Thermodynamic Properties of Molecular Borane Phosphines, Alane Amines, and Phosphine Alanes and the $[BH_4^-][PH_4^+]$, $[AlH_4^-][NH_4^+]$, and $[AlH_4^-][PH_4^+]$ Salts for Chemical Hydrogen Storage Systems from ab Initio Electronic Structure Theory

Daniel J. Grant and David A. Dixon*,†

Department of Chemistry, University of Alabama, P.O. Box 870336, Tuscaloosa, Alabama 35487-0336

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The heats of formation for the molecules BH_3PH_3, BH_2PH_2, HBPH, AlH_3NH_3, AlH_2NH_2, HAlNH, AlH_3PH_3, AlH_2PH_2, HAlPH, AlH_4^-, PH_3, PH_4, and PH_4^+, as well as the diatomics BP, AlN, and AlP, have been calculated by using ab initio molecular orbital theory. The coupled cluster with single and double excitations and perturbative triples method (CCSD(T)) was 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. Additional d core functions were used for Al and P. 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 of the salts $[BH_4^-][PH_4^+]$(s), $[AlH_4^-][NH_4^+]$(s), and $[AlH_4^-][PH_4^+]$(s) have 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 AlH_3NH_3(g) and $[AlH_4^-][NH_4^+]$(s) can serve as good hydrogen storage systems that release H_2 in a slightly exothermic process. In addition, AlH_3PH_3 and the salts $[AlH_4^-][PH_4^+]$ and $[BH_4^-][PH_4^+]$ have the potential to serve as H_2 storage systems. The hydride affinity of AlH_3 is calculated to be −70.4 kcal/mol at 298 K. The proton affinity of PH_3 is calculated to be 187.8 kcal/mol at 298 K in excellent agreement with the experimental value of 188 kcal/mol. PH_4 is calculated to be barely stable with respect to loss of a hydrogen to form PH_3.

Introduction

There is clear interest in the development of H_2-based fuel cells to provide economic, energy, and environmental security benefits to the United States. 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] 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. The suitability of the NH_xBH_x ($x = 1-4$) compounds for hydrogen storage has recently been evaluated using theoretical methods.[2−4] The calculations showed that BH_3NH_3(g), BH_3NH_3(s), 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 from the energetics for release of H_2 from C_2H_6. In addition, calculations on the solid materials show that they may all be good systems for H_2 storage. These prior results show that the thermoneutrality of hydrogen release from the NH_xBH_x compounds is in significant contrast to hydrolysis pathways of boron based hydrogen storage materials.[5] In addition, recent work has shown that nanoscaffolds can be used to mediate the release of hydrogen from amine boranes.[6] Our current interest is to search for other candidates for H_2 storage systems to identify alternatives that may be easier to synthesize and for which we can design new catalysts. We have chosen to study the molecular systems isoelectronic to the previously studied amine boranes, BH_3NH_3, BH_2NH_2, and HBNH, those compounds containing Al, P, B, and N.

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, i.e., addition of H_2 back to the H_2 depleted material. We have been developing an approach[7−20] 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 includes a perturbative triples correction (CCSD(T)),[21−23] combined with the correlation-consistent basis sets[24,25] 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 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[26] and the appropriate corrections for the heat of formation of the atoms.[27]

In the present study, we present data for the molecular compounds BH_3PH_3, BH_2PH_2, HBPH, AlH_3NH_3, AlH_2NH_2,

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† E-mail: dadixon@bama.ua.edu.

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HAlNH, AlH_3PH_3, AlH_2PH_2, HAlPH, AlH_4^-, PH_3, PH_4, and PH_4^+ as well as the diatomics BP, AlN, and AlP. We have recently used a combined computational chemistry/empirical modeling approach[28] to predict the lattice energy of the $N_3^-N_5^+$ and $N_5^-N_5^+$ salts[29] and that of $[BH_4^-][NH_4^+](s)$.[4] We employ this same approach to calculate the lattice energy for the $[BH_4^-][PH_4^+](s)$, $[AlH_4^-][NH_4^+](s)$, and $[AlH_4^-][PH_4^+](s)$ salts.

There have been previous experimental and computational studies of a number of the molecules under study. The molecule BH_3PH_3 has been shown to be the monomer in the molten state at 37 °C and in the solid on the basis of NMR, infrared, and Raman studies.[30] Jungwirth and Zahradnik[31] calculated the geometries for BH_3NH_3, BH_3PH_3, AlH_3NH_3, and AlH_3PH_3 at the MP2/6-31G* level and evaluated bond energies at the QCISD(T)/6-31G* level with a BSSE correction. They find X−Y bond distances of 1.661, 1.944, 2.083, and 2.544 Å respectively and X−Y bond energies of 20.9, 15.6, 22.4, and 8.8 kcal/mol, respectively. The dissociation energy to form $BH_3 + PH_3$ has been calculated to be 18.0 kcal/mol at the MP4(STDQ)/6-31++G(d,p)//MP2/6-31++G(d,p) level.[32] The B−P bond distance has been calculated to be 1.947 Å. Similarly, AlH_3PH_3 has been calculated to have a bond distance of 2.555 Å and a Al−P bond energy of 12.8 kcal/mol. The structures and frequencies of AlH_3PH_3 have been calculated at the CISD/DZP level and for AlH_2PH_2 at the CISD/TZ2P level. The geometries were also calculated at the CCSD/TZ2P level, and the Al−P bond is 2.576 Å for AlH_3PH_3 and 2.335 Å for AlH_2PH_2 with a decidedly nonplanar structure for the latter. The AlHPH isomer has been predicted to be 13 kcal/mol higher in energy than the $AlPH_2$ isomer at the CCSD/TZ2P level.[33] The Al−P bond distance for $Me_3Al{-}PMe_3$ has been found to be 2.53(4) Å on the basis of an electron diffraction study.[34] The best calculated value for D_0 for the Al−P bond energy in AlH_3PH_3 is the CCSD/TZ2P value of 11.0 kcal/mol.[33] This group also calculated a dehydrogenation energy of 3.3 kcal/mol at the CCSD/TZ2P level with zero point corrections for loss of H_2 from AlH_3PH_3 to form AlH_2PH_2. The structures and energetics of $AlNH_y$ have been calculated at the CISD and CCSD levels with basis sets up to TZ2P.[35] The heat of hydrogenation of AlH_2NH_2 is −4 kcal/mol and for AlHNH is −62 kcal/mol at the CCSD/DZP level. The bond energy is AlH_3NH_3 has been calculated to be 26 kcal/mol at the CCSD/DZP level.[36] At the MP2/cc-pVDZ level, the bond distance in AlH_3NH_3 has been calculated to be 2.116 Å and 2.111 Å at the B3LYP/cc-pVDZ level. These values were obtained in a study of the dimers.[37] Watts et al.[38] studied the molecule HB═PH and found a cis structure to be the global minimum with a variety of methods up through CCSD(T) with the cc-pVTZ basis set. The cis structure is best described as an H bridging the B and P although it is not described as such in the reference. Kerrins et al.[39] also found a similar cisoid structure to be the most stable with geometries optimized at the HF/6-31G** level and energies obtained at the MP4/6-31++G** level. Their cisoid structure has less P−H bond bridging than the correlated one. The AlN molecule has been studied by Langhoff et al.[40] at the CASSCF and MRCI levels with a focus on the spectrum. The AlN bond energy for the $^3\Pi$ state has been calculated to be 63.2 kcal/mol at the density functional theory level with the Becke exchange and Perdew−Wang correlation functional (BPW) and the DNP basis set.[41] Costales et al. used the same method to calculate the properties of AlP for the $^3\Sigma^-$ state.[42]

