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Lewis Acidities and Hydride, Fluoride, and X^- Affinities of the $BH_{3-n}X_n$ Compounds for (X = F, Cl, Br, I, NH_2, OH, and SH) from Coupled Cluster Theory

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Atomization energies at 0 K and enthalpies of formation at 0 and 298 K are predicted for the $BH_{4-n}X_n^-$ and the $BH_{3-n}X_nF^-$ compounds for (X = F, Cl, Br, I, NH_2, OH, and SH) from coupled cluster theory (CCSD(T)) calculations with correlation-consistent basis sets and with an effective core potential on I. To achieve near chemical accuracy (±1.0 kcal/mol), additional corrections were added to the complete basis set binding energies. The hydride, fluoride, and X^- affinities of the $BH_{3-n}X_n$ compounds were predicted. Although the hydride and fluoride affinities differ somewhat in their magnitudes, they show very similar trends and are both suitable for judging the Lewis acidities of compounds. The only significant differences in their acidity strength orders are found for the boranes substituted with the strongly electron withdrawing and back-donating fluorine and hydroxyl ligands. The highest H^- and F^- affinities are found for BI_3 and the lowest ones for $B(NH_2)_3$. Within the boron trihalide series, the Lewis acidity increases monotonically with increasing atomic weight of the halogen, that is, BI_3 is a considerably stronger Lewis acid than BF_3. For the X^- affinities in the BX_3, HBX_2, and H_2BX series, the fluorides show the highest values, whereas the amino and mercapto compounds show the lowest ones. Hydride and fluoride affinities of the $BH_{3-n}X_n$ compounds exhibit linear correlations with the proton affinity of X^- for most X ligands. Reasons for the correlation are discussed. A detailed analysis of the individual contributions to the Lewis acidities of these substituted boranes shows that the dominant effect in the magnitude of the acidity is the strength of the $BX_3^-{-}F$ bond. The main contributor to the relative differences in the Lewis acidities of BX_3 for X, a halogen, is the electron affinity of BX_3 with a secondary contribution from the distortion energy from planar to pyramidal BX_3. The B−F bond dissociation energy of $X_3B{-}F^-$ and the distortion energy from pyramidal to tetrahedral BX_3^- are of less importance in determining the relative acidities. Because the electron affinity of BX_3 is strongly influenced by the charge density in the empty p_z lowest unoccupied molecular orbital of boron, the amount of π-back-donation from the halogen to boron is crucial and explains why the Lewis acidity of BF_3 is significantly lower than those of BX_3 with X = Cl, Br, and I.

Introduction

We have recently reported the calculated enthalpies of formation and the B−X and B−H bond dissociation energies (BDEs) for the BX_3, HBX_2, and H_2BX compounds with X = F, Cl, Br, I, NH_2, OH, and SH together with the different radicals involved in the bond breaking process[1] as part of an effort to predict the thermodynamics of regeneration schemes for spent fuel derived from loss of H_2 from ammonia borane. In addition, these compounds have many practical applications and are of substantial interest as model systems.[2] To further understand the chemistry of these compounds, we investigated the hydride (HA) and fluoride (FA) affinities as well as the X^- affinities (XA) of these substituted borane

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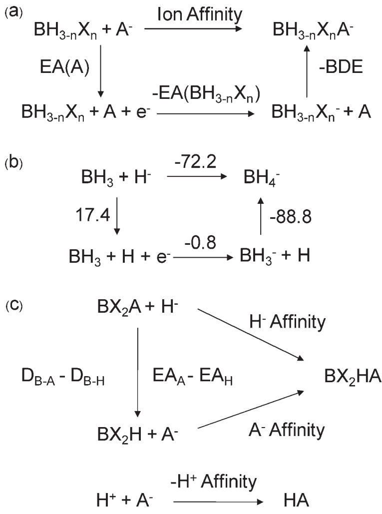

Figure 1. (a) Three step thermodynamic cycle for the A^- ion affinities of $BH_{3-n}X_n$: (1) the first ionization potential of A^-, (2) the electron affinity of $BH_{3-n}X_n$, and (3) the homolytic BDE of the B−A bond in the corresponding $BH_{3-n}X_nA^-$ anion. (b) Representative three step thermodynamic cycle for the hydride affinity of BH_3: (1) the electron affinity of the H radical, (2) the electron affinity of BH_3, and (3) the homolytic BDE of the B−H bond in BH_4^-. Energies in kcal/mol. (c) Thermodynamic cycle relating the hydride affinity of X_2BA to the anion affinity of X_2BH. The two reactions are linked by a metathesis reaction for which the energetics can be related to the homolytic bond energies of $X_2B{-}A$ and $X_2B{-}H$ and the electron affinities of A and H.

compounds. Furthermore, the fluoride ion[3] or hydride[4] affinities offer unique measures of the strength as a Lewis acid.

The most thorough and relevant previous study on this subject was carried out by Vianello and Maksic,[4] who calculated the H^- affinities of BH_3 and the fluoro, chloro, bromo, hydroxo, and methyl substituted boranes using the G2(MP2) method. They wrote a three step thermodynamic cycle (shown in Figures 1(a) for the general case and in 1(b) for the H^- affinities). For BH_3, this is (1) the pruning of an electron from H^-, which equals to 17.4 kcal/mol, the first ionization potential of H^- (or the electron affinity (EA) of H), (2) the attachment of the electron to BH_3 (the negative of the EA of BH_3), and (3) the homolytic chemical bond formation resulting from the combination of the BH_3^- and H radicals. For compounds with a calculated negative EA, they used these negative values, not the more appropriate value of 0 in the cycle. Since the electron is not bound when the EA ≤ 0, such an approach is non-physical and somewhat arbitrary as the size of the negative EA is strongly method and basis set dependent. They showed that F, OH, and CH_3 substitution reduces the hydride affinity (Lewis acidity) of the boranes, whereas Cl and Br substitution enhances the acidity, and that BBr_3 was the most acidic one of the compounds studied. Vianello and Maksic[4] also reported that the HA of the $BH_{3-n}X_n$ compounds with X = halogen, OH, and Me show a correlation with the EA with the inclusion of negative electron affinities.

In our present study, the scope of the previous investigation[4] for the HA was expanded by including the additional ligands, I, NH_2, and SH, and all calculations were done at a higher level. The F^- affinities for all compounds were also calculated and compared to the H^- values. Furthermore, the Cl^-, Br^-, I^-, NH_2^-, OH^-, and SH^- affinities were determined for the BX_3, HBX_2, H_2BX, and BH_3 series. It was found that H^- affinities correlate linearly with the proton affinities (PA) of X^-, except for H and F. The reasons for the correlation and the deviations from it are discussed. Since PAs for a number of anions are known or readily calculated, the H^- affinity of $BH_{3-n}X_n$ compounds with other X groups may be readily estimated.

Modern computational chemistry methods implemented on high performance computer architectures can now provide reliable predictions of chemical bond energies to within about 1 kcal/mol for most compounds that are not dominated by multireference character. We use the approach that we have been developing with collaborators at Pacific Northwest Laboratory and Washington State University for the prediction of accurate molecular thermochemistry[5] to determine accurate thermodynamic data for these compounds, including total atomization energies (TAE = $\sum D_0$), enthalpies of formation, BDEs, HAs, and FAs. As we have shown previously,[1] the experimental enthalpies of formation for a number of the molecules under study, specifically the neutral analogues, are available allowing for comparison to our calculated theoretical values. The experimental enthalpies of formation for the hydrogen halides,[6] the haloboranes,[7] the dihaloboranes (with the exception of diiodoborane),[7] the dihaloboryl radicals,[7] the trihaloboranes,[6,7] trihydroxyborane,[7] and the dihydroxyboryl radical[7] have been reported. Our theoretical calculations on the enthalpies of formation show excellent agreement with the reported experimental values.

