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Heats of Formation and Bond Energies of the $H_{(3-n)}BX_n$ Compounds for (X = F, Cl, Br, I, NH_2, OH, and SH)

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Atomization energies at 0 K and heats of formation at 0 and 298 K are predicted for the borane compounds $H_{(3-n)}BX_n$ for (X = F, Cl, Br, I, NH_2, OH, and SH) and various radicals from coupled cluster theory (CCSD(T)) calculations with an effective core potential correlation-consistent basis set for I. In order to achieve near chemical accuracy (±1.5 kcal/mol), three corrections were added to the complete basis set binding energies calculated from frozen core coupled cluster theory energies: a correction for core-valence effects, a correction for scalar relativistic effects, and a correction for first-order atomic spin−orbit effects. Vibrational zero point energies were computed at the MP2 level. The calculated heats of formation are in excellent agreement with the available experimental data for the closed shell molecules, but show larger differences with the reported "experimental" values for the BX_2 radicals. The heats of formation of the BX_2 radicals were also calculated at the G3(MP2) level of theory, and the values were in excellent agreement with the more accurate CCSD(T) values. On the basis of extensive comparisons with experiment for a wide range of compounds, our calculated values for these radicals should be good to ± 1.5 kcal/mol and thus are to be preferred over the experimental values. The accurately calculated heats of formation allow us to predict the B−X and B−H adiabatic bond dissociation energies (BDEs) to within ± 1.5 kcal/mol. The B−F BDEs in the $H_{(3-n)}BF_n$ compounds and in BF ($^1\Sigma^+$) are the largest BDEs in comparison to the other substituents that were investigated. The second and third largest B−X BDEs in the $H_{(3-n)}BX_n$ and BX compounds are predicted for X = OH and NH_2, respectively. The substituents have a minimal effect on the B−H BDEs in HBX_2 and H_2BX compared to the first B−H BDE of borane. The differences in adiabatic and diabatic BDEs, which are related to the reorganization energy in the product, can be estimated from singlet−triplet splittings in these molecules, and can account for the large fluctuations in adiabatic BDEs observed, specifically for the BX_2 and HBX radicals, during the stepwise loss of the respective substituents.

Introduction

There is substantial interest in the energetics of borane compounds as intermediates in regeneration cycles for chemical hydrogen storage systems. We are especially interested in the B−X and B−H bond dissociation energies (BDEs) in the BX_3, HBX_2, and H_2BX compounds, as well as the radicals BX_2 and HBX, which are products of varying bond breaking processes, where X = F, Cl, Br, I, NH_2, OH, and SH, for use in the investigation of the thermodynamics of regeneration schemes for spent fuel derived from ammonia borane. These compounds have other applications and are of substantial interest as model systems.[1] Following our recent work[2] on the BDEs in the PF_xO_y and SF_xO_y compounds, we define the diabatic BDE as dissociation to the configurations most closely representing the bonding configuration in the reactant and the adiabatic BDE as dissociation to the ground-state of the separated species. The adiabatic BDE will always be equal to or less than the diabatic BDE. Because it can be difficult to measure BDEs, high-level theoretical calculations of these quantities offer a unique opportunity to obtain accurate self-consistent values for these processes.

There have been a number of measurements of BDEs for these borane compounds, but many of them have not been as accurate as one would hope for.[3] The experimental dissociation energies for the diatomic haloboranes have been summarized by Huber and Herzberg.[4] The experimental heats of formation for the hydrogen halides,[5] the haloboranes,[6] the dihaloboranes (with the exception of diiodoborane),[6] the dihaloboryl radicals,[6] the trihaloboranes,[5,6] trihydroxyborane,[6] and the dihydroxyboryl radical[6] have been reported. The BDEs of the borane compounds $B(H)_x{-}H$ for x = 0, 1, and 2 have been reported.[7−9]

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.[10] We can 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[11] to predict BDEs in these boron compounds. Our approach is based on calculating the total atomization energy of a molecule and using this value with known heats of formation of the atoms to calculate the heat of formation at 0 K. The approach starts with coupled cluster theory with single and double excitations and includes a perturbative triples correction (CCSD(T)),[12−14] combined with the correlation-consistent basis sets[15,16] extrapolated to the complete basis set limit to treat the correlation energy of the valence electrons. This is followed by a number of smaller additive corrections including core−valence interactions and relativistic effects, both scalar and spin−orbit. The zero point energy can be obtained from experiment, theory, or a combination of the two. Corrections to 298 K can then be calculated by

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using standard thermodynamic and statistical mechanics expressions in the rigid rotor−harmonic oscillator approximation[17] and appropriate corrections for the heat of formation of the atoms.[18]

There have been several theoretical investigations into a couple of the molecules under study. The heats of formation of some small halogenated compounds, including the hydrogen halides, have been previously calculated using a similar approach at the CCSD(T)/CBS level plus additional corrections.[19] The authors noted that the largest errors in the calculated heats of formation were found for the molecules containing the I atom. In our recent study of the iodofluorides,[20] we found that it was necessary to correlate the core electrons with the aug-cc-pwCV*n*Z basis sets for n = D, T, or Q in order to extrapolate these quantities to the CBS limit to predict accurate heats of formation. The molecular atomization energies of BF_3 and BCl_3 have previously been reported at a comparable composite CCSD(T)/CBS level.[11i] Martin and Taylor have reported on the atomization energies of BF and BF_3 using the CCSD(T) method and used these results in an analysis of the heat of formation of the boron atom.[21] Bauschlicher and Ricca have reported CCSD(T)/CBS heats of formation on the basis of the atomization energies obtained with the cc-pV*n*Z basis sets up through n = 5 for BF_n, BF_n^+, BCl, and BCl_n^+ for $n = 1-3$.[22] Schlegel and Harris have reported the heats of formation of the BH_mCl_n species at the G-2 level of theory.[23] Rablen and Hartwig have reported on the sequential BDEs of borane compounds at the G-2 and CBS-4 levels of theory.[24] Baeck and Bartlett have studied BCl_3, BCl_2 BCl, and their anions and cations using the coupled-cluster and MBPT levels of theory and looked at their structure, spectra, and decomposition paths.[25]

Computational Approach. 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.[15,16] It has recently been found that tight *d* functions are necessary for calculating accurate atomization energies for second row elements,[26] 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. The CCSD(T) total energies were extrapolated in the normal way to the CBS limit by using a mixed exponential/Gaussian function of the form:

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

with n = 2 (aVDZ), 3 (aVTZ), and 4 (aVQZ), as first proposed by Peterson et al.[27]

In order to achieve thermochemical properties within ± 1 kcal/mol of experiment, it is necessary to account for core−valence correlation energy effects. Core−valence (CV) calculations were carried out with the weighted core−valence basis set cc-pwCVTZ.[28] 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 due to issues described elsewhere.[20] For I, we used the new effective core potential/correlation consistent basis sets developed by Peterson and co-workers.[29] 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 complete basis set 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-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. For the molecules containing I as a substituent, we also 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.

We also performed additional calculations for molecules containing Br using the new effective core potential/correlation consistent basis sets developed by Peterson and co-workers.[29] 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, and only the (ns^2, np^5) electrons are active in our valence correlation treatment. In these calculations, we will use aV*n*Z-PP to represent the combination of the aug-cc-pV*n*Z basis set on H and B and the aug-cc-pV*n*Z-PP basis set on Br. Core−valence calculations were also carried out with the weighted core−valence basis set cc-pwCVTZ for H and B,[28] and the cc-pwCVTZ-PP basis set for Br, which is based on the cc-pVTZ-PP basis set and accompanying small core RECP. For Br, the cc-pwCVTZ-PP basis set includes up through g-functions in order to provide a consistent degree of angular correlation for the active 4d electrons. The core−valence calculations for Br involve all 25 electrons outside the RECP core.

All of the current work was performed with the MOLPRO suite of programs.[30] The open-shell CCSD(T) calculations for the atoms were carried out at the R/UCCSD(T) level. In this approach, a restricted open-shell Hartree−Fock (ROHF) calculation was initially performed, and the spin constraint was relaxed in the coupled cluster calculation.[31−33] 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.

