The Electrical Conduction of Iodine Complexes of Aromatic Diamines*

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In our previous work[1], we have studied the electrical properties of the *p*-phenylenediamine (*p*-PDA) - iodine complex system. The magnitude and the temperature dependence of the electrical resistivity of this system is dependent upon the iodine content.

As part of the study of a series of aromatic diamine - iodine complex systems, in this paper we have studied the electrical properties of iodine complexes of aromatic diamines, which contain two benzene rings. To examine the effects of the molecular structures of donors, we have selected four compounds from three different types of aromatic diamines: (a) 1, 5-naphthylenediamine (NDA), from diaminopolyacenes, (b) benzidine (BEN) and *o*-tolidine (TOL), from polyphenylenediamines, and (c) *p*, *p*'-diaminodiphenylmethane (APM), from non-conjugated diamines.

Experimental

Materials. — The aromatic diamines and iodine were purified by means of two recrystallizations or sublimations. The complexes were prepared in the following way. A diamine and iodine were dissolved separately in benzene, and then the two

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1) S. Nishizaki and H. Kusakawa, This Bulletin, **36**, 1681 (1963).

solutions were mixed in four different proportions, so that the mole ratios of iodine to diamine in the mixtures were 3/4, 4/4, 5/4 and 6/4 respectively. After the mixtures had been kept standing for one day, the precipitates were collected by filtration and dried. In the case of the APM-iodine system, however, no precipitate could be obtained from the solution. Thus to prepare this complex system, the two components were blended in a test tube and heated to the melting point. The iodine contents of the complexes prepared from the solutions were determined by the microanalytical method.

Resistivity Measurements. — The experimental method and the conditions for the measurement of the magnitude and the temperature dependence of the electrical resistivity were similar to those described in the previous paper[1] except that, in the present case, the temperature range was from −70°C to 20°C, and carbon electrodes were used instead of the metal electrodes for BEN and TOL complexes. All specimens of the APM and iodine systems are of flowage, so only the resistivity at room temperature was obtained.

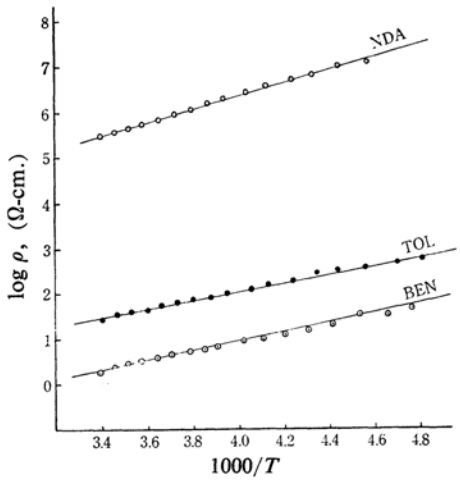

Fig. 1. Temperature dependence of conductivity of aromatic diamine complexes: for determination of thermal activation energy for conduction.

Results and Discussion

The aromatic diamine - iodine complexes do not have a constant coordination number, and their resistivities are dependent on their iodine content. The correlation of resistivities at room temperature with iodine content is shown in Table I.

Examples of the experimental data on the temperature dependence of the electrical resistivity are shown in Fig. 1. The mole ratio of iodine in the examples shown this figure are 1.01 in the NDA-iodine system, 1.26 in the BEN-iodine system, and 1.29 in the TOL-iodine system. The activation energy, E_c, was determined from the experimental data according to the following equation:

$$\rho = \rho_0 \exp(E_c/kT) \qquad (1)$$

The results obtained are listed in the last column of Table I. The resistivity of the complex of BEN with iodine is not in agreement with that obtained by van der Hoek and his coworkers.[2] When metal electrodes were used, however, we also obtained a value similar to that reported by them ($10^2\Omega$-cm. at 20°C). It seems that a reaction takes place between metal electrodes and the specimen during the resistivity measurement, thus causing a high resistivity region in the neighborhood of the electrodes, and hence, an increase in the apparent resistivity.

