The Electrical Conduction of 10-Methylacridinium Polyiodides

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In a previous paper,[1] it was indicated that the specific resistivities at 20°C and the band gap energies of organic polyiodides decrease with the number of iodine atoms in the polyiodide anion, not very much difference in these values being observed with different kinds of cations. It was also established that the iodine framework in the crystal structure is of primary importance in determining the electrical conductivity.

The present investigation has been made to find what influences, if any the size and shape of the cation has on the conduction.

Preparation.—*10-Methylacridinium Monoiodide.*—Monoiodide was prepared by the action of methyl iodide on acridine. The melting point agreed with the compound reported in the literature.[2]

10-Methylacridinium Polyiodides.—A hot solution of the required amount of iodine and 1.00 g. of monoiodide in 145 ml. of 99% alcohol was cooled to yield the product.

10-Methylacridinium Triiodide.—From 1.03 g. of iodine, 1.75 g. of triiodide was obtained. It was then recrystallized from the alcohol-tetrahydrofuran mixture. Dark brown crystals; m. p. 170°C.

Found: C, 28.35; H, 2.40; N, 3.07; I, 65.58. Calcd. for $C_{14}H_{12}NI_3$: C, 29.25; H, 2.10; N, 2.44; I, 66.21%.

10-Methylacridinium Pentaiodide.—The reaction of 2.85 g. of iodine gave 2.20 g. of pentaiodide. It was then recrystallized from the iodine-alcohol-tetrahydrofuran solution. Dark purple crystals, m. p. 94.5°C.

Found: C, 21.48; H, 1.92; N, 2.29; I, 74.40. Calcd. for $C_{14}H_{12}NI_5$. C, 20.29; H, 1.46; N, 1.69; I, 76.56%.

10-Methylacridinium Heptaiodide.—4.74 g. of iodine yielded 2.32 g. of heptaiodide. It was then recrystallized in the same way as pentaiodide. Dark green crystals; m. p. 86°C.

Found: C, 17.84; H, 1.51; N, 1.36; I, 79.51. Calcd. for $C_{14}H_{12}NI_7$: C, 15.53; H, 1.12; N, 1.29; I, 82.06%.

A drying of the crystal for analyses inevitably causes some loss of iodine, thus decreasing slightly the analytical iodine content.

Absorption Spectra.—The absorption spectra of 10-methylacridinium polyiodides are shown in Fig. 1. In a tetrahydrofuran solution all three spectra were nearly identical, except that the molar extinction coefficicients were slighly different. The main peaks are at 259, 295 and 360 mμ. Subtracting from this absorption curve the absorption due to acridinium ion, which has main absorption peaks at 259 and 360 mμ, one obtains a curve with peaks at 295 and 360 mμ, peaks which conform fairly well with the absorption curves reported for the tetramethylammonium polyiodides in ethylene chloride[3] and several triiodides in various solvents.[4] Therefore, in the 10-methylacridinium polyiodides as well as in the tetramethylammonium polyiodides, these facts are consistent with the interpretation that the triiodide is the only polyiodide stable in a dilute solution.

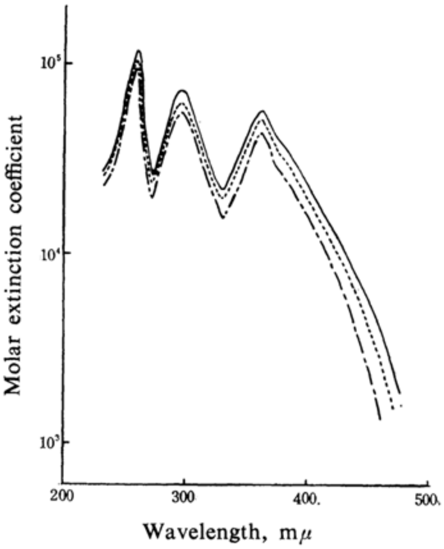

Fig. 1. Absorption spectra of 10-methylacridinium poyiodides in tetrahydrofuran.

