Charge Carriers in Pyrene Crystals

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(Received September 25, 1962)

The experimental studies on the electrical behaviours of the organic semiconductors have been carried out by a number of investigators$^{1)}$. The work on the determination of signs of charge carriers in molecular crystals have already been reported with association of a several methods. For anthracene, Chynoweth and Schneider$^{2)}$ found it to be positive by the rectifying behaviour of photoconduction and also Schneider and Waddington$^{3)}$ found the identical result by means of a charge carrier generation in the crystal by absorption of gases.

Applying the rectifying effect of the photoconduction, on the other hand, the predominant charge carrier in violanthrene ($C_{34}H_{18}$) was found to be negative by the present author$^{1)}$. Further, the charge carrier in pentacene, hexacene, ovalene or violanthrene was negative one and in anthracene, pyrene, chrysene, naphthacene or anthanthrene was found to be positive by Northrop and Simpson$^{4)}$. Recently, Kepler$^{5)}$ and LeBlanc$^{6)}$ reported that positive charge carriers are more mobile than negative ones in anthracene single crystals from an observation of the drift mobility.

As is described above, there are some discrepancies among the different investigators concerning the signs of charge carriers. One of the reasons for such discrepancies may be related to the purity of specimen. In this paper, the authors are presenting the effect of impurities on the sign of the charge carriers in pyrene single crystal and in pyrene thin film.

Experimental

Crude pyrene (A) was provided by Rütgerswerke-Aktiengesellschaft A. G., Germany. Among the methods of purifying pyrene crystals, the techniques of recrystallization from xylene or toluene, sublimation in vacuo and chromatography with benzene or benzene-petroleum ether were effectively applied to make specimens for measuring the electronic

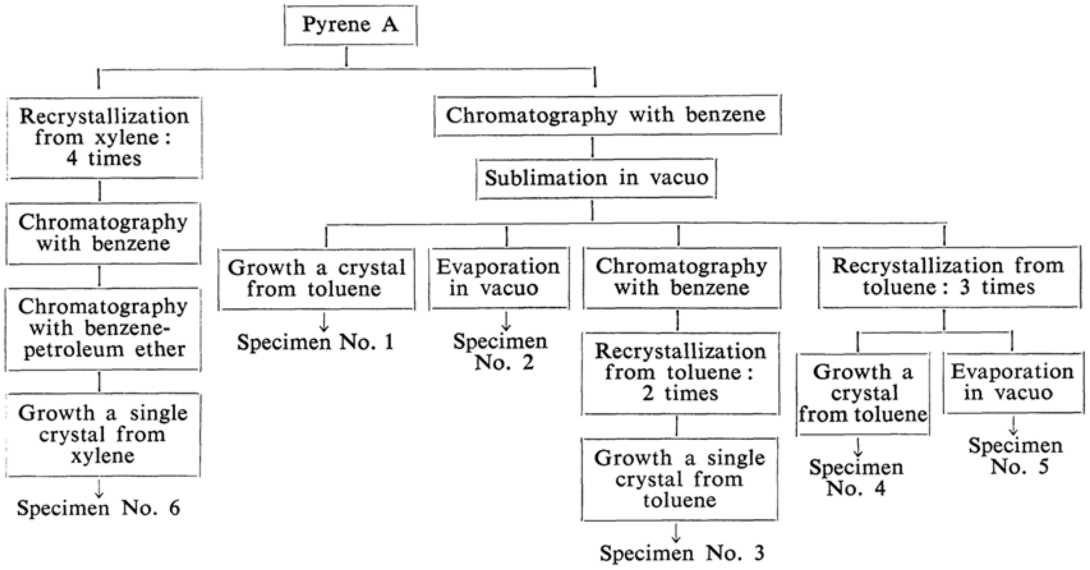

Fig. 1. The purification process of pyrene.

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1) H. Inokuchi and H. Akamatu; Electrical Conductivity of Organic Semiconductors in "Solid State Physics", Vol. 12, Academic Press Inc., New York (1961), p. 93.

2) A. G. Chynoweth and W. G. Schneider, *J. Chem. Phys.*, **22**, 1021 (1954).

3) W. G. Schneider and T. C. Waddington, ibid., **25**, 358 (1956).

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

5) R. G. Kepler, *Phys. Rev.* **119**, 1226 (1960).

6) O. H. LeBlanc, Jr., *J. Chem. Phys.*, **33**, 626 (1960).

properties with combination and repeat of the above purification methods six sorts of specimens, single crystals and evaporated thin films, were prepared as shown in the chart, Fig. 1.

