XPS Study on the Charge Distribution in Chromium(0) Complexes

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Binding energies of core electrons in $Cr(C_6H_6)_2$, $Cr(C_6H_6)(CO)_3$, and $Cr(CO)_6$ were measured by means of X-ray photoelectron spectroscopic method in solid phase. By comparison with their UPS spectra observed in gasous phase, binding energies referred to vacuum level can be obtained. On the basis of this result, charge distribution in these complexes are estimated. The intramolecular relaxation energy of $Cr(C_6H_6)_2$ is also discussed.

The study of X-ray photoelectron spectroscopic, (XPS), spectra of solid material reveals that the observed binding energy of a core electron is a function of not only the charge density on an atom but also the matrix effects such as Madelung energy, polarization energy, and work function.[1] Therefore, the evalutaion of the matrix effects is required so as to elucidate the charge density on atom from the observed binding energy by XPS method.

In this paper, results of XPS measurements of bis-(benzene) chromiun, chromium benzene tricarbonyl, and chromium hexacarbonyl in solid phase are reported. The matrix effects on observed binding energy were calibrated by comparing the observed valence bands of these compounds to their UPS spectra in gasous phase. This correction made it possible to estimate the effective charge on each atom except for hydrogen atom. Finally, these resullts were examined by comparison of the predicted chemical shift in binding energy of Cr 3p electrons with that of the observed energy. Estimation of the difference of relaxation energies of C ls electrons between benzene and bis-benzene chromium was also attempted.

Exprimental

Bisbenzene chromium[2] and chromium benzene tricarbonyl[3] were prepared, and identified by the elemental analysis and mass spectrometric analysis. Those were stored in sealed samples. Chromium hexacarbonyl was of commercial source (Sterm Chemicals Inc.) and used without any further purification. Thin film of samples was prepared by condensing the sublimated compounds under a vacuum of 10^{-2} Pa on the sample-holder. The surface of the sample-holder was covered with vacuum deposited gold and kept at a temperature of 200 K during XPS measurement.

All of the XPS spectra were recorded by means of an AEI ES 200 type photoelectron spectrometer with aluminium target as an X-ray source. During measurements of XPS spectra the spectrometer was kept at the pressure lower than 10^{-5} Pa. An Au $4f_{7/2}$ peak (83.8 eV), which came from the surface of the sample-holder, was measured simultaneously with XPS spectra of sample and used as a reference of bending energy.

Results and Discussion

The compounds investigated have sufficient vapor pressure to measure XPS spectra in gaseous phase at the moderately elevated temperature. However, the partial decomposition of the sample by heat and/or X-ray irradiation and deposition of thin layer of metallic chromium of non-volatile compounds on aluminum X-ray window was observed. This not only gave the unreliable XPS data but also caused serious damage to XPS spectrometer preventing a prolonged XPS measurement. The XPS measurement in solid phase at low temperature did not cause any trouble and the surface of samples was continuously renewed by the slight evaporation of samples.

The valence region of XPS spectra of these compounds are shown in Fig. 1. The energy level diagrams thus obtained are illustrated in Fig. 2, together with results of UPS spectra in gaseous phase.[4,5] In UPS spectra, chromium benzenene tricarbonyl and hexacarbonyl give the well difined first band separating from the succeeding bands, but the first and second bands in UPS spectrum of bis-benzene chromium close to each other and are observed as a single peak in its XPS spectrum.

When compounds form molecular crystals and the interaction beween molecules in crystal is very weak, their MO's would not encounter with serious perturbation and ionization potentials or binding energies in both solid and gaseous phase would be coincident with each other. Then, the difference of binding energies between gaseous and solid phase should be brought solely by the matrix effects. Of these effects, Madelung energy must be so small that it might be disregarded. Seki *et al.*[6] show that the polarization energy in molecular crystals of some aromatic compounds lies around 1.1 eV within the range of 0.2 eV. Very similar results were obtained by Lyons and Mackie.[7] Therefore the main part of the observed difference of binding energies between gaseous and solid phase is considered to come from the work function.

