Electron Donor-acceptor Complexes between Group IV Tetrahalides and Methylbenzenes

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The charge-transfer bands of the loose complexes between Group IV tetrahalides (chlorides and bromides) and methylbenzenes were observed, and the electron affinities of these tetrahalides were systematically evaluated from these observed charge-transfer bands. The semi-empirical molecular orbital calculations (the extended Hückel method) for these tetrahalides revealed that the tetrahalides interact with the benzene ring using the vacant molecular orbital involving the empty *d* atomic orbital of the halogen atom in the tetrahalides. Moreover, the meanings of the electron affinities estimated in this study were discussed in terms of the molecular orbitals, by comparing them with the values of the electron affinities evaluated by other methods.

Extensive studies have been made of the complexes between Group IV tetrahalides and *n*-donors by means of the thermodynamic[1] and the spectroscopic measurements, such as IR[2] and NMR.[3] Since Mulliken developed the theory of the donor-acceptor complex,[4] it has been reported that these tetrahalides form not only stable complexes with *n*-donors, but also loose complexes with aromatic π-donors.

As for the carbon tetrachloride and carbon tetrabromide, many workers have studied the formation of loose complexes with π-donors.[5-8] The formation of loose complexes between tin tetrachloride and aromatic hydrocarbons has been studied by Tsubomura[9] and by Myher and Russell.[10] By the spectroscopic measurements, Krauss and his co-workers have found that the titanium tetrachloride and vanadium tetrachloride form loose complexes with π-donors.[11]

Although there have been many investigations of the tetrahalide complexes, many essential problems have not yet been solved. Some of them are as follows:

i) What are the structures of these complexes?

ii) What is the order of the electron affinities of the tetrahalides, which are evaluated from the charge-transfer bands, and what are the meanings of these electron affinities?

iii) What are the molecular orbitals of the tetrahalides which are used to accept the aromatic π-electrons of the donors?

The aim of the present study is to settle some of these problems as definitely as possible. In order to accomplish this purpose, we undertook to measure the UV and visible spectra and to carry out some molecular orbital calculations on these tetrahalides.

Experimental

Materials. Cyclohexane of a spectral-use grade was refluxed over calcium hydride and was distilled and stored under nitrogen gas. The hexamethylbenzene (HMB) and pentamethylbenzene (PMB) were recrystallized and sublimated twice, whereas durene purified by zone-refining was used without further purification. The Mesitylene was refluxed, distilled, and stored in a sealed vessel under nitrogen gas. All the tetrachlorides and tetrabromides, of an extra pure grade, were distilled *in vacuo* and then were immediately used.

Procedure. After the glass apparatus had been dried in a high vaccum and baked to a high temperature, the donor and acceptor solutions were made separately, with air excluded, in glass apparatus, and then degassed in a high vaccum to follow the mixing of both solutions. The concentrations of the solutions were varied over a wide range to obtain the new absorption bands clearly. The absorption spectra were measured by a Cary model 14M recording spectrophotometer, and fused quartz cells with a light-path length of 0.1—10 mm were used.

Experimental Results and Discussion

Electron Donor-acceptor Complexes between Tin Tetrachloride and Methylbenzenes. The mixed solutions of tin tetrachloride and methylbenzenes, *i.e.*, mesitylene, durene, PMB, and HMB, in cyclohexane showed significant absorption bands in the UV and visible regions, where solutions of the individual components show negligible absorption; only in the appropriate concentrations of the donor (0.050—0.075 mol/*l*) and those of the acceptor (0.025—0.050 mol/*l*) solutions were new absorption maxima clearly separated, as is shown in Fig. 1.

The plotting of the transition energies of the new absorption bands ($h\nu_{CT}$) against the ionization potentials(I_P)[12] of the corresponding donors exhibits a linear relationship, as is shown in Fig. 2-I. A similar linear relationship has been established in the iodine molecular

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[1] D. P. N. Satchell and R. S. Satchell, *Chem. Rev.*, **69**, 251 (1969).

[2] D. G. Brown, R. S. Drago, and T. F. Bolles, *J. Amer. Chem. Soc.*, **90**, 5706 (1968).

[3] J. F. Deters, P. A. McCusker, and R. C. Pilger, *ibid.*, **90**, 4583 (1968).

[4] R. S. Mulliken, *ibid.*, **74**, 811 (1952).

[5] F. J. Striter and D. H. Templeton, *J. Chem. Phys.*, **37**, 161 (1962).

[6] F. Dorr and G. Buttgereit, *Ber. Bunsenges. Physik. Chem.*, **67**, 867 (1963).

[7] R. F. Weimer and J. M. Fransnitz, *J. Chem. Phys.*, **42**, 3643 (1965).

[8] K. M. C. Davis and M. F. Farmer, *J. Chem. Soc., B*, **1967**, 28.

[9] H. Tsubomura, This Bulletin, **27**, 1 (1954).

[10] J. J. Myher and K. E. Russell, *Can. J. Chem.*, **42**, 1555 (1964).

[11] a) H. L. Krauss and H. Hüttmann, *Z. Naturforsch.*, **18b**, 976 (1963); b) H. L. Krauss and J. Nickl, *ibid.*, **20b**, 630 (1965). c) H. L. Krauss and H. Hüttmann, *ibid.*, **21b**, 490 (1966).

