J. Phys. Chem. A **2005,** *109,* 5129−5135

Thermodynamic Properties of Molecular Borane Amines and the $[BH_4^-][NH_4^+]$ Salt for Chemical Hydrogen Storage Systems from ab Initio Electronic Structure Theory

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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 $\Delta H_f(BH_3NH_3) = -9.1$, $\Delta H_f(BH_2NH_2) = -15.9$, $\Delta H_f(BHNH) = 13.6$, $\Delta H_f(BN) = 146.4$, and $\Delta H_f(BH_4^-) = -11.6$. The reported experimental value for ΔH_f(BN) is clearly in error. The heat of formation of the salt $[BH_4^-][NH_4^+]$(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 BH_3NH_3(g) and $[BH_4^-][NH_4^+]$(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 $BH_4^-NH_4^+$[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

$$3NaBH_4 + 2Fe_2O_3 \rightarrow 3NaBO_2 + 4Fe + 6H_2$$

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, $(NH_4)_2SO_4$.[4] The $NaBH_4/(NH_4)_2SO_4$ combination could produce up to 8.5 wt % of H_2. In addition, they[4] 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 $(NH_4)(BH_4)$ 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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10.1021/jp0445627 CCC: $30.25

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 approximation[32] 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 boranes[25] and nitrogen hydrides[26] 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 approach[36] 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 $NH_4^+BH_4^-$ salt.

Computational Approach

For the current study, we used the augmented correlation consistent basis sets aug-cc-pV*n*Z for H, B, and N (n = D, T, Q).[30,31] For the sake of brevity, we abbreviate the names to aV*n*Z. 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:

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

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 ($\Delta H_f^0(N) = 112.53 \pm 0.02$ kcal mol^{-1}, $\Delta H_f^0(B) = 136.2 \pm 0.2$ kcal mol^{-1}, and $\Delta H_f^0(H) = 51.63$ kcal mol^{-1}),[47] we can derive ΔH_f^0 values for the molecules under study in the gas phase. The value for $\Delta H_f^0(B)$ has only recently been revised. The older JANAF value[47] 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 expression[36]

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

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 nm^3, respectively.[36] The calculated volume[8] per formula unit at the density functional theory level is 0.098 nm^3, which is in reasonable agreement with the sum 0.089 ± 0.030 nm^3 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}	∠HNH	r_{BH}	∠HBH	r_{BN}
NH_3 (^{1}A1)	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_3NH_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_2NH_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($^3\Pi$)	aVDZ					1.3493
	aVTZ					1.3365
	aVQZ					1.3299
	expt[57]					1.329
BN($^1\Sigma$)	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 BH_3NH_3.[62] For BH_3NH_3, there are an additional three modes which differ substantially from experiment.[62] These modes are the two lowest a_1 modes and the second lowest e mode. This has previously been observed by Jagielska et al.[65] The second lowest a_1 mode is calculated to be too high by ~130 cm^{-1} and the lowest a_1 mode is calculated to be too low by more than 300 cm^{-1}. The lowest a_1 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 BH_2NH_2, the calculated lowest a_1 bend is below the gas-phase experimental assignment[60] 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 b_1 and both b_2 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 $\omega_e\chi_e$. 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 $^1\Sigma$ state as found by Martin et al.[34] and subsequently by Peterson.[35] At the CCSD(T)/CBS level, the $^1\Sigma$ state is lower than that of the $^3\Pi$ state by 0.7 kcal/mol. A similar result was found by Martin et al.,[34] who calculated that the $^1\Sigma$ state is lower than that of the $^3\Pi$ 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 $^3\Pi$ state to be lower than the $^1\Sigma$ 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 $^3\Pi$ ground state of 105.2 kcal/mol based on the dissociation energy of the $^1\Sigma$ state and their value of T_e.[34] A later MRCI/CBS calculation by Peterson[35] gave $T_e = 190 \pm 100$ cm^{-1} (0.54 kcal/mol) with a $^3\Pi$ 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 $^3\Pi$ 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 $^3\Pi$ 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 Peterson[35] 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]
	e'	2675.6	2601.6[54,63]
NH_3	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	
	π	428	460[59]
BH_2NH_2	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]
	b_2	725	742,[60] 608[61]
BH_3NH_3	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
	a_2	253	
BH_4^-	a	2261	
	t	2240	
	e	1185	
	t	1086	
$BN(^3\Pi)$	σ	1510.6	1496[57]
		13.1 ($\omega_e\chi_e$)	
$BN(^1\Sigma)$	σ	1735.9	1712[56]
		17.83 ($\omega_e\chi_e$)	