Computational Approach

Our approach is based on calculating the TAE of a molecule and using this value with known enthalpies of formation of the atoms to calculate the enthalpy of formation at 0 K. The approach starts with coupled cluster theory with single and double excitations and including a perturbative triples correction (CCSD(T)),[8−10] combined with the correlation-consistent basis sets[11,12] extrapolated to the complete basis set (CBS) limit to treat the correlation energy of the valence electrons. This is followed by a number of smaller additive

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corrections including core−valence interactions and relativistic effects, both scalar and spin−orbit. The zero point energy is obtained from experiment, theory, or a combination of the two. Corrections to 298 K can then be calculated by using standard thermodynamic and statistical mechanics expressions in the rigid rotor-harmonic oscillator approximation[13] and appropriate corrections for the enthalpy of formation of the atoms.[14] All of the current work was performed with the MOLPRO suite of programs.[15] The open-shell CCSD(T) calculations for the atoms were carried out at the R/UCCSD(T) level.[16−18] All of the calculations were done on the 144 processor Cray XD-1 computer system at the Alabama Supercomputer Center or a Dell Cluster at the University of Alabama.

For the current study, we used the augmented correlation consistent basis sets aug-cc-pV*n*Z (n = D, T, Q) for H, B N, O, F, and Br.[12] In addition, it has recently been found that tight d functions are necessary for calculating accurate atomization energies for second row elements,[19] so we also included additional tight d functions in our calculations giving the aug-cc-pV(n+d)Z basis set on the second row atoms S and Cl. We use aV*n*Z to represent the combination of aug-cc-pV*n*Z on H, B, N, O, F, and Br, and aug-cc-pV (n+d)Z on the second row atoms S and Cl. Only the spherical components of the Cartesian basis functions were used. The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form:

$$E(n) = E_{\mathrm{CBS}} + A\exp[-(n-1)] + B\exp[-(n-1)^2] \quad (1)$$

with n = 2 (aVDZ), 3 (aVTZ), and 4 (aVQZ), as first proposed by Peterson et al.[20]

Core−valence (CV) calculations were carried out with the weighted core−valence basis set cc-pwCVTZ.[21] The core−valence correction is then taken as the difference in energy between the valence electron correlation calculation and that with the appropriate core electrons included using basis sets with additional functions. For molecules containing I as a substituent, we used a different approach because of issues described elsewhere.[22] We used the new effective core potential/correlation consistent basis sets developed by Peterson and co-workers.[23] These basis sets were developed in combination with the small core relativistic effective core potentials (RECPs) from the Stuttgart/Köln group. The RECP for I subsumes the ($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$) orbital space into the 28-electron core set, leaving the ($4s^2$, $4p^6$, $5s^2$, $4d^{10}$, and $5p^5$) space with 25 electrons to be handled explicitly. We performed our CBS extrapolation with the aug-cc-pwCV*n*Z basis sets for n = D, T, Q with 25 active electrons on each I atom so the core−valence correction is automatically included in the CBS extrapolation. We use aV*n*Z to represent the combination of aug-cc-pwCV*n*Z on the other atoms and aug-cc-pwCV*n*Z-PP on I.

For Br, we also performed additional calculations using the new effective core potential/correlation consistent basis sets.[23] For Br, the RECP subsumes the ($1s^2$, $2s^2$, $2p^6$) orbital space into the 10-electron core set, leaving the ($3s^2$, $3p^6$, $4s^2$, $3d^{10}$, and $4p^5$) space with 25 electrons to be handled explicitly. Only the ($4s^2$, $4p^5$) electrons are active in our valence correlation treatment. We use aV*n*Z-PP to represent the combination of aug-cc-pV*n*Z basis set on the other atoms and the aug-cc-pV*n*Z-PP basis set on Br. Core−valence (CV) calculations (all 25 electrons outside the RECP core) were also carried out with the weighted core−valence basis set cc-pwCVTZ for H and B,[21] and the cc-pwCVTZ-PP basis set for Br.

Geometry optimizations were performed at the MP2/aVTZ or MP2/aVTZ-PP level.[24] The vibrational frequencies were calculated at the sameMP2/aVTZ level to obtain the zero point energies and the thermal corrections at 298 K and were used without scaling except for calculating the electron affinity of BH_3. For the calculation of the electron affinity of BH_3, the zero point corrections for BH_3 and BH_3^- were obtained from the calculated harmonic stretching frequencies scaled by a factor of 0.96, (the average of the CCSD(T)/aVTZ and experimental values[25] of BH_3 divided by the average by the theoretical value).[26] The Gaussian program system[27] was used for the MP2 calculations. The MP2/aVTZ geometries were used in the single point CCSD(T)/aV*n*Z (n = D, T, Q) calculations.

Two adjustments to the TAE are necessary to account for relativistic effects in atoms and molecules. The atomic spin−orbit corrections are $\Delta E_{\mathrm{SO}}(\mathrm{B})$ = 0.03 kcal/mol, $\Delta E_{\mathrm{SO}}(\mathrm{O})$ = 0.22 kcal/mol, $\Delta E_{\mathrm{SO}}(\mathrm{F})$ = 0.39 kcal/mol, $\Delta E_{\mathrm{SO}}(\mathrm{S})$ = 0.56 kcal/mol, $\Delta E_{\mathrm{SO}}(\mathrm{Cl})$ = 0.84 kcal/mol, $\Delta E_{\mathrm{SO}}(\mathrm{Br})$ = 3.50 kcal/mol, and $\Delta E_{\mathrm{SO}}(\mathrm{I})$ = 7.24 kcal/mol from the tables of Moore.[28] A second relativistic correction to the TAE accounts for molecular scalar relativistic effects, ΔE_{SR}. ΔE_{SR} is taken as the sum of the mass-velocity and 1-electron Darwin (MVD) terms in the Breit-Pauli Hamiltonian.[29] For the molecules containing Br, the molecular scalar relativistic correction ΔE_{SR} was calculated using the spin-free, one-electron Douglas−Kroll−Hess (DKH) Hamiltonian.[30−32] ΔE_{SR} was defined as the difference in the atomization energy between the results obtained from basis sets recontracted for DKH calculations[31] and the atomization energy obtained with the normal valence basis set of the same quality. DKH calculations were carried out at the CCSD(T)/cc-pVTZ and the CCSD(T)/cc-pVTZ-DK levels of theory.

By combining our computed $\sum D_0$ values with the best available enthalpies of formation at 0 K for the elements $\Delta H_f^0(\mathrm{H})$ = 51.63 kcal mol^{-1}, $\Delta H_f^0(\mathrm{B})$ = 135.1 ± 0.2 kcal mol^{-1},[33] $\Delta H_f^0(\mathrm{N})$ = 112.53 kcal mol^{-1}, $\Delta H_f^0(\mathrm{O})$ = 58.99 kcal mol^{-1}, $\Delta H_f^0(\mathrm{F})$ = 18.47 kcal mol^{-1}, $\Delta H_f^0(\mathrm{S})$ = 65.66 kcal

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mol^{-1}, ΔH_f^0(Cl) = 28.59 kcal mol^{-1}, ΔH_f^0(Br) = 28.19 kcal mol^{-1}, and ΔH_f^0(I) = 25.61 kcal mol^{-1}, we can derive ΔH_f^0 values for the molecules under study in the gas phase.

Results and Discussion

The calculated geometry parameters, total energies and vibrational frequencies are given in the Supporting Information (Tables SI-1, SI-2, SI-3 and SI-4). The energetic components for predicting the TAE are given in Table 1 along with the point groups and ground-state symmetry labels. We first describe some trends in the various components for the TAE. The ΔE_{CV} corrections are all positive and range from 1.13 (BH_3^-) to 4.16 (BBr_4^-) kcal/mol. The ΔE_{SR} corrections are all negative and range from −0.09 (BH_3^-) to −1.86 kcal/mol (BBr_4^-). We estimate that the error bars for the calculated enthalpies of formation are ± 1.5 kcal/mol considering errors in the energy extrapolation, frequencies, and other electronic energy components. Quantities such as the fluoride affinities should be good to ± 1.0 kcal/mol as the errors in adding F^- are smaller. An estimate of the potential for significant multireference character in the wave function can be obtained from the T_1 diagnostic[34] for the CCSD calculation. The value for the T_1 diagnostics are small (< 0.02) for most molecules showing that the wave function is dominated by a single configuration. The T1 diagnostics for BH_3^-, BH_2F^-, and BHF_2^- are all substantially higher. In the case of BH_2F^- and BHF_2^- this is not surprising because, as discussed below, the parent neutral does not bind an electron. BH_3 does have a positive electron affinity so the large T_1 diagnostic was somewhat surprising. However, the predicted small electron affinity is within 0.01 eV of the experimental value[35] so this is not a serious issue for BH_3^-. The T_1 diagnostics for the molecules are given as Supporting Information (Table SI-6).