The geometries were optimized numerically for most of the molecules at the frozen core CCSD(T) level with the aVDZ and aVTZ correlation-consistent basis sets. The CCSD(T)/aVTZ geometries were then used in single-point CCSD(T)/aVQZ calculations. Diatomics were further optimized at the CCSD(T)/aVQZ level, and bond distances, harmonic frequencies, and anharmonic corrections were obtained from a fifth-order fit of the potential energy surface (PES) at this level. For the molecules containing I as a substituent, geometry optimizations were performed at the CCSD(T) level with the aVDZ-PP and aVTZ-PP basis sets and additionally with the aVQZ-PP basis set for the diatomic with a fit of the PES performed at this level. The CCSD(T)/aVTZ-PP geometery was then used in single-point CCSD(T)/aV*n*Z (n = D, T, Q) calculations. For $H_{(3-n)}BX_n$ (X = OH, NH_2), geometry optimizations were performed at the MP2/aVTZ level,[34] and the MP2/aVTZ geometry was consequently used in single-point CCSD(T)/aV*n*Z (n = D, T, Q) calculations.

The vibrational frequencies of the polyatomic molecules were calculated at the MP2/aVTZ level[34] using the Gaussian program system[35] in order to obtain the zero point energies and the thermal corrections at 298 K.

Two adjustments to the total atomization energy (TAE = ΣD_0) are necessary in order to account for relativistic effects in atoms and molecules. The first correction lowers the sum of the atomic energies (decreasing TAE) by replacing energies that correspond to an average over the available spin multiplets with energies for the lowest multiplets, as most electronic structure codes produce only spin multiplet averaged wave functions. The atomic spin−orbit corrections are $\Delta E_{\text{SO}}(\text{B}) = 0.03$ kcal/mol,

$\Delta E_{SO}(O) = 0.22$ kcal/mol, $\Delta E_{SO}(F) = 0.39$ kcal/mol, $\Delta E_{SO}(S) = 0.56$ kcal/mol, $\Delta E_{SO}(Cl) = 0.84$ kcal/mol, $\Delta E_{SO}(Br) = 3.50$ kcal/mol, and $\Delta E_{SO}(I) = 7.24$ kcal/mol from the tables of Moore.[36] A second relativistic correction to the atomization energy accounts for molecular scalar relativistic effects, ΔE_{SR}. ΔE_{SR} is taken as the sum of the mass-velocity and one-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[37] We evaluated ΔE_{SR} by using expectation values for the two dominant terms in the Breit−Pauli Hamiltonian, the so-called MVD corrections from configuration interaction singles and doubles (CISD) calculations. The quantity ΔE_{SR} was obtained from CISD wave function with a VTZ basis set at the CCSD(T)/aVTZ, CCSD(T)/aVTZ-PP, or MP2/aVTZ geometry. The CISD(MVD) approach generally yields ΔE_{SR} values in good agreement (±0.3 kcal/mol) with more accurate values from, for example, Douglass−Kroll−Hess (DKH) calculations, for most molecules. A potential problem arises in computing the scalar relativistic corrections for the molecules in this study, as there is the possibility of "double counting" the relativistic effect on I when applying an MVD correction to an energy that already includes most of the relativistic effects via the RECP. Because the MVD operators mainly sample the core region where the pseudo-orbitals are small, we assume any double counting to be small. For the molecules containing Br, the molecular scalar relativistic correction ΔE_{SR} was calculated using the spin-free, one-electron DKH Hamiltonian.[38−40] ΔE_{SR} was defined as the difference in the atomization energy between the results obtained from basis sets recontracted for DKH calculations[39] 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 CCSD(T)/cc-pVTZ-DK levels of theory.

By combining our computed ΣD_0 values with the known heats of formation at 0 K for the elements[6] $\Delta H_f^0(H) = 51.63$ kcal mol^{-1}, $\Delta H_f^0(B) = 135.1 \pm 0.2$ kcal mol^{-1},[41] $\Delta H_f^0(N) = 112.53$ kcal mol^{-1}, $\Delta H_f^0(O) = 58.99$ kcal mol^{-1}, $\Delta H_f^0(F) = 18.47$ kcal mol^{-1}, $\Delta H_f^0(S) = 65.66$ kcal mol^{-1}, $\Delta H_f^0(Cl) = 28.59$ kcal mol^{-1}, $\Delta H_f^0(Br) = 28.19$ kcal mol^{-1}, and $\Delta H_f^0(I) = 25.61$ kcal mol^{-1}, we can derive ΔH_f^0 values for the molecules under study in the gas phase. The heat of formation of the boron atom has changed over time. The original JANF value[6] was $\Delta H_f^0(0\text{ K,B}) = 132.7 \pm 2.9$ kcal/mol. Storms and Mueller[42] recommended a much larger value of 136.2 ± 0.2 kcal/mol, which, on the basis of the analysis of Ruscic and co-workers,[43] we have used in our previous work.[44−46] Martin and Taylor[47] calculated the atomization energies of BF and BF_3 using a composite approach based on CCSD(T), used these results to analyze of the heat of formation of the boron atom, and came to a similar conclusion as that of Ruscic.[43] More recently, Karton and Martin[41] revised their heat of formation of the B atom to 135.1 ± 0.2 kcal/mol on the basis of the experimental heats of formation of BF_3[5] and B_2H_6[48] coupled with W4 calculations of their total atomization energies, and this is the value we have used. We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.[18]

Results and Discussion

Geometries. The calculated geometry parameters with the aVTZ basis set are given in Table 1 and are in excellent agreement with the available structural data.[49] The electronic states and symmetry of the molecules are also given in Table 1 and consequently have been excluded from the other tables. The bond distance for the halide acids calculated with the aVDZ and aVTZ basis sets are given as Supporting Information (Table SM-1), and those for the remaining molecules calculated with the aVDZ basis set are also given in the Supporting Information (Table SM-2). The total CCSD(T) energies as a function of the aV*n*Z and aV*n*Z-PP (*n* = D, T, Q) basis sets are given in the Supporting Information in Tables SM-3 and SM-4, respectively. The calculated harmonic vibrational frequencies are also given as Supporting Information (Table SM-5). Finally, the components for the calculated atomization energies for the halide acids are given as Supporting Information (Table SM-6).

Heats of Formation. The energetic components for predicting the total molecular dissociation energies are given in Table 2, and we first describe some trends in the different components. The core−valence corrections for the molecules are all positive and range from 0.42 (BCl) to 3.44 kcal/mol ($B(NH_2)_3$). The scalar relativistic corrections are all small and negative, and range in values from −0.01 (BI) to −1.18 ($B(OH)_3$) kcal/mol, except for BBr with a 0.01 kcal/mol correction. We estimate that the error bars for the calculated heats of formation are ± 1.5 kcal/mol considering errors in the energy extrapolation, frequencies, and other electronic energy components. An estimate of the potential for significant multireference character in the wave function can be obtained from the T_1 diagnostic[50] for the CCSD calculation. The value for the T_1 diagnostics are small (<0.03) showing that the wave function is dominated by a single configuration. The T_1 diagnostics for the molecules are given as Supporting Information (Table SM-9).

The calculated heats of formation[51] at 0 and 298 K are given in Table 3, where they are compared with available experimental data. We use the calculated values at 298 K in our discussions below unless specified otherwise. Our calculated heats of formation for the hydrogen halides HX (X = F, Cl, Br, I) are in excellent agreement with the previously calculated[19] and experimental values.[5] Including the core electrons in the correlation and employing the weighted core basis sets for the CBS extrapolation, our calculated ΔH_f(HI) overestimates the experimental value by 0.5 kcal/mol.[5] Using the new heat of formation of the boron atom, we recalculated the values of ΔH_f(BH),[45] ΔH_f(BH_2),[45] ΔH_f(BH_3),[44] and ΔH_f(BH_2NH_2),[44] as given in Table 3.

