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Core–Electron Binding Energies for Compounds of Boron, Carbon, and Chromium

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Boron 1s and chromium 3p binding energies have been measured for 25 boron compounds and 17 chromium compounds. The data correlate linearly with calculated atomic charges. A linear correlation is also demonstrated for CNDO-calculated atomic charges and carbon 1s binding energies determined by other workers.

Introduction

Core–electron binding energies for several elements in a wide variety of compounds have been determined by X-ray photoelectron spectroscopy (XPS).[1] These energies have been correlated with atomic charges calculated from molecular orbital eigenfunctions.[2,3] Although it has been pointed[4] out that, from theoretical considerations, one cannot expect better than a rough correlation between core–electron binding energy and atomic charge, such rough correlations are fairly easy to make and can give useful information about the bonding and structure of compounds. In this paper we report boron 1s and chromium 3p binding energies and show that they can be roughly correlated with atomic charges calculated by various molecular orbital methods. A CNDO-calculated charge correlation is also demonstrated for some carbon 1s binding energies that were determined in another work.[3]

Experimental Section

The experimental aspects of the determination of inner-electron binding energies have been reviewed by Siegbahn, *et al.*[1] Mg Kα X-radiation (1253.6 eV) was used in this work. All compounds were solid and were treated as before[2] except where noted below. The precision of the measurements was ±0.2 eV. The chromium 3p peaks appeared to be slightly broader (by 0.2 or 0.3 eV) than the carbon 1s and boron 1s peaks. This result may possibly indicate a slight participation of the chromium 3p electrons in the valence molecular orbitals; in future work the binding energies of deeper levels should probably be measured.

It was necessary to cool the samples of $(CH_3)_3NBF_3$, $B_{10}H_{14}$, and $Cr(CO)_6$ to prevent their sublimation in the spectrometer. These samples were loaded into the spectrometer source house under dry nitrogen and cooled to $\sim -60°$ before evacuation.

Photoelectrons originate from sites near the surface;[1] thus it was necessary to clean the surface of a piece of chromium foil continuously in order to see a peak that could be assigned to the unoxidized metal. This was accomplished by heating the chromium foil to ~650° in hydrogen at 10^{-2} Torr. The disappearance of the oxide layer was monitored by the O 1s line. Chromium hydride formation need not be considered because of the low solubility of hydrogen in chromium metal at 650°.[5]

The work function for the spectrometer material (aluminum) was assigned the value 4.0 eV, as in previous work.[2]

Compounds were either purchased or were gifts. Samples of many boron compounds were kindly supplied by Professor M. F. Hawthorne and Dr. S. Trofimenko.

Calculations

CNDO molecular orbital eigenfunctions[6] were obtained for some of the carbon and boron compounds.[7] Simple extended Hückel calculations[7,8] were also made for some of the boron compounds. In the extended Hückel method, Coulomb integrals, H_{ii}, were approximated by the valence-state ionization potentials (VSIP) calculated by Hinze and Jaffé.[9] The off-diagonal elements were assigned as

$$H_{ij} = 1.75S_{ij}(H_{ii} + H_{jj})/2$$

where S_{ij} is the overlap integral between the ith and jth atomic orbitals. Slater's rules[10] were used to calculate orbital exponents for atomic orbitals. Boron nitride was treated in an approximate manner.[2]

Simple iterative extended Hückel molecular orbital calculations[11] were completed for a few chromium compounds. Coulomb integrals for ligand orbitals were set equal to the negative of the appropriate neutral atom VSIP's[9] corrected in each cycle for net atomic charge q_i

$$H_{ii} = H_{ii}^0 - (2.0 \text{ eV/charge})q_i \qquad (1)$$

Chromium coulomb integrals (except where noted) were calculated for a neutral atom in a d^5p configuration;[12] charge correction of these values was made using eq 1 on each iterative cycle. Both the metal and ligand

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[1] A review of many aspects of XPS can be found in K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, J. Lindgren, and B. Lindberg, "ESCA Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells AB, Stockholm, 1967.

[2] (a) For nitrogen compounds see: J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, *J. Chem. Phys.*, **49**, 3315 (1968); D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*; **8**, 2642 (1969). (b) For phosphorus compounds see: M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, **74**, 1116 (1970).

[3] For carbon compounds see: R. Nordberg, U. Gelius, P. F. Hedén, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, submitted for publication.

