Electrical Conduction in the Violanthrene-Iodine System

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With relation to the nature of conductive electrons or the mechanism of electrical conduction in organic solids, the intermolecular charge transfer complexes are interesting, because the complex formation results in a remarkably low electrical resistivity compared with that of the constituents[1-5]. However, there is a variety in their electrical properties, which depend on the combination of the electron donor compounds and the acceptor compounds. The complexes which possess a relatively high conductivity are those which belong to the "strong" charge transfer complexes, whereas the "weak" charge transfer complexes possess a relatively high resistivity. The former can be characterized by its strong electron spin resonance absorption at room temperature; a correlation between the charge carriers and the unpaired electrons has even been suggested. The typical examples with which we are concerned here are the complexes between polycyclic aromatic hydrocarbons and halogens. Most of these complexes consist of definite stoichiometic compositions in the solid state, for instance, pyrene-iodine (1:1 and 1:2), perylene-iodine (2:3 and 1:3), pyranthrene-iodine (1:2), etc. Under X-ray diffraction,

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[1] H. Akamatu, H. Inokuchi and Y. Matsunaga, *Nature*, **173**, 168 (1954); This Bulletin, **29**, 213 (1956).

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

[3] M. M. Labes, R. Sehr and M. Bose, *J. Chem. Phys.*, **33**, 868 (1960).

[4] J. Komanduer and F. R. Hall, ibid., **34**, 129 (1961).

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

these complexes show particular crystal patterns. In contrast to these complexes, violanthrene forms a complex with iodine, which has a non-stoichiometric composition; furthermore, X-ray diffraction indicates that it is completely amorphous. The structure of the violanthrene-iodine complex has been discussed in a previous paper[6], where we concluded that this complex is to be regarded as the solid solution between iodine and violanthrene. From the view point of semiconducting material, a system like this is specially interesting, because iodine molecules (acceptor) can be distributed homogeneously among violanthrene molecules (host matrix) at any concentration. This will result in a semiconducting system which is analogous to an impurity semiconductor or a valence-controlled semiconductor, lithium-nickel oxide, for instance.

Experimental and Results

Preparation.—Violanthrene was prepared from violanthrone by reduction with zinc-dust. After the usual purification, it was carefully purified by repeated sublimation in vacuo. In order to vary the iodine content in the complex widely, the following two procedures were applied according to the iodine concentration.

For High Iodine Content Complex.—Crystalline powder of violanthrene was suspended in a benzene solution of iodine and boiled for about 30 min. using a reflux condenser. After cooling, the black-colored precipitate was filtered off with a glass filter. (When this precipitate was heated, iodine was liberated and the original hydrocarbon could be recovered. This indicates that the black precipitate was not a substitutional product but a molecular additional compound.) The quantity of added iodine was determined from the difference in weight between the original hydrocarbon and the precipitate. The amount of violanthrene dissolved into the benzene solution was disregarded as being too small compared with the total amount of the sample.

For Low Iodine Content Complex.—Finely powdered violanthrene was suspended in a carbon tetrachloride solution of iodine and, being kept at room temperature for more than three days, was shaken from time to time. Then the precipitate was filtered off with a glass filter. The amount of added iodine was determined from the difference between the initial and the final concentration of dissolved iodine, which difference was measured by iodometry with sodium thiosulfate.

In both procedures, the iodine content in the precipitates could be varied by controlling the amounts of dissolved iodine in the initial solutions. The high iodine content complex was black colored, while, as the iodine content decreased, the color approched that of the original hydrocarbon (dark red).

Electrical Resistivity.—The measurement of electrical resistivity was made with a sample packed into an ebonite pipe (3 mm. in diameter), both ends of which were attached to electrodes of platinum or silver-coated copper. At least 116 kg./cm^2 pressure was applied to the sample in order to reduce the contact resistance at the grain boundary. The resistance was read with an ohmmeter for the samples with low resistivity, while it was measured also with a galvanometer for the samples possessing higher values of resistivity. The applied voltage was less than 20 V./cm., at which the electrolysis did not take place.

The resistivities at room temperature are shown in the third column in Table I. The second column denotes the composition of the sample in the mole ratio of iodine to violanthrene.

All the specimens showed a negative temperature coefficient of resistivity and changed in value in accordance with the formula $\rho=\rho_0\exp(E/kT)$. The observed values for activation energy, E, for the electrical conduction are shown in the fourth column in Table I. The temperature ranges for these observations are indicated in the last column.

