PHOTOCONDUCTIVITY OF ORGANIC DYES AT A FREQUENCY OF \(10^{10}\) Hz

Physics

1966

SovietRxiv

Abstract

Full Text

UDC 535.215

Physics

L. N. IONOV, I. A. AKIMOV, Academician A. N. TERENIN

PHOTOCONDUCTIVITY OF ORGANIC DYES AT A FREQUENCY OF 10^{10} Hz

Determining the mechanism of photoconductivity in organic dyes is greatly complicated by the fact that the studies are usually carried out on powders or films, which constitute a heterogeneous system. The measurements may then be distorted by such effects as the resistances of intercrystalline contacts, phenomena at electrodes, surface conductivity, etc. Confirmation of this is provided by the experimentally observed strong dependence of the semiconductor properties of organic substances on the influence of the surrounding atmosphere and on the structure of the layer, the dependence of the resistance of specimens on the frequency of the electric field and on pressure, the influence of the nature of the contacts on the conductivity, and so forth. Bulk conductivity can be investigated on single-crystal specimens; however, such measurements have been made only for phthalocyanines [1–3].

Another approach is to measure the electrical conductivity of polycrystalline specimens with high-frequency alternating current, when the influence of intercrystalline barriers between individual grains is eliminated by shunting them with intercrystalline capacitances. Indeed, for phthalocyanine powders an increase in conductivity with the frequency of the external field was found up to frequencies of 10^8 Hz [4]. Earlier, the broad possibilities for applying microwave techniques to the study of photoeffects in such heterogeneous systems as lead sulfide photoresistors [5] and photographic layers [6] had been demonstrated. However, the electrical conductivity and photoconductivity of organic substances at microwave frequencies had not previously been studied. In the present work, microwave photoconductivity ($\Delta\sigma_\sim$) of organic dyes of various classes has been detected and investigated.

For measuring $\Delta\sigma_\sim$, an EPR radiospectrograph with a transmission resonator and without the use of a magnetic field was employed [6]. A dye specimen in the form of a thin layer (10^{-4}—10^{-3} cm) on a mica disk 5.3 cm in diameter was placed at the maximum of the electric field of a cylindrical resonator of the H_{012} type (quality factor with specimen 10^4). The microwave power generated by a klystron (ν = 9600 MHz, P = 50 mW) passed through the resonator with the specimen and was recorded by a bolometer. When the specimen was illuminated through an aperture in the resonator, a microwave photocurrent

Figure 1. Spectral distribution of photoconductivity at microwave frequencies ($\Delta\sigma_{\sim}$) of copper polyphenylacetylenide.

Figure 1: Figure 1. Spectral distribution of photoconductivity at microwave frequencies ($\Delta\sigma_{\sim}$) of copper polyphenylacetylenide.

arose in the specimen, causing an increase in losses in the resonator and a corresponding decrease in the microwave power passing through it. When the specimen was illuminated with light modulated at a frequency of 150 Hz, the bolometric detector selected a signal of the same frequency, proportional to the microwave photoconductivity. The signal was amplified by a narrow-band amplifier and, after rectification by a synchronous detector, was recorded by a self-recording potentiometer. The circuit employed automatic tuning of the klystron frequency, which made it possible to eliminate its frequency noise. The specimens were illuminated by a tungsten incandescent lamp through a water filter. For spectral measurements a set of interference filters was used, followed by recalculation of the $\Delta\sigma_{\sim}$ spectrum to equal incident energy. In the present work the temperature of the specimen was varied from $+100$ to -170° and was measured with a copper–constantan thermocouple, one of whose junctions

which was in contact with the layer under investigation inside the resonator. The silver-plated resonator made of invar was placed in a casing which, for cooling, was filled with liquid nitrogen. The resonator was heated by an electric furnace wound on its outer surface. The resonator was sealed and could be pumped down to 10^{-3} torr. The intensity of the microwave electric field on the sample was kept constant at all times as the Q factor of the resonator changed with temperature. The kinetics of photoconductivity at microwave frequencies was studied under steady illumination on another setup assembled according to a scheme analogous to (7).

