Photoconductivity of Polycyclic Aromatic Compounds

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Since Akamatu and Inokuchi reported the photoconductivity of violanthrone[1], a number of investigations have been made on the photoconductive phenomena in aromatic compounds[2-7]. These investigations, however, have been concentrated mainly on compounds consisting of a small number of rings, such as anthracene and pyrene, which possess resistivities as high as 10^{20} ohm. cm. at room temperature[3]; hence, they may be classified as insulation photoconductors rather than semiconductors. Recently Kallmann and Pope[8] showed

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[1] H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **20**, 1481 (1952).

[2] H. Inokuchi, This Bulletin, **27**, 22 (1954).

[3] H. Inokuchi, ibid., **29**, 131 (1956).

[4] D. M. J. Compton, T. C. Waddington and W. G. Schneider, *J. Chem. Phys.*, **27**, 160 (1957).

[5] L. E. Lyons and G. C. Morris, *J. Chem. Soc.*, **1957**, 3648.

[6] B. Rosenberg, *J. Chem. Phys.*, **29**, 1108 (1958).

[7] D. C. Northrop and O. Simpson, *Proc. Roy. Soc.*. A **244**, 377 (1958).

[8] H. Kallmann and M. Pope, *J. Chem. Phys.*, **32**, 300 (1960).

that the injected holes from an electrode contributed to the major conduction in anthracene, and Moore and Silver[9] concluded that anthracene is an extrinsic photoconductor rather than the intrinsic one.

On the other hand, relatively little work has been done on the photoconductive behaviors in multi-ring compounds, though it is known that the semiconductive properties are enhanced with the increase of the number of rings.

Experimental

Materials.—Most of the materials were synthetized by Drs. Handa and Aoki in our laboratory. All of them were carefully purified by recrystallization from solutions. To the final process of the purification the vacuum sublimation method was applied repeatedly.

Procedures. — Two types of photocells, i. e., the surface-type cell and the sandwich-type cell, were employed for the investigation of photoconduction. The surface-type cell consisted of a uniform film of aromatic compound with a thickness of about one micron and an area of 15×15 mm². The film was deposited on a pyrex glass plate (the dimension of which was 20 mm.×25 mm.) by slow sublimation in vacuo. Colloidal graphite, "Aquadag", was applied on the film to serve as the electrodes, which were 1 cm. in length and about 3 mm. in width, with a gap of 1 mm. between them. The sandwich-type cell was formed by sublimation of the compound onto a pyrex plate on which a transparent aluminum conducting film had been previously deposited. The second aluminum film, lying entirely on the organic film, completed a photocell with an area of 10×5 mm² and a thickness of a few microns.

The sublimation of organic compounds was carried out in vacuo (10^{-3} mmHg) without decomposition over temperatures ranging from 80 to 380°C. The growth of a film was followed by observing the color of reflected light, and in this way the thickness could be estimated accurately enough to prepare an appropriate film for photoconduction.

Most of the aromatics employed absorb the light intensely in the spectrum region extending from near ultraviolet to near infrared, so that a tungsten lamp is one of the most convenient light sources. The Mazda 750-watt projector lamp was used, being associated with second-order interference filters to isolate narrow particular wavelength regions. The maximum transmissive wavelengths of the regions, which were 9∼16 mμ in half band width, ranged from 392 to 1324 mμ, with an interval of 50∼100 mμ.

Absolute measurements of intensity of incident light on an organic photocell were made with the Nihonbunko vacuum thermopile which was placed at the position of the photocell. The sensitivity of the thermopile was 5.6 microvolts per one microwatt with the time constant of 33 milliseconds and the resistance of 4.2 ohm. A germanium phototransistor and a PbS photocell were used as auxiliary instruments for the measurement of light intensity, because these detectors endure a higher intensity of light better than the thermopile. The maximum intensity, 6×10^{18} photons/sec·cm², was obtained for the light which was isolated by the 1324 mμ filter.

Measurements of electric current were made with association of the Takeda Model V-IM dc amplifier. The ampplifier has the input resistance ranging from 4.5×10^5 to 4.4×10^{11} ohm. The voltage source applying to an organic photocell was a battery of dry elements with voltage of up to 700 V.

The apparatus, as illustrated in Fig. 1, consisted of five parts; the outer glass cylinder, the liquid nitrogen container with the photocell holder, the radiation shield, the optical windows and four conducting leads. The photocell was mounted on the holder by being pressed with a polystyrene plate and nuts.

Measurements of temperature were made with the germanium resistor which had been calibrated with a pentane direct-readings thermometer. The resistance of the resistor changed from 27 to 10 ohm. following the temperature change from +15 to −196°C. The complete evacuation and the heat radiation shield prevented condensation of moisture on the surface of optical window. The apparatus was placed in a metal box, which served for shutting out the photocell from light and also for preventing electrical disturbance.