[4] W. L. Jolly and D. N. Hendrickson, *J. Am. Chem. Soc.*, in press.

[5] T. R. P. Gibb, Jr., *Progr. Inorg. Chem.*, 315 (1962).

[6] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129, S136 (1965). A modified CNDO/1 version involving empirically evaluated repulsion integrals was used: P. M. Kuznesof and D. F. Shriver, *J. Am. Chem. Soc.*, **90**, 1683 (1968). Calculational details can be found in this latter reference.

[7] We did not vary the orbital exponents or the formulation of H_{ij} because earlier work with nitrogen[2a] and phosphorus[2b] had shown that such variations did not significantly change the correlation of binding energy with atomic charge.

[8] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[9] J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

[10] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

[11] The method was essentially that used for phosphorus compounds by P. C. Van der Voorn and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 3255 (1966).

[12] H. Basch, A. Viste, and H. B. Gray, *Theoret. Chim. Acta* (Berlin), **3**, 458 (1965).

orbital exponents were taken as neutral atom orbital values, μ_i^0 (assigned by Slater's rules[10]), corrected for charge

$$\mu_i = \mu_i^0 + 0.35q_i/n^*$$

Here n^* is the effective principal quantum number. The off-diagonal Hamiltonian elements were assigned by Cusachs' approximation[13]

$$H_{ij} = S_{ij}(H_{ii} + H_{jj})(2 - |S_{ij}|)/2$$

Atomic charges q_i were obtained in each cycle by an application of Mulliken's population analysis.[14] Iterations were made on the chromium compounds until the atomic charges were self-consistent to at least 0.05.

Program PROXYZ[15] was used to obtain Cartesian coordinates when necessary; the molecular parameters were obtained from crystal structure determinations[16] or from estimates.

Core–electron binding energies (the differences in energy between the Fermi level and the atomic level for the solids) were calculated from the relation[1]

$$E_B = E_{h\nu} - E_{\text{kin}} - \phi_{\text{sp}}$$

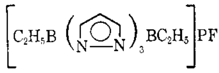
Here $E_{h\nu}$ is the X-ray energy, E_{kin} is the kinetic energy of the photoelectron in the spectrometer, and ϕ_{sp} is the work function of the spectrometer material.

Results and Discussion

Boron Compounds.—Boron 1s electron binding energies were measured for some 25 compounds and are listed in Tables I and II. The range of boron 1s shifts is 8.4 eV, which is comparable to the observed phosphorus 2p shift range (~8.5 eV).[4] Larger shift ranges have been observed for nitrogen (~10.8 eV),[2] carbon (~15.9 eV),[3] and sulfur (~15 eV).[1]

TABLE I

BORON 1s BINDING ENERGIES AND CALCULATED CHARGES

Compound no.	Compound	Binding energy, eV	Calcd boron atom charge	
			CNDO	Extended Hückel
1	$NaBF_4$	195.1	+0.754	+2.361
2	$(CH_3)_3NBF_3$	193.8	+0.756	+2.161
3	$B(OH)_3$	193.2	+0.651	+2.122
4	$NaBH(OCH_3)_3$	192.3	+0.404	+1.724
5	$Na_3B_3O_6$	192.2	+0.321	+2.098
6	p-$FC_6H_4B(OH)_2$	191.9	+0.498	+1.715
7	p-$ClC_6H_4B(OH)_2$	191.9		+1.713
8		191.9		+1.228
9	BN	190.2		+1.48
10	$K_2BH_3CO_2$	187.5	−0.024	+1.604
11	$(CH_3)_4NB_3H_8$	187.4	+0.165[a] −0.007	+0.518[a] +0.078
12	$NaBH_4$	187.4	0.000	+0.138
13	B_{amor}	187.5	≡0	≡0

[a] There are two structurally different B atoms in the $B_3H_8^-$ ion; the first boron charge refers to the unique boron. For purposes of plotting, a weighted average was used.

