

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT DIVISION, AMERICAN VISCOSE CORPORATION, MARCUS HOOK, PENNA.]

Preparation and Electrical Conductivity of Copper Tetra-2,3-pyridinoporphyrazine and Copper Tetra-2,3-pyrazinoporphyrazine

BY M. J. DANZIG, C. Y. LIANG AND E. PASSAGLIA¹

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In order to relate semiconduction of organic substances to structure, copper tetra-2,3-porphyrazines were made containing pyridine and pyrazine rings. The resistivity of copper phthalocyanine, Cu-tetra-2,3-pyridinoporphyrazine and Cu-tetra-2,3-pyrazinoporphyrazine has been shown to follow the equation $\rho = \rho_0 \exp(E_d/2kT)$. It is found that E_d for the three substances are 1.3, 1.17 and 0.81 e.v., respectively, and that ρ_0 is the same for the three substances. It is deduced from these results that the mobility for the materials is an activated process. The photocurrents for these samples were found to be proportional to the applied voltage at various temperatures.

I. Introduction

The semiconductive and photoconductive properties of the phthalocyanines have been the object of study by many workers.^{2,3} The basic structure of the materials is well known and they can be obtained in pure and crystalline forms. Measurements have been carried out either on pressed powders or single crystals of metal-free phthalocyanine or phthalocyanine containing various metals. The dark conductivity is found to obey the equation $\rho = \rho_0 \exp(E_d/2kT)$, where ρ_0 is a constant and E_d is an activation energy, and has a value ranging from 0.5 e.v. to 2 e.v. The steady state photocurrent in metal-free phthalocyanine was found to obey the equation $i = i_0 \exp(-E_p/kT)$, with an activation energy E_p estimated to be 0.2 e.v. Many, Harnik and Gerlich⁴ estimated the carrier mobility to be 1 cm.²/volt-sec. for metal-free phthalocyanine and 10 cm.²/volt-sec. for copper phthalocyanine, but Kearns and Calvin⁵ using pulse-light technique estimated the carrier mobility to be of the order of 10^{-3} to 10^{-2} cm.²/volt-sec. In common with other organic semiconductors the majority of carriers are positive holes.

In a system which has been so well studied we decided to investigate the effect of systematic changes in molecular structure on the electrical properties. Such systematic changes could be expected to lead to changes in the mobility of the carriers, the activation energy, or both, and hence the dark conductivity and possibly the photoconductivity. The first investigation undertaken in this study was the synthesis of a series of phthalocyanines in which the ring R has been altered in the following sequence: benzene (I), pyridine (II) and pyrazine (III) (see Fig. 1).

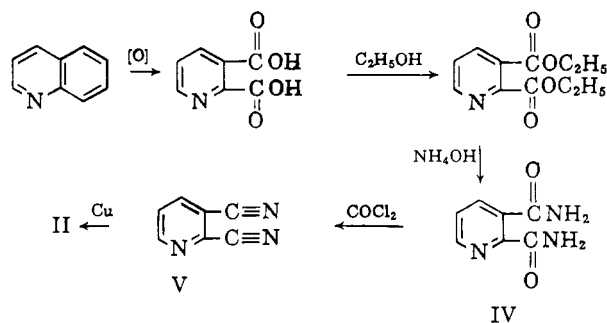
The chemistry of the phthalocyanines is well known, and they have been extensively studied as dyestuffs. The phthalocyanines of interest to us have been reported by Linstead and co-workers.^{6,7} However, the pyridine analog II was not characterized, and we have developed an easier synthetic route to the pyrazine analog III.

Copper tetraazoporphyrazine (Cu phthalocyanine) (I) was prepared by the method of Linstead.⁶ The resulting dye was purified by solution in concentrated sulfuric acid followed by precipitation in ice, after which it was dried and sublimed.