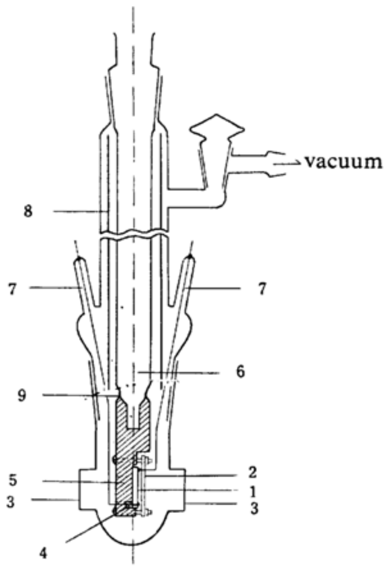

Fig. 1. The apparatus for conductivity measurement.

1 Photocell
2 Polystyrene plate
3 Optical windows
4 Germanium-registor thermometer
5 Specimen holder
6 Liquid nitrogen container
7 Conducting leads
8 Radiation shield
9 Copper-soft glass joint

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[9] W. Moore and M. Silver, ibid., 33, 1671 (1960).

Results

Change in Photocurrent with Electric Potential. —The electric current was measured as a function of applied potential under the illumination of monochromatic light. Most of the observations were made with surface-type photocells in vacuo, to avoid the effects of space charge which were occasionally observed with sandwich-type photocells.

The current responded to potential variation instantaneously and then remained constant with time. The potential dependence of photocurrent was reproducible, as in the case of dark current similarly. When the logarithm of the current i was plotted against the logarithm of the applied potential V, a linear relationship was obtained. This is illustrated in Fig. 2 for pyranthrene. From this, the potential-current relation could be expressed by the following formula,

$$i \propto V^{\alpha}$$

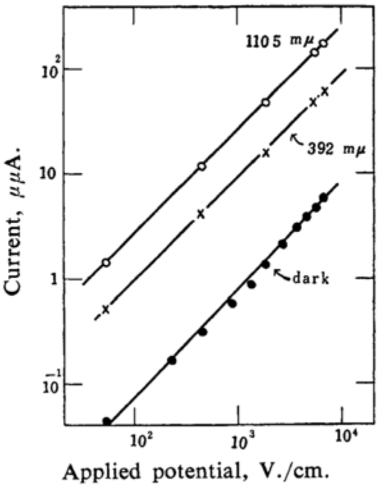

Fig. 2. The relation between current and applied potential for pyranthrene.

TABLE I. THE α-VALUE FOR SURFACE-TYPE PHOTOCELLS

	Illumination		
	Wave-length mμ	Intensity photons/sec. cm²	α-Value
Pyranthrene (film)	Dark	—	1.05
	392	10^{15}	1.01
	529	10^{13}	1.14
	1055	10^{15}	1.10
	1105	10^{17}	1.00
Violanthrene (film)	Dark	—	1.11
	557	10^{13}	1.15
Perylene (film)	470	10^{13}	1.20
Perylene (single crystal)	392	10^{16}	1.17
	403	10^{16}	1.15
	502	10^{16}	1.17
	502	10^{17}	1.19

The values of α for pyranthrene, violanthrene and perylene are shown in Table I. In this table, it is seen that α is approximately unity, under different conditions of illumination with regard to wavelength and intensity of light. Hence, it can be concluded that the photocurrent obeys Ohm's law over the range of potential applied up to 7×10^3 V./cm.

Change in Photocurrent with Light Intensity. — The photocurrent in surface-type photocells was observed as a function of light intensity. The relation between photocurrent and light intensity yielded two regions generally, as illustrated in Figs. 3 and 4. In each region, the relationship between the photocurrent i_p and the light intensity L could be expressed by the formula,

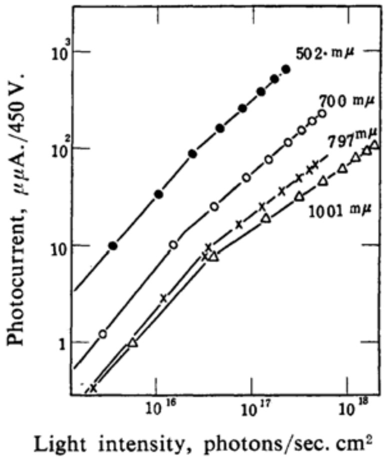

Fig. 3. The relation between photocurrent and light intensity for pyranthrene (surface-type photocell).

