289. *The Electrical Conductivity of Phosphonitrilic Chlorides.**

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As aromatic-type systems, the cyclic phosphonitrilic chlorides might be expected to show a small electronic conductivity. In addition there is the possibility of ionic conductivity by chloride ions. In this paper, measurements are reported of the electrical conductivities of compressed polycrystalline samples using a d.c. technique. The compounds show an exponential variation of resistance with reciprocal of absolute temperature. Evidence is presented favouring an ionic mechanism for conduction.

A very large number of organic compounds possessing π electrons, particularly in aromatic systems, show a small but definite electrical conductivity in the solid state.[1] This conductivity has been attributed to the intermolecular tunnelling of activated π electrons. The variation of resistivity, ρ, with temperature follows the usual relation for electronic semiconductors:

$$\rho = \rho_0 e^{\Delta E/2kT}$$

where ΔE is the energy-gap, k the Boltzmann constant, and T the absolute temperature. The value of ΔE is dependent on the electronic structure of the molecule and the molecular interactions. In general, the more π electrons there are in the molecule, the lower the energy gap and the higher the conductivity.

At present there is considerable interest in the conductivity of polymeric materials, particularly those with thermal stability. The cyclic phosphonitrilic chlorides are known to possess some aromatic character.[2] By analogy with organic systems it is possible to predict that the trimeric and tetrameric chlorides will show an extremely small electronic conductivity and a very high energy-gap (>3 ev). On the other hand there exists the possibility of ionic conductance by chloride ions.

The purpose of this work is to examine the electrical conductivity in order to elucidate the nature of the charge carriers, and to compare the behaviour of these compounds with those of organic analogues.

Experimental

Preparation of Materials.—Samples of $(PNCl_2)_3$ and $(PNCl_2)_4$ were provided by N. L. Paddock of Albright & Wilson, Ltd., and were subsequently purified by a zone-melting method similar to that described by Beynon and Saunders for organic compounds.[3] The sample, in a tube 15 cm. long and 4 mm. internal diameter, was drawn through a heating loop at the rate of 3 cm. per hr. The heater was adjusted so that the molten zone was 2 cm. long. Successive refinements produced a marked increase in crystal size in the upper parts of the tube, which is an indication of increased purity. No further improvement was observed after the first 12 passages, and so the refinement was stopped at this point. Although no absolute criterion of purity is available, it is significant that the zone refinement produced a marked sharpening of the melting point.

It was thought that defects frozen in during the zone-melting might influence the conductivity. A zone-refined sample of $(PNCl_2)_4$ was recrystallised from light petroleum (b. p. 40—60°) for comparison.

d.c. Measurements of Variation of Resistance with Temperature.—The method was basically that described by Cardew and Eley.[4] Polycrystalline specimens of the purified material were compressed between aluminium electrodes of area 7 mm.^{2} in a glass and silica cell. The silica was used so that the resistance of the cell should be much greater than that of the specimen.

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* This paper was read at the Chemical Society Symposium on Inorganic Polymers, Nottingham, 1961.

[1] Eley, *Research*, 1959, **12**, 293.

[2] Craig and Paddock, *Nature*, 1958, **181**, 1052.

[3] Beynon and Saunders, *Brit. J. Appl. Phys.*, 1960, **11**, 128.

[4] Eley and Cardew, *Discuss. Faraday. Soc.*, 1959, **27**, 115.

Hydrostatic pressure of 80 kg./cm.^{2} was applied with a nickel–Monic 90 spring to overcome intercrystalline resistances. The resistance of the specimen was measured by using a valve voltmeter capable of measuring resistances up to 10^{15} ohms with an applied potential of 120 v.

Measurements under vacuum conditions were unsatisfactory as the samples tended to sublime on heating. Measurements were, therefore, made under 10—15 cm. of pure nitrogen.

The specimen was heated to a suitable temperature below the melting point and measurements of the resistance were made as it cooled slowly. This method has been shown to give satisfactory results provided that the cooling rate does not exceed 1° per min.

RESULTS

1. *Effect of Applied Voltage*.—(*a*) When a voltage was applied, a marked polarisation occurred. This is shown by an increase in resistance with time, equilibrium being reached after 15—20 min. at a resistance of approximately twice the initial value. This polarisation is not strongly field-dependent. Fig. 1 shows the effect of applied voltage on the variation of resistance with time for a sample of $(PNCl_2)_4$.