TABLE II

BORON 1s BINDING ENERGIES

Compound no.	Compound	Binding energy, eV
14	$Na_2B_4O_7 \cdot 10H_2O$	192.8
15		191.9
16	$(CH_3)_4N[(8,9,12\text{-}Br_3\text{-}1,2\text{-}B_9C_2H_8)_2Co]$	189.5
17	$Cs[Co(1,2\text{-}B_9C_2H_{10}\text{-}8\text{-}S)_2]$	188.9
18	$Rb[Co(1,2\text{-}B_9C_2H_{11})(B_8C_2H_{10})]$	188.4
19	$C_2B_9H_{11} \cdot C_5H_5N$	188.4
20	$Cs[(1,2\text{-}B_9C_2H_{11})_2Co]$	188.2
21	$B_{10}H_{14}$	188.0
22	$Na_2B_{12}H_{12} \cdot xH_2O$	187.7
23	$NaB(C_6H_5)_4$	187.7
24	$Cs_2B_{10}H_{10}$	187.6
25	B_4C	186.7

Simple extended Hückel molecular orbital (EHMO) calculations were completed for 12 of the boron compounds. A fair linear correlation between measured boron 1s electron binding energy and boron atom charge from the EHMO eigenfunctions is shown in Figure 1.

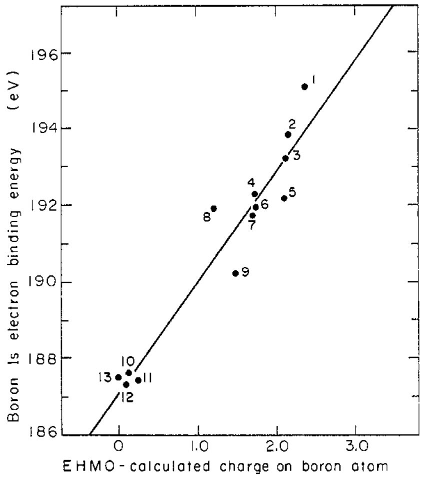


Figure 1.—Plot of boron 1s binding energy *vs.* extended-Hückel-calculated charges on boron atoms. The line is a least-squares fit to the points.

The tetramethylammonium salt of the octahydrotriborate ion ($B_3H_8^-$) with two geometrically different borons gave a single broad boron 1s peak with no structure, and therefore only a single point represents this ion in Figure 1. The boron atom charges (*via* the EHMO method) range from near neutrality in the borohydrides to almost +2.4 in BF_4^-.

In our nitrogen studies[2] we found that the EHMO method tended to overemphasize charge separations in molecules. The CNDO nitrogen atom charge range was one-fourth to one-fifth as large as that obtained by the EHMO method for a series of nitrogen compounds. CNDO calculations were made for some of the boron compounds treated by the EHMO method. The results are given in Table I. Again the CNDO-calculated atom charge range is about four times smaller than that obtained using EHMO eigenfunctions. The greater charge separations obtained using the simple EHMO method are probably the result of using charge-independent Coulomb integrals.

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(13) L. Cusachs, *J. Chem. Phys.*, **44**, 835 (1966).

(14) R. S. Mulliken, *ibid.*, **23**, 1833, 1841, 2338, 2343 (1955).

(15) P. M. Kuznesof," Quantum Chemistry Program Exchange," QCPE 94, Indiana University, Bloomington, Ind., 1966.

(16) L. E. Sutton, Ed., "Table of Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958; No. 18, Supplement, 1965.

A fairly good correlation exists between the measured boron 1s binding energies and the CNDO-calculated boron charges, as can be seen in Figure 2. Using this CNDO correlation line and the boron binding energy for BN, we infer a boron charge of ~+0.29. The measured nitrogen 1s binding energy for BN[2] correlates with a nitrogen charge of −0.25. This result is a good indication of internal consistency; the sum of the charges should equal zero. Unfortunately, the number of boron compounds was insufficient to permit the distinguishing of two lines (one characteristic of anions and the other of neutral molecules), as observed in our nitrogen work.[2] However it is perhaps significant that the points for the three neutral molecules (**2**, **3**, and **6**) fall below the line in Figure 2.

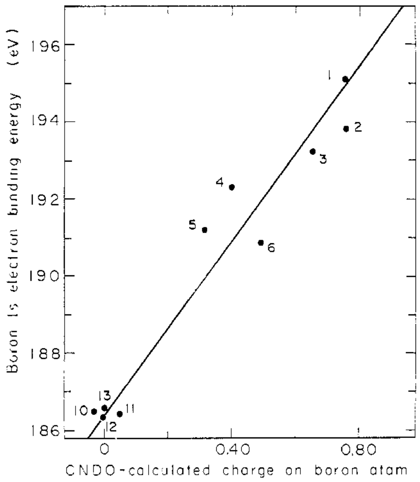

Figure 2.—Plot of boron 1s binding energy *vs.* CNDO-calculated charges on boron atoms. The line is a least-squares fit to the points.

