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The Bulk Photoconductivity of Violanthrene Single Crystals

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The bulk photoconductivity of single crystals of aromatic hydrocarbons in contact with the electrolyte electrode has been the subject of serveral reports.[1] This arrangement of electrodes has proved to have some advantages in distinguishing whether the charge carriers are produced in the bulk of the crystal or on the interface between the crystal and the electrodes.[2] So far, however, these works have been confined to the crystals of relatively small aromatic molecules and have not been extended to include crystals of large aromatic molecules, which are expected to have different electronic properties. In this note some peculiar features of the bulk photoconductivity in the single crystals of violanthrene, which has nine condensed aromatic rings, in contact with the liquid electrodes will be reported.

The violanthrene (violanthrene A, 1,2,9,10-dibenzoperopyrene) single crystals were prepared as follows. Powdered crystals of violanthrene which had been purified by repeated sublimation in a vacuum were sealed off in a glass tube with several cmHg of nitrogen gas. The tube was then placed in an electric furnace which was designed to attain an appropriate temperature gradient, after which the bottom of the tube was heated to a temperature slightly below the melting point of violanthrene (478°C) in order to sublime it. The single crystals grew on the upper wall of the tube at lower temperatures. Thus, single crystals with an area of approximately 0.1 cm^2 and a thickness below few hundred microns were easily obtained.

Measuring procedures were similar to the method described previously.[3] A violanthrene crystal was mounted between the two polystyrene half cells which were the modified types of Kallmann and Pope's cell.[4] Each half cell was filled with liquid which acted as an elctrode for the crystal. The crystal was illuminated by a 750 W tungsten lamp with metal interference filters through the electrode. The half width of the light transmitted through the filters ranged from 110 to 160 Å.

The dc photocurrent[5] was more than fifty times as large as the dark current at 5990 Å, intensity of incident light being 2.7×10^{15} photons/cm^2·sec. The photocurrent-voltage characteristics were similar for the wavelength range studied (4000 to 7000 Å). The photocurrent was proportional to the applied voltage in the lower-voltage region (ohmic region) up to the applied voltage of 10^4 V/cm; it began to deviate from Ohm's law to be dependent on the voltage superlinearly in the higher-voltage region (non-ohmic region). The photocurrent depended little on the direction of the applied field. This was especially true in the ohmic region. Moreover, in the ohmic region, the photocurrent was insensitive to the electrode conditions, such as the electrode material or the addition of chemicals. For example, when the aqueous electrode was replaced by alcoholic electrodes, such as methanol or ethanol, the photocurrent was almost unchanged; nor did the addition of ceric ion, iodine, or o-chloranil, which are ready to act as electron acceptor or hole injector to the crystal, affect the photocurrent in the ohmic region.

Figure 1 shows the spectral dependence of the photocurrent at the constant light intensity of 2.9×10^{14} photons/cm^2·sec. The absorption sepctra of a thin single crystal and of a solution[6] of violantherne are shown for comparison. The spectral response was dependent on the thickness of the crystal. When the thinner crystals were used, the maximum in the spectral response shifted towards a shorter wavelength, and for the crystals thicker than 20 μ (up to 150μ) the maximum at 5990 Å was emphasized. The current changed sublinearly with the intensity of the incident light. The slope of the photocurrent-intensity curve decreased with an increase in the intensity. The sublinear dependence of the photocurrent on the incident light intensity suggests that the bimolecular decay of the charge carriers plays an important role.

All the above findings suggest that the charge carriers produced in the bulk of the violanthrene crystal predominate at least in the ohmic region. This is in con-

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[1] H. Kallmann and M. Pope, *J. Chem. Phys.*, **32**, 300 (1960); P. Mark and W. Helfrich, *J. Appl. Phys.*, **33**, 205 (1962); J. W. Steketee and J. de Jonge, *Phillips Res. Reports*, **17**, 363 (1962); W. Mehl and J. M. Hale, *Discuss. Faraday Soc.*, **45**, 30 (1967).

[2] N. Geacintov and M. Pope, *J. Chem. Phys.*, **45**, 3884 (1965); N. Geacintov and M. Pope, *ibid.*, **50**, 814 (1969).

[3] M. Soma, *J. Amer. Chem. Soc.*, **92**, 3289 (1970).

