

Thermodynamic Properties of Molecular Borane Amines and the $[\text{BH}_4^-][\text{NH}_4^+]$ Salt for Chemical Hydrogen Storage Systems from *ab Initio* Electronic Structure Theory

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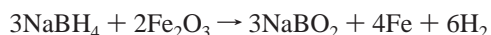
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Received: November 30, 2004; In Final Form: March 25, 2005

The heats of formation for the borane amines BH_3NH_3 , BH_2NH_2 , and HBNH , tetrahedral BH_4^- , and the BN molecule have been calculated by using *ab initio* molecular orbital theory. Coupled cluster calculations with single and double excitations and perturbative triples (CCSD(T)) were employed for the total valence electronic energies. Correlation consistent basis sets were used, up through the augmented quadruple- ζ , to extrapolate to the complete basis set limit. Core/valence, scalar relativistic, and spin-orbit corrections were included in an additive fashion to predict the atomization energies. Geometries were calculated at the CCSD(T) level up through at least aug-cc-pVTZ and frequencies were calculated at the CCSD(T)/aug-cc-pVDZ level. The heats of formation (in kcal/mol) at 0 K in the gas phase are $\Delta H_f(\text{BH}_3\text{NH}_3) = -9.1$, $\Delta H_f(\text{BH}_2\text{NH}_2) = -15.9$, $\Delta H_f(\text{HBNH}) = 13.6$, $\Delta H_f(\text{BN}) = 146.4$, and $\Delta H_f(\text{BH}_4^-) = -11.6$. The reported experimental value for $\Delta H_f(\text{BN})$ is clearly in error. The heat of formation of the salt $[\text{BH}_4^-][\text{NH}_4^+](\text{s})$ has been estimated by using an empirical expression for the lattice energy and the calculated heats of formation of the two component ions. The calculations show that both $\text{BH}_3\text{NH}_3(\text{g})$ and $[\text{BH}_4^-][\text{NH}_4^+](\text{s})$ can serve as good hydrogen storage systems which release H_2 in a slightly exothermic process. The hydride affinity of BH_3 is calculated to be 72.2 kcal/mol, in excellent agreement with the experimental value at 298 K of 74.2 ± 2.8 kcal/mol.

Introduction

The development of H_2 -based fuel cells promises clear economic, energy, and environmental security benefits to the United States. Diversifying our energy resources, particularly through the expansion of a domestic resource such as H_2 , will stimulate new markets and strengthen U.S. flexibility and economic resiliency in all sectors, as well as meet specific national security needs. There is a critical need to develop new chemical H_2 storage materials and novel approaches for the release/uptake of H_2 for use in on-board transportation systems.¹ A significant effort in the 1970s by the military was made to develop clean sources of H_2 for use in HF lasers. An important part of this effort was the use of compounds containing B or B and N as hydrogen sources based on the original synthesis of compounds such as the ammonium borohydride salt $\text{BH}_4^- \text{NH}_4^+$ ² and ammonia borane NH_3BH_3 .³ For example, work at the Redstone Arsenal and Edwards Air Force Base showed that the following reaction



provided a good source of H_2 for the chemical HF laser system.⁴ This reaction yields 3 wt % of H_2 , somewhat low in terms of the Department of Energy's requirements for realistic H_2 storage/release materials of 6 wt %. In other work, the Redstone Arsenal workers looked at formulations containing NaBH_4 in combination with various ammonium salts, for example, $(\text{NH}_4)_2\text{SO}_4$.⁴ The $\text{NaBH}_4/(\text{NH}_4)_2\text{SO}_4$ combination could produce up to 8.5 wt % of H_2 . In addition, they⁴ and others^{5,6} also studied amine boranes as possible H_2 sources.

