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Thermochemistry of Molecules in the B−N−Cl−H System: *Ab Initio* Predictions Using the BAC-MP4 Method

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A self-consistent set of thermochemical data for 33 molecules in the B−N−Cl−H system are obtained from a combination of *ab initio* electronic structure calculations and empirical corrections. Calculations were performed for both stable and radical species. Good agreement is found between the calculations and experimental heats of formation for most molecules containing B, H, and Cl. In addition, the BAC-MP4 and experimental heats of formation for $H_3B{:}NH_3$ are also in reasonable agreement, suggesting that the bond additivity parameters chosen for B−N bonds will provide reasonably accurate heats of formation for compounds containing this type of bond. Transition-state energies for two reactions involving BCl_3 and NH_3 are also predicted. Polynomial fits of the predicted thermodynamic data over the 300−4000 K temperature range are included in the Supporting Information.

I. Introduction

Compounds containing boron and nitrogen have been of interest to chemists for nearly two centuries, with complexes between boron halides and ammonia constituting the first-known examples of coordination compounds.[1−3] Besides this intrinsic interest, boron−nitrogen chemistry also has practical value and is used to manufacture materials such as ceramic composites,[4] thin films,[5] and coatings[6] of boron nitride. Accurate thermodynamic data are essential both to achieving an in-depth understanding of the chemical reactions in the boron−nitrogen system and for developing and optimizing new industrial processes that make use of this chemistry.

Reliable thermodynamic data are particularly important in modeling the chemical vapor deposition (CVD) of boron nitride, since these processes operate at temperatures up to 2000 °C.[7] BCl_3 and NH_3 are the most commonly used precursors,[8−13] although a wide range of both boron- and nitrogen-containing compounds have been used.[14] It has been shown that BCl_3 and NH_3 react in the gas phase at low temperatures (298−350 K),[15,16] forming aminodichloroborane (Cl_2BNH_2). Species containing B−N bonds are also observed under CVD conditions (1173−1373 K).[12,17] These experiments and the predictions of a kinetics model[18] suggest that gas-phase chemical reactions play an important role in determining which species interact with the deposition surface. Thus, accurate thermochemical data for compounds in the B−N−Cl−H system are necessary to determine the importance of these reactions and to develop models that can simulate BN CVD processes.

Unfortunately, reliable heats of formation, enthalpies, entropies, and heat capacities are unavailable for almost all compounds in the B−N−Cl−H series. Thermochemical data based on experimental measurements for most species in the BH_nCl_m (n, $m = 0-3$) series are available, although only the heat of formation of BCl_3 can be considered well established. These data are thoroughly reviewed elsewhere.[19,20] There are also numerous high-level calculations of the heats of atomization for BH_n ($n = 1-3$) compounds[21−30] as well as a recent study of the thermochemistry of molecules in the BH_nCl_m (n, $m = 0-3$) series using the G-2 method.[31] However, data for compounds containing B−N bonds are much more sparse; to our knowledge, heats of formation have been measured for only BN, $H_3B{:}NH_3$, and $B_3N_3H_6$.[20] There are several theoretical treatments reported for molecules with B−N bonds, but the objective of these investigations was not to predict thermochemistry for a wide range of compounds.[1,32−40] Complicating this situation is the fact that the uncertainty in the heat of formation of gas-phase boron atoms, which is required to convert theoretical atomization energies into heats of formation, is larger than what is typical for most gas-phase atomic species.[19−21]

The ability of high-level *ab initio* calculations to predict heats of formation for gas-phase molecules has been demonstrated in numerous studies published in the last decade.[30,31,41−51] In our work, we have used *ab initio* calculations coupled with empirically derived bond-additivity corrections to predict thermochemical quantities for a very large number of first- and second-row elements. This method is known as the BAC-MP4 method (for bond-additivity-corrected−fourth-order Møller−Plesset perturbation theory), and to date we have applied it to first-row compounds[48] and the Si−H,[44−46] Si−H−Cl,[44,46] Si−F−H,[46] Si−N−F−H,[49] Si−C−H,[41] Si−C−Cl−H,[42] Si−O−H,[52,53] and Si−O−C−H[47,52] systems. In this work, we extend the BAC-MP4 method to compounds in the B−N−Cl−H system. We also discuss the energetics of several transition states relevant to reactions between BCl_3 and NH_3. To maximize the usefulness of the predicted thermochemical data, we include polynomial fits that describe the temperature dependence of the heat capacity, enthalpy, and entropy for all compounds in the study. The results provide a self-consistent set of thermochemical values that will be useful for future studies of the chemical reactions of this system.