The calculated enthalpies of formation of the borane-derived anions are given in Table 2 at 0 and 298 K, together with those of the neutral parent molecules[1] for completeness. For our calculations on molecules containing Br, we note a ~0.8 kcal/mol difference per Br atom in the valence electronic energy extrapolated to the CBS limit based on the aV*n*Z and aV*n*Z-PP basis sets, respectively. The largest difference in the calculated enthalpies of formation based on both approaches was 1.4 kcal/mol for BBr_3^- (Supporting Information, Table SI-5). For the enthalpies of formation for the I containing molecules, the inclusion of the core electrons into the treatment of the correlation energy and employing the weighted core basis sets for the CBS extrapolation yields calculated values for the enthalpies of formation that are on average within 0.2 kcal/mol of the calculated value for the enthalpies of formation using the aV*n*Z-PP basis sets and just correlating the valence electrons (Supporting Information, Table SI-5). In general, the agreement between calculated and experimental enthalpies of formation is excellent. The only significant deviation, 9 kcal/mol, was found for BI_3, which is attributed to the very large uncertainty of 12 kcal/mol in the experimental value.

Given the calculated enthalpies of formation and the experimental enthalpies of formation of the hydride ($\Delta H_f^0(H^-)$ (298 K) = 34.7 kcal mol^{-1}) and fluoride ($\Delta H_f^0(F^-)$ (298 K) = 59.5 kcal mol^{-1}) anions, we can predict the HA and FA of the neutral molecules. We use the values of the ions without any energy attached to the electron. We define the HA and FA as $-\Delta H$ for the following respective reactions:

$$BH_{3-n}X_n + H^- \rightarrow BH_{4-n}X_n^- \quad (2)$$

$$BH_{3-n}X_n + F^- \rightarrow BH_{3-n}X_nF^- \quad (3)$$

The calculated HAs and FAs are summarized in Table 3 and depicted in Figure 2. The values at 298 K are used in our discussion below except as noted. The HA of BH_3 has been previously reported using the same approach as here.[36] The highest H^- and F^- affinities are found for BI_3 and the lowest ones for $B(NH_2)_3$, and within the boron trihalide series, the Lewis acidity increases monotonically with increasing atomic weight of the halogen, that is, BI_3 is a considerably stronger Lewis acid than BF_3.

In addition, we predict the chloride, bromide, iodide, amide, hydroxide, and bisulfide anion affinities, XA, where X = Cl, Br, I, NH_2, OH, and SH, respectively. We define the XA as $-\Delta H$ for the reaction

$$BH_{3-n}X_n + X^- \rightarrow BH_{3-n}X_{n+1}^- \quad (4)$$

The calculated XA values are presented in Table 4. For the X^- affinities in the BX_3, HBX_2, and H_2BX series, the fluorides show the highest values, while the amides, iodides, and bisulfides show the lowest ones. If X is a halogen, the X^- affinity increases with increasing X content of the molecule, that is, from H_2BX to HBX_2 and BX_3. However, if X is OH, the OH^- affinity decreases from $H_2B(OH)$ to $B(OH)_3$ with $HB(OH)_2$ and $B(OH)_3$ having essentially the same value. For X = SH, there is a substantial increase from H_2BX to HBX_2 and only a small increase to BX_3. For X = NH_2, the X^- affinity is a maximum for $HB(NH_2)_2$ with respect to $H_2B(NH_2)$ and $B(NH_2)_3$.

As can be seen from the data in Table 3, the FAs and HAs have similar values. The largest differences are observed for the boranes substituted with the strongly electron withdrawing and backdonating fluorine and hydroxyl ligands. These compounds exhibit large distortion energies upon addition of an electron to BX_3 or HBX_2.[4] In the case of F^- addition, this distortion energy loss can be recovered to a large extent by the high energy of the newly formed B−F bond, which is not the case for the weaker and more polar B−H bond. Therefore, the HAs for the fluoro- or hydroxo-boranes are considerably lower than the corresponding FAs. The largest differences in the opposite direction, that is, the HA being significantly higher than the FA, is seen for BH_3. In BH_4^-, all four ligands are identical and form strong covalent bonds, whereas in BH_3F^-, the B−F bond becomes highly polar and, therefore, weaker. A comparison of our HAs with the less comprehensive data set of reference 4 shows very good agreement with the deviations being 2 kcal/mol or less, except for $B(OH)_3$ where the difference is 3.4 kcal/mol. Furthermore, the range of the previously reported acidities for the boranes has been extended at both ends of the scale, BI_3 becoming the strongest acid and $B(NH_2)_3$ becoming the weakest one.

As discussed in the Introduction, Vianello and Maksic[4] provided a thermodynamic scheme for the HAs with three steps, the ionization of H^- to a hydrogen radical and an

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Table 1. Components for Calculated Atomization Energies in kcal/mol

