Photoelectric Emission and Electrical Conductivity of the Cesium Complex with Pyrene Derivatives

By Kyohei OGINO, Satoshi IWASHIMA, Hiroo INOKUCHI and Yoshiya HARADA

(Received August 17, 1964)

The efficiency of the photoelectric emission of an alkali metal was promoted by the evaporation of a hydrocarbon, naphthalene or anthracene onto a sodium (or potassium) film.[1]

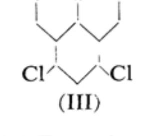
In the 1950's, Ubbelohde investigated the electronic properties of the solid-state complexes of polycyclic aromatics involving an alkali metal; sodium, potassium or lithium.[2]

Recently, we have found a strong photoelectric emission and a high quantum efficiency of the complexes between cesium and polycyclic aromatic compounds in the region with wavelengths shorter than 600 mμ.[3]

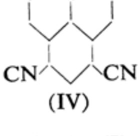
On the basis of the charge transfer process of the complexes, the selection of the types of the two components—the electron donor and the acceptor—may help to yield a group of materials with higher conductivities. In this article, we will discuss the photoemission and the electronic conduction of the cesium complexes with pyrene derivatives in an attempt to understand better the mechanism of the charge transfer process.

Experimental Procedures

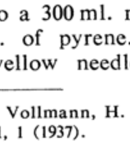
Though preparations of the pyrene derivatives have already been reported,[4] the descriptions are not reliable. The pyrene derivatives applied in this experiment were synthesized as follows:



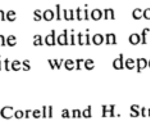
(I)



(II)



(III)



(IV)

1, 3, 6, 8-Tetranitropyrene (TNO_2P) (I). — One hundred grams of nitric acid ($d=1.5$) was added slowly to a 300 ml. nitrobenzene solution containing 30 g. of pyrene. With the addition of nitric oxide, yellow needle crystallites were deposited.

---

[1] R. Suhrmann, *Z. Phys.*, **94**, 742 (1935); **111**, 18 (1937).

[2] W. A. Holmes-Walker and A. R. Ubbelohde, *J. Chem. Soc.*, **1954**, 720; G. C. Martin, N. D. Parkyns and A. R. Ubbelohde, ibid., **1961**, 4958.

[3] H. Inokuchi and Y. Harada, *Nature*, **198**, 477 (1963).

[4] H. Vollmann, H. Becker, M. Corell and H. Streeck, *Ann.*, **531**, 1 (1937).

TABLE I. THE CHANGE OF COLOUR BY THE FORMATION OF THE COMPLEXES

Complex		Change of colour	
Donor	Acceptor	After formation 30 min.	1 day
Cs	Pyrene (white)	Pink	Blue
Cs	TNO_2P (orange yellow)	Dark brown	Dark brown
Cs	TCNP (yellow)	Orange yellow	Dark violet
Cs	TClP (pale yellow)	Bluish brown	Bluish brown
Cs	TBrP (pale yellow)	Dark brown	Dark brown

After the solution had been stirred for 4—5 hr. at 110—120°C, the crystallites were separated with a glass-filter. Through sublimation in vacuo, purified crystallites, m. p. 334—336°C, were obtained.

1, 3, 6, 8-Tetrabromopyrene (TBrP) (II).—Twenty grams of pyrene was dissolved in 300 ml. of nitrobenzene. Seventy grams of bromine was then stirred drop by drop into the solution. Through continuous shaking at 120—125°C, pale yellow crystallites separated from the solution as precipitates. These crystallites were filtered and washed with ethanol. The melting point of tetrabromopyrene, which was purified by sublimation under a pressure of 10^{-4} mmHg, was 399—404°C.

1, 3, 6, 8-Tetrachloropyrene (TClP) (III).—Thirty-eight grams of 1,3,6,8-tetranitropyrene (I) and 150 g. of phosphorus pentachloride were dissolved in 150 ml. of trichlorobenzene and heated at around 150°C for 8—9 hr. while being continuously stirred. During the operation, a large amount of gas was removed from the solution and the colour of solution changed from pale brown to dark brown. Dark brown crystallites were separated from the solution as precipitates. Through vacuum sublimation, purified compounds, for which the melting point was 358—360°C, were pale yellow-coloured crystallites.

