*Semiconducting Properties of Organic Polyiodides**

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A new class of organic salts, formed from the radical anion of tetracyanoquinodimethane (abbreviated as TCNQ, or simply as T) and various cations has been reported,[1] and the electrical resistivties of these compounds have also been reported.[2] Quinolinium TCNQ anion radical salt ($M^+T^{\div}$), for example, has a resistivity of $10^4\Omega$ cm., whereas quinolinium TCNQ anion radical complex salt ($M^+T^{\div}T$), which contains one molecule of neutral TCNQ in addition to $M^+T^{\div}$, has such a low resistivity as $10^{-2}\Omega$ cm.

The mechanism of the electrical conduction of $M^+T^{\div}T$ salt is presumed to be essentially the successive electron transfer between $T^{\div}$ and T, resulting in a delocalization of the electrons through the crystal. The M^+ cation seems to be of subordinate importance in the conduction mechanism, acting merely to keep the entity electrically neutral. In other words, the electrical conduction of $M^+T^{\div}T$ salt is primarily the conduction through the charge transfer complex $T_2^{\div}$, with $T^{\div}$ acting as a donor and T acting as an acceptor. In this sense, $M^+T^{\div}T$ may also be written as $M^+T_2^{\div}$.

Organic polyiodides, $M^+I_x^-$, are a class of compound analogous to TCNQ anion radical complex salts. The only difference between TCNQ complex salt and the polyiodide, except for their different crystal structures, is that the

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[1] D. S. Acker, R. J. Harder, W. R. Hertler, W. Mahler, L. R. Melby, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, **82**, 6408 (1960).

[2] R. G. Kepler, P. E. Bierstedt and R. E. Merrifield, *Phys. Rev. Letters*, **5**, 503 (1960).

former is an anion radical salt containing π-electron system and the latter is an ionic salt of a highly-polarized polyatomic ion. The crystal structures of these four organic polyiodides have been analysed: tetraphenylarsonium triiode,[3] tetramethylammonium pentaiodide,[4] tetraethylammonium heptaiodide[5] and tetramethylammonium enneaiodide[6]. The structure of tetramethylammonium pentaiodide, for example, consists of layers of iodine atoms, with V-shaped pentaiodide ions arranged so as to form a nearly square net of iodine. The iodine-iodine distances within an ion are 2.81 and 3.17 Å, whereas the shortest distance between the iodine atoms belonging to the nearest neighboring ions is 3.63 Å; however, the net to net distance is 4.3 Å. The nets are so arranged as to leave large holes for the tetramethylammonium cations.

As for the crystalline polyiodides stated above, it is generally observed that the iodine-iodine distances within each ion are longer than the I–I distance of the I_2 molecule in crystalline iodine (2.68 Å),[7] and that they are considerably smaller than the sum of the normal ionic radius of the I^- ion, 2.16 Å[8], and the covalent radius of iodine, 1.34 Å. These facts show that, as Hach and Rundle have suggested[4], polyiodide ions result from the interaction of a negative iodide ion with a highly-polarizable iodine molecule, the interaction leading to a partial charge transfer through the resonance of the covalent bond. Furthermore, the interpretation of the structure of polyiodide by the molecular orbital method has confirmed the possibility of the delocalization of the outer p-electron.[4,9]

Although quite a large number of organic semiconductors have already been investigated, not so many ionic compounds have been investigated except for some ionic dyes. The present paper will, therefore, deal with the electrical properties of organic polyiodides.

Experimental

Material.—*Monoiodides.*— Tetramethylammonium iodide, trimethylphenylammonium iodide, 1-methyl-2-picolinium iodide and 1-methylquinolinium iodide were prepared by the method of Vogel[10] by the action of methyl iodide on the parent tertiary amines. These were recrystallized three times from water or alcohol. The melting points agreed with those reported in the literature.

Polyiodides.—The following polyiodides were prepared from iodine and monoiodides and were recrystallized twice from alcohol or an iodine-alcohol solution. Single crystals of several polyiodides were grown from a solution over a several-weeks period. *Tetramethylammonium Polyiodides* were prepared by the method of Buckles, Yuk and Popov.[11] The melting points found (and those reported in the literature) are as follows. Triiodide, 116.5∼117.5°C (117.0∼117.2°C); pentaiodide, 129∼130°C (129∼130°C). *Trimethylphenylammonium Polyiodides* were prepared by the method of Geuther.[12] Triiodide, 117.0∼117.5°C (115°C); pentaiodide, 83.3∼83.6°C (82°C); heptaiodide, 63.5∼64.0°C (65°C). *1-Methyl-2-picolinium Polyiodides* were prepared by the method of Murrill.[13] Triiodide, 135.5∼136.0°C (134°C); pentaiodide, 61.5∼62.5°C (60°C); heptaiodide, 57.5∼59.0°C (57°C). *1-Methylquinolinium Polyiodides* were prepared by the method of Trowbridge.[14] Triiodide, 109.1∼109.3°C (108.6∼109.6°C[15]); pentaiodide, 70.5∼71.5°C (70°C).