The suitability of the NH_xBH_x ($x = 1-4$) compounds as solids for hydrogen storage has recently been evaluated by using theoretical methods.^{7,8} The amine boranes have excellent weight percent storage for H_2 with BH_3NH_3 having 19% if 3 molecules of H_2 are produced and the salt $(\text{NH}_4)(\text{BH}_4)$ having 24% if 4 molecules of H_2 are produced. In both cases, the final product would be BN . Thus, the NH_xBH_x series of compounds ($x = 1-4$) are attractive targets for chemical H_2 storage materials. Since the BN unit is isoelectronic with the CC unit, these materials can be viewed as inorganic analogues of hydrocarbons. However, the NH_xBH_x compounds are solids rather than gases at ambient temperatures, due to the greater polarity and the stronger intermolecular interactions as compared to the C_2 organic analogues which are gases. The inherent polarity is dictated by the different electronegativities of the B and N atoms, 2.0 and 3.0, respectively.⁹ As solids, they provide far more favorable volumetric densities compared to the corresponding gaseous hydrocarbons.⁸

The computational results, obtained at the density functional level of theory, for the solids NH_4BH_4 , NH_3BH_3 , and BN and polymers NH_2BH_2 and NHBH , indicate that the NH_xBH_x compounds also display favorable thermodynamics: all four subsequent steps of hydrogen release from NH_xBH_x for x ranging from 4 to 1 are thermoneutral to within 10 kcal/mol.^{7,8} These theoretical results are supported by experimental work that shows the reaction enthalpy for H_2 loss from NH_3BH_3 is exothermic by only 5 kcal/mol.⁵ The close thermoneutrality of hydrogen release from the NH_xBH_x compounds is in significant contrast to hydrolysis pathways of boron based hydrogen storage materials.¹⁰ Finally, it has recently been demonstrated that nanophase NH_3BH_3 deposited in a silica scaffold displays even more favorable kinetics and thermodynamics of hydrogen release than neat NH_3BH_3 .^{11,12} The specific nanophase structure

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of NH_xBH_x and the chemical properties of the scaffold provide additional controls on the release and uptake of hydrogen. The sum of these properties make the NH_xBH_x compounds promising candidates for on-board hydrogen storage materials.

An important need for understanding these materials and their performance is accurate thermodynamic data. Such data are needed in designing not only the release process but also the regeneration system. We have been developing an approach^{13–26} to the reliable calculation of molecular thermodynamic properties, notably heats of formation, based on ab initio molecular orbital theory. Our approach is based on calculating the total atomization energy of a molecule and using this with known heats of formation of the atoms to calculate the heat of formation at 0 K. This approach starts with coupled cluster theory with single and double excitations and including a perturbative triples correction (CCSD(T)),^{27–29} combined with the correlation-consistent basis sets^{30,31} 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. Finally, one must include the zero-point energy obtained either from experiment, theory, or some combination. The standard heats of formation of compounds at 298 K can then be calculated by using standard thermodynamic and statistical mechanics expressions in the rigid rotor-harmonic oscillator approximation³² and the appropriate corrections for the heat of formation of the atoms.³³

We have previously reported the calculation by using the above methods of the heats of formation of a number of the species needed to calculate reliable thermodynamic properties of some boranes²⁵ and nitrogen hydrides²⁶ including BH_3 , B_2H_6 , NH_3 , and NH_4^+ . In the present study, we present data for the molecular amine boranes, BH_3NH_3 , BH_2NH_2 , and HBNH , and tetrahedral BH_4^- . We also report results for the BN molecule, which has previously been studied in detail by Martin et al.³⁴ and Peterson.³⁵ In their work using multireference calculations, they showed that the ground state is the $^3\Pi$ and we predict the heat of formation of BN based on this state. We have recently used a combined computational chemistry/empirical modeling approach³⁶ to predict the lattice energy of the N_3^-N_5^+ and N_5^-N_5^+ salts.³⁷ We employ this same approach to calculate the lattice energy for the $\text{NH}_4^+\text{BH}_4^-$ salt.

Computational Approach

For the current study, we used the augmented correlation consistent basis sets aug-cc-pVnZ for H, B, and N ($n = \text{D, T, Q}$).^{30,31} For the sake of brevity, we abbreviate the names to aVnZ. Only the spherical components (5-d, 7-f, 9-g and 11-h) of the Cartesian basis functions were used. All of the current work was performed with the MOLPRO suite of programs.³⁸ All of the calculations were done on a massively parallel HP Linux cluster with Itanium-2 processors or on a 16-processor SGI computer system.