1, 3, 6, 8-Tetracyanopyrene (TCNP) (IV).—Twelve grams of tetrabromopyrene (II) and 90 g. of copper cyanide (CuCN) were dissolved in 120 ml. of benzyl cyanide ($C_6H_5CH_2CN$) which had been purified by vacuum distillation. The solution was heated at 100°C for half an hour and then at 234°C (the boiling point of benzyl cyanide) for 4 hr. while being continuously stirred. Through these reactions, the color of the solution changed from pale brown to dark brown. One hundred millilitres of ethanol was added to the solution at 80—90°C for 1—1.5 hr. with stirring continuously. The precipitates which separated from the solution were washed with 30 per cent nitric acid to eliminate the residue of copper and then repeatedly washed with ethanol. The melting point of compound, sublimed in vacuo, was 445—448°C.

The Preparation of a Cesium Complex Photocell (Fig. 1). — A vapour of cesium metal (8), prepared from a reaction between cesium chloride and calcium metal, was brought in contact with a thin film (3) of pyrene derivatives which had previously been deposited on the surface of a glass plate with two aluminium electrodes. By the contact between the aromatic compound and cesium vapour, an abrupt change in the colour occurred, as Table I shows.

The formation of a complex was terminated by the saturation of the cesium metal involved. All preparations of the complexes were carried out at room temperature except that of the cesium-pyrene complex. In the latter, the thin film of the hydrocarbon had to be kept at a low temperature (around 0°C) in order to decrease the vapour pressure of the compound. The ratio of the components of cesium-tetranitropyrene, Cs/TNO_2P, was found to be two by chemical analysis.

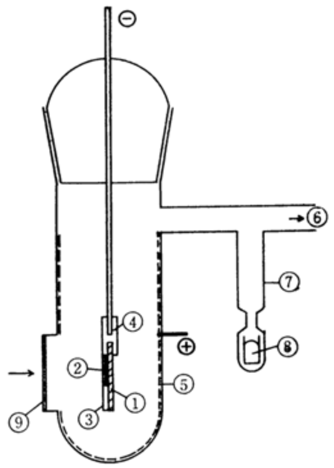


Fig. 1. The cesium complex photocell: 1, glass plate; 2, aluminium electrode; 3, organic thin film; 4, electrode connector; 5, collector (silver film); 6, to connect vacuum system, 7, annex glass for reaction; 8, CsCl+Ca mixture; 9, quartz window.

Under illumination by a visible and an ultraviolet light from a Hitachi spectrometer through a quartz window (9), a strong photoemission from the surface of the complex was found when an electric field (1—30 V.) between a specimen and a collector (5), deposited as a silver film, was applied.

The Observation of the Quantum Yield of Photoemission.—The quantum efficiency (Y) derives from the ratio between a number of incident photons (n_p) and a number of emissive electrons (n_e) observed in a photocurrent;

$$Y=\frac{n_e}{n_p} \tag{1}$$

The photocurrent, 10^{-14}—10^{-6} amp., was observed by means of a Cary model 32 vibrating reed electrometer.*

---

* One ampere corresponds to 1.6×10^{19} electrons/sec. in this experiment.

The incident photons (n_p) were measured by means of the thermoelectric power of the thermopile:

$$n_p = \frac{V\lambda}{vc\boldsymbol{h}} \times 10^7 \text{ photons/sec.} \qquad (2)$$

where v(μV./μW. cm^2) is the sensitivity of the thermopile, V is an applied potential on the photocell, λ is a wavelength of light, c is the light velocity and $\boldsymbol{h}$ is Plank's constant.

When a Nipponbunko thermopile was applied (its sensitivity was 7.0×10^2 μV./μW. cm^2), the spectral response of the quantum efficiency of cesium-aromatics complexes in the wavelength range from 200 mμ to 900 mμ was obtained.

The Measurement of the Electrical Resistivity of the Complexes.—The thin organic film evaporated on a silica plate, with two aluminium electrodes as a surface-type cell, came in contact with the vapour of cesium gas in vacuo. The resistivity of the cell was measured with a Kawaguchi Denki model MMA III-13 vibrating reed electrometer.

The absorption spectra of the thin complex films were observed with a Cary recording spectrometer model 14.

Experimental Results

A variation in the emission current as a function of the applied potential for a Cs-(TBrP) photocell under illumination by monochromatic light (550 mμ), its intensity being 3.6×10^{11} photons/sec., is illustrated in Fig. 2. From an irregularity in the geometrical arrangement of the photocell, as is shown in Fig. 1, the saturation potential of the photoemission was found to be around ten volts. Therefore, the observation has been carried out under an applied potential of 10 V. An ageing of the emission was found.

