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Heats of Formation of Simple Boron Compounds

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The heats of formation of BH, BH_2, BH_3, and B_2H_6 have been obtained from ab initio coupled cluster calculations by using a systematic sequence of correlation consistent Gaussian basis sets. The best values were obtained by extrapolating the finite basis set results to the complete basis set limit and by incorporating an estimate of core/valence correlation effects. In general, the largest calculations in this study utilized quadruple-ζ-level basis sets that were augmented by an additional shell of diffuse functions. Even larger basis set calculations were performed on the smallest of the four systems in order to test the accuracy of the complete basis set extrapolation. Vibrational zero point energies were taken from experiment when available. Missing values were replaced by theoretical harmonic frequencies scaled to more closely approximate the experimental values. The calculated heats of formation are $\Delta H_f{}^0(BH) = 106.2 \pm 0.3$ kcal/mol, $\Delta H_f{}^0(BH_2) = 78.4 \pm 0.6$ kcal/mol, $\Delta H_f{}^0(BH_3) = 25.8 \pm 0.7$ kcal/mol, and $\Delta H_f{}^0(B_2H_6) = 13.7 \pm 1.4$ kcal/mol.

Introduction

Boron compounds have wide application in many technological areas such as separations (e.g., the proposed "In-Tank Precipitation" process at the U.S. Department of Energy's Savannah River Site), catalyst promoters, and radiation therapy and as potential high-energy fuels. Although thermochemistry data is available for some of the simpler boron compounds,[1] significant gaps in our knowledge exist for many of the larger substituted systems. Accurate heats of formation of simple compounds are needed (1) as the base on which to build group additivity methods, (2) as test cases for new methods for predicting heats of formation, and (3) for use in isodesmic reactions. Unrecognized errors in the experimental data for these simple systems can be propagated throughout an isodesmic reaction series for larger compounds leading eventually to unacceptable errors in the final heats of formation. We are especially interested in calculating the heats of formation of boron compounds in order to predict reaction pathways related to the global decomposition of organo-boron compounds in the presence of water.

Due to its small size, BH has been the subject of a large number of theoretical studies. Although a thorough review of this literature is beyond the scope of the present work, we will briefly discuss several recent high-accuracy investigations of the $^1\Sigma^+$ ground state. Bauschlicher et al.[2] used $4e^-$/9-orbital complete active space multireference configuration interaction (MR−CI) wave functions to obtain a value for the dissociation energy, D_e, of 84.35 kcal/mol. The one-particle basis set consisted of a [5s,6p,5d,2f,1g/4s,3p,2d] atomic natural orbital contraction, where the notation [*x*/*y*] indicates the use of basis set *x* on boron and *y* on hydrogen. Their best D_0 value, including estimates of core/core and core/valence effects, was 81.5 ± 0.5 kcal/mol. The same value had been reported earlier by Curtiss and Pople,[3] who used the Gaussian-1 procedure. Bauschlicher et al.[2] were able to recommend a revised "experimental" D_0 of 81.6 ± 0.6 kcal/mol by combining a theoretical estimate for the predissociation barrier from the A $^1\Pi$ state with the experimental data of Johns et al.,[4] considerably larger than the 78.9 kcal/mol given by Huber and Herzberg.[5]

Frozen core (FC) MR−CI wave functions were also used by Peterson et al.[6] in conjunction with a sequence of correlation consistent basis sets to calculate the dissociation energy.[7] The systematic convergence behavior associated with these basis sets enabled a complete basis set (CBS) estimate for D_e (84.4 kcal/mol) to be obtained from an exponential extrapolation based on double-through quintuple-ζ basis set energies.

Martin and Taylor[8] selected MR−CI and single and double excitation coupled cluster theory, including a perturbative estimate of triple excitations (CCSD(T)),[9] to examine the basis set dependence of r_e and the harmonic frequency (ω_e). Martin[10] has also reported total atomization energies for BH, BH_2, and BH_3 obtained from CCSD(T) calculations with the correlation consistent basis sets.[7] While this paper was in preparation, we learned of work in press by Martin[11] focusing on nonadiabatic effects in the ground states of BH and BeH. By using CCSD(T) with large correlation consistent basis sets and full configuration interaction (FCI) with the more modest cc-pVTZ basis, he obtained a variety of spectroscopic properties (r_e, ω_e, $\omega_e\chi_e$, and α_e) in excellent agreement with the available experimental data. Nonadiabatic effects resulted in a 0.0025 Å lengthening of r_e, bringing the best theoretical value (1.2320 Å) to within a few ten thousandths of an angstrom of the 1.2324 Å value of Huber and Herzberg[5] or the 1.2322 Å value of Fernando and Bernath.[12] The high level of agreement between theory and experiment for BH constitutes strong evidence that the CCSD(T) method should provide an accurate tool for studying the four systems that are the focus of the present work.