Measurements.—Measurements were mainly carried out on a compressed disk of crystalline powder. Since it is inert to iodine or iodides, graphite was used as the electrode material. The electrode assembly is shown in Fig. 1. Two disk electrodes, 0.4∼0.5 mm. thick and 8 mm. in diameter, were prepared first by pressing graphite powder with a 5t/cm^2 apparatus. Crystalline powder was then

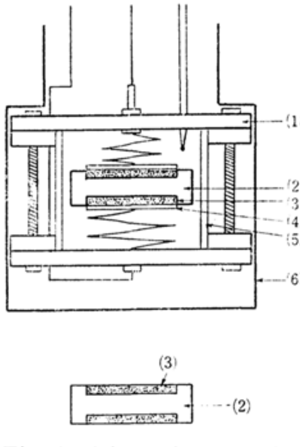

Fig. 1. Electrode assembly.

(1) Teflon (2) Specimen (3) Graphite electrode (4) Platinum plate (5) Glass tube (6) Shield box

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[3] R. C. L. Mooney Slater, *Acta Cryst.*, **12**, 187 (1959).

[4] R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951); J. Broekema, E. E. Havinga and E. H. Wiebenga, *Acta Cryst.*, **10**, 596 (1957).

[5] E. E. Havinga and E. H. Wiebenga, *Proc. Roy. Ac. Amsterdam*, B, **58**, 412 (1955); E. E. Havinga and E. H. Wiebenga, *Acta Cryst.*, **11**, 733 (1958).

[6] W. J. James, R. J. Hach, D. French and R. E. Rundle, *Acta Cryst.*, **8**, 814 (1955).

[7] A. I. Kitaĭgorodskiĭ, T. L. Khotsyanova and Yu. T. Struchkov, *Zhur. Fiz. Khim.*, **27**, 780 (1953) from *Chem. Abstr.*, **49**, 2145 (1955).

[8] L. C. Pauing, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, New York (1960), p. 518.

[9] E. E. Havinga and E. H. Wiebenga, *Rec. Trav. Chem.*, **78**, 724 (1959); G. C. Pimentel, *J, Chem. Phys.*, **19**, 446 (1951).

[10] A. I. Vogel, "A Text-book of Practical Organic Chemistry," Longmans, Green and Co., London (1951), p. 631.

[11] R. E. Buckles, J. P. Yuk and A. I. Popov, *J. Am. Chem. Soc.*, **74**, 4379 (1952).

[12] A. Geuther, *Ann.*, **240**, 66 (1887).

[13] P. Murrill, *J. Am. Chem. Soc.*, **21**, 828 (1899).

[14] P. F. Trowbridge, ibid., **21**, 66 (1899).

[15] C. Schall, *Z. Elektrochem.*, **14**, 397 (1908).

packed between these two graphite electrodes in a mold with a diameter of 13 mm. and pressed at 2.7 t/cm² in a vacuum. The thickness of the specimen-between-electrodes thus obtained was about 0.5 mm. Platinum plates with lead wires were attached to the graphite electrodes. In the case of a single crystal, both ends of the crystal rod were wrapped with graphite powder and held with platinum plates. A copper-constantan thermocouple was placed near one of the platinum plates. The whole was closed in a Teflon container of a 3 cc. capacity. The electrode assembly was entirely shielded and placed in a glass vessel.

The resistance was measured by the d. c. method with a Toa Denpa Model PM 18 microvolt-ammeter for the specimens with a high resistivity. A National Model PV 910 A vacuum-tube voltmeter was used for the specimens with a lower resistivity. The applied voltage was less than 70 V./cm. The temperature range of the measurements was from room temperature to about 10∼20°C below the melting point.

As graphite had to be used as the electrode material, it was impossible to apply a guard ring electrode. The surface leakage current is, however, negligible, because ε values, the band-gap energy of electrical conduction, do not change, even after the heating and cooling cycles which accompany the slight color change of the material surface, bulk conduction evidently being predominant.