The results show that the conductivity is enhanced by the addition of a small quantity of iodine and increases monotonously with the increase in iodine content (Fig. 1), while the activation energy has a nearly constant value in the range of low iodine content. If the iodine molecules are assumed to be distributed homogeneously in the host matrix, they might be separated from each other by 13 molecules of violanthrene (about 100 Å) in the sample with the least iodine content.

Qualitative observation for thermoelectric power was attempted to know the sign of the predominant charge carriers. Both electrodes of the specimen cell, the mole ratio of which was 1.90, were connected to a galvanometer. By heating one side of the electrodes, a minute current flow was observed. The direction of the flow through the galvanometer was from the cold side electrode to the hot side electrode. Namely, the contribution of the positive holes was more predominant than that of the electrons to the conduction in this complex, while the opposite was observed in pure violanthrene.

Hall Effect.—The Hall effect has not been observed in semiconductive simple organic compounds because of their high resistivities. The only report presented has been on a rather special compound, poly-copper-phthalocyanine[7].

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[6] H. Akamatu, Y. Matsunaga and H. Kuroda, ibid., 30, 618 (1957).

[7] A. Epstein and B. S. Wildi, *J. Chem. Phys.*, 32, 324 (1960).

TABLE I. ELECTRICAL RESISTIVITY AT ROOM TEMPERATURE AND ACTIVATION ENERGY OF VIOLANTHRENE-IODINE

Sample No.	Mole ratio	Resistivity ohm cm.	E eV.	Temp. range °C
1	3.17	127	0.12_5	$-180\sim15$
2	1.90	18.0	0.07_5	$-180\sim15$
3	1.31	24.0	0.09	$-180\sim15$
4	0.118	2.2×10^2	0.09	$-180\sim15$
5	1.0×10^{-2}	3.1×10^5	0.22_5	$15\sim90$
6	3.6×10^{-3}	2.8×10^7	0.22_5	$15\sim90$
7	$8\ \times10^{-4}$	6.0×10^8	—	—
8	$5\ \times10^{-4}$	1.4×10^9	0.22	$15\sim65$
	Violanthrene	2.0×10^{14}	0.47	$60\sim200$

TABLE II. NUMBER OF SPINS AND CHARGE CARRIERS

Sample No.	Iodine concn. N_{I_2} per cc.	Spin concn. N_{spin} per cc.	Line width gauss	Carrier concn. N^* per cc. (calcd.)	Mobility μ cm²/V. sec. (calcd.)
1	4.48×10^{21}	8.0×10^{19}	18	2.93×10^{19}	1.7×10^{-3}
2	2.63×10^{21}	9.0×10^{19}	14	1.29×10^{20}	2.7×10^{-3}
3	1.79×10^{21}	1.0×10^{20}	11	4.79×10^{19}	5.4×10^{-3}
4	2.27×10^{20}	$4\ \times10^{18}$	10	6.07×10^{18}	4.7×10^{-3}
5	$2.1\ \times10^{19}$	$<10^{18}$	—	$2.4\ \times10^{15}$	8.4×10^{-3}
6	$7.4\ \times10^{18}$	—	—	$8.7\ \times10^{14}$	2.6×10^{-4}
7	$1.7\ \times10^{18}$	—	—	$1.9\ \times10^{14}$	5.4×10^{-5}
8	$1.0\ \times10^{18}$	—	—	$1.5\ \times10^{14}$	3.0×10^{-5}

It was hoped to observe the Hall effect successfully in the halogen-complexes, because they possess low resistivities. The attempt was made with a sample with the mole ratio of 1.90. The specimen powder was pressed into a frame of Bakelite plate with a load of 1000 kg. The dimensions of the specimen were $5\times20\times1.73$ (t) mm. Platinum electrodes and leads were mounted in the frame. The electrical resistance of the specimen was 140 ohm between current leads and 700 ohm between potential leads. This frame was placed between poles of a magnet. The applied electrical current (I) was 8.5 mamp. The magnetic field (H) was 8000 oersted. For the electromotive force measurement, a Leed & Northrup potentiometer was employed in association with a galvanometer (Kaken) possessing the sensitivity of 4.6×10^{-8} V. All the apparatus was carefully insulated from the ground to avoid a slight irregular current.