Copper-tetra-2,3-pyridinoporphyrazine was also reported by Linstead and co-workers,⁷ but they could not obtain a pure product. The synthetic methods used were treatment of an impure 2,3-dicyanopyridine

(V) with copper or by heating cuprous chloride, quinolinamide and ammonium aminosulfonate together. In order to obtain a pure sample of II, it was felt that the synthesis of the uncharacterized 2,3-dicyanopyridine should be undertaken. With this synthesis completed a pure pyridinophthalocyanine could be prepared. Attempts to prepare 2,3-dicyanopyridine by the classical dehydration techniques of quinolinamide gave very poor or no yield of an impure material which formed a blue pigment when heated with copper, or 2(or 3)-cyanopyridine-3(or 2)-carboxamide which also gave blue colors with copper.⁶ The character of these pigments is unknown.

We were able to dehydrate quinolinamide (IV) in 65% yield by using phosgene as a reagent. The 2,3-dicyanopyridine (V) was then obtained for the first time in pure form and this readily gave a pure phthalocyanine analog on treatment with copper.



By using a similar reaction scheme 2,3-dicyanopyrazine was prepared from quinoxaline and subsequently converted to the Cu-tetra-2,3-pyrazinoporphyrazine III.

II. Preparation of the Samples

2,3-Dicyanopyridine (V).—In a 3-neck flask fitted with a stirrer, gas inlet tube and a condenser with a gas exit was placed 39.2 g. of quinolinic acid diamide⁸ in 1 liter of dimethylformamide. The flask was cooled to 10° and phosgene was bubbled into it for 2 hours. The temperature was raised to 40° and the phosgene addition was continued for 5 hours. Upon completion of the addition of the gas the stirring was continued for another hour. The resulting red liquid was poured into ice-water and neutralized with 10% sodium carbonate. There was obtained on filtration 13.1 g. of dicyanopyridine melting at 79°. The filtrate was extracted with ether and an additional 6.43 g. melting at 80° was isolated; total yield 19.5 g. (63.7%). The product was recrystallized from a solution of 50% benzene and petroleum ether; m.p. 80°.

Anal. Calcd. for $C_7H_3N_3$: C, 65.1; H, 2.32; N, 32.5. Found: C, 65.3; H, 2.62; N, 32.6.

Copper Tetra-2,3-pyridinoporphyrazine (II).—In a flask was placed 2.58 g. of 2,3-dicyanopyridine, 0.32 g. of copper powder and 15 cc. of quinoline. The suspension was stirred and heated to 212° for 4 hours. Upon completion of the reaction the mixture was poured into methanol and filtered. This almost pure dye was suspended in methanol and stirred. The heavier unreacted copper settled quickly and the dye was decanted off. This was continued repeatedly until the dye was removed from any un-

(1) National Bureau of Standards, Washington 25, D. C.

(2) C. G. B. Garrett, "Semiconductors," N. B. Hannay, Ed., Reinhold Publishing Corp., New York, N. Y., 1959.

(3) H. Inokuchi and H. Akamatsu, "Solid State Physics," F. Seitz and D. Turnbull, Eds., Vol. 12, Academic Press, Inc., New York, N. Y., 1961.

(4) A. Many, E. Harnik and D. Gerlich, *J. Chem. Phys.*, **23**, 1733 (1955).

(5) D. R. Kearns and M. Calvin, *ibid.*, **34**, 2022 (1961).

(6) R. P. Linstead, *et al.*, *J. Chem. Soc.*, 1016 (1934).

(7) R. P. Linstead, E. G. Noble and J. M. Wright, *ibid.*, 911 (1937).

(8) C. Engler, *Ber.*, **27**, 1784 (1894).

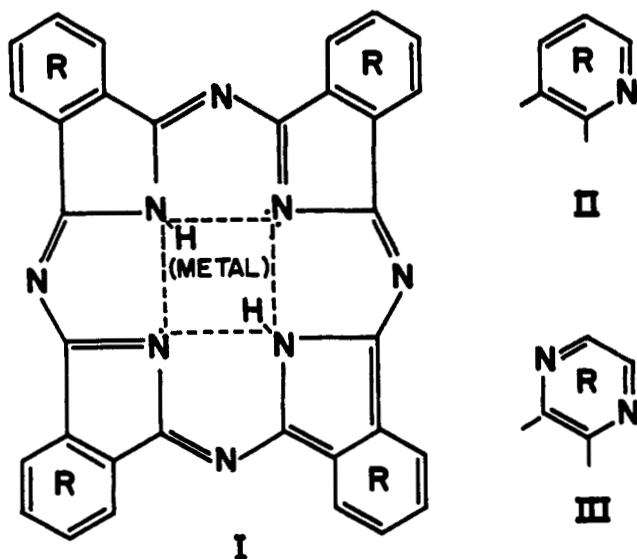


Fig. 1.—Chemical structures of Cu-phthalocyanine (I), Cu-tetra-2,3-pyridinoporphyrazine (II) and Cu-tetra-2,3-pyrazinoporphyrazine (III).

reacted copper. The dye was filtered and dried at 195° for 2 hours to give 2.67 g. (92%) of copper tetra-2,3-pyridinoporphyrazine.