Results and Discussion

In tetramethylammonium pentaiodide, for example, a linear relationship was observed between current and applied voltage as long as the voltage was kept below about 2000 V./cm.

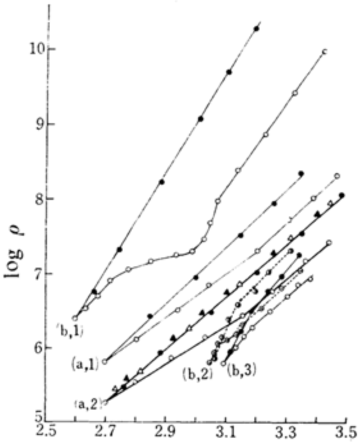


Fig. 2. Temperature dependence of the electrical resistivity of organic polyiodides.

(a) Tetramethylammonium polyiodides
(b) 1-Methyl-2-picolinium polyiodides
(1) Triiodide (2) Pentaiodide (3) Heptaiodide
○ or ⊙ first heating, ● or ◑ first cooling, △ second heating, ▲ second cooling

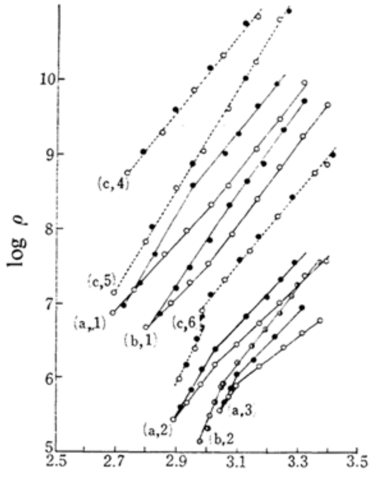


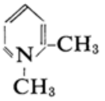
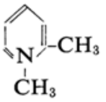
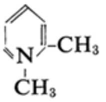
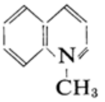
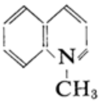
Fig. 3. Temperature dependence of the electrical resistivity of organic polyiodides.

(a) Trimethylphenylammonium polyiodides
(b) 1-Methylquinolinium polyiodides
(c) Single crystal of trimethylphenylammonium polyiodides (Values of log ρ are arbitrary.)
(1) Triiodide (2) Pentaiodide (3) Heptaiodide
(4) Parallel to the cleavage plane of triiodide
(5) Normal to the cleavage plane of triiodide
(6) Parallel to the cleavage plane of pentaiodide
○ or ⊙ heating, ● or ◑ cooling

The relationship between the logarithm of resistivity and the reciprocal of temperature is shown for various compounds in Figs. 2 and 3. Generally speaking, the plots obtained for the heating cycle do not agree with those for the cooling cycle. For the reasons to be discussed below, the values of the resistivities and the slopes observed at relatively low temperature for the heating cycle seem to be correct. The specific resistivities at 20°C (ρ_{20}) and the band-gap energy (ε) as calculated from the low temperature slope by the equation $\rho=\rho_0 \exp(\varepsilon/2kT)$ are tabulated in Table I. The values of the specific resistivity and the band-gap energy for several organic polyiodides range between $10^7\sim10^{10}$ Ωcm. and 1.3∼2.6 eV. respectively.

On the Shape of log ρ versus $1/T$ Curves.—Curve (a, 2) of Fig. 2. shows the log ρ versus $1/T$ curve for tetramethylammonium pentaiodide, where the heating and cooling cycles are repeated successively twice. During the first course of the heating cycle, a distinct break was observed. Moreover, different ρ values were observed in the heating and cooling cycles. However, the plots of the second heating and cooling cycles were found on the same line and coincided with the plots in the first cooling cycle. Besides, no change in ε