The geometries were optimized numerically at the frozen core CCSD(T) level with the aug-cc-pVDZ and aug-cc-pVTZ correlation-consistent basis sets. The vibrational frequencies were calculated numerically at the CCSD(T)/aug-cc-pVDZ level. For BN , the geometry and frequency were calculated at the aug-cc-pVQZ level from a 6th degree Dunham fit of the potential energy surface.³⁹ The CCSD(T)/aug-cc-pVTZ geometries were then used in single-point CCSD(T)/aug-cc-pVQZ calculations. 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.^{40–42} The CCSD(T) total energies were extrapolated 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 $n = 2$ (DZ), 3 (TZ), and 4 (QZ), as first proposed by Peterson et al.⁴³ This extrapolation method has been shown to yield atomization energies in the closest agreement with experiment (by a small amount) as compared to other extrapolation approaches up through $n = 4$. For BH_4^- , we also calculated the energy with the aug-cc-pV5Z basis set.

Core-valence corrections, ΔE_{CV} , were obtained at the CCSD(T)/cc-pCVTZ level of theory.⁴⁴ Scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI-SD (configuration interaction singles and doubles) level of theory by using the cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass-velocity and 1-electron Darwin (MVD) terms in the Breit-Pauli Hamiltonian.⁴⁵ Most calculations using available electronic structure computer codes do not correctly describe the lowest energy spin multiplet of an atomic state as spin-orbit in the atom is usually not included. Instead, the energy is a weighted average of the available multiplets. For N in the ^4S state, no spin-orbit correction is needed, but a correction of 0.03 kcal/mol is needed for B, taken from the excitation energies of Moore.⁴⁶

By combining our computed ΣD_0 (total atomization energies) values with the known heats of formation at 0 K for the elements ($\Delta H_f^0(\text{N}) = 112.53 \pm 0.02$ kcal mol⁻¹, $\Delta H_f^0(\text{B}) = 136.2 \pm 0.2$ kcal mol⁻¹, and $\Delta H_f^0(\text{H}) = 51.63$ kcal mol⁻¹),⁴⁷ we can derive ΔH_f^0 values for the molecules under study in the gas phase. The value for $\Delta H_f^0(\text{B})$ has only recently been revised. The older JANAF value⁴⁷ was 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), which we have used.⁴⁸ We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.³³

To predict the lattice energies needed for predicting the heat of formation of a salt, we can use the empirical expression³⁶

$$U_L = 2I[V_m^{-1/3} + \beta] \quad (2)$$

to estimate the lattice energy, U_L , of the salt, where I is the ionic strength ($I = 1$), V_m is the molecular (formula unit) volume of the lattices involved, which is equal to the sum of the individual ion volumes of the cation, V_+ , and anion, V_- , and $\alpha = 117.3$ kJ mol⁻¹ nm and $\beta = 51.9$ kJ mol⁻¹ are parameters. The individual ion volumes for NH_4^+ and BH_4^- can be taken from an ion volume database and are 0.021 ± 0.15 and 0.066 ± 0.15 nm³, respectively.³⁶ The calculated volume⁸ per formula unit at the density functional theory level is 0.098 nm³, which is in reasonable agreement with the sum 0.089 ± 0.030 nm³ of the separate ionic volumes. The empirical expression is probably good to ± 5 kcal/mol based on comparing lattice energies from it with those obtained from experimental data based on a Born-Haber cycle. For example, for NH_4CN , KI , and LiF the values are essentially identical within 1 kcal/mol as shown by Jenkins et al.³⁶ based on the values reported by Jenkins.⁴⁹

Results and Discussion

The calculated geometries are given in Table 1, the calculated vibrational frequencies in Table 2, the calculated total valence CCSD(T) as a function of basis set in Table 3, and the calculated

TABLE 1: Optimized CCSD(T) Bond Lengths (Å) and Bond Angles (deg)

molecule	basis set	r_{NH}	$\angle\text{HNB}$	r_{BH}	$\angle\text{HBH}$	r_{BN}
NH ₃ (¹ A ₁)	aVDZ	1.0237	105.9			
	aVTZ	1.0149	106.4			
	expt ⁵⁴	1.0116	106.7			
BH ₃	aVDZ			1.2062	120.0	
	aVTZ			1.1914	120.0	
	expt ⁵¹			1.185	120.0	
BH ₄ ⁻	aVDZ			1.2549	109.5	
	aVTZ			1.2397	109.5	
	aVQZ			1.2381	109.5	
NH ₄ ⁺	aVDZ	1.0282	109.5			
	aVTZ	1.0235	109.5			
	aVQZ	1.0218	109.5			
	expt ⁵⁵	1.0208 ± 0.002	109.5			
BH ₃ NH ₃	aVDZ	1.0230	107.70	1.2246	104.37	1.6768
	aVTZ	1.0157	107.92	1.2110	104.74	1.6575
	expt ⁵⁰	1.0140 ± 0.0020		1.2160 ± 0.0017		1.6576 ± 0.0016
BH ₂ NH ₂	aVDZ	1.0145	113.82	1.2082	122.73	1.4068
	aVTZ	1.0065	113.65	1.1947	122.49	1.3970
	expt ⁵²					1.403
HBNH	aVDZ	1.0022		1.1818		1.2542
	aVTZ	0.9927		1.1700		1.2445
	expt ⁵³					1.2381
BN(³ Π)	aVDZ					1.3493
	aVTZ					1.3365
	aVQZ					1.3299
	expt ⁵⁷					1.329
BN(¹ Σ)	aVDZ					1.2853
	aVTZ					1.2750
	aVQZ					1.2701
	expt ⁵⁶					1.281