Anal. Calcd. for $C_{28}H_{12}N_{12}Cu$: C, 57.99; H, 2.07; N, 28.99. Found: C, 58.0; H, 2.47; N, 28.4.

2,3-Dicyanopyrazine.—In a 3-neck flask fitted with a stirrer, gas inlet tube and a condenser fitted with an exit tube was placed 12.0 g. of 2,3-pyrazinedicarboxylic acid diamide⁹ in 300 ml. of dimethylformamide. The flask was cooled to 5° and phosgene was bubbled into the solution for 1 hour. The temperature was controlled by the reaction heat and it reached a maximum of 30°. Upon completion of the phosgene addition the contents were poured into ice and water, and upon filtration of the solid there was obtained 5.0 (53.3% yield) of dicyanopyrazine melting at 134–135°. An additional 0.84 g. of product was obtained by extracting the aqueous solution with ether; total yield 5.84 g. (62% yield). A sample was purified for analysis; m.p. 135° by recrystallization from water.

Anal. Calcd. for $C_4H_2N_4$: C, 55.4; H, 1.54; N, 43.1. Found: C, 55.1; H, 1.55; N, 43.2.

Copper Tetra-2,3-pyrazinoporphyrazine (III).—In a flask was placed 3.56 g. of 2,3-dicyanopyrazine, 0.32 g. of copper powder and 75 ml. of quinoline. The mixture was heated to 200° and stirred for 3 hours. Upon completion of the reaction, the mixture was poured into methanol and the dye was filtered off. The crude dye was dissolved in concentrated H_2SO_4 at 0°, filtered and poured over an excess of ice. After the ice melted the dye was centrifuged away from the water, washed with water, dilute ammonium hydroxide and water until neutral, followed by acetone washings. The product was then dried in vacuum at 195° with a pressure of less than 10^{-5} mm. for 2 days and was then allowed to pump overnight at this pressure at room temperature. Attempts to dehydrate the porphyrazine failed. Linstead was also unsuccessful in his attempts to dehydrate this dye.

Anal. Calcd. for $C_{24}H_8N_{16}Cu \cdot H_2O$: C, 47.9; H, 1.66. Found: C, 47.5; H, 1.95.

III. Electrical Conductivity Measurement

A. Experimental.—The polycrystalline samples were prepared in the form of pressed disks at approximately 4000 p.s.i. The back electrode was tin foil and the front electrode was conducting glass. The pressed disk with electrodes was clamped between two polished stainless steel plates, with a hole in the center of the top plate to serve as a window for illumination, and it was insulated with Teflon sheets. Conductivity at various temperatures was measured by placing the sample in a temperature-controlled vacuum chamber having a quartz window. The cell was clamped on the heated metal block with its front electrode facing the quartz window of the container. The container was evacuated during measurements.

The light source used for photocurrent measurement was either a tungsten lamp with focusing lens or a Perkin-Elmer model 12B infrared spectrometer equipped with a quartz prism. The plain mirror behind the exit slit of the spectrometer was replaced by a flat quartz plate. The transmitted light from the quartz plate was condensed by a quartz lens onto the conducting glass elec-