Computational Approach

For the current study, we used the augmented correlation consistent basis sets aug-cc-pVnZ for H, B, and N (n = D, T, Q).[24,25] For the sake of brevity, we abbreviate the names to aVnZ. Only the spherical components (5d, 7f, and 9g) of the Cartesian basis functions were used. All of the current work was performed with the MOLPRO suite of programs.[43] 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.[44−46] All of the calculations were done on a massively parallel HP Linux cluster with 1970 Itanium-2 processors in the Molecular Sciences Computing Facility in the William R. Wiley Environmental Molecular Sciences Laboratory or on the 144 processor Cray XD-1 computer system at the Alabama Supercomputer Center.

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 CCSD(T)/aug-cc-pVTZ geometries were then used in single point CCSD(T)/aug-cc-pVQZ calculations. Harmonic frequencies and anharmonic constants for the diatomic molecules were obtained from a fifth-order fit of the potential energy surface at the CCSD(T)/aug-cc-pV(Q+d)Z level. For a few molecules, the harmonic frequencies were calculated at the CCSD(T)/aug-cc-pVDZ to get scaling parameters for the zero point energies. All of the vibrational frequencies were calculated at the MP2/cc-pVTZ level[47] using the Gaussian program system.[48] These were used for the zero point energies except for the diatomics and for the thermal corrections and entropies.

It has recently been found that tight d functions are necessary for calculating accurate atomization energies for second row elements,[49] so we also included additional tight d functions in our calculations. Basis sets containing extra tight d functions are denoted aug-cc-pV(n+d)Z in analogy to the original augmented correlation consistent basis sets. We will use aug-cc-pV(n+d)Z to represent the combination of aug-cc-pV(n+d)Z (on the second row atoms Al and P) and aug-cc-pVnZ (on H, B, and N) basis sets and abbreviate this as aV(n+d)Z. The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form

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

with $n = 2$ (DZ), 3 (TZ), and 4 (QZ), as first proposed by Peterson et al.[50] 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 $n = 4$.

Core-valence corrections, ΔE_{CV}, were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[51] 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 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.[52] 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 or P in the ^4S state, no spin−orbit correction is needed, but a correction of 0.03 kcal/mol is needed for B and one of 0.21 kcal/mol for Al, taken from the excitation energies of Moore.[53]

By combining our computed ΣD_0 (total atomization energies) values with the known heats of formation at 0 K for the elements

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

molecule	basis set	r_{MH}	∠HMH
AlH_3	aVDZ	1.5921	120.0
	aVTZ	1.5855	120.0
AlH_4^-	aVDZ	1.6547	109.5
	aVTZ	1.6482	109.5
PH_3 ($^1A1$)[a]	aVDZ	1.4343	93.45
	aVTZ	1.4195	93.46
	expt[a]	1.413	93.45
PH_4 (C_{2v})	aVDZ	1.5488ax	170.66ax
		1.4238eq	99.06eq
	aVTZ	1.5241ax	170.63ax
		1.4091eq	99.79eq
PH_4^+	aVDZ	1.4103	109.5
	aVTZ	1.3972	109.5

[a] *Structure of Free Polyatomic Molecules−Basic Data*; Kuchitsu, K., Ed.; Springer: Berlin, 1998; p 66.

($\Delta H_f{}^0$(N) = 112.53 ± 0.02 kcal mol^{-1}, $\Delta H_f{}^0$(B) = 136.2 ± 0.2 kcal mol^{-1}, $\Delta H_f{}^0$(P) = 75.42 ± 0.24 kcal mol^{-1}, $\Delta H_f{}^0$(Al) = 78.23 ± 1.0 kcal mol^{-1}, and $\Delta H_f{}^0$(H) = 51.63 kcal mol^{-1},[54] we can derive $\Delta H_f{}^0$ values for the molecules under study in the gas phase. We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.[27]

To predict the lattice energies needed for predicting the heat of formation of a salt, we can use the empirical expression[28]

$$U_L = 2I[\alpha V_m{}^{-1/3} + \beta] \tag{2}$$

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 α = 28.0 kcal mol^{-1} nm and β = 12.4 kcal mol^{-1} for 1:1 salts. Most of the individual ion volumes for can be taken from an ion volume database and are $V(BH_4^-)$ = 0.066 ± 0.015, $V(NH_4^+)$ = 0.021 ± 0.015, $V(AlH_4^-)$ = 0.067 nm^3.[28] The volume for PH_4^+ was calculated on the basis of the volumes that we have used in free energy of solvation calculations.[55] The electron densities were calculated at the B3LYP/6-31+G* level[56] and the volume was taken to be that inside the 0.001 au contour of the electron density, giving $V(PH_4^+)$ = 0.025 nm^3. The empirical expression is probably good to ±5 kcal/mol on the basis of 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.,[28] on the basis of the values reported by Jenkins.[57]

