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Photoconductive Properties of Organic Polyiodides

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The photoconductive properties of $(CH_3)_4N^+I_5^-$, $(CH_3)_3(C_6H_5)N^+I_5^-$, *N*-methylacridinium pentaiodide and *N*-methylquinolinium pentaiodide were investigated by both a sandwich type cell and a single crystal cell. In the former arrangement, the photoresponse observed was the overlap of photoconductive response and photovoltaic response. The single crystal gave pure photoconductive response. Tetramethylammonium pentaiodide was the most photoconductive among the polyiodides. Spectral dependence of the photocondutcivity of this compound revealed that the threshold is at about 1000 mμ (1.24 eV). This value is in good agreement with the band gap energy 1.36 eV obtained from the temperature dependence of the dark current and 1.20—1.26 eV from calculation. Semiconductive properties of the organic polyiodides are explained by applying the band model.

Semiconductive properties of thirteen organic polyiodides including tetramethylammonium, trimethylphenylammonium, *N*-methylpicolinium, and *N*-methylacridinium polyiodides were investigated.[1,2] Two inorganic polyiodides, caesium triiodide[3] and tetraiodide,[4] were investigated. The effect of X- and γ-irradiations on the electrical conductivity of tetramethylammonium pentaiodide was also investigated.[5] Specific resistivity of the polyiodides was of the order 10^5—10^{12} Ωcm and had close connection with the number of the iodine atoms of the polyiodide anion. The framework of the polyiodide anion in the crystal is, therefore, considered to be of primary importance in determining the electrical

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[1] S. Kusabayashi, H. Mikawa, S. Kawai, M. Uchida and R. Kiriyama, This Bulletin, **37**, 811 (1964).

[2] S. Kusabayashi and H. Mikawa, *ibid.*, **38**, 1410 (1965).

[3] M. Hayashi, H. Mikawa and S. Kusabayashi, Preprints for the 19th Annual Meeting of the Chemical Society of Japan (Yokohama, 1966), 1S010.

[4] R. Matsuyama, S. Kusabayashi and H. Mikawa, Preprints for the 21st Annual Meeting of the Chemical Society of Japan (Suita, 1967), 2O227.

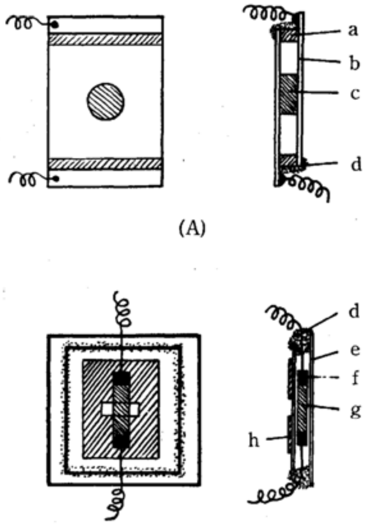
[5] S. Kawai, R. Kiriyama, M. Uchida, S. Kusabayashi and H. Mikawa, This Bulletin, **38**, 799 (1965).

conductivity of the crystals. Energy band calculation of tetramethylammonium pentaiodide was carried out by the simple LCAO approximation method.[6] Calculation of the energy band was carried out with caesium triiodide[3] and caesium tetraiodide (Cs_2I_8).[4] Although in these calculations only the iodine framework was considered, without taking into consideration the effect of cations, values of the energy gap were found to be nearly the same as the observed value. This fact confirmed again the primary importance of the iodine framework in determining the electrical properties of the polyiodides.

The authors have already pointed out that some of the organic polyiodides have photoconductive response. In the present investigation, the photoconductive properties of tetramethylammonium pentaiodide (I), trimethylphenylammonium pentaiodide(II), *N*-methylquinolinium pentaiodide(III) and *N*-methylacridinium pentaiodide (IV) are reported. The threshold wavelength of the photoconductivity of I is in agreement with the band gap energy from the dark conductivity and the calculated band gap energy.

Experimental

Materials. The pentaiodides (I—IV) were prepared by the method reported[1,2] and used as the samples for photoconductivity measurement after recrystallizing repeatedly from water-alcohol (I, II, III) or alcohol-tetrahydrofuran (IV).



(A)

(B)

Fig. 1. Sandwich cell (A) and Single crystal cell (B).
a mica sheet, b nesa coated glass or quartz, c sample (melted and solidified), d paraffin, e glass or quartz, f silver paste, g crystal, h mask for the light

Sandwich-type Cell. The sandwich type cell (0.3—0.6 cm^2 in area and 10^{-2} cm in thickness) was made by melting and solidifying the polyiodide material between two nesa quartz plates (Fig. 1). The polyiodide materials sandwiched were in polycrystalline state.