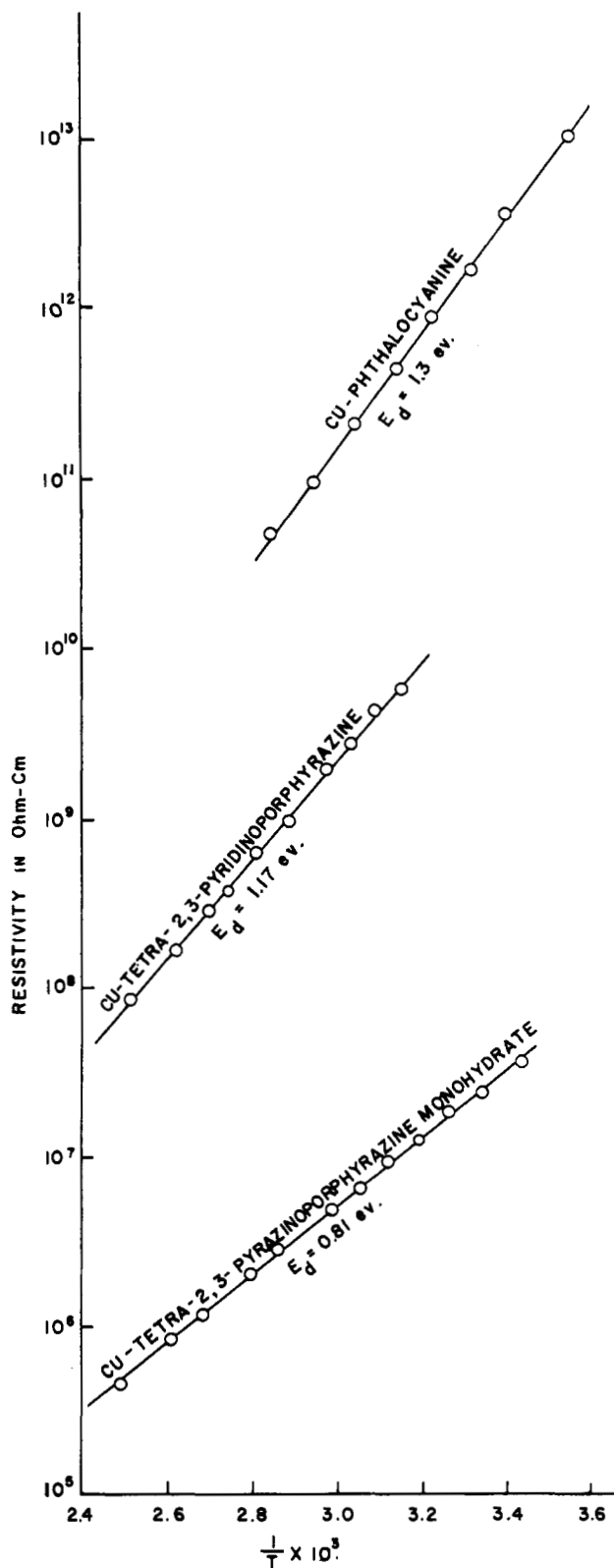


Fig. 2.—Resistivity of Cu-phthalocyanine, Cu-tetra-2,3-pyridinoporphyrazine and Cu-tetra-2,3-pyrazinoporphyrazine monohydrate vs. reciprocal of absolute temperature.

trode of the sample cell. In order to correct the incident light on the sample to a constant intensity at different wave lengths, the intensity of the small percentage of the reflected light from the quartz plate was measured by a thermocouple.

The dark and photocurrents of the samples were measured using a vibrating reed electrometer. A bias potential was connected to the feedback terminal and was used to balance the dark current in order to make the photocurrent measurement in a sensitive scale.

(9) S. Gabriel and A. Sonn. *Ber.*, **40**, 4850 (1907).

TABLE I
DIMENSIONS, RESISTIVITY AND ACTIVATION ENERGY OF PRESSED DISKS OF COPPER PHTHALOCYANINE DERIVATIVES

Sample	Diameter, cm.	Thickness, cm.	ρ , ohm-cm.	E_d , e.v.	ρ_1/ρ , obsd.	ρ_1/ρ , calcd.	E_p , e.v.
Cu-phthalocyanine (I)	1.27	0.136	$\sim 10^{12}$	1.3			0.15
Cu-tetra-2,3-pyridinoporphyrazine (II)	1.27	.157	2.89×10^{10}	1.17	35	13	.20
Cu-tetra-2,3-pyrazinoporphyrazine (III)	1.27	.222	2.97×10^7	0.81	3.4×10^4	1.5×10^4	.27

B. Temperature Dependence of Resistivity.—The temperature dependence of the resistivities of the samples is shown in Fig. 2. The results for each sample can be expressed by the well known equation $\rho = \rho_0 \exp(E_d/2kT)$. The room temperature resistivity and activation energy are given in Table I for each of the samples. The reason for the differences in the E_d will be discussed later.