Results and Discussion

The calculated geometries are given in Tables 1−4 and the calculated vibrational frequencies in Tables 5−8. The molecular structures are shown in Figure 1. The calculated geometries show some interesting behavior. The molecules BH_3PH_3, AlH_3NH_3, and AlH_3PH_3 all have long dative bonds between the group IIIA and group VA atoms. As a consequence, the HPH angles become a little less pyramidal than in PH_3 and the HAlH and HBH bond angles become more pyramidal and move away from the D_{3h} angle of 120.0°. The molecule AlH_2NH_2 remains planar, as found for BH_2NH_2 but the molecules BH_2PH_2 and AlH_2PH_2 become nonplanar. The nonplanarity occurs at the PH_2− moiety and is consistent with the much higher inversion barrier in PH_3 as compared to NH_3.[58] The nonplanar form of BH_2PH_2 is 6.5 kcal/mol more stable than the planar structure at the CBS valence electronic energy level and the nonplanar form of AlH_2PH_2 is 5.0 more stable than the planar structure at the same level. The molecules BHPH and AlHPH are clearly bent with the bent structures 28.4 and 25.9 kcal/mol more stable than the linear structures at the CBS valence electronic energy level, respectively. The bent structure HBPH forms a BHP bridge-bond with a PH distance of 1.529 Å, which is slightly larger than the PH bond distance obtained for PH_3 of 1.4195 Å. Also, the ∠BHP of 70.1° is smaller than the ∠BHB of 84.3° obtained in diborane. This structure for the minimum is essentially the same as the one predicted by Watts et al.[38] The molecule AlHNH has more complicated energetics with the bent and linear forms having the same energy at the CBS valence electronic energy level. The bent AlHNH molecule has a trans structure with a ∠HNAl of 147.2° further from linear compared to the ∠HAlN of 161.4°. The bent structure HAlPH has a ∠HPAl of 78.0° with the HAlP angle remaining linear. The PH bond distance of 1.449 Å is larger than the PH bond distance obtained in PH_3 of 1.4195 Å.

Huber and Herzberg[59] report a bond length of 1.786 Å for the bond length of the $^3\Pi$ state for AlN and our best calculated value is a little long by 0.02 Å. The calculated and experimental values for ω_e are in excellent agreement with each other for the $^3\Pi$ state. Langhoff et al.[40] calculated a number of states for AlN at the CASSCF and MRCI levels and suggest that the ground state is $^3\Pi$ with the $^3\Sigma^-$ slightly higher in energy. Their spectroscopic constants of R_e = 1.817 Å and ω_e = 737 cm^{-1}

TABLE 2: Optimized CCSD(T) Bond Lengths (Å) and Bond Angles (deg) for BPH_x

molecule	basis set	r_{PH}	∠HPH	∠HPB	r_{BH}	∠HBH	∠HBP	r_{BP}
BP($^3\Pi$)	aVDZ							1.7858
	aVTZ							1.7602
	aVQZ							1.7521
BP($^3\Sigma$)	aVDZ							1.9976
	aVTZ							1.9728
	aVQZ							1.9643
BP($^1\Sigma$)	aVDZ							1.7133
	aVTZ							1.6880
	aVQZ							1.6799
HBPH (linear)	aVDZ	1.3967			1.1841			1.6701
	aVTZ	1.3855			1.1717			1.6507
HBPH (nonlinear)	aVDZ	1.5454		52.70	1.1910		176.38	1.7307
	aVTZ	1.5288		52.57	1.1778		176.49	1.7066
BH_2PH_2 (planar)	aVDZ	1.4071	109.23	125.39	1.2029	124.61	117.69	1.8140
	aVTZ	1.3939	109.03	125.49	1.1888	124.69	117.67	1.7943
BH_2PH_2 (nonplanar)	aVDZ	1.4246	99.70	102.53	1.2056	120.70	119.65	1.8997
	aVTZ	1.4101	100.16	103.18	1.1913	120.86	119.57	1.8783
BH_3PH_3	aVDZ	1.4205	99.98	117.82	1.2215	115.01	103.11	1.9818
	aVTZ	1.4062	99.99	117.81	1.2079	114.87	103.30	1.9491

TABLE 3: Optimized CCSD(T) Bond Lengths (Å) and Bond Angles (deg) for AlNH$_x$

molecule	basis set	r_{NH}	∠HNH	∠HNAl	r_{AlH}	∠HAlH	∠HAlN	r_{AlN}
AlN($^3\Pi$)	aVDZ							1.8597
	aVTZ							1.8141
	aVQZ							1.8031
AlN($^3\Sigma$)	aVDZ							1.9894
	aVTZ							1.9400
	aVQZ							1.9287
AlN($^1\Sigma$)	aVDZ							1.7186
	aVTZ							1.6863
	aVQZ							1.6771
HAlNH (linear)	aVDZ	1.0080			1.5630			1.6530
	aVTZ	0.9990			1.5590			1.6312
HAlNH (nonlinear)	aVDZ	1.0175		137.67	1.5730		157.30	1.6974
	aVTZ	1.0046		147.21	1.5646		161.37	1.6579
AlH_2NH_2 (planar)	aVDZ	1.0168	110.02	124.99	1.5888	124.78	117.61	1.8087
	aVTZ	1.0090	109.77	125.11	1.5833	124.38	117.81	1.7812
AlH_3NH_3	aVDZ	1.0238	107.09	111.76	1.6087	117.71	98.78	2.1220
	aVTZ	1.0164	107.36	111.51	1.6038	117.51	99.18	2.0714