TABLE I. ELECTRICAL PROPERTIES OF ORGANIC POLYIODIDES

Substance	ρ_{20} Ω cm.	ε, eV. Heating cycle		ε, eV. Cooling cycle		Temp. range
		Low temp.	High temp.	Low temp.	High temp.	
$(CH_3)_4N\ I_3$	1.2×10^8	1.58	1.17	1.64		16— 97
$(CH_3)_4N\ I_5$	2.1×10^7	1.36	1.00	1.37		16— 97
$(CH_3)_3C_6H_5N\ I_3$	2.7×10^{10}	2.09	1.89	2.04	3.10	29—100
$(CH_3)_3C_6H_5N\ I_3$	*	2.65		2.65		36—100
$(CH_3)_3C_6H_5N\ I_3$	**	2.00		2.00		41— 91
$(CH_3)_3C_6H_5N\ I_5$	5.2×10^7	1.63	2.15	1.73	3.30	24— 71
$(CH_3)_3C_6H_5N\ I_5$	**	2.03	3.43	2.03	3.43	26— 71
$(CH_3)_3C_6H_5N\ I_7$	8.2×10^6	1.29	2.96	2.12	3.68	25— 56
 I_3	9.6×10^9	2.25	1.81	2.68		20—104
 I_5	2.2×10^7	1.65	4.97	1.73	5.22	26— 55
 I_7	1.2×10^7	1.39	1.98	2.19	3.48	24— 50
 I_3	7.0×10^9	2.08	1.74	2.14	2.66	21— 85
 I_5	7.2×10^7	1.96	4.33	1.96	4.33	25— 63

* Single crystal: normal to the cleavage plane.
** Single crystal: parallel to the cleavage plane along the growth axis.

values was observed throughout all the cycles except just after the break in the first heating cycle.

One possible explanation for the break and the difference in ρ values is the annealing of the strain originally existing in the virgin specimen, i. e. that caused by some unstable grain contact which existed first; the thermal annealing gradually removed such unstable contact in the temperature region higher than a certain temperature. In the case of single crystals, the reproducibility was observed in the $\log\rho$ versus $1/T$ plots, as is shown in Fig. 3, as can be well understood from the assumption that no unstable contact exists in a single crystal.

After the measurement, the surface of the specimen showed some color change, evidently because some iodine was lost from the surface of the material. No color change was observed in the inner part of the specimen, however, and the X-ray powder pattern also remained quite unchanged. As the contact surface between the material and the electrode graphite is deep in the specimen, as Fig. 1 show, it may safely be assumed that the values obtained, especially at relatively low temperatures, are correct.

The general features of the shape of the $\log\rho$ versus $1/T$ plots just explained above using tetramethylammonium pentaiodide as an example are about the same as those observed in other pentaiodides as well as those in the several triiodides investigated, as Figs. 2 and 3 show. The values of ρ and ε calculated at a relatively low temperature seem to be correct for these compounds also.

For heptaiodides the slopes of the plots for the heating and cooling cycles do not agree, as is shown in Figs. 2 and 3. As heptaiodide is the most unstable compound among the polyiodides investigated, the difference in the slopes of the plots for the heating and cooling cycles seems to be due to the slight irreversible decomposition of the compound. Here again the values calculated at low temperatures will be the correct ones.

Although the possible annealing of the strain which originally existed in the specimen was suggested as the cause of the rather complex feature of the log ρ versus $1/T$ plots observed with almost every polyiodides, the effects of, say, impurities, lattice defects and a phase transition during the measurements should not be left out of consideration.

Single Crystal.—For the trimethylphenylammonium triiodide single crystal, a considerable anisotropy was observed in ε values between the normal direction and that parallel to the cleavage plane along the growth axis. Although in some organic semiconductors a considerable anisotropy is reported in conductivity, ε values remain isotropic without exception.[2,16] This is natural because the energy gap should remain isotropic in so far as an energy-band scheme is applicable to the conduction in diferent directions. Hence, it is possible that band-scheme conduction and hopping conduction are taking place in different directions, in the hopping conduction some excess activation energy for hopping being required in addition to the energy of carrier formation.

It is interesting to note that the ε value of a specimen tablet made of powdered trimethylphenylammonium triiodide at a low temperature is about the same as the value of the single crystal measured parallel to the cleavage plane along the growth axis. The absolute value of the specific resistivity can not be estimated at present with a single crystal, because the estimation of the electrode area is not possible. Thereby, it is impossible to ascertain the anisotropy in specific resistivity. To find this, a large single crystal is now being grown.

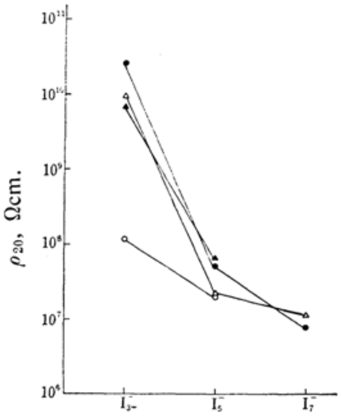


Fig. 4. Resistivities of organic polyiodides.