[12] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

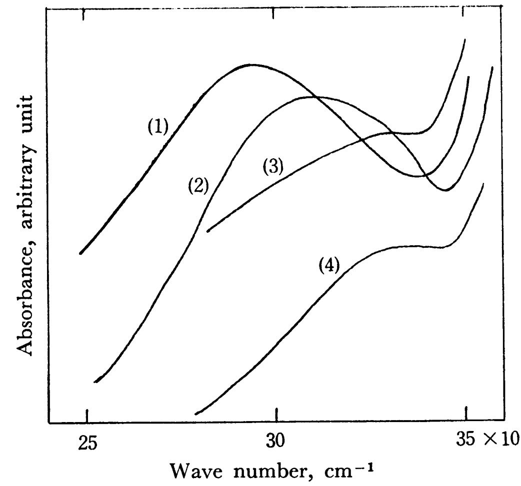

Fig. 1. Absorption spectra of various donors with $SnCl_4$ in cyclohexane (at 24.5°C).
(1) HMB, (2) PMB, (3) durene, (4) mesitylene.

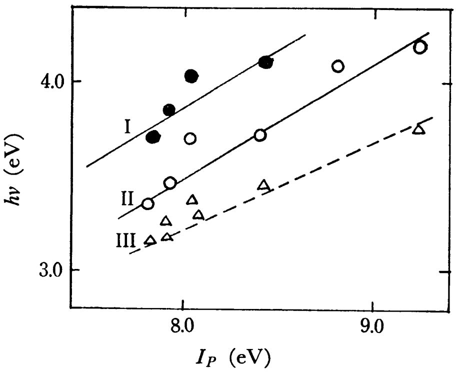

Fig. 2. Relationships between transition energies and I_P of aromatics.
I: $SnCl_4$-aromatics
II: I_2-aromatics
III: σ-complexes or protonated carbonium ions of aromatics

complexes with methylbenzenes (Fig. 2-II).[13] The transition energies of the absorption bands for the σ-complexes or protonated carbonium ions of methylbenzenes are also plotted in Fig. 2-III against I_P.[14-16] From a comparision of I with II and III in Fig. 2, it could be confirmed that the new absorption bands are due not to the σ-complexes or protonated carbonium ions, but to the electron donor-acceptor complexes.[17] Moreover, the similarity of the slopes of I and II in Fig. 2 suggests that the properties of these tin tetrachloride complexes resemble those of the iodine molecular complexes.

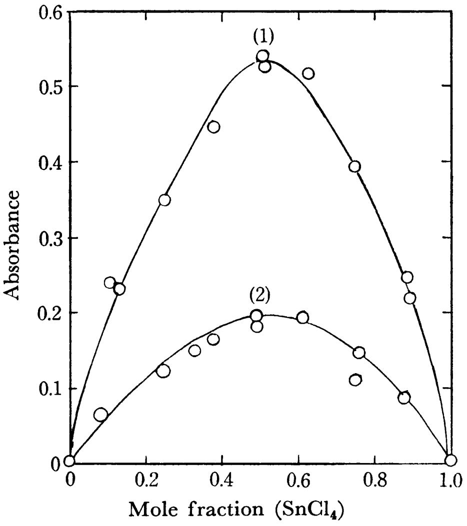

Fig. 3. Continuous variation plots for the absorbance of $SnCl_4$-HMB solution in cyclohexane.
$SnCl_4$+HMB=0.2 mol/l, (1) at 33.3 kK (absorption maximum), (2) at 31.3 kK.

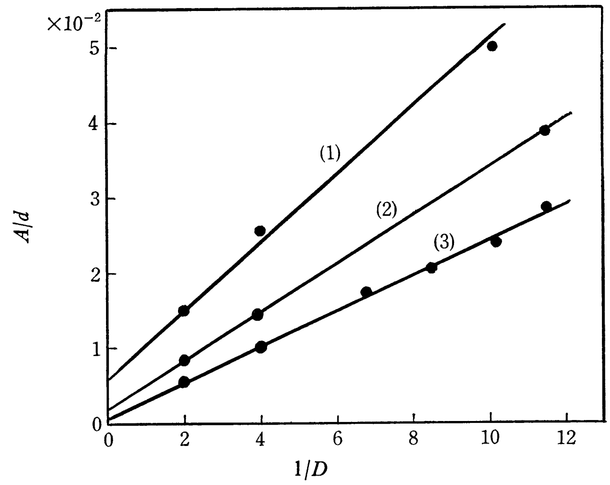

Fig. 4. Plots of Benesi-Hildebrand for $SnCl_4$-mesitylene at high concentration of mesitylene in cyclohexane (24.5°C).

$$\frac{A}{d}=\frac{1}{\varepsilon K}\cdot\frac{1}{D}+\frac{1}{\varepsilon}$$

A,D: concentrations of acceptor and donor, respectively, d: absorbance, ε: molar extinction coefficient, K: formation constant, (1) 340 nm, (2) 320 nm, (3) 300 nm

Continuous variation plots for the absorbance of the solutions of tin tetrachloride and HMB in cyclohexane are given in Fig. 3. At both 300 nm (a maximum of the charge-transfer absorption) and 320 nm, these plottings indicate that a 1 : 1 complex is formed in this system; this finding is consistent with that of Myher and Russell.[10] Since the formation of a 1 : 1 complex was confirmed, the Benesi-Hildebrand plots for this system were attempted, as is shown in Fig. 4, which shows straight lines. The formation constant and molar extinction coefficient of this complex were estimated to be as shown in Table 1, in which the formation constants varied greatly with the wavelength. It has been reported that the dependence of the formation constants on the wavelength occur, when a contact charge-transfer complex or another com-

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[13] G. Briegleb, "Electron-Donor-Acceptor-Komplexe," Springer, Berlin (1961).