energy components for the total atomization energies in Table 4. The calculated geometries (Table 1) are all in good agreement with the available experimental data.^{50–57}

The calculated frequencies for the molecules under consideration at the CCSD(T)/aug-cc-pVDZ level (Table 2) are in reasonable agreement with experiment^{54,58–64} for most of the frequencies. As expected, the N–H and B–H calculated harmonic stretching frequencies are greater than the experimental anharmonic frequencies by up to almost 200 cm⁻¹ for BH₃NH₃.⁶² For BH₃NH₃, there are an additional three modes which differ substantially from experiment.⁶² These modes are the two lowest a₁ modes and the second lowest e mode. This has previously been observed by Jagielska et al.⁶⁵ The second lowest a₁ mode is calculated to be too high by ~130 cm⁻¹ and the lowest a₁ mode is calculated to be too low by more than 300 cm⁻¹. The lowest a₁ mode is the B–N stretch and it is very anharmonic as noted by Jagielska et al.,⁶⁵ who did a one-dimensional calculation of this mode and obtained much better agreement with experiment, calculated 1005 cm⁻¹ as compared to 968 cm⁻¹. The second lowest e mode is calculated to be too low by ~130 cm⁻¹.

There are other deviations from the experimental frequencies in the other molecules. For HBNH, the lowest calculated frequency is below experiment.⁵⁹ For BH₂NH₂, the calculated lowest a₁ bend is below the gas-phase experimental assignment⁶⁰ by almost 100 cm⁻¹ but is in excellent agreement with the matrix-isolated assignment.⁶¹ We do not support the reassignment of the lowest b₁ and both b₂ bands made from the matrix-isolated measurements.⁶¹

To estimate zero-point energies, we followed our previous procedure of averaging the calculated harmonic and experimental anharmonic frequencies. For BN, we use just the calculated frequency as we have also calculated $\omega_e x_e$. As the largest anharmonic corrections are found for the stretches involving the N–H and B–H bonds, we average these values and use experimental values for the other modes filling in with

the computed values if the experimental ones are missing. We estimate that the error introduced in the heats of formation due to the zero-point energies is a maximum of ±0.4 kcal/mol.

The results for the prediction of the ground state of BN are complicated due to the presence of large multireference character in the ¹Σ state as found by Martin et al.³⁴ and subsequently by Peterson.³⁵ At the CCSD(T)/CBS level, the ¹Σ state is lower than that of the ³Π state by 0.7 kcal/mol. A similar result was found by Martin et al.,³⁴ who calculated that the ¹Σ state is lower than that of the ³Π state by 0.5 kcal/mol at the CCSD(T) level with a [4321] contracted basis set. At the multireference averaged coupled pair functional level with the same [4321] basis set, Martin et al.³⁴ find the ³Π state to be lower than the ¹Σ state with $T_e = 1.32$ kcal/mol (461 cm⁻¹) and provide a best estimate of $T_e = 1.1$ kcal/mol (381 cm⁻¹). They calculated a D_e for the ³Π ground state of 105.2 kcal/mol based on the dissociation energy of the ¹Σ state and their value of T_e .³⁴ A later MRCI/CBS calculation by Peterson³⁵ gave $T_e = 190 \pm 100$ cm⁻¹ (0.54 kcal/mol) with a ³Π ground state and a bond dissociation energy at the MRCI/CBS limit of 104.2 kcal/mol. On the basis of the photoelectron spectroscopy of the BN⁻ ion, T_e has been measured as 0.031 ± 0.004 eV (0.71 kcal/mol).⁶⁶ It is apparent that the CCSD(T) method overestimates the stability of the singlet state. Our CCSD(T)/CBS result for D_e of the ³Π state (104.03 kcal/mol) is in excellent agreement with that of Peterson at the MRCI/CBS level so we use this value to calculate the heat of formation of BN. Using the values given in Table 4 and the spin-orbit coupling constant for the ³Π state (25.1 cm⁻¹),⁵⁶ we find a D_e of 104.5 kcal/mol in good agreement with the available values and $D_0 = 102.4$ kcal/mol. The bond energy of BN is within the range of 92.2 ± 11.5 kcal/mol reported by Gaydon,⁶⁷ where we would recommend the higher end of the range. Our calculated geometries and frequencies agree with those of Martin et al.³⁴ and Peterson³⁵ for BN. For BN, the calculated heat of formation of 146.4 kcal/mol at 0 K

