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CALCULATION OF THE RELATIVE LEWIS ACIDITIES OF THE GROUP IV TETRAHALIDES

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The order of the formation energies of the adducts between one Lewis base and the group IV tetrahalides calculated by the extended Hückel method agreed with the observed relative Lewis acidities. The Lewis acidities of the group IV tetrahalides are governed by both the steric factor and the electronic factor.

In our preceding paper, the charge-transfer complexes between the group IV tetrahalides and methylbenzenes were studied by the electronic absorption spectra and an extended Hückel molecular orbital calculations, and it was concluded that the π-electron acceptor abilities of the group IV tetrahalides are related to the vacant orbitals on the halogen atom rather than those on the central atom in the tetrahalides.[1,2] On the other hand, it is well known that toward the n-donors(Lewis bases) the tetrahalides form the adducts and behave as Lewis acids.[3] The relative Lewis acidities of many Lewis acids have been discussed in relation to the catalytic activity. For the acidities of metal ions, Misono, Ochiai, Saito and Yoneda have proposed a theoretical representation in terms of the electronegativity and "softness".[4] For the group III trihalides, some theoretical calculations of the Lewis acidities in relation to the reorganization energies have been reported.[5] However, any theoretical elucidation of the relative Lewis acidities of the tetrahalides has not been made. In this letter, we performed the extended Hückel molecular orbital calculations to elucidate the factor determining the relative Lewis acidities of the tetrahalides.

In general, with n-donors the tetrahalides form 1:2 adducts which have the structures as shown in equation (2).[6] Two factors may be expected in determining the relative Lewis acidities of the tetrahalides. One of them is the steric

factor which depends on a geometrical change from the tetrahedral $MX_4(T_d)$ to the square planar $MX_4(D_{4h})$. The other is the electronic factor which depends on the bonding energy between the lone pair electrons of the Lewis base and the vacant orbital on the central atom of the square planer $MX_4(D_{4h})$. In order to discriminate between the steric factor and the electronic factor, the formation energy(ΔH_{AB}) of the adduct was calculated by the following two steps;

$$MX_4\ (T_d) \xrightarrow{\Delta H_I} MX_4\ (D_{4h}) \qquad (1)$$

$$MX_4\ (D_{4h}) + 2B \xrightarrow{\Delta H_{II}} \begin{matrix} & B & \\ X & M & X \\ X & & X \\ & B & \end{matrix} \qquad (2)$$

ΔH_I is steric factor and can be evaluated by the difference of the total energy of the tetrahedral MX_4 and that of the square planar MX_4, where each of them was calculated by the extended Hückel method. Total energies of $MX_4(T_d)$ were calculated by using the valence state ionization potentials and distances between the central atom and halogen atoms described in our preceding paper.[2] For the calculations of the total energies of $MX_4(D_{4h})$, the distances between the central atom and halogen atoms were assumed to be same as $MX_4(T_d)$. In these calculations, the d orbitals of the central atom in both $MX_4(T_d)$ and $MX_4(D_{4h})$ were included. The valence state ionization potentials of these orbitals were estimated by the method of Bach, Viste and Gray.[7] The calculated ΔH_I values were summarized in Table 1 for the tetrachlorides and tetrabromides. In the calculated ΔH_I values, some negative values appear in Table 1, since the suitable repulsion energies between halogen atoms were not included in the calculations of the total energies. However, these calculated ΔH_I values may be sufficient for elucidating the relative Lewis acidities.

In the calculation of ΔH_{II}(electronic factor), as a Lewis base(B) the lone pair electron of oxygen atom(2p) whose valence state ionization potential is -11.31 eV, was chosen. It was assumed that these lone pair electrons coordinated to the vacant d_{z^2} and p_z orbitals on the central atom of $MX_4(D_{4h})$ perpendicular to the plane including the four halogen atoms. The bond length between M and B was assumed to 2.0 Å by reference to the bond length of Sb - O bond in the adduct of $SbF_5 \cdot OSO$.[8] The calculated ΔH_{II} values were summarized

Table 1. The calculated values of ΔH_I, ΔH_{II} and ΔH_{AB} and the observed relative Lewis acidities for tetrahalides.

	$SiCl_4$	$GeCl_4$	$SnCl_4$	$TiCl_4$	$SiBr_4$	$GeBr_4$	$SnBr_4$	$TiBr_4$
ΔH_I(eV)	0.36	-0.91	-0/76	0.59	2.45	0.34	-0.15	-1.33
ΔH_{II}(eV)	-0.94	-0.42	-0.70	-2.30	-0.88	-0.18	-0.34	-1.88
ΔH_{AB}(eV)	-0.58	-1.33	-1.46	-1.71	1.57	0.16	-0.49	-3.19
NMR shift[a]	0	0	51	70	—	—	40	—
IR shift[b]	28	24	60	—	—	—	—	—

a) Toward n-buthyl ether(BCl_3 = 100), reference 9.

b) Toward ethyl acetate(BCl_3 = 100), reference 5.

in Table 1. The formation energy(ΔH_{AB}) of the adduct is given as follows from equations (1) and (2);

$$\Delta H_{AB} = \Delta H_I + \Delta H_{II} \qquad (3)$$

The calculated formation energies were shown in Table 1. These calculated ΔH_{AB} values give slightly larger values than the observed formation energies, since the reported formation energies of the adducts generally range in the value from 10 kcal/mole to 20 kcal/mole.[3,5]

Deters, McCusker and Pilger reported a scale of relative Lewis acidities for a number of inorganic halides bases on the ratios of changes in the NMR chemical shifts of the α-protons of ethers on adduct formation(a value of 100 is assigned to BCl_3).[9] These reported values are shown in a column in Table 1. Brown, Drago and Bolles reported a linear correlation between ethyl acetate carbonyl frequency shift in the infrared spectrum upon complexation and the enthalpy of adduct formation for a series of Lewis acids.[5] From their observed carbonyl frequency shifts, the relative Lewis acidities of the tetrachlorides(a value of 100 is assigned to BCl_3) were evaluated as shown in Table 1.

The calculated ΔH_I values(steric factor) increase in the order, $GeCl_4$ <

$SnCl_4$ < $SiCl_4$ < $TiCl_4$, from which the observed relative Lewis acidities could not be explained. Only by the calculated ΔH_{II} values(electronic factor) the observed relative Lewis acidities also could not be explained. The calculated ΔH_{AB} increased in the order, $SiCl_4$ < $GeCl_4$ < $SnCl_4$ < $TiCl_4$, which may explain the order of the observed relative Lewis acidities excepting that the $SiCl_4$ is stronger than $GeCl_4$. The observed Lewis acidity of $SnCl_4$ is stronger than that of $SnBr_4$, which coincides with the order of the calculated ΔH_{AB} values. The discussions for a series of the tetrabromides could not be made, since the relative Lewis acidities for a series of the tetrabromides have not been reported in the literature.

Deters, McCusker and Pilger concluded from their NMR study that for the group III trichlorides the sterically open planar structure makes the empty p orbital readily accessible to the Lewis base, and that the electronic factors are dominant in determining relative Lewis acidities, while the tetrahedral structure of the group IV tetrahalides results in dominance of the steric factors in relative Lewis acidities.[9] Indeed, the calculated ΔH_I values (steric factor) play important roles in determining the order of the formation energies (ΔH_{AB}) of the adducts between tetrahalides and Lewis base. However, the calculated formation energies in this study indicate that the observed relative Lewis acidities of the group IV tetrahalides could be determined not only by the steric factor (ΔH_I), but also the electronic factor (ΔH_{II}).

A more detail study is in progress.

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