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Methods

A long term goal of this study is the development of accurate and reliable methods for predicting a variety of thermodynamic quantities, including heats of formation, without recourse to empirical parameters. Such parameters might unnecessarily restrict the scope of the methodology to chemical systems similar to those used to derive the parameters.[13−15] The approach we follow begins with known values and then proceeds to calculate reaction energies by using levels of theory that have been demonstrated to yield high accuracy for well-characterized systems. Our primary energetics are obtained from highly correlated methods, such as MR−CI and CCSD(T), used in combination with the correlation consistent sequence of basis sets. CCSD(T) is capable of recovering a large fraction (>98%) of the empirical valence correlation energy for first- and second-period elements. When account is taken of the effects due to core/valence correlation and the remaining error due to the use of finite basis sets, CCSD(T) appears capable of providing better than 1 kcal/mol accuracy for most atomization energies of compounds composed of first- through third-period elements.[16]

This approach differs from the Gaussian-1 (G1) and Gaussian-2 (G2) procedures[17,18] which attempt to compute energetics with an accuracy comparable to a quadratic configuration interaction calculation performed with a 6-311+G(2df,p) basis set. Both of the Gaussian methods make assumptions about the additivity of basis set and correlation corrections and include a “higher-order” empirical correction to minimize the error with respect to a body of reliable experimental atomization energies. The only empirical scaling that enters into our approach is in the treatment of the theoretical zero point vibrational energies (ZPEs) when reliable experimental values are not available. A practical disadvantage of the present approach, compared with G1 and G2, is the significant increase in computer time it required. As a consequence, current hardware limits the range of applicability of the procedures followed in this work to chemical systems with fewer than six second- and third-period atoms. We will discuss several time-saving approximations that can be exploited and their impact on the accuracy of the energetics.

CCSD(T) calculations were performed with the Gaussian-94[19] and MOLPRO-96[20] programs on Silicon Graphics PowerChallenge computer servers and Cray vector supercomputers. As previously mentioned, the one-particle basis sets were chosen from the correlation consistent collection of basis sets.[7] Only the spherical components (5-d, 7-f, 9-g, 11-h, and 13-i) of the Cartesian Gaussian functions were used. Unless otherwise noted, the boron 1s inner shell pairs were treated as frozen cores, i.e., they were excluded from the correlation treatment. Dissociation energies were computed with respect to both restricted[21] and unrestricted open shell ^{2}P energies for the boron atom. Fully unrestricted boron energies are denoted UCCSD(T), whereas results based on restricted open shell Hartree−Fock atomic orbitals and unrestricted coupled cluster theory are denoted R/UCCSD(T). Orbital symmetry and equivalence restrictions on the 2p atomic orbitals were not imposed. Atomic energies are listed in Table 1.

The geometries were optimized at the second-order Møller−Plesset (MP2) level of perturbation theory[22] with the cc-pVTZ basis set unless noted below. Harmonic frequencies were also calculated at this level to augment the available experimental values. This geometry was used for single-point CCSD(T) calculations with the correlation consistent basis sets (cc-pVxZ for x = D, T, or Q, corresponding to the double-, triple-, and quadruple-ζ levels). In a number of cases for the smaller compounds, we were able to optimize the geometry and obtain frequencies at the CCSD(T) level. These values are given where appropriate.

TABLE 1: Frozen Core Atomic Energies[a]

		B (^{2}P)	
basis set	H (^{2}S) RHF	UCCSD(T)	RCCSD(T)
cc-pVDZ	−0.499278	−24.589408	−24.589378
cc-pVTZ	−0.499810	−24.598101	−24.598021
cc-pVQZ	−0.499946	−24.600836	−24.600747
cc-pV5Z	−0.499995	−24.601552	−24.601462
cc-pV6Z	−0.499999	−24.601789	−24.601699
CBS(DTQ/e^{-x})	−0.50000	−24.6021	−24.6020
CBS(TQ/l_{max})	−0.50000	−24.6024	−24.6023
CBS(Q56/e^{-x})	−0.50000	−24.6018	−24.6018
CBS(56/l_{max})	−0.50000	−24.6022	−24.6020
aug-cc-pVDZ	−0.499334	−24.591102	
aug-cc-pVTZ	−0.499821	−24.598450	
aug-cc-pVQZ	−0.499948	−24.600948	
aug-cc-pV5Z	−0.499995	−24.601603	
CBS(aDTQ/e^{-x})	−0.50000	−24.6022	
CBS(aTQ5/e^{-x})	−0.50000	−24.6018	
CBS(aTQ/l_{max})	−0.50000	−24.6024	
CBS(aQ5/l_{max})	−0.50000	−24.6021	
CBS(aDTQ/mix)	−0.50000	−24.6024	
CBS(aTQ5/mix)	−0.50000	−24.6020	

[a] Energies are given in hartrees.

To estimate properties at the CBS limit we used a variety of 2- and 3-parameter functional forms.[23] The first was an exponential of the form

$$F(x) = A_{CBS} + B\exp(-Cx) \tag{1}$$

where, in general, A_{CBS}, B, and C are determined by a nonlinear least-squares fit and x = 2, 3, or 4 for the DZ, TZ, and QZ basis sets. Values estimated by this procedure will be denoted CBS(DTQ/e^{-x}) or denoted CBS(aDTQ/e^{-x}) if the augmented sets are used. An alternative expression based on the asymptotic limit of the two-electron cusp[24] is given by

$$F(x) = A_{CBS} + B/(l_{max} + 1/2)^4 \tag{2}$$

where l_{max} is the maximum l value for the basis set (l = 0, 1, 2, etc. for s, p, d, etc.).[25] In the present work, we used (2) to fit results from TZ and QZ basis sets, ignoring the DZ values since their inclusion in the fitting procedure produces noticeably poorer CBS estimates. These results are denoted CBS(TQ/l_{max}). Finally, we also used a mixed exponential/Gaussian function:

$$F(x) = A_{CBS} + B\exp[-(x-1)] + C\exp[-(x-1)^2] \tag{3}$$

which was first proposed by Peterson et al.[26] Results based on eq 3 will be denoted CBS(aDTQ/mix).