Single Crystal Cell. The single crystal cell was made by putting between two quartz plates a single crystal (1.5 mm in width, 1 mm in thickness and 4 mm in length) with the electrodes attached by using silver paste (Fig. 1). The light illumination was effected perpendicular to the cleavage plane (*ab*-plane) of the crystal. To prevent the incident light from reaching the electrodes area an appropriate screen was attached to the single crystal cell. The sample was shut out from air with a paraffin seal between the two quartz plates, as shown in Fig. 1.

A monochromatic light from a 500 W xenon lamp with the intensity distribution shown in Fig. 2 was used, its intensity being controlled by neutral filters. Electrical measurements were carried out as usual at 20°C. In measuring the photocurrent, the dark current was potentiometrically compensated when necessary.

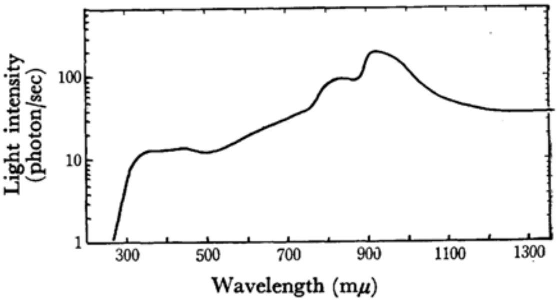


Fig. 2. Energy distribution of the light of the xenon lamp measured by a thermopile (Reedeer 8858 USA) using a monochrometer. For light of 300—320 mμ and 500—1200 mμ the slit width was kept 2 mm and 0.48 mm respectively. For 320—500 mμ the width of the wave length was kept 10 mμ. Absolute intensity of the light with this wave length width at 350—450 mμ region is 3.3×10^{14} photon/sec, when measured at the outlet of the monochrometer.

Results and Discussion

With the sandwich type cell the photoresponse consisted of both photoconductive response and photovoltaic response. It was revealed that the photoresponse of tetramethylammonium pentaiodide (I) is two to three orders of magnitude larger than the other three pentaiodides (II—IV). The photoresponse of I is very large when the positive side is illuminated, and small when illuminated at the negative side. Then sign of this rectifying effect in photoconductivity is in agreement with the positive sign of the thermoelectric power.[1] The predominant carrier in this material seems to be a hole rather

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6) S. Kusabayashi and H. Mikawa, This Bulletin, **39**, 736 (1966); S. Kusabayashi, H. Mikawa, M. Konda and M. Hayashi, *ibid.*, **39**, 1383 (1966).