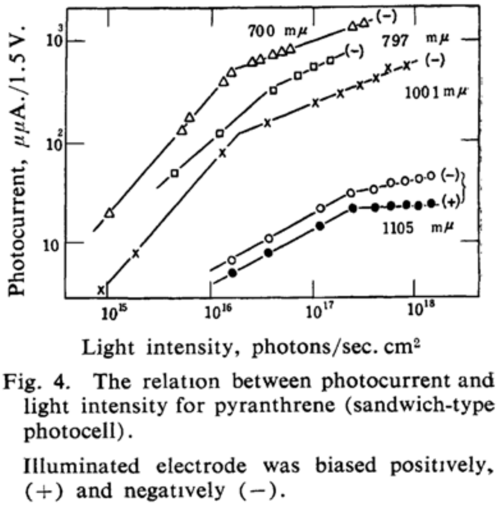

Fig. 4. The relation between photocurrent and light intensity for pyranthrene (sandwich-type photocell).

Illuminated electrode was biased positively, (+) and negatively (−).

$$i_p \propto L^n$$

In the region of low light intensity, usually not much exceeding 10^{16} photons/sec. cm^2, the photocurrent changed approximately in linearity with the light intensity, i. e., the exponent n was nearly unity. This relation was seemingly independent of the wavelength of incident light, the atmosphere, the applied potential and the temperature.

While in the region of high light intensity, n possessed a smaller value than unity, and was dependent on the wavelength of illumination. Nevertheless, no appreciable difference of n-value was noted according to the variation of temperature, potential, or atmosphere. The n-values are summarized in Table II.

No indication of saturation was observed with surface-type photocells even in the region of the highest light intensity, around 10^{18} photons/sec. cm^2. However, sandwich-type photocells showed the saturation of photocurrent at the light intensity of 2×10^{17} photons/sec. cm^2, as illustrated in Fig. 4.

TABLE II. THE n-VALUE FOR PYRANTHRENE AND PERYLENE SURFACE-TYPE PHOTOCELLS IN THE REGION OF HIGH LIGHT INTENSITY

Wave-length of illumination mμ	Pyranthrene film			Perylene single crystal	
	In vacuo*		In dry air	In vacuo*	In dry air
	290°K	185°K	290°K	290°K	290°K
403	0.86			0.98	0.87
450	0.84			0.95	0.87
502	0.95		1.06	1.12	1.15
552	1.00	1.03		1.10	1.02
599	0.89			0.86	0.82
655	0.82			0.79	0.68
700	0.85	0.81	0.87		
747	0.77				
797	0.77		0.74		
853	0.61				
901	0.62				
945	0.73				
1001	0.67		0.63	0.78	
1105	0.76	0.78		0.79	
1195	0.78			0.78	
1324	0.92	0.91	0.88		

* 10^{-3} mmHg after being flushed with argon gas.

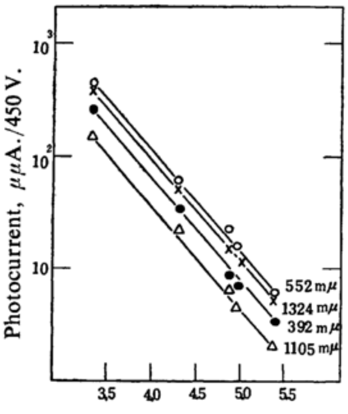

Fig. 5. The photocurrent vs. temperature for pyranthrene (surface-type photocell).

Change in Photocurrent with Temperature.—The temperature dependence for photocurrent was measured over the range from 173 to 290°K. The surface-type photocell was employed with association of the apparatus which is shown in Fig. 1. The photocurrent increased with an increase in the temperature. Plots of the logarithm of photocurrent i_p against the reciprocal of temperature gave a straight line (Fig. 5), and the relation follows the equation,

$$i_p = i_0 \exp(-E/kT)$$

where E is the activation energy of photocurrent.

It is of interest that the activation energy, e. g., 0.18 eV. for pyranthrene, was found to be independent of the intensity and the wavelength of incident light over the range from 392 to 1324 mμ employed.

Generation of Charge Carriers.—An attempt was made to measure the photocurrent which was produced by the illumination onto a limited area of the aromatic film between the electrodes of surface-type photocell. Aquadag electrodes were painted on the pyranthrene film with a gap of 7 mm. between them. When the whole area between the electrodes was illuminated, the maximum photocurrent, of the value of 12×10^{-12} A./450 V., was observed. When the illumination was made onto the half part of the area between the electrodes by masking the other half, the magnitude of photocurrent was smaller than that expected if the photons in the same number had been uniformly distributed over the whole area. When the illumination was focused onto one of the electrodes alone, the increase of current was hardly observed. In addition, when the light fell onto a small limited area of the film, the magnitude of photocurrent assigned per unit area was nearly equal to that of the photocurrent produced by the illumination on the half area. Consequently it might be concluded that the charge carriers are not produced in a particular portion such as the Aquadag electrode or the contact area, but in the area between both elctrodes. Nevertheless, there is no explanation for the fact that the maximum photocurrent was produced by the illumination on the whole area. Probably the difference is related to the decay pocess of charge carriers.