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

TABLE 3: Total CCSD(T) Energies (E_h) as a Function of Basis Set[a]

system	basis set	energy
BH_3NH_3	aVDZ	−82.985 576 1
	aVTZ	−83.069 257 4
	aVQZ	−83.091 339 2
	CBS	−83.103 365
BH_2NH_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
	CBS	−27.198 177
BH_3	aVDZ	−26.512 759 7
	aVTZ	−26.539 081 7
	aVQZ	−26.545 468 5
	CBS	−26.548 873
NH_3	aVDZ	−56.425 519 7
	aVTZ	−56.480 562 4
	aVQZ	−56.495 732 3
	CBS	−56.504 079
NH_4^+	aVDZ	−56.762 100 4
	aVTZ	−56.818 013 4
	aVQZ	−56.833 285 1
	CBS	−56.841 671
$BN(^3\Pi)$	aVDZ	−79.217 735 6
	aVTZ	−79.271 668 9
	aVQZ	−79.288 619 9
	CBS	−79.298 211
$BN(^1\Sigma)$	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_3NH_3	609.27	42.92	1.66	−0.39	−0.03	567.59
BH_2NH_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
$BN(^3\Pi)$	104.03	2.15	0.66	−0.15	0.0	102.36
$BN(^1\Sigma)$	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 $BN(^3\Pi)$ were calculated with the R/UCCSD(T) method. [b] Extrapolated by using eq 1 with aug-cc-PV*n*Z, 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 BH_4^- and NH_4^+,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 BH_4^- and NH_4^+, 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 ΣD_0(0K).

does not agree with the JANAF value[47] 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 BH_3 and NH_3 are in excellent agreement with experiment[47] as we have previously shown.[25,26] Our current value for $\Delta H_f^0(BH_3) = 26.4$ kcal/mol is in excellent agreement with our previously calculated value[25] of 25.9 ± 0.7 kcal/mol. We note that Ruscic and co-workers[48] 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 BH_3 based on the heat of formation of B from Storms and Mueller[48] is thus 25.8 ± 1.7 kcal/mol. Our current value for $\Delta H_f^0(NH_3) = -9.6$ kcal/mol can be compared with our value[26] of −9.1 ± 0.17 kcal/mol obtained at an even higher level. The latest experimental value for the heat of formation of NH_3 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 BH_3NH_3 has been estimated to be 31.1 ± 1 kcal/mol based on the binding energy for the adduct of BH_3 with $N(CH_3)_3$.[70] Our calculated value at 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	$\Delta H_f(0K)_{theory}$	$\Delta H_f(0K)_{expt}$	$\Delta H_f(298K)_{theory}$	$\Delta H_f(298K)_{expt}$
BH_3NH_3	−9.1 ± 1.0		−13.5 ± 1.0	
BH_2NH_2	−15.9 ± 1.0		−18.6 ± 1.0	
HBNH	13.6 ± 0.7		12.8 ± 0.7	
BN($^3\Pi$)	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 NH_3 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 BH_3NH_3 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, BH_3NH_3.