Our calculated value for the ΔH_f(BF) is in excellent agreement with the value from a spectroscopic measurement,[4] the experimental value derived from a mass spectrometry study of the BF_2 radical,[52] and the JANAF[6] value (within the ± 3.3 kcal/mol error bars of the latter). Our calculated value is in excellent agreement with the high-level theoretical values[21,22] at the CCSD(T)/CBS level using basis sets up through aug-cc-pV6Z. The ΔH_f(BF) at the lower G-2 and CBS-4 levels[24] are in good agreement with our CCSD(T)/CBS value. Our calculated value for the ΔH_f(BCl) is in excellent agreement with the experimental value derived from a thermochemical analysis of the dissociation energy of BCl,[53] but differs from the JANAF value[6] by 9.6 kcal/mol and from the spectroscopically derived value[4] by 5.8 kcal/mol. The JANAF value was derived from the Cl_2B-Cl BDE and employing a ratio of the $D_0°(B-F)$/average bond energy of BF_3. Our value should be accurate to ±1.0 kcal/mol and supports the thermochemical value[53] as the preferred experimental one. Our calculated value is also in excellent agreement with the CCSD(T)/CBS (V*n*Z) theoretical value,[22] and the G-2 value is in agreement with our more accurately calculated value.[23] Our calculated values for the ΔH_f(BBr) and ΔH_f(BI) are in excellent agreement with the JANAF values[6] within the rather large error bar limits of ± 10.0 kcal/mol, and we expect our values to be accurate to within ± 1.5 kcal/mol. Our ΔH_f(BBr) differs by 2.5 and 8.8 kcal/mol, respectively, from the spectroscopically derived values from Huber and Herzberg[4]

TABLE 1: Optimized CCSD(T) Bond Lengths (Å) and Bond Angles (°) for BX, HBX, BX_2, and $H_{(3-n)}BX_n$ for (X = F, Cl, Br, I, NH_2, OH, and SH)

molecule	basis set	R_{HX}	R_{HB}	R_{BX}	∠HBX	∠HXB	∠XBX
BF ($^1\Sigma^+ - C_{\infty v}$)	aVTZ			1.2747			
	aVQZ			1.2686			
	expt.[a]			1.2625_9			
HBF ($^2A' - C_s$)	aVTZ		1.2027	1.3094	121.0		
H_2BF ($^1A_1 - C_{2v}$)	aVTZ		1.1933	1.3250	117.8		
HBF_2 ($^1A_1 - C_{2v}$)	aVTZ		1.1861	1.3190	121.0		118.0
	expt[b]		1.189(10)	1.311(5)			118.3(10)
BF_2 ($^2A_1 - C_{2v}$)	aVTZ			1.3124			121.1
BF_3 ($^1A'_1 - D_{3h}$)	aVTZ			1.3153			120.0
	expt[b]			1.3070(1)			
BCl ($^1\Sigma^+ - C_{\infty v}$)	aVTZ			1.7283			
	aVQZ			1.7239			
	expt.[a]			1.715_9			
HBCl ($^2A' - C_s$)	aVTZ		1.1909	1.7238	123.3		
H_2BCl ($^1A_1 - C_{2v}$)	aVTZ		1.1869	1.7435	118.1		
$HBCl_2$ ($^1A_1 - C_{2v}$)	aVTZ		1.1826	1.7423	119.7		120.7
	expt[b]		1.13(20)	1.75			119.7(30)
BCl_2 ($^2A_1 - C_{2v}$)	aVTZ			1.7291			125.5
BCl_3 ($^1A'_1 - D_{3h}$)	aVTZ			1.7446			120.0
	expt[b]			1.7421(44)			
BBr ($^1\Sigma^+ - C_{\infty v}$)	aVTZ			1.9062			
	aVQZ			1.9044			
	expt.[a]			1.888_2			
HBBr ($^2A' - C_s$)	aVTZ		1.1900	1.8804	123.6		
H_2BBr ($^1A_1 - C_{2v}$)	aVTZ		1.9035	1.1856	117.9		
$HBBr_2$ ($^1A_1 - C_{2v}$)	aVTZ		1.1819	1.9026	119.3		121.4
	expt[b]		1.20	1.87			119.3(20)
BBr_2 ($^2A_1 - C_{2v}$)	aVTZ			1.8910			126.2
BBr_3 ($^1A'_1 - D_{3h}$)	aVTZ			1.9081			120.0
	expt[b]			1.8932(54)			
BI ($^1\Sigma^+ - C_{\infty v}$)	aVTZ			2.1501			
	aVQZ			2.1484			
HBI ($^2A' - C_s$)	aVTZ		1.1902	2.0943	124.3		
H_2BI ($^1A_1 - C_{2v}$)	aVTZ		1.1853	2.1182	117.8		
HBI_2 ($^1A_1 - C_{2v}$)	aVTZ		1.1830	2.1200	118.7		
BI_2 ($^2A_1 - C_{2v}$)	aVTZ			2.1087			128.2
BI_3 ($^1A'_1 - D_{3h}$)	aVTZ			2.1315			120.0
	expt[b]			2.118(5)			
$B(NH_2)$ ($^1A_1 - C_{2v}$)	aVTZ	1.0115		1.3875		122.8	
$HB(NH_2)$ ($^2A' - C_s$)	aVTZ	1.0071/1.0111	1.1941	1.3872	124.3	123.2/123.4	
$HB(NH_2)_2$ ($^1A_1 - C_{2v}$)[c]	aVTZ	1.0012/1.0033	1.1932	1.4143	118.6	121.9/124.4	122.7
	expt[b]	1.000(1)/1.002(2)	1.193(1)	1.414(1)		121.1(1)/123.7(6)	122.0(3)
$B(NH_2)_2$ ($^1A_1 - C_{2v}$)[c]	aVTZ	1.0081/1.0023		1.4075		124.0/122.4	126.2
$B(NH_2)_3$ ($^1A' - C_s$)[c]	aVTZ	1.0031/1.0023		1.4341/1.4309		120.7/121.6	119.9/120.2
B(OH) ($^1A' - C_s$)	aVTZ	0.9653		1.3130		120.7	
HB(OH) ($^2A' - C_s$)	aVTZ	0.9626	1.1976	1.3466	120.7	113.6	
$H_2B(OH)$ ($^1A' - C_s$)[c]	aVTZ	0.9620	1.1887/1.1941	1.3607	116.6/120.5	112.5	
	expt[b]	0.967(14)	1.200/1.200	1.352(4)	117.2(8)/121.8(8)	112.0(17)	
$HB(OH)_2$ ($^1A' - C_s$)[c]	aVTZ	0.9641/0.9605	1.1898	1.3635/1.3741	118.5/122.4	111.5/112.4	119.1
	expt[b]	0.9590(8)/0.9498(4)	1.1972(3)	1.359(9)/1.365(9)	118.2(12)/122.8(12)	111.8(13)/113.3(17)	119.1(13)
$B(OH)_2$ ($^2A' - C_s$)[c]	aVTZ	0.9610/0.9673		1.3662/1.3536		112.6/112.4	122.6
$B(OH)_3$ ($^1A' - C_{3h}$)[c]	aVTZ	0.9614		1.3745		111.5	120.0
B(SH) ($^1A' - C_s$)	aVTZ	1.3492		1.8213		86.3	
HB(SH) ($^2A' - C_s$)	aVTZ	1.3432	1.1878	1.7571	124.4	99.0	
$H_2B(SH)$ ($^1A' - C_s$)	aVTZ	1.3411	1.1893/1.1882	1.7782	123.0/116.1	98.5	
$HB(SH)_2$ ($^1A' - C_s$)	aVTZ	1.3431/1.3400	1.1873	1.7960/1.7988	116.7/121.2	98.2/96.8	122.1
$B(SH)_2$ ($^2A' - C_s$)[c]	aVTZ	1.3439/1.3360		1.7675/1.7714		99.1/97.0	129.9
$B(SH)_3$ ($^1A' - C_{3h}$)	aVTZ	1.3418		1.8121		97.2	120.0

[a] Reference 4. [b] Reference 49. [c] Geometry parameters were obtained at the MP2 level.

and an infrared diode laser spectroscopy study of the vibrational levels, which were used to construct a potential energy curve.[54]

Our calculated values for the $\Delta H_f(BF_3)$, $\Delta H_f(BCl_3)$, and $\Delta H_f(BBr_3)$ are in excellent agreement with the reported experimental values,[6] within 0.5 kcal/mol. Two high level calculated values[11i,21] from similar CCSD(T)/CBS approaches are in agreement with our $\Delta H_f(BF_3)$ value. Our $\Delta H_f(BCl_3)$ is within 0.5 kcal/mol of the previously reported value at the RCCSD(T)/CBS level.[11i] The G2 value[23] for the $\Delta H_f(BCl_3)$ is in good agreement with our higher level CCSD(T)/CBS value. Our $\Delta H_f(BI_3)$ is in agreement with the experimental value,[6] determined from measuring the appearance potential of the B^+ ion from BI_3, within the rather large error bar limits of ± 12.0 kcal/mol. The $\Delta H_f(B(OH)_3)$ is calculated to be within 2.6 kcal/mol of the experimental value obtained from the heat of formation of the crystal and an average of the enthalpy of sublimation.[6]

Our calculated values for the $\Delta H_f(HBF_2)$ and $\Delta H_f(HBCl_2)$ are within 0.3 kcal/mol of the experimental values,[6] while the $\Delta H_f(HBBr_2)$ differs by 2.2 kcal/mol. The G2 values[23] for $\Delta H_f(HBCl_2)$ and $\Delta H_f(H_2BCl)$ are in good agreement with our CCSD(T)/CBS values.