[14] H. H. Perdampus and T. H. Kranz, *Z. Physik. Chem. Neue Folge*, **38**, 295 (1963).

[15] C. Dallinger, E. L. Macker, and A. A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958).

[16] In Fig. 2-III, it seems as if the plots for σ-complexes fit a linear relationship, but it has been established that, for aromatic hydrocarbons with lower I_P values, such as polyacenes, the plots deviate from this linearity.[13]

[17] M. Hatano and O. Ito, This Bulletin, **42**, 1780 (1969).

TABLE 1. FORMATION CONSTANT (K) AND MOLAR EXTINCTION COEFFICIENT (ε) FOR $SnCl_4$-MESITYLENE AT 24.5°C

Wavelength (nm)	K(mol^{-1} l)	ε
300[a]	0.43	1000
320	0.95	357
340	1.30	167

a) Absorption maximum.

TABLE 2. FORMATION CONSTANTS (mol^{-1} l) FOR $SnCl_4$ AND CCl_4 COMPLEXES WITH METHYLBENZENES OR BENZENE

	HMB	Mesitylene	Benzene
$SnCl_4$[a]	1.68	0.43	—
CCl_4[b]	0.64	0.113	0.0009

a) Values estimated at the maxima of charge-transfer bands in cyclohexane at 24.5°C.

b) Ref. 7, values estimated near the maxima of charge-transfer bands in n-hexane at 25°C.

position is included in the system,[18,19] but we could not determine which case is more likely in this system. However, when the formation constant of one system is compared with that of another system, only the values obtained at or near the maxima of the charge-transfer absorptions may be suitable. The estimated values of the formation constants at the absorption maxima are shown in Table 2, together with the literature values for the carbon tetrachloride complexes, which were measured near the maxima of the charge-transfer bands.[7] Moreover, from the temperature changes of the formation constants, the formation enthalpy for this system was estimated to be −2.8 kcal/mol; this value was comparable with the previously reported values.[9,10]

The Charge-transfer Bands of the Other Tetrahalide Complexes with HMB. As for the other tetrachloride complexes and tetrabromide complexes with HMB, all the spectra except the carbon tetrahalide complex were measured (Fig. 5—10); the absorption maxima of the newly-appearing absorption bands are summarized in Table 3, together with the reported charge-transfer bands. The shapes and positions of these absorption spectra are characteristic of the charge-transfer bands. In the case of silicon tetrahalides, the approximate values are shown in Table 3, since the new absorptions seemed to overlap with those of the donor.

In the systems of titanium tetrahalides and methylbenzenes (Figs. 8 and 9), two absorption peaks appeared, as had been reported by Dijkgraaf[20] and by Ott and his co-workers.[21] Since a peak at a shorter wavelength changed its position with a variation in the concentrations of the donor and the acceptor, this

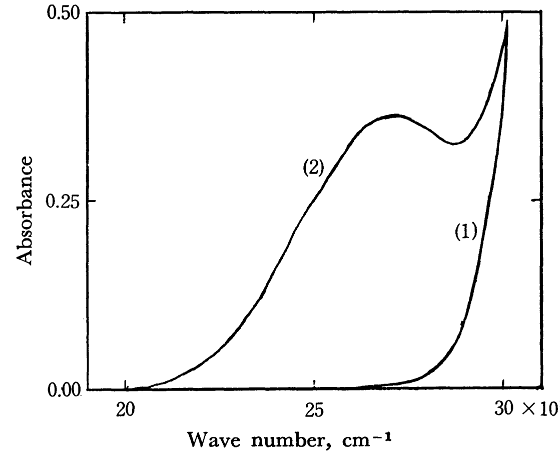

Fig. 5. Absorption spectra of $SnBr_4$-HMB in cyclohexane.
(1) $SnCl_4$(2.5×10^{-2} mol/l) in cyclohexane
(2) $SnCl_4$(2.5×10^{-2} mol/l)+HMB(7.5×10^{-2} mol/l) 10 mm cell

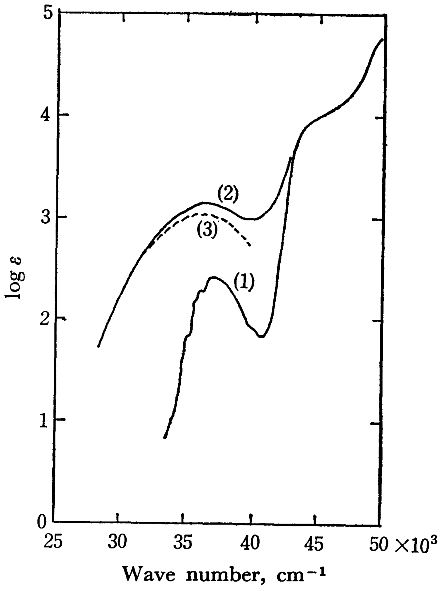

Fig. 6. Absorption spectra of $GeCl_4$-HMB in cyclohexane.
(1) HMB in cyclohexane
(2) HMB in mixed system ($GeCl_4$: cyclohexane=1:1)
(3) (2)—(1)