Based on the calculated values, we can calculate the energy for the sequential release of H_2 from these molecules in the gas phase

$$BH_3NH_3 \rightarrow BH_2NH_2 + H_2 \qquad \Delta H = -6.8\ (0\ K),\ -5.1\ (298\ K)\ kcal/mol \quad (3)$$

$$BH_2NH_2 \rightarrow HBNH + H_2 \qquad \Delta H = 29.5\ (0\ K),\ 31.4\ (298\ K)\ kcal/mol \quad (4)$$

$$HBNH \rightarrow BN + H_2 \qquad \Delta H = 132.8\ (0\ K),\ 134.3\ (298\ K)\ kcal/mol \quad (5)$$

Clearly, BH_3NH_3 will be a good source of H_2 as the release of H_2 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

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad \Delta H = 30.9\ (0\ K),\ 32.6\ (298\ K)\ kcal/mol \quad (6)$$

$$C_2H_4 \rightarrow C_2H_2 + H_2 \qquad \Delta H = 41.2\ (0\ K),\ 42.0\ (298\ K)\ kcal/mol \quad (7)$$

$$C_2H_2 \rightarrow C_2 + H_2 \qquad \Delta H = 141.9\ (0\ K),\ 145.7\ (298\ K)\ kcal/mol \quad (8)$$

On the basis of these results, it is clear that the C_2 gaseous hydrocarbons cannot release H_2. 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 C_2 have lowest singlet and triplet states that are essentially degenerate.[35]

Another possibility for an H_2 storage system is the salt $[BH_4^-][NH_4^+]$.[7,8] We can estimate the lattice energy of the salt from eq 2 by using the estimated volumes of 0.066 ± 0.015 nm^3 for BH_4^- and 0.021 ± 0.015 nm^3 for NH_4^+. 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 nm^3 for solid $[BH_4^-][NH_4^+]$,[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 $[BH_4^-][NH_4^+]$ although the qualitative discussion is not strongly dependent on which value is used. The reaction from the ionic solid to the gas-phase products

$$[BH_4^-][NH_4^+](s) \rightarrow BH_3NH_3 + H_2 \qquad \Delta H(0\ K) = 0.2\ kcal/mol \quad (9)$$

is essentially thermoneutral and the salt would be a good source of H_2. In order for the salt to be stable, we need to look at the possibility of electron transfer. The electron affinity (EA) of NH_4^+ is very low as NH_4 is a Rydberg molecule with only a weak binding of H to NH_3 if at all. Thus we can estimate the EA(NH_4^+) as the energy of the reaction

$$NH_4^+ + e^- \rightarrow NH_3 + H \quad (10)$$

giving −111.6 kcal/mol (4.84 eV). The ionization potential of BH_4^- is given by the reaction

$$BH_4^- \rightarrow BH_3 + H + e^- \quad (11)$$

as BH_4 is also a very weakly bonded system and the electron affinity of BH_3 is very small (0.038 ± 0.015 eV = 0.88 ± 0.35 kcal/mol).[72] The ionization potential of BH_4^- is low, 89.6 kcal/mol (3.89 eV). The fact that the electron affinity of NH_4^+ and the ionization potential of BH_4^- 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 H_2(g) is formation of NH_3BH_3(s) as shown in reaction 12.

$$[BH_4^-][NH_4^+](s) \rightarrow BH_3NH_3(s) + H_2 \qquad \Delta H(0\ K) = -16.8\ kcal/mol \quad (12)$$

The calculated cohesive energy for BH_3NH_3 is 17 kcal/mol[8] and the enthalpy change for the hydrogen release reaction is substantially more exothermic than if BH_3NH_3(g) is produced.

From the heats of formation of BH_4^- and BH_3 together with the heat of formation of H^- (34.2 kcal/mol at 298 K), we can calculate the hydride affinity of BH_3. This value is 72.2 kcal/mol, which shows that BH_3 is a good hydride acceptor as expected. The experimental value[73] at 298 K is 74.2 ± 2.8 in excellent agreement with our calculated value. The total atomization energy for BH_4^- was also obtained by extrapolating the aug-cc-pVQZ and aug-cc-pVQ5Z values, using the formula[74]

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

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 $[BH_4^-][NH_4^+]$(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 BH_3NH_3(g) and $[BH_4^-][NH_4^+]$(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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