○ Tetramethylammonium
● Trimethylphenylammonium
△ 1-Methyl-2-picolinium
▲ 1-Methylquinolinium

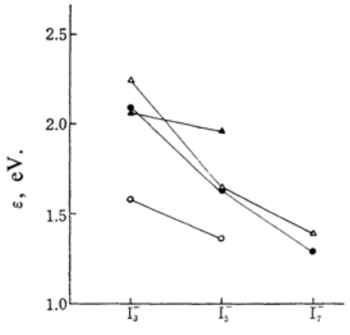


Fig. 5. Band-gap energies of organic polyiodides.

○ Tetramethylammonium
● Trimethylphenylammonium
△ 1-Methyl-2-picolinium
▲ 1-Methylquinolinium

Electrical Properties and Crystal Structure.—Figures 4 and 5 show how the values of ρ_{20} and ε change with the number of iodine atoms in polyiodide anions. It is indicated clearly that both values decrease with an increase in the number of iodine atoms, the influence of cations being of subordinate importance. That iodine has an important effect upon the conduction of polyiodides is understandable in the light of the crystal structure of the polyiodides. With regard to enneaiodide, the details will be discussed in a forthcoming paper.

As has been stated previously, the crystal structures of tetraphenylarsonium triiodide, tetramethylammonium pentaiodide, tetraethylammonium heptaiodide and tertamethylammonium enneaiodide are known. Although it is sure that the structure of many other polyiodides will deform according to the difference in the nature of the cations, it is certain that the structure will remain essentially similar to the known structures.

The structure of the molecular crystal of iodine itself is also known. In its layer structure, the I–I bond length and the I_2–I_2 intermolecular distance in the layer are 2.68 and 3.56Å respectively.[7] The values of the electrical resistivity at room temperature are 2×10^{11} and $6\times10^{7}\,\Omega$ cm. for both the normal direction and the direction parallel to the cleavage plane,[17] while the ε value is 1.24∼1.30 eV.[18]

As is evident from Table II, the shortest

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[16] H. Mette and H. Pick, *Z. Physik.*, **134**, 566 (1953); P. L. Kronick and M. M. Labes, *J. Chem. Phys.*, **35**, 2016 (1961); G. H. Heilmeier, G. Warfield, S. E. Harrison and J. Assour, Abstracts of Organic Crystal Symposium. Ottawa, October, 1962., p. 133; H. Kokado, K. Hasegawa and W. G. Schneider, ibid., p. 186; Y. Maruyama, H. Inokuchi and Y. Harada, This Bulletin, **36**, 1193 (1963).

[17] R. Bersohn, *J. Chem. Phys.*, **36**, 3445 (1962).

[18] T. S. Moss "Photoconductivity in the Elements," Butterworths, London (1952), p. 240.

TABLE II. SHORTEST DISTANCE BETWEEN NEIGHBORING POLYIODIDE ANIONS IN ORGANIC POLYIODIDE CRYSTALS OF KNOWN STRUCTURE

Polyiodide		Shortest distance Å
Anion	Cation	
Triiodide	tetraphenylarsonium	5.29[3] ($I_3^- - I_3^-$)
Triiodide	(caesium)	4.03* ($I_3^- - I_3^-$)
Pentaiodide	tetramethylammonium	3.63[4] ($I_5^- - I_5^-$)
Heptaiodide	tetraethylammonium	3.47[7] ($I_3^- - I_2$)**
(Iodine)		3.56[7] ($I_2 - I_2$)

* Value reported for CsI_3 (H. A. Tasman and K. H. Boswijk, *Acta Cryst.*, **8**, 59 (1955).). $I_3^- - I_3^-$ distances of organic polyiodides investigated for electrical properties in the present report may come, because of the bulkiness of the cation, between 4∼5Å.

** I_7^- anion in crystal is better understood as being composed of I_3^- and I_2.

distances between neighboring polyiodide anions in crystsal decrease with an increase in the number of iodine atoms of polyiodide anions. In so far as the electrical conduction is effected through the overlap of molecular orbitals of polyiodide anions, it is quite understandable that the ρ_{20} and ε values of these compounds decrease with an increase in the number of iodine atoms in polyiodide anions.

Although, as has been discussed above, the iodine framework may be of primary importance in the electrical conduction in the crystal, it is possible that the cation has some influence on the conduction, although it should be remembered that the iodine framework itself is being deformed by the differences in the size and shape of the cations. It is possible, for example, that some cation with conjugated double bonds may form a charge transfer complex with the polyiodide anion.