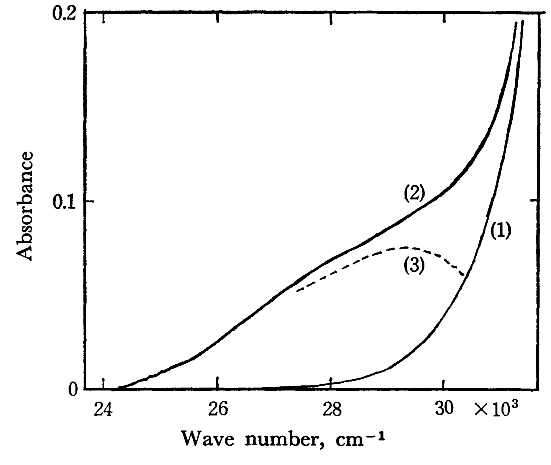

Fig. 7. Absorption spectra of $GeBr_4$-HMB in cyclohexane.
(1) mixed system ($GeBr_4$: cyclohexane=1:1)
(2) HMB (5.0×10^{-2} mol/l) in mixed system of (1)
(3) (2)—(1), 0.1 mm cell

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18) G. Dana Johnson and Ronald E. Bowen, *J. Amer. Chem. Soc.*, **87**, 1655 (1965).

19) M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron, Suppl.*, **no. 7**, 97 (1966).

20) C. Dijkgraaf, *J., Phys. Chem.*, **69**, 660 (1965).

21) J. B. Ott, J. R. Goates, R. J. Jensen, and N. F. Mangelson, *J. Inorg. Nucl. Chem.*, **27**, 2005 (1965).

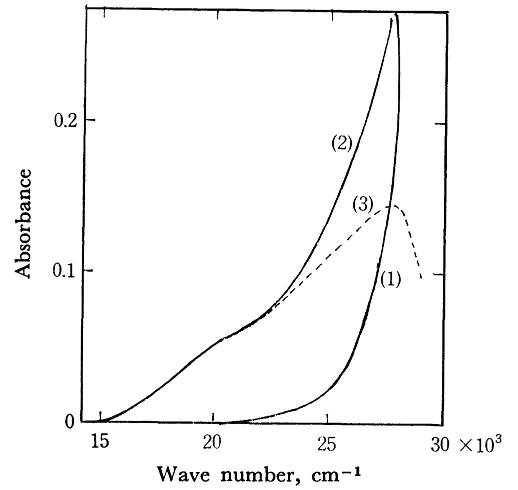

Fig. 8. Absorption spectra of $TiCl_4$-HMB in cyclohexane.
(1) $TiCl_4$ (2.7×10^{-3} mol/l)
(2) $TiCl_4$ (2.7×10^{-3} mol/l)+HMB(5.0×10^{-2} mol/l)
(3) (2)—(1), 2 mm cell

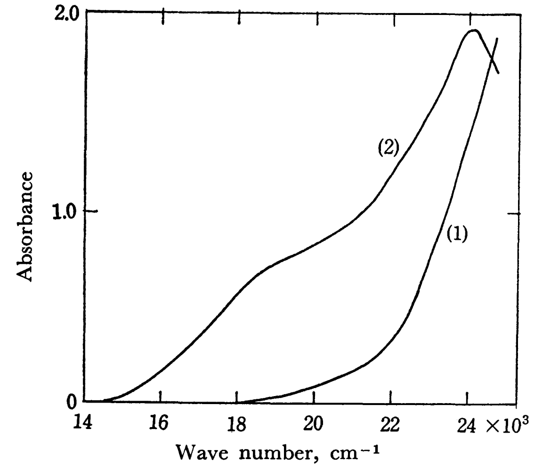

Fig. 9. Absorption spectra of $TiBr_4$-HMB in cyclohexane.
(1) $TiBr_4$ (2.5×10^{-2} mol/l)
(2) $TiBr_4$ (2.5×10^{-2} mol/l)+HMB (7.5×10^{-2} mol/l)
ref. $TiBr_4$ (1), 10 mm cell

peak was deduced to be an apparent absorption peak which emerged from the difference between the absorption of titanium tetrahalide in the complex system and that of titanium tetrahalide itself in cyclohexane. Therefore, only the absorptions at longer wavelengths were deduced to be the charge-transfer bands which correspond to the values reported by Krauss and his co-workers.[11]

On the basis of these measurements, it may be pointed out that the charge-transfer bands of the tetrabromides appear in a longer-wavelength region than those of the corresponding tetrachlorides and the charge-transfer bands of tetrahalides including the transition elements appear in a longer-wavelength region than those of tetrahalides including non-transition elements.

Evaluation of Electron Affinities of the Tetrahalides from the Charge-transfer Bands. The electron affinities

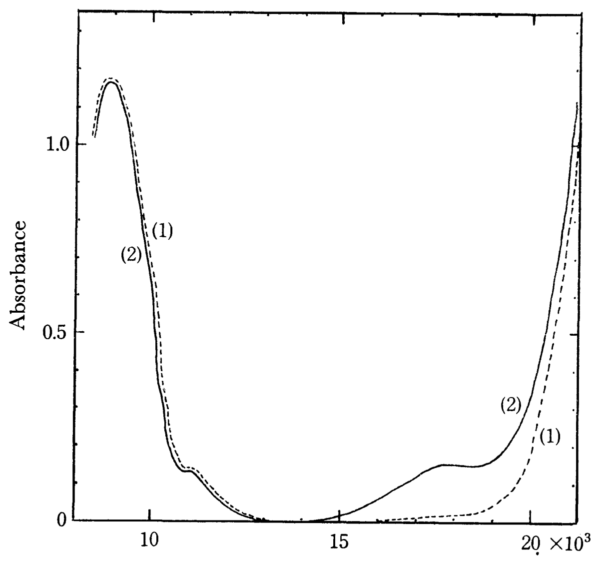

Fig. 10. Absorption spectra of VCl_4-HMB in cyclohexane.
(1) VCl_4 (2.5×10^{-2} mol/l)
(2) VCl_4 (2.5×10^{-2} mol/l)+HMB (5.0×10^{-2} mol/l), 1 mm cell