TABLE 4: Optimized CCSD(T) Bond Lengths (Å) and Bond Angles (deg) for AlPH$_x$

molecule	basis set	r_{PH}	∠HPH	∠HPAl	r_{AlH}	∠HAlH	∠HAlP	r_{AlP}
AlP($^3\Pi$)	aVDZ							2.2743
	aVTZ							2.2366
	aVQZ							2.2197
AlP($^3\Sigma$)	aVDZ							2.4773
	aVTZ							2.4374
	aVQZ							2.4232
AlP($^1\Sigma$)	aVDZ							2.1399
	aVTZ							2.1108
	aVQZ							2.0967
HAlPH (linear)	aVDZ	1.4013			1.5623			2.0532
	aVTZ	1.3890			1.5576			2.0315
HAlPH (nonlinear)	aVDZ	1.4592		80.04	1.5881		180.0	2.1865
	aVTZ	1.4487		78.01	1.5817		180.0	2.1585
AlH_2PH_2 (planar)	aVDZ	1.4097	107.28	126.36	1.5835	127.82	116.09	2.2573
	aVTZ	1.3971	106.95	126.53	1.5775	127.50	116.25	2.2373
AlH_2PH_2 (nonplanar)	aVDZ	1.4352	95.16	94.02	1.5919	121.34	119.33	2.3651
	aVTZ	1.4213	95.01	93.55	1.5855	121.09	119.46	2.3402
AlH_3PH_3	aVDZ	1.4229	98.44	119.03	1.6033	118.75	96.46	2.6231
	aVTZ	1.4087	98.63	118.86	1.5979	118.65	96.73	2.5673

for the $^3\Pi$ state are in good agreement with ours, and our values of $R_e = 1.8031$ Å and $\omega_e = 745$ cm^{-1} for the $^3\Pi$ state show a slightly shorter bond distance and higher frequency as a consequence. Costales et al.[42] calculated the properties of AlP for the $^3\Sigma^-$ state at the BPW/DNP level and obtain $R_e = 2.46$ Å and $\omega_e = 348$ cm^{-1}, in qualitative agreement with our values as their bond length is too long and their frequency too low.

The calculated frequencies for the molecules under consideration are given in Tables 5−8. Where comparisons can be made, the values are in reasonable agreement with the experimental values.[60−62] Based on our previous calculations on BNH$_x$ compounds[4] as well as those of others,[63] the largest error in the calculated frequencies would be in the bond between the group IIIA and group VA atoms in the compound $H_3X{-}YH_3$. However, because the bonds are longer in the compounds under consideration, the error is smaller in an absolute sense. To calculate the zero point energy correction, we scaled the M−H frequencies by the factors 0.96 for M = B and M = N, 0.95 for M = P, and 0.954 for M = Al. These scale factors were obtained by taking the average of the CCSD(T)/aug-cc-pVTZ values and the experimental values for the M−H stretches for the MH_3 compounds and dividing them by the MP2/cc-pVTZ value. Thus we estimate that the error introduced in the heats of formation due to the zero point energies is a maximum of ±0.5 kcal/mol.

The calculated total valence CCSD(T) energies as a function of basis set are given as Supporting Information, and the calculated energy components for the total atomization energies

TABLE 5: Calculated Vibrational MP2/(CCSD(T)/aug-cc-pVDZ) Frequencies (cm^{-1}) for AlH$_x$ and PH$_x$[a]

molecule	symmetry	calc	expt
AlH_3	a_1'	1894.0/1904.5	
	a_2''	732.1/721.7	697.8[60]
	e'	1896.2/1911.2	1882.8
	e'	807.3/787.0	783.4
AlH_4^-	a	1692.5/1702.8	
	e	778.3/750.5	750.0[60]
	t	1614.0/1620.4	1609.3
	t	802.9/767.9	766.6
PH_3	a_1	2352.6/2385.0	2323[61]
	a_1	1020.4/1005.0	992
	e	2364.5/2398.1	2328
	e	1161.6/1133.4	1118
PH_4	a_1	2402.7	
	a_1	1791.2	
	a_1	1027.7	
	a_1	919.4	
	a_2	1218.8	
	b_1	2418.7	
	b_1	856.7	
	b_2	1441.5	
	b_2	1128.0	
PH_4^+	a	2449.9	
	e	1166.5	
	t	2502.5	
	t	1020.1	

[a] Calculated values at the CCSD(T)/aug-cc-pVDZ level are given after the "/".

TABLE 6: Calculated Vibrational MP2/cc-pVTZ Level Frequencies (cm^{-1}) for BPH$_x$

molecule	symmetry	calc
$BP(^3\Pi)^a$	σ	941.1
		6.21($\omega_e\chi_e$)
$BP(^3\Sigma)^a$	σ	638.7
		4.41($\omega_e\chi_e$)
$BP(^1\Sigma)^a$	σ	1043.4
		6.26($\omega_e\chi_e$)
HBPH (linear)	σ	2749.0
	σ	2551.0
	σ	1145.4
	π	650.7
	π	574.9i
HBPH (nonlinear)	a_1	2708.0
	a_1	1978.7
	a_1	1068.9
	a_1	1050.0
	a_1	759.0
	a_2	658.5
BH_2PH_2 (planar)	a_1	2550.0
	a_1	2485.9
	a_1	1194.6
	a_1	1088.2
	a_1	828.5
	a_2	720.4
	b_1	891.4
	b_1	340.8i
	b_2	2656.3
	b_2	2518.4
	b_2	823.8
	b_2	438.8
BH_2PH_2 (nonplanar)	a_1	2540.3
	a_1	2398.5
	a_1	1224.3
	a_1	1136.5
	a_1	950.7
	a_1	750.2
	a_1	403.5
	a_2	2633.8
	a_2	2419.4
	a_2	896.5
	a_2	536.8
	a_2	491.3
BH_3PH_3	a_1	2442.6
	a_1	2403.0
	a_1	1118.2
	a_1	1037.4
	a_1	547.7
	a_2	245.4
	e	2492.5
	e	2430.1
	e	1186.7
	e	1163.4
	e	850.7
	e	385.3

[a] Diatomic molecule frequencies calculated at the CCSD(T)/aug-cc-pV(Q+d)Z level with a fifth-order fit.

TABLE 7: Calculated Vibrational MP2/(CCSD(T)/aug-cc-pVDZ) Frequencies (cm^{-1}) for AlNH$_x$^{a}

molecule	symmetry	calc	expt
$AlN(^3\Pi)^b$	σ	745.06	746.9[59]
		5.65($\omega_e\chi_e$)	
$AlN(^3\Sigma)^b$	σ	622.54	
		4.54($\omega_e\chi_e$)	
$AlN(^1\Sigma)^b$	σ	970.7	
		6.04($\omega_e\chi_e$)	
HAlNH (linear)	σ	3630.7	
	σ	2000.8	
	σ	1106.2	
	π	531.5	
	π	216.1i	
HAlNH (nonlinear)	a_1	3563.5	
	a_1	1977.0	
	a_1	1051.3	
	a_1	486.2	
	a_1	296.8	
	a_2	517.4	
AlH_2NH_2 (planar)	a_1	3469.5/3499.7	3558.1[62]
	a_1	1897.9/1891.0	1921.5
	a_1	1573.0/1541.6	1566.6
	a_1	839.3/801.4	818.7
	a_1	764.8/742.8	755.0
	a_2	499.4/498.8	
	b_1	629.8/627.2	608.7
	b_1	427.8/411.7	518.3
	b_2	3567.6/3657.7	
	b_2	1900.1/1925.9	1899.3
	b_2	735.0/745.1	769.8
	b_2	424.1/435.1	
AlH_3NH_3	a_1	3354.9	
	a_1	1827.4	
	a_1	1263.5	
	a_1	791.2	
	a_1	422.3	
	a_2	125.6	
	e	3483.4	
	e	1808.8	
	e	1664.8	
	e	800.2	
	e	709.6	
	e	373.2	