molecule	CBS[a]	ΔE_{ZPE}[b]	ΔE_{CV}[c]	ΔE_{SR}[d]	ΔE_{SO}[e]	$\sum D_0(0\ K)$[f]
BH_3^- ($^2A_2''$ - D_{3h})	278.80	14.31[h]	1.13	−0.09	−0.03	265.51
BH_4^- ($^1A_1$ - T_d)[g]	373.88	20.69	1.28	−0.09	−0.03	354.35
H_2BF^- ($^2B_1$ - C_{2v})	330.18	12.55	1.31	−0.41	−0.42	318.12
H_3BF^- ($^1A_1$ - C_{3v})	426.60	18.66	1.23	−0.42	−0.42	408.33
$H_2BF_2^-$ ($^1A_1$ - C_{2v})	490.62	16.08	1.30	−0.75	−0.81	474.28
H_2BCl^- ($^2A'$ - C_s)	297.73	11.73	1.21	−0.38	−0.87	285.95
H_3BCl^- ($^1A_1$ - C_{3v})	400.11	18.69	1.31	−0.38	−0.87	381.48
H_2BClF^- ($^1A'$ - C_s)	457.55	15.58	1.33	−0.70	−1.26	441.34
H_2BBr^- ($^2A'$ - C_s)	287.59	11.62	1.58	−0.93	−3.53	273.33
H_3BBr^- ($^1A_1$ - C_{3v})	390.98	18.56	1.77	−0.88	−3.53	369.78
H_2BBrF^- ($^1A'$ - C_s)	447.17	15.40	1.83	−0.98	−3.92	428.69
H_2BI^- ($^2A'$ - C_s)	278.35	11.46		−0.09	−7.27	259.53
H_3BI^- ($^1A_1$ - C_{3v})	382.49	18.37		−0.09	−7.27	356.76
H_2BIF^- ($^1A'$ - C_s)	437.32	15.23		−0.67	−7.66	413.77
$H_3B(NH_2)^-$ ($^1A'$ - C_s)	557.49	33.72	1.73	−0.38	−0.03	525.09
$H_2B(NH_2)F^-$ ($^1A'$ - C_s)	618.56	30.99	1.79	−0.71	−0.42	588.23
$H_3B(OH)^-$ (^1A - C_1)	502.57	26.02	1.45	−0.43	−0.25	477.33
$H_2B(OH)F^-$ (^1A - C_1)	566.72	23.33	1.50	−0.77	−0.64	543.49
$H_3B(SH)^-$ ($^1A'$ - C_s)	465.78	23.70	1.51	−0.49	−0.59	442.51
$H_2B(SH)F^-$ (^1A - C_1)	521.89	20.64	1.53	−0.80	−0.98	500.99
HBF_2^- ($^2A'$ - C_s)	388.47	9.10	1.39	−0.73	−0.81	379.21
HBF_2^- ($^2B_1$ - C_{2v})	386.54	10.67	1.51	−0.76	−0.81	375.80
HBF_3^- ($^1A_1$ - C_{3v})	561.43	12.74	1.42	−1.11	−1.20	547.80
$HBCl_2^-$ ($^2A'$ - C_s)	317.91	8.27	1.28	−0.62	−1.71	308.59
$H_2BCl_2^-$ ($^1A_1$ - C_{2v})	422.99	14.99	1.42	−0.63	−1.71	407.07
$HBCl_2F^-$ ($^1A'$ - C_s)	482.06	11.23	1.47	−0.94	−2.10	469.27
$HBBr_2^-$ ($^2A'$ - C_s)	294.86	7.83	2.32	−1.47	−7.03	281.21
$H_2BBr_2^-$ ($^1A_1$ - C_{2v})	400.03	14.56	2.48	−1.40	−7.03	379.52
$HBBr_2F^-$ ($^1A'$ - C_s)	456.48	10.72	2.61	−1.43	−7.42	439.52
HBI_2^- ($^2A'$ - C_s)	272.08	7.44		−0.10	−14.51	250.03
$H_2BI_2^-$ ($^1A_1$ - C_{2v})	376.86	14.09		−0.11	−14.51	348.15
HBI_2F^- ($^1A'$ - C_s)	430.32	11.32		−0.67	−14.90	403.44
$H_2B(NH_2)_2^-$ ($^1A'$ - C_s)	748.21	45.54	2.25	−0.68	−0.03	704.21
$HB(NH_2)_2F^-$ ($^1A'$ - C_s)	811.82	41.89	2.30	−1.02	−0.42	770.79
$H_2B(OH)_2^-$ (^1A - C_2)	643.16	30.61	1.69	−0.78	−0.47	612.99
$HB(OH)_2F^-$ (^1A - C_1)	712.39	27.10	1.80	−1.14	−0.86	685.10
$H_2B(SH)_2^-$ (^1A - C_2)	556.26	25.24	1.80	−0.87	−1.15	530.81
$HB(SH)_2F^-$ ($^1A'$ - C_s)	610.93	21.33	1.84	−1.18	−1.54	588.72
BF_3^- ($^2A_1$ - C_{3v})	453.58	6.14	1.38	−1.07	−1.20	446.55
BF_4^- ($^1A_1$ - T_d)	631.23	8.90	1.58	−1.50	−1.59	620.82
BCl_3^- ($^2A_1$ - C_{3v})	335.80	3.86	1.45	−0.81	−2.55	330.04
$HBCl_3^-$ ($^1A_1$ - C_{3v})	441.60	10.47	1.56	−0.83	−2.55	429.32
BCl_3F^- ($^1A_1$ - C_{3v})	499.68	6.22	1.64	−1.15	−2.94	491.01
BCl_4^- ($^1A_1$ - T_d)	455.10	5.33	1.73	−0.99	−3.39	447.12
BBr_3^- ($^2A_1$ - C_{3v})	297.52	3.08	3.30	−1.75	−10.53	285.46
$HBBr_3^-$ ($^1A_1$ - C_{3v})	402.29	9.67	3.30	−1.72	−10.53	383.68
BBr_3F^- ($^1A_1$ - C_{3v})	457.37	5.31	3.44	−1.75	−10.92	442.82
BBr_4^- ($^1A_1$ - T_d)	398.42	4.10	4.16	−1.86	−14.03	382.58
BI_3^- ($^2A_1$ - C_{3v})	260.33	2.59		−0.11	−21.75	235.88
HBI_3^- ($^1A_1$ - C_{3v})	363.00	9.04		−0.12	−21.75	332.09
BI_3F^- ($^1A_1$ - C_{3v})	414.65	4.73		−0.67	−22.14	387.11
BI_4^- ($^1A_1$ - T_d)	342.84	3.36		−0.14	−28.99	310.36
$HB(NH_2)_3^-$ ($^1A'$ - C_s)	943.30	57.14	2.80	−0.98	−0.03	887.95
$B(NH_2)_3F^-$ ($^1A'$ - C_s)	1010.16	53.59	2.92	−1.34	−0.42	957.72
$B(NH_2)_4^-$ ($^1A_1$ - D_{2d})	1139.00	68.67	3.38	−1.30	−0.03	1072.38
$HB(OH)_3^-$ (^1A - C_3)	785.95	33.72	2.00	−1.16	−0.69	752.38
$B(OH)_3F^-$ (^1A - C_3)	857.05	30.39	2.15	−1.54	−1.08	826.19
$B(OH)_4^-$ (^1A - S_4)	933.82	38.04	2.34	−1.56	−0.91	895.64
$HB(SH)_3^-$ (^1A - C_3)	641.63	26.04	2.13	−1.19	−1.71	614.82
$B(SH)_3F^-$ (^1A - C_3)	697.99	21.99	2.06	−1.52	−2.10	674.43
$B(SH)_4^-$ (^1A - S_4)	726.49	26.63	2.48	−1.54	−2.27	698.53

[a] Extrapolated by using eq 1 with aV*n*Z, n = D, T, Q. [b] The zero point energies were obtained as described in the text. [c] Core−valence corrections were obtained with the cc-pwCVTZ (B, N, O, F, S, Cl, and Br) and cc-pwCVTZ-PP (I) basis sets at the optimized MP2/aVTZ geometries. [d] The scalar relativistic correction is based on a CISD(FC)/VTZ MVD calculation and is expressed relative to the CISD result without the MVD correction, that is, including the existing relativistic effects resulting from the use of a relativistic effective core potential. For molecules containing Br, the scalar relativistic correction was calculated using the DKH method as described in the text. [e] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on C. Moore's Tables, Reference 28. [f] The theoretical value of the dissociation energy to atoms $\sum D_0(0K)$. [g] Reference 36. [h] Unscaled ZPE is 14.73 kcal/mol.

electron (step 1), the capture of the electron by the Lewis acid (LA) including the reorganization energy resulting from the structural change from LA to LA^- (step 2), and the subsequent formation of the $[LA{-}H]^-$ bond (step 3). As described above, there are issues with the use of the appropriate value for step 2. For the thermodynamic cycle depicted

Table 2. Enthalpies of Formation (kcal/mol) at 0 and 298 K[a]

molecule	$\Delta H_f(0\ K)_{theory}$	$\Delta H_f(298\ K)_{theory}$
BH_3[b]	25.3	24.4[25.5 ± 2.4[c]]
BH_3^-	24.5	23.7
BH_4^-[b]	−12.7	−14.6
H_3BF^-	−99.9	−101.7
H_2BF	−72.3	−73.3
H_2BF^-	−61.3	−62.2
$H_2BF_2^-$	−199.0	−200.7
H_2BCl	−17.6	−18.5
H_2BCl^-	−19.0	−19.7
H_3BCl^-	−62.9	−64.7
H_2BClF^-	−155.9	−157.5
H_2BBr	0.1	−2.6
H_2BBr^-	−6.8	−9.3
H_3BBr^-	−51.6	−55.2
H_2BBrF^-	−143.7	−147.0
H_2BI	17.6	16.3
H_2BI^-	4.4	3.3
H_3BI^-	−41.2	−43.3
H_2BIF^-	−131.3	−133.2
$H_2B(NH_2)$[b]	−17.0	−19.7
$H_3B(NH_2)^-$	−19.3	−22.8
$H_2B(NH_2)F^-$	−115.6	−118.9
$H_2B(OH)$	−63.7	−65.6
$H_3B(OH)^-$	−76.7	−79.2
$H_2B(OH)F^-$	−176.0	−178.4
$H_2B(SH)$	−0.7	−2.4
$H_3B(SH)^-$	−35.2	−37.6
$H_2B(SH)F^-$	−126.9	−129.0
HBF_2	−174.6	−175.5[-175.4 ± 0.8[c]]
HBF_2^-	−155.5	−156.3
HBF_3^-	−305.7	−307.1
$HBCl_2$	−58.9	−59.6[-59.3 ± 1.0[c]]
$HBCl_2^-$	−64.7	−65.2
$H_2BCl_2^-$	−111.5	−113.0
$HBCl_2F^-$	−206.9	−208.0
$HBBr_2$	−23.0	−27.2[-25.0 ± 1.2[c]]
$HBBr_2^-$	−38.1	−42.1
$H_2BBr_2^-$	−84.8	−89.8
$HBBr_2F^-$	−178.0	−182.5
HBI_2	12.0	10.6
HBI_2^-	−12.1	−13.3
$H_2BI_2^-$	−58.6	−60.7
HBI_2F^-	−147.0	−148.8
$HB(NH_2)_2$	−45.9	−49.9
$H_2B(NH_2)_2^-$	−34.3	−39.1
$HB(NH_2)_2F^-$	−134.0	−138.4
$HB(OH)_2$	−152.0	−154.6
$H_2B(OH)_2^-$	−153.4	−156.5
$HB(OH)_2F^-$	−258.7	−261.4
$HB(SH)_2$	−20.4	−22.5
$H_2B(SH)_2^-$	−57.9	−60.5
$HB(SH)_2F^-$	−148.9	−151.0
BF_3	−270.7	−271.4[-271.5 ± 0.2[d]]
BF_3^-	−256.0	−256.5
BF_4^-	−411.8	−413.0
BCl_3	−96.4	−96.7[-96.3 ± 0.5[c]]
BCl_3^-	−109.2	−109.2
$HBCl_3^-$	−156.8	−157.8
BCl_3F^-	−251.7	−252.2
BCl_4^-	−197.7	−198.0
BBr_3	−43.0	−48.3[-48.8 ± 0.05[c]]
BBr_3^-	−65.8	−71.0
$HBBr_3^-$	−112.4	−118.5
BBr_3F^-	−204.7	−210.3
BBr_4^-	−134.7	−141.8
BI_3	8.6	7.6[17 ± 12[c]]
BI_3^-	−23.9	−24.8
HBI_3^-	−68.5	−70.3
BI_3F^-	−156.7	−157.9
BI_4^-	−72.8	−74.7
$B(NH_2)_3$	−70.1	−74.9
$HB(NH_2)_3^-$	−53.9	−60.0
$B(NH_2)_3F^-$	−156.8	−162.5
$B(NH_2)_4^-$	−74.1	−81.5
$B(OH)_3$	−236.7	−239.8[-237.2 ± 0.6[c]]
$HB(OH)_3^-$	−233.8	−236.9
$B(OH)_3F^-$	−340.8	−343.7
$B(OH)_4^-$	−318.1	−321.9
$B(SH)_3$	−36.3	−38.4
$HB(SH)_3^-$	−76.2	−78.8
$B(SH)_3F^-$	−169.0	−171.2
$B(SH)_4^-$	−94.3	−96.9