For all of the compounds listed in Table II it was possible to detect only a single relatively sharp boron peak. The carboranes (compounds **16–20**) have geometrically different boron atoms, but in an unsubstituted carborane (as in compound **20** where two 1,2-dicarbollide ions are bound to a single cobalt atom) delocalization of charge would be expected to make the charges on the boron atoms similar. It can be seen that as we substitute one S atom for an H atom on the 1,2-dicarbollide ion (as in compound **17**) the boron 1s binding energy is increased appreciably. Substitution of three bromines for three hydrogens on this same cage increases the boron binding energy even more, but still only one sharp peak can be seen. Presumably delocalization of charge occurs in this 1,2-dicarbollide cage.

TABLE III

CARBON 1s BINDING ENERGIES AND CALCULATED CHARGES

Compound no.	Compound	Binding energy,[a] eV	CNDO-calculated carbon atom charge
1	CF_4	300.7 (296.1[b])	+0.831
2	CF_2O	294.1	+0.720
3	CF_3H	295.1 (293.5[b])	+0.656
4	CF_3COCH_3	292.8	+0.637
5	CO_2	292.5	+0.576
6	CF_3CO_2Na	292.3	+0.569
7	$NaHCO_3$	290.2	+0.409
8	Na_2CO_3	289.7	+0.226
9	CH_3CO_2Na	289.1	+0.437
6	CF_3CO_2Na	289.1	+0.401
10	CH_3CO_2Na	288.8	+0.320
4	CF_3COCH_3	288.7	+0.363
11	NH_4HCO_2	288.6	+0.318
12	CH_3COCH_3	288.0	+0.302
13	CH_2O	287.9	+0.329
10	CH_3CO_2Na	285.0	+0.072
14	CH_4	285.0	+0.098
15	KCN	285.0	−0.482
12	CH_3COCH_3	284.9	+0.098
9	CH_3CO_2H	284.8	+0.125

[a] Binding energies taken from ref 3 except where noted. [b] T. D. Thomas, unpublished work.

Carbon Compounds.—Nordberg, *et al.*,[3] have recently reported carbon 1s binding energies. They found that the carbon binding energies roughly correlate with carbon fractional atomic charges calculated by a modification of Pauling's method and with carbon atom charges calculated from simple EHMO eigenfunctions. The results of our CNDO calculations for some of the compounds treated by Nordberg, *et al.*,[3] are given in Table III. The carbon 1s binding energies for these compounds are plotted *vs.* the CNDO-calculated carbon charges in Figure 3. In the cases of CF_4 and CHF_3, the binding energies obtained by Professor T. D. Thomas (measured *vs.* Xe as well as CH_4) were found to fit the correlation better and were used instead of the values given by Nordberg, *et al.* We draw two conclusions. First, the CNDO carbon charges seem more realistic (*i.e.*, not as large) than those obtained by the EHMO method. Second, a somewhat improved straight-line correlation is obtained in the CNDO plot. Only two points fall off the line (*i.e.*, not within experimental uncertainty), the points for KCN and Na_2CO_3.

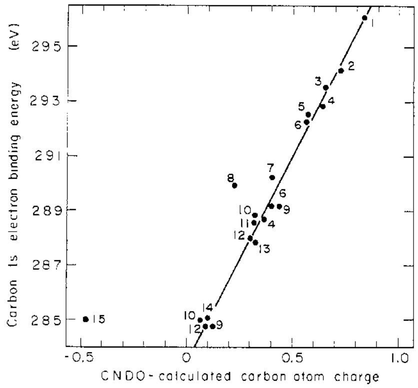

Figure 3.—Plot of carbon 1s binding energies *vs.* CNDO-calculated charges on carbon atoms. The line is a least-squares fit to the points.