[a] Calculated values at the CCSD(T)/aug-cc-pVDZ level are given after the "/". [b] Diatomic molecule frequencies calculated at the CCSD(T)/aug-cc-pV(Q+d)Z level with a fifth-order fit.

in Table 9. The relativistic corrections are all negative and reasonably small ranging from 0 to −1 kcal/mol. The core-valence corrections are positive for the BPH$_x$ series and range from 1 to 1.6 kcal/mol. For the AlNH$_x$ series the core valence corrections are negative and range from 0 to −1 kcal/mol. For the AlPH$_x$ series, the core valence corrections are positive for the compounds containing PH$_3$ and are negative for the remaining compounds. The calculated heats of formation are given in Table 10. The calculated value for $\Delta H_f(PH_3)$ is in excellent agreement with the experimental value. Our estimated error bars for the heats of formation are ±1.0 kcal/mol.

The diatomic BN molecule has a $^3\Pi$ ground state with the $^1\Sigma^+$ 0.54 kcal/mol higher in energy.[64] The diatomic BP has a $^3\Pi$ ground state with the $^1\Sigma^+$ 7.5 kcal/mol higher in energy and the $^3\Sigma^-$ 20.9 kcal/mol higher in energy. The AlN molecule has a near degeneracy between the $^3\Pi$ and the $^3\Sigma^-$, and we predict the $^3\Sigma^-$ to be slightly lower in energy. The $^1\Sigma^+$ state is 9.5 kcal/mol higher in energy. Both the $^3\Pi$ and $^1\Sigma^+$ states have substantial multireference character, as noted by the large T_1 diagnostics.[65] The $^3\Sigma^-$ state does not have substantial multireference character. The AlP molecule is very similar to the AlN molecules with the two triplet states essentially isoenergetic and the $^3\Sigma^-$ is the ground state. The $^1\Sigma^+$ state is 12.0 kcal/mol higher in energy than the ground state. Although the AlP $^1\Sigma^+$ state does have some multireference character, it is substantially smaller than in BN or AlN. The $^3\Pi$ state for AlP has a little multireference character but it is not large and the $^3\Sigma^-$ has very little. The BP bond energy is substantially higher than the AlN or AlP bond energies. The multireference character in the three states for BP is like that in AlP.

The dissociation energy for AlN has been measured spectroscopically to be 66 ± 9 kcal/mol.[54,66] Our value of 57.3 kcal/mol is consistent with the lower range of the experimental value. The higher experimental dissociation energy leads to a value of $\Delta H_f{}^0(AlN) = 125.0$ kcal/mol, lower than our calculated value as expected on the basis of the difference in dissociation energies. Our value of $D_e = 58.1$ kcal/

TABLE 8: Calculated Vibrational MP2/(CCSD(T)/aug-cc-pVDZ) Frequencies (cm^{-1}) for AlPH$_x$

molecule	symmetry	calc
AlP($^3\Pi$)[a]	σ	466.7 0.85($\omega_e\chi_e$)
AlP($^3\Sigma$)[a]	σ	372.76 1.67($\omega_e\chi_e$)
AlP($^1\Sigma$)[a]	σ	560.1 2.93($\omega_e\chi_e$)
HAlPH (linear)	σ	2521.2
	σ	1996.0
	σ	687.9
	π	441.1
	π	565.3i
HAlPH (nonlinear)	a_1	2155.8
	a_1	1905.8
	a_1	636.8
	a_1	534.2
	a_1	300.5
	a_2	391.1
AlH_2PH_2 (planar)	a_1	2463.8
	a_1	1910.3
	a_1	1079.8
	a_1	747.2
	a_1	494.5
	a_2	440.2
	b_1	594.9
	b_1	413.8i
	b_2	2493.0
	b_2	1926.0
	b_2	546.5
	b_2	318.6
AlH_2PH_2 (nonplanar)	a_1	2337.5
	a_1	1884.1
	a_1	1105.4
	a_1	791.9
	a_1	632.1
	a_1	432.1
	a_1	417.0
	a_2	2351.5
	a_2	1893.4
	a_2	665.4
	a_2	373.4
	a_2	203.9
AlH_3PH_3	a_1	2430.5
	a_1	1842.2
	a_1	1016.7
	a_1	730.6
	a_1	241.1
	a_2	125.2
	e	2424.1
	e	1833.2
	e	1153.6
	e	777.8
	e	516.0
	e	220.6

[a] Diatomic molecule frequencies calculated at the CCSD(T)/aug-cc-pV(Q+d)Z level with a fifth-order fit.

mol for the $^3\Pi$ state is consistent with the value calculated by Langhoff et al.[40] of 54.2 kcal/mol at the MRCI+Q level with a [5s4p2d1f(N)/6s5p2d1f(Al)] basis set. Langhoff et al.[40] find the $^1\Sigma^+$ state to be 13.3 kcal/mol above the $^3\Pi$, a few kcal/mol higher than our energy difference. At the BPW/DNP level the bond energy for AlN is calculated to be about 6 kcal/mol higher than our more accurately calculated value.[41] The BP bond energy has been measured to be 82.0 ± 4 kcal/mol on the basis of Knudsen cell measurements, in reasonable agreement with our value of 76.4 kcal/mol.[67] The dissociation energy for AlP has been measured to be 50.8 ± 3 kcal/mol, in excellent agreement with our calculated value of 50.7 kcal/mol.[68]

