Magnetochemical Study of Violanthrene-iodine System

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Introduction

As reported in the preceding paper[1], it has been found that polycyclic aromatic hydrocarbons form molecular complexes with bromine or iodine, and these complexes behave as typical semiconductors with high conductivity. For instance, the electrical resistivity of perylene-bromine complex is as low as several ohm-cm. at room temperature with the energy gap for conductivity of 0.13 e.v., and that of violanthrene-iodine complex is about 40 ohm-cm. with the energy gap of 0.15 e.V.

In connection with the investigation for the electrical conductivity of these molecular

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[1] H. Akamatu, H. Inokuchi and Y. Matsunaga, *Nature*, **173**, 168 (1954), see also This Bulletin to be published.

complexes, we have studied the magnetic susceptibility of violanthrene-iodine complex as a function of iodine concentration in it. Included also are the following complexes, benzanthrone-bromine, perylene-bromine, perylene-iodine, and violanthrene-bromine.

Experimental

Materials

Benzanthrone-bromine.—Brass and Clar prepared this complex by addition of bromine to benzene solution of benzanthrone[2], but our sample was prepared by direct absorption of bromine vapor to a known quantity of crystalline powder of benzanthrone. The complex containing excess bromine was left in a desiccator, and its weight was measured from time to time. The change of composition with time shows that a complex is formed containing one molecule of benzanthrone and one atom of bromine (cf. Fig. 1). This result agrees well with that reported by Brass and Clar, though we prepared it by a different method.

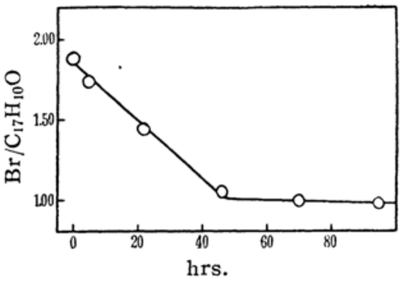

Fig. 1. Change of bromine content of benzanthrone-bromine complex by preservation in a desiccator.

Perylene-bromine.—The sample used in this study was prepared by direct absorption of bromine vapor[3]. The complex containing excess bromine was left over potassium hydroxide in a desiccator for a week. Therefore, the sample may be dibromoperylene-bromine complex with a little amount of free dibromoperylene[1].

Perylene-iodine.—This complex was prepared by addition of iodine to benzene solution of perylene[4]. To determine the composition of complex, we dissolved its known quantity in benzene, added potassium iodide and water, and titrated the liberated iodine with the standard solution of sodium thiosulfate.

Violanthrene-bromine.—This complex was also prepared by absorption of bromine vapor, and left in a desiccator until the change of weight due to the decomposition became so small that we could ignore it during the time required for the magnetic measurement. We have not yet prepared the complex which can be considered to have a definite composition. However, it is sure that a part of bromine which combines with violanthrene is used for substitution and the other part for the formation of molecular complex.

Violanthrene-iodine.—The crystalline powder of violanthrene was treated with benzene solution of iodine for some minutes at boiling point, or with carbon tetrachloride solution for a few days at room temperature. The precipitated complex was filtered and dried in vacuo at room temperature. The samples which have varied compositions were obtained by the change of iodine concentration of solution. Solubility of violanthrene and its complex to cold benzene and carbon tetrachloride is very small, so that in the calculation of its composition, we can leave out of consideration the loss of violanthrene during this treatment.

Magnetic measurement

The susceptibilities were measured using a Gouy balance as previously described[5]. The field was calibrated at two current strengths with distilled water. Fields of about 16 and 23 kilo-oersteds were used, and each sample was measured in two field strengths to detect any ferromagnetic impurities. The samples which exhibited field strength dependence of susceptibility were discarded.

Taking water as the standand substance (-0.720×10^{-6}), the susceptibility of a sample per gram (χ) is calculated by

$$-\chi\cdot10^6=0.749\times\frac{V}{M}\times\frac{F}{F_0}-\frac{0.029}{D}\qquad\text{(at 20°C)}$$

where F_0 and F are the resultant forces on water and the sample in g., respectively, V is the volume of water in cc. and the same volume is occupied by M g. of the sample, and D is the true density of the sample.