When the magnetic field was applied, a slight potential difference was recognized between the potential leads. Although the magnitude was very small (about 0.5 mm. movement on the scale of the galvanometer), a quite definite change in direction of the electromotive force was noted following alternation of the direction of the magnetic field or electric current in the specimen. This direction indicated the hole conduction, which was consistent with the results of the thermoelectric power. From this, it might be concluded that a very weak Hall effect was perceived in the violanthrene-iodine complex. However, the Hall voltage was small, restricted by the limits for the sensitivity of the galvanometer, $\varDelta V<4.6\times10^{-8}$ V. Thus, the Hall coefficient was $R=10^8\cdot\varDelta Vt/HI<1.2\times10^{-2}$ cm³/coulomb. If the conduction is assumed to be carried by positive holes, the number of carriers and the mobility might be estimated as:

$$n_h=\frac{3\pi}{8}\frac{1}{Re}>7\times10^{20}\ \mathrm{cm}^{-3}$$

$$\mu_h=\frac{8}{3\pi}R\sigma<1.6\times10^{-3}\ \mathrm{cm^2/V.\,sec.}$$

This indicates that the mobility possesses a very small value, and this is the reason for the difficulty of Hall effect measurement for these organic compounds. These values quoted the lower limit and the upper limit respectively due to the sensitivity of the galvanometer. However, they are perhaps not far from the real values, which will be discussed in a later section.

ESR Absorption.—The electron spin resonance absorption was observed at room temperature with a Hitachi MPS-1 ESR X-band spectrometer. All the samples showed absorption and, consequently, the existence of unpaired electrons. No fine structure was found in the absorption line.

The g-value was determined by referring to a standard sample of ultramarine ($g=2.028$). The g-value of the violanthrene-iodine system was 2.0035, regardless of the composition, which is very close to the value of the free electron or of organic free radicals. The spin concentration of the samples was determined from the integral areas of absorption lines by comparison with that of a standard sample of diphenylpicrylhydrazyl. The observed values are summarized in Table II. For the samples of lower iodine content, the estimationof spin numbers could not be made quantitatively because of their weak absorptions. Violanthrene usually shows a weak absorption (for a reason unknown at present), and the values quoted in Table II are those for which correction has been made for the absorption of violanthrene (2×10^{18}/g.). Such being the case, a spin concentration of less than 10^{18} per cc. (for sample 5) is not reliable.

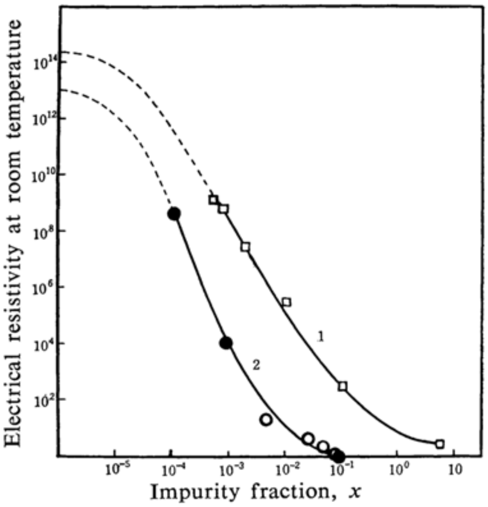

Fig. 1. Electrical resistivity for various impurity content.
Curve 1 : Violanthrene-iodine. Curve 2 : $Li_xNi_{(1-x)}O$. (After Morin. Ref. 9, p. 622). Impurity content is represented by the fractional number x for both curves.

Discussion

It has been found that a small amount of iodine added to violanthrene enhances the electrical conduction remarkably, and that the resistivity decreases monotonously with an increase in the iodine concentration until the mole ratio 1 : 2, where the intermolecular pseudo-compound is formed⁶⁾. This effect of iodine is almost comparable to that of lithium oxide added to nickel(II) oxide. The resistivity of pure oxide nickel is 10^{13} ohm-cm. at room temperature, which is comparable to that of violanthrene, 10^{14} ohm-cm. It is well known[8,9] that the alloying of lithium oxide with nickel-(II) oxide in a homogeneous solid solution leads to a semiconducting material (the so-called valence control semiconductor) with a remarkable range of resistivity depending on the lithium concentration. In Fig. 1, the variation of resistivity with the concentration of the impurity is illustrated for the systems of both violanthrene-iodine and nickel(II) oxide-lithium oxide. One can see that the two curves are quite similar to each other. Moreover, a few common characteristics can be noted between these two systems. In the nickel oxide system, the activation energy for electrical conduction is as small as around 0.1 eV. and depends on the lithium content; the conduction is carried by positive holes, and its mobility is so small that the Hall effect could hardly be observed. However, from the Seebeck effect it has been estimated as 10^{-3} cm²/V. sec. at room temperature, depending on the lithium content.

The mechanism of electrical conduction in the nickel oxide system has long been discussed as a typical example to which the energy band model could not be applied. Recently, the "hopping" type electrical conduction theory has been proposed and has been quite successful[10]. Thus, it might be interesting to speculate on the conduction mechanism in the violanthrene-iodine system on the analogy of the nickel(II) oxide-lithium oxide system.

