and decay of the photocurrent does not obey an exponential law.

With the aid of an exponential sweep, on individual sections of the decay curve one can distinguish three exponents with a short time constant

$\tau_1^{\text{decay}} = 3 \cdot 10^{-5}$ sec and longer $\tau_2^{\text{decay}} = 6 \cdot 10^{-3}$ sec, $\tau_3^{\text{decay}} = 1.7 \cdot 10^{-2}$ sec. Determination of the form of the law of photocurrent decay in the objects under study was carried out using the plot of "instantaneous" relaxation times (4). In Fig. 2, 1 the decay of the photocurrent with time is shown for a layer of chlorophyll $(a+b)$ in air, measured on a tau-meter with exponential sweep by the method of "partial times." Curve $1'$ of the same figure gives the "instantaneous" relaxation times θ, characterizing the reciprocal value of the logarithmic derivative of the photocurrent with respect to time. Analysis of the decay curves using such plots showed that, in the interval of fast times from several microseconds to 10^{-3} sec, the decay of the photocurrent obeys the hyperbolic law

Fig. 1. Kinetics of the photoconductivity of chlorophyll $(a+b)$: a—chlorophyll $(a+b)$ in air at $+20^\circ$, $\tau_1^{\text{decay}} = 3 \cdot 10^{-5}$ sec (1), $\tau^{\text{hl}} = 5 \cdot 10^{-3}$ sec (2); b—the same layer as in a, in a vacuum of 10^{-5} mm Hg, $\tau_1^{\text{decay}} < 5 \cdot 10^{-6}$ sec (1), $\tau_3^{\text{decay}} = 2 \cdot 10^{-2}$ sec (2); c—the same layer as in b, after admission of air, $\tau_1^{\text{decay}} = 5 \cdot 10^{-6}$ sec (1), $\tau^{\text{hl}} = 2.6 \cdot 10^{-3}$ sec (2)

$$I_{\text{decay}} = I_0/(1+at)^{\alpha},$$

which indicates a bimolecular process of charge recombination. This basic result was obtained for different layers of crystalline chlorophyll under different conditions.

Experiments showed that the same layers of chlorophyll $(a+b)$, after removal of air by pumping even at room temperature, sharply reduce their inertia. Figure 1b shows curves of the change of the photocurrent with time in vacuum upon

Figure 2

Figure 2: Figure 2

switching the light on and off for one of the tested layers of crystalline chlorophyll $(a+b)$, in linear (A) and exponential (B) sweeps.

From the data presented it is evident that the fraction of the slow component of photocurrent decay in vacuum amounts to 50% of the stationary value, while the inertia of the fast and slow components decreases by a factor of 5 or more. At the very initial stages, the rise and decay of the photocurrent proceed at a rate exceeding the time constant of the instrument itself. In the curves of photocurrent rise under vacuum conditions, "instantaneous" jumps of the photocurrent are observed, apparently caused by additional transitions of electrons, possessing greater duration, from finer levels of the crystal*. The rise of the photocurrent proceeds at a higher rate than the decay.

In the exponential sweep, on individual sections of the decay curves one can distinguish three exponents with very short (less than a microsecond) and longer times $\tau_2^{\text{hl}} = 10^{-4}$ sec.** and $\tau_3^{\text{decay}} = 1.2 \cdot 10^{-2}$ sec. As in air, the decay of the photocurrent in vacuum after the illumination is switched off is described in chlorophyll layers by a hyperbolic law (Fig. 2, 2 and 2′). The phenomenon is reversible, and after admission of air the duration of the photoelectric processes again increases (Fig. 1c). Adsorbed quinone vapors at a pressure of about 0.02 mm Hg have the same effect on the kinetics of photoconductivity as air. In contrast, the admission of water vapor at a pressure of 14 mm Hg to a previously evacuated chlorophyll sample has no noticeable effect on the relaxation of the pho-

* This question requires more detailed investigation.

** τ_2^{hl}—half-life time.

does not affect the photoconductivity. Apparently, in air or in quinone vapor, the electrons in the chlorophyll molecules are localized at trapping levels, which increases the duration of recombination processes.

2. Experiments with films of crystalline methylchlorophyllide $(a+b)$, containing a small amount of carotenoids—lutein and violaxanthin—showed that the rise and decay of the photocurrent, as in chlorophyll, proceed over a broad time interval. In Fig. 3a, typical curves are given for the rise and decay of the photocurrent with time for methylchlorophyllide $(a+b)$ on linear (A) and exponential (B) sweeps with two different time constants. $\tau_1^{\text{decay}} = 2 \cdot 10^{-4}$ sec. $(B, 1)$; $\tau^{\text{rise}} = 1.3 \cdot 10^{-3}$ sec. $(B, 2)$.