The other hydrocarbons applied in this work, violanthrene, dibenzpentacene and quaterrylene, were also purified through the above techniques.

The cell applied in this experiment was prepared by evaporating an organic film on a Pyrex glass which has been coated in advance with a metal film to provide an electrode. For a single crystal specimen, an electrode of metal film was prepared on the crystal directly by means of a vacuum evaporation. The second electrode was formed thereafter by evaporation of a metal onto the surface of the specimen film or single crystal. In order to determine the sign of the predominant charge carrier, the rectifying effects of the photocurrent of the sandwhich-type cells were observed with association of a Cary vibrating-reed electrometer, model-32.

Results and Discussion

It is known that the charge carriers are generated predominately at the thin surface layer closed to the illuminated electrode. Therefore, when the illuminated electrode is charged in negative, the negative charge carriers, electrons, traverse the crystal to reach the other electrode and when the electrode is positive, the positive carriers, holes, will traverse. (It is denoted that the former current is forward one, I_f, and the latter is reverse, I_r.) Therefore, when there is a difference in the mobilities of both signs of charge carriers, the rectifying effects are found.

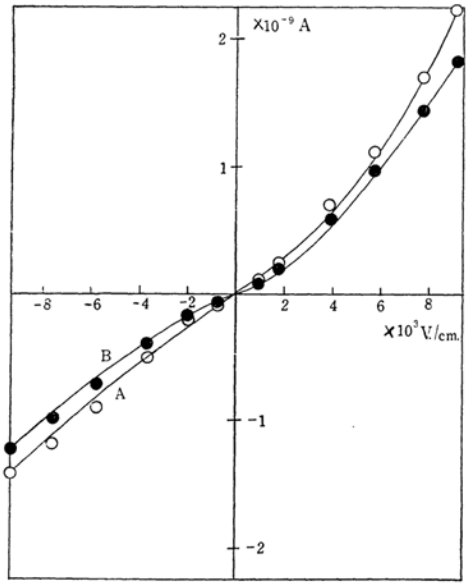

Fig. 2. The variation of the photocurrent with the applied voltage for the pyrene crystal; -●- illuminated with mercury lamp, 3650 Å, and -○- with tungsten lamp.

The variation of the photocurrent (I_p) of the crystal, pyrene, with the applied voltage obeyed the following equation:

$$I_p \propto V^{1.2} \tag{1}$$

As an example, this variation for specimen No. 1 is illustrated in Fig. 2. When two light sources*, 1000 W tungsten lamp and monochromatic mercury one (3650 Å) were applied no significant difference of the voltage-photocurrent curve was found as shown in the figure. It is suggested that photocarriers are generated only at the surface, even for wavelengths at which it would expect volume generation. For the convenience of understanding, the relation between the photocurrent and the applied voltage is illustrated with logarithmic scale in Fig. 3. Two curves, forward photocurrent and reverse one, are nearly linear except for the highest field applied in the work and are parallel with each other, that is to say, no change of the ratio of these forward and reverse currents, I_f/I_r, is found within the applied electric field.

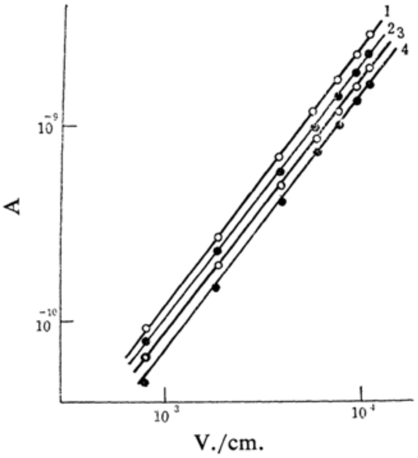

Fig. 3. The photocurrent-voltage curves for pyrene No. 1 with logarithmic scale; -●- illuminated with mercury lamp and -○- with tungsten lamp. Curves 1 and 2 are the reverse photocurrent, 3 and 4 are the forward one.

Following the consideration of transient photoconductivity in ionic crystals, I_f/I_r is described as⁷⁾,

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* The intensities of these sources were approximately $10^{15} \sim 10^{16}$ photons/cm² sec.