CBS dissociation energies can be obtained by subtracting the individually extrapolated CBS atomic energies from the energy of the molecule or by directly extrapolating the D_e values. Differences are typically small (≤0.1 kcal/mol).[13,16] In this work we have adopted the former approach. This approach to estimating the complete basis set limit is not to be confused with the CBS atomic pair natural orbital techniques of G. A. Petersson and co-workers.[27]

Unless otherwise noted, core/valence corrections to the dissociation energy were obtained from fully correlated CCSD(T) calculations with the cc-pCVTZ and cc-pCVQZ basis sets at CCSD(T)(FC)/aug-cc-pVTZ geometries. Comparison of core/valence corrections obtained by this procedure with corrections obtained from larger basis set calculations at core/

TABLE 2: Frozen Core CCSD(T) Results for (X $^1\Sigma^+$) BH

basis set	energy	D_e (kcal/mol)[a]	D_0 (kcal/mol)
cc-pVDZ	−25.214841	79.18	75.87
cc-pVTZ	−25.230615	83.32	79.99
cc-pVQZ	−25.235064	84.32	80.98
cc-pV5Z	−25.236212	84.56	81.22
cc-pV6Z	−25.236612	84.66	81.32
CBS(Q56/e^{-x})	−25.2368	84.7 (84.9)[b]	81.4 (81.6)[b]
CBS(56/l_{max})	−25.2370	84.8 (85.0)[b]	81.5 (81.7)[b]
aug-cc-pVDZ	−25.217900	79.99	76.71
aug-cc-pVTZ	−25.231479	83.59	80.27
aug-cc-pVQZ	−25.235341	84.37	81.03
aug-cc-pV5Z	−25.236342	84.55	81.20
CBS(aDTQ/e^{-x})	−25.2369	84.6 (84.8)[b]	81.3 (81.5)[b]
CBS(aTQ5/e^{-x})	−25.2367	84.7 (84.9)[b]	81.4 (81.6)[b]
CBS(aTQ/l_{max})	−25.2376	84.8 (85.0)[b]	81.5 (81.7)[b]
CBS(aQ5/l_{max})	−25.2372	84.8 (85.0)[b]	81.5 (81.7)[b]
CBS(aDTQ/mix)	−25.2375	84.8 (85.0)[b]	81.5 (81.7)[b]
CBS(aTQ5/mix)	−25.2369	84.7 (84.9)[b]	81.4 (81.6)[b]
Martin best est.[c]		84.78	81.49
experiment		85.0 ± 0.6[d]	81.6 ± 0.6[e] 78.9[f] 78.2 ± 0.9[g]

[a] Dissociation energies for the cc-pV*x*Z basis sets were obtained with respect to restricted open shell ^{2}P energies for the boron atom. Dissociation energies for the aug-cc-pV*x*Z basis sets were obtained with respect to unrestricted open shell calculations on B. Calculations on BH were performed at the CCSD(T) optimal bond lengths: 1.2560 Å (VDZ), 1.2354 Å (VTZ), 1.2333 Å (VQZ), 1.2327 Å (V5Z), 1.2326 Å (V6Z), 1.2531 Å (aVDZ), 1.2333 Å (aVQZ), 1.2327 Å (aV5Z). [b] Value corrected for the effects of core/valence correlation, as described in the text. [c] Martin, ref 10. These values are based on CCSD(T) calculations up through aug-cc-pV5Z(B)/cc-pV5Z(H), a ZPE of 3.35 kcal/mol, and a core/valence correction of 0.16 kcal/mol. It was not clear from ref 10 how the atomic asymptotes were treated, but based on a private communication, they were declared to be R/UCCSD(T). [d] Based on $D_0 = 81.6 \pm 0.6$ kcal/mol, ZPE = 3.35 kcal/mol, and spin−orbit = 0.03 kcal/mol. [e] Recommended by Bauschlicher et al., ref 2, which in turn is based on the predissociation limit (82.5 ± 0.4 kcal/mol) of Johns et al., ref 4. [f] Huber and Herzberg, ref 5. [g] JANAF tables, ref 1.

valence optimized geometries show typical errors of ~20% for the cc-pCVTZ basis set and ~8% for the cc-pCVQZ set.

Results

BH. BH, the simplest of the four compounds studied, is formed by adding a hydrogen to the singly occupied 2p orbital on boron (X $^1\Sigma^+$: $1\sigma^2\ 2\sigma^2\ 3\sigma^2$). As seen in Table 2, the values of D_e obtained by extrapolating the cc-pV*x*Z and aug-cc-pV*x*Z basis set sequences differ by no more than 0.1 kcal/mol and are essentially identical to the experimental value (85.0 ± 0.6 kcal/mol). CBS estimates of the total energy show little variation with basis set size. The cc-pCVTZ core/valence correction is 0.15 kcal/mol, slightly smaller than the 0.19 kcal/mol correction obtained with the cc-pCVQZ basis set. The addition of the core/valence correction increases D_e, i.e., there is more core/valence correlation energy in BH than in the boron atom. Finally, inclusion of the experimental ZPE[5] yields D_0 values in the range of 81.5−81.7 kcal/mol, depending upon which CBS extrapolation is used.