[a] Experimental values are given in square brackets. [b] Reference 36. [c] Reference 7. [d] Reference 6.

Table 3. Calculated Hydride (HA) and Fluoride (FA) Affinities in kcal/mol at 0 and 298 K

	HA		FA	
molecule	(0 K)	(298 K)	(0 K)	(298 K)
H_3B	72.3	73.7	65.2	66.6
H_2BF	61.8	63.2	66.7	67.9
H_2BCl	79.5	80.9	78.3	79.4
H_2BBr	86.0	87.3	83.8	84.9
H_2BI	93.0	94.3	88.9	89.9
H_2BNH_2	36.6	37.8	38.6	39.7
H_2BOH	47.2	48.4	52.3	53.3
H_2BSH	68.8	69.8	66.2	67.0
HBF_2	58.6	60.0	71.0	72.1
$HBCl_2$	86.9	88.1	88.0	88.9
$HBBr_2$	96.0	97.3	95.0	95.8
HBI_2	104.8	106.0	99.0	99.9
$HB(NH_2)_2$	22.6	24.0	28.1	29.0
$HB(OH)_2$	35.6	36.6	46.6	47.3
$HB(SH)_2$	71.7	72.7	68.5	69.0
BF_3	69.2	70.5	81.1	82.1
BCl_3	94.6	95.8	95.2	96.0
BBr_3	103.6	104.9	101.7	102.4
BI_3	111.4	112.6	105.3	105.9
$B(NH_2)_3$	18.0	19.8	26.7	28.1
$B(OH)_3$	31.3	31.8	44.1	44.4
$B(SH)_3$	74.2	75.2	72.7	73.3

in Figure 1(a), we predicted the electron affinities of all of the compounds in our study (Table 5) at the density functional theory (DFT) level with the B3LYP exchange-correlation functional[37] and the aVTZ basis set, and, for some, at the CCSD(T)/CBS level. We employ the usual convention that a positive EA signifies that a molecule will bind an extra electron and a negative EA that it will not. In a thermodynamic cycle, this means that if a molecule has a positive EA that the detachment energy is positive and the attachment energy is negative. The DFT values are in good agreement with the CCSD(T)/CBS values for the larger positive EAs and differ somewhat more for negative EAs or weakly positive EAs. BH_3 is predicted to weakly bind an electron with a very small positive EA value of 0.8 kcal/mol, about 1 kcal/mol less than that for CH_3.[38] This value is in excellent agreement with experiment within 0.01 eV.[35] Substitution of one to three H atoms by F atoms to form H_2BF, HBF_2 and BF_3 yields negative EAs, so these boranes will not bind a free

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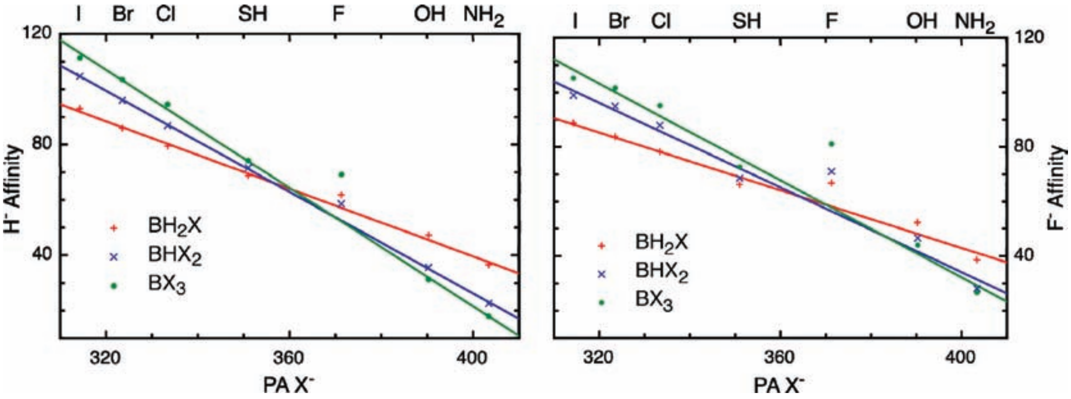

Figure 2. Hydride and fluoride affinities of the $BH_{3-n}X_n$ compounds in kcal/mol at 0 K show a linear correlation with the proton affinity of X^-. Values for X = F deviate from the trend line drawn through the points for I, Br, Cl, SH, OH, and NH_2.

Table 4. Calculated X^- Affinities (XA; X = Cl, Br, I, NH_2, OH, and SH) in kcal/mol at 0 and 298 K

molecule	X	(0 K)	(298 K)
H_3B	Cl	33.4	33.2
H_3B	Br	27.5	27.2
H_3B	I	21.5	21.2
H_3B	NH_2	72.0	73.9
H_3B	OH	69.2	69.3
H_3B	SH	39.7	41.2
H_2BF	Cl	28.8	28.3
H_2BF	Br	21.9	21.4
H_2BF	I	14.1	13.4
H_2BF	NH_2	70.7	72.4
H_2BF	OH	70.9	70.9
H_2BF	SH	33.8	35.0
H_2BCl	Cl	39.1	38.6
H_2BBr	Br	35.5	34.8
H_2BI	I	31.3	30.5
H_2BNH_2	NH_2	15.8	16.0
H_2BOH	OH	56.8	56.6
H_2BSH	SH	16.7	17.2
$HBCl_2$	Cl	43.1	42.3
$HBBr_2$	Br	39.3	38.3
HBI_2	I	35.6	34.4
$HB(NH_2)_2$	NH_2	35.4	36.9
$HB(OH)_2$	OH	48.9	48.0
$HB(SH)_2$	SH	35.0	35.6
BCl_3	Cl	46.4	45.4
BBr_3	Br	42.3	41.1
BI_3	I	36.9	36.2
$B(NH_2)_3$	NH_2	31.4	33.3
$B(OH)_3$	OH	48.5	47.7
$B(SH)_3$	SH	37.2	37.7

electron and the appropriate value for use in step 2 is thus 0. The EAs of the BX_3 compounds for X = Cl, Br, and I are all positive so they will bind an electron. The calculated EAs for BCl_3 and BBr_3 are in good agreement with the experimental values[39] considering the rather large error bars. For BCl_3, we would recommend a value at the higher end of the experimental range. The EA increases with increasing atomic number of the substituent, with BI_3 having the highest EA. The EAs of the BX_3 compounds for X = halogen correlate directly with the B−X bond order, which decreases with increasing atomic number. The decrease in bond order is due to decreasing back-donation of electron density from the halogen ligand to boron so that the vacant orbital on the B is more available to add a negatively charged species such as an electron, H^-, or F^-. The changes in the relative HA and FA values mirror the changes in the positive EAs so step 2 in the cycles 1(a) and 1(b) of Figure 1 is important in providing the relative ordering the HA or FA values if the borane binds an electron.

