Intermolecular Charge-Transfer Spectra. V. Halogen-Polymethylbenzene Complexes

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In the first paper of this series[1], we studied the spectroscopic features of halogen-aromatic complexes such as $X_2 \cdot C_6H_{(6-n)}(CH_3)_n$ in which $n=0, 1, 2$. Now we extend the previous discussions over the cases of $n=3, 4, 5, 6$ and compare the predicted value of molar extinction coefficient ϵ_c of intermolecular charge-transfer spectra with the observed results. Next, the foregoing idealized treatment will be discussed from the more general point of view in relation to the previous discussions on pressure effect[2,3] and the recent result by Ham[4].

Statistical Consideration

As can easily be seen, the electronic structure of π-electron system in methyl-benzene is practically the same as that in benzene itself. Consequently, in case of halogen-alkylbenzene complex, the observed behaviour of ϵ_c cannot be explained from the viewpoint of the electronic structure of the aromatic component. In order to solve this difficulty, we have already introduced the statistical treatment on the relative configuration between the two components[1]. That is, we considered the two relative configurations such as Model (α) and Model (β). In Model (α), the halogen molecule is resting on the benzene ring with its axis parallel to the plane of benzene and its center on the six-fold axis of benzene. In Model (β), the center of the halogen molecule is shifted towards the methyl group on account of van der Waals attraction of it (see Fig. 1 in reference 1). Since the degree of overlapping between orbital functions which are essential to charge-transfer interaction is considerably different for Models (α) and (β), it is reasonable to assume that each configuration has its own molar extinction coefficient $\epsilon_c^{(\alpha)}$ and $\epsilon_c^{(\beta)}$, respectively.

Next we postulate, as we have already done in our previous paper[1], that these two configurations (α) and (β) have almost the same stability and exist in solution with almost equal statistical weight. This assumption is reasonable so long as the contribution of the van der Waals type interaction is predominant compared with that of the charge-transfer type interaction[5]. Considering these conditions, we can give the following general formula for the observed molar extinction coefficient ϵ_c of molecular complexes as statistical mean,

$$\epsilon_c = (\epsilon_c^{(\alpha)} + n\epsilon_c^{(\beta)})/(1+n) \qquad (1)$$

where n is the number of substituted methyl groups and arbitrary integer between 0 and 6. At the present stage, the exact evaluation of $\epsilon_c^{(\beta)}$ is somewhat difficult and remains as parameter. Hence, we retain the previous relation[1]

$$\epsilon_c^{(\beta)} \simeq \epsilon_c^{(\alpha)}/2 \qquad (2)$$

as a reasonable one. The value of $\epsilon_c^{(\alpha)}$ is approximated by the observed molar extinction coefficient of halogen-benzene complex ($n=0$). Then, Eqs. (1) and (2) enable us to predict the observed molar extinction coefficient ϵ_c for any value of n. The results are shown in Table I together with the experimental results. At present, we have two sets of experimental results. The one is by Andrews and Keefer[6] and the other is by Tamres et al.[7]

As is seen in Table I, the order of magnitude of predicted values corresponds well to either of the two observations. The most essential feature of theoretical prediction is the decrease of ϵ_c with the increase of n. This interesting feature is well established in the data of Tamres et al. although it is not established in those of Andrews and Keefer. Strictly speaking, the rate of decrease of observed ϵ_c is greater than that of theoreticol prediction. If this difference is significant, it may probably be due to the contribution of the configurations in which the halogen molecule is rather resting on the

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TABLE I

EXPERIMENTAL AND THEORETICAL MOLAR EXTINCTION COEFFICIENTS OF IODINE-POLYMETHYLBENZENE COMPLEXES (IN CCl_4 SOLUTION)

Aromatic Component	ϵ_c (obs.) Andrews et al.[6]	ϵ_c (calc.)	ϵ_c (obs.) Tamres et al.[7]	ϵ_c (calc.)
Benzene	16400	(16400)	14700	(14700)
Mesitylene	8850	10250	10200	9190
Durene	9000	9840	8700[a]	8820
Pentamethylbenzene	9260	9570	7770	8580
Hexamethylbenzene	8200	9370	6690	8400

a) The value for isodurene.

two adjacent methyl groups and its own molar extinction coefficient is smaller than $\epsilon_c^{(\beta)}$.