For our calculations on molecules containing Br, we note that there is a difference of ~0.5 kcal/mol per Br atom in the valence electronic energy extrapolated to the CBS limit based on the aV*n*Z and aV*n*Z-PP (Table SM-7) basis sets, respectively. However, much of the difference is recovered in the various components of the atomization energy, and the largest difference in the calculated heats of formation based on both approaches

TABLE 2: Components for Calculated Atomization Energies in kcal/mol

Molecule	CBS[a]	ΔE_{ZPE}[b]	ΔE_{CV}[c]	ΔE_{SR}[d]	ΔE_{SO}[e]	ΣD_0 (0 K)[f]
BF	182.05	1.98	0.54	−0.24	−0.42	179.92
BCl	122.70	1.19	0.42	−0.07	−0.87	120.99
BBr	104.72	1.01	0.92	0.01	−3.53	101.11
BI	86.56	0.82		−0.01	−7.27	78.47
$B(NH_2)$	313.47	15.75	1.17	−0.31	−0.03	298.54
B(OH)	264.99	8.34	0.87	−0.34	−0.25	256.92
B(SH)	184.30	5.70	0.59	−0.23	−0.59	178.37
HBF	232.76	7.08	0.92	−0.35	−0.42	225.83
HBCl	187.47	6.40	0.95	−0.24	−0.87	180.91
HBBr	172.52	6.16	1.38	−0.48	−3.53	163.73
HBI	157.52	5.92		−0.07	−7.27	144.25
$HB(NH_2)$	387.92	23.13	1.66	−0.38	−0.03	366.04
HB(OH)	324.59	15.15	1.24	−0.40	−0.25	310.03
HB(SH)	265.77	12.41	1.19	−0.39	−0.59	253.56
H_2BF	343.22	14.40	1.13	−0.37	−0.42	329.16
H_2BCl	298.01	13.51	1.18	−0.27	−0.87	284.54
H_2BBr	282.05	13.22	1.66	−0.54	−3.53	266.42
H_2BI	266.57	12.87		−0.08	−7.27	246.35
$H_2B(OH)$	434.32	22.42	1.45	−0.40	−0.25	412.69
$H_2B(SH)$	374.88	18.97	1.42	−0.39	−0.59	356.36
HBF_2	409.82	11.36	1.33	−0.69	−0.81	398.29
$HBCl_2$	313.02	9.48	1.40	−0.44	−1.71	302.80
$HBBr_2$	280.49	8.88	2.40	−0.88	−7.03	266.11
HBI_2	248.87	8.27		−0.10	−14.51	225.99
$HB(NH_2)_2$	704.14	41.91	2.71	−0.72	−0.03	664.19
$HB(OH)_2$	586.17	26.80	1.89	−0.78	−0.47	560.00
$HB(SH)_2$	462.06	20.23	1.81	−0.74	−1.15	441.74
BF_2	295.71	4.42	1.11	−0.67	−0.81	290.92
BCl_2	203.18	2.86	1.17	−0.40	−1.71	199.38
BBr_2	172.11	2.33	2.05	−0.75	−7.03	164.04
BI_2	142.64	2.05		−0.09	−14.51	125.99
$B(NH_2)_2$	591.19	34.62	2.49	−0.73	−0.03	558.31
$B(OH)_2$	473.28	19.60	1.68	−0.77	−0.47	454.12
$B(SH)_2$	353.20	13.83	1.64	−0.73	−1.15	339.13
BF_3	469.75	7.80	1.53	−1.05	−1.20	461.23
BCl_3	323.71	4.88	1.61	−0.60	−2.55	317.30
BBr_3	275.04	3.86	3.14	−1.16	−10.53	262.63
BI_3	228.36	3.16		−0.11	−21.75	203.34
$B(NH_2)_3$	902.25	52.00	3.44	−1.07	−0.03	852.60
$B(OH)_3$	733.80	30.59	2.33	−1.18	−0.69	703.67
$B(SH)_3$	545.23	21.37	2.17	−1.09	−1.71	523.22

[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, Br) and cc-pwCVTZ basis sets at the optimized CCSD(T)/aVTZ or MP2/aVTZ geometries. For the compounds containing I, the CV correction is included in the CBS value, see text. [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, i.e., including the existing relativistic effects resulting from the use of an RECP. [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, ref 36. [f] The theoretical value of the dissociation energy to atoms ΣD_0 (0 K).

was 0.7 kcal/mol for BBr_3. The predicted heat of formation of BBr_3 (aV*n*Z-PP) of −47.6 kcal/mol shows a larger difference of 1.2 kcal/mol from the experimental value.[6] For the heats of formation for the I-containing molecules, the inclusion of the core electrons and the CBS extrapolation with the weighted core basis sets yields calculated values for the heats of formation that are on average within 0.3 kcal/mol of the heats of formation calculated using the aV*n*Z-PP basis sets and just correlating the valence electrons. The largest difference between the predicted heats of formation based on both approaches was 0.5 kcal/mol for BI_3, where the heats of formation were predicted to be 8.6 (awCV*n*Z) and 9.1 (aV*n*Z-PP) kcal/mol, respectively, at 0 K.

Our calculated $\Delta H_f(BF_2)$ is in excellent agreement with the experimental value obtained from the thermochemical analysis of the BF_2 radical by mass spectrometry differing by 1.3 kcal/mol and within the error bar limits.[52] The JANAF value differs by 22 kcal/mol and is clearly incorrect.[6] The JANAF value[6] was calculated based on combining the appearance potential of BF_2^+ from BF_3 and the ionization potential for BF_2. Using the same method, Margrave[55] obtained a value of $\Delta_f H^o(BF_2, g) \leq -124 \pm 9$ kcal/mol, in better agreement with our reliably calculated value. Our $\Delta H_f(BF_2)$ is in excellent agreement with the CCSD(T)/CBS (V*n*Z) value.[22] For the $\Delta H_f(BCl_2)$, there is a large difference of 12 kcal/mol between the JANAF[6] and our calculated theoretical value. The JANAF value was determined based on an analysis of the equilibrium constants, which were obtained from ion intensity data, for the reaction BCl_3 (g) + BCl (g) = $2BCl_2$ (g) in combination with the experimental enthalpies of formation for BCl_3 (g) and BCl (g).[6] Our calculated value for the $\Delta H_f(BCl_2)$ is in excellent agreement with the CCSD(T)/CBS (V*n*Z)[22] and G2 values.[23] Our $\Delta H_f(BBr_2)$ and $\Delta H_f(BI_2)$ differ by 9.2 and 1.8 kcal/mol from the estimated experimental values, which were based on an analogy with BF_3, employing the ratio $\Delta_r H^o(BX_3 \rightarrow BX_2 + X)/\Delta_r H^o(BX_3 \rightarrow B + 3X)$.[6] Our $\Delta H_f(B(OH)_2)$ differs from the estimated experimental value by 15 kcal/mol, which was calculated using the bond energy, D_0^o(B−OH), of 132.7 kcal/mol and the enthalpies of formation of B (g) and OH (g) as 132.80 and 9.33 kcal/mol, respectively.[6] We recalculated the "experimental" $\Delta H_f(B(OH)_2)$ using the new value for $\Delta H_f^0(B)$ of 135.1 ± 0.2 kcal/mol[41] and $\Delta H_f^0(OH)$ = 8.85 kcal/mol,[11k] and obtain a value of −112.6 kcal/mol, and still do not find agreement with our value. On the basis of extensive comparisons with experiment for a wide range of compounds, our calculated values for these radicals should be good to ±1.5 kcal/mol and thus are to be preferred over the experimental values when there are large differences.