TABLE 2: Calculated Vibrational CCSD(T)/aug-cc-pVDZ Frequencies (cm⁻¹)^a

molecule	symmetry	calcd	exptl
BH ₃	a ₂ ''	1145.7	1140.9 ^{54,63}
	e'	1202.6	(1199) ⁵⁸
	a ₁ '	2545.8	(2475) ⁵⁸
NH ₃	e'	2675.6	2601.6 ^{54,63}
	a ₁	1070.1	932/968 ⁶⁴
	e	1649.7	1626 ⁶⁴
	a ₁	3433.9	3337 ⁶⁴
	e	3571.4	3444 ⁶⁴
HBNH	σ	3841	3700 ⁵⁹
	σ	2852	
	σ	1780	1786.2 ⁵³
	π	729	
BH ₂ NH ₂	π	428	460 ⁵⁹
	a ₁	3578	3451 ⁶⁰
	a ₁	2568	2495 ⁶⁰
	a ₁	1643	1625 ⁶⁰
	a ₁	1339	1337.5 ⁶⁰
	a ₁	1138	1225, ⁶⁰ 1116 ⁶¹
	a ₂	845	820 ⁵⁸
	b ₁	1000	1005 ⁶⁰
	b ₁	590	612, ⁶⁰ 705 ⁶¹
	b ₂	3686	3534 ⁶⁰
	b ₂	2649	2564 ⁶⁰
	b ₂	1129	1131, ⁶⁰ 1022 ⁶¹
	BH ₃ NH ₃	b ₂	725
e		3562	3386 ⁶²
a ₁		3440	3337
e		2494	2415
a ₁		2436	2340
e		1655	1608
a ₁		1324	1343
e		1191	1301
a ₁		1187	1052
e		1054	1186
a ₁		638	968
e		630	603
BH ₄ ⁻		a ₂	253
	a	2261	
	t	2240	
	e	1185	
BN(³ Π)	t	1086	
	σ	1510.6	1496 ⁵⁷
BN(¹ Σ)		13.1 (ω _e χ _e)	
	σ	1735.9	1712 ⁵⁶
		17.83 (ω _e χ _e)	

^a The frequencies for BN were obtained with the aug-cc-pVQZ basis set.

does not agree with the JANAF value⁴⁷ of 113 ± 30 kcal/mol taken from the value of $D_0^0 = 5.7$ eV of Douglas and Herzberg.⁶⁸

The calculated heats of formation for BH₃ and NH₃ are in excellent agreement with experiment⁴⁷ as we have previously shown.^{25,26} Our current value for $\Delta H_f^0(\text{BH}_3) = 26.4$ kcal/mol is in excellent agreement with our previously calculated value²⁵ of 25.9 ± 0.7 kcal/mol. We note that Ruscic and co-workers⁴⁸ obtained a total dissociation energy of 265.3 ± 1.7 kcal/mol in excellent agreement with our value of 264.6 kcal/mol. The experimental heat of formation of BH₃ based on the heat of formation of B from Storms and Mueller⁴⁸ is thus 25.8 ± 1.7 kcal/mol. Our current value for $\Delta H_f^0(\text{NH}_3) = -9.6$ kcal/mol can be compared with our value²⁶ of -9.1 ± 0.17 kcal/mol obtained at an even higher level. The latest experimental value for the heat of formation of NH₃ is from Ruscic, who using the Active Thermochemical Tables approach finds -9.219 ± 0.007 kcal/mol at 0 K.⁶⁹ The dissociation energy of BH₃NH₃ has been estimated to be 31.1 ± 1 kcal/mol based on the binding energy for the adduct of BH₃ with N(CH₃)₃.⁷⁰ Our calculated value at