When the weighted mean values of binding energies of the very closed orbitals observed by He(II) or He(I) UPS were compared with the binding energies of the corresponding bands in XPS spectra, the shifts are paralled and the difference falled within ± 0.2 eV. In Fig. 2, the calibrated binding energies of XPS data were given by broken lines. In the case of bis-benzene chromium, the binding energy of the first band in XPS spectra was set equal to the weighted average of those of the first and second bands in He(II) UPS spectrum. The calibrated binding energies agree well with the binding energies of the corresponding bands in UPS spectra. According to Guest *et al.*[4] the first band of $Cr(C_6H_6)_2$ should be assigned to t_{2g} orbital mainly localized on a chromium atom and the bands below the third bands come from MO's on ligands. A similar assignments were made for $Cr(C_6H_6)(CO)_3$[4] and $Cr(CO)_6$.[5]

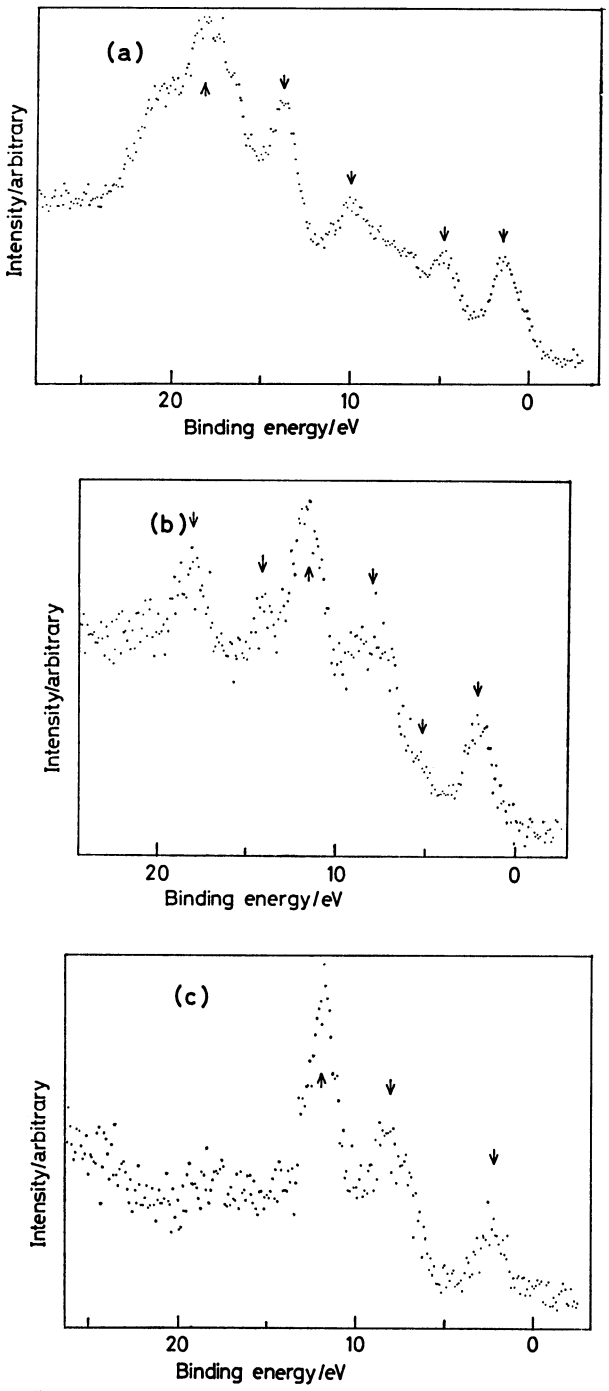


Fig. 1. The valence region of XPS spectra of a) Cr $(C_6H_6)_2$, b) $Cr(C_6H_6)(CO)_3$, and c) $Cr(CO)_6$.

The fact that the binding energies localized on both a central metal atom and ligands give the same shift shows that the magnitude of the matrix effects is constant over a molecule, and that the observed binding energies are little affected by Madelung and polarization energies which may depend upon the lattice points.

The fact must be also true in the case of core electrons, that is, we could obtain the binding energies of core electrons referred to vacuum level as given in Table 1.

The Estimation of the Charge Distribution from XPS Data. It has been shown that the binding energy, BE, of a carbon 1s electron can be expressed as follows in terms

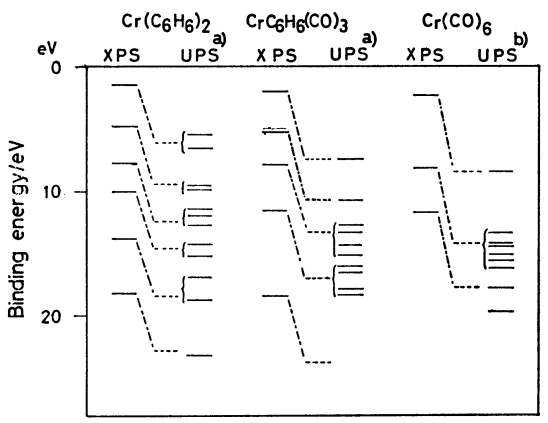


Fig. 2. The comparison of the energy level diagrams observed by XPS method and UPS method. Broken lines denote the corrected binding energies. a) : Ref. 4. b) : Ref. 5.