For the *p*-PDA-iodine system both the resistivity and the activation energy showed

TABLE I. IODINE CONTENTS OF SPECIMENS AND THEIR ELECTRICAL RESISTIVITIES AND ACTIVATION ENERGIES

Donor	I_2/diamine mixed mole ratio	Iodine content	Resistivity at 20°C Ω-cm.	Activation energy, eV.
NDA	0.75	0.70	6.1×10^{7}	0.66
	1.00	0.86	1.6×10^{6}	0.42
	1.25	0.90	1.0×10^{6}	0.40
	1.50	1.01	3.1×10^{5}	0.32
BEN	0.75	0.78	1.6×10^{5}	0.34
	1.00	0.94	6.2×10^{2}	0.19
	1.25	1.26	2.2×10^{0}	0.19
	1.50	1.49	1.2×10^{1}	0.19
TOL	0.75	0.94	3.5×10^{3}	0.27
	1.00	1.02	2.9×10^{2}	0.24
	1.25	1.29	2.9×10^{1}	0.18
	1.50	1.53	9.1×10^{1}	0.18
APM	0.75	—	8×10^{10}	—
	1.00	—	3×10^{9}	—
	1.25	—	2×10^{8}	—
	1.50	—	6×10^{7}	—

2) J. A. van der Hoek, J. H. Lupinski and L. J. Oosterheff, *Mol. Phys.*, 3, 299 (1960).

TABLE II. CORELATION BETWEEN *Ec* AND ρ_0 ON AROMATIC DIAMINE IODINE COMPLEXES

Donor	*p*-PDA	NDA	BEN	TOL
Activation energy, eV.	0.41	0.32	0.19	0.18
ρ_0 in Eq. 1, Ω-cm.	2.6×10^{-2}	8.0×10^{-1}	1.2×10^{-3}	2.3×10^{-2}
Iodine content	0.82	1.01	1.26	1.29

minimum values at an iodine mole ratio of 0.8. In the cases of these aromatic diamines, the minimum appears at a mole ratio above 1.0. This is reasonable because the molecules of these aromatic diamines are longer than that of *p*-PDA.

When a non-conjugated diamine such as APM is used as the electron donor, the charge transfer complex of iodine does not possess a high electrical conductivity at room temperature. In this case, there was no minimum in the resistivity vs. iodine content curve in a 3/4—6/4 range of the mole ratio of iodine to amine. The resistivity of this system decreases with an increase in the iodine content, as with polyiodides.[3]

The results shown in Table II demonstrate that the activation energy, E_c, increases in the order; TOL, BEN, NDA and *p*-PDA, but this order is not in agreement with the order of their specific resistivities at room temperature. A linear relation can often be found between the activation energy, E_c, and the logarithm of ρ_0 in Eq. 1,[4,5] but such a relation can not be observed for aromatic diamine-iodine complexes.

The results obtained in this investigation indicate that polyphenylenediamines, such as BEN and TOL, are better than diaminopolyacenes, represented by NDA, as electron donors for iodine. It is well known that the charge transfer complex, which shows the remarkable electrical conduction, can be formed from the interaction of a strong electron donor with a strong electron acceptor. In the case of aromatic hydrocarbon, the ionization potential of naphthalene is lower than those of biphenyl[6] and benzene.[7] However, not only is the NDA-iodine complex poor in electrical conduction but also its energy of charge transfer transition[8] in the solid state is large compared with that of the BEN-iodine complex. Considering these facts, it is imaginable that the pendant amino group of polyacenes does not interact with iodine so strongly as does that of polyphenylene diamines.

Foster and Thompson have reported[9] that for chloranil, the donor character of *N,N,N',N'*-tetramethylbenzidine is as strong as that of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine. In the case of non-substituted compounds for iodine, BEN is a very strong donor compared with *p*-PDA. On the other hand, if chloranil is used as the acceptor, BEN and TOL behave as weak donors,[10] but the *p*-PDA-chloranil complex shows a conspicuous signal of electron-spin resonance.[11] Concerning the charge transfer complexes of a given donor, its strength of charge transfer interaction seems to vary with the acceptor molecule, depending on its molecule, depending on its molecular size and other properties.

Summary

The magnitudes and temperature dependence of the electrical resistivities of aromatic diamine - iodine complexes have been studied on four aromatic diamines; 1,5-naphthylenediamine (NDA), benzidine (BEN), *o*-tolidine (TOL) and *p,p'*-diaminodiphenylmethane (APM).

As the donor is a non-conjugated molecule, the electrical conductivity of its iodine complex is inferior to that of the conjugated diamine.

BEN and TOL, which are polyphenylenediamines, are better electron donors for iodine than NDA, a diaminopolyacene; the characteristics of the electron donor for iodine of NDA are as strong as those of *p*-PDA.

The resistivity shows a minimum value at an iodine mole ratio above 1.0 in the cases of the conjugated aromatic diamine which involve two benzene rings. These iodine contents are higher than the corresponding value *p*-PDA-iodine, 0.8.

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