Chemical Shifts in Boron 1s Binding Energies of Some Gaseous Compounds

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Abstract: Chemical shifts in boron 1s electron binding energies for gaseous BF_3, BCl_3, $B(OCH_3)_3$, B_2H_6, $B(CH_3)_3$, BH_3CO, and $H_3BN(CH_3)_3$ are shown to be linearly related to boron atom charges estimated by Pauling, CNDO, and extended Hückel methods. The best correlation is found with the extended Hückel charges, with inclusion of the interatomic "Madelung potential" (average deviation from straight-line relation, ±0.83 eV). By application of the thermodynamic method (based on the approximation that $\Delta E = 0$ for the interchange of a pair of equally charged atomic cores between two different chemical species), the chemical shifts are estimated with an average error of ±0.57 eV. There is no obvious correlation between the 1s binding energy chemical shifts and published ^{11}B nmr chemical shifts.

Recently we reported[1] the nitrogen 1s electron binding energies for a series of gaseous nitrogen compounds and correlated the experimental values with calculated atomic charges and thermodynamic data. In this study we have measured the boron 1s electron binding energies of a series of gaseous boron compounds in order to provide data for further tests of the correlation of binding energies with atomic charges and thermodynamic data. We have also compared the boron 1s binding energies with boron-11 nuclear magnetic resonance chemical shifts.

Experimental Section

Magnesium Kα X-radiation was used for photoionization. Kinetic energies of the photoelectrons were measured with an iron-free, double-focusing magnetic spectrometer.[2] Each compound was first studied alone to determine the approximate magnitude of the photoelectron kinetic energy. Then an approximately 1:1 mixture of the compound and a reference compound, usually boron trifluoride, was studied. Because absolute binding energies were not determined, all the reported binding energies are relative. The width of each channel was 0.3 eV; the counting times were such that approximately 1000 counts were recorded in the channel nearest the signal peak. Signal-to-noise ratios were 2.0–4.0, and the widths of the photoelectron lines at half-height were 1.2–1.8 eV. Most samples were run twice; no peak position changed more than 0.1 eV.

Trimethyl borate was obtained from Alfa Inorganics, Inc., trimethylamine-borane from Callery Chemical Co., and boron trifluoride and boron trichloride from the Matheson Co. Borane carbonyl,[3] diborane,[4] and boron trimethyl[5] were prepared by literature procedures. The purity of the samples was checked by mass spectroscopy and by infrared spectroscopy.[6-12]

Results and Discussion

The measured boron 1s electron binding energies, relative to that of boron trifluoride, are listed in Table I.

Atomic Charge Method. Pauling, CNDO, and extended Hückel methods were used for calculating boron atomic charges to permit a comparison of their correlations with experimental binding energies.

The Pauling method is based on a relation between the ionic character of a bond and the difference in the electronegativities of the atoms.[13] Using Pauling's technique[14] for estimating the electronegativities of charged atoms, the calculations were iterated until consistent sets of charges and electronegativities were obtained. The calculated charges are listed in column 4 of Table I. The least-squares fitted straight line relation between binding energy and Pauling charge, $E_B = 4.35q - 4.39$, fits the data with an average error of ±1.23 eV. A similar poor correlation with Pauling charges was found previously[1] for nitrogen compounds.

Using a FORTRAN IV program, the CNDO molecular orbital charge calculations[15] were made with a CDC 6400 computer, using Cartesian cooridinates obtained from program PROXYZ[16] coupled with literature values for the molecular parameters.[17] The calculated CNDO atomic charges are listed in column 5 of Table I. The least-squares fitted straight line relation between binding energy and CNDO charge, $E_B = 7.58q - 6.37$, fits the points with an average error of ±1.45 eV (worse than in the Pauling charge correlation).

Extended Hückel calculations were made with a CDC 6600 computer using a FORTRAN IV program.[18] The Slater exponents used were 1.2, 2.6, 3.25, 3.9, 4.55, 5.2, and 4.5 for H, B, C, N, O, F, and Cl, respectively.

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Table I. Boron 1s Chemical Shifts, Estimated Boron Charges, ^{11}B Nmr Chemical Shifts, and Thermochemically Estimated Chemical Shifts

Compd no.	Compd	Relative binding energy, eV	Pauling charge	CNDO charge	Extended Hückel charge	^{11}B nmr chemical shifts, ppm	Thermo-chemical energy, eV
1	BF_3	0	0.92	0.70	1.65	6.6	0
2	BCl_3	−2.3	−0.22	0.25	0.81	−29.2	−2.42
3	$B(OCH_3)_3$	−4.4	0.36	0.49	1.13	0.0	−3.02
4	B_2H_6	−6.3	−0.29	−0.03	−0.01	0.5	−5.42
5	$B(CH_3)_3$	−6.4	−0.62	0.13	0.31	−68.2	−6.86
6	BH_3CO	−7.6	−0.78	−0.43	0.15		−8.03
7	$BH_3N(CH_3)_3$	−9.1	−0.60	−0.08	−0.19	24.9	−9.46