Due to the scarcity of results obtained with extremely large basis sets (i.e., basis sets larger than sextuple-ζ) or alternative methods, such as the R12 techniques proposed by Klopper,[28] it is difficult to judge the relative merits of eqs 1, 2, or 3 for estimating the CBS limit. Agreement with high-accuracy experimental binding energies may be adopted as an alternative measure by which to judge competing CBS estimates, but only if one is willing to assume that the intrinsic error in the CCSD(T) method is negligible compared to the desired accuracy in the final results. A comparison of 30 G2 atomization energies in the EMSL Computational Results Database[16] produced mean absolute deviations (ϵ_{MAD}) with respect to experiment of 0.66 (e^{-x}), 0.48 (mix), and 0.51 (l_{max}) kcal/mol after accounting for core/valence effects at the cc-pCVQZ level. The CBS(aTQ/l_{max}) extrapolation technique overestimates ΣD_e in 20 cases, whereas the mixed Gaussian/exponential form overestimates and underestimates in the same number of cases. SO_2 is a particularly difficult molecule in terms of basis set convergence, with errors more than twice as large as the next worst case. If we remove $\Sigma D_e(SO_2)$ from the set of atomization energies, the average deviation for the mixed extrapolation becomes 0.02 kcal/mol, compared with 0.16 kcal/mol for the $1/l_{max}$ method.

It should be emphasized that the magnitude of the errors at such a high level of treatment are small enough that the choice of how one treats the separated atoms becomes significant. The use of UCCSD(T) atomic energies ensures the lowest asymptotic dissociated limit and thus favors the $1/l_{max}$ extrapolation. If we were to use R/UCCSD(T) or RCCSD(T) atomic energies, the balance would be shifted back toward the exponential or mixed extrapolations. Differences in atomic energies can be as large as 0.3 kcal/mol per atom between UCCSD(T) and RCCSD(T).

On the basis of the statistical evidence, we tentatively adopt the CBS(aDTQ/mix) values as our best estimates of the complete basis set limit for atomization energies when combined with UCCSD(T) atomic energies. As seen in Table 2, the complete basis extrapolations based on the augmented double-through quadruple-ζ basis sets yield D_e values that differ by no more than 0.1 kcal/mol from the results obtained with even larger basis sets.

Furthermore, the variation among the various CBS estimates can be taken as a crude measure of the inherent uncertainy in the extrapolations. We adopt half of this variation as an estimate of the error limit. By doing so, we make the implicit assumption that the inherent error associated with the CCSD(T) method is small by comparison. It is difficult to judge the inherent error of CCSD(T) because its overall agreement with accurate experimental measurements is very good and its agreement with other high-level theoretical methods, e.g., MR−CI, is similarly good. Bauschlicher et al.[2] performed full CI calculations using a triple-ζ quality basis set and a fixed bond length of 1.2436 Å in order to gauge the accuracy of their MR−CI dissociation energies. We have performed full CI calculations with the cc-pVTZ basis set at the full CI and CCSD(T) optimal bond lengths. The BH full CI energy at $R_e = 1.2356$ Å is $-25.231136\ E_h$, yielding a D_e of 83.35 kcal/mol, compared to the CCSD(T) value of 83.32 kcal/mol at $R_e = 1.2354$ Å. This difference of 0.03 kcal/mol is indeed much smaller than the error limits obtained by considering the uncertainty in the CBS extrapolations. Thus, our best theoretical value for D_0(BH) is 81.6 ± 0.1 kcal/mol.

The corresponding experimental values are (1) 78.9 kcal/mol given by Huber and Herzberg,[5] (2) 78.2 ± 0.9 kcal/mol obtained from the JANAF tables,[1] and (3) 81.6 ± 0.6 kcal/mol on the basis of the work of Bauschlicher et al.[2] and Johns et al.[4] The present work supports the revision of the experimental value reflected in (3). The current lower limit for D_0 is in exact agreement with the value predicted by Martin.[10] He used the R/UCCSD(T) method for treating the boron atom.[47] G2 gives a D_0 which differs from our best estimate by ~1 kcal/mol (D_0 = 82.8 kcal/mol), while the CBS-4[29] method underestimates D_0 by the same amount (D_0 = 80.7 kcal/mol).

TABLE 3. Frozen Core CCSD(T) Results for (X $^2A_1$) BH_2[a]

				normal mode frequencies			
basis set	energy	R_{BH}	∠HBH	A_1	A_1	B_2	ΣD_e
aug-cc-pVDZ	−25.844082	1.2051	128.3	1016.8	2561.4	2721.5	159.58
aug-cc-pVTZ	−25.864193	1.1893	128.9	1011.8	2587.0	2749.7	166.98
aug-cc-pVQZ	−25.869343	1.1877	128.9	1011.6	2593.0	2756.1	168.49
CBS(aDTQ/e^{-x})	−25.8711	1.1876	128.9	1011.4	2594.8	2758.3	168.7 (169.5)[b]
CBS(aTQ/l_{max})	−25.8723						169.4 (170.2)[b]
CBS(aDTQ/mix)	−25.8721						169.3 (170.1)[b]
Martin best est.[c]							169.86
experiment		1.181	131.0				

[a] Bond lengths are in angstroms and angles are in degrees. Frequencies are in cm^{-1}. D_e is given in kcal/mol. Dissociation energies were obtained with respect to unrestricted open shell calculations on B. [b] Including core/valence correction obtained from CCSD(T)/cc-pCVQZ calculations. [c] Martin, ref 10. This value is based on CCSD(T) calculations up through aug-cc-pV5Z(B)/cc-pV5Z(H), a ZPE of 9.05 kcal/mol, and a core/valence correction of 0.79 kcal/mol.