Bond Dissociation Energies. From the calculated heats of formation, we can predict the various B−X and B−H adiabatic BDEs at 0 K for BX_3, HBX_2, H_2BX, BX, and HX as well as for the various radicals involved in the bond-breaking processes. The results are presented in Table 4 for comparison with the available experimental data, which is largely taken from the compilation of Luo[3] and references therein. On the basis of the results for the heats of formation of the BX_2 radicals, we expect that there are large errors in the experimental BDEs. We define the calculated BDE as the adiabatic value at 0 K. We first examine the BDEs in the diatomics (B−X), as they are representative of the strength of a single bond in these compounds. Our calculated value for the BDE of BF ($^1\Sigma^+$) is in excellent agreement with the value from Huber and Herzberg,[4] the reported experimental value of Hildebrand and Lau,[52] and other calculations (CCSD(T)/CBS, G2, and CBS-4)[21,22,24] The B−F BDE is the largest B−X bond energy. Our calculated BCl ($^1\Sigma^+$) BDE differs by 1.2 kcal/mol from the thermochemical value,[53] 5.8 kcal/mol from that of Huber and Herzber,[4] and 8.0 kcal/mol from the JANAF value.[6] Our calculated value is within 0.5 kcal/mol of another CCSD(T)/CBS value.[22] The BDE of BBr ($^1\Sigma^+$) falls within the range of the available experimental BDEs.[6,54,56] The predicted BI ($^1\Sigma^+$) BDE differs from the experimental value by 8 kcal/mol.[3] Given the previously calculated $\Delta H_f(NH_2)$[11m] and the experimental ΔH_f(OH)[11k] and ΔH_f(SH),[6] the B−X BDE in the pseudodiatomic molecules $B(NH_2)$, B(OH), and B(SH) are calculated with the predicted B−OH BDE lying just outside the error bar limits of the reported experimental value.[48]

BF_3 is predicted to have the largest X_2B-X BDE, and this B−F BDE is slightly less stable than the calculated BF ($^1\Sigma^+$) BDE. Our calculated F_2B-F BDE is in excellent agreement

TABLE 3: Heats of Formation (kcal/mol) at 0 and 298 K[a]

molecule	$\Delta H_f(0\ K)_{theory}$	$\Delta H_f(298\ K)_{theory}$	$\Delta H_f(298\ K)_{expt}$	$\Delta H_f(298\ K)_{other\_theory}$
HF	−65.5	−64.8	−65.32± 0.17[b]	−65.2[c]
HCl	−22.1	−22.1	−22.06 ± 0.024[b]	−22.6[c]
HBr	−6.6	−8.5	−8.674 ± 0.038[b]	−8.6[c]
HI	7.3	6.8	6.334 ± 0.024[b]	5.5[c]
BH	105.1	105.9	105.8± 2.0[e]	
BF	−26.4	−25.6	−27.7 ± 3.3,[e] −25.3,[f] (−26.5)[g]	(−25.5),[h] −25.9,[i] (−26.1),[j] (−24.1)[j]
BCl	42.7	43.4	33.8 ± 4.0,[e] (36.9),[g] (43.5)[k]	44.9,[i] 42.5[l]
BBr	62.2	61.1	55.9 ± 10.0,[e] (59.7),[g] (71.0)[m]	
BI	82.2	82.5	72.9 ± 10.0[e]	
$B(NH_2)$	52.3	51.7		
B(OH)	−11.2	−11.1		
B(SH)	74.0	74.2		
HBF	−20.6	−20.6		
HBCl	34.4	34.4		34.5[l]
HBBr	51.2	51.2		
HBI	68.1	67.7		
$HB(NH_2)$	36.5	34.7		
HB(OH)	−12.7	−13.6		
HB(SH)	50.5	49.7		
H_2B[d]	77.4	77.5	48.0 ± 15.1[e]	
H_2BF	−72.3	−73.3		
H_2BCl	−17.6	−18.5		−19.0[l]
H_2BBr	0.1	−2.6		
H_2BI	17.6	16.3		
$H_2B(NH_2)$[n]	−17.0	−19.7		
$H_2B(OH)$	−63.7	−65.6		
$H_2B(SH)$	−0.7	−2.4		
HBF_2	−174.6	−175.5	−175.4 ± 0.8[e]	
$HBCl_2$	−58.9	−59.6	−59.3 ± 1.0[e]	−60.7[l]
$HBBr_2$	−23.0	−27.2	−25.0 ± 1.2[e]	
HBI_2	12.0	10.6		
$HB(NH_2)_2$	−45.9	−49.9		
$HB(OH)_2$	−152.0	−154.6		
$HB(SH)_2$	−20.4	−22.5		
BF_2	−118.9	−118.7	−141.0 ± 3.1,[e] −120.0 ± 4,[f] ≤ −124 ± 9[o]	−118.9,[i] −118.2[p]
BCl_2	−7.1	−6.9	−19.0 ± 3.0[e]	−5.9,[i] −6.8,[l] −6.8[p]
BBr_2	27.4	24.2	15.0 ± 3.6[e]	
BI_2	60.3	59.9	58.1 ± 15.1[e]	
$B(NH_2)_2$	8.4	5.5		
$B(OH)_2$	−97.8	−99.3	−114.00 ± 3.6[e]	−97.4[p]
$B(SH)_2$	30.5	29.5		
BH_3[n]	25.3	24.4	25.5 ± 2.4[e]	
BF_3	−270.7	−271.4	−271.4 ± 0.4[e]	(−271.0),[h] (−269.8)[q]
BCl_3	−96.4	−96.7	−96.3 ± 0.5[e]	−98.6,[l] (−95.8)[q]
BBr_3	−43.0	−48.3	−48.8 ± 0.05[e]	
BI_3	8.6	7.6	17.0 ± 12.0[e]	
$B(NH_2)_3$	−70.1	−74.9		
$B(OH)_3$	−236.7	−239.8	−237.2 ± 0.6[e]	
$B(SH)_3$	−36.3	−38.4		

[a] Values given in parenthesis are at 0 K. [b] Reference 5. [c] Reference 19. [d] Reference 45. [e] Reference 6. [f] Reference 52. [g] Reference 4. [h] Reference 21. [i] Reference 22. [j] Reference 24. [k] Reference 53. [l] Reference 23. [m] Reference 54. [n] Reference 44. [o] Reference 55. [p] Calculated at the G3(MP2) level in this work (ref 62). [q] Reference 11i.

with the experimental value derived from a mass spectrometry study[52] but differs by 20 kcal/mol from the other available experimental values,[57,6] because of errors in the experimental $\Delta H_f(BF_2)$. The F_2B-F BDE is 9.6 kcal/mol less than the BDE of BF ($^1\Sigma^+$). The strong bond is consistent with back-bonding from the F lone pairs to the vacant B out-of-plane p orbital.[58] Our calculated value is in good agreement with previous calculations.[22,24] The Cl_2B-Cl BDE is calculated to be 12 and 8 kcal/mol larger, respectively, than the reported experimental values[6,57] and 3.1 kcal/mol less than the BDE of BCl ($^1\Sigma^+$). Our calculated value is within 0.6 kcal/mol of a previously reported CCSD(T)/CBS value.[22] The Br_2B-Br and I_2B-I BDEs are calculated to be 8.6 and 10.8 kcal/mol larger than the JANAF values[6] and only 2.6 and 1.2 kcal/mol smaller than the BBr ($^1\Sigma^+$) and BI ($^1\Sigma^+$) BDEs, respectively, showing that the other halide substituents have only a small effect on the B−X BDE. The I_2B-I BDE is predicted to be 93 kcal/mol smaller than the F_2B-F BDE. For the Group VIIA substituents, there is the expected decrease in X_2B-X BDE as one increases the atomic number.

The second highest B−X BDE of the BX_3 compounds is predicted for the hydroxyl substituent, which is isoelectronic with fluorine. The $(HO)_2B-OH$ BDE is 15.7 kcal/mol larger than the JANAF value.[6] The $(HO)_2B-OH$ BDE is 7.4 kcal/