If methyl groups are replaced with ethyl groups, one can expect the larger contribution of such configurations (which have smaller ϵ_c than $\epsilon_c^{(\beta)}$). Moreover, as was pointed out by Andrews and Keefer and also by Tamres et al., the steric hindrance of ethyl groups prevent the configuration such as Model (α) (which has greater ϵ_c than $\epsilon_c^{(\beta)}$). Consequently, one can predict the smaller ϵ_c for $X_2 \cdot C_6(C_2H_5)_6$ than for $X_2 \cdot C_6(CH_3)_6$. In fact, Tamres et al. observed the much smaller ϵ_c for $X_2 \cdot C_6(C_2H_5)_6$ ($\epsilon_c \sim 4570$) than for $X_2 \cdot C_6(CH_3)_6$ ($\epsilon_c \sim 6690$). On the contrary, Andrews and Keefer observed the reverse, that is, $\epsilon_c \sim 16700$ for the former complex. Judging from the regular behaviour of the observed ϵ_c and K, the results by Tamres et al. seem to be more reliable. At any rate, further experimental study is very desirable.

Generalization and Pressure Effect

In the foregoing discussion, we considered only two configurations such as Model (α) and Model (β). This corresponds to the idealized limiting case and is not exact enough. From the more general point of view, the observed molar extinction coefficient ϵ_c is given as follows:

$$\epsilon_c=\sum_i W_i \epsilon_c^{(i)} / \sum_i W_i \qquad (3)$$

where $\epsilon_c^{(i)}$ is the molar extinction coefficient for the any configuration (i) and W_i is the statistical weight of this configuration in solution. In case of non-substituted benzene complex, the value of W_i which corresponds to such a configuration as Model (β) may be much smaller than that of Model (α). On the other hand, in case of substituted benzene complex, the former value may become comparable to the latter one. Then, if one assumes that W_i of all the configurations except those of Model (α) and Model (β) are equal to zero, Eq. (3) reduces essentially to Eq. (1)*. In practice, any of W_i may be unequal to zero although it may be small enough. Consequently, when one uses the observed ϵ_c of halogen-nonsubstituted benzene complex as the value of $\epsilon_c^{(\alpha)}$ in Eq. (1), one should always remember that such a value of $\epsilon_c^{(\alpha)}$ has already included the statistical effect more or less (the assumed value of $\epsilon_c^{(\beta)}$ should also be considered as effective value which includes statistical effect).

This situation seems to have special importance for the explanation of pressure effect. In fact, it is reasonable to consider that the high pressure favours the compact configurations and makes the values of W_i of compact configurations greater. In case of halogen-aromatic complexes, the more compact configuration may have the greater $\epsilon_c^{(i)}$. Taking these factors into account, one can predict the increase of ϵ_c with increase of pressure. These considerations correspond to the special case of pressure effect which was discussed in the second paper of this series and seems to explain the recent work by Ham in which he observed the slight increase of optical density under the high pressure for iodine-aromatic complexes in *n*-heptane solution.

According to our opinion, the above-described explanation is more correct than that of Ham which postulated the alteration of equilibrium constant K and the constancy of ϵ_c with increase of pressure. At least, we should emphasize that Ham's explanation is rather macroscopic or phenomenological and does not take the microscopic situation into account: such as relative configuration between two components which seems to be essential to the value of ϵ_c. Especially, Ham's discussion seems to be inadequate for the case of Gibson and Loeffler's experiment in

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* If one takes the contribution of Model (γ) into account—see Part I of this series—the contribution of Model (α) and Model (β) should decrease by the corresponding amount.

which 50%, 50% mixture of nitrobenzene and aniline was used (without solvent). In such a condition as the above, the degree of intensification of ϵ_c may become much greater than that in Ham's experiment which was performed as dilute solution (solvent was *n*-heptane). Moreover, Gibson and Loeffler observed that the elevation of temperature at constant volume causes the same result as the high pressure at constant temperature. It is almost certain that the elevation of temperature tends to break up the molecular complex in the usual concept even at constant volume. Consequently, the concept or definition of molecular complex should be generalized as was discussed by Gibson and Loeffler from the kinetic point of view. If one admits this generalization, the previous explanation in the second Part of this series seems to be most probable.

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