The calculated heat of formation of PH_3 of 1.4 kcal/mol at 298 K is in excellent with the experimental value of 1.3 kcal/mol.[54] Similarly, the calculated heat of formation of AlH_3 of 30.3 kcal/mol at 298 K is in excellent agreement with the experimental value of 30.8 kcal/mol,[54] especially considering the error bars for the heat of formation of the Al atom. We have previously shown that the calculated heats of formation of BH_3 and NH_3 are in good agreement with experiment.[4,19,20]

The dissociation energy of AlH_3NH_3 to form $AlH_3 + NH_3$ is calculated to be 26.1 kcal/mol, comparable to the calculated value of 25.9 kcal/mol for BH_3NH_3.[4] The dissociation energy of BH_3PH_3 to form $BH_3 + PH_3$ is calculated to be somewhat lower at 21.1 kcal/mol, and the dissociation energy of AlH_3PH_3 to form $AlH_3 + PH_3$ is calculated to be even lower at 14.0 kcal/mol. These values are in general higher than those obtained by workers using lower level methods.[31−36]

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

$$AlH_3NH_3 \rightarrow AlH_2NH_2 + H_2 \quad \Delta H = 3.5\ (0\ K),\ 5.0\ (298\ K)\ kcal/mol \tag{3}$$

$$AlH_2NH_2 \rightarrow HAlNH + H_2 \quad \Delta H = 60.7\ (0\ K),\ 61.9\ (298\ K)\ kcal/mol \tag{4}$$

$$AlHNH \rightarrow AlN + H_2 \quad \Delta H = 73.1\ (0\ K),\ 74.9(298\ K)\ kcal/mol \tag{5}$$

$$BH_3PH_3 \rightarrow BH_2PH_2 + H_2 \quad \Delta H = 15.8\ (0\ K),\ 17.4\ (298\ K)\ kcal/mol \tag{6}$$

$$BH_2PH_2 \rightarrow HBPH + H_2 \quad \Delta H = 29.2\ (0\ K),\ 31.4\ (298\ K)\ kcal/mol \tag{7}$$

$$BHPH \rightarrow BP + H_2 \quad \Delta H = 81.6\ (0\ K),\ 82.5\ (298\ K)\ kcal/mol \tag{8}$$

$$AlH_3PH_3 \rightarrow AlH_2PH_2 + H_2 \quad \Delta H = 4.3\ (0\ K),\ 5.6\ (298\ K)\ kcal/mol \tag{9}$$

$$AlH_2PH_2 \rightarrow HAlPH + H_2 \quad \Delta H = 33.2\ (0\ K),\ 34.6\ (298\ K)\ kcal/mol \tag{10}$$

$$AlHPH \rightarrow AlP + H_2 \quad \Delta H = 44.1\ (0\ K),\ 45.4(298\ K)\ kcal/mol \tag{11}$$

Simply on the basis of the value of ΔH, only reaction 3 involving AlH_3NH_3 and reaction 9 involving AlH_3PH_3 might be possible sources for H_2 release, as they are close to thermoneutral. However, one must also consider the values of the free energy. The formation of two gas-phase products will lead to a substantial $T\Delta S$ term, which will make H_2 generation more favorable. The values of S for each molecule are given in Table 11 and the values of $-T\Delta S$ at $T = 298$ K for reactions 3−11 are given in Table 12. These values clearly show that reactions 3 and 9 are potential sources for H_2.

Another possibility for an H_2 storage system are the salts [BH_4^-][PH_4^+], [AlH_4^-] [NH_4^+], and [AlH_4^-][PH_4^+]. We[4] and others[2,3] have previously predicted that the salt [BH_4^-][NH_4^+] can readily release H_2 to form either solid or gaseous BH_3NH_3 exothermically. We can estimate the lattice energy of the salts from eq 2 by using the volumes given above. Use of these values in eq 2 gives lattice energies for [BH_4^-][PH_4^+], [AlH_4^-] [NH_4^+], and [AlH_4^-][PH_4^+] of 149.3, 150.7, and 148.9 kcal/mol, respectively, and calculated heats of formation of the salts at

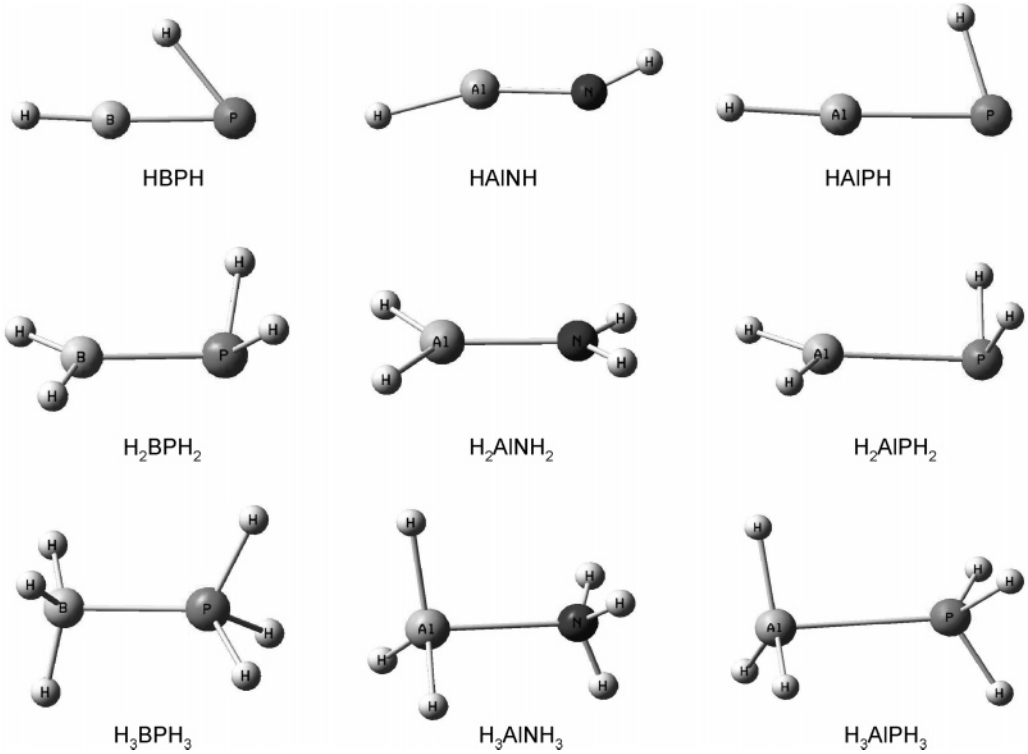

Figure 1. Optimized molecular structures for HBPH, HAlNH, HAlPH, BH_2PH_2, AlH_2NH_2, AlH_2PH_2, BH_3PH_3, AlH_3NH_3, and AlH_3PH_3.