TABLE 3. SYSTEMATIC DATA FOR THE ELECTRON DONOR-ACCEPTOR COMPLEXES BETWEEN TETRAHALIDES AND AROMATIC HYDROCARBONS

	$h\nu_{CT}$(HMB) in nm	$E_A{}^{CT}$ in eV	ΔH(HMB) in kcal/mol	R(M-X)[c] in Å
CCl_4	242[a]	0.15	−0.54[a]	1.767
$SiCl_4$	230	−0.3	—	2.019
$GeCl_4$	280	0.87	—	2.113
$SnCl_4$	339	1.57	−2.8	2.31
$TiCl_4$	510	2.87	−1.8[b]	2.169
VCl_4	550	3.27	—	2.137
CBr_4	303[a]	1.17	—	1.942
$SiBr_4$	250	0.13	—	2.15
$GeBr_4$	342	1.60	—	2.266
$SnBr_4$	370	1.92	—	2.44
$TiBr_4$	540	2.97	—	2.31

a) Ref. 8.
b) Toward phenanthlene in CCl_4, Ref. 11.
c) R(M-X) means M-X distance (Ref. 30).

of electron acceptors have been evaluated on the basis of the charge-transfer bands by many investigators.[22,23] Using the same donor, neglecting the differences in the coulombic interaction energies between the components in the complexes, and neglecting the contributions of the local excitations to the charge-transfer transition, the following approximate equation can be derived:

$$(E_A)_i - (E_A)_0 = (h\nu_{CT})_0 - (h\nu_{CT})_i \qquad (1)$$

Here, the suffixes *o* and *i* indicate the standard and any given acceptor respectively. Since the "vertical" ionization potential and electron affinity should be involved in the charge-transfer transition according to Mulliken's theory,[4] the values used here and evaluated on the basis of Eq. (1) are not "adiabatic"

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[22] M. Batley and L. E. Lyons, *Nature*, **196**, 573 (1962).
[23] G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).

but "vertical." Here, choosing the iodine molecule and HMB as the standard system, and assuming the electron affinity of the iodine molecule to be 1.8_0 eV[22] and the charge-transfer transition energy of this system to be 3.4_7 eV,[13] the electron affinities of all the tetrachlorides and tetrabromides could be evaluated systematically, as is shown in Table 3.

The electron affinities of titanium tetrachloride and vanadium tetrachloride evaluated by Krauss and his co-workers[11] are smaller by 1 eV than the values evaluated in this study, because they evaluated them assuming the electron affinity of iodine molecule to be 0.8 eV[23] and used that value as the standard in Eq. (1). Therefore, these electron affinities are meaningful only as relative values. As was expected from the transition energies of the charge-transfer bands, the electron affinities of transition-element tetrahalides are larger than those of non-transition element tetrahalides, and the electron affinities of bromides are larger than those of chlorides.

TABLE 4. ELECTRON AFFINITY OF CARBON TETRACHLORIDE AND *p*-BENZOQUINONE ESTIMATED FROM DIFFERENT METHODS

	E_A^{CT} (eV)[a]	E_A^{mag}(eV)[b]	ΔH(HMB) in kcal/mol
CCl_4	0.15	2.1[d]	−0.54[e]
p-Benzoquinone	2.02[c]	1.4[d]	−1.8[f]

a) Electron affinity estimated from charge-transfer band.
b) Electron affinity estimated by magnetron method.
c) Ref. 21, d) Refs. 24 and 25, e) Ref. 8, f) Ref. 13.

Moreover, it was pointed out by Davis and Farmer[8] that the electron affinity of carbon tetrachloride as evaluated from the charge-transfer band was smaller than the corresponding values of *p*-benzoquinone; on the other hand, this order was reversed when the electron affinity was evaluated by the magnetron method (Table 4).[24,25] In the following section we will attempt to explain this anomaly in terms of the molecular orbital.

Structure of the Loose Complexes between Tetrahalides and Methylbenzenes. In general, tetrahalides form 1 : 2 stable complexes with *n*-donors, the structures being as shown in Fig. 11-A,[26] while, with aromatic π-donors, tetrahalides form loose complexes, whose structures have not yet been made clear except a carbon tetrabromide complex with *p*-xylene (Fig. 11-B).[5] If tetrahalides form A-type complexes, some spectral changes might occur accompanying a conformational change from the T_d to the D_{4h} of tetrahalides. These changes in the electronic spectra were indicated by Bridgland and McGregor in their study of vanadium tetrachloride complexes with *N*-oxides;[27] that is, in a ligand field with a D_{4h} symmetry of vanadium tetrachloride in the A-type complex, the $2T_{2g}-2E_g$ intramolecular charge transition of the T_d symmetry split into two transitions. However, in the case of the vanadium tetrachloride-HMB complex, the spectral change was not observed, as is shown in Fig. 10; this indicates that vanadium tetrachloride retains the T_d symmetry even in the complex with methylbenzenes. As for the tetrachlorides, since the order of the atomic distance between the central atom and the halogen atom of tetrachlorides is $CCl_4<SiCl_4<GeCl_4<TiCl_4<VCl_4<SnCl_4$ (Table 3), it may be presumed that tetrachlorides, whose distance are smaller than vanadium tetrachloride, will tend to form a structure similar to that of the vanadium tetrachloride complex with methylbenzenes, that is, a B-type structure (Fig. 11).