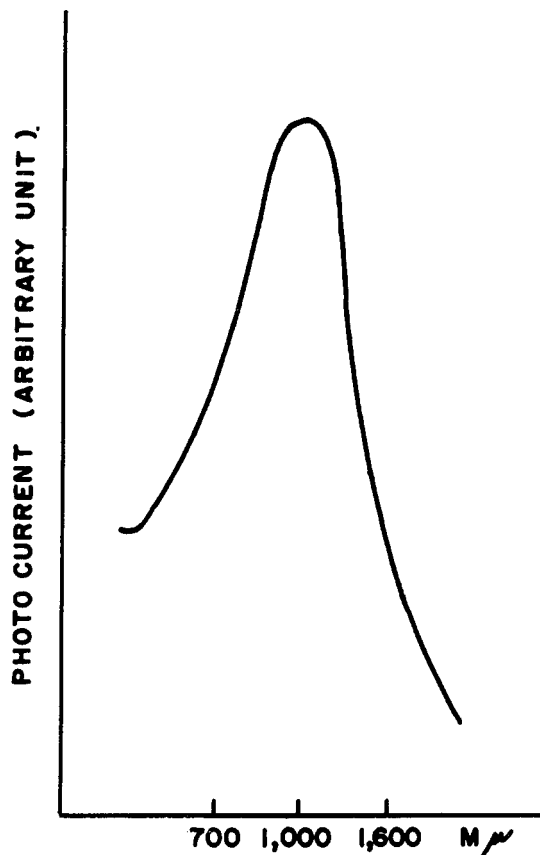


Fig. 3.—Wave length dependence of photocurrent of Cu-tetra-2,3-pyrazinoporphyrazine monohydrate.

C. Wave Length Dependence of Photoconductivity.—The wave length dependence of the photocurrent for Cu-tetra-2,3-pyrazinoporphyrazine monohydrate is shown in Fig. 3. The photocurrent peak is measured near 1000 mμ. Calibration for constant light intensity at different wave length was not made. The peak intensity of the tungsten lamp was observed near 1200 mμ and hence the peak photocurrent near 1000 mμ was characteristic of the sample.

The photocurrent peak for Cu-tetra-2,3-pyridinoporphyrazine was not accurately determined because the photocurrent was too weak to be measured with the present equipment. The photocurrent peaks of a sample of Cu-phthalocyanine were found near 700 and 1100 mμ.

D. Photoconductivity at Different Electrical Fields and Temperatures.—Several authors¹⁰⁻¹² have reported

(10) G. Tollin, D. R. Kearns and M. Clavin, *J. Chem. Phys.*, **32**, 1013, 1020 (1960).

(11) J. Kommandeur, G. J. Korinek and W. G. Schneider, *Can. J. Chem.*, **35**, 998 (1957).

(12) B. Rosenberg, *J. Chem. Phys.*, **29**, 1108 (1958).

temperature dependence of photocurrent on organic semiconductors. They found that the photocurrent satisfied the equation $i = i_0 \exp(-E_p/kT)$ where i_0 is a constant. The photocurrent activation energy E_p is of the order of 0.2 e.v. and is interpreted as due to potential barriers hindering carrier transport.¹¹