We searched for other possible energetic properties that would correlate with the HA and FA to develop qualitative predictors. Properties such as atomic charges and molecular orbital energies of the $BH_{3-n}X_n$ compounds were found to be generally poor predictors of HA, probably because such properties of either the initial A or the final HA^- are inadequate to capture the effects of R substitution on both initial and final states.

We did observe that the HA and FA of $BH_{3-n}X_n$ tended to correlate linearly with the PA of the substituent X^- (the enthalpic component of the gas phase acidity), which equates directly to the enthalpy for dissociation of HX into H^+ and X^- (the enthalpic component of the gas phase acidity of HX). Figure 2 shows the HA and FA from Table 3 plotted against literature values[40] for PA(X). Different lines (6 in all) are obtained for the HA and FA and for different values of *n*. Each line is a linear fit to the data except for X = F and X = H. The data points for X = F (i.e., $BH_{3-n}F_n$) deviate from the respective lines and the deviation increases with *n*. The data points for X = H corresponding to HA and FA of BH_3 are not plotted in Figure 2 as they deviate significantly from the trend lines. Like the data for X = F, the affinity of BH_3 for H^- is greater than predicted by the PA of H^-. The acidity of HX can be considered in part to be a measure of the ability of a group X to stabilize negative charge. From this perspective, the F when attached to B, as a group, is better at stabilizing negative charge than when it is by itself. This is also the case for H and Me. We will comment on this after discussing reasons for the observed correlation.

The thermodynamic cycle shown in Figure 1(a) shows that we can calculate the BDE for the B−A bond in $BH_{3-n}X_n$−A^- by use of the other quantities in the cycle, which we already have. These BDEs are given in Table 6 where we set the EA = 0 if the corresponding Lewis acid repels an electron, that is, the EA is negative. From the data in Table 6, it is clear that the dominant component of determining the absolute magnitude of the hydride, fluoride, or X^- affinities of the boranes is the $BH_{3-n}X_n$−A^- bond dissociation energy.

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Table 5. Calculated Electron Affinities at 0 K at the CCSD(T)/CBS and B3LYP/aVTZ Levels

molecule	CCSD(T) kcal/mol	CCSD(T) eV	B3LYP kcal/mol	B3LYP eV	expt. eV
BH_3	0.8	0.031	4.5	0.17	0.038 ± 0.015[a]
H_2BF	−11.0	−0.42	−15.9	−0.61	
H_2BCl	1.4	0.05	4.7	0.18	
H_2BBr	6.6	0.26	8.6	0.33	
H_2BI	13.2	0.51	14.7	0.56	
HBF_2	−19.1	−0.73	−13.4	−0.51	
$HBCl_2$	5.8	0.22	9.0	0.35	
$HBBr_2$	14.8	0.57	15.7	0.60	
HBI_2	24.0	0.92	25.0	0.96	
BF_3	−14.7	−0.56	−8.9	−0.34	
BCl_3	12.7	0.49	14.4	0.55	0.33 ± 0.20[b]
BBr_3	22.5	0.86	23.2	0.89	0.82 ± 0.20[b]
BI_3	32.5	1.25	33.0	1.27	
H_2BNH_2			−8.6	−0.33	
H_2BOH			−8.8	−0.34	
H_2BSH			−4.6	−0.17	
$HB(NH_2)_2$			−7.9	−0.30	
$HB(OH)_2$			−6.2	−0.24	
$HB(SH)_2$			−4.6	−0.18	
$B(NH_2)_3$			−6.1	−0.24	
$B(OH)_3$			−5.3	−0.20	
$B(SH)_3$			1.8	0.07	

[a] Reference 35. Laser photoelectron spectroscopy. [b] Reference 39. Neutral beam ionization potentials.

We looked for but did not find a thermodynamic cycle to equate the HA of $BH_{3-n}X_n$ with the PA of the X^- group. We did observe, however, that the HA of $BH_{3-n}X_n$ (n = 0, 1, 2, or 3) can be related to the anion affinity of $BH_{3-n}X_n$ via the thermodynamic cycle shown in Figure 1(c). Therefore, since the proton is a Lewis acid, it seems reasonable that the affinities of anions for protons and for the $BH_{3-n}X_n$ Lewis acids may exhibit a good correlation. Anane, Boutalib, and co-workers have demonstrated correlations of B dative bond energies with the PA of Lewis base ligands.[41] Consistent with this relationship, the plot in Figure 3 shows that the anion affinities of BH_3 and the PA of these anions, PA(X^-), are well correlated; the only exception being F^- for which the reaction with BH_3 releases more energy than expected.

As shown by the cycle of Figure 1(c), the difference between the HA of $BH_{3-n}X_n$ and the anion affinities of $BH_{3-n}X_n$ amounts to the differences in the homolytic B−X and B−H BDEs and the EAs of X and H. Therefore, the goodness of the correlation between HA or FA of $BH_{3-n}X_n$ and the PA of X^- depends on how well the differences between the BDE and EA changes exhibit the same trends as the PAs of X^-.

In the plots shown in Figures 2 and 3, the compounds with X = F deviate from the trends followed by the other atoms and groups. This deviation might be caused by anomalies in the homolytic B−F BDEs and/or the EA of F that determine the PA of F^-.[42] As can be seen from Figure 4, which shows plots of the EAs of the halogen atoms and of the B−X BDEs of BH_2X and BHX_2 against the homolytic BDEs of the corresponding acids, D(HX), the main culprit for the deviation is the anomalously low EA of F.[43] The EAs of the halogens increase linearly with D(HX) for I, Br, and Cl, but falls considerably below the trend line for F. For the EA of F to be on the trend line, the BDE of HF would have to be close to that of HBr. As we had calculated the homolytic BDEs of the $[BH_3{-}X]^-$ and $BH_2{-}X$ compounds,[1] we also plotted them against the HX BDEs in Figure 4. The values including those for the F-substituted compounds follow linear trends suggesting that the B−F BDEs are normal. Finally, we note that the HAs of BH_3 and BMe_3[4] also deviate significantly from the trend lines plotted in Figure 2. The values deviate upward from the lines indicating that the PAs of H^- and Me^- also are not good predictors. As with F, the EAs of H and CH_3 are also low, whereas the B−H and B−C bond dissociation energies follow the expected trend lines. The low values for the EAs show that the free gas phase radicals H and CH_3 do not stabilize excess negative charge as well as when bonded as substituents to boron.

One of the more interesting results is that the fluoride affinities of the boron trihalides BX_3 increase with increasing atomic number of X, so that BF_3 has the lowest FA and BI_3 has the highest FA. This trend has been discussed previously[44] for other Lewis acid strength descriptors, such as the NH_3 affinities of BF_3 and BCl_3, and several authors have offered different explanations for this observation. These include the energy of the BX_3 LUMO[45] and the distortion energy for the BX_3 to form the complex BH_3A (ligand close packing).[46] Brinck et al.[47] suggested that the larger BDE for NH_3BCl_3 is due to increased charge capacity in BCl_3 and not to the stronger overlap of the out of plane p orbitals on F with the vacant p orbital on B. Hirao et al.[48] argue that the backbonding to the unoccupied p orbital on B is not the major factor but that the LUMO is more stable and thus more available (lower acidic hardness) leading to a larger

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[41] Anane, H.; Boutalib, A.; Tomas, F. *J. Phys. Chem. A* **1997**, *101*, 7879. Anane, H.; El Houssame, S.; El Guerraze, A.; Guermoune, A.; Boutalib, A.; Jarid, A.; Nebot-Gil, I.; Tomas, F. *Cent. Eur. J. Chem.* **2008**, *6*, 400.

[42] PA(X^-) = D(X−H) − EA(X) + IP(H) where D(X−H) is the enthalpy for homolysis of the X−H bond, EA(X) is the electron affinity of X, and IP is the ionization energy of H; by convention EA is a positive number if the electron is bound.