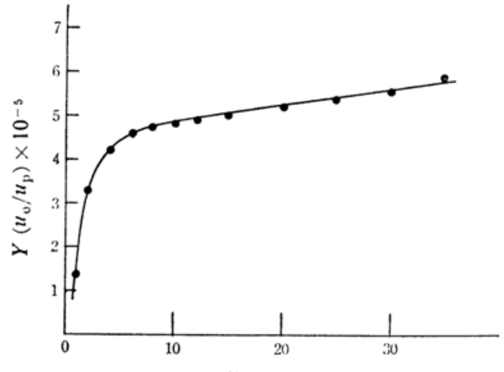


Fig. 2. The variation of photoemission as a function of applied potential for Cs-TBrP.

The spectral responses of the photo-emissive current were curves decreasing gradually from the short wavelength side to the long wavelength side as Fig. 3 shows. However, the response curves changed with time at an initial stage of the complex formation, as is shown in the figure, and converged to the stable state.

The electrical resistivity of the complexes, which was observed with a surface-type cell,5) possessed a wide range of values, depending on the pyrene derivatives applied as acceptors. The temperature dependence of the resistivity was semiconductive in character ($\rho = \rho_0 \exp \Delta\varepsilon/2\boldsymbol{KT}$), as Table II demonstrates.

TABLE II. THE SEMICONDUCTIVITY OF PYRENE-CESIUM COMPLEXES

Complex	ρ, Ω cm. at 15°C	$\Delta\varepsilon$, eV.
Pyrene-Cs	2.1×10^4	0.42
TClP-Cs	8	0.34
TBrP-Cs	1.6×10^1	0.35
TNO$_2$P-Cs	2×10^6	0.94
TCNP-Cs	6×10^5	0.70

Discussion

The threshold values of the spectral response of the photoemission of the cesium complexes which correspond to the ionization potential are situated around 1.6×10^4 cm^{-1}. The pure cesium metal has a strong response peak at around 2.5×10^4 cm^{-1}. Further, the threshold value of the photoemission of pyrene was reported to be around 4.7×10^4 cm^{-1}.6) Therefore, it is reasonable to consider that the emission from a cesium-aromatics system, observed in the experiment, occurs from new compounds.

The formation of complexes demonstrated an increase in the quantum yield of photoemission from 10^{-3}—10^{-4}, the values for pure cesium metal and also for pure aromatic compounds, to 10^{-1}—10^{-2}, an increase shown in Fig. 3. These promotions may take place from the electron transfer from a cesium metal to a partner molecule.

The transfer charge carriers depends roughly on the energy difference between the ionization potential of metal, 1.9 eV. for cesium, and the electron affinity of the acceptor, pyrene derivatives. On the basis of organic chemistry, the order of the values of electron affinity is;