To determine the enthalpy of formation at 0 K, $\Delta H_f{}^0$(BH), we combine D_0(BH) and the heats of formation of H and B in the gas phase. Although the 0 K heat of formation of H(g) is well-established at 51.63 kcal/mol (52.10 kcal/mol at 298 K),[1] the value for B(g) is less certain. The older JANAF value is 132.6 ± 2.9 kcal/mol (133.8 at 298 K), while the newer value is 136.2 ± 0.2 kcal/mol (137.7 at 298 K).[29,30] We thus obtain $\Delta H_f{}^0$(BH) = 106.2 ± 0.3 kcal/mol (0 K) by using the newer value of $\Delta H_f{}^0$(B). This can be compared to the JANAF value of 105.0 ± 2 kcal/mol. Consequently, we suggest increasing ΔH_f(BH) by 1.2 kcal/mol. Our error limits are based on the ±0.2 kcal/mol uncertainty in $\Delta H_f{}^0$(B) and an estimate of ±0.1 kcal/mol uncertainty in the complete basis set energies.

BH_2. UCCSD(T) values of the optimized geometry, harmonic frequencies, and total atomization energy, ΣD_e, for the $^2A_1$ state of BH_2 are shown in Table 3. The UCCSD(T)/CBS(aDTQ/mix) value of ΣD_e for BH_2 is 170.1 ± 0.35 kcal/mol, including core/valence corrections. We estimate the D_e bond strength for a single B−H bond in BH_2 to be 85.0 ± 0.4 kcal/mol, on the basis of CBS(aDTQ/mix) energies and correcting for core/valence effects. This value is very similar to the dissociation energy of BH. The uncertainty is obtained from the spread in CBS values, which show a range of 0.7 kcal/mol from the smallest (CBS(aDTQ/e^{-x})) to the largest (CBS(aTQ/l_{max})). The cc-pCVQZ core/valence correction (0.57 kcal/mol) in BH_2 is larger than that in BH, again leading to an increase in D_e compared with the uncorrected D_e.

Since experimental vibrational frequencies for BH_2 have not been reported, we relied on the UCCSD(T)/CBS harmonic frequencies listed in Table 3. These were obtained by using an exponential extrapolation of the double-through quadruple-ζ frequencies. It should be noted that the correction due to anharmonicity in the vibrational frequency of BH was small, amounting to only 0.04 kcal/mol. Therefore, we estimate that the true zero point energy is 0.1 kcal/mol less than the value obtained from the harmonic frequencies, or $ZPE_{BH_2} = 9.0$ kcal/mol. This value is in excellent agreement with the value of 9.05 kcal/mol reported by Kolbuszewski et al.[30] Subtracting the differential vibrational energy (5.6 kcal/mol) to D_e, one obtains a D_0 value for the HB−H bond strength of 79.4 kcal/mol, about 2 kcal/mol smaller than the value in BH. The difference in the bond energies is due entirely to variations in the ZPE's. By comparison, the G2 value (77.4 kcal/mol) and CBS-4 value (78.9 kcal/mol) are slightly smaller. Combining ΣD_e and ZPE_{BH_2} leads to a ΣD_0 of 161.1 kcal/mol, in good agreement with the value predicted by Martin.[10] The G2 value of 160.1 kcal/mol is about 1 kcal/mol lower. Thus, our best theoretical value for $\Delta H_f{}^0(BH_2)$ is 78.4 ± 0.4 kcal/mol, on the basis of ±0.2 kcal/mol from the error limit on $\Delta H_f{}^0$(B) discussed above and ±0.2 kcal/mol from the electronic energies. This value is significantly larger than the experimental JANAF value of 48.3 ± 15 kcal/mol.

BH_3. The optimized BH bond length, frequencies, and ΣD_e values for BH_3 are listed in Table 4. At the frozen core CCSD(T)/CBS(aDTQ/e^{-x}) level of theory, the predicted value of R_{BH} is 0.004 Å longer than the experimental value of Kawaguchi,[31] but core/valence effects are expected to decrease this by ∼0.003 Å.[11] There are two known BH_3 experimental frequencies, the a_2'' bend (inversion) and the e' asymmetric stretch.[32−34] Scaling factors of 0.965 and 0.985, based on the ν/ω_{theory} ratios for the a_2'' and e' modes, respectively, were applied to the CCSD(T)/aug-cc-pVTZ frequencies for the a_1' stretch and the e' bend modes. These scaling factors were based on the ratio of the experimental to the calculated harmonic frequencies and lead to a combined experimental/theoretical $ZPE_{BH3} = 16.0$ kcal/mol, computed as $1/2\Sigma(\nu_{expt})$. This value is in good agreement with the 16.3 kcal/mol taken from Schwenke's analysis[35] of the CCSD(T)/cc-pVTZ quartic force field of Martin and Lee.[36] If the e' and a_1' theoretical frequencies are not scaled, the resulting ZPE is 16.5 kcal/mol.

