*The Electrical Conduction of the p-Phenylenediamine Iodine Complex**

By Shun-ichiro NISHIZAKI and Hideaki KUSAKAWA

(Received August 2, 1963)

Extensive work has by now been carried out on the electronic conduction in molecular complexes of aromatic hydrocarbon with iodine,[1-5] or antimony pentachloride,[6] and amines with quinones,[7-9] but on complexes of amines with iodine, except in solutions, there have been only a few papers.[10]

It seems that iodine is stronger as an electron acceptor[11] than are quinones, therefore, it is to be expected that the complexes constituted of amine and iodine have a lower electrical resistivity than that of amine and quinone.

This paper will report on the electrical conductivity of the complex of paraphenylenediamine with iodine. This complex appeared to have a nonstoichiometrical composition, and its electrical resistivity varied according to the iodine contents. Therefore, it was the objective of the present work to investigate the relation between the magnitude and temperature dependence of the electrical resistivities and the coordination numbers of the iodine.

Experimental

Materials.—The purification of *p*-phenylenediamine (*p*-PDA) and iodine (I_2) was carried out by distillation and sublimation, which were repeated twice.

p-PDA and iodine were dissolved in benzene. When both solutions were mixed, dark-colored complexes of *p*-PDA with iodine precipitated. In order to vary the iodine content in the complexes, the mole ratio of iodine/amine was arranged at 2/4, 3/4, 4/4, 5/4, 6/4 and 7/4. The complexes precipitated were left to stand for 24 hr. in the mixed solution, they were then filtered and dried.

All the complexes gave a rich yield above 90% for the mixed *p*-PDA and iodine, especially in cases of the mixed mole ratios of 2/4 and 3/4, when the yield was approximately 99%.

Electrical Conduction.—The electrical resistivities of the complexes were measured by means of the dc method, using crystalline powder which had been packed into a glass capillary (about 2 mm.) in a dry box and compressed with a pressure of 15 kg. between metal electrodes, the diameters of which were 2.0 mm. (about 500 kg./cm^2). This electrode cell was exposed to an atmosphere of dry air. By applying a dc field of about 50 V./cm. across the electrodes, the current through the specimen was measured with a micro or electronic micro-micro ammeter.

In order to isolate the ionic conduction, for over 15 hr. the d. c. field was applied through the specimen at room temperature (about 30°C). After this treatment, there was no change in the infrared absorption spectra of the specimens, the temperature of the specimen, which was controlled with an electric furnace placed around the cell, was raised to 85°C.

The relation between the electrical resistivities and the temperature for calculating the activation energy was measured during the first cooling.

Apparent Densities.—The apparent densities of the complexes were measured with tablets which had been compressed in a manner similar to that used potassium bromide tablet for the infrared-spectrum. The tablet of the potassium bromide compressed under the same conditions indicated 2.52 g./cm^3 at 30°C, but the density of potassium bromide is 2.7 g./cm^3 at 25°C.

Results and Discussion

The results of this investigation are shown in Fig. 1, as semilogarithmic plots of the resistivity vs. temperature for the complexes. In this case the coordination numbers of iodine (Table I) are noted on the figure. The activation energy for the electrical conduction process, E_c, can be calculated from the slope of the plots, $\rho=\rho_0 \exp(E/kT)$, their values are listed in the last column in Table I.

It may be seen that the electrical conductivities of complexes are remarkably enhanced with a small increase in the iodine content in complexes and that a minimum value for both

---

* This paper has been presented in part at the 16th Annual Meeting of the Chemical Society of Japan, April, Tokyo.

[1] H. Akamatu, H. Inokuchi and Y. Matsunaga, *Nature*, 173, 168 (1954).

[2] H. Akamatu, H. Inokuchi and Y. Matsunaga, This Bulletin, 29, 213 (1956).

[3] J. Kommandeur and F. R. Hall, *J. Chem. Phys.*, 34, 129 (1961).

[4] T. Uchida and H. Akamatu, This Bulletin, 34, 1015 (1961).

[5] T. Uchida and H. Akamatu, ibid., 35, 981 (1962).

[6] G. E. Blongrein and J. Kommandeur, *J. Chem. Phys.*, 35, 1635 (1962).

[7] M. M. Labes, R. Sehr and M. Bose, ibid., 32, 1570 (1960).

[8] D. L. Kronik and M. M. Labes, ibid.. 35, 2016 (1961).

[9] D. D. Eley, H. Inokuchi and M. P. Wilis, *Discussions Faraday Soc.*, 28, 54 (1959).

[10] J. A. Van Der Hoek, J. H. Lupinski and L. J. Oosterhoff, *Mol. Phys.*, 3, 299 (1960).

[11] D. C. Heosterey, *J. Chem. Phys.*, 36, 557 (1962).

TABLE I. ELECTRICAL RESISTIVITY AT ROOM TEMPERATURE (30°C)
Activation energy and density of p-PDA-I_2 complexes

Sample No.	Coordination No. of I	30°C ohm-cm.	ρ_0 ohm-cm.	E_c eV.	Density g./cm³
1	0.45	5.9×10^{9}	3.3×10^{-4}	0.80	2.54
2	0.67	3.5×10^{7}	2.9×10^{-3}	0.61	2.62
3	0.82	1.7×10^{5}	2.4×10^{-2}	0.41	2.81
4	1.03	2.7×10^{5}	1.56×10^{-2}	0.44	3.78
5	1.36	1.04×10^{6}	1.07×10^{-2}	0.48	2.57
6	1.62	5.4×10^{6}	8.5×10^{-3}	0.59	1.88

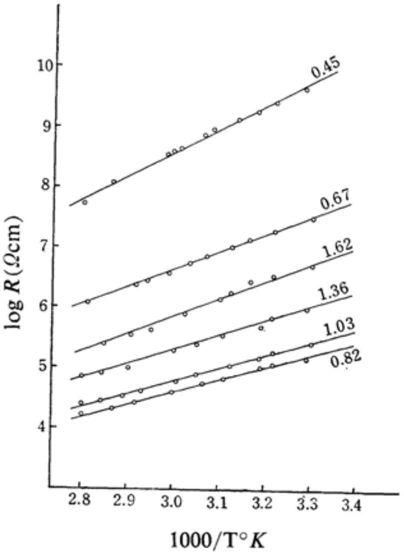

Fig. 1. Electrical resistivities vs. temperature for p-PDA-I_2 complexes.