Table 1. Binding energies of core electrons refered to the vacuum level (eV)

Compound	C 1s	O 1s	Cr 3p
$Cr(CO)_6$	292.9	539.2	50.8
$Cr(C_6H_6)(CO)_3$	292.0	538.4	49.8
	290.1[a]		
$Cr(C_6H_6)_2$	289.7	—	47.9

a) the C 1s binding energy due to carbon atom in benzene.

of the charge density q_C on the carbon atom of the interest:[8]

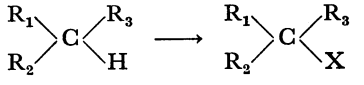
$$BE = k_C q_C + V + E_R + l_C \quad (1)$$

where V denotes the electrostatic potential at the nuclear caused by surrounding atoms and E_R gives relaxation energy based on the sudden approximation. k_C and l_C are constant to be decided from experiments. Snyder[9] and Gelius[10] suggestes that E_R may also be expressed in terms of q_C. For the group of carefully selected compounds, such a linear relation can be found in Fig. 3 where calculated relaxation energies[11] were plotted against the charge density on the carbon atom obtained by CNDO/2 method. This is expected on the basis of the study of relaxation energies done by H. Siegbahn *et al.*[12] According to their notation, the following equation may be settled for a certain authorized group

$$k^T \cdot \Delta q_A(j) + \Delta V_A(j) + l^T - l = \text{const.}$$

where the constants of k and l for the transition state are denoted by k^T and l^T. In other words, it can be said that the flow of charge onto the ionized atom and potential energy change at the site of the ionized atom as a result of charge reorganization in the rest of the molecule are similar within a certain group.

When the following substitution reaction proceeds



the carge density on the carbon atom may increase by amounts of Δq. It is shown that the chemical shift in

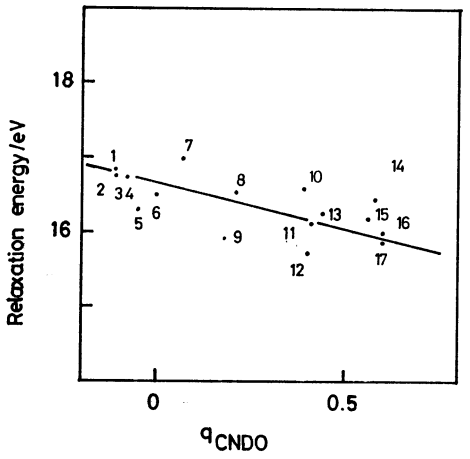


Fig. 3. The correlation between the relaxation energy and the charge density on carbon atom of the compounds : 1) $C^*H_2CF_2$; 2) $C^*H_3CF_3$; 3) $C^*H_3CHF_2$; 4) $C^*H_3CHF_2$; 5) $CH_3C^*H_2F$; 6) C_2H_6; 7) $C^*HF=CF_2$; 8) $CH_2=C^*HF$; 9) CH_3F; 10) $CHF=C^*F_2$; 11) $CH_3C^*HF_2$; 12) CH_2F_2; 13) $CH_2=C^*F_2$; 14) $C^*F_3CF_2CF_3$; 15) CF_3CF_3; 16) $C^*F_3CH_2NH_2$; 17) $CH_3C^*F_3$: [after Ref. 11].

C 1s bind eningergies could be given by the sum of group shifts.[13] This reflects that the σ-bond is strongly localized, and leads to the conclusion that most of Δq come from the substituent X, and that the charge distribution on both the substituent and residual groups remains almost constant. Most of the second row elements attach to a carbon atom with the bond length ranging from 1.1 Å to 1.5 Å. Then, in the case where molecules have a similar skeletal structure and do not have polar bonds, it might be expected that the change in V of Eq. 1 can be given as a linear function of the charge density on the carbon atom concerned. Under such circumstances, Eq. 1 can be rewritten as follows:

$$BE = k' \cdot q_C + l' \qquad (2)$$

as has been given by K. Siehgbahn *et al.* in the XPS study of free molecules.[14] For the present purposes, we selected the observed C 1s binding energies for the sp^2 carbon taken from the reliable data and reproduced in the plots of *BE vs.* q_C (Fig. 4.), (the same plot for O 1s binding energies was also given in Fig. 5).