To compute $\Delta H_f{}^0(BH_3)$ for the $^1A_1'$ ground state of BH_3 we followed the same procedure outlined above for BH_2. The CCSD(T)/CBS(aDTQ/mix) value of ΣD_e is 281.2 kcal/mol, including a core/valence correction of 1.03 kcal/mol. The smaller cc-pCVTZ basis set predicts a correction of 0.76 kcal/mol. The energy required to break the first B−H bond in this molecule is much larger than the corresponding values in BH or BH_2. The CBS(aDTQ/mix) extrapolation predicts a value for $D_e(BH_3 \rightarrow BH_2 + H)$ of 111.2 ± 0.5 kcal/mol, including a 0.27 kcal/mol core/valence correction. Adding the differential ZPE (7.0 kcal/mol) results in a final value for $\Delta H°(BH_3 \rightarrow BH_2 + H) = 104.2$ kcal/mol and $\Delta H_f{}^0(BH_3)$ of 25.8 ± 0.7 kcal/mol. The G2 and CBS-4 values for $\Delta H°(BH_3 \rightarrow BH_2 + H)$ are 105.2 and 104.0 kcal/mol, respectively.

The G2 $\Sigma D_0(BH_3)$ is 265.3 kcal/mol, in close agreement with the 264.6 kcal/mol predicted by Martin[10] and the present value of 265.2 ± 0.5 kcal/mol. Part of the difference in our ΣD_0 value and that of Martin[10] is due to the differences in the ZPEs. By combining the atomization energy and the atomic heats of formation, we arrive at a value of $\Delta H_f{}^0(BH_3) = 25.9 \pm 0.7$ kcal/mol. The calculated $\Delta H_f{}^0(BH_3)$ is in excellent agreement with the experimental value of 26.4 ± 2.4 kcal/mol.[1] Use of the slightly larger ZPE(BH_3) of Schwenke[35] would yield a $\Delta H_f{}^0(BH_3)$ of 25.6 kcal/mol.

B_2H_6. B_2H_6 is the largest of the boron hydrides examined in this study. At the aug-cc-pVQZ basis set level, it required a calculation with 436 basis functions. Experimentally, the heat of formation of the X ^1A_g state ($1a_g{}^2\ 1b_{3u}{}^2\ 2a_g{}^2\ 2b_{3u}{}^2\ 1b_{1u}{}^2\ 1b_{2u}{}^2$

TABLE 4: Frozen Core CCSD(T) Results for ($^1A_1'$) BH_3[a]

				normal mode frequencies			
basis set	energy	R_{BH}	a_2''	e′	a_1'	e′	ΣD_e
aug-cc-pVDZ	−26.512760	1.2062	1145.7	1202.6	2545.8	2675.6	265.85
aug-cc-pVTZ	−26.539082	1.1914	1158.3	1217.1	2564.5	2695.2	276.84
aug-cc-pVQZ	−26.545469	1.1900					279.04
CBS(aDTQ/e^{-x})	−26.5475	1.189					279.4 (280.4)[b]
CBS(aTQ/l_{max})	−26.5492						280.4 (281.4)[b]
CBS(aDTQ/mix)	−26.5489						280.2 (281.2)[b]
cc-pVDZ	−26.508066	MP2[c]					264.07
cc-pVTZ	−26.537699	MP2[c]					276.21
cc-pVQZ	−26.545047	MP2[c]					278.84
CBS(DTQ/e^{-x})	−26.5475	MP2[c]					279.5
aug-cc-pVDZ	−26.512220	MP2[c]					265.51
aug-cc-pVTZ	−26.539047	MP2[c]					276.82
aug-cc-pVQZ	−26.545450	MP2[c]					279.03
CBS(aDTQ/e^{-x})	−26.5475	MP2[c]					279.4
Martin best est.[d]							280.98
experiment		1.185[e]	1140.9[f]	(1199)	(2475)	2601.6[f]	278.7[g]

[a] Bond lengths are in angstroms. Frequencies are in cm^{-1}. D_e is given in kcal/mol. Dissociation energies were obtained with respect to unrestricted open shell calculations on B. [b] Including core/valence correction obtained from CCSD(T)/cc-pCVQZ calculations. [c] Calculation carried out at the optimal MP2/cc-pVTZ geometry, $R_{BH} = 1.1868$ Å. For comparison, MP2/cc-pVTZ frequencies are 1175.7, 1241.7, 2611.3, and 2749.9 cm^{-1}. [d] Martin, ref 10. This value is based on CCSD(T) calculations up through aug-cc-pV5Z(B)/cc-pV5Z(H), a ZPE of 16.32 kcal/mol, and a core/valence correction of 1.05 kcal/mol. [e] Kawaguchi, ref 32. [f] Kawaguchi, ref 32, Kawaguchi et al., ref 33, and Jacox et al., ref 34. [g] Based on JANAF tables, $\Delta H_f{}^0 = 26.4 \pm 2.4$ kcal/mol, and a ZPE of 16.0 kcal/mol.