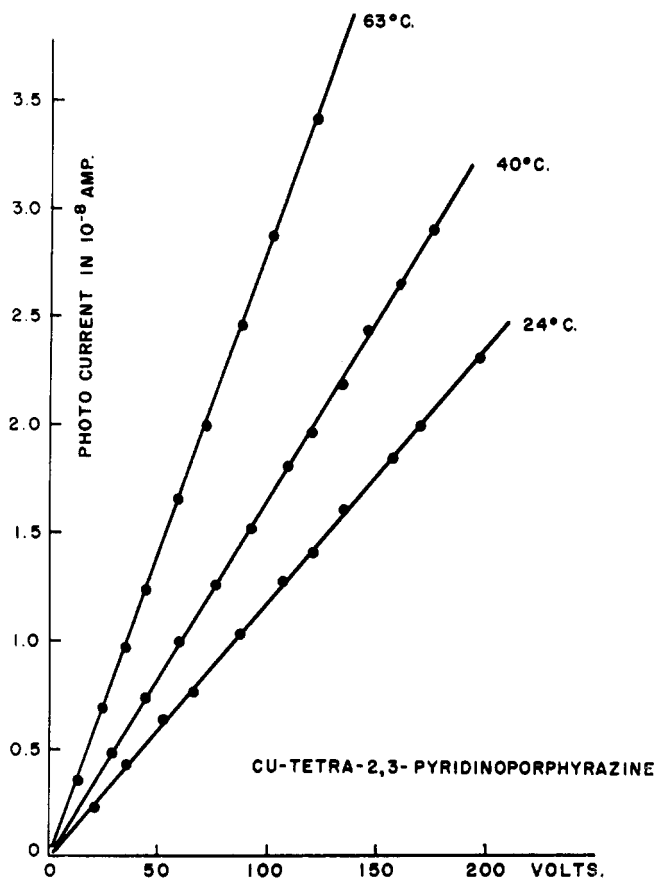


Fig. 4.—Photocurrent vs. voltage for Cu-tetra-2,3-pyridinoporphyrazine.

Using tungsten lamp illumination, the photocurrents at various temperatures for the samples were measured. The photocurrent increases as the temperature increases from room temperature to about 50°. At high temperature, the photocurrent decreases. Since it has been noted that the resistance of the sample decreases at higher temperature, the voltage across the sample thus becomes small. In order to observe the photocurrent at different temperature with the same voltage across the sample, the following measurements were made: The samples were kept at a certain chosen temperature, and the photocurrents were measured at various applied voltages. These measurements were then plotted on a graph of photocurrent against voltage across the sample. Similar measurements made for the sample at other temperatures are plotted on the same graph. Selecting a certain value of voltage, the photocurrent at different temperatures can be obtained from the graph.

The photocurrent vs. voltage at temperatures 24, 40 and 63° for Cu-tetra-2,3-pyridinoporphyrazine is shown in Fig. 4. The photocurrent is found to increase

linearly with the increase of applied voltage and to increase with the increase of temperature. The logarithms of the photocurrents at temperatures 24, 40 and 63° at a certain voltage are plotted against the inverse of absolute temperature. It was found that the three points lie approximately in a straight line. The photocurrent can thus be assumed to follow the equation $i = i_0 (-E_p/kT)$ and the activation energy E_p was found to be about 0.20 e.v. It may be noted that the photocurrent activation energy E_p is independent of the applied voltage.

The photocurrent plotted against voltage at 19, 40 and 60° for Cu-tetra-2,3-pyrazinoporphyrazine monohydrate is shown in Fig. 5. Again the photocurrent was found to increase linearly with the increase in applied voltage and to increase with the increase in temperature. The photocurrent activation energy E_p was estimated to be about 0.27 e.v.

Similar measurements were made for a Cu-phthalocyanine sample and the photocurrent activation energy was estimated to be about 0.15 e.v.

IV. Discussion

If these materials are considered to be intrinsic semiconductors, the resistivity is written

$$\rho = \rho_0 \exp (E_d/2kT) \quad (1)$$

and the ratio of the resistivities of two samples, ρ_1 and ρ_2 , is given by

$$\rho_1/\rho_2 = \frac{\rho_{01}}{\rho_{02}} \exp \left(\frac{E_{d1} - E_{d2}}{2kT} \right) \quad (2)$$

The ratio at room temperature as observed is given in Table I along with the ratio calculated on the assumption $\rho_{01} = \rho_{02}$. It will be noted that the observed value taking I as the reference sample is 2 to 3 times the value calculated on this basis. The calculated resistivity ratio from samples II and III is 1.1×10^3 and the observed value is 0.97×10^3 , values which are remarkably similar. Moreover, the room temperature resistivity of sample I was not reproducible within a factor of two, so that from these experiments there is reason to believe that ρ_0 for these materials is approximately a constant, which indicates that the primary factor in determining the differences in conductivity is the activation process.