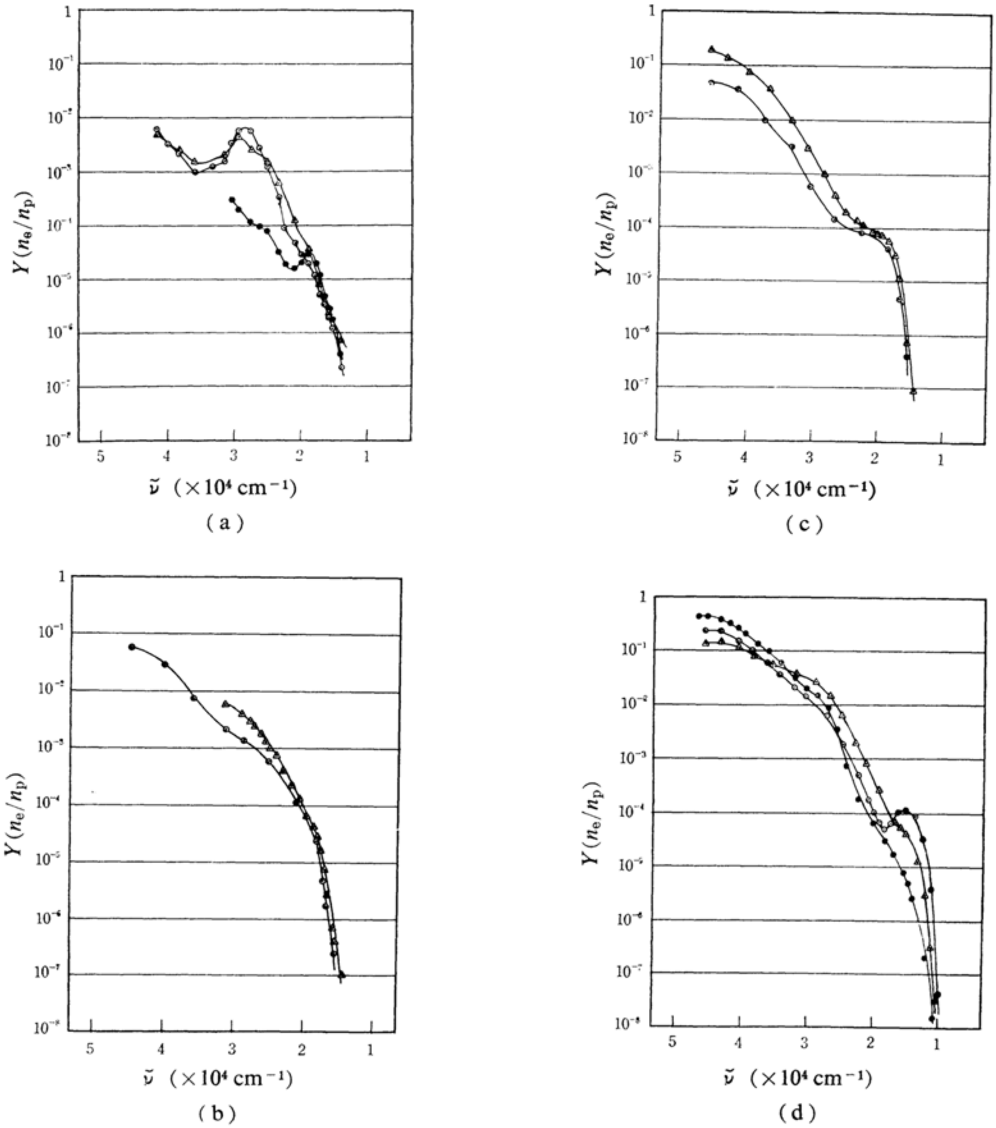
tetracyanopyrene > tetranitropyrene > tetrabromopyrene $\geqq$ tetrachloropyrene > pyrene

The velocity of complex formation followed the above relation qualitatively, and also the quantum yield of the photoemission was increased in roughly the above order. The spin

---

5) H. Inokuchi, "Organic Semiconductors," Makishoten, Tokyo (1964), p. 45.

6) L. E. Lyons and G. C. Morris, *J. Chem. Soc.*, **1960**, 5192.



(a) (c)

(b) (d)

Fig. 3. The spectral response of the photoemission.

(a) Cs-pyrene : ● immediately after reaction, ⊙ 3 days, ◬ 4 days
(b) Saturated photoemission curve for ⊙ Cs-TBrP and ◬ for Cs-TClP
(c) Cs-TNO$_2$P : ◬ immediately after reaction, ⊙ 3 days
(d) Cs-TCNP : ● immediately after reaction, ⊙ 2 days, ◬ 10 days

concentrations of the Cs-complexes, which will be reported elsewhere,⁷⁾ were also increased in the order of the above relation.

As mentioned above, the changed in the spectral response of the photoemission occured gradually. In the case of cesium-tetracyanopyrene, the response peak, around 1.7×10^4—1.8×10^4 cm^{-1}, was found during the formation of the complex, as Fig. 3 shows. This peak may be produced by cesium metal and was disappeared with time. Sometimes, the peak around 2.8×10^4 cm^{-1} was found in the spectral response of the photoemission and was independent of the nature of the organic acceptors applied. Similar peaks, 2.87×10^4 cm^{-1} for naphthalene-Cs and 2.87×10^4 cm^{-1} for hydrogenated cesium, have already been observed by Suhrmann.¹⁾ The source of the peak may be atomic cesium dispersed in the acceptors.

The absorption spectra of the Cs-aromatics complexes in th solid phase also gradually changed with time ; a strong new absorption

---

7) K. Ohigashi, S. Iwashima and H. Inokuchi, Private Communication.