Photoconductivity at microwave frequencies was found in a large number of the dyes investigated, belonging to various classes—triphenylmethane, xanthene, cyanine, porphyrin, and others. $\Delta\sigma_{\sim}$ was observed both under modulated and under steady illumination. It should be noted that, in the apparatus used, automatic adjustment of the klystron frequency in the case of steady illumination completely rules out manifestation of the photoelectric effect, and the recorded signal is due to free carriers of the photocurrent. Photoconductivity at microwave frequencies was observed not only in synthetic organic dyes, but also in natural pigments of the green leaf. In this case the specific capabilities of microwave techniques made it possible to observe the photoconductivity of pigments not only in cases where they were isolated as microcrystalline powders, but also for pigments extracted together with lipoids, and even directly in the green leaf. In the latter case, before a fresh green leaf was placed in the resonator, it had to be somewhat dried in order to reduce absorption of microwave power by water. $\Delta\sigma_{\sim}$ was observed for the following samples: crystalline chlorophyll a + b—

Fig. 1. Spectral distribution of photoconductivity at microwave frequencies ($\Delta\sigma_{\sim}$) of copper polyphenylacetylenide

Table 1

No.	Dye	Form of aggregation of the sample	Temperature interval, °C	Activation energy E_1, eV	Temperature interval, °C	Deactivation energy E_2, eV
1	Basic bright-green oxalate	Polycryst.	+100 ÷ −70	0.10	–	–
1	Basic bright-green oxalate	Polycryst.	−70 ÷ −150	0.03	–	–
2	Malachite green oxalate	Amorph.	+100 ÷ −70	0.10	–	–
3	[[structural formula]] *	Polycryst.	+100 ÷ −70	0.10	–	–
4	Metal-free phthalocyanine	Polycryst. (α-form)	+100 ÷ −50	0.05-0.15	–	–
5	Basic bright-green sulfate	Amorph.	+40 ÷ −100	0.09	+85 ÷ +45	0.16
6	Crystal violet	Polycryst.	−15 ÷ −120	0.09	+20 ÷ −15	0.22
7	3,3′-Diethyl-4,5,4′,5′-dibenzoxacarbocyanine-*n*-toluenesulfonate	Same	0 ÷ −70	0.12	+100 ÷ 0	0.12
8	2,2′-Diethylthiacarbocyanine iodide	» »	+45 ÷ −100	0.18	+100 ÷ +45	0.38
9	Pinacyanol iodide	» »	−10 ÷ −90	0.05	+100 ÷ −10	0.12

Figure 2

Figure 2: Figure 2

No.	Dye	Form of aggregation of the sample	Temperature interval, °C	Activation energy E_1, eV	Temperature interval, °C	Deactivation energy E_2, eV
10	Basic bright-green sulfate	» »	−20 ÷ −50	0.20	+20 ÷ −20	0.22
10	Basic bright-green sulfate	» »	−140 ÷ −170	0.09	−50 ÷ −120	0.02
11	Copper polyphenylacetylenide	» »	–	–	+20 ÷ −90	0.06

* Macrocyclic pigment synthesized by R. P. Smirnov (Ivanovo, Chemical-Technological Institute).

crystalline, chlorophyll + lipids + quinone, xanthophylls, a mixture of pigments with lipoids extracted from petroleum (or sulfur) ether, chloroplasts of blue-green algae, and green leaves of various plants*.

The study of the inertia of $\Delta\sigma_{\sim}$ on an apparatus with constant illumination showed that the kinetic curves for different dyes are approximately similar. They contain both fast and slow stages of rise and decay of the photocurrent (from 10^{-3} to 10^{2} sec.). The photoconductivity of dye layers varied with illumination according to the law $\Delta\sigma_{\sim} = kL^{\alpha}$, where α decreased from 1 to 0.5 with increasing illumination L, i.e., in the same way as for photoconductivity at direct current ($\Delta\sigma_{=}$). The region of spectral sensitivity of $\Delta\sigma_{\sim}$ corresponded to the absorption spectra of the layers and $\Delta\sigma_{=}$. Fig. 1 gives the spectral curve of $\Delta\sigma_{\sim}$ for copper polyphenylacetylide*. It is similar to the spectral distribution of dc photoconductivity for this polymer ([8]).

Fig. 2. Temperature dependence of microwave photoconductivity ($\Delta\sigma_{\sim}$) of crystalline and amorphous dye layers (the numbers of the curves indicate the ordinal number in Table 1; for convenience, the curves are arbitrarily shifted along the ordinate axis)

A considerable part of the work was devoted to studying the dependence of photoconductivity on temperature. The results of the measurements are shown

in Fig. 2 and in Table 1. The investigated substances can be divided into three groups according to the temperature dependence of $\Delta\sigma_{\sim}$.

The first group includes dyes whose photoconductivity increased with increasing temperature over the entire investigated temperature range. A similar dependence is usually observed for the photoconductivity of dyes under constant voltage. The values of the thermal activation energy of microwave photoconductivity, determined from Fig. 2 by the formula

$$\Delta\sigma_{\sim} = Ae^{-E_1/kT},$$

are given in Table 1.