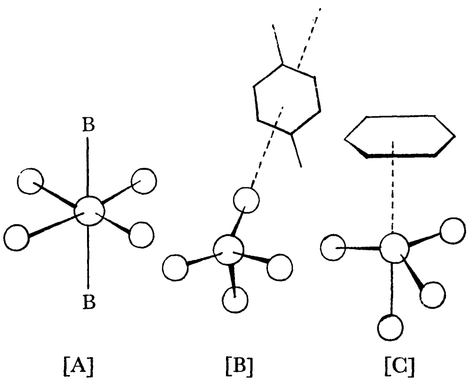

Fig. 11. Structures of tetrahalide complexes.
[A] a stable complex toward *n*-donors
[B] a loose complex between CBr_4 and *p*-xylene proposed by Striter and Templeton[5]
[C] a possible structure between $SnCl_4$ and methylbenzene

The only remaining problem here is, then, the analysis for the tin tetrachloride complex, for which Tsubomura[9] assumed that the tin atom may be coordinated directly to either one or two benzene rings. On the other hand, it has been reported that, although the stable complexes show a 1 : 2 composition, the loose complexes show a 1 : 1 composition. Even in the case of the tin tetrachloride complexes with methylbenzenes, the formation of 1 : 1 complexes was confirmed (Fig. 3); this suggests that the tetrachlorides composed of a relatively large-sized central atom such as tin tetrachloride also form B-type complexes. This suggestion was supported by the order of the formation constants, which increase in the same order as those of the carbon tetrachloride complexes (Table 2), whose structures were presumed to be B-type.[5]

Since the unstability accompanying the conformational change from the T_d to the D_{4h} or from the T_d to the "Pyramidal" of tetrachloride is too large to form a complex between the central atom and the benzene ring, the A- and C-type structures may be excluded. The same discussions may be extended to the tetrabromide complexes.

Theoretical Considerations and Discussions

It has been presumed by some workers that the carbon tetrahalides accept the π-electron of the benzene ring using the empty *d* atomic orbitals of halogen

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[24] A. F. Gaines, J. Kay, and F. M. Page, *Trans. Faraday Soc.*, **62**, 874 (1966).
[25] A. L. Farragher and F. M. Page, *ibid.*, **62**, 3072 (1966).
[26] S. Ichiba, M. Mishima, and H. Negita, This Bulletin, **42**, 1486 (1969).
[27] B. E. Bridgland and W. R. McGregor, *J. Inorg. Nucl. Chem.*, **31**, 43 (1969).

Table 5. Valence state ionization potentials of group IV elements and halogen atoms in eV

	C	Si	Ge	Sn	Ti	V	Cl	Br
s	20.78[a]	17.31[a]	17.90[b]	17.75[b]	9.86[c]	9.99[c]	25.27[d]	23.81[d]
p	11.31[a]	9.19[a]	7.40[b]	8.19[b]	5.62[c]	6.89[c]	13.69[d]	11.85[d]
d	—	—	—	—	—	—	1.61[e]	1.74[e]

a) J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962).
b) C. E. Moore, "Atomic Energy Levels," *N. B. S. Circular*, (1948).
c) H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, **44**, 10 (1966).
d) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).
e) W. Kauzman, "Quantum Chemistry," Academic Press Inc., New York (1957), p. 326.

atoms (3*d* for chlorides and 4*d* for bromides).[28] To ascertain the truth of this assumption for all tetrahalide complexes, molecular orbital calculations were carried out by an extended Hückel method for tetrachlorides and tetrabromides.[29] In these calculations, in addition to *s* and *p* atomic orbitals, empty *d* atomic orbitals of halogen atoms were considered. All the valence state ionization potentials used in this study are summarized in Table 5, together with the literatures.

The distances between the central atoms and the halogen atoms are shown in Table 3.[30] The overlap integrals were calculated using the Slater-type atomic orbitals by means of the method of Roothaan,[31] whose program was reported by Offenhartz.[32,33]

Table 6. Some results of extended Hückel calculations of some T_d symmetry tetrachlorides

	$E_{\text{H.O.}}$ (eV)[a]	I_p (obsd)[b]	$E_{\text{L.V.}}$ (eV)[c]	E_A^{CT} (eV)	S_{AD}[d]
CCl_4	−13.29	11.47	−10.7	0.15	0.017
$SiCl_4$	−11.51	11.6	−8.8	−0.3	0.022
$GeCl_4$	−13.58	11.0	−6.7	0.87	0.011
$SnCl_4$	−13.64	10.5	−7.7	1.57	0.011
$TiCl_4$	−13.16	11.7	−8.2	2.67	0.030

a) Energy level of the highest occupied orbital.
b) From Ref. 34.
c) Energy level of the lowest vacant orbital.
d) Overlap integral in complex.