[43] Cox, J. D.; Wagman, D. D.; Medvedev, V. A., *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Corp.: New York, 1984, p 1.

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[46] Rowsell, B. D.; Gillespie, R. J.; Heard, G. L. *Inorg. Chem.* **1999**, *38*, 4659.

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Table 6. Calculated $BH_{3-n}X_n-A^-$ Bond Dissociation Energies in kcal/mol at 0 K[a]

molecule	A	(0 K)
H_3B	H	88.8
H_2BF	H	79.2 (90.2)
H_2BCl	H	92.3
H_2BBr	H	96.7
H_2BI	H	97.2
H_2BNH_2	H	53.9
H_2BOH	H	64.6
H_2BSH	H	86.2
HBF_2	H	76.0 (95.1)
$HBCl_2$	H	98.5
$HBBr_2$	H	98.6
HBI_2	H	98.1
$HB(NH_2)_2$	H	40.0
$HB(OH)_2$	H	53.0
$HB(SH)_2$	H	89.1
BF_3	H	86.6 (101.2)
BCl_3	H	99.3
BBr_3	H	98.6
BI_3	H	96.3
$B(NH_2)_3$	H	35.4
$B(OH)_3$	H	48.7
$B(SH)_3$	H	91.6
H_3B	F	142.8
H_2BF	F	145.1 (156.1)
H_2BCl	F	155.4
H_2BBr	F	155.6
H_2BI	F	154.2
H_2BNH_2	F	117.0
H_2BOH	F	130.8
H_2BSH	F	144.6
HBF_2	F	149.5 (168.5)
$HBCl_2$	F	160.6
$HBBr_2$	F	158.6
HBI_2	F	153.4
$HB(NH_2)_2$	F	106.6
$HB(OH)_2$	F	125.1
$HB(SH)_2$	F	146.9
BF_3	F	159.5 (174.2)
BCl_3	F	160.9
BBr_3	F	157.7
BI_3	F	151.3
$B(NH_2)_3$	F	105.1
$B(OH)_3$	F	122.5
$B(SH)_3$	F	151.2
H_3B	Cl	115.9
H_2BF	Cl	112.1 (123.1)
H_2BCl	Cl	121.0
$HBCl_2$	Cl	120.6
BCl_3	Cl	117.0
H_3B	Br	104.2
H_2BF	Br	99.5 (110.5)
H_2BBr	Br	106.4
$HBBr_2$	Br	102.1
BBr_3	Br	97.4
H_3B	I	91.3
H_2BF	I	84.6 (95.7)
H_2BI	I	88.6
HBI_2	I	82.1
BI_3	I	74.9
H_3B	NH_2	89.0
H_2BF	NH_2	88.5 (99.5)
H_2BNH_2	NH_2	33.6
$HB(NH_2)_2$	NH_2	53.1
$B(NH_2)_3$	NH_2	49.1
H_3B	OH	110.5
H_2BF	OH	113.0 (124.1)
H_2BOH	OH	99.0
$HB(OH)_2$	OH	91.1
$B(OH)_3$	OH	90.7
H_3B	SH	92.4
H_2BF	SH	87.2 (98.2)
H_2BSH	SH	70.1
$HB(SH)_2$	SH	88.4
$B(SH)_3$	SH	90.7

[a] Values in parentheses include calculated negative EA values of the fluoroboranes.

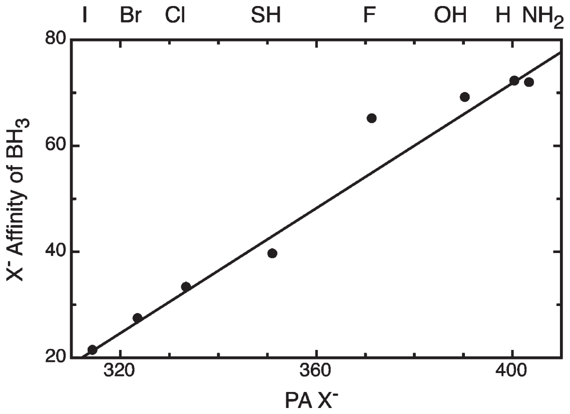

Figure 3. I^-, Br^-, Cl^-, SH^-, OH^-, and NH_2^- anion affinities of BH_3 in kcal/mol at 0 K correlate linearly with the PAs of these anions, but the point for F^- deviates from the trend line.

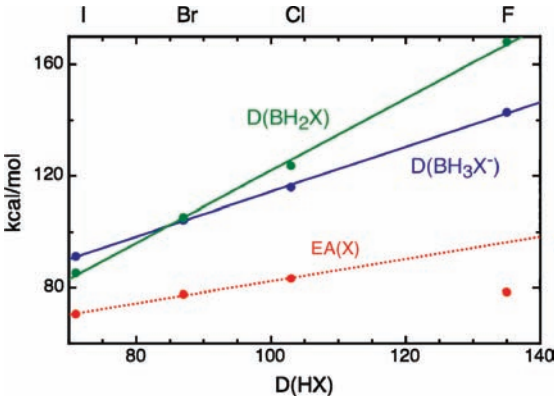

Figure 4. Plots of the homolytic B−X BDEs for BH_2X and BH_3X^- against the homolytic HX BDEs for the halogen series. For I, Br, and Cl, the EAs increase linearly with the homolytic HX BDEs; however, the EA for F falls way below the trend line suggesting that it is anomalously low.

BDE. Branchadell and Oliva[49] used charge density analysis to predict that the increase in Lewis acidity from BF_3 to BBr_3 is due to the EA differences and the nature of the boron-halogen bond. They calculated the distortion energy to reach an angle of 113.5° and showed that BF_3 requires more energy than BBr_3.

Our analysis shows that, on the basis of the charge distributions alone, BF_3 should have the highest FA as it has the largest positive natural orbital[50] charge on B (BF_3(1.53 e), BCl_3(0.41 e), BBr_3(0.05 e), and BI_3(−0.40 e)) and BI_3 the smallest one. However, the calculated EAs (Table 5) show that BF_3 cannot bind an electron and that the EAs increase from BCl_3 to BI_3. The NBO charge distribution tends to exaggerate the ionic character of a bond. The large positive charge on the B in BF_3 can be explained by the strong electron withdrawing inductive effect of the highly electronegative fluorine ligands (sigma effect). However, for the electron affinity, this sigma effect is outweighed by the strong back-donation from the out-of-plane p orbital of fluorine into the empty p orbital on B, which has the opposite effect and leads to an inability to bind an electron. As shown

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(49) Branchadell, V.; Oliva, A. *J. Mol. Struct.: THEOCHEM* **1991**, *236*, 75.

(50) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

Table 7. Distortion Energies at 0 K in kcal/mol at the B3LYP/aVDZ and CCSD(T)/aVTZ Levels

molecule	$\Delta E_{\mathrm{distort}}1(\mathrm{BX_3}^-)^a$ B3LYP	$\Delta E_{\mathrm{distort}}1(\mathrm{BX_3}^-)^a$ CCSD(T)	$\Delta E_{\mathrm{distort}}2(\mathrm{BX_3F}^-)^b$ B3LYP	$\Delta E_{\mathrm{distort}}2(\mathrm{BX_3F}^-)^b$ CCSD(T)
BF_3	34.4	38.1	42.6	47.1
BCl_3	26.6	29.1	37.8	40.9
BBr_3	20.2	22.1	31.1	33.5
BI_3	14.7	16.3	26.9	29.0

[a] Distortion Energy1 = *E*(distorted Structure BX_3^- geometry) − *E*(planar, ground state minimum BX_3)). [b] Distortion Energy2 = *E*(distorted Structure BX_3F^- geometry) − *E*(planar, ground state minimum BX_3)).