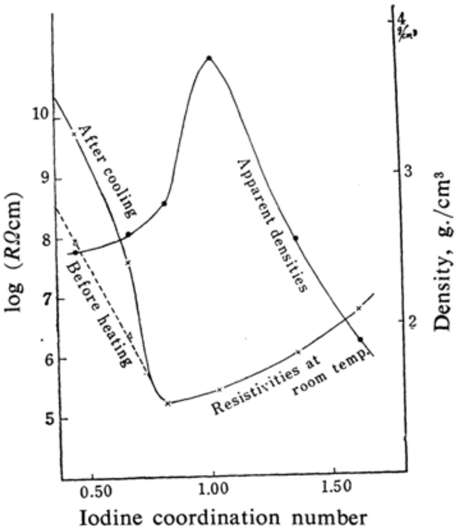

Fig. 2. The relationship between the I_2 coordination number and electrical resitivities, density.

the magnitude and the temperature dependence of the electrical resistivity appears in the complex the coordination number of the iodine of which is around 0.8. Over this range, the magnitude and temperature dependence of the resistivity gradually increase with the iodine content. However, on the other hand, the maximum value of density exists in the vicinity of the coordination number 1.0. These results are shown in Fig. 2.

In view of the fact that the resistivities increased with time when the current was run through the specimens the coordination numbers of which were 0.45 and 0.67, and so did not follow Ohm's law, it seems that ionic conduction formed most of the conduction in these complexes. The different values of resistivities between before heating and after cooling were especially conspicuous in these cases. However, even if these specimens were heated and cooled twice, there was no remarkable change in resistivity.

In the complexes the iodine coordination number of which was above the neighborhood of 0.8, ionic conduction was inferior to electronic conduction, because the current ran in an Ohmic pattern and the resistivity did not change between before heating and after cooling.

As Table II shows, the values for both the magnitude and the temperature dependence of the resistivity of an amine-iodine complex are smaller than those of an amine-chloranil complex[12] when the amine is p-PDA. On the other hand, the redox potential of iodine is 0.536 V. and that of chloranil is 0.742 V. From this point of view, chloranil seems to be a

TABLE II. COMPARISON WITH p-PDA-I_2 AND p-PDA-CHLORANIL ON THE ELECTRICAL RESISTIVITY AND ACTIVATION ENERGY

	$\rho_{25°C}$ ohm-cm.	ρ_0 ohm-cm.	E_c eV.
p-PDA-I_2	2.1×10^{5}	2.4×10^{-2}	0.41
p-PDA-Chloranil	6×10^{6}	1.9×10^{-5}	0.67

---

[12] R. Sehr, M. M. Labes, M. Bose and H. Ur. F. Wilhelm, "Symposium on Electrical Conductivity in Organic Solid," John Wiley & Sons Inc., New York (1961) p. 309.

stronger oxidative reagent than iodine, although, as an electron-acceptor, iodine is superior to chloranil for *p*-PDA. In the cases of bromine and iodine with benzidine,[10,13] one can see the same results. For this reason it is presumed that the polarization terms in the following equation play an important role[3,14].

$$2E_c \simeq \varepsilon = [I_G(\mathrm{D}) - A_G(\mathrm{A})] - [P(\mathrm{D}_+) + P(\mathrm{A}_-)]$$

where ε is the energy of charge transfer band, $I_G(\mathrm{D})$ is the ionization potential of the donor, $A_G(\mathrm{A})$ is the electron affinity of the acceptor in the gas phase, and the contributions, $P(\mathrm{D}_+)$ and $P(\mathrm{A}_-)$, from the polarization energy around the positive and negative ion are represented.

The complexes of *p*-PDA with iodine were thermally stable up to the vicinity of 120°C, and their melting points were not lower than those of the two conpenents (*p*-PDA: 140°C iodine: 114°C). Iodine had been freed upon being heated before the complexes were melted therefore, the phase diagram for *p*-PDA-iodine could not be obtained in this atmosphere.

Summary

In the case of a complex of *p*-phenylenediamine with iodine, a nonstoichiometrical composition has been established; the minimum values for both the magnitude and the temperature dependence of resistivity exist on the complex the coordination number of which is around 0.8. On the other hand, the maximum value of the apparent density appears in the vicinity of 1.0.

In comparison with the complex of *p*-phenylenediamine-iodine and that of *p*-phenylenediamine-chloranil, even though the redox potential of chloranil is larger than that of iodine, the resistivity and the activation energy of the *p*-phenylenediamine-iodine system are smaller than those of the chloranil complex.

Mitsubishi Electric Corporation
Research Laboratory
Amagasaki, Hyogo

---

[13] H. Kusakawa, unpublished.

[14] H. Kuroda, *J. Japanese Chem. (Kagaku no Ryoiki)* **17**, 113 (1963).