Results

The hydrocarbons and complexes under consideration together with the experimental molar susceptibilities are given in Table I

TABLE I

MOLAR SUSCEPTIBILITIES OF SOME MOLECULAR COMPLEXES AND RELATED COMPOUNDS

Substance	Formula	Molar suscept. ($-\chi_M\times10^6$) observed	estimated
benzanthrone	(1)	143	
benzanthrone-0.97 Br.		171	173
perylene	(2)	167	
dibromoperylene	(3)	216	215
perylene-3.87 Br.		62	286
perylene-2.67 I.		210	286
violanthrene	(4)	304*	
violanthrene-4.36 Br.		180	437
violanthrene-4.00 I.		308	482
bromine (1/2 Br_2 or Br)**		30.6	(Pascal's constants)
iodine (1/2 I_2 or I)**		44.6	

* The previously reported value is 273, the new datum may be more correct.

** The constant for halogen is half the molar susceptibility.

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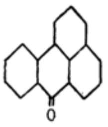
[2] K. Brass and E. Clar, *Ber.*, **69**, 690 (1936).

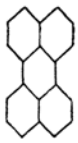
[3] A. Zinke and A. Pongratz, ibid., **69**, 1591 (1936).

[4] K. Brass and E. Clar, ibid., **65**, 1660 (1932).

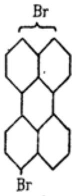
[5] H. Akamatu and Y. Matsunaga, This Bulletin, **26**, 364 (1953).



(1)



(2)



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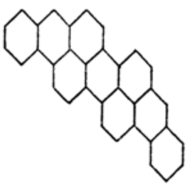

(4)

columns one and two. The molar susceptibilities of complexes estimated from the measurements on hydrocarbons and Pascal's constants for halogens by direct application of the additivity law are given in column three.

The experimental molar susceptibilities of benzanthrone-bromine complex and dibromoperylene are in accordance with the estimated ones within the errors of the experiments and the estimations. But, in the others, the estimated values are all in serious disagreement with the experimental ones.

Most of complexes which show such a large discrepancy are not stable, bromine complexes change spontaneously to brominated hydrocarbons evolving hydrogen bromide, and perylene-iodine complex loses iodine slowly and leaves the original hydrocarbon. Only violanthrene-iodine complex is so stable that we have no need to consider the change of composition with time. In Fig. 2, its susceptibility per gram is plotted against the concentration of iodine varied from 0 to 67.1 per cent in twelve steps. The dotted line shows the calculated susceptibility derived by the additivity law, and the susceptibility of iodine (-0.36×10^{-6}) is taken from "International Critical Tables"[6]. The actual susceptibility decreases lineary as a function of iodine concentration, but deviates remarkably from the dotted line. When iodine concentration exceeds 55 per cent, the susceptibility increases very slowly and approaches that of pure iodine. The maximum deviation amounting to over 35 per cent occurs at 55 per cent iodine, suggests that a complex is formed containing one molecule of violanthrene and two of iodine. The molecular complex which has this composition will show the most typical properties of this two-component system. If we assume merely the existence of the compound which has the above mentioned concentration of iodine, the linearity of susceptibility-composition curve below and above 55 per cent iodine will be explained. The linearity, whilst consistent with the assumption, can not be regarded as the evidence for non-existence of other complexes in this two-component system.

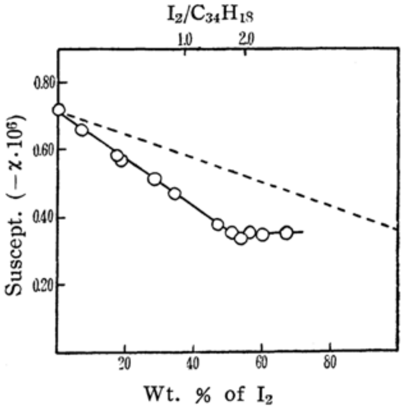

Fig. 2. Magnetic susceptibility of violanthrene-iodine complex as a function of iodine concentration.