0 K of +21.8, −0.5, and +30.4 kcal/mol, respectively. We note that the error bars for using eq 2 are probably ±5 kcal/mol. The reaction energies starting from the ionic solid to form the gas-phase products are

$$[BH_4^-][PH_4^+](s) \rightarrow BH_3PH_3 + H_2 \quad \Delta H(0\ K) = -13.2\ kcal/mol \quad (12)$$

$$[AlH_4^-][NH_4^+](s) \rightarrow AlH_3NH_3 + H_2 \quad \Delta H(0\ K) = -3.3\ kcal/mol \quad (13)$$

$$[AlH_4^-][PH_4^+](s) \rightarrow AlH_3PH_3 + H_2 \quad \Delta H(0\ K) = -9.3\ kcal/mol \quad (14)$$

All of the reactions involving the salts releasing H_2 are predicted to be exothermic, as found for $[BH_4^-][NH_4^+]$. Thus they may serve as H_2 storage systems. The reaction starting from $[AlH_4^-][NH_4^+](s)$ is close to thermoneutral, so this salt might be a good source of H_2, as it will be easier to manage the heat release.

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 estimate the EA(NH_4^+) as the energy of the reaction

$$NH_4^+ + e^- \rightarrow NH_3 + H \quad (15)$$

giving −111.6 kcal/mol (4.84 eV). The ionization potential of BH_4^- can be estimated from the reaction

$$BH_4^- \rightarrow BH_3 + H + e^- \rightarrow BH_4 + e^- \quad (16)$$

as BH_4 is a weakly bonded system with a predicted dissociation energy of 12.9 kcal/mol to form BH_3 + H and a dissociation energy to form $BH_2 + H_2$ of 14.8 kcal/mol at the UMP4/6-311G(df,p) level.[69] The electron affinity of BH_3 is very small

TABLE 9: Components for Calculated Atomization Energies (kcal/mol)[a]

molecule	CBS[b]	ΔE_{ZPE}[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	$\Sigma D_0(0K)$[g]
BP($^3\Pi$)	77.19	1.34	0.78	−0.16	−0.03	76.44
BP($^3\Sigma^-$)	56.24	0.91	0.35	−0.07	−0.03	55.58
BP($^1\Sigma^+$)	69.83	1.50	0.81	−0.13	−0.03	68.98
AlN($^3\Pi$)	58.23	1.06	0.24	−0.13	−0.21	57.07
AlN($^3\Sigma^-$)	58.51	0.89	−0.01	−0.14	−0.21	57.26
AlN($^1\Sigma^+$)	49.94	1.40	−0.42	−0.13	−0.21	47.78
AlP($^3\Pi$)	51.63	0.67	0.12	−0.13	−0.21	50.74
AlP($^3\Sigma^-$)	51.72	0.53	0.07	−0.12	−0.21	50.93
AlP($^1\Sigma^+$)	40.53	0.80	−0.46	−0.16	−0.21	38.90
HBPH (linear)	243.35	11.07	1.23	−0.64	−0.03	232.84
HBPH (nonlinear)	271.79	11.75	1.48	−0.23	−0.03	261.26
HAlNH (linear)	245.89	11.14	−0.29	−0.63	−0.21	233.62
HAlNH (nonlinear)	245.88	11.27	−0.27	−0.57	−0.21	233.56
HAlPH (linear)	181.89	8.70	−0.88	−1.00	−0.21	171.10
HAlPH (nonlinear)	207.80	8.46	−0.31	−0.48	−0.21	198.34
BH_2PH_2 (planar)	409.82	23.14	1.39	−0.66	−0.03	387.38
BH_2PH_2 (nonplanar)	416.31	23.40	1.35	−0.53	−0.03	393.70
AlH_2NH_2 (planar)	422.57	23.90	−0.21	−0.69	−0.21	397.56
AlH_2PH_2 (planar)	345.97	18.59	−0.74	−0.96	−0.21	325.42
AlH_2PH_2 (nonplanar)	354.92	18.70	−0.60	−0.72	−0.21	334.69
BH_3PH_3	547.28	35.45	1.57	−0.61	−0.03	512.76
AlH_3NH_3	541.80	36.38	−0.15	−0.73	−0.21	504.33
AlH_3PH_3	472.00	28.91	0.27	−0.86	−0.21	442.29
AlH_3	214.27	11.48	−1.00	−0.33	−0.21	201.25
AlH_4^-	304.76	15.00	−0.99	−0.48	−0.21	288.10
PH_3	242.01	14.89	0.27	−0.36	0.00	227.03
PH_4	250.81	18.86	0.09	−0.61	0.00	231.43
PH_4^+	121.89	21.93	−0.08	−0.62	0.00	99.26

[a] The energies of the atomic asymptotes and the open shell states of the diatomics 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. [e] The scalar relativistic correction is based on a CISD(FC)/cc-pVTZ MVD calculation. [f] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on Moore's tables.[53] [g] The theoretical value of the dissociation energy to atoms ΣD_0(0K).

TABLE 10: Calculated Heats of Formation (kcal/mol) at 0 and 298 K[a]

molecule	$\Delta H_f(0K)_{theory}$	$\Delta H_f(298K)_{theory}$
$BP(^3\Pi)$[b]	135.2	135.7
$AlN(^3\Pi)$[c]	133.7	133.7
$AlN(^3\Sigma)$	133.5	133.5
$AlP(^3\Pi)$[d]	102.9	102.8
$AlP(^3\Sigma)$	102.7	102.6
HBPH (nonlinear)[e]	53.6	53.2
HAlNH (nonlinear)[f]	60.4	58.6
HAlPH (nonlinear)[g]	58.6	57.2
BH_2PH_2 (nonplanar)[h]	24.4	21.8
AlH_2NH_2 (planar)	−0.3	−3.3
AlH_2PH_2 (nonplanar)[i]	25.4	22.6
BH_3PH_3	8.6	4.4
AlH_3NH_3	−3.8	−8.3
AlH_3PH_3	21.1	17.0
AlH_3	31.9	30.3
AlH_4^-	−3.4	−5.9
PH_3	3.3	1.4
PH_4	50.5	47.7
PH_4^+	182.7	179.8
BH_3	26.4	25.5
BH_4^-	−11.6	−13.5
NH_3	−9.6	−11.3
NH_4^+	153.6	150.9