In the second group of dyes, usually in the low-temperature region, $\Delta\sigma_{\sim}$ at first also increased with increasing temperature, and then, beginning at some temperature, $\Delta\sigma_{\sim}$ decreased as the temperature rose. For these dyes, the table gives both the activation energy E_1 and the deactivation energy E_2, determined from the formula

$$\Delta\sigma_{\sim} = Ae^{-E_1/kT} + Be^{E_2/kT},$$

with indication of the corresponding temperature intervals. Let us note that in polycrystalline

* We express our gratitude to E. K. Putseiko and I. A. Popova for providing pigment samples and to A. M. Sladkov for providing the polymer.

layers of the dye basic bright green sulfate, the intervals of increase and decrease of $\Delta\sigma_{\sim}$ alternate twice as T increases.

Finally, in the case of copper polyphenylacetylenide, $\Delta\sigma_{\sim}$ decreased with increasing temperature over the entire temperature interval investigated.

The fact that $\Delta\sigma_{\sim}$ exists indicates the possibility of the formation of free photocurrent carriers in the volume of crystals and amorphous layers and the presence of bulk photoconductivity in dyes. Some properties of $\Delta\sigma_{\sim}$ are analogous to the properties of $\Delta\sigma_{=}$, but there are also substantial features. As is known, $\Delta\sigma_{=}$ of dyes has a positive temperature coefficient with a thermal activation energy of the order of 0.2-0.5 eV ([9]). According to the assumption ([10,11]), the temperature dependence of $\Delta\sigma_{=}$ is determined by the fact that the quantum yield of the photoeffect and the mobility of the photocurrent carriers depend exponentially on temperature, with activation energies of 0.05-0.2 and 0.2-0.5 eV, respectively. The results of the temperature studies of $\Delta\sigma_{\sim}$ indicate the necessity of thermal activation of bulk photoconductivity in dyes. The values of this energy for the dyes studied, as is seen from Table 1, lie in the interval 0.05-0.2 eV. This thermal energy is apparently needed for dissociation of the exciton in accordance with the assumption ([10,11]), and possibly also for intermolecular displacements of the photocurrent carriers in the dye crystal. Temperature

quenching of the photoconductivity in the case of copper polyphenylacetylenide over the entire temperature range investigated evidently indicates the direct formation of photocurrent carriers under the action of absorbed photons without additional thermal activation, analogous to the photoeffect in inorganic semiconductors. In the more complicated case of the second group of dyes, following the process of thermal activation of photoconductivity with an energy of 0.05-0.2 eV, a process of deactivation of $\Delta\sigma_{\sim}$ with an energy of 0.1-0.4 eV appears. The mechanism of this quenching of $\Delta\sigma_{\sim}$ in dyes with temperature is not yet clear and requires additional studies. It should be noted that an analogous temperature dependence with similar activation and deactivation energies has been established for the photoinduced EPR signal in dyes, which characterizes the concentration of light-excited current carriers ([10,12]).

The discovery of bulk photoconductivity in a living green leaf is important, since it unambiguously testifies to the occurrence of free current carriers in the granules of the leaf as a result of absorption of visible light. In this respect the photocurrents in granules are similar to photocurrents in microcrystals of isolated pigments. Further application of microwave techniques, with their specific capabilities, appears promising for the study of photosemiconductor phenomena in connection with the process of photosynthesis not in model systems, but directly in natural objects.

We express our gratitude to V. E. Kholmogorov for discussions of the work.

Received
1 IV 1966

REFERENCES CITED

1. P. E. Fielding, F. Gutman, J. Chem. Phys., **26**, 411 (1957); P. E. Fielding, A. G. MacKay, J. Chem. Phys., **38**, 2777 (1963).

2. J. Curry, E. P. Cassid , J. Chem. Phys., **37**, 2454 (1963).

3. G. H. Heilmeier, G. Warfield, J. Chem. Phys., **38**, 163, 897 (1963).

4. C. M. Huggins, A. H. Sharbaugh, J. Chem. Phys., **38**, 393 (1963).

5. V. G. Erofeichev, L. N. Kurbatov, FTT, **3**, 595, 3329 (1961); Collection: *Physics of the Solid State*, **1**, 1959, p. 133.

6. E. V. Baranov, I. A. Akimov, DAN, **154**, 184 (1964).

7. E. M. Trukhan, *Instruments and Experimental Techniques*, No. 4, 198 (1965).

8. V. S. Mylnikov, A. N. Terenin, DAN, **153**, 1381 (1963).

9. A. T. Vartanyan, *Izv. AN SSSR, ser. fiz.*, **16**, 169 (1952); **20**, 1541 (1956).

10. A. M. Meshkov, V. E. Kholmogorov, DAN, **160**, 394 (1965).

11. A. M. Meshkov, FTT, **7**, 3468 (1965).

12. B.-Y. Cho, R. C. Nelson, L. C. Brown, J. Chem. Phys., **39**, 499 (1963).

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