TABLE 4: B−X and B−H BDEs in kcal/mol at 0 K

bond	BDE_{calc} (this work)	BDE_{expt}	BDE_{other_theory}
$BF_3 \rightarrow BF_2 + F$	170.3	150.0,[a] 149.4,[b] 169[c]	170.2,[d] 172.0,[e] 171.0[e]
$BCl_3 \rightarrow BCl_2 + Cl$	117.9	106.3,[b] 110.0[a]	118.5[d]
$BBr_3 \rightarrow BBr_2 + Br$	98.3	89.7[b]	
$BI_3 \rightarrow BI_2 + I$	77.3	66.5[b]	
$B(NH_2)_3 \rightarrow B(NH_2)_2 + NH_2$	123.8		
$B(OH)_3 \rightarrow B(OH)_2 + OH$	147.8	132.1 ± 7[b]	
$B(SH)_3 \rightarrow B(SH)_2 + SH$	99.4		
$HBF_2 \rightarrow HBF + F$	172.5		174.0,[e] 172.2[e]
$HBCl_2 \rightarrow HBCl + Cl$	121.9		
$HBBr_2 \rightarrow HBBr + Br$	102.1		
$HBI_2 \rightarrow HBI + I$	81.7		
$HB(NH_2)_2 \rightarrow HB(NH_2) + NH_2$	127.6		
$HB(OH)_2 \rightarrow HB(OH) + OH$	148.2		
$HB(SH)_2 \rightarrow HB(SH) + SH$	103.5		
$BF_2 \rightarrow BF + F$	111.0	136,[a] 132.3,[b] 110[c]	110.9[d], 109.7,[e] 110.2[e]
$BCl_2 \rightarrow BCl + Cl$	78.4	81.8,[b] 93[a]	78.9[d]
$BBr_2 \rightarrow BBr + Br$	62.7	67.7[b]	
$BI_2 \rightarrow BI + I$	47.5	40.5[b]	
$B(NH_2)_2 \rightarrow B(NH_2) + NH_2$	89.2		
$B(OH)_2 \rightarrow B(OH) + OH$	95.4	121.3 ± 7[b]	
$B(SH)_2 \rightarrow B(SH) + SH$	76.1		
$H_2BF \rightarrow BH_2 + F$	168.2	144.4 ± 6[f]	169.9,[e] 167.8[e]
$H_2BCl \rightarrow BH_2 + Cl$	123.6		
$H_2BBr \rightarrow BH_2 + Br$	105.2		
$H_2BI \rightarrow BH_2 + I$	85.4		
$H_2B(NH_2) \rightarrow BH_2 + NH_2$	139.7		
$H_2B(OH) \rightarrow BH_2 + OH$	150.0		
$H_2B(SH) \rightarrow BH_2 + SH$	110.7		
$HBF \rightarrow BH + F$	144.2	145.5 ± 6[f]	142.5,[e] 143.3[e]
$HBCl \rightarrow BH + Cl$	99.3		
$HBBr \rightarrow BH + Br$	81.9		
$HBI \rightarrow BH + I$	62.6		
$HB(NH_2) \rightarrow BH + NH_2$	113.9		
$HB(OH) \rightarrow BH + OH$	126.6		
$HB(SH) \rightarrow BH + SH$	87.3		
$BF \rightarrow B + F$	179.9	180.0,[c] 180.1[g]	181.0 ± 0.2,[h] 179.9,[d] 180.8,[e] 178.8[e]
$BCl \rightarrow B + Cl$	121.0	122.2 ± 1.1,[i] 126.8,[g] 129[b]	121.5[d]
$BBr \rightarrow B + Br$	100.9	104.6,[b] 103.5,[g] 93.4 ± 0.1,[j] 94.6[k]	
$BI \rightarrow B + I$	78.5	86.4[b]	
$B(NH_2) \rightarrow B + NH_2$	128.0		
$B(OH) \rightarrow B + OH$	155.2	144.3 ± 7[f]	
$B(SH) \rightarrow B + SH$	93.7		
$BH \rightarrow B + H$	81.6	83.9,[l] 81.3,[m] 82.5 ± 0.6[n]	
$HF \rightarrow F + H$	135.6	135.2 ± 0.2[b]	
$HCl \rightarrow Cl + H$	102.3	102.23 ± 0.05[b]	
$HBr \rightarrow Br + H$	86.3	86.64 ± 0.04[b]	
$HI \rightarrow I + H$	69.9	70.42 ± 0.05[b]	
$BH_3 \rightarrow BH_2 + H$	103.7	74.6,[b] 82.6[l]	
$NH_3 \rightarrow NH_2 + H$	106.5		
$H_2O \rightarrow OH + H$	117.6		
$H_2S \rightarrow SH + H$	88.5		
$HBF_2 \rightarrow BF_2 + H$	107.4	86.5[b]	108.8,[e] 107.1[e]
$HBCl_2 \rightarrow BCl_2 + H$	103.4		
$HBBr_2 \rightarrow BBr_2 + H$	102.1		
$HBI_2 \rightarrow BI_2 + H$	100.0		
$HB(NH_2)_2 \rightarrow B(NH_2)_2 + H$	105.9		
$HB(OH)_2 \rightarrow B(OH)_2 + H$	105.9		
$HB(SH)_2 \rightarrow B(SH)_2 + H$	102.6		
$H_2BF \rightarrow HBF + H$	103.3		104.8,[e] 103.4[e]
$H_2BCl \rightarrow HBCl + H$	103.6		
$H_2BBr \rightarrow HBBr + H$	102.7		
$H_2BI \rightarrow HBI + H$	102.1		
$H_2B(NH_2) \rightarrow HB(NH_2) + H$	105.1		
$H_2B(OH) \rightarrow HB(OH) + H$	102.7		
$H_2B(SH) \rightarrow HB(SH) + H$	102.8		
$BH_2 \rightarrow BH + H$	79.3	109.9,[b] 89.9[l]	
$HBF \rightarrow BF + H$	45.9		44.5,[e] 45.2[e]
$HBCl \rightarrow BCl + H$	59.9		
$HBBr \rightarrow BBr + H$	62.6		
$HBI \rightarrow BI + H$	65.8		
$HB(NH_2) \rightarrow BNH_2 + H$	67.5		
$HB(OH) \rightarrow BOH + H$	53.1		
$HB(SH) \rightarrow BSH + H$	75.2		

[a] Reference 57. [b] Reference 6. [c] Reference 52. [d] Reference 22. [e] Reference 24. [f] Reference 48. [g] Reference 4. [h] Reference 21. [i] Reference 53. [j] Reference 54. [k] Reference 56. [l] Reference 7. [m] Reference 8. [n] Reference 9.

mol less than the B−OH BDE and 23 kcal/mol less than the F_2B-F BDE. The $(H_2N)_2B-NH_2$ and $(HS)_2B-SH$ BDEs are predicted to be 4 kcal/mol lower and 6 kcal/mol higher than the $B-NH_2$ and B−SH BDEs, respectively, and 47 and 71 kcal/mol lower, respectively, than the F_2B-F BDE.

Similar trends were found in the HBX−X BDE of the HBX_2 molecules. Substitution of H for X to form HBX_2 leads to an average increase of 3 kcal/mol in the HBX−X BDE of the HBX_2 molecules relative to the BX_3 molecules. The HBF−F BDE is again the largest HBX−X BDE and is calculated to be slightly larger than the F_2B-F BDE and 7.4 kcal/mol less than the BDE in BF ($^1\Sigma^+$). The G-2 and CBS-4 values are in good agreement with our calculated value for the HBF−F BDE.[24] The HBCl−Cl and HBBr−Br BDEs are calculated to be 1 kcal/mol more stable than the corresponding diatomic BDEs. There is a decrease in the HBX−X BDE with halide substitution, with the HBI−I BDE predicted to be the lowest, 91 kcal/mol less than the HBF−F BDE. The HBI−I BDE is 4 and 3 kcal/mol more stable than the first B−I BDE in BI_3 and BI ($^1\Sigma^+$), respectively.

The HB(OH)−OH BDE is calculated to be slightly higher than the $(HO)_2B-OH$ BDE, 7 kcal/mol less than the B−OH BDE, and 24 kcal/mol less than the HBF−F BDE. The $HB(NH_2)-NH_2$ and HB(SH)−SH BDEs are predicted to be 4 kcal/mol larger than the analogous first BDE in $B(NH_2)_3$ and $B(SH)_3$, respectively. The $HB(NH_2)-NH_2$ BDE is predicted to be approximately the same as the BDE in $B-NH_2$, while the HB(SH)−SH BDE is 10 kcal/mol larger than the B−SH BDE. The $HB(NH_2)-NH_2$ and HB(SH)−SH BDEs are calculated to be 45 and 69 kcal/mol less than the HBF−F BDE, respectively.

The highest and lowest B−H BDEs for the HBX_2 compounds were calculated for $H-BF_2$ and $H-BI_2$, respectively, bracketing the $H-BH_2$ BDE obtained from the calculated $\Delta H_f(BH_3)$ and $\Delta H_f(BH_2)$, indicating only a small substituent effect on the B−H BDEs. Our calculated value for the $H-BF_2$ BDE is in good agreement with the lower level G-2 and CBS-4 values.[24] For all of the HBX_2 molecules, the HBX−X BDE is larger than the X_2B-H BDE, except in $HBBr_2$ where the Br_2B-H and HBBr−Br BDEs are the same and in HBI_2 where the I_2B-H BDE is larger than the HBI−I BDE by 18 kcal/mol.

