A Study of the Charge-Transfer Complexes. VI. A Question on the Concept of the Weak Charge-Transfer Complexes[*1]

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In the recent years, several criticisms have been made on the reliability of the equilibrium constant (K) and the extinction coefficient (ε) for weak charge-transfer (CT) complex as estimated by the Benesi-Hildebrand (B-H) equation or the modified ones.1–4) The disbelief in the B-H equation has mainly come from the three facts: (1) the dependence of the K-value on the ratio between the concentrations of donor and acceptor molecules,1) (2) the variation of the K-value with the wavelength of the absorption band which the B-H equation is applied to,2,3) and (3) the inconsistent relationship between the K- and ε-values.1,4) All of these criticisms may be summarized to indicate that the basic assumptions inherent to the B-H equation do not hold in the actual cases of weak CT complexes. In other words, the fundamental concept of weak CT complexes might have been in error. Dewar and Thompson, in this connection, have lately emphasized that the appearance of CT absorption band does not necessarily mean that the CT interaction is the main driving force in the formation of molecular complexes.5) The present authors have reached similar conclusions as described below.

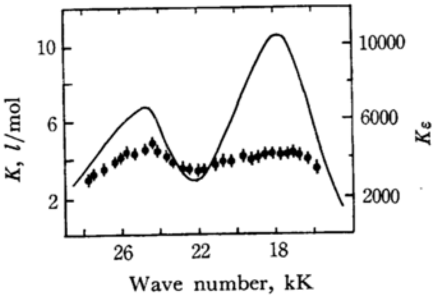

Fig. 1. The K- and $K\varepsilon$-values for TCNE complex of *p*-methylanisole. ●, K; —, $K\varepsilon$. The short, vertical line across the dot represents the standard deviation for the K.

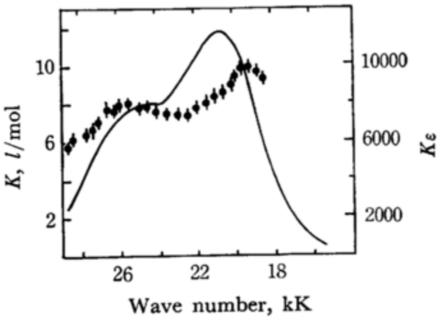

Fig. 2. The K- and $K\varepsilon$-values for TCNE complex of *t*-butyl *p*-tolyl ether. ●, K; —, $K\varepsilon$.

The CT absorption bands of tetracyanoethylene (TCNE) complexes with *p*-methylanisole (I) and *t*-butyl *p*-tolyl ether (II) have been measured in carbon tetrachloride. The ordinary B-H equation has been used to obtain the K- and $K\varepsilon$-values for the complexes as summarized in Figs. 1 and 2. If the K-values at the absorption maxima are compared, as usual, the TCNE complex with II is more stable than that with I. As to the CT bands themselves, on the other hand, the absorption maximum for the complex II is at considerably larger wave numbers than that for the complex I. This is a very peculiar situation. On the basis of the ordinary concept of CT complexes, it is expected that the more stable the complex becomes, the smaller the wave numbers at the absorption maximum are. The apparent contradiction to the expectation, as observed here, may be easily understood however if the associations are essentially due to the van der Waals forces as suggested by Dewar and Thompson.5) If this assumption is correct, the CT absorption is expected to occur simply because the pair of donor- acceptor molecules are held at close distance where CT forces contribute additional stabilizing effects on the association. In the present case, the relative importance of CT interaction in the association may be considerably different between the two complexes.

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One of the present authors has found, in his study of the NMR solvent effects also, that the CT forces are merely complementary ones in the interaction between solvent benzene and polar solute such as maleic anhydride or *p*-benzoquinone.[6,7] It should be recalled further that the heats of formation for the weak CT complexes are of the order of a few kcal/mol, in general. Therefore, one can hardly distinguishes the energy of weak CT interaction from that of van der Waals interaction.

On the basis of the above discussion, the present authors propose a revised model for weak CT complexes as follows. The donor and acceptor molecules at close distance may be held each other mainly by the van der Waals-type forces. Then, the configurations (or mutual orientations) of the pair will follow a statistical distribution. The most stable configuration in the distribution is not necessarily the most favored one from the view points of CT interactions. The apparent CT bands in solution are considered to be originated from such assembly of the associated species. In short, the spectra may not be taken to represent a simple, rigid complex. The three problems about the B-H equation, as described in the beginning, have appeared to be reasonably solved by Foster and his associates who have assumed that the absorption of CT complexes deviates*[3] from Beer's law.[1,2] It is suggested here that the deviation occurs simply because the relative importances among the configurations of the associated species vary with the change in the environment.

Experimental

Chemicals. *p*-Methylanisole and *t*-butyl *p*-tolyl ether were prepared from *p*-cresol by the use of dimethyl sulfate and *t*-butyl alcohol (together with concentrated sulfuric acid), respectively. The products were repeatedly purified by fractional distillations, and were identified by the IR and NMR spectra. The purities were proven to be above 99% by the gas chromatography. TCNE were prepared from malononitrile by the method of Carboni (mp 199—200°C).[8] Carbon tetrachloride was purified by the standard procedure.

Measurements. The spectra were measured under the temperature regulation (25±0.5°C) with a Hitachi model EPS-2U recording spectrophotometer. The K- and $K\varepsilon$-values were obtained by the least-square-mean method as applied to the B-H equation.

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*[3] The magnitude of the deviation has been suggested to depend on the wavelength.

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