TABLE 3: Total CCSD(T) Energies (E_n) as a Function of Basis Set^a

system	basis set	energy
BH ₃ NH ₃	aVDZ	-82.985 576 1
	aVTZ	-83.069 257 4
	aVQZ	-83.091 339 2
	CBS	-83.103 365
BH ₂ NH ₂	aVDZ	-81.818 269 0
	aVTZ	-81.895 303 4
	aVQZ	-81.916 794 7
	CBS	-81.928 653
HBNH	aVDZ	-80.592 278 2
	aVTZ	-80.661 667 3
	aVQZ	-80.682 462 8
	CBS	-80.694 117
BN	aVDZ	-79.217 735 6
	aVTZ	-79.271 668 9
	aVQZ	-79.288 619 9
	CBS	-79.298 211
BH ₄ ⁻	aVDZ	-27.154 512 1
	aVTZ	-27.186 223 9
	aVQZ	-27.194 011 9
	aV5Z	-27.196 076 8
BH ₃	CBS	-27.198 177
	aVDZ	-26.512 759 7
	aVTZ	-26.539 081 7
	aVQZ	-26.545 468 5
NH ₃	CBS	-26.548 873
	aVDZ	-56.425 519 7
	aVTZ	-56.480 562 4
	aVQZ	-56.495 732 3
NH ₄ ⁺	CBS	-56.504 079
	aVDZ	-56.762 100 4
	aVTZ	-56.818 013 4
	aVQZ	-56.833 285 1
BN(³ Π)	CBS	-56.841 671
	aVDZ	-79.217 735 6
	aVTZ	-79.271 668 9
	aVQZ	-79.288 619 9
BN(¹ Σ)	CBS	-79.298 211
	aVDZ	-79.216 310 0
	aVTZ	-79.272 004 5
	aVQZ	-79.289 424 9
	CBS	-79.299 275

^a Complete basis set limit (CBS) from eq 1.

TABLE 4: Components for Calculated Atomization Energies (kcal/mol)^a

molecule	CBS ^b	ΔE _{ZPE} ^c	ΔE _{CV} ^d	ΔE _{SR} ^e	ΔE _{SO} ^f	ΣD ₀ (0K) ^g
BH ₃ NH ₃	609.27	42.92	1.66	-0.39	-0.03	567.59
BH ₂ NH ₂	499.63	29.69	1.61	-0.38	-0.03	471.13
HBNH	352.46	15.35	1.63	-0.32	-0.03	338.39
BN(³ Π)	104.03	2.15	0.66	-0.15	0.0	102.36
BN(¹ Σ)	104.70	2.47	0.73	-0.16	-0.03	102.77
BH ₄ ⁻	373.88	20.69	1.28	-0.09	-0.03	354.35
BH ₃	280.19	16.20	0.76	-0.07	-0.03	264.65
NH ₃	297.44	20.86	0.70	-0.26	0.0	277.02
NH ₄ ⁺	195.53	30.48	0.72	-0.29	0.0	165.48

^a The energies of the atomic asymptotes and BN(³Π) were calculated with the R/UCCSD(T) method. ^b Extrapolated by using eq 1 with aug-cc-pVnZ, n = D, T, Q. ^c The zero-point energies were obtained as described in the text. ^d Core/valence corrections were obtained with the cc-pwCVTZ basis sets at the optimized geometries except for BH₄⁻ and NH₄⁺, where ΔE_{CV} was obtained with the aug-cc-pwCVTZ basis set. ^e The scalar relativistic correction is based on a CISD(FC)/cc-pVTZ MVD calculation except for BH₄⁻ and NH₄⁺, where ΔE_{CV} was obtained with the aug-cc-pVTZ basis set. ^f 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 46. ^g The theoretical value of the dissociation energy to atoms ΣD₀(0K).