TABLE 5: CCSD(T) Results for (X ^1A_g) B_2H_6

basis set	energy	R_{BB}	R_{BH}	$R_{BH(br)}$	∠HBH	ΣD_e
cc-pVDZ	−53.078799	MP2[b]				567.47
cc-pVTZ	−53.143194	MP2[b]				594.96
cc-pVQZ	−53.159064	MP2[b]				600.98
CBS(DTQ/e^{-x})	−53.1643	MP2[b]				602.5
CBS(TQ/l_{max})	−53.1682	MP2[b]				604.5
aug-cc-pVDZ	−53.088453	MP2[b]				
aug-cc-pVTZ	−53.146408	MP2[b]				
aug-cc-pVQZ	−53.160090	MP2[b]				
CBS(aDTQ/e^{-x})	−53.1643	MP2[b]				602.3
CBS(aTQ/l_{max})	−53.1680	MP2[b]				604.4
aug-cc-pVDZ	−53.089683	1.7928	1.2028	1.3306	122.6	571.96
aug-cc-pVTZ	−53.146478	1.7630	1.1887	1.3153	122.4	596.54
aug-cc-pVQZ	−53.160118	1.7581	1.1873	1.3137	122.3	601.49
CBS(aDTQ/e^{-x})	−53.1644	1.7569	1.1872	1.3134	122.3	602.4 (605.1)[c]
CBS(TQ/l_{max})	−53.1680					604.4 (607.1)[c]
CBS(aDTQ/mix)	−53.1674					604.0 (606.7)[c]
experiment		1.763[d]	1.201[d]	1.320[d]	121.0[d]	606.9 ± 4[d]

[a] Bond lengths are in angstroms and angles are in degrees. D_e is given in kcal/mol. Dissociation energies were obtained with respect to unrestricted open shell calculations on B. [b] Calculation carried out at the optimal MP2(FC)/cc-pVTZ geometry, $R_{BB} = 1.7541$ Å, $R_{BH} = 1.1845$ Å, $R_{BH(br)} = 1.3097$ Å, and ∠HBH = 122.2°. [c] Including core/valence correction obtained from CCSD(T)/cc-pCVQZ calculations. [d] Callomon, ref 46. [e] Experimental ΣD_e is based on the $\Delta H_f{}^0$ taken from the JANAF tables, the "experimental" ZPE, and a spin−orbit correction for the boron atoms of 2 × 0.03 kcal/mol.

$1a_g{}^2\ 1b_{1g}{}^2$) can be obtained from the dimerization energy of BH_3, i.e., $2BH_3 \rightarrow B_2H_6$. Using the CCSD(T)/CBS(aDTQ/mix) values for ΣD_e listed in Table 5, we obtain a ΔE_{dimer} of −44.3 kcal/mol for this reaction, including a −0.59 kcal/mol core/valence correction. The calculated geometry at the CBS limit is in reasonable agreement with experiment, considering the type of experimental measurement and the associated error bars (up to ±0.01 Å and ±1°).[37,46]

To determine the enthalpy of dimerization at 0 K, we need to include zero point energy differences. Harmonic vibrational frequencies were obtained at the MP2/cc-pVTZ level and CCSD(T)/aug-cc-pVDZ levels of theory and compared with the B_2H_6 experimental data.[38] As seen in Table 6, the agreement between both levels of theory and experiment is good, with the CCSD(T) frequencies generally within 3% of experiment. The ν/ω_{theory} ratios remain relatively constant across the 18 modes. The largest deviations between theory and experiment were observed in the b_{2g} and b_{3u} bands, where the first and second modes involve motions of the bridging hydrogens. At the MP2 level of theory both ratios are near 0.91. CCSD(T) improves the b_{2g} ratio to 0.944, but the b_{3u} ratio is still noticeably poorer than the other values. Anharmonic effects may be significant for this mode. Thus, since the theoretical frequencies appear to confirm the experimental assignments, we have chosen to use $1/2\Sigma(\nu_{expt}) = 38.2$ kcal/mol for the B_2H_6 zero point energy. We note that the experimental frequencies that we have used differ somewhat from those used in the JANAF tables.[1]

The resulting ZPE correction for the dimerization energy is 6.2 kcal/mol, i.e., it decreases the magnitude of ΔH. Thus, we calculate $\Delta H_{dimer}{}^0 = -38.1$ kcal/mol, in good agreement with the 0 K values estimated from the photoionization work of Ruscic et al.[39] which lie in the range −34.3 to −39.1 ± 2 kcal/

TABLE 6: Frequencies for B_2H_6[a]

symmetry	ω_{MP2}	$\omega_{CCSD(T)}$	ν_{expt}[b]	ν/ω_{MP2}	$\nu/\omega_{CCSD(T)}$	IR intensity
a_g	2669.1	2603.8	2524	0.946	0.969	0
	2218.8	2159.9	2104	0.948	0.974	0
	1230.6	1190.7	1180	0.959	0.991	0
	829.8	800.9	794	0.957	0.991	0
a_u	871.0	832.7	833	0.956	1.000	0
b_{1g}	2751.2	2680.2	2591[c]	0.942	0.967	0
	956.3	923.1	915[c]	0.957	0.991	0
b_{2g}	1940.0	1872.9	1768[d]	0.911	0.944	0
	916.6	875.9	850[d]	0.927	0.970	0
b_{3g}	1075.0	1051.2	1012	0.941	0.963	0
b_{1u}	2048.2	1979.1	1915[e]	0.935	0.968	9
	1008.8	981.6	973[e]	0.965	0.991	27
b_{2u}	2764.9	2696.6	2612[f]	0.945	0.969	166
	981.9	962.2	950[f]	0.968	0.987	1
	372.7	366.5	368	0.987	1.004	16
b_{3u}	2653.0	2587.7	2525	0.952	0.976	145
	1770.5	1740.8	1602	0.905	0.920	492
	1218.2	1174.5	1177	0.966	1.002	78