Discussion

It is apparent that benzanthrone-bromine complex and the other complexes shown in Table I belong to different types of molecular complexes from each other. In the former case, the susceptibility follows the additivity law strictly, although stoichiometrical formula of this complex $C_{17}H_{10}O\cdot Br$ suggests the existence of unpaired electron, as Brass and Clar named these complexes "unpaarige Halogenide"[2,4]. For this reason, benzanthrone-bromine complex should be represented by doubled formula. The same conclusion had already been obtained by Müller and Wiesemann within the limits of their rather large experimental errors[7]. Schwab and Schwab-Agallidis applied the ortho-para conversion of hydrogen, and concluded also that this compound was not a radical[8].

On the other hand, the complexes between perylene or violanthrene and halogens, which are colored almost black and show surprisingly high electrical conductivities, are also very anomalous in magnetic behavior. In view of the peculiar and characteristic change of these properties, there can be little doubt

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[6] International Critical Tables, vol. 6, p. 355.

[7] E. Müller and W. Wiesemann, *Ber.*, 69, 2173 (1936).

[8] G. M. Schwab and E. Schwab-Agallidis, *Z. physik. Chem.*, B, 49, 196 (1941).

that in their complexes, hydrocarbons and halogens are present with very large changes in their electronic states. Dibromoperylene does not show such anomalies, and we can analyse perylene-iodine complex by titration with standard solution of sodium thiosulfate, so in these complexes, there is no doubt that halogens are not substituted in aromatic nuclei.

The decrease of molar susceptibility in these complexes is not explainable by the localization of π-electrons which have large orbital radii in aromatic molecules, as the contribution of these electrons to the susceptibilities of original hydrocarbons are no more than -65×10^{-6} in perylene and -137×10^{-6} in violanthrene. Therefore, these large decreases must be attributed to the occurrence of constituents or complex as a whole in the paramagnetic state, such as atomic halogen, hydrocarbon positive ion, triplet state or free electrons.

To make further examination of magnetic state, we estimate the depression of diamagnetism at the apparent composition containing one molecule of hydrocarbon and four atoms of halogen in each complex from the data shown in Table I, assuming that perylene-bromine, perylene-iodine and violanthrene-bromine behave like violanthrene-iodine in the susceptibility-composition curve. This assumption is not improbable in perylene-bromine and perylene-iodine, as the composition of the former complex is $C_{20}H_{12}\cdot 2Br_2$ or $C_{20}H_{10}Br_2\cdot Br_2$ as described in the previous paper and that of the latter complex reported by Pestemer and Treiber is $C_{20}H_{12}\cdot 2I_2$[9]. Violanthrene-bromine complex shown in Table I contains more halogen compared to the standard composition, so that the required value may be equal to the observed decrease. The estimated depressions are shown in Table II. In this Table, we regarded perylene-bromine complex as pure dibromoperylene-bromine complex, so the depression was estimated for $C_{20}H_{10}Br_2\cdot Br_2$.

TABLE II

THE ESTIMATED DEPRESSION OF MOLAR SUSCEPTIBILITY OF COMPLEX AT THE APPARENT COMPOSITION OF ArH-4X

Substance	Estimated depression of molar suscept.
perylene-bromine	240×10^{-6}
perylene-iodine	110×10^{-6}
violanthrene-bromine	260×10^{-6}
violanthrene-iodine	170×10^{-6}

We can find from Table II that bromine is more effective to the depression of diamagnetism than iodine, and violanthrene is affected more than perylene by these two halogens. Consequently, it is not probable that the occurrence of paramagnetism is due to the dissociation of halogen molecule, as the bond energy of bromine is larger than that of iodine, and if so, iodine should be more effective. The order of depression of diamagnetism is not compatible with that of the electronegativity of halogen and besides probably with that of the ionization potential of aromatic molecule. The partial ionization of constituents may be sufficient to explain the above data. But this explanation is inconsistent with the data on the electronic conduction described in the previous paper.

