Soviet-era science, translated into English

PHYSICAL CHEMISTRY

V. S. MYLNIKOV, Academician A. N. TERENIN

1963

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196301.04407

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. S. MYLNIKOV, Academician A. N. TERENIN

PHOTON-SEMICONDUCTOR PROPERTIES OF METAL ACETYLIDES

Interest in the study of the semiconductor properties of organic compounds is steadily increasing. In our laboratory, an internal photoeffect was discovered ([1]) in polymers containing triple bonds in the conjugation chain.* In subsequent works ([6,7]), the spectral characteristics of the diffusion photo-emf, photoconductivity, and also the relaxation of photoconductivity and other properties of certain polyynes were studied. The dark semiconductor properties of polyacetylenes were also studied ([3,8]). Until now only polymers and oligomers with triple bonds had been investigated. To clarify the mechanism of the generation and transfer of charge in these substances, the following monomers with triple bonds, synthesized by A. M. Sladkov and co-workers ([2]), were examined: copper phenylacetylide (I), copper *p*-phenylenediacetylide (II), silver phenylacetylide (III), and silver *p*-phenylenediacetylide (IV).

$$\mathrm{Cu-C\equiv C-C_6H_5} \qquad \text{(I)}$$

$$\mathrm{Cu-C\equiv C-C_6H_4-C\equiv C-Cu} \qquad \text{(II)}$$

$$\mathrm{Ag-C\equiv C-C_6H_5} \qquad \text{(III)}$$

$$\mathrm{Ag-C\equiv C-C_6H_4-C\equiv C-Ag} \qquad \text{(IV)}$$

Measurements of the photoelectric sensitivity were carried out by the method of diffusion photo-emf in a capacitor ([9,10]) with a modulation frequency of 300 Hz, and by the method of transverse photoconductivity under direct current in air and in vacuum of 10^{-4}–10^{-5} mm Hg. In studying the diffusion photo-emf, compounds (I–IV) were used in the form of powders. Photoresistors for the photoconductivity method were prepared by depositing suspensions of substances I–IV in dimethylformamide onto quartz substrates with platinum electrodes. The platinum electrodes had the form of two "combs," each with 10 teeth, with a distance between neighboring teeth of 0.1 mm. The layer thickness was 1–5 μ. When measuring photoconductivity, for thermostating purposes, the quartz

SovietRxiv

Fig. 1. Kinetics of the photoconductivity of copper phenylacetylide: 1—in air, 2—in vacuum

Figure 1: Fig. 1. Kinetics of the photoconductivity of copper phenylacetylide: 1—in air, 2—in vacuum

substrate 1 mm thick was pressed against the flat polished face of a glass finger filled with water and located inside a glass vessel with a quartz window for illuminating the sample. A voltage of 10—30 V was applied to the electrodes of the photoresistor. To measure the spectral distribution of photoconductivity and photo-emf in the region 300—700 mμ, a monochromator with a diffraction grating of luminosity 1:5 was used. The source was a xenon lamp GSVd-120. The spectral distribution of the radiation varied over the spectrum from 10^{12} to 10^{15} quanta/sec. The spectral curves of photo-emf and photoconductivity were recalculated to the same number of incident quanta; for this purpose, by changing the widths of the monochromator slits, spectra were recorded at intensities for which the dependence of the photo-emf and photoconductivity on illumination was linear with an accuracy of up to 10%. The reflection spectrum of copper phenylacetylide was measured on an SF-4.

In all the substances studied, I-IV, a diffusion photo-emf and photoconductivity were found in the visible and ultraviolet regions of the spectrum. In this case the photosensitivity decreased in going from I to IV. It should be noted that III, IV, containing silver atoms, proved photochemically sensitive and, in detail, could not be studied by this method. Therefore our main attention was devoted to compounds containing copper atoms, and especially to copper phenylacetylide, which was the most photoelectrically sensitive.

Fig. 1. Kinetics of the photoconductivity of copper phenylacetylide: **1**—in air, **2**—in vacuum.