Chromium Compounds.—Chromium 3p electron binding energies are given in Table IV. Qualitatively the chromium 3p binding energies increase with increasing oxidation state, the exception being $Cr(CO)_6$. Chromium 3p binding energies are somewhat more difficult to obtain than nitrogen, carbon, phosphorus, or

TABLE IV

CHROMIUM 3p BINDING ENERGIES

Compound	Binding energy, eV	Compound	Binding energy, eV
$K_2Cr_2O_7$	48.7	$K_3[Cr(CN)_5NO]$	44.8
CrO_3	48.2	$Cr(NH_3)_6Cl_3$	44.7
$Na_2CrO_4 \cdot 4H_2O$	47.9	$Cr_2O_3 \cdot xH_2O$	44.6
$Cr_2(SO_4)_3 \cdot xH_2O$	46.9	*trans*-$[Cr(H_2O)_4Cl_2]Cl$	44.5
$Cr(CO)_6$	45.8	$Cr_2(CH_3CO_2)_4(H_2O)_2$	44.5
$[Cr(H_2O)_6](NO_3)_3 \cdot 3H_2O$	45.4	Cr foil (unreduced)	43.9
$CrCl_3 \cdot 6H_2O$	45.4	Cr_2O_3	43.5
$[Cr(H_2O)_5Cl]Cl_2$	45.2	CrN	43.2
$K_3[Cr(CN)_6]$	44.8	Cr foil (reduced)	43.2

boron core–electron binding energies, because the lower energies associated with ionization of a chromium 3p electron give a lower photoionization cross section when using the same X-radiation.[1] Equally troublesome is the asymmetric background probably due to bremstrahlung (inelastically scattered electrons).

Some preliminary iterative extended Hückel calculations (see Calculations) were completed for a few of the chromium compounds; the results are given in Table V. In all cases the configuration of the chromium atom was assumed, and the calculations were iterated until all atom charges in the molecule were self-consistent to within 0.05. Two modifications of the metal input parameters were considered—one using Slater orbital exponents[10] coupled with neutral atom chromium valence orbital ionization potentials for d^5p configuration[12] and the other using essentially changed metal orbital exponents. In both cases (see Figure 4) only a very rough correlation between chromium 3p binding energy and calculated chromium atom charge was found.

TABLE V

ITERATIVE EXTENDED-HÜCKEL-CALCULATED CHROMIUM ATOM CHARGES

Molecule	Calcd chromium atom charges	
	d^5p confign[a]	Modified d^5p confign[b]
$Cr_2O_7^{2-}$	2.526	2.741
CrO_4^{2-}	2.430	2.618
$Cr(CN)_6^{3-}$	2.055	1.598
$Cr(CO)_6$	1.500	1.400

[a] Slater exponents used[9] (H_{ii} for metal): 3d, −8.40 eV; 4s, −8.01 eV; 4p, −3.52 eV. See ref 12 for a neutral-atom d^5p configuration. [b] Metal orbital exponents: 3d, 2.22; 4s and 4p, 0.733. H_{ii} for metal: 3d, −8.40 eV; 4s, −9.27 eV; 4p, −3.52 eV.

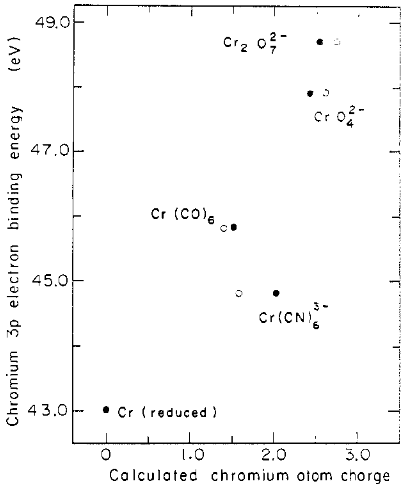

Figure 4.—Plot of chromium 3p binding energies *vs.* iterative extended-Hückel-calculated charges on chromium atoms. The symbols ○ and ● refer to two different sets of input data as given in footnotes *a* and *b*, respectively, in Table V.

The chromium 3p binding energies of $K_3[Cr(CN)_6]$ and $K_3[Cr(CN)_5NO]$ are identical and therefore one might conclude that the latter compound is a Cr(III) compound, contrary to its usual formulation as a Cr(I) compound.[17] The assignment of the +3 oxidation state to chromium corresponds to a formal NO^- group. This conclusion is consistent with our nitrogen 1s work, where we found the charge on the NO nitrogen in K_3-$[Cr(CN)_5NO]$ to be more negative than expected for an NO^+ group.[2]

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(17) This conclusion has also been reached on the basis of bond lengths, etc.: R. D. Feltham, private communication.