The Photovoltaic Behavior in Organic Compounds

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(Received January 17, 1961)

The study on the photo-electrical behavior in organic semiconductors produced by excitation accompanying absorption of light, especially the investigation of the photoconduction, has been carried out by several workers⁽¹⁾. However, relatively little is known about the photovoltaic phenomena of these organic compounds⁽²⁾.

In one of the few articles on this subject, Nelson⁽³⁾ reported a photovoltaic behavior of junctions between organic compounds and cadmium sulfide in association with optical sensitization in photography. The author proposed that the induced photovoltage is related to the difference in energy between the conduction band of the organics (dye) and that of cadmium sulfide. On the other hand, Calvin and Kearns⁽⁴⁾ reported interesting results on photovoltaic organic junctions: Mg-phthalocyanine ‖ tetramethyl-p-phenylene diamine and coronene ‖ chloranil junctions.

In this paper, we show that the photovoltaic behaviors have been observed with a simple cell, consisting of a junction between aromatic compounds and metal or stannic oxide. Further, in comparison with other semiconductive behaviors of polycyclic aromatic compounds, the produced electromotive force will be discussed.

Experimental Procedures

For an observation of photo-electromotive force between organic semiconductor and metal or metal

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(2) H. Baba, K. Chitoku and K. Nitta, *Nature*, **177**, 672 (1956).

(3) R. C. Nelson, *J. Chem. Phys.*, **22**, 885, 890, 892 (1954), **29**, 388 (1958); *J. Opt. Soc. Am.*, **45**, 774 (1955); **46**, 13 (1956).

(4) M. Calvin and D. Kearns, *J. Chem. Phys.*, **29**, 950 (1958).

oxide, a sandwich-type cell was applied. This cell was made by sandwiching aromatic compounds between two electrodes: The evaporated film of aromatic compounds was deposited onto a glass plate which had been coated in advance with a thin metal film or onto a stannic oxide conducting layer to provide a junction electrode. The specimen film was usually one or two microns in thickness. Further, the second electrode was evaporated onto the specimen film. The conducting path between these electrodes extended through the specimen film. The resulting construction of the cell was illustrated in Fig. 1 of the previous report[5].

For the preparation of alkali metal-aromatics junction, as shown in Fig. 1, the alkali metal, evaporated onto organic film as a second electrode under less than 10^{-5} mmHg, acted as a junction electrode. After the evaporation of alkali metal, all observations of their electromotive forces were carried out under a high vacuum to avoid a decomposition of the alkali metal by an action of moisture. However, a fluctuation was frequently introduced concerning the direction of electromotive force. For the elimination of this fluctuation, the construction of a more precise apparatus is in due course.

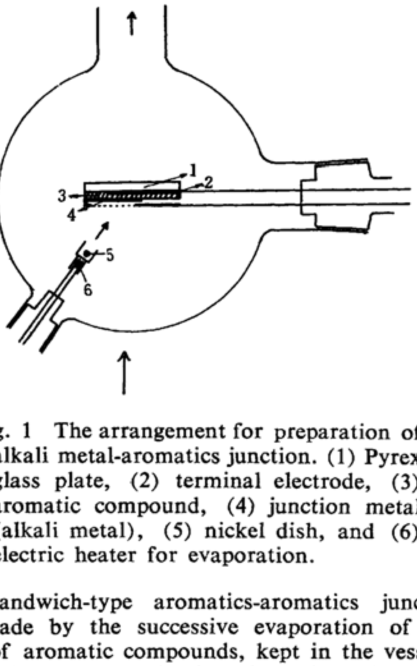

Fig. 1 The arrangement for preparation of alkali metal-aromatics junction. (1) Pyrex glass plate, (2) terminal electrode, (3) aromatic compound, (4) junction metal (alkali metal), (5) nickel dish, and (6) electric heater for evaporation.

The sandwich-type aromatics-aromatics junction was made by the successive evaporation of two sorts of aromatic compounds, kept in the vessel 5 of Fig. 1, onto a conducting glass plate without an intrusion of air into the contact area between these two compounds.