Fig. 2. 1—decay of the photocurrent of chlorophyll $(a+b)$ in air on an exponential sweep; 2—the same as 1, in vacuum. "Instantaneous relaxation times" of chlorophyll $(a+b)$: 1′—in air $(\alpha = 0.28)$, 2′—in vacuum $(\alpha_1 = 0.45$ and $\alpha_2 = 0.125)$.

Figure 3

Figure 3: Figure 3

Fig. 4

Figure 4: Fig. 4

Likewise, as in the case of chlorophyll $(a + b)$, evacuation of air in films of methylchlorophyllide $(a + b)$ noticeably reduces the inertia. Under vacuum conditions, the fraction of the fast component reaches 50% of the stationary value of the photocurrent, while the inertia of the slow component decreases by a factor of 3 or more (Fig. 3b).

Fig. 3. Kinetics of photoconductivity:
a—methylchlorophyllide $(a + b)$ in a mixture with carotenoids (lutein, violaxanthin) in air at +20°, $\tau_1^{\text{decay}} = 2 \cdot 10^{-4}$ sec. (1), $\tau^{\text{rise}} = 1.3 \cdot 10^{-3}$ sec. (2);
b—the same layer as in a, in vacuum 10^{-5} mm Hg, $\tau_1^{\text{decay}} = 7 \cdot 10^{-5}$ sec. (1), $\tau^{\text{rise}} = 8 \cdot 10^{-4}$ sec. (2);
c—pigments of the green leaf in air at +20°, $\tau_1^{\text{decay}} = 4 \cdot 10^{-6}$ sec. (1), $\tau_3^{\text{decay}} = 1.2 \cdot 10^{-2}$ sec. (2).

Analysis of the photocurrent decay curves in layers of methylchlorophyllide with the aid of a plot of "instantaneous" relaxation times shows that, both in air and in vacuum, the initial stages of the photoconductivity decay follow a hyperbolic law (Fig. 4, 1 and 1′).

3. In contrast to crystalline layers of chlorophyll and methylchlorophyllide $(a + b)$, leaf pigments isolated from an extract of green leaves of plants already in air exhibit considerably shorter relaxation times. In Fig. 3c, curves are given for the rise and decay of the photocurrent in leaf pigments with time upon switching on and

turning off the light at time intervals of 0.02 sec. As is evident from these curves, for leaf pigments containing a mixture of chlorophyll $(a+b)$ with carotenoids (β-carotene, violaxanthin, lutein, and neoxanthin) and the lipoprotein fraction of destroyed chloroplasts, the rise of the photocurrent occurs more rapidly than the decay. As with chlorophyll in vacuum, in the curve of the rise of the photocurrent of leaf pigments in air, "instantaneous" jumps are observed. During illumination for 10^{-2} sec, the photocurrent very rapidly reaches its stationary value. After the illumination is switched off, at the very initial moment the photocurrent drops sharply, shows a bend, and then slowly approaches the initial value. In the exponential sweep, in individual portions of the photocurrent decay one can distinguish two time constants—a very short one, $\tau_1^{\text{decay}} = 4 \cdot 10^{-6}$ sec, and a longer one, $\tau_3^{\text{decay}} = 10^{-2}$ sec.

Fig. 4. 1—decay of the photocurrent of methylchlorophyllide $(a + b)$ with carotenoids (lutein, violaxanthin) in vacuum in an exponential sweep; 2—the

same as 1 for green-leaf pigments; "instantaneous relaxation times" : $1'$—methylchlorophyllide $(a+b)$ $(\alpha = 0.8)$, $2'$—green-leaf pigments $(\alpha_1 = 0.32$ and $\alpha_2 = 0.20)$.

As with crystalline chlorophyll $(a+b)$ in vacuum, the decay of the photocurrent in the case of an extract of green-leaf pigments in the time interval from 10^{-5} to 10^{-3} sec in air can be approximated by the sum of two hyperbolas (Fig. 4, 2 and $2'$) with $\alpha_1 = 0.32$ and $\alpha_2 = 0.20$.

The small inertia of the processes of release and disappearance of electronic vacancies (positive holes) in solid films of chlorophyll $(a+b)$, methylchlorophyllide $(a+b)$, and leaf pigments established in this work[5] shows that we are dealing with a primary process. The pronounced dependence of the relaxation of photoconductivity in these pigments on adsorbed vapors and gases indicates capture of electrons from the excited chlorophyll molecule by traps present in pigment crystals. Experiments with an extract of green-leaf pigments show that the residues of chloroplast lipoproteins, on which carotenoids and chlorophyll are fixed, not only do not hinder the motion of charges, but make this process in air less inertial.

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