The resistance of a layer of copper phenylacetylide in the dark was, for different specimens, 10^9-10^{10} Ω. On illumination with monochromatic light ($\lambda = 500$ mμ) the resistance fell to 10^7-10^8 Ω. Thus, in individual cases the photocurrents reached 10^{-6} A. Figure 1 shows the course of the rise and decay of the photocurrent in a layer of copper phenylacetylide in air (1) and in vacuum (2) at the same intensity of monochromatic illumination ($\lambda = 500$ mμ). It is seen from the figure that, when the light is switched on, the photocurrent reaches a stationary value in approximately 2 min, while the decay of the photocurrent after the light is switched off requires up to 10 min. Pumping the air out of the vessel leads to an increase in the inertia of the photoconductivity relaxation. It was

---

* The polymers were synthesized in the laboratory of V. V. Korshak at the Institute of Organoelement Compounds of the Academy of Sciences of the USSR under the direction of A. M. Sladkov ($^{2-5}$).

SovietRxiv

Fig. 2. 1—absorption spectrum of copper phenylacetylide. Spectral distribution of the photoconductivity of copper phenylacetylide (2), photo-emf of copper phenylacetylide (3)

Figure 2: Fig. 2. 1—absorption spectrum of copper phenylacetylide. Spectral distribution of the photoconductivity of copper phenylacetylide (2), photo-emf of copper phenylacetylide (3)

also established that in vacuum the dark conductivity of copper phenylacetylide increases by 1-1.5 orders of magnitude compared with the conductivity in air.

Figure 2 (1) gives the spectral distribution of the absorption of copper phenylacetylide, calculated by the formula $(1-R)$, where R is the coefficient of diffuse reflection. In the same Fig. 2, in arbitrary units, are given the spectral distribution of the photoconductivity (curve 2) and of the diffusion photo-emf (curve 3). In air and in vacuum the form of the photoconductivity and photo-emf spectra is preserved. The spectral curve of the photoconductivity has two clearly expressed maxima at 430 mμ and 500 mμ (Fig. 2 (2)). Attention is drawn to the fact that the photoconductivity falls in the region of strong absorption and reaches its maximum value when the absorption decreases. Such a relationship between the spectral course of absorption and the photoconductivity spectrum, as is known, is quite common in photosemiconductors and is explained by a decrease in the lifetime of the photocurrent carriers in the region of strong absorption owing to an increase in the rate of surface recombination. We note that an analogous character of the spectral course of absorption and photoconductivity was obtained by us also for polymeric compounds with triple bonds in the conjugation chain (7). If the magnitude of the optical activation energy is estimated by Moss’ s method (11), then it should be taken as equal to 2.40 ± 0.02 eV. The threshold value for the appearance of the diffusion photo-e.m.f. also corresponds to this energy (Fig. 2(3)). The spectrum of the diffusion photo-e.m.f., like the photoconductivity spectrum, shows two maxima, namely at 390 and 460 mμ. Moreover, each maximum in the photo-e.m.f. spectrum is shifted relative to the corresponding maximum of the photoconductivity spectrum by 40 mμ. The appearance of maxima in the photoconductivity spectrum (430 mμ and 500 mμ) and in the photo-e.m.f. (390 mμ and 460 mμ) is probably due to the presence of photoactive impurities remaining in the substance during synthesis. It should be noted that, in contrast to photoconductivity, the photo-e.m.f. increases in the ultraviolet direction with increasing absorption of copper phenylacetylide, which is explained by an increase in the concentration gradient of the carriers of the diffusion photocurrent with increasing absorption coefficient. A shift of the photoconductivity spectrum toward longer wavelengths relative to the

Fig. 2. **1**—absorption spectrum of copper phenylacetylide. Spectral distribution of the photoconductivity of copper phenylacetylide (**2**), photo-emf of copper phenylacetylide (**3**).

SovietRxiv

Fig. 3. Spectral distribution of the photo-e.m.f. of copper
n-phenylenediacetylide

Figure 3: Fig. 3. Spectral distribution of the photo-e.m.f. of copper *n*-phenylenediacetylide

photo-e.m.f. spectrum was also observed for polyynes (^{7}), as well as for other semiconductors (^{12}).