In nickel oxide, neighboring Ni^{2+} ions are so far separated from each other that the overlap of 3d wave functions is very small and the 3d charge carriers can be considered to occupy energy levels localized on the cations. In consequence, pure nickel oxide possesses a high resistivity. However, nickel oxide can be made conducting by introducing Ni^{3+} ions into the lattice by the substitution of Li^+ ions for some of the Ni^{2+} ions. The Ni^{3+} ions (holes) are not bound to definite positions in the lattice, but can wander through the crystal by jumping from ion to ion if there is some overlap between hole wave functions localized on neighboring ions. However, the hole tends to be "self-trapped" in the crystal as a result of the polarization of the surrounding lattice, and when the hole can jump, the polarization associated with the hole must jump with it. The jumping process is then

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[8] E. J. W. Verwey, "Semiconducting Material", Ed. by H. K. Henisch, Butterworths Scientific Publications, London (1951), p. 151.

[9] F. J. Morin, "Semiconductors", Ed. by N. B. Hannay, Reinhold Pub. Co., New York (1959), p. 600.

[10] J. Yamashita and T. Kurosawa, *J. Chem. Phys. Solids*, 5, 34 (1958).

expected to involve an activation energy associated with the self-trapping of the holes.

In the violanthrene-iodine system, the electron transfer takes place from violanthrene (D) to neighboring iodine (A) through an overlap of molecular orbitals by the quantum mechanical resonance; the dative structure (D^+A^-) will result, in which the violanthrene molecule can be regarded as a positive ion. The dative structure may not be bound to a definite donor molecule, but may wander by the resonance among the neighboring molecules; thus resulting in a positive hole. However, the hole may be localized (trapping) around the acceptor molecule (I_2^-), and an activation energy is then expected to make it the " free " hole, which gives rise to electrical conduction by the jumping process. In transport of this type one may expect low mobility and a low value of activation energy because of the polarization effect, as in the case of nickel oxide.

In such a scheme, as many dative structures will be produced as the number of iodine molecules in the violanthrene matrix, but the number of free holes must be smaller than this. This is characteristic of the charge transfer complexes which possess a relatively high conductivity; i. e., a strong ESR absorption is generally observed. Singer and Kommanduer[11] have found, for the complex of pyrene-iodine and perylene-iodine, that the spin concentration increases with the temperature and that the activation energy for the spin generation is in accordance with that for the electrical conduction. Calvin et at.[12] assumed that the number of charge carriers is the same as the number of unpaired spins in the phthalocyanine-chloranil complex. The origin of the observed spins in the charge transfer complex has not yet been clarified; however, a close relation between these unpaired spins and the charge carriers can be presumed. The observable number of unpaired spins is much less than the number of iodine molecules added to violanthrene, and just a small percentage of it at room temperature. If one can assume that the trapped holes are thermally excited and give rise to the free holes, then the number of free holes N^* might be given by $N_{I_2}\exp(-E/kT)$, where N_{I_2} is the number of iodine molecules and E is the activation energy for electrical conduction. In Table II, the calculated values of N^* are shown. These values are almost comparable with the observed numbers of spins in samples 1, 2, 3 and 4, whose spin concentration could be measured quantitatively.

Further speculation can be made on the mobility of charge carriers, which can be given by $\mu=\sigma/N^*e$. The calculated values for the mobility are shown in the last column of Table II. These values are likely reasonable and consistent with the results of the measurement of the Hall effect. In this speculation, it has been assumed that the unpaired spins are observable only when associated with the free holes, but no spin is observable when the hole is trapped by the acceptor ion. Furthermore, the observed activation energy is assumed to be associated predominantly with the delocalization of the hole, rather than with the polarization effect in the transportation process.

Summary

Electrical conduction and ESR absorption in the violanthrene-iodine system have been investigated, varying the iodine content. Observation of the Hall effect has been attempted, but the Hall voltage was so small that the effect could not be determined. It was pointed out that, concerning conductive behaviors, the violanthrene-iodine system is analogous with the nickel(II) oxide-lithium oxide solid solution, and that the hopping model of electrical conduction can be applied. From such a view point, the correlation between the observed unpaired spins and charge carriers has been estimated.

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[11] L. S. Singer and J. Kommandeur, *J. Chem. Phys.*, **34**, 133 (1961).

[12] D. R. Kearns, G. Tollin and M. Calvin, ibid., **32**, 1020 (1960).