Nowadays, it is well known that aromatic hydrocarbons as benzene[10], naphthalene[11], and phenanthrene[12] form complexes with halogens. The bonding power in these complexes is named by Mulliken as "intermolecular charge-transfer force"[13]. He showed also that the theory predicts the possibility of highly intense absorption even for very loose complexes. Benzene, naphthalene and their derivatives form only loose complexes in solutions, so that the charge-transfer may be limited in one complex molecule. If the complex molecules are packed together closely as in our solid complexes, the charge-transfer will not be limited in one complex molecule, but spread out more widely and strongly. In such a case, the complexes have to be extremely deeply colored and show very intense absorption. The occurrence of the excited form with unpaired electrons by thermal excitation may be plausible. The order of difference between observed and estimated molar susceptibilities seems to be consistent with this theory We are not yet ready to state whether the electrical conductivity is explainable by triplet state or not, but we can conclude confidently that the excited state relates to the electrical conductivity of these complexes from its temperature dependence.

If we assume that the difference between observed and estimated molar susceptibilities is equal to the paramagnetic contribution of unpaired electrons and all unpaired electrons behave as free electrons, the excitation energy 0.17 e.V. for violanthrene-iodine complex ($C_{34}H_{18}\cdot 2I_2$) is anticipated from it[14].

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[9] M. Pestemer and E. Treiber, *Ber.*, **74**, 964 (1941).

[10] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

[11] N. W. Blake, H. Winston and J. A. Patterson, ibid., **73**, 4437 (1951).

[12] L. J. Andrews and R. M. Keefer, ibid., **74**, 4500 (1952).

[13] R. S. Mulliken, ibid., **74**, 811 (1952), *J. Phys. Chem.*, **56**, 801 (1952).

[14] Assuming that the paramagnetic contribution of one mole of free electron is equal to 1270×10^{-6}, the relation between the depression of molar susceptibility ($\varDelta\chi_M$ and the excitation energy ($\varDelta\epsilon$) is approximated by $\varDelta\chi_M/2\times1270\times10^{-6}=2\cdot\exp(-\varDelta\epsilon/2kT)$.

This is in good accordance with that obtained from the temperature dependence of electrical conductivity.

Bhatnagar and Lakra[15], and Rao and Govindarajan[16] studied the magnetic susceptibility of benzene solution of iodine. Both of them found that the susceptibility of solution is more diamagnetic than expected from the additivity law. The apparent susceptibility per gram of iodine reported by the former investigators is -0.51×10^{-6}. This increase of apparent susceptibility is not inconsistent with the above explanation, as, in this case, the interaction between complex molecules may be negligibly small and the charge-transfer in a complex molecule will bring about only the expansion of the orbital radii of π-electrons, namely, the increase of diamagnetism, and not the occurrence of a paramagnetic state.

If we take into consideration the expansion of the orbital radii of π-electrons in our complexes, the contribution of paramagnetism to molar susceptibility will increase and the excitation energy will decrease to a little extent. For example, if we take the apparent susceptibility of iodine in violanthrene-iodine complex for -0.60×10^{-6}, calculated from the apparent susceptibility in benzene solution and the formation constant of benzene-iodine complex[10], assuming that the susceptibility of iodine not tied up as complex is equal to -0.36×10^{-6}, the magnitude of paramagnetism will be 300×10^{-6}, and the excitation energy 0.15 e.V. The agreement between the final estimated value of excitation energy and that obtained from the temperature dependence of electrical conductivity is surprisingly good.

Summary

The magnetic susceptibility of violanthrene-iodine complex was measured as a function of iodine concentration. This complex shows the large discrepancy between the observed susceptibility and the estimated one which was derived by direct application of the additivity law. Perylene-bromine, perylene-iodine, and violanthrene-bromine show a similar behavior also. The susceptibility-composition curve in violanthrene-iodine system suggests the existence of molecular complex containing one molecule of violanthrene and two of iodine. At that composition, the discrepancy exceeds 35 per cent. This depression of diamagnetism is so large that we can not explain it by the localization of π-electrons in aromatic molecule. The occurrence of paramagnetic state is taken into consideration, and the nature of this state is discussed. The large difference between observed and estimated susceptibilities is attributed to the partial cancellation of diamagnetism by the paramagnetic contribution of free electrons produced by the intermolecular charge-transfer force which spreads out widely and strongly in this solid complex.

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[15] S. S. Bhatnagar and C. L. Lakra, *Indian J. Phys.*, 8, 43 (1933).

[16] S. R. Rao and S. R. Govindarajan, *Proc. Indian Acad., Sci.*, **15**, A. 35, (1942).