Fig. 3. Spectral distribution of the photo-e.m.f. of copper *n*-phenylenediacetylide

The sign of the carriers of the diffusion photocurrent, determined by the method described earlier (^{10}), is positive. In vacuum the magnitude of the photo-e.m.f. increases by a factor of 3–5 compared with the signal in air. It might have been expected that in a hole semiconductor, under the action of oxygen, which is an electron acceptor, the photo-e.m.f. in air would be greater than in vacuum. In the present case the photo-e.m.f. slowly increases as the vacuum improves. It is possible that this is due to the pumping out of water vapor from the vessel. This, apparently, should also explain the greater inertia of the photoconductivity and the increase in the dark conductivity of copper phenylacetylide in vacuum compared with the inertia and dark conductivity in air, which should not occur for a hole semiconductor if it is assumed that the sign of the dark and light carriers is the same and that oxygen affects the photoeffect.

The hole nature of the photocurrent carriers has also been established for copper *n*-phenylenediacetylide (II), whose diffusion photo-e.m.f. spectrum is shown in Fig. 3. The photo-e.m.f. spectrum of copper *n*-phenylenediacetylide is shifted toward the long-wavelength side in comparison with the photo-e.m.f. spectrum of copper phenylacetylide and likewise has two maxima on the falling part of the curve, at 380 and 470 mμ, which is probably also due to the action of photoactive impurities. The presence, in copper *n*-phenylenediacetylide, of a maximum at 320 mμ suggests that in copper phenylacetylide as well, at wavelengths shorter than 300 mμ, a decline of the photo-e.m.f. will be observed.

In contrast to the previously investigated polyynes (^{1}, ^{6}, ^{7}), the monomers studied do not show the characteristic increase in photoelectric sensitivity after preliminary illumination with ultraviolet light.

The metal acetylides investigated, despite the small extent of their conjugated bond system, possess photoconductivity and a photo-e.m.f. exceeding those observed in polymers of the polyacetylene class (^{1}, ^{6}, ^{7}). This clearly shows that in the present case the determining factor for phototransport is not a great length of conjugated bonds in the molecule, but intermolecular configurational interactions that lower the potential barriers at the boundaries between macromolecules. In these compounds with heavy metals, such interaction between molecula-

is effected by bridges of π-complexes of electron-acceptor copper atoms with

SovietRxiv

acetylene bonds, functioning as electron donors (2).

In conclusion, we express our gratitude to V. V. Korshak and A. M. Sladkov for providing the acetylides.

Received
20 VI 1963

References

1. V. S. Mylnikov, A. M. Sladkov et al., DAN, **144**, No. 4, 840 (1962).
2. V. V. Korshak, A. M. Sladkov, Yu. P. Kudryavtsev, *Vysokomolek. soed.*, **2**, No. 12, 1824 (1960).
3. V. V. Korshak, V. I. Kasatochkin et al., DAN, **136**, No. 6, 1342 (1961).
4. V. V. Korshak, A. M. Sladkov, Yu. P. Kudryavtsev, DAN, **144**, No. 1, 115 (1962).
5. V. V. Korshak, A. M. Sladkov, L. K. Luneva, *Izv. AN SSSR, OKhN*, **1962**, 4, 728.
6. V. S. Mylnikov, DAN, **148**, No. 3 (1963).
7. V. S. Mylnikov, E. K. Putseiko, A. N. Terenin, DAN, **149**, No. 4, 897 (1963).
8. Masahiro Hatano, Shu Kambara, *J. Polym. Sci.*, **51**, 526 (1961).
9. E. K. Putseiko, DAN, **59**, 471 (1948).
10. A. Terenin, E. Putzeiko, I. Akimov, *J. Chem. Phys.*, **25**, 716 (1957).
11. T. S. Moss, *Photoconductivity in Elements*, London, 1952.
12. I. A. Akimov, E. K. Putseiko, *Fiz. tverd. tela*, **4**, No. 6, 1542 (1962).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.