SHORT COMMUNICATIONS

Photoconductivity in an Organic Liquid Solution

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Semi- and photo-conductivity in organic substances have been studied for several years, but most of the experiments have been concerned with the crystalline state[1]. Recently, however, the electronic conduction has been investigated in liquid benzene[2], pyrene[3] and *n*-hexane[4]. The electronic mobility in the liquid was samller by three orders of magnitude than that in the solid[3]. However, the conductivity itself rose sharply at the melting point[5,6]. The rise in the conductivity could not be attributed to the increase in the mobility at the melting point, but it might be due to the enormous increase in the number of charge carriers. In the present experiment the photoconductivity of solutions was investigated preliminarily in relation to the intermolecular energy transfer.

Measurement was made with benzene solutions of pyranthrene (3.3×10^{-5} mol./l.), tetracene (2.0×10^{-5} mol./l.), and pyrene (1.3×10^{-1} mol./l.), all of which show intense absorption spectra in the range of 370~500 mμ. A photocell was made of Teflon, with two parallel Nesa-glass electrodes (1.3 cm^2 in area), forming a sandwich-type cell. The distance between the electrodes was fixed at 3 mm. Through one of the electrodes the solution was illuminated by monochromatized light. The currents were measured by a d. c. method.

The dark currents through the solutions, as well as the benzene, followed Ohm's law below the electric field of 10^2 V./cm. The specific conductivity of benzene was $6.4\times10^{-14}\Omega^{-1}\cdot$cm^{-1}, judging from the observed current in this ohmic range. Beyond the electric field of the above value, the current increased nonlinearly and showed a tendency to saturate in accordance with an applied voltage. Similar behavior was found in the photocurrent in the solutions, as is shown in Fig. 1.

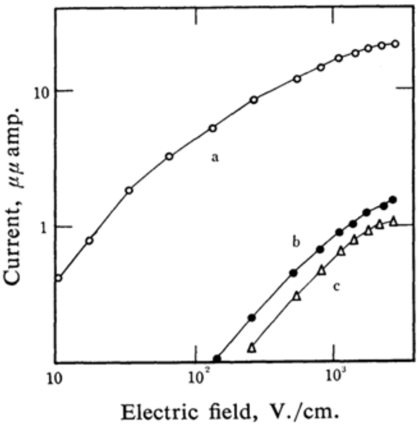

Fig. 1. The relation between current and electric field for the benzene solution of pyranthrene; (a) dark current, (b), (c) photocurrents produced by 450 and 403mμ illuminations, respectively.

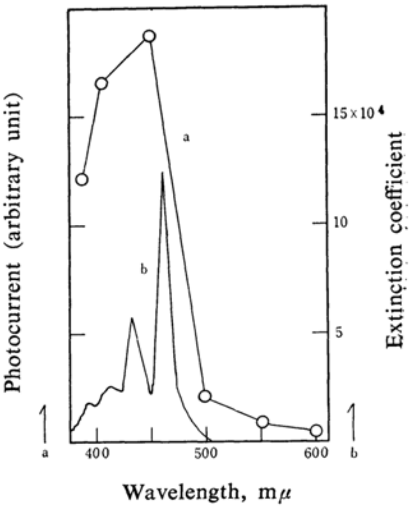

Fig. 2. The spectral responses of (a) photocurrent and (b) extinction coefficient for the benzene solution of pyranthrene.

Benzene itself did not show any response to illumination in the visible spectral region. However, when benzene dissolved pyranthrene, for instance, the solution was found to be

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[3] O. H. LeBlanc, Jr., ibid., 37, 916 (1962).

[4] O. H. LeBlanc, Jr., ibid., 30, 1443 (1959).

[5] J. Kommandeur, G. J. Korinek and W. G. Schneider, *Can. J. Chem.*, 36, 513 (1958).

[6] J. A. Bornmann, *J. Chem. Phys.*, 36, 1691 (1962).

photosensitive in the spectral region. As is shown in Fig. 2, the benzene solution of pyranthrene exhibited a remarkable photocurrent in the spectral region between 400 and 500 mμ. The spectral response of photocurrent is located in the absorption region of the pyranthrene molecule. Therefore, the result indicates the contribution of the solute molecules in the first singlet excited state to the photoconduction. The photocurrent depended linearly on the light intensity below 3×10^{17} photons/sec. cm^2. The linearity was independent of the wavelength of the illumination and of the applied voltage, even if the measurement was made outside the ohmic range.

It is uncertain whether the solute molecules facilitate an injection of charge carriers from the electrode, or whether charge carriers are produced by the interaction between the excited solute molecules and the solvent. The presence of solute molecules at the surface of electrode may, however, reduce the work of emitting electrons from the elecrode. This reduction of the work function is probably induced by the excited molecules. It must also be considered that the conducting state of the solvent is located below the first singlet excited state of the solute, and that the excitation energy is transferred from the excited solute molecule to the solvent by interaction, generating the charge carriers. These different patterns of behavior could not, however, be separated in this preliminary experiment.

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