Coulomb integrals were obtained from valence orbital ionization potentials.[19] The calculated charges are listed in column 6 of Table I. The least-squares fitted straight line relation, $E_B = 4.34q - 7.54$, provides the best fit of the three atomic charge methods with an average error ±1.04 eV. For nitrogen compounds the extended Hückel method also gives the best fit.[20]

By inclusion of the interatomic "Madelung potential," M,[21] the linear relationships between binding energy and atomic charge are improved. The improvement is negligible for the Pauling charges, yielding an average error ±1.20 eV for the least-squares fitted straight line $E_B - M = 4.98q - 4.37$. The average errors for the CNDO least-squares fitted straight line, $E_B - M = 8.29q - 6.04$, and the extended Hückel straight line, $E_B - M = 5.15q - 7.48$, are significantly reduced to ±1.21 and ±0.83 eV, respectively.

Nmr Chemical Shifts. The ^{11}B nmr chemical shifts reported by Phillips, Miller, and Muetterties[22] relative to methyl borate are listed in column 7 of Table I. There seems to be no correlation whatsoever between these data and the relative binding energies, even when considering the planar molecules alone.

Thermodynamic Method. The difference in the boron 1s electron binding energies of boron trichloride and boron trifluoride is the energy of reaction 1.

$$BCl_3 + BF_3^{+*} \longrightarrow BF_3 + BCl_3^{+*} \qquad (1)$$

(An asterisk denotes removal of a core electron.) The basis of the thermodynamic method is the approximation that $\Delta E = 0$ for the interchange of a pair of equally charged atomic cores between two different chemical species, specifically, for the case in which one atomic core lacks one electron and the other has a complete set of electrons but has a nuclear charge one unit higher. Application of this approximation to the present set of data corresponds to the assumption that $\Delta E = 0$ for the interchange of B^{4+*} and C^{4+} cores between different species. Thus we take $\Delta E = 0$ for reaction 2. The

$$CF_3^+ + BCl_3^{+*} \longrightarrow BF_3^{+*} + CCl_3^+ \qquad (2)$$

sum of reactions 1 and 2 is reaction 3, for which, to

$$BCl_3 + CF_3^+ \longrightarrow BF_3 + CCl_3^+ \qquad (3)$$

the accuracy of our approximation, ΔE is the chemical shift in binding energy between BF_3 and BCl_3. Reactions analogous to reaction 3 can be written for all the other boron compounds studied. The corresponding energies, calculated from literature data,[23-30] are given in column 8 of Table I. A plot of the experimental relative binding energies *vs.* the thermodynamically estimated relative binding energies is presented in Figure 1. The least-squares fitted straight line drawn through the data, forced to have a slope of unity, corresponds to the relation $E_B(\text{exptl}) = E_B(\text{calcd}) - 0.13$. The average deviation between the experimental and calculated values is ±0.57 eV.

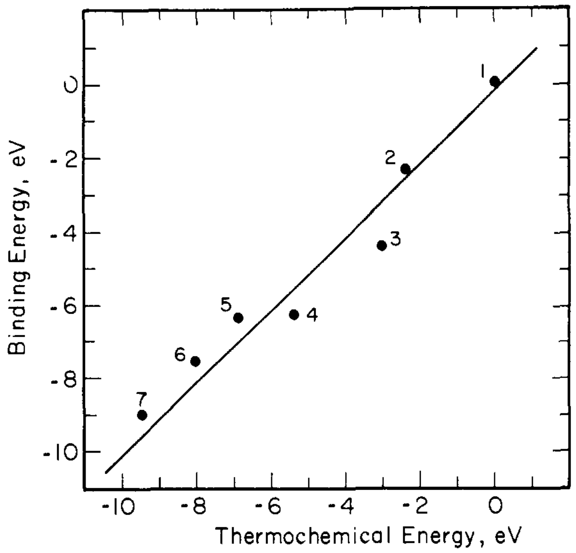

Figure 1. Plot of boron 1s binding energies *vs.* thermodynamically estimated binding energies.

Thermodynamic Calculations. Most of the heats of formation used to calculate the relative binding energies were taken from the literature.[23-25] However, not all the data required for diborane (B_2H_6) and trimethylamine-borane [$H_3BN(CH_3)_3$] are available, and it was necessary to make further approximations in these cases.