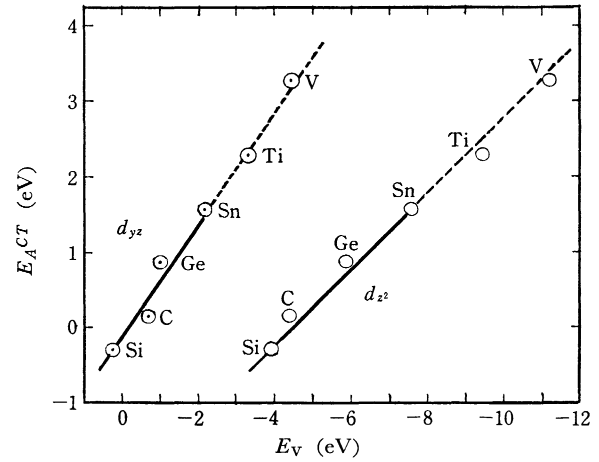

Fig. 12. Plots of E_A^{CT} against energies of vacant molecular orbitals of tetrachlorides, (E_V), which are used to accept aromatic π-electrons.
d_{z^2}: molecular orbitals involving $3d_{z^2}$ of chlorine atom
d_{yz}: molecular orbitals involving $3d_{yz}$ of chlorine atom

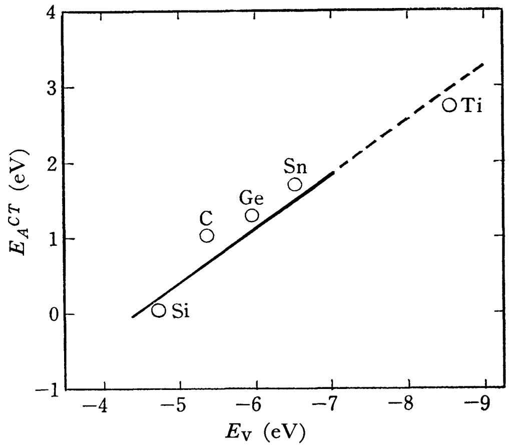

Fig. 13. Plots of E_A^{CT} against energies of vacant molecular orbitals of tetrabromides(E_V), which are used to accept aromatic π-electrons.
d_{z^2}: molecular orbitals involving $4d_{z^2}$ of bromine atom

Some of the results of the calculations are shown in Table 6. The calculated ionization potentials of tetrachlorides may be compared with the measured values;[34] the agreement is as good as is generally achieved for this quantity. On the other hand, the electron affinity calculated by the extended Hückel method could not be compared directly with the measured values, but it may be possible to compare them relatively. However, no correlation, not even a relative one, could be found between the lowest vacant orbital energies and the electron affinities evaluated from the charge-transfer bands. As for the non-transition element tetrahalides, when the vacant molecular orbitals (E_V) involving the *d* atomic orbital of the halogen atom, which appeared at a higher energy level than those of the lowest vacant orbital, are plotted against

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TABLE 7. MOLECULAR ORBITALS, INVOLVING $3d_{z^2}$ OF Cl, WHICH FIT A LINEAR RELATIONSHIP AGAINST E_A^{CT} IN FIG. 13

	M[a)]	X_1[a)]	S_{AD}[b)]
CCl_4	$-0.28\,s + \cdots +$	$0.09\,s - 0.02\,p_z + 0.46\,d_{z^2} + \cdots$	0.06
$SiCl_4$	$-0.20\,s + \cdots +$	$0.08\,s - 0.20\,p_z + 0.41\,d_{z^2} + \cdots$	0.05
$GeCl_4$	$-0.54\,s + \cdots +$	$0.13\,s - 0.28\,p_z + 0.30\,d_{z^2} + \cdots$	0.04
$SnCl_4$	$-0.71\,s + \cdots +$	$0.20\,s - 0.38\,p_z + 0.17\,d_{z^2} + \cdots$	0.04
$TiCl_4$	$-0.86\,s + \cdots +$	$0.20\,s - 0.10\,p_z + \cdots\cdots \quad \cdots$	0.03
VCl_4	$-0.49\,s + 0.86\,d_{z^2}$	$\cdots\cdots + 0.10\,p_z + \cdots\cdots \quad \cdots$	0.03

a) M and X mean the central atom and halogen atom, respectively.
b) Overlap integral in complexes (*AD*).

TABLE 8. MOLECULAR ORBITALS, $3d_{yz}$ OF Cl, WHICH FIT A LINEAR RELATIONSHIP AGAINST E_A^{CT} IN FIG. 13

	M	X_1-X_2
CCl_4	$0.22(p_x+p_y)+\cdots$	$+(0.74(d_{yz}(X_1)-d_{yz}(X_2)+\cdots)$
$SiCl_4$	$0.36(p_x+p_y)+\cdots$	$+(0.78(d_{yz}(X_1)-d_{yz}(X_2)+\cdots)$
$GeCl_4$	$0.25(p_x+p_y)+\cdots$	$+(0.73(d_{yz}(X_1)-d_{yz}(X_2)+\cdots)$
$SnCl_4$	$0.13(p_x+p_y)+\cdots$	$+(0.99(d_{yz}(X_1)-d_{yz}(X_2)+\cdots)$
$TiCl_4$	$0.58\,p_x+\cdots\cdots\cdots$	$+(0.22(d_{yz}(X_1)-d_{yz}(X_2)+\cdots)$
VCl_4	$0.61\,p_x+\cdots\cdots\cdots$	$+(0.20(d_{yz}(X_1)-d_{yz}(X_2)+\cdots)$