[4] H. Kallmann and M. Pope, *Rev. Sci. Instr.*, **30**, 44 (1959).

[5] When the term "photocurrent" is used, the dark current is always subtracted.

[6] E. Clar, "Aromatische Kohlenwasserstoffe," Springer Verlag, Berlin (1952).

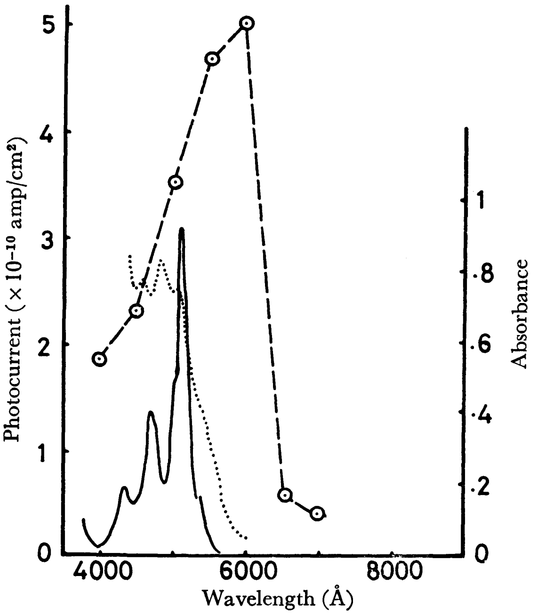

Fig. 1. Spectral dependence of the photocurrent in violanthrene crystal. Intensity of incident light, 2.9×10^{14} photons/cm·sec. Crystal thickness, 20 μ. Applied voltage, 6 V (in ohmic region). Dotted line shows the absorption spectrum of violanthrene single crystal of 2 μ thick in units of 10^4 cm^{-1}. Full line is the absorption spectrum of violanthrene in benzene (longer wavelength part, in 1-methylnaphthalene) in units of 10^5 l/mol·cm.[6]

trast with the cases of anthracene crystals in similar electrode arrangements. In that case, in the wavelength region corresponding to the first singlet excited state of anthracene the charge injection from the electrode always predominates.[1,3]

The bimolecular decay of carriers offers a qualitative explanation of the spectral response of the photocurrent. If we simply assume that the carriers are produced *via* one exciton mechanism in the bulk of the crystal and that they decay bimolecularly, the steady-state approximation for the carrier concentration gives, neglecting the diffusion of both the exciton and the carries;

$$\frac{\mathrm{d}n(x)}{\mathrm{d}t}=\alpha I_0\mathrm{e}^{-\epsilon x}-Rn(x)^2=0 \tag{1}$$

where $n(x)$ is the carrier concentration at a certain distance, x, from the surface of the crystal $\mathrm{d}n(x)/\mathrm{d}t$ its time derivative, ϵ the absorption coefficient of the crystal, I_0 the incident light intensity, α the constant relating to the carrier production, and R is the bimolecular rate constant. The total number of carriers, N_C, in the crystal with a thickness of L and a unit area is expressed as follows:

$$N_c=\int_0^L n(x)\mathrm{d}x \tag{2}$$

From (1) and (2), we get:

$$N_c=2\sqrt{\frac{\alpha I_0}{\mathrm{R}}}\,[1-e^{-1/2\epsilon L}] \tag{3}$$

N_0 has a maximum between $\epsilon=2/L$ and $\epsilon=3/L$. For the crystal 20 μ thick, these optical densities in the decadic unit are 4.3×10^2 and 6.4×10^2 cm^{-1} respectively. The corresponding value for the violanthrene crystal appears around the abosrption threshold above 5500 Å; this is in accordance with the observed spectral dependence of the photocurrent.

Whether the carrier generation process is an intrinsic one or an extrinsic one involving some impurities or defects is obscure at present. In this connection, it should be noted, however, that the fall-off in the photocurrent at 6000 Å for the thicker crystals corresponds in its energy (2.1 eV) roughly to the energy gap determined from the temperature dependecne of the dark conductivity (1.95 eV).[7]

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[7] Y. Hori, Y. Maruyama, and H. Inokuchi, presented at Symposium on Molecular Structure, Fukuoka (1969).