[a] Frequencies are in cm^{-1}. MP2 IR intensities are in km/mol. MP2 frequencies were obtained with the cc-pVTZ basis set. CCSD(T) frequencies were obtained with the aug-cc-pVDZ basis set. The zero point energies are 40.4 (MP2), 39.2 (CCSD(T)), and 38.2 (expt) kcal/mol. [b] Experimental frequencies are taken from Shimanouchi, ref 38. [c] b_{2g} symmetry type in ref 38. [d] b_{1g} symmetry type in ref 38. [e] b_{2u} symmetry type in ref 38. [f] b_{1u} symmetry type in ref 38.

mol. The B_2H_6 CCSD(T)/CBS(aDTQ/mix) value of ΣD_e is 606.7 ± 1.0 kcal/mol, including a 2.66 kcal/mol core/valence correction, whereas the smaller cc-pCVTZ basis set predicts a core/valence correction of 2.10 kcal/mol. The G2 value reported by Rablen and Hartwig[40] is 604.3 kcal/mol. Combining the CCSD(T) value for the atomization energy with the experimental $\Delta H_f{}^0(B)$ and $\Delta H_f{}^0(H)$ yields $\Delta H_f{}^0(B_2H_6) = 13.7 \pm 1.4$ kcal/mol. Although the same value could have been obtained from the dimerization of BH_3, it would have been somewhat more difficult to estimate the error limits, since an estimate of the error in the BH_3 energy would been required. By using −3.75 kcal/mol as the difference in $\Delta H_f(B_2H_6)$ between $T = 0$ K and $T = 298$ K,[1] we obtain a value of $\Delta H_f{}^{298}(B_2H_6) = 8.3$ kcal/mol. Experimental[1] measurements of $\Delta H_f{}^0(B_2H_6)$ provide a value of 13.6 ± 4 kcal/mol and a dimerization energy of −39.2 ± 8.8 kcal/mol at 0 K.

A number of authors have calculated the dimerization energy of BH_3. Early work by Hall et al.[41] established the Hartree−Fock limit to be approximately −19.0 kcal/mol, whereas we compute −22.0 kca/mol. CEPA calculations by Ahlrichs[42] predicted a value of $\Delta E_{dimer} = -36.6$ kcal/mol. Fourth-order, many body perturbation theory calculation (no triple excitations) with a polarized triple-ζ basis set gave −37.4 kcal/mol.[43] A third-order perturbation theory calculation with the 6-311G** basis set gave −40.3 kcal/mol.[44] The most recent value is −43.14 kcal/mol obtained by Page et al.[45] at the MP4/6-311G++(3df,3pd) level, to be compared with our value of −44.3 kcal/mol. Page et al. used scaled HF frequencies to get a zero point energy difference of 6.1 kcal/mol for the dimerization reaction, in excellent agreement with our value. We note that the authors used the older value of $\Delta H_f{}^{298}(B)$ in obtaining their $\Delta H_f{}^{298}(B_2H_6)$ of 2.7 kcal/mol from their atomization energy $\Sigma D_e = -603.7$ kcal/mol. Combining the 3.75 kcal/mol quoted in the JANAF tables as the 298 → 0 K difference in $\Delta H_f(B_2H_6)$ with the $\Delta H_f{}^{298}(B_2H_6)$ value reported by Page et al. yields a value of $\Delta H_f{}^0(B_2H_6)$ of 6.4 kcal/mol, compared to our value of 13.7 kcal/mol. The difference of ∼7 kcal/mol can be chiefly attributed to differences in $\Delta H_f{}^0(B)$.

To avoid the very time-consuming process of optimizing the molecular geometry with big basis sets at the CCSD(T) level of theory, where analytical first derivatives are not available, we have investigated the possibility of using MP2 geometries obtained with the more modest cc-pVTZ basis set. As seen in Table 5, the CBS estimates for ΣD_e obtained at the optimal MP2/cc-pVTZ geometry from either the cc-pVxZ sequence of basis sets or the aug-cc-pVxZ sequence are within 0.1−0.2 kcal/mol of the values obtained at the optimal CCSD(T) geometries. The small size of the error introduced by using a fixed MP2 geometry is due, in part, to a fortuitous cancelation of errors. The MP2/cc-pVTZ geometry is much closer to the CCSD(T)/aug-cc-pVQZ geometry than MP2 geometries determined with either the double- or quadruple-ζ basis set. Agreement between the MP2 and CCSD(T) optimized geometries and the experimental geometry reported by Callomon et al.[46] is reasonably good.

Conclusion

The total binding enthalpies and heats of formation for four simple boron hydrides were obtained from high-level ab initio calculations at the coupled cluster level of theory. After accounting for the errors due to (1) the finite basis set expansion, (2) the nonnegligible effects of core/valence correlation, (3) the use of fixed geometries obtained at a lower level of theory, (4) the uncertainties due to missing experimental zero point vibrational energies, and (5) errors in $\Delta H_f{}^0(B)$, we arrived at final values of $\Delta H_f{}^0(BH) = 106.2 \pm 0.3$ kcal/mol, $\Delta H_f{}^0(BH_2) = 78.4$ kcal/mol ± 0.4 kcal/mol, $\Delta H_f{}^0(BH_3) = 25.8 \pm 0.7$ kcal/mol, and $\Delta H_f{}^0(B_2H_6) = 13.7 \pm 1.4$ kcal/mol. These calculated values significantly reduce the error limits in comparison to the experimental values and further demonstrate the difficulty in computing thermodynamic quantities such as $\Delta H_f{}^0$ via ab initio techniques.

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