TABLE 9. MOLECULAR ORBITALS, INVOLVING $4d_{z^2}$ OF Br, WHICH FIT A LINEAR RELATIONSHIP AGAINST E_A^{CT} IN FIG. 14

	M	Br_1	$+\cdots$
CBr_4	$-0.17\,s + \cdots\cdots$	$(-0.26\,p_z+0.36\,d_{z^2}+\cdots)$	$+\cdots$
$SiBr_4$	$-0.14\,s + \cdots\cdots$	$(-0.19\,p_z+0.39\,d_{z^2}+\cdots)$	$+\cdots$
$GeBr_4$	$-0.56\,p_x + \cdots\cdots$	$(-0.05\,p_z+0.16\,d_{z^2}+\cdots)$	$+\cdots$
$SnBr_4$	$-0.58\,p_x + \cdots\cdots$	$(-0.06\,p_z+0.11\,d_{z^2}+\cdots)$	$+\cdots$
$TiBr_4$	$-0.82\,d_{xy} + \cdots\cdots$	$(-0.15\,s\ +0.16\,p_z\ +\cdots)$	$+\cdots$

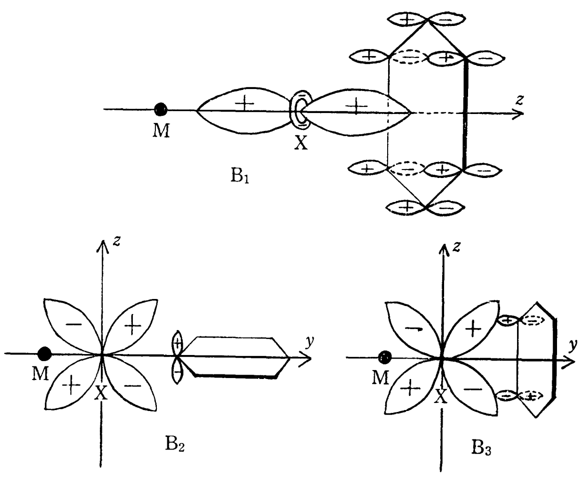

Fig. 14. Assumed structures of loose complexes between tetrahalides and methylbenzenes.
[B_1]: d_{z^2} orbital on halogen atom,
[B_2] and [B_3]: d_{yz} orbital on halogen atom.

the electron affinities evaluated from the charge-transfer bands, the molecular orbitals involving the $3d_{z^2}$ and $3d_{yz}$ of chlorides or the $4d_{z^2}$ of bromides all satisfy a linear relationship, as is shown in Figs. 12 and 13 respectively. The corresponding vacant molecular orbitals of the transition-element tetrahalides, which could be found by extrapolating the plots for the non-transition-element halides, do not always involve empty *d* atomic orbitals on the halogen atoms. These molecular orbitals are summarized in Tables 7 and 8 for the chlorides and in Table 9 for the bromides. From the geometry of the empty *d* atomic orbitals, some structures of the complexes with benzene rings could be presumed, as is illustrated in Fig. 14.

Since it has been accepted that the charge-transfer force is determined mainly by the electron affinity and the overlap integral (S_{AD}) between the donor and the acceptor orbital, these overlap integrals were evaluated approximately, assuming an a_{2u} molecular orbital of benzene as the donor orbital and using the coordination system shown in Fig. 14-B_1. These results are shown in Tables 6 and 7. Since the overlap integrals for the lowest vacant orbitals are very small compared with that of the iodine-benzene complex, which was evaluated by Aono to be 0.11,[35)] it is not considered that these molecular orbitals of tetrachlorides accept the π-electrons of the donor. However, the overlap integrals of the molecular orbitals in Table 7 are suitable values for explaining the formations of the weak complexes. Since the electron affinities of titanium tetrachloride and vanadium tetrachloride are larger than these of tin tetrachloride and carbon tetrachloride, and since the order of the overlap integrals are reversed, the compensation between the electron affinity and the overlap integral might induce the lack of variation in the formation enthalpies in the complexes.

On the basis of these results, we could explain the anomaly in the meaning of the electron affinity shown in Table 4. That is, although carbon tetrachloride accepts the free electron by using the lowest vacant orbital, and although the result of this process might correspond to the value measured by the magnetron method, the π-electrons of the benzene ring are accepted by the molecular orbital involving the empty *d* orbital of the chlorine atom in carbon tetrachloride; this process corresponds to the charge-transfer transition. On the other hand, an organic π-acceptor such as *p*-benzoquinone accepts both the free electron and the π-electrons of the donor by using the lowest vacant orbital, for this orbital expands outside of the acceptor molecule.

As has been discussed above, the results on the struc-

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tures of the complexes and on the molecular orbitals of tetrahalides permit the explanation of many phenomena, such as the order of the electron affinities and formation enthalpies; therefore, it may safely be concluded that the tetrahalides interact with the benzene ring using the vacant molecular orbitals involving empty *d* atomic orbitals on halogen atoms of tetrahalides. Moreover, this conclusion suggests that the weak other charge-transfer bands from the donor orbital to the lowest vacant orbital of tetrahalide may appear in a wavelength region longer than those observed in this study. However, more detailed studies of the shapes of the charge-transfer bands, especially of their tails, are needed.

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