The illumination of white light was produced from a tungsten lamp onto the side of the junction metal. The measurement of induced photovoltage had to be associated with a vibration-reed electrometer because its produced electric power was extremely low. By means of a quartz-prism monochrometer and also of interference filters, a spectral response of photo-electromotive force in the range from 350 mμ to 1300 mμ was observed.

The applied aromatic compounds, perylene, violanthrene and violanthrone, were provided from Drs. T. Handa and also J. Aoki. Coronene, a seven membered aromatic hydrocarbon, was provided from Badisch Anilin und Soda Fabrik, Germany. These organic compounds were purified with a combination of three methods; recrystallization, sublimation and chromatography.

Results and Discussions

When the contact between an organic semiconductor and a metal was illuminated with white light from a tungsten lamp, the induced electromotive force reached immediately a saturated value and this was kept quite steadily for a long period. However, in the alkali metal-aromatics junction it was found that its electromotive force decreased to a value smaller than the original one. This behavior would be introduced from a high reactivity of alkali metal with moisture and/or from a formation of charge transfer complex between the metal and the aromatic compound.

For the noble metal-aromatics junction, the observed photoelectromotive force varied from a few millivolts to 10 mV. depending on the sorts of metals applied to the junction and also on the condition of preparation technique as illustrated in Table I. In all of these photocells, the junction metal acted as a negative electrode against the terminal electrode; thereby, at the junction, electrons flowed from the hydrocarbons to the junction metals under the illumination.

On the other hand, a quite stable photovoltage was produced at the contact between perylene and stannic oxide, and its saturated value reached 80 mV. when a light was incident on it through the transparent stannic oxide electrode (electrical conducting glass electrode). The spectral response of this electromotive force was a curve which is in good coincidence with the optical absorbance curve and also with the response curve of photoconduction for solid perylene as illustrated in Fig. 2.

Similar behavior of the photovoltaic effect was found in the junction between coronene, violanthrene or violanthrone and stannic oxide, whose electromotive forces were 20, 450 and 80 mV. respectively. These four hydrocarbons acted as electron acceptors with respect to stannic oxide under illumination of panchromatic light. However, the spectral response of photovoltage of violanthrone junction was a quite peculiar one as shown in Fig. 3. Its threshold value was found to be around 0.9 eV., which is in agreement with that of the photoconduction of its aromatic compound.

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[5] H. Inokuchi, H. Kuroda and H. Akamatu, This Bulletin, **34**, 749 (1961).

TABLE I. THE PHOTOVOLTAGE OF METAL-AROMATICS JUNCTIONS

Photovoltaic junction		Photo-emf	
Aromatics (sign)	Metal (sign)	Voltage, mV.	Wattage, W.
Violanthrene (+)	Pt (−)	2~ 3	$\sim 10^{-17}$
Violanthrene (+)	Au (−)	6~ 9*	$\sim 10^{-16}$
Violanthrene (+)	Ag (−)	Detectable	
Violanthrene (+)	Sn (−)	2~ 8	$\sim 10^{-16}$
Violanthrene (+)	Pb (−)	4~14	$\sim 10^{-16}$

* As a special case, emf reached to 50 mV.

TABLE II. THE PHOTO-ELECTROMOTIVE FORCE OF ALKALI METAL-AROMATICS JUNCTIONS

Photovoltaic junction		Photo-emf		
Aromatics (sign)	Metal (sign)	Voltage, V.	Wattage, W.	$\Delta\varepsilon/2$, eV.
Perylene (−)	Li (+)	0.3~1.0	$\sim 10^{-10}$	1.0
Coronene (−)	Li (+)	0.3	$\sim 10^{-10}$	0.8
Violanthrene (−)	Li (+)	0.3~0.8	$\sim 10^{-9}$	0.43
Violanthrone (−)	Li (+)	0.2~0.9	$\sim 10^{-10}$	0.39
Perylene (+)	Na (−)	0.3~1.0	$\sim 10^{-11}$	1.0
Violanthrene (+)	Na (−)	0.3~0.8	$\sim 10^{-10}$	0.43
Violanthrone (±)	Na (∓)	0.1~0.5	$\sim 10^{-8}$	0.39
Perylene (±)	K (∓)	0.2~0.9	$\sim 10^{-10}$	1.0
Violanthrene (+)	K (−)	0.2~0.8	$\sim 10^{-10}$	0.43
Violanthrone (−)	K (+)	0.2~0.5	$\sim 10^{-9}$	0.39