0 K with zero-point effects included is 25.9 kcal/mol, which is about 5 kcal/mol lower than the estimated value. Our binding

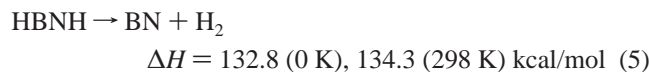
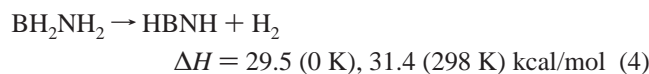
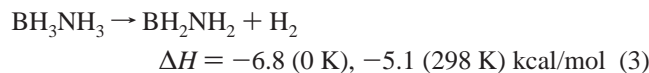
TABLE 5: Heats of Formation (kcal/mol) at 0 and 298 K^a

molecule	$\Delta H_f(0K)_{\text{theory}}$	$\Delta H_f(0K)_{\text{expt}}$	$\Delta H_f(298K)_{\text{theory}}$	$\Delta H_f(298K)_{\text{expt}}$
BH ₃ NH ₃	-9.1 ± 1.0		-13.5 ± 1.0	
BH ₂ NH ₂	-15.9 ± 1.0		-18.6 ± 1.0	
HBNH	13.6 ± 0.7		12.8 ± 0.7	
BN(³ I)	146.4 ± 0.3	113 ± 30 ⁴⁷	147.1 ± 0.3	114 ± 30 ⁴⁷
BH ₄ ⁻	-11.6 ± 0.7		-13.5 ± 0.7	
BH ₃	26.4 ± 0.7	26.4 ± 2.4 ⁴⁷ 25.8 ± 1.7 ⁴⁸	25.5 ± 0.7	25.5 ± 2.4 ⁴⁷
NH ₃	-9.6 ± 0.5	-9.30 ± 0.10 ⁴⁷ -9.219 ± 0.007 ⁶⁹	-11.3 ± 0.5	-10.97 ± 0.10 ⁴⁷ -10.891 ± 0.007 ⁶⁹
NH ₄ ⁺	153.6 ± 0.5		150.9 ± 0.7	

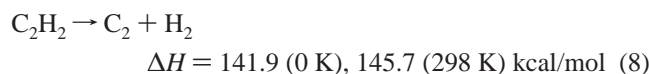
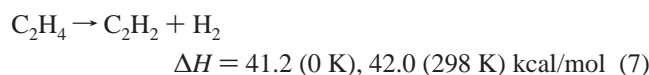
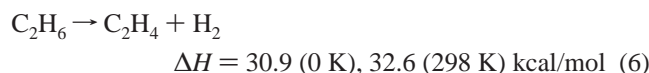
^a The calculated values are the recommended values except for NH₃ where the experimental values take precedence, especially the more recent ones from ref 69.

energy is about 3 kcal/mol higher than the value of Jagielska et al.⁶⁵ obtained at the CCSD(T)/aug-cc-pVTZ level. We suggest that our value for the binding energy of BH₃NH₃ is the best available value and, hence, our heat of formation is the best available value. Our estimated error bar due to ZPE is ±0.4 kcal/mol and we estimate that the errors in our extrapolation procedure and other electronic effects are a maximum of 0.6 ± kcal/mol, giving a maximum estimated error of ±1.0 kcal/mol with the largest error for the largest compound, BH₃NH₃.

Based on the calculated values, we can calculate the energy for the sequential release of H₂ from these molecules in the gas phase



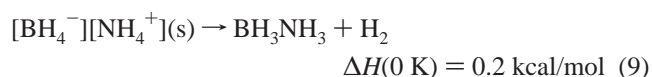
Clearly, BH₃NH₃ will be a good source of H₂ as the release of H₂ from this species is not far from thermoneutral. For comparison, we list the energies of the following gas-phase reactions^{47,71} based on hydrocarbons



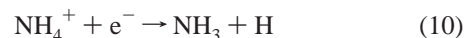
On the basis of these results, it is clear that the C₂ gaseous hydrocarbons cannot release H₂. What is surprising is how close the reaction energies are for reactions 4 and 7 and reactions 5 and 8. This is a manifestation of the similarity of the isoelectronic CCH_m and BNH_m systems. We also note that diatomic BN and diatomic C₂ have lowest singlet and triplet states that are essentially degenerate.³⁵

Another possibility for an H₂ storage system is the salt [BH₄⁻][NH₄⁺].^{7,8} We can estimate the lattice energy of the salt from eq 2 by using the estimated volumes of 0.066 ± 0.015 nm³ for BH₄⁻ and 0.021 ± 0.015 nm³ for NH₄⁺. Use of these values in eq 2 gives a lattice energy of 151.3 kcal/mol and a calculated heat of formation of the salt at 0 K of -9.3 kcal/mol. Alternatively, we may use the calculated volume at the DFT level of 0.098 nm³ for solid [BH₄⁻][NH₄⁺],⁸ which leads