(*b*) In Fig. 1 it can be seen that the resistance (as calculated from volts/amps) increases with applied voltage, resulting in a negative deviation from Ohm's law (*i.e.*, the plot of equilibrium current against applied voltage is curved and falls *below* the line expected from Ohm's law). This deviation is negligible compared with changes of resistance produced by temperature, and can be neglected in semiconductivity measurements.

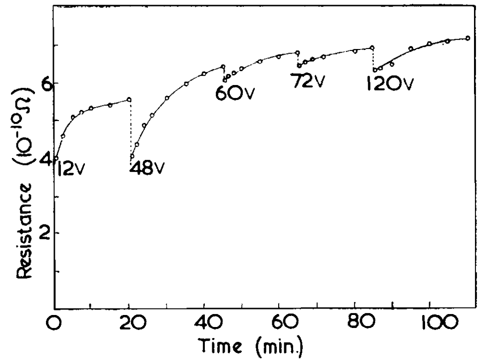

FIG. 1. The influence of applied voltage on polarisation in $(PNCl_3)_4$.

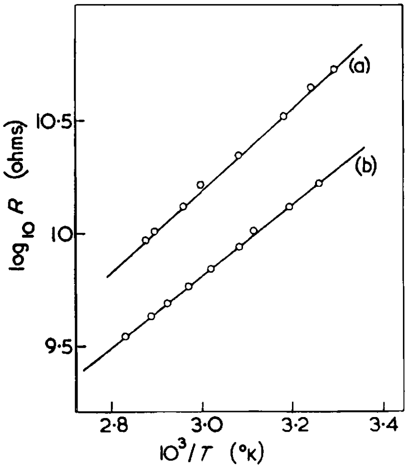

FIG. 2. The dependence on temperature of the resistance of (a) $(PNCl_2)_3$ and (b) $(PNCl_2)_4$.

However, the usual technique for investigating non-ohmic behaviour is to allow the sample to reach equilibrium at the highest voltage used, and then to measure the variation of current as the voltage is rapidly decreased. In this way variations due to polarisation and the heating effect of the current are minimised, and a small positive deviation from Ohm's law is observed which is similar to that found for other molecular crystals.[5]

2. *The Variation of Resistance with Temperature* (*d.c. Method*).—The crude samples of $(PNCl_2)_3$ and $(PNCl_2)_4$ showed a non-linear relationship between log (Resistance) and $1/T$. On purification, the resistance was reduced and a linear variation was observed (Fig. 2). Thus the compounds obeyed the relation $\rho = \rho_0 \exp (\Delta E/2kT)$:

	ΔE	ρ_0	ρ at 20°
$(PNCl_2)_3$	0·71 ev	6·3 × 10^4 ohm cm.	8·0 × 10^{10} ohm cm.
$(PNCl_2)_4$	0·61 ev	3·5 × 10^5 ohm cm.	5·3 × 10^{10} ohm cm.

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[5] Eley and Willis, " Symposium on Electrical Conductivity in Organic Solids," ed. H. Kallmann, Interscience, New York, 1961, p. 257; Eley and Spivey, *Trans. Faraday Soc.*, 1960, **56**, 1432.

Measurements on a sample of $(PNCl_2)_4$ recrystallised from light petroleum (b. p. 40—60°) showed anomalous behaviour on the first run, but subsequent runs were virtually identical with those of the zone-refined sample.

DISCUSSION

The first problem is to determine the nature of the charge-carriers. The high resistance virtually excludes any measurements of mass transport. However, from the results presented it is possible to draw certain conclusions. The conductivity could be either electronic or ionic in nature. Let us consider each possibility in turn.

1. *Electronic Conductivity.*—(a) *Intrinsic.* From studies on organic systems it can be predicted that an energy-gap of >3 ev. This energy-gap is lower than, but related to the energy required to excite a π electron. Since it is known that the lowest $\pi \longrightarrow \pi^*$ transition in the phosphonitrilic chlorides occurs at >6 ev,[6] the energy-gap for intrinsic semiconduction would be very much greater than is observed. We can, therefore, rule out this possibility.

(b) *Impurity conduction.* The fact that the conductivity is increased and the energy-gap decreased on zone refinement indicates that the conduction is not controlled by impurity. If decomposition occurred during melting, the length of the polycrystalline zone at the bottom of the zone-refining tube would steadily increase. This was not observed.