Thermoelectric Power.—To ascertain the sign of the majority carriers, a preliminary examination of the thermoelectric power was made. The flow of the current was clearly observed in pentaiodides, heptaiodides and tetramethylammonium enneaiodide. The direction of the current indicated that the positive hole contributed more to the current than the electron. In other polyiodides the results were not so clear as in the compounds stated above; the positive hole seems, however, to be the main carrier there also. It has been reported that, in the space-charge-limited photocurrent in iodine, the hole conduction was predominant over the electron conduction.[19]

Details of the measurement of thermoelectric power will be reported on in a forthcoming paper.

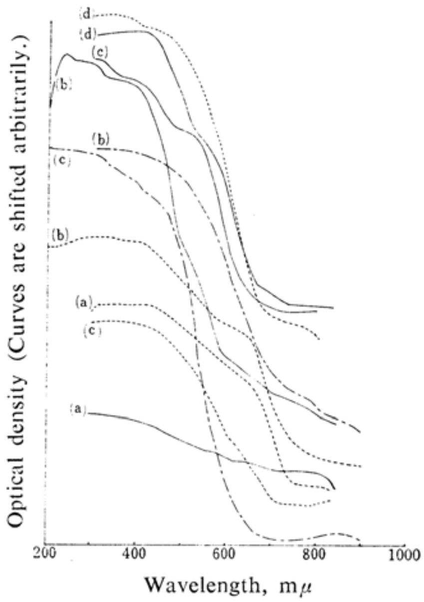

Fig. 6. Absorption spectra of organic polyiodides.

—— Triiodides
- - - Pentaiodides
-·-· Heptaiodides
(a) Tetramethylammonium
(b) Trimethylphenylammonium
(c) 1-Methyl-2-picolinium
(d) 1-Methylquinolinium

Optical Properties. — The optical absorption spectra of quaternary ammonium polyiodides in various solvents have been reported.[11,20] As in connection with the electrical properties of a solid, we are interested in the absorption spectra of solid; they were measured and are shown in Fig. 6. Polyiodides were melted between two glass or quartz plates and then cooled slowly, and the absorption was measured with the usual spectrophotometer. The absorption curves are rather diffuse, and the band-gap energies, as calculated from the temperature dependence of the electrical resistivity, do not agree with the absorption maxima, being grouped rather near the very beginning of the first absorption.

Preliminarily it is observed that all the

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[19] A. Many, M. Simhony, S. Z. Weisz and J. Levinson, *J. Phys. Chem. Solids*, **22**, 285 (1961).

[20] C. K. Tinkler, *J. Chem. Soc.*, **1908**, 1611; F. L. Gilbert, R. R. Goldstein and T. M. Lowry, ibid., **1931**, 1092; R. E. Buckles and J. F. Mills, *J. Am. Chem. Soc.*, **76**, 6021 (1954).

polyiodides investigated show a photoconductivity response. Details will be published later.

Summary

1) The electrical conductivities of ten organic polyiodides have been measured: tetramethylammonium triiodide, tetramethylammonium pentaiodide, trimethylphenylammonium triiodide, trimethylphenylammonium pentaiodide, trimethylphenylammonium heptaiodide, 1-methyl-2-picolinium triiodide, 1-methyl-2-picolinium pentaiodide, 1-methyl-2-picolinium heptaiodide, 1-methylquinolinium triiodide and 1-methylquinolinium pentaiodide. At the room temperature specific resistivities are $10^7 \sim 10^{10}\Omega$ cm. and the band-gap energies, as calculated from $\rho = \rho_0 \exp(\varepsilon/2kT)$, are $1.3 \sim 2.6$ eV.

2) Both ε and ρ_{20} decrease with an increase in the number of iodine atoms in the polyiodide anion, not so much difference in these values being observed with different kinds of cations. The iodine framework in the crystal structure is of primary importance in determining the electrical conductivity.

3) For the trimethylphenylammonium triiodide single crystal, an anisotropy of ε values was observed between the normal direction and the direction parallel to the cleavage plane along the growth axis.

4) Preliminary thermoelectric power measurements show that the majority carrier is the hole.

5) The solid absorption spectra of polyiodides have been measured. The band-gap energy, ε, does not agree with the absorption maximum, being rather near the very beginning of the first absorption.

6) All the polyiodides investigated show a photoconductivity response.

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