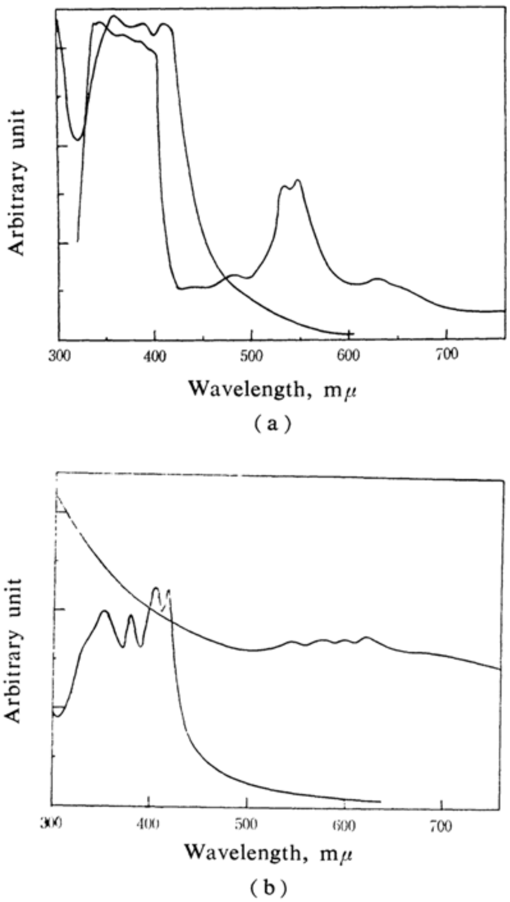


Fig. 4. The absorption spectra of the thin film of Cs-aromatics complex and its aromatic component.
(a) Cs-TCNP; curve I aromatic component and II the complex
(b) Cs-TBrP; curve I aromatic component and II the complex

peak, $1.7\times10^4\,\mathrm{cm}^{-1}$ for (TCNP) or $1.85\times10^4\,\mathrm{cm}^{-1}$ for ($\mathrm{TNO_2P}$), was found after the complex formation had been completed. However, only a very weak peak for (TBrP) was detected or no new peak for (TClP) (Fig. 4). The behaviour is also explained by the order of the electron affinity of the organic compounds.

The charge-transfer absorption peaks resemble to that of the mono-negative pyrene ion;[8] that is, the results suggest that the components in the complex are charged as $[\mathrm{Cs}^{+}] \curvearrowright [\mathrm{aromatics}^{-}]$, as was described in our previous work.[3]

The electrical resistivity of the complexes has a fairly strange result, as is illustrated in Table II. The electrical conduction of (TBrP)-Cs or (TClP)-Cs is higher than that of ($\mathrm{TNO_2P}$)-Cs or (TCNP)-Cs; in the case of the latter, the contribution of the dative-bond character to the interaction between donor and acceptor may be larger than the contributions of the former compounds. Because of the strong coupling between two components, it may be expected that the mobile carriers contributing to the electronic conduction will decrease.

Summary

On the basis o the charge transfer process of the complexes, the photoemission and the electronic conduction of the complexes between cesium and pyrene derivatives, tetranitropyrene ($\mathrm{TNO_2P}$), tetrachloropyrene (TClP), tetrabromopyrene (TBrP) and tetracyanopyrene (TCNP) have been measured. A strong increase in the quantum yield of photoemission, from 10^{-3}—10^{-4} to 10^{-1}—10^{-2}, resulting from the formation of the complexes, has been found. The promotion may take place by means of an electron transfer from cesium metal to a partner molecule; $[\mathrm{Cs}^{+}] \curvearrowright [\mathrm{Aromatics}^{-}]$. The assumption is supported by the findings concerning electron spin resonance absorption and charge-transfer spectra.

The electrical resistivity of the complexes, ρ at 15°C of pyrene-Cs$=2.1\times10^4\,\Omega$cm., (TClP)-Cs$=8\,\Omega$cm., (TBrP)-Cs$=1.6\times10^1\,\Omega$cm., ($\mathrm{TNO_2P}$)-Cs$=2\times10^6\,\Omega$cm. and (TCNP)-Cs$=6\times10^5\,\Omega$cm., is strongly affected by the contribution of the dative-bond character of the complexes.

The Institute for Solid State Physics
The University of Tokyo
Azabu, Tokyo

---

[8] P. Balk, S. de Bruijn and G. J. Hoijtink, *Rec. Trav. Chim.*, **76**, 907 (1957).