(c) *Extrinsic conduction resulting from defects.* It is possible that zone refinement gives a sample with a high concentration of defects frozen in at the melting point. To investigate this, a zone-refined sample of the tetramer was recrystallised from light petroleum (b. p. 40—60°). The first run on the sample gave an anomalously high slope, but on the second run it returned to its former value. This behaviour is consistent with the presence of occluded solvent which is slowly removed by heating under reduced pressure.

It thus appears that, unless there exists a low-lying electronic state which is optically forbidden, the conductivity cannot be explained by an electronic mechanism.

2. *Ionic Conductivity.*—The marked polarisation observed on applying a potential difference is suggestive of ionic conduction. The fact that the extent of polarisation is not proportional to the applied field, and the rate of attainment of equilibrium is slow, indicates that the polarisation process is due to a redistribution of ions rather than orientation or distortion effects. It thus appears that the cyclic phosphonitrilic chlorides are members of a small class of compound which exhibit ionic conductivity in a molecular lattice. Ice is another example of this type, although the crystal is hydrogen bonded.[7]

Whereas the conductivity of ionic crystals is controlled by the number and mobility of lattice defects, the conductivity in these compounds will depend on the number of chloride ions present and their mobility in a molecular lattice.

Let us consider, for example, the trimer $(PNCl_2)_3$. For ionic conductivity to occur it is necessary for the process:

$$(PNCl_2)_3 \longrightarrow P_3N_3Cl_5^+ + Cl^-$$

to occur to a small extent in the solid state. There is no direct evidence for this, although a comparison with phosphorus oxychloride indicates that this suggestion is reasonable. Phosphorus oxychloride [8] has some similarity in bonding with the phosphonitrilic chlorides, and is known to be capable of ionisation to form chloride ions.[9] The P–Cl bond lengths emphasize the similarity in bond type. The P–Cl distance in phosphorus oxychloride is

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[6] Paddock and Searle, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 347.

[7] Eigen and De Maeyer, *Proc. Roy. Soc.*, 1958, *A*, **247**, 505.

[8] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

[9] Baaz and Gutmann, *Monatsh.*, 1959, **90**, 426.

1·99 Å [10] and in $(PNCl_2)_3$ it is 1·97 Å,[11] which agree within the limits of experimental error. Thus, although the phosphonitrilic chlorides have a covalent ground state, an ionic state is likely to be one of reasonably low energy.

Thus we can suggest a conduction mechanism which is initiated by the ionisation of a molecule to give a chloride ion. This chloride ion can then move through the lattice under the influence of the applied field. This ion is likely to interact only weakly with the neutral molecules. Thus we have a process analogous to electron transport in semiconductors. " Hole " type conduction could also occur by the transfer of a chloride ion from a neutral to an ionised molecule, although the potential-energy barrier for this process is likely to be high. We may represent the potential-energy path of the current carriers as shown in Fig. 3.

A similar type of mechanism has been suggested by Eigen and De Maeyer for ice.[7] The energy required to initiate the process is thus ΔE. Since the process liberates two current carriers (*i.e.*, "Hole" and ion) we are justified in using an equation directly analogous to that used for semiconductors, *i.e.*,

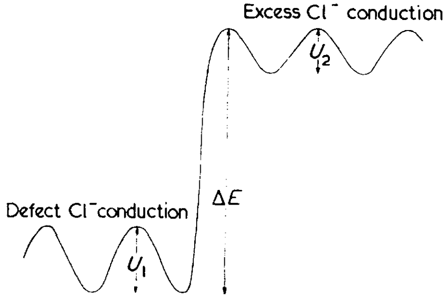

FIG. 3. Potential-energy path for conduction by chloride ions. U_1 is the barrier height of defect Cl^- conduction and U_2 the barrier height for excess Cl^- conduction.

$$\rho = \rho_0 e^{\Delta E/2kT}$$

where ΔE is a function of the energy change for the process and the barrier height. An upper limit for the maximum number of charge carriers can be obtained from Nd/M, where N is Avogadro's number, d the density, and M the molecular weight. This gives a value of 4×10^{-7} cm.^{2} v^{-1} sec^{-1}. for the mobility of the charge carrier. This is of the low order which might be expected for an ion.

It thus seems that, in the absence of a suitably low-energy electronic transition, the conductivity is most readily explained in terms of an ionic mechanism.

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[10] Badgley and Livingston, *J. Amer. Chem. Soc.*, 1954, **76**, 261.
[11] Wilson and Carroll, *J.*, 1960, 2548.