– – – Triiodide ······ Pentaiodide
——— Heptaiodide

The absorption spectra of the solid were also measured. However, the absorption band was very broad, extending over about a 500 mμ region from the ultraviolet region.

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

[2] A. I. Vogel, "A Text-Book of Practical Organic Chemistry," Longmans, Green and Co., London (1951), p. 634.

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

[4] C. K. Tinkler, *J. Chem. Soc.*, **1908**, 1611; F. L. Gilbert, R. R. Goldstein and T. M. Lowry, ibid., **1931**, 1092; A. D. Awtrey and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 1842 (1951); A. I. Popov and R. E. Swensen, ibid., **77**, 3724 (1955).

Electrical Conduction.—The electrical resistivity was measured on a compressed disk of crystalline powder by the DC method. The apparatus and method were the same as have been described previously.

The relation between the current and the applied voltage obeyed Ohm's law up to 2000 V./cm. at least.

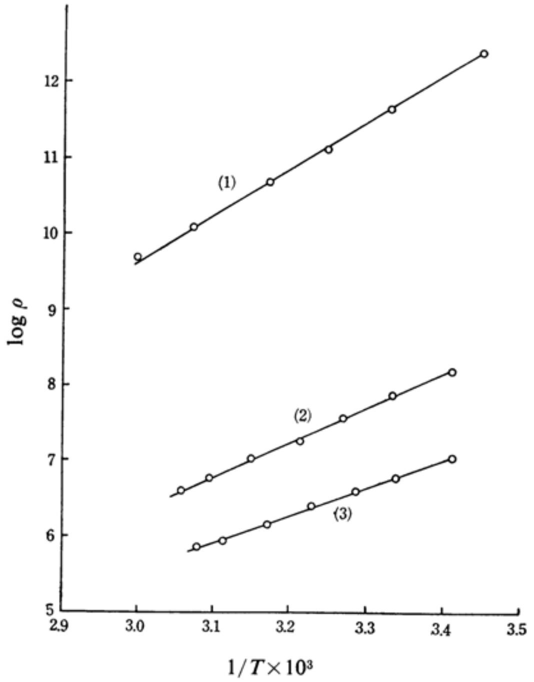

Fig. 2. Temperature dependence of the resistivity of 10-methylacridinium polyiodides.

(1) Triiodide (2) Pentaiodide
(3) Heptaiodide

The relationship between the logarithm of resistivity and the reciprocal of temperature is shown in Fig. 2. The specific resistivity at 20°C (ρ_{20}) and the band-gap energy (ε), as calculated from the temperature dependence of the resistivity by the equation $\rho=\rho_0 \exp(\varepsilon/2kT)$, are tabulated in Table I.

TABLE I. ELECTRICAL PROPERTIES OF 10-METHYLACRIDINIUM POLYIODIDES

Substance	ρ_{20} Ω cm.	ε eV.	Temp. range °C
Triiodide	1.6×10^{12}	2.49	17—60
Pentaiodide	1.5×10^{8}	1.72	20—55
Heptaiodide	1.2×10^{7}	1.47	20—52

The values of ρ_{20} and ε decrease with an increase in the number of iodine atoms. This is similar to the previous finding. However, generally the present values of ρ_{20} and ε are larger than those reported for other polyiodides.

The size of the acridinium cation is the largest of all the polyiodides investigated. Therefore, it is possible that the iodine framework is deformed by the size and shape of the cation and that the shortest distance between anions is larger than those of other polyiodides. As has been shown in the previous paper, the shortest distances between neighboring polyiodide anions of the known crystal structures decrease with an increase in the number of the iodine atoms of polyiodide anions. In so far as the electrical conduction is effected through the overlap of the molecular orbitals of polyiodide anions, it is understandable that the values of ρ_{20} and ε are larger than those reported for other polyiodides.

On the basis of the present and previous papers, it is certain that the iodine framework in the crystal structure is of primary importance in determining the electrical conductivity; the theory has obtained an additional confirmation in the present paper's finding that the size of the cation increases the deformation of the iodine framework and, as expected, influences the electrical properties.

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