[a] Values for BH_3, BH_4^-, NH_3, and NH_4^+ from ref 4. [b] $\Delta H_f(0K)$ $BP(^3\Sigma^-) = 156.0$ kcal/mol, $\Delta H(0K)$ $BP(^1\Sigma^+) = 142.6$ kcal/mol. [c] $\Delta H(0K)$ $AlN(^1\Sigma^+) = 143.0$ kcal/mol. [d] $\Delta H(0K)$ $AlP(^1\Sigma^+) = 114.8$ kcal/mol. [e] $\Delta H(0K)$ HBPH (linear) = 82.0 kcal/mol. [f] $\Delta H(0K)$ HAlNH (linear) = 60.4 kcal/mol. [g] $\Delta H(0K)$ HAlPH (linear) = 86.1 kcal/mol. [h] $\Delta H(0K)$ BH_2PH_2 (planar) = 31.0 kcal/mol. [i] $\Delta H(0K)$ AlH_2PH_2 (planar) = 35.4 kcal/mol.

TABLE 11: Calculated Entropies [cal/(mol K)] at the MP2/cc-pVTZ Level

molecule	$S(298K)_{theory}$
$BP(^3\Pi)$	52.64
$AlN(^3\Pi)$	53.28
$AlN(^3\Sigma)$	53.28
$AlP(^3\Pi)$	56.40
$AlP(^3\Sigma)$	56.40
HBPH (nonlinear)	56.74
HAlNH (nonlinear)	52.38
HAlPH (nonlinear)	62.40
BH_2PH_2 (nonplanar)	60.88
AlH_2NH_2 (planar)	60.11
AlH_2PH_2 (nonplanar)	66.87
BH_3PH_3	61.79
AlH_3NH_3	64.50
AlH_3PH_3	70.66
AlH_3	49.49
AlH_4^-	49.87
PH_3	50.16
PH_4	53.76
PH_4^+	48.52
BH_3	44.96
BH_4^-	45.17
NH_3	45.94
NH_4^+	44.39
H_2	31.23

TABLE 12: $T\Delta S$ (kcal/mol) Corrections for Reactions 3−11

reaction	$-T\Delta S(298K)$
3	8.0
4	7.0
5	9.6
6	9.0
7	8.1
8	8.1
9	8.2
10	8.0
11	7.5

(0.038 ± 0.015 eV = 0.88 ± 0.35 kcal/mol).[70] The ionization potential of BH_4^- is thus predicted to be quite low, 76.7 kcal/mol (3.33 eV).[71] The fact that the electron affinity of NH_4^+ and the ionization potential of BH_4^- are comparable within 1.5 eV of each other is consistent with the fact that this salt can be produced as we have previously reported.

The molecule AlH_4 is predicted to be only weakly bound by 1 kcal/mol (without zero point energy (ZPE) corrections and unbound with ZPE corrections included) with respect to $AlH_2 + H_2$ at the UMP4/6-311+G(MC)(2df,p) level and is predicted to be bound by 17.9 kcal/mol with respect to AlH_3 + H.[72] The ionization potential of AlH_4^- can be estimated by the reaction

$$AlH_4^- \rightarrow AlH_3 + H + e^- \rightarrow AlH_4 + e^- \qquad (17)$$

giving a value of 69.0 kcal/mol (2.99 eV), which is similar to the value found for BH_4^-. The EA of PH_4^+ is given by

$$PH_4^+ + e^- \rightarrow PH_3 + H \rightarrow PH_4 \qquad (18)$$

where the first half of the reaction gives 127.8 kcal/mol (5.54 eV), which is reduced by 4.4 kcal/mol (0.19 eV) by the ability of PH_3 to bind H to give a final value of 5.35 eV. PH_4 ($^2A_1$) is barely stable with a P−H bond energy of 4.4 kcal/mol with respect to PH_3 + H.

Use of these ionization and electron attachment values for (12)−(14) gives electron transfer energies of 2.02, 1.85, and 2.36 eV, respectively. These values are substantially less than the lattice energies so that electron transfer is unlikely to occur and the salts are expected to be stable in terms of their ionic components.

From the heats of formation of AlH_4^- and AlH_3 together with the heat of formation of H^- (34.2 kcal/mol at 298 K), we can calculate the hydride affinity of AlH_3 defined as $-\Delta H$ for the reaction $AlH_3 + H^- \rightarrow AlH_4^-$. This value is 70.4 kcal/mol, which shows that AlH_3 is a good hydride acceptor as expected. There is a very recent experimental value[73] (published after this paper was initially submitted) based on a flowing afterglow mass spectrometric measurement for the hydride affinity of 75 ± 4 kcal/mol, in reasonable agreement with our computational value. The value[4] for the hydride affinity of BH_3 of 72.2 kcal/mol is very similar to that for AlH_3. From the heats of formation of PH_4^+ and PH_3 together with the heat of formation of H^+ (367.2 kcal/mol at 298 K), we calculate the proton affinity of PH_3 to be 187.8 kcal/mol, in excellent agreement with the experimental value of 188 kcal/mol.[74]

Conclusions

Ab initio molecular orbital theory at the CCSD(T)/CBS level plus additional corrections has been used to predict the heats of formation of a number of borane phosphines, alane amines, and phosphine alanes. The heat of formation of the salts $[BH_4^-][PH_4^+]$, $[AlH_4^-]$ $[NH_4^+]$, and $[AlH_4^-][PH_4^+]$ (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 AlH_3NH_3(g) and $[AlH_4^-]NH_4^+]$(s) can serve as good hydrogen storage systems. In addition, AlH_3PH_3 and the salts $[AlH_4^-][PH_4^+]$ and $[BH_4^-][PH_4^+]$ have the potential to serve as H_2 storage systems. The hydride affinity for AlH_3 and the proton affinity for PH_3 were also calculated, and the latter value is found to be in good agreement with the available experimental result. The P−H bond energy in PH_4 of 4.4 kcal/mol shows that PH_4 is only weakly bound with respect to the H + PH_3 asymptote.

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Supporting Information Available: Total CCSD(T) energies (E_h) as a function of basis set. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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