The B−X BDEs in the H_2BX molecules were calculated using our revised $\Delta H_f(BH_2)$[45] with the new heat of formation of the B atom. The substitution of a second H for X to form H_2BX leads to an increase in the H_2B-X BDE compared to the HBX−X BDE except for X = F, where a decrease of 4 kcal/mol is predicted for the H_2B-F BDE compared to the HBF−F BDE. There is also a general increase in the H_2B-X BDE compared to the B−X BDE in the diatomic molecules except for X = F and OH with a predicted decrease of 12 and 5 kcal/mol in the H_2B-F and H_2B-OH BDEs compared to the analogous BDEs in BF ($^1\Sigma^+$) and B(OH), respectively. The H_2B-F BDE differs by 24 kcal/mol from the reported experimental value. The H_2B-F BDE is the highest BDE predicted for the H_2BX molecules, and similar trends are noted as found for the BDEs of BX_3 and HBX_2. Our calculated value for the H_2B-F BDE is in good agreement with the lower level G-2 and CBS-4 values.[24] There is a general decrease in the H_2B-X BDE down the group for the halide substituents, with that of iodine predicted to have the smallest H_2B-X BDE, 83 kcal/mol less than the H_2B-F BDE but 7 kcal/mol more stable than the BDE of BI ($^1\Sigma^+$). The H_2B-NH_2 and H_2B-SH BDEs are calculated to be 29 and 58 kcal/mol smaller than the H_2B-F BDE, respectively, and 12 and 17 kcal/mol larger than the corresponding BDEs in $B(NH_2)$ and B(SH), respectively.

As for the HBX_2 compounds, the effect of the substituent on the first B−H BDE in H_2BX is small when compared to the first B−H BDE in BH_3. The largest difference is predicted for the HBI−H BDE, which is only 1.6 kcal/mol less than the $H-BH_2$ BDE. The HBF−H BDE has been calculated at the G-2 and CBS-4 levels,[24] and show good agreement with our higher level CCSD(T)/CBS value. For the H_2BX molecules, the H_2B-X BDE is larger than the HBX−H BDE except for H_2BI where the H_2B-I BDE is 17 kcal/mol less than the HBI−H BDE.

We also predicted the B−X and B−H BDEs in the BX_2 and HBX radicals. Although the XB−X and HB−X BDEs follow similar trends to those discussed above, there is a considerable decrease in the strength of both compared to the corresponding X_2B-X, HBX−X, H_2B-X, and B−X BDEs. Our calculated FB−F BDE is in excellent agreement with the experimental value derived from a mass spectrometry study of the BF_2 radical,[52] but differs from the other experimental values,[3,6] due to errors in $\Delta H_f(BF_2)$. Our calculated value is in good agreement with other calculated values.[22,24] The FB−F BDE is significantly lower than the BDE in BF ($^1\Sigma^+$) by 70 kcal/mol. The calculated ClB−Cl BDE is within 3.4 kcal/mol of one of the reported experimental value and 15 kcal/mol of the other reported value,[3] and smaller than the BCl ($^1\Sigma^+$) BDE by 43 kcal/mol. Our calculated value is in excellent agreement with the reported CCSD(T)/CBS value.[22] The BrB−Br and IB−I BDEs differ by 5 and 7 kcal/mol from the reported experimental values, respectively,[3] and are predicted to be 38 and 31 kcal/mol less stable than the analogous BDEs in BBr ($^1\Sigma^+$) and BI ($^1\Sigma^+$), respectively. Our calculated value for the (HO)B−OH BDE is not in agreement with the reported experimental value.[6]

The first B−F adiabatic BDEs of all the fluoroboranes are large except for BF_2, which is much lower due to the relative instability of the BF_2 radical and the stability of the closed-shell singlet diatomic BF. The adiabatic B−F BDE for $^2BF_2$ produces BF ($^1\Sigma^+$) and F(^{2}P). Following our previous study on the BDEs in the PF_xO_y and SF_xO_y compounds,[2] in order to compare the BDEs, it may be more appropriate to consider the diabatic BDE with the formation of ^3BF where there are two unpaired electrons: one from the unpaired electron on BF_2 and one from the B−F bond that was broken. Inclusion of the singlet−triplet splitting for BF obtained at the CCSD(T)/CBS//MP2/aVTZ level (Supporting Information, Table SM-8) provides an estimate of the reorganization energy. We then obtain a diabatic BDE of 193.4 kcal/mol, which is more consistent with the other B−F BDEs, 23 and 14 kcal/mol larger than the first B−F BDE in BF_3 and BF ($^1\Sigma^+$), respectively. The reorganization energy in this case is the pairing of the two electrons to form the lone pair on BF to give the singlet structure. Our calculated diabatic BF−F BDE is in good agreement with the G-2 and CBS-4 diabatic BF−F BDEs of 195.5 and 193.2 kcal/mol, respectively.[24] For the other molecules, we can also consider dissociation to the diabatic limit given by the reaction $^2BX_2 \rightarrow {}^3BX + {}^2X$. We calculated the singlet−triplet splitting for the BX molecules at the CCSD(T)/CBS//MP2/aVTZ level (Supporting Information, Table SM-8). Use of the singlet−triplet splitting in the BX molecules leads to diabatic BX−X BDEs of 136.3, 116.1, 94.5, 137.0, 165.7, and 109.5 kcal/mol for X = Cl, Br, I, NH_2, OH, and SH, respectively. These values are comparable and on average about 16 kcal/mol larger than the corresponding first B−X BDE in BX_3.

The HB−F BDE is the largest for the HBX molecules and is in excellent agreement with the reported experimental[48] and G-2 and CBS-4 theoretical values.[24] The B−X BDE decreases down the group, and the HB−I BDE is calculated to be 82 kcal/mol smaller than the HB−F BDE. The HB−X BDEs where X = OH, NH_2, and SH are calculated to be 18, 30, and 57 kcal/mol smaller than the HB−F BDE, respectively.

The HB−F BDE is 24 and 36 kcal/mol smaller than the H_2B−F and B−F BDEs, respectively. Again, it is appropriate to consider dissociation of the products to the diabatic limit. We define the diabatic B−F BDE in HBF as occurring with dissociation to the excited $^3\Pi$ state of BH, which has two unpaired electrons: one from the unpaired electron on HBF and one from the B−F bond that was broken. The experimental singlet−triplet splitting of the BH radical is 10 410 cm^{-1} (29.7 kcal/mol),[59] giving a diabatic B−F BDE in HBF of 173.9 kcal/mol, consistent with the predicted B−F BDEs in BF_3, HBF_2, H_2BF, and BF. The HB−F diabatic BDE has been calculated at the G-2 and CBS-4 levels, and the results are in good agreement with our CCSD(T)/CBS value.[24] We predict the HB−X diabatic BDEs for X = Cl, Br, I, NH_2, OH, and SH to be 129.0, 111.6, 92.3, 143.6, 156.4, and 117.0 kcal/mol. These diabatic HB−X BDEs are on average 6 kcal/mol larger than the analogous H_2B−X BDE.

The corresponding B−H BDEs of the HBX molecules are also considerably less than the B−H BDE in BH_3. The smallest H−BX BDE is predicted for H−BF, 58 kcal/mol less than the H−BH_2 BDE. Our calculated value of the H−BF BDE is in good agreement with the lower level G-2 and CBS-4 values.[24] We consider dissociation to the diabatic asymptote defined by the reaction $^2HBX \rightarrow {}^3BX + {}^2H$. Use of the singlet−triplet splittings (Table SM-8) yields diabatic B−H BDEs that are considerably larger than the B−H BDE in BH_3 by as much as 26 kcal/mol in HBF, which suggests that use of this diabatic model may not be appropriate. Our calculated diabatic H−BF BDE of 129.3 kcal/mol is in good agreement with the G-2 and CBS-4 values of 130.3 and 128.2 kcal/mol, respectively.[24] For HB(SH), we find the B−H diabatic BDE to be only 5 kcal/mol larger than the H−BH_2 BDE. Comparison of the B−X and B−H BDEs in the HBX molecules shows that the HB−X BDE is larger than the XB−H BDE, except for HBI where the HB−I BDE is smaller than the H−BI BDE by 6.1 kcal/mol.

Regeneration of Spent Fuel from Ammonia Borane. On the basis of the BDEs, it is unlikely that B−X to B−H conversion will occur for any of the substituted HBX_2, H_2BX, and HBX molecules studied. The iodine derivatives were the most favorable for B−X to B−H conversion as the B−H BDEs in HBI_2, H_2BI, and BHI were more stable than the corresponding B−I BDEs, respectively, and the B−I BDE in BI_3 was the smallest.