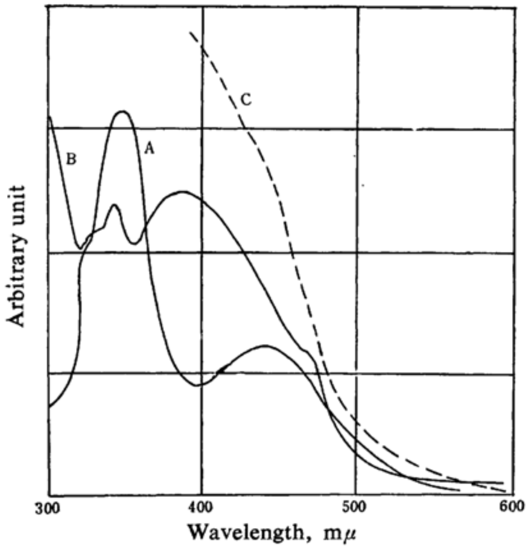

Fig. 2 The spectral response curves of photoconductivity (A), absorption spectrum (B) and photovoltage (C) for perylene in solid phase.

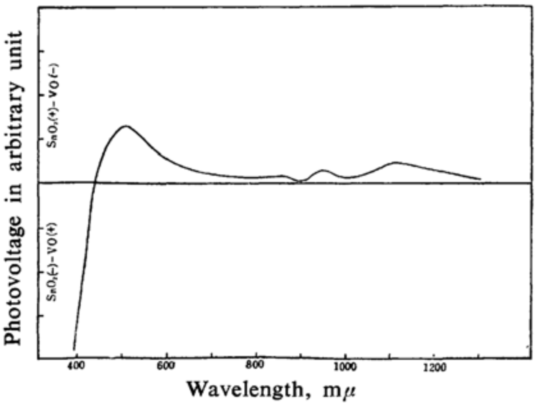

Fig. 3 The spectral response curve of photovoltage for the SnO_2-violanthrone (SnO_2-VO) junction.

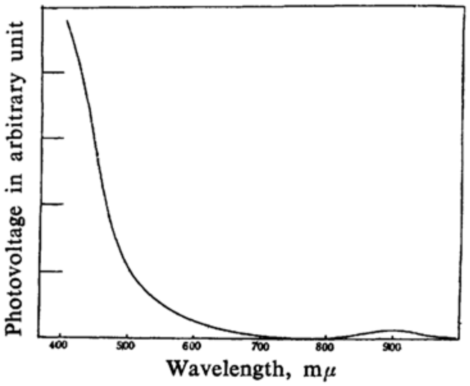

Fig. 4 The spectral response of photovoltage produced at the junction between sodium metal and violanthrene.

These results imply that the spectral responses of the photovoltage are predominated by the electronic structure of polycyclic aromatic compounds but not by that of stannic oxide. In this connection, no optical absorption in stannic oxide film was found in a visible region longer than 390 mμ.

In the alkali metal-aromatics junction, the induced photo-electromotive force reached to almost one volt as listed in Table II. Its spectral response was a curve falling monotonously from short wavelength to long wavelength side. An extrapolation of this decrement found a tentative threshold value, which is sited in a range from 600 to 700 mμ as shown in Fig. 4.