The binding energy of B_2H_6, relative to that of BF_3, is taken to be the energy of reaction 4, where BCH_6^+ is

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$$B_2H_6 + CF_3^+ \longrightarrow BF_3 + BCH_6^+ \quad (4)$$

the species formed by replacing a boron atom in B_2H_6 with a C^+ ion. The heat of formation of this species is unknown. We have assumed that its heat of formation from BH_3 and CH_3^+ is equal to the heat of formation of the isoelectronic species, B_2H_6, from two BH_3 molecules.

The binding energy of $H_3BN(CH_3)_3$, relative to that of BF_3, is taken to be the energy of reaction 5. Although the heat of the formation of the gaseous tetramethylammonium ion apparently has not been recorded, it can be estimated from a Born-Haber cycle for tetramethylammonium nitrate. The sum of reactions 6, 7, and 8 is reaction 9, for which $\Delta H°$ is the heat of formation of the gaseous tetramethylammonium ion. Médard and Thomas[26] have determined $\Delta H°_6$ to be −80.8 kcal/mol. The value of $\Delta H°_7$ (117.2 kcal/mol) was estimated by the formula of Kapustinsky, which, for salts of univalent anions, is[27]

$$H_3BN(CH_3)_3 + CF_3^+ \longrightarrow BF_3 + N(CH_3)_4^+ \quad (5)$$

$$\frac{3}{2}O_2(g) + N_2(g) + 4C(s) + 6H_2(g) \longrightarrow [(CH_3)_4N]NO_3(s) \quad (6)$$

$$[(CH_3)_4N]NO_3(s) \longrightarrow N(CH_3)_4^+(g) + NO_3^-(g) \quad (7)$$

$$NO_3^-(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) + e^-(g) \quad (8)$$

$$\frac{1}{2}N_2(g) + 4C(s) + 6H_2(g) \longrightarrow N(CH_3)_4^+(g) + e^-(g) \quad (9)$$

$$U = 287.2\left[\frac{n(n + 1)}{(r_+ + r_-)}\right]\left[1 - \frac{0.345}{(r_+ + r_-)}\right]$$

where n is the charge on the cation and r_+ and r_- are the cationic and anionic radii. The radius of the tetramethylammonium ion (2.43 Å) was calculated from the lattice constants for the chloride, bromide, and iodide salts[28,29] and the halide ionic radii,[30] and the nitrate ion radius was taken as 2.10 Å.[27] A previously calculated value of $\Delta H°_8$ (89.0 kcal/mol[27]) was used. The resulting value for the heat of formation of $N(CH_3)_4^+(g)$ is 125.4 kcal/mol.

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Structure and Dynamics in Metal Tetrahydroborates. I. Nuclear Magnetic Resonance Studies of Zirconium and Hafnium Tetrakis(tetrahydroborates)

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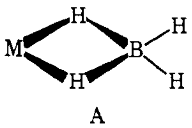
Abstract: The identical temperature dependence of the pmr spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ is due to the variable rate of ^{10}B and ^{11}B quadrupolar spin-lattice relaxation. Intramolecular rearrangement processes are still rapid at −80°. Quantitative analysis of the spectra as a function of solution viscosity yields results at least partially in accord with the hydrodynamic model for molecular reorientation, though inertial effects are also probably operative. Within experimental error, both molecules have the same nuclear quadrupole coupling constants, which are estimated to be: ^{10}B, 3.5 ± 0.6 MHz; ^{11}B, 1.7 ± 0.3 MHz, and the same activation energies for molecular reorientation, 3.1 ± 0.1 kcal/mol.

A number of transition metal hydroborate compounds are now known,[1] which, unlike their more familar salt-like alkali metal cogeners, possess characteristics typical of covalent molecules (solubility in nonpolar solvents, high volatility). These molecules are of interest in that they may serve as simple models for numerous organometallic systems of multicenter metal–ligand interactions. Their structural, chemical, and dynamical properties may also shed light on the nature of the hydrogen-transfer process both in borohydride reductions and in transition metal catalyzed hydrogenations. Finally, these molecules are of interest in that they appear to undergo a rapid, degenerate permutation of bridging and terminal hydrogen atoms,[1] possibly making them some of the most rapid fluxional[2] molecules yet discovered.

Studies of transition metal tetrahydroborates have been complicated by a number of factors. A structural problem has always existed in distinguishing between bidentate (A) and tridentate (B) bonding configurations. The difficulty in locating hydrogen atoms near a heavy metal has impaired the accuracy of X-ray diffraction studies[3,4] employed to completely resolve problems of this sort in the solid state. To date, the full potential of infrared and Raman spectroscopy as structural tools in these systems has not been realized. Nuclear magnetic resonance spectroscopy of metal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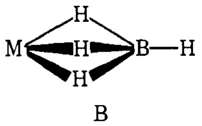
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