The observed values of dark conductivity activation energy need not be the quantity which is related to a "band-gap," if such a thing exists for these materials. If the mobility itself is an activated process, the resistivity may be written where N is the charge carrier

$$\rho = \frac{1}{N\mu} = \frac{1}{N_0\mu_0} \exp \left(\frac{\epsilon}{kT} + \frac{E_g}{2kT} \right) \quad (3)$$

concentration, μ is the carrier mobility, ϵ is the activation energy for mobility and E_g is the forbidden band-gap. If the mobility activation energy is the same as the photocurrent activation energy, then the band gap is related to the observed values by the equation

$$E_g = E_d - 2E_p \quad (4)$$

From this we may calculate E_g (I) $\cong 1.0$ e.v., E_g (II) $\cong 0.77$ e.v. and E_g (III) $\cong 0.27$ e.v. The threshold energies estimated from the photoconductivity is

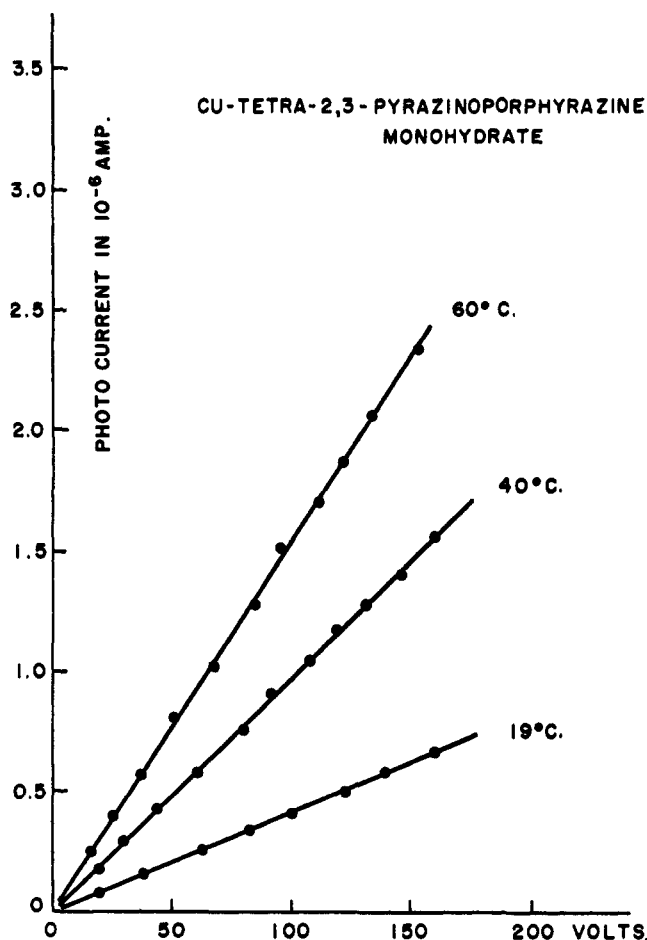


Fig. 5.—Photocurrent vs. voltage for Cu-tetra-2,3-pyrazinoporphyrazine.

about 0.9 e.v. for I and 0.4 e.v. for III. Because of the weak photoconduction a similar comparison for II could not be made. From the above data the threshold energy is approximately equal to the calculated band gap (E_g).

The constancy of ρ_0 or the product $\mu_0 N_0$ is all the more remarkable for the following reasons: (a) the X-ray diffraction pattern for II is different from that for I, indicating a different crystal structure, and the X-ray diffraction pattern of III indicates a disordered structure—it would be expected that this would have a significant effect on the resistivity,^{13,14} and possibly the mobility; (b) the water molecule in III, which may form a hydrogen-bonding bridge between two molecules in the material; and (c) the level of impurities in the sample.

The present results are interpreted to mean that the mobility is an activated process, for this merely requires the constancy of $\mu_0 N_0$, but it has not been shown that the activation energy for mobility is the same as the photocurrent activation energy.

(13) D. D. Eley and G. D. Parfitt, *Trans. Faraday Soc.*, **51**, 1529 (1955).

(14) K. Wihksne and A. E. Newkirk, *J. Chem. Phys.*, **34**, 2184 (1961).