A weak but definite response of photovoltage was found in a longer wavelength region than the extrapolation value. However, further investigations are restricted by fluctuation concerning the direction of electromotive force and also by the lack of stability of the force. In the lithium-aromatics junction, the metal acted as a positive electrode relative to the terminal electrode. Most of the aromatic compounds in the sodium-aromatics junction, however, acted as a positive electrode with respect to sodium; that is to say, electrons were transferred from the hydrocarbons to the junction metal at the junction and then the organic solids acted as electron donors. In the potassium-aromatics junction, the direction of photo-electromotive force was changed depending on the sorts of organic solids and also on the wavelength of incident light.

These values of photovoltage decreased to a small value in time. This decrease may be introduced from the complex formation between aromatic compound and alkali metal and/or may be produced by a decomposition of the junction. These fluctuations on the observed values may be eliminated by means of the application of ultra-high vacuum.

As a preliminary work of aromatics-aromatics junction, we have found that a fairly large electromotive force ($10\sim10^2$ mV.) was produced at the contact between two pure aromatic hydrocarbons; for instance, perylene and violanthrene, under illumination. The details of this work will appear elsewhere.

When a contact between semiconductive material (band gap : $\Delta\varepsilon$) and metal is made, it is believed that the flow of charge carrier, $I_o \exp[-\Delta\varepsilon/2kT]$, happended at the contact and a potential barrier occurs at the boundary layer. On illuminating the contact of junction, the flows of forward and backward currents, I_f and I_b, are expressed as

$$I_f = I_o \exp[-(\Delta\varepsilon/2 - eV_{op})/kT] \qquad (1)$$

$$I_b = I_o \exp[-(\Delta\varepsilon/2)/kT] + I_L \qquad (2)$$

respectively, where I_L is the excess flow of charge carrier under illumination and V_{op} is photo-electromotive force, measured for an open circuit condition. At an equilibrium condition, V_{op} is expressed as

$$V_{op} = \frac{kT}{e} \ln\left[1 + \frac{I_L}{I_o \exp[-(\Delta\varepsilon/2)/kT]}\right] \qquad (3)$$

because of $I_f = I_b$.

When the induced current I_L under illumination of light is large, Eq. 3 is rewritten as

$$V_{op} \fallingdotseq \frac{\Delta\varepsilon}{2e} + \frac{kT}{e} \ln\frac{I_L}{I_o} \approx \frac{\Delta\varepsilon}{2e} (kT \ll e) \qquad (4)$$

$$V_{op} \fallingdotseq \frac{kT}{e} \frac{I_L}{I_o} \exp[-(\Delta\varepsilon/2)/kT] \ll 1 \qquad (5)$$

For the alkali metal-aromatics junction, it is expected the produced photovoltage, V_{op}, follows Eq. 4 because the excess flow of illuminated current is great. On the contrary, the minute photovoltage for the noble metal-aromatics junctions is explained by Eq. 5 tentatively.

Summary

When a contact between a semiconductive material and a metal is made, it is expected that a potential barrier occurs at the boundary layer and the photovoltaic effect which is observed with illumination on this barrier. It has been found that this is the case for organic semiconductors. The photovoltaic cell was made with aromatic compounds sandwiched between two metal layers or metal and stannic oxide. One of them was a terminal electrode and the other, the junction electrode, was made with evaporated film of platinum, gold, silver, tin, lead or alkali metal. All observations of photovoltage were carried out in vacuo or in an atmosphere of inert gas.

With the illumination of white light from a tungsten lamp, the induced photovoltage varied from several millivolts to one volt, depending on the sorts of metals applied to the junctions. In most of these junctions, the organic solids acted as positive electrodes with respect to the junction metal.

In the alkali metal-aromatics system, a fluctuation was frequently observed concerning the direction of electromotive force, but the value of photovoltage was generally much higher than in the case of the other metals; thus the spectral response of the voltage was measurable. This response was less dependent on the sorts of organic solids but dependent on the sorts of metals. On the other hand, the spectral response in the junction between organic solid and stannic oxide, was a curve which is in good coincidence with the optical absorption curve for solid organics.

The cost of this research has been defrayed from the Grant in Aid for Fundamental Scientific Research from the Ministry of Education, to which the author's thanks are due.

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