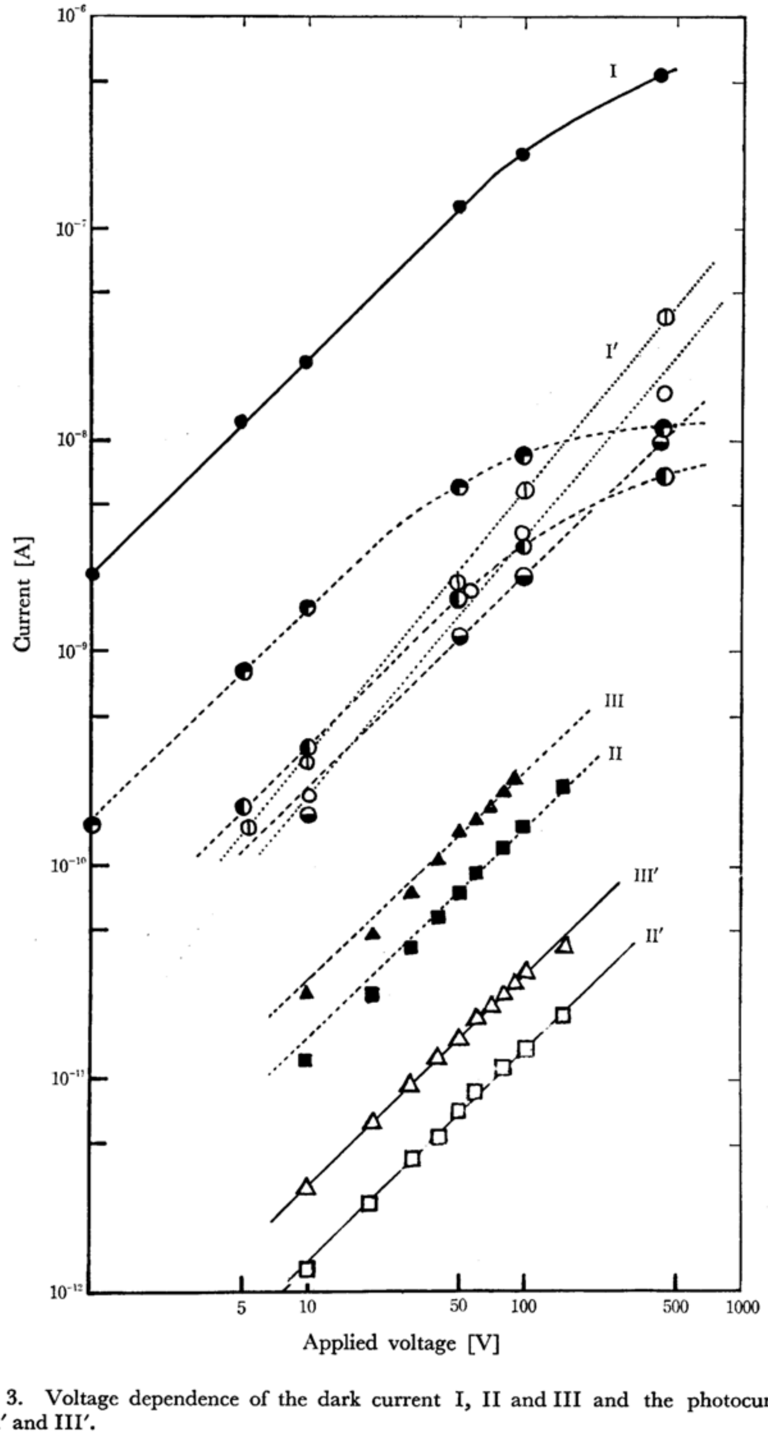

Fig. 3. Voltage dependence of the dark current I, II and III and the photocurrent I′, II′ and III′.
Tetramethylammonium pentaiodide (I and I′) with the monochromatic light of ◕ 850 mμ, ◐ 700 mμ, ◒ 600 mμ, ⦶ 450 mμ, ○ 350 mμ. Trimethylphenylammonium pentaiodide (II and II′) and *N*-methylquinolinium pentaiodide (III and III′) with the light from a 500 W xenon lamp with the filter passing the light longer than 550 mμ. All values of the photocurrent are not normalized for the light intensity.

than an electron. At the higher applied voltage region, the photocurrents of II, III and IV are very small in comparison with the dark current, and the photocurrent due to the photovoltaic effect seems to be predominant.

With the single cyrstal cells no photoresponse was observed when illuminated with no applied potential. Under applied potential the steady state photocurrent with comparatively sharp rise and decay characteristics was observed with the light on or off. As the contact area between the electrode and the material is not illuminated in the single crystal cell, it might be concluded that the polyiodide materials are photoconductive. Photoresponse was in the order I ≫ II, III, IV, being in the same order as for the sandwich type cell.

The photocurrent with the monochromatic light was very small for the compounds II, III and IV, when compared with the dark current, being in the order of 10^{-11}—10^{-12} A. Total light with $\lambda > 550$ mμ was, therefore, used to measure the voltage dependence of the photocurrent of these compounds. Both the dark current and the photocurrent thus measured were proportional to the applied voltage, as shown by the curves II, II′, III and III′ in Fig. 3. The dark current and the photocurrent of compound I was nearly proportional to the applied voltage, as shown by the curves I and I′ in Fig. 3. As the photocurrent of this compound is rather large, monochromatic light was used. When illuminated with the light of the longer wavelength (700 mμ and 850 mμ), saturation of the photocurrent occurs in the higher voltage region. As the length of the single crystal was about 4 mm, the field strength remained within several hundred volt per cm even when 100 V was applied.

The light intensity dependence of the photocurrent changes as shown in Fig. 4 and Table 1 according to the applied voltage and the wave-

TABLE 1. THE LIGHT INTENSITY (L) DEPENDENCE OF THE PHOTOCURRENT OF $(CH_3)_4{}^+I_5{}^-$

The numbers represent n in $I_{pn} \propto L^n$.