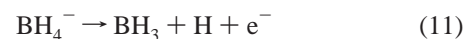
to a lattice energy of 146.1 kcal/mol and a heat of formation of the salt at 0 K of -4.1 kcal/mol. We note that the error bars for using eq 2 are probably ±5 kcal/mol. For the discussion below we use the former set of data for [BH₄⁻][NH₄⁺] although the qualitative discussion is not strongly dependent on which value is used. The reaction from the ionic solid to the gas-phase products



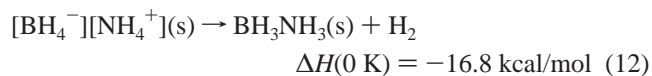
is essentially thermoneutral and the salt would be a good source of H₂. In order for the salt to be stable, we need to look at the possibility of electron transfer. The electron affinity (EA) of NH₄⁺ is very low as NH₄ is a Rydberg molecule with only a weak binding of H to NH₃ if at all. Thus we can estimate the EA(NH₄⁺) as the energy of the reaction



giving -111.6 kcal/mol (4.84 eV). The ionization potential of BH₄⁻ is given by the reaction



as BH₄ is also a very weakly bonded system and the electron affinity of BH₃ is very small (0.038 ± 0.015 eV = 0.88 ± 0.35 kcal/mol).⁷² The ionization potential of BH₄⁻ is low, 89.6 kcal/mol (3.89 eV). The fact that the electron affinity of NH₄⁺ and the ionization potential of BH₄⁻ are comparable within 1 eV of each other is consistent with the fact that this salt can be produced. Another possibility for the formation of H₂(g) is formation of NH₃BH₃(s) as shown in reaction 12.



The calculated cohesive energy for BH₃NH₃ is 17 kcal/mol⁸ and the enthalpy change for the hydrogen release reaction is substantially more exothermic than if BH₃NH₃(g) is produced.

From the heats of formation of BH₄⁻ and BH₃ together with the heat of formation of H⁻ (34.2 kcal/mol at 298 K), we can calculate the hydride affinity of BH₃. This value is 72.2 kcal/mol, which shows that BH₃ is a good hydride acceptor as expected. The experimental value⁷³ at 298 K is 74.2 ± 2.8 in excellent agreement with our calculated value. The total atomization energy for BH₄⁻ was also obtained by extrapolating the aug-cc-pVQZ and aug-cc-pVQ5Z values, using the formula⁷⁴

$$E(I_{\text{max}}) = E_{\text{CBS}} + B/I_{\text{max}}^3 \quad (13)$$

The CBS value obtained in this way is $-27.198\ 243$ au yielding a value for the valence electronic component of the dissociation energy of 373.98 kcal/mol, in excellent agreement with the value of 373.88 kcal/mol obtained with eq 1.

Conclusions

Ab initio molecular orbital theory at the CCSD(T)/CBS level plus additional corrections have been used to predict the heats of formation of a number of borane amines. The calculated heats of formation of the gas-phase boron amines with hydrogen are the best available values. The value for the bond energy of BN and hence its heat of formation is consistent with the best available values. The heat of formation of the salt $[\text{BH}_4^-]\text{[NH}_4^+](\text{s})$ has been estimated by using an empirical expression for the lattice energy and the calculated heats of formation of the two component ions. The calculations show that both $\text{BH}_3\text{-NH}_3(\text{g})$ and $[\text{BH}_4^-]\text{[NH}_4^+](\text{s})$ can serve as good hydrogen storage systems. The energetics for release of H_2 were calculated and the energetics for release of H_2 from BH_3NH_3 is predicted to be substantially different than the energetics for release of H_2 from C_2H_6 . However, the release of H_2 from the C_2 and BN analogues with a lower number of hydrogens is predicted to be comparable and substantially endothermic. The hydride affinity for BH_3 was also calculated and the value is found to be large and in good agreement with the available experimental result.

Acknowledgment. We thank Dr. Branko Ruscic for providing his unpublished value for the experimental heat of formation of NH_3 . This work has been supported in part by the LDRD program at the PNNL. This research was performed in part using the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory. Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle.

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