We can calculate the heats of reaction for the disproportionation step in proposed reprocessing schemes for the regeneration of ammonia borane. The results are in Table 5. The generic disproportionation reactions are

$$2HBX_2 \rightarrow H_2BX + BX_3 \tag{2}$$

$$H_2BX + HBX_2 \rightarrow BH_3 + BX_3 \tag{3}$$

$$2H_2BX \rightarrow BH_3 + HBX_2 \tag{4}$$

The disproportionation reactions involving the halide and hydroxyl derivatives are all relatively close to thermoneutral. Reaction 4, involving the F substituent, was the only exothermic reaction. These are model reactions for these processes, and BH_3 and BH_2Cl may form dimers in an actual system depending on the temperature. For example, Christe demonstrated the chemical transformation of B_2H_5Cl to B_2H_6 and BCl_3 ($6B_2H_5Cl \leftrightarrow 5B_2H_6 + 2BCl_3$) in the gas phase using a platinum catalyst at temperatures between 200 and 520 °C.[60] Another group has reported similar transformations for boron trihalides over Group IB metals at even higher temperatures, 550−750 °C.[61]

TABLE 5: Disproportionation Reactions in kcal/mol at 0 and 298 K

disproportionation reactions	ΔH_{rxn} (0 K)$_{theory}$	ΔH_{rxn} (298 K)$_{theory}$
$2HBF_2 \rightarrow H_2BF + BF_3$	6.2	6.3
$H_2BF + HBF_2 \rightarrow BH_3 + BF_3$	1.5	2.7
$2H_2BF \rightarrow BH_3 + HBF_2$	−4.7	−3.6
$2HBCl_2 \rightarrow H_2BCl + BCl_3$	3.7	4.0
$H_2BCl + HBCl_2 \rightarrow BH_3 + BCl_3$	5.4	6.7
$2H_2BCl \rightarrow BH_3 + HBCl_2$	1.6	2.8
$2HBBr_2 \rightarrow H_2BBr + BBr_3$	3.3	3.6
$H_2BBr + HBBr_2 \rightarrow BH_3 + BBr_3$	5.3	6.8
$2H_2BBr \rightarrow BH_3 + HBBr_2$	2.0	3.3
$2HBI_2 \rightarrow H_2BI + BI_3$	2.3	2.7
$H_2BI + HBI_2 \rightarrow BH_3 + BI_3$	4.3	6.0
$2H_2BI \rightarrow BH_3 + HBI_2$	2.0	3.3
$2HB(NH_2)_2 \rightarrow H_2B(NH_2) + B(NH_2)_3$	4.6	5.1
$H_2B(NH_2) + HB(NH_2)_2 \rightarrow BH_3 + B(NH_2)_3$	18.0	19.0
$2H_2B(NH_2) \rightarrow BH_3 + HB(NH_2)_2$	13.4	13.9
$2HB(OH)_2 \rightarrow H_2B(OH) + B(OH)_3$	3.6	3.8
$H_2B(OH) + HB(OH)_2 \rightarrow BH_3 + B(OH)_3$	4.3	5.6
$2H_2B(OH) \rightarrow BH_3 + HB(OH)_2$	0.7	1.9
$2HB(SH)_2 \rightarrow H_2B(SH) + B(SH)_3$	3.9	4.2
$H_2B(SH) + HB(SH)_2 \rightarrow BH_3 + B(SH)_3$	10.2	11.9
$2H_2B(SH) \rightarrow BH_3 + HB(SH)_2$	6.3	7.7

We can predict the thermodynamics for the digestion reaction of borazine with the halide acids at 298 K in kcal/mol given the recalculated heat of formation of borazine[46] (using the new value for the heat of formation of the boron atom) of −118.8 kcal/mol at 298 K in the gas phase. The reactions with NH_3,[44] H_2O,[6] and SH_2[6] are also given for comparison.

$$\text{c-}(BHNH)_3 + 6HF \rightarrow 3NH_3 + 3HBF_2 \qquad \Delta H = -56.3 \tag{5}$$

$$\text{c-}(BHNH)_3 + 6HCl \rightarrow 3NH_3 + 3HBCl_2 \qquad \Delta H = 35.6 \tag{6}$$

$$\text{c-}(BHNH)_3 + 6HBr \rightarrow 3NH_3 + 3HBBr_2 \qquad \Delta H = 51.2 \tag{7}$$

$$\text{c-}(BHNH)_3 + 6HI \rightarrow 3NH_3 + 3HBI_2 \qquad \Delta H = 71.7 \tag{8}$$

$$\text{c-}(BHNH)_3 + 6NH_3 \rightarrow 3NH_3 + 3HB(NH_2)_2 \qquad \Delta H = -0.2 \tag{9}$$

$$\text{c-}(BHNH)_3 + 6H_2O \rightarrow 3NH_3 + 3HB(OH)_2 \qquad \Delta H = -35.4 \tag{10}$$

$$\text{c-}(BHNH)_3 + 6SH_2 \rightarrow 3NH_3 + 3HB(SH)_2 \qquad \Delta H = 43.5 \tag{11}$$

We predict the reaction of borazine with hydrofluoric acid to be considerably more exothermic as compared to the other halide acids. In order to better understand the digestion chemistry and the energetics for the borazine reactions, one can compare the various bond energies for the respective halide acid reactants and the HBX_2 products. Breaking an HF bond compared to an HCl bond is more endothermic by 33 kcal/mol; however, much of this energy difference in the HF/BF_3 system is gained back on forming HBF_2. More notably, there is a difference of 96 kcal/mol in the cumulative reaction sequence BH + X → HBX + X → HBX_2 between X = F and X = Cl. Similarly, breaking an HBr bond is about 49 kcal/mol less endothermic than breaking an HF bond; however, the cumulative reaction to form $HBBr_2$ ($BH + Br \rightarrow HBBr + Br \rightarrow HBBr_2$) is only exothermic by 184 kcal/mol as compared to 317 kcal/mol for the analagous fluorine reaction. Although breaking an HI bond is considerably less endothermic than breaking an HF bond by 66 kcal/mol, only 144 kcal/mol is regained in forming HBI_2, and this value is less than half the equivalent reaction for the fluoride derivatives. The digestion reaction involving H_2O is also exothermic, but is ~21 kcal/mol less compared to the reaction with HF. The reactions involving NH_3 are thermoneutral, and the reactions involving SH_2 are endothermic.

Conclusions

The heats of formation at 0 and 298 K are predicted for a range of substituted borane compounds, BX_3, HBX_2, and H_2BX, and the radicals, BX_2 and HBX, 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 values should be good to ±1.5 kcal/mol. The calculated heats of formation are in excellent agreement with the available experimental data for the closed-shell molecules, but show larger differences with the reported experimental values for the BX_2 radicals. However, on the basis of extensive comparisons with experiment for a wide range of compounds, our calculated values for these radicals are to be preferred over the experimental values. Our calculated heats of formation allow us to predict the adiabatic BDEs for all of the compounds to within ±1.5 kcal/mol, dramatically improving the estimates of these important quantities, particularly for the radicals.

The calculated BDEs provide insight into the reactivity of these molecules. The B−F BDE is the largest B−X BDE predicted for BX_2, HBX_2, and H_2BX, and for the halogens, there is the expected decrease in B−X BDE with increasing atomic number. For ammonia borane spent fuel regeneration processes, B−X to B−H conversion will most likely not occur for any of the substituted HBX_2, H_2BX, and HBX molecules studied, except for the iodine derivatives, which were the most favorable with the B−H BDEs in HBI_2, H_2BI, and HBI larger than the corresponding B−I BDEs, respectively, and the B−I BDE in BI_3 being the lowest for all of the substituents studied.

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Supporting Information Available: Geometry paramaters for HX (X = F, Cl, Br, and I). Geometry parameters for BX, HBX, BX_2, and $H_{3-n}BX_n$ for (X = F, Cl, Br, I, NH_2, OH, and SH) at the CCSD(T)/aVDZ level. 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}). Components for calculated atomization energies for HX (X = F, Cl, Br, and I). Components for calculated atomization energies for BX, HBX, BX_2, and $H_{3-n}BX_n$ for X = Br and I. Electronic contribution to the CCSD(T) singlet−triplet splitting for the HBX compounds. T_1 diagnostics calculated at the CCSD(T)/aVQZ level. This material is available free of charge via the Internet at http://pubs.acs.org.

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