Equation 2 may be used to get the charge distribution in the present compounds from binding energies given in Table 1. Some objection may exist to the utility of Eq. 2 for those compounds owing to 1) the difference of the skeletal structure of bisbenzene chromium from that of the compounds used to induce Eq. 2, and 2) smaller relaxation energy for a C 1s electron in free CO. Bis-benzene chromium forms a π-complex with the separation of 2.19 Å between carbon and chromium atoms. However, in the case of bis-benzene chromium, positive potential at ionized carbon caused by a chromium atom is reduced by negative potential caused by other eleven carbon atoms. This makes the situation simply as the substitution by the twelfth part of chromium with a bond length of 0.8 Å.

The binding energy of a C 1s electron in free CO lies significantly far from the relation given by Eq. 2 as clearly seen from Fig. 4. Davis and Shirley[11] have shown that the relaxation energy of a C 1s electron in CO is the smallest of the compounds of all they studied. According to their results, the relaxation energy of a C 1s electron in CO is smaller than the average of relaxation energies calculated for C 1s electrons in various compounds by amounts of 4.8 eV.

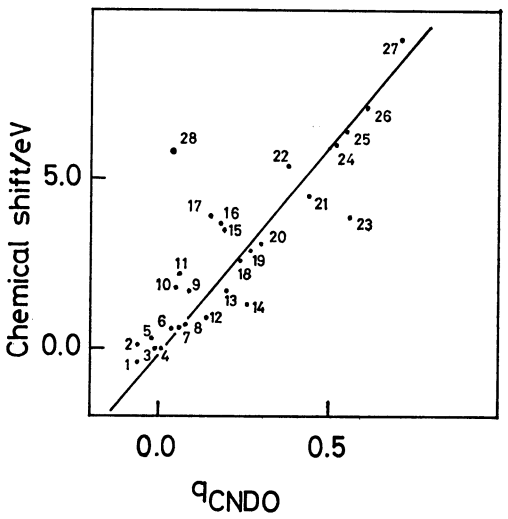


Fig. 4. The correlation between chage density on carbon atom calculated by CNDO/2 method and chemical shift in C 1s binding energy relative to that of benzene: 1)pyrrole, (β-carbon); 2) furan, (β-carbon); 3) thiophene, (β-carbon) ; 5) thiophene, (α-carbon) ; 14) furan, (α-carbon); 23) pyrrole, (α-carbon): [after Ref. 18]; 4) benzene; 6) toluene, (α-carbon); 8) $C_6H_5C^*N$; 9) chlorobenzene, (α-carbon); 12) aniline, (α-carbon); 13) phenol, (α-carbon); 18) fluorobenzene, (α-carbon): [after Ref. 17]; 15) C_6O_6; 16) $CF_3C^*OCH_3$; 17) C_6F_6; 19) H_2C^*O; 20) $(CH_3)_2C^*O$; 21) CH_3C^*OOH; 23) $(NH_2)_2C^*O$; 24) $C_2H_5OC^*OCl$; 25) $(CH_3O)_2C^*O$; 26) CO_2; 27) F_2CO: [after Ref. 13]; 28) CO: [after Ref. 11].

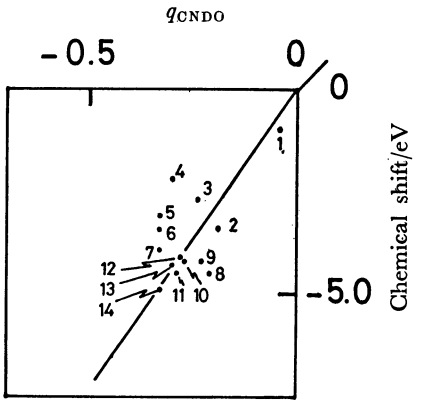


Fig. 5. The correlation between charge density on oxygen atom calculated by CNDO/2 method and chemical shift in O 1s binding energy relative to that of O_2 : 1) CO; 2) NNO; 4) CO_2 ; 5) CH_3CO^*OH 6) H_2O; 10) CH_3OH; 11) C_2H_5OH; 12) $(CH_3)_2CO$; 14) CH_3COO^*H: [after Ref. 19]; 3) $HCOO^*H$; 7) CH_3NO_2; 8) C_2H_4O; 9) $(C_2H_5)_2O$; 13) HCO^*OH : [after Ref. 11].