7) R. S. Van Heyningen and F. C. Brown, *Phys. Rev.*, **111**, 462 (1958).

$$\frac{I_{\mathrm{f}}}{I_{\mathrm{r}}}=\left[\omega_{\mathrm{e}}\left\{1-\frac{\mathrm{e}^{-Kl}}{1-K\omega_{\mathrm{e}}}+\frac{K\omega_{\mathrm{e}}}{1-K\omega_{\mathrm{e}}}\,\mathrm{e}^{-l/\omega_{\mathrm{e}}}\right\}\right.$$
$$\left.+\,\omega_{\mathrm{h}}\left\{\frac{1}{1+K\omega_{\mathrm{h}}}+\frac{K\omega_{\mathrm{h}}}{1+K\omega_{\mathrm{h}}}\,\mathrm{e}^{-(K+(1/\omega_{\mathrm{h}}))l}-\mathrm{e}^{-Kl}\right\}\right]\Big/$$
$$\left[\omega_{\mathrm{e}}\left\{\frac{1}{1+K\omega_{\mathrm{e}}}+\frac{K\omega_{\mathrm{e}}}{1+K\omega_{\mathrm{e}}}\,\mathrm{e}^{-(K+(1/\omega_{\mathrm{e}}))l}-\mathrm{e}^{-Kl}\right\}\right.$$
$$\left.+\,\omega_{\mathrm{h}}\left\{1-\frac{\mathrm{e}^{-Kl}}{1-K\omega_{\mathrm{h}}}+\frac{K\omega_{\mathrm{h}}}{1-K\omega_{\mathrm{h}}}\,\mathrm{e}^{-l/\omega_{\mathrm{h}}}\right\}\right] \qquad (2)$$

where K is an absorption constant ($10^4\,\mathrm{cm}^{-1}$ at $365\,\mathrm{m}\mu$ for pyrene), l is a thickness of crystal, $\omega_{\mathrm{e}}=\mu_{\mathrm{e}}E\tau_{\mathrm{e}}$, $\omega_{\mathrm{h}}=\mu_{\mathrm{h}}E\tau_{\mathrm{h}}$. Furthermore, μ_{e} and μ_{h} are the mobilities of electron and hole respectively, τ_{e} and τ_{h} are the meantimes for trapping of electron and hole. $E=V/l$, where V is an applied field.

In rough approximation*, this ratio, $I_{\mathrm{f}}/I_{\mathrm{r}}$, reduces as follows:

$$\frac{I_{\mathrm{f}}}{I_{\mathrm{r}}}\propto\frac{1+K\omega_{\mathrm{e}}}{1+K\omega_{\mathrm{h}}} \qquad (3)$$

The ratios for pyrene specimens are summarized in Table I. These results suggests that the ratio reaches over a unity with repeating the purification, that is, the predominant charge carrier is changed from hole to electron with increasing the purity of the crystals. It is expected that the impurities, which may be compounds comprised oxygen**, provide trapping centres for electrons or catch the negative charge carriers. Thereby, it is observed the positive charge carriers in impure crystal are more mobile than the negative one. Recently, Hoesterey has reported the impurity in anthracene acts as an additional dissociation centre capable of trapping the electron component of the exciton[8]. These ratios, $I_{\mathrm{f}}/I_{\mathrm{r}}$, for violanthrene, dibenzpentacene and quaterrylene were 5∼10, 4 and 1.0, respectively. The ratio of pyranthrene ($C_{30}H_{16}$) was found to be 1.5 by Sano[9].

TABLE I. THE RATIOS FOR A NUMBER OF PYRENE CRYSTALS

Sample No.	Form	$I_{\mathrm{f}}/I_{\mathrm{r}}$
1	Single crystal	0.8
2	Evaporated film	0.9
3	Single crystal	0.6
4	Single crystal	1.3
5	Evaporated film	2.4
6	Single crystal	1.2

To avoid the effect of electrodes and also to estimate the charge mobility in organic crystals, the observation of transient photoconductivity of the organic single crystal sandwiched with two blocking layers is in due course. Further, in comparison with the experimental results, the calculation of overlap integrals between the molecular orbitals of different pyrene molecules in the crystal lattice will be appeared elsewhere.

Summary

From the rectifying behaviour of photoconduction, the sign of charge carriers in molecular crystals is estimated; the ratio of forward photocurrent and reverse one corresponds to the ratio of mobilities $\mu_{\mathrm{e}}/\mu_{\mathrm{h}}$, where μ_{e} is the mobility of electron and μ_{h} is that of hole. The ratio for pyrene crystal reaches over a unity with repeating the purification, that is, the predominant charge carrier changed from hole to electron with increasing the purity of the crystals. For violanthrene or dibenzpentacene, the ratio is larger than 4 and for quaterrylene, that is almost a unity.

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* When we introduce $Kl\gg 1$ and $\omega\ll l$, Eq. 2 reduces to Eq. 3.

** The chemical analysis of the contaminants is progressed.

[8] D. C. Hoesterey, *J. Chem. Phys.*, **36**, 557 (1962).

[9] M. Sano, This Bulletin, **34**, 1668 (1961).