Voltage	Wavelength mμ		
	$\lambda < 500$	$500 < \lambda < 700$	$700 < \lambda$
High (100—450 V)	0.5	0.5—1.0	1.0
Low (1—100 V)	0.4—0.5	0.5—0.7	0.7—0.9

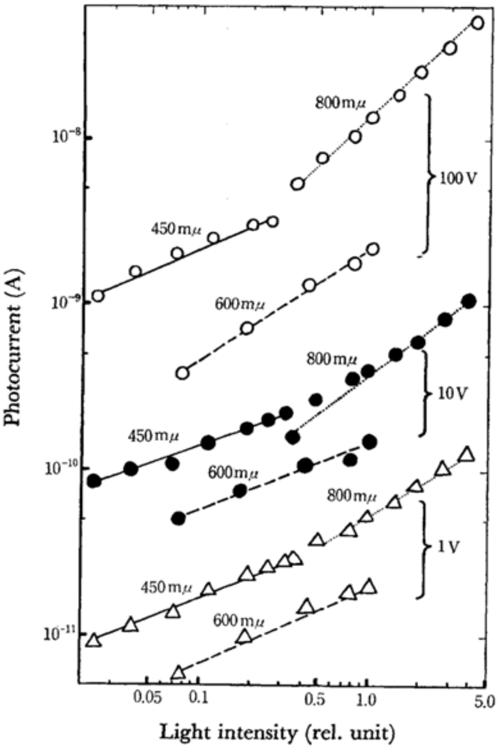

Fig. 4. Dependence of the photocurrent of tetramethylammonium pentaiodide on light intensity. Voltages shown in the figure are the potentials applied across the crystal of *ca.* 4 mm length.

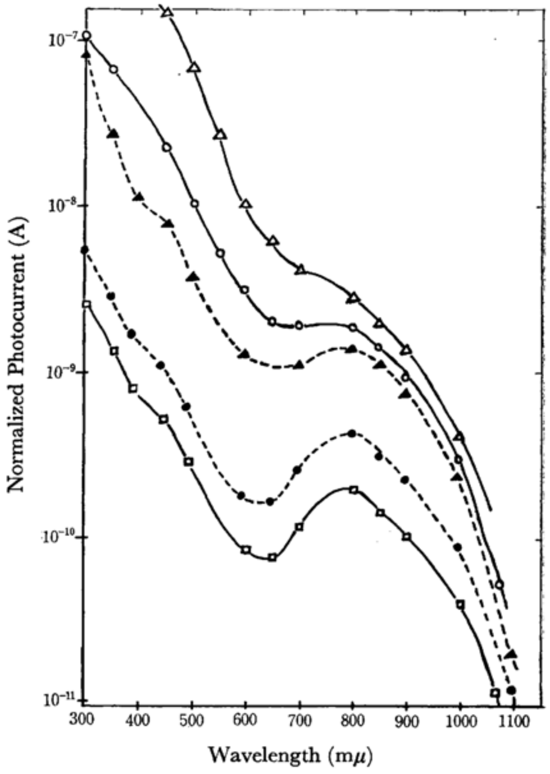

Fig. 5. Spectral dependence of the photocurrent of tetramethylammonium pentaiodide normalized for light intensity. Voltages shown in the figure are the potentials applied across the crystal of *ca.* 4 mm length.

——△—— 450 V ——○—— 100 V
——▲—— 50 V ------●------ 10 V
——□—— 5 V

length. When illuminated with the light shorter than 500 mμ, the photocurrent was proportional to the 0.5 power of the light intensity, probably because the photocurrent was recombination limited in this region, the light being strongly absorbed, generating the carriers in very high concentration at the crystal surface. On the other hand the wavelength longer than 700 mμ is absorbed weakly, generating the carriers penetrating rather deep in the bulk of the crystal. This condition gives $n=1.0$. In the intermediate region from 500—700 mμ, n becomes 0.5—1.0.

The wavelength dependence of the photocurrent normalized for the light intensity L is shown in Fig. 5. The normalization was made by assuming the relation $I_{ph} \propto L^{1.0}$, the current at 600 mμ being taken as the standard. As the photocurrent is proportional to the light intensity in the region longer than 700 mμ at 100—450 V as shown in Fig. 4, this normalization may be reasonable at least in this region.

The apparent quantum yield of the photocurrent of tetramethylammonium pentaiodide was calculated to be 1.5×10^{-5} at 1000 mμ under 450 V. The threshold of the photocurrent seems to be about 1000 mμ. If the mechanism of the photoconduction is to be explained by the band model, the energy of the threshold (1.24 eV) must be equal to the band-gap energy. This value is in good agreement with the band-gap energy value 1.36 eV1) estimated from the temperature dependence of the dark current and the band-gap energy value 1.20—1.26 eV estimated from the calculation.6) These facts suggest that the band model is applicable to the photoconduction of the tetramethylammonium pentaiodide. Moreover, this result gives additional support to our previous suggestion that the iodine framework in the crystal structure is of primary importance in determining the conductivity of polyiodides.