On the other hand, Baerends and Ros[15] showed in the study of metal carbonyls by DVM Xα-SCF MO calculation that the relaxation energy for a C 1s electron in $Cr(CO)_6$ is larger than that in free CO by amounts of 4.0 eV. Therefore, it might be said that the relaxation energy for C 1s electron in $Cr(CO)_6$ is comparable to that found in molecules used to decide Eq. 2.

The Estimation of Chemical Shifts in Cr 3p Binding Energies. The charge distribution in $Cr(CO)_6$, $Cr(C_6H_6)(CO)_3$, and $Cr(C_6H_6)_2$ are given in Table 2. It is presumed that the charge density on a hydrogen atom in benzene remains constant before and after the formation of a complex because a benzene molecule attached to a chromium atom through its π-orbital. Standing on this assumption we determined the charge density on a chromium atom. Assuming that the relaxation energy of 3p electron in these compounds is constant, chemical shifts in Cr 3p binding energy relative to bis-benzene chromium may be obtained to substitute the above obtained charge densities into the equation similar to the Eq. 1. The *k*-value for Cr 3p electron is decided to be 22 eV/unit charge calculating the Coulomb integral between Cr 3p and 3d electrons with Slater orbitals. The calculated chemical shifts are given in Table 3. It should be noted that the binding energy of Cr 3p electron in $Cr(CO)_6$ is larger than that in $Cr(C_6H_6)(CO)_3$, whereas the charge density on chromium atom in $Cr(CO)_6$ is smaller than in $Cr(C_6H_6)(CO)_3$, that is, the later is more positive than the former. The observed chemical shifts agreed well with the calculated chemical shifts. In other words, the relation given by Eq. 2 is no longer applied to the chemical shift in Cr 3p electrons. Evidently, this is due to the difference in molecular structure. CO coordinated through the carbon atom which is more positive than that in benzene. Furthermore, the distance between Cr and C for benzene is larger than that between Cr and C for CO. Therefore, electrostatic potential felt by a chromium atom in $Cr(CO)_6$ is more positive than that in $Cr(C_6H_6)(CO)_3$.

The Relaxation Energy for C 1s Electron in $Cr(C_6H_6)_2$. The difference between the relaxation energies in free and coordinated benzenes, ΔE_R, was obtained to be 0.4 eV to substitute above obtained charge distribution in bis-benzene chromium into Eq. 1. The relaxation energy is given by the equation[11]

$$E_R = \frac{1}{2}(V^* - V)$$

where V^* and V are respectively, the electrostatic potential at ionized carbon in the relaxed hole state and in the ground state. The hole state was expressed by equivalent core model. V^* and V caused by surrounding atoms were calculated on the basis of the potential model. For the atom which has a 1s hole, $1/2(V^* - V)$ was calculated by using the equation given by Basch.[16] The results of these calculation predict that $\Delta E_R = -0.9$ eV. ΔE_R can be estimated also from Fig. 3, which gives $\Delta E_R = -0.1$ eV. The values of ΔE_R obtained by each method may be considered to show a rather agreement with each other.

Table 2. The charge density on atoms estimated from XPS data, (in unit of |e|)

Compound	q_C	q_O	q_{Cr}
$Cr(CO)_6$	0.23	−0.24	0.06
$Cr(C_6H_6)(CO)_3$	0.15	−0.29	0.54
	−0.02[a]		
$Cr(C_6H_6)_2$	−0.05	—	0.60

a) The charge density on carbon atom in benzene.

Table 3. Comparison of the estimated chemical shift in Cr 3p electron with that of observed, (in unit of eV).

Compound	Calcd	Obsd
$Cr(C_6H_6)_2$	0.0	0.0
$Cr(C_6H_6)(CO_3)$	1.1	1.9
$Cr(CO)_6$	2.7	2.9

Conclusion

We could obtain the binding energy of a core electron referred to vacuum level by calibrating the binding energy of a valence band observed in solid phase with that in gaseous phase. Within certain selected molecules, the change in binding energy can be directly correlated to the change in charge density. This relation could be applied to the results of XPS measurements of the present compounds for the estimation of charge distribution in these compounds.

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