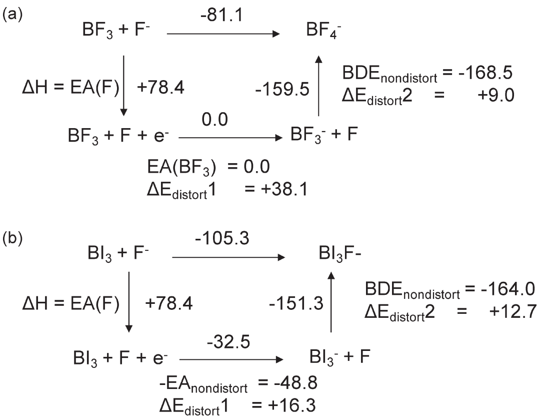

Figure 5. Born−Haber cycles for the FAs of BF_3 and BI_3. For each step, the total energies and the energies of each component are given in kcal/mol. The values for the overall reaction are the sums of steps 1−3 given by the values inside the square defined by the arrows. The values outside the square defined by the arrows are the conceptual values, which include the effect of the distortion energies calculated for BX_3 at the BX_3^- and BX_3F^- geometries (CCSD(T) values from Table 7). These values are provided as guidelines for understanding the roles of the various terms. The EA of BF_3 is negative so it is set to 0.

in the orbital diagrams in the Supporting Information, the amount of back-donation in BF_3 is stronger than that in BI_3. Using average covalent atomic radii,[51] we find that the B−F bond distance[1] (1.315 Å) in BF_3 is 10% shorter than the sum of the covalent radii (1.46 Å). The B−Cl (1.745 Å), B−Br (1.908 Å), and B−I (2.132 Å) bond distances[1] are shorter by 7%, 6%, and 4% in BCl_3, BBr_3, and BI_3, respectively, than the sum of the covalent radii. This is consistent with the larger pi backbonding in BF_3.

A second energetic effect that plays an important role is the energy needed to distort the geometry at the boron from planar BX_3 to tetrahedral BX_3F^-. This distortion energy can be broken down into two components. The first component is the energy required to distort BX_3 from its planar structure to a pyramidal structure having the same geometry as in BX_3^-. The second component is the distortion from pyramidal to tetrahedral BX_3^-, which has the same geometry as the BX_3 part of BX_3F^-. These distortion energies were calculated and are summarized in Table 7. Using these values, additional components can be included in the various steps in the Born−Haber cycles we have written for the F^- affinities of BF_3 and BI_3 (see Figure 5 for X = F and I). This allows a quantitative analysis of the relative contributions of EAs, BDEs, and distortion energies to the Lewis acidities of BF_3 and BI_3, thus providing more detailed energetic insight as to why BI_3 is a stronger Lewis acid than BF_3.

As can be seen from Figure 5, the energies of step 1 (the ionization potential of F^-) are identical for both X = F and X = I. The energies of step 3 (conceptually the sum of an "undistorted" B−F BDE in BX_3^-−F and the distortion energy from the pyramidal to the tetrahedral geometry of BX_3^-) are also comparable. The major difference between the cycle for X = F and that for X = I arises from step 2, which is the EA of BX_3 (conceptually the sum of the undistorted EA of BX_3 and the associated distortion energy from planar to pyramidal BX_3). For the purpose of the Born−Haber cycles, step 2 of the BF_3 cycle was set equal to zero because a negative EA (positive value for the reaction enthalpy due to a repulsive interaction between BF_3 and the electron) is physically not meaningful. Thus, step 2 is responsible for the higher Lewis acidity of BI_3, and the EA of BX_3 makes by far the largest contribution to the relative differences in the acidities. The fact that the EA of BI_3 is higher than that of BF_3 can be explained by the fact that fluorine is a better π-backdonor than iodine, resulting in a higher occupation of the empty p_z orbital (LUMO) of boron. The calculations show that the large distortion energy in BF_3 is important in preventing BF_3 from readily binding an electron. Although, the energetics of step 2 govern the relative acidities, the overall magnitudes are governed by the strength of the X_3B^-−F bonds, which are quite large, consistent with the large value for the BF_2−F bond energy of 170.3 kcal/mol at 0 K.[1]

Conclusions

The enthalpies of formation at 0 and 298 K are predicted for a range of anionic substituted borane compounds, $BH_{4-n}X_n^-$ and $BH_{3-n}X_nF^-$ for X = F, Cl, Br, I, NH_2, OH, and SH, on the basis of coupled cluster theory (CCSD(T)) calculations extrapolated to the complete basis set limit. The calculated enthalpies of formation allow the prediction of the H^-, F^-, and X^- affinities to within ±1.0 kcal/mol, dramatically improving the previous estimates of these important quantities. The hydride affinity is defined as $-\Delta H$ for the reaction $BH_{3-n}X_n + H^- \rightarrow BH_{4-n}X_n^-$, with similar considerations for the fluoride and X^- affinities. For the BX_3 series, the highest hydride and fluoride affinities are predicted for BI_3 at 112.6 and 105.9 kcal/mol, respectively, and the lowest ones for $B(NH_2)_3$ at 19.8 and 28.1 kcal/mol, respectively, at 298 K. The highest X^- affinity within the BX_3 series to form BX_4^- is found for BF_3 at 82.1 kcal/mol and the lowest one for $B(NH_2)_3$ at 33.3 kcal/mol, at 298 K. For the HBX_2 compounds, HBI_2 has the highest hydride and fluoride affinities at 106.0 and 99.9 kcal/mol, respectively, and $HB(NH_2)_2$ has the lowest ones at 24.0 and 29.0 kcal/mol, respectively, at 298 K. The highest X^- affinity is predicted for HBF_2 at 72.1 kcal/mol at 298 K, while HBI_2 is predicted to have the lowest one at 34.4 kcal/mol at 298 K. Similar

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(51) Emsley, J., *The Elements*, 2nd ed.; Clarendon Press: Oxford, 1994.

trends were observed for the H_2BX compounds with the highest H^- and F^- affinities predicted for H_2BI at 94.3 and 89.9 kcal/mol, respectively, and the lowest ones for H_2BNH_2 at 37.8 and 39.7 kcal/mol, respectively, at 298 K, while H_2BF and H_2BNH_2 are predicted to have the highest and lowest X^- affinities at 67.9 and 16.0 kcal/mol, respectively, at 298 K.

The dominant component of determining the absolute magnitude of the hydride, fluoride, or X^- affinities of the boranes is the $BH_{3-n}X_n{-}A^-$ bond dissociation energy. The H^- and F^- affinities of $BH_{3-n}X_n$, that is, their Lewis acidities, correlate linearly with the proton affinities of the substituent X^-, that is, their gas phase Brønsted acidities. A decreasing proton affinity of the corresponding base, X^-, corresponds to an increase in the Brønsted acidity of HX and in the Lewis acidities of $BH_{3-n}X_n$ although the absolute values go in opposite directions because of their different definitions. This correlation also accounts for the fact that BI_3 is the strongest Lewis acid in our series, in the same way as HI is the strongest gas phase Brønsted acid. The only deviations from this correlation are observed for X being H and F. These deviations can be attributed to the anomalous values of the electron affinities of the F and H atoms relative to the homolytic bond dissociation energies of the B−F and B−H bonds, respectively, that determine the proton affinities of the corresponding X^- anions. The fact that BI_3 is a stronger Lewis acid than BF_3 is primarily due to its higher electron affinity, which is influenced to some extent by the distortion energy from planar to pyramidal BX_3. The roles of the $X_3B^-{-}F$ bond dissociation energy and the concomitant distortion energy from pyramidal to tetrahedral BX_3^- in determining the relative acidities are considerably smaller. Since the electron affinity of BX_3 is strongly influenced by the charge density in the empty p_z LUMO of boron, the π-backdonation from the halogen to boron plays a very important role.

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Supporting Information Available: Full author citations for References 15 and 27. Optimized MP2/aVTZ geometry parameters for the $BH_{4-n}X_n^-$, $BH_{3-n}X_nF^-$, and $BH_{3-n}X_{n+1}^-$ compounds. Total CCSD(T) energies as a function of basis set. Total CCSD(T)/aV*n*Z-PP energies as a function of basis set. Calculated MP2/aVTZ frequencies (cm^{-1}). Enthalpies of formation (kcal/mol) at 0 and 298 K for the $BH_{4-n}X_n^-$, $BH_{3-n}X_nF^-$, and $BH_{3-n}X_{n+1}^-$ compounds where X = Br and I based on CCSD(T)/aV*n*Z-PP extrapolation. T_1 diagnostics calculated at the CCSD(T)/aVQZ level. Natural bond orbital analysis of the trihaloboranes at the B3LYP/aug-cc-pVDZ Level. Top view of occupied out-of-plane lone pair orbital on BX_3 and side view of empty p orbital on BX_3 for X a halogen. This material is available free of charge via the Internet at http://pubs.acs.org.