Interaction of Stannic Chloride with Polymethylbenzenes

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In a number of papers, it has been found that inorganic acceptors, such as $SnCl_4$, $TiCl_4$, $VOCl_3$, and VCl_4, form charge-transfer (CT) complexes with various organic donors including aromatics.[1-5] The formation of these CT complexes has been confirmed using spectroscopic and other physicochemical methods. Since these inorganic acceptors are also a group of Lewis acids, it may be expected that the electron affinities of these inorganic acceptors, E_A, which are estimated from transition energies of CT absorption ($h\nu_{CT}$), will be of importance as effective measures of the strength of Lewis acids.

Although there have been some investigations of the CT interaction between $SnCl_4$ and aromatics as donors,[1,2,5] no CT absorption maximum has been separated; hence, the E_A of $SnCl_4$ has not yet been estimated. In the present communication we report that, in the systems of $SnCl_4$ and some polymethylbenzenes, new absorption bands were successfully separated from the absorption of the components and that these new bands were assigned and the E_A of $SnCl_4$ estimated.

Mixtures of $SnCl_4$ and hexamethylbenzene (HMB), pentamethylbenzene (PMB), durene, or mesitylene in a cyclohexane solution absorb significantly in the UV and visible region, where solutions of the individual components show negligible absorption. All the absorption spectra are summarized in Fig. 1.

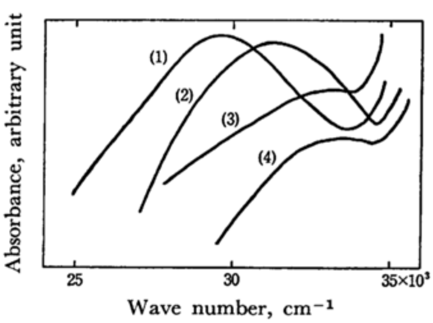

Fig. 1. Spectra of various donors with $SnCl_4$ in cyclohexane; (1), HMB (2), PMB; (3), durene; (4), mesitylene: (at 24.5°C)

The transition energies which were estimated from new absorption bands appearing in the systems of $SnCl_4$-polymethylbenzenes are also plotted against the ionization potentials (I_P) of the corresponding aromatic hydrocarbons in Fig. 2-I, where a linear relationship can be seen. The similar linear relationship of $h\nu_{CT}$ *vs.* I_P has been estsblished in the system of I_2-aromatics, as may be seen in Fig. 2-II. The transition energies of absorption bands due to σ-complexes or protonated carbonium ions of polymethylbenzenes are also plotted in Fig. 2-III against I_P.[6]

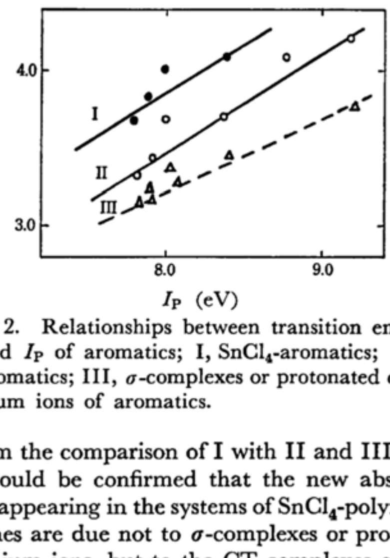

Fig. 2. Relationships between transition energies and I_P of aromatics; I, $SnCl_4$-aromatics; II, I_2-aromatics; III, σ-complexes or protonated carbonium ions of aromatics.

From the comparison of I with II and III in Fig. 2, it could be confirmed that the new absorption bands appearing in the systems of $SnCl_4$-polymethylbenzenes are due not to σ-complexes or protonated carbonium ions, but to the CT complexes of $SnCl_4$ with aromatics, as in the case of I_2-aromatics.

Using the same donor, the E_A value of any given acceptor or can be estimated by means of the following approximate equation;

$$(h\nu_{CT})_0-(h\nu_{CT})_i = (E_A)_i-(E_A)_0$$

where the suffixes 0 and i indicate those for the standard and for any given acceptor respectively. Here, I_2 and mesitylene were chosen as the standard acceptor and donor, and the E_A of I_2 was assumed to be 1.8_0 eV; hence the E_A of $SnCl_4$ could be estimated to be 1.4_6 eV.

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