The photocurrent produced by an asymmetric illumination with respect to the polarity of ppalied potential was also measured. Onto a pyranthrene surface-type cell an image of slit of monochromatic light was collimated so that the illuminated strip lay parallel to the electrodes. Keeping the applied potential ($2.25\times\times10^2$ V./cm.) and light intensity (2.8×10^{17} photons/sec. cm^2 for 552 mμ illumination) constant, the photocurrent was measured as the image was moved from one electrode to the other. The photocurrent was always greater when the illuminated portion was located close to the negatively biased electrode. In this case, the photoelectromotive force due to the asymmetric illumination was undetectable, even under the illumination of the highest light intensity.

Also, a sandwich-type photocell possesses the asymmetry in itself, because the light intensity of illumination is diminished successively along the electric potential. The photocurrent of a pyranthrene film (about 10 μ in thickness), which was sandwiched between two evaporated aluminum films, was 1.5 times greater when the illuminated side was negatively biased than when it was positively biased at the applied potential of 1.5×10^3 V./cm.

The thermoelectromotive force, which was observed with compressed powder of isoviolanthrone, was of the order of 10^{-4} V./deg., indicating conduction predominantly by electrons.

Discussion

The semiconductive behaviors of polycyclic aromatic compounds have been fairly extensively studied, but the theoretical interpretation of their electronic conduction has not been completed, because the intermolecular interactions in the solid state are scarcely known. However, a significant part of the behavior of organic semiconductors can be discussed, for convenience, in terms of the band model. It may be postulated that the empty band and the full band are formed from the energy levels of the excited states and the ground state of π-electrons of the molecule respectively. In this case, the band widths might be narrow; especially the width of the full band is so narrow because of poor overlapping of the wave functions for the ground state, that the full band may be regarded as a series of discrete levels. Consequently it is quite probable that the holes are almost confined to the particular molecules in which they are generated, and most of the electric current is conducted by electrons through the crystal. The model was supported by the signs of the thermoelectromotive force and the polarity for the maximum photocurrent which was produced by an asymmetric illumination. In addition, as the ohmic nature of photocurrent as well as the experiment on the limited-area illumination indicated, the generation of charge carriers took place in the bulk of aromatic film, neither from the electrode nor the electrode-film contact. Hence, the multi-ring compounds are seemingly intrinsic photoconductors. The light intensity dependence for photocurrent has been usually accounted for by the concept of the trapping process of charge carriers. For instance, Rose(10) explained the variation of the exponent n from 1 to 0.5 by the population of the effective trapping centers which varies depending on the intensity of illumination. Our result showed that n possesses unity at a low light intensity and possesses a smaller value than unity at a high light intensity. This result is coincident qualitatively with that shown by Rose. The temperature dependence for photocurrent can not be easily interpreted because more than one parameter can change with temperature. However, the activation energy of photocurrent was independent on the wavelength of light. This result seems to indicate that the activation energy is not associated with the formation of charge carriers, such as the dissociation of electron-hole pairs, but with the transport process of carriers. If the trapping centers are assumed to be of the same depth below the empty band, and the temperature dependence could be ascribed to the variation of the mobility of carriers, the activation energy indicates the depth of trapping center. However, the nature of the centers has not been established. As suggested by Nelson(11) for the case of cationic dyestuff, every molecule might be regarded as a trapping center in the polycyclic aromatic compounds.

Summary

The voltage, light intensity, and temperature dependences for photocurrent in multi-ring compounds were studied as well as the photocurrent produced by the limited-area illumination. The photocurrent was found to be ohmic over the range of voltage employed. The photocurrent increased linearly with the intensity of light in the region of low light intensity, while it increased as the fractional power of the light intensity in the region of high intensity. The photocurrent increased with an increase of the temperature, and the activation energy of the photocurrent was found to be independent of the wavelength and the intensity of illumination.

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(10) A. Rose, *RCA Review*, **12**, 362 (1951).

(11) R. C. Nelson, *J. Chem. Phys.*, **30**, 406 (1959).

The signs of the thermoelectric power as well as the polarity for the maximum photocurrent, and the experiment on the limited-area illumination indicated that the conduction in polycyclic aromatic compounds was due predominantly to electrons which were generated in the bulk of aromatic film.

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