II. Theoretical Methods

We describe the theoretical methods used here in detail in earlier works,[46,48] so we present only a short description here. Electronic structure calculations were performed using Gaussian 92[46,48,54] and earlier versions of these quantum chemistry codes. Equilibrium geometries and harmonic vibrational frequencies were obtained at the HF/6-31G* level of theory. Restricted Hartree−Fock theory (RHF)[55] was applied for the closed shell molecules and unrestricted Hartree−Fock theory (UHF)[56] was

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TABLE 1: BAC Parameters for the BAC-MP4 (SDTQ) Level of Theory

bond	A_{ij}(MP4)[a]	α_{ij}(MP4)[b]
B−H	31.120	2.00
B−N	370.100	2.84
B−Cl	172.490	2.00
N−H	70.08	2.00

atom	B_k
B	0.20
N	0.20
Cl	0.42
H	0.00

[a] In kcal mol^{-1}. [b] In Å^{-1}.

applied for the open shell molecules, using the 6-31G* basis set.[57,58] Vibrational frequencies calculated at this level of theory are known to be systematically larger than experimental values; thus, each calculated frequency was scaled by dividing it by 1.12.[58]

To determine atomization enthalpies and thus heats of formation, the effects of electron correlation are included by performing single-point calculations, using Møller−Plesset perturbation theory and the HF/6-31G* geometries. MP4(SDTQ)/6-31G** calculations (fourth-order perturbation theory using the 6-31G** basis set with single, double, triple, and quadruple substitutions) were performed to obtain electronic energies. This level of theory has been used in most of our previous work; the errors remaining in the total energies are sufficiently systematic that empirical bond additivity corrections can provide enthalpies accurate to a few kcal mol^{-1}. The form of the BAC parameters α_{ij}, A_{ij}, and B_{ij} used to calculate the corrections for individual molecules is given in eqs 1−4, using the example of a bond between atoms X_i and X_j in a molecule of the form $X_k-X_i-X_j$:

$$E_{\mathrm{BAC}}(X_i - X_j) = f_{ij} g_{kij} \tag{1}$$

where

$$f_{ij} = A_{ij}\exp(-\alpha_{ij}R_{ij}) \tag{2}$$

$$g_{kij} = (1 - h_{ik}h_{ij}) \tag{3}$$

$$h_{ik} = B_k \exp\{-\alpha_{ik}(R_{ik} - 1.4\ \text{Å})\} \tag{4}$$

A_{ij} and α_{ij} are empirically derived parameters that depend on the X_i-X_j bond type and R_{ij} is the bond distance (Å). The factor B_k in eq 4 is used to derive a correction for the effects of neighboring atoms on the X_i-X_j bond (eq 3) and depends on the identity of atom k.

Table 1 lists the parameters A_{ij}, α_{ij}, and B_k used in this work for each bond type. Parameters for N−H bonds were established in previous studies.[48,49] The values for B−Cl bonds were determined by using the heat of formation of BCl_3 recommended by Gurvich et al.[20] as a reference, for which the uncertainty is low (±0.3 kcal mol^{-1}). In the case of B−H bonds, since uncertainties in the recommended heats of formation for BH_n ($n = 1-3$) compounds are large (see discussion below), we determined the B−H bond correction by using the heat of atomization for BH_3 obtained from a G-2 calculation as a reference. Values of A and α for B−N "single" bonds were determined by using the heat of formation of borazole ($B_3N_3H_6$) recommended by Gurvich et al.[20] as a reference (note that, for compounds such as H_2BNH_2, the order of these bonds actually approaches 2; see, for example, Dill et al.[40] and the discussion in section III). Although the uncertainty in this value is fairly high (±3 kcal mol^{-1}), it is lower than that reported for H_3B:NH_3. Complexes such as H_3B:NH_3 are also unsuitable as references since the effectiveness of the BAC-MP4 method for compounds of this type has not been adequately characterized. An additional advantage of using borazole instead of BN as a reference compound, which has three B−N bonds, is that it minimizes the accumulation of errors that results when multiple corrections are applied to molecules with more than one B−N bond. In the case of unsaturated BN compounds, the only compound for which experimental data exist is BN. Unfortunately, the uncertainties in recommended heats of formation[19,20] are very high (14−30 kcal mol^{-1}). Thus, corrections for higher order B−N bonds were determined by using, as a reference, the heat of atomization of HBNH predicted by a G-2 calculation.

Table 2 lists calculated bond lengths for each species, as well as the MP4(SDTQ) BACs corresponding to each bond in the molecule and any spin corrections.[46] The sum of the BACs is combined with the MP4(SDTQ) electronic energy and the unscaled zero-point energy to obtain the heats of atomization and formation at 0 K ($\sum D_0$ and $\Delta H_f°(0\ \mathrm{K})$, respectively). Entropies, heat capacities, enthalpies, and free energies as a function of temperature were calculated using the heats of formation at 0 K, equations derived from statistical mechanics, and the calculated geometries and scaled frequencies. For consistency with our earlier reports,[41−49] the unscaled frequencies are used for determining $\Delta H_f°(0\ \mathrm{K})$, while the scaled frequencies are used to calculate thermochemistry at higher temperatures. Minor differences that would result from using the scaled frequencies to calculate $\Delta H_f°(0)$ are incorporated into the BACs.

To obtain heats of formation from the calculated atomization energies, the heat of formation for each atom type in a given compound is required. Values used here for H, N, and Cl atoms are given in Table 4 and were taken from the *JANAF Tables*.[19] The heat of formation of gas-phase boron atoms is a matter of some debate. The value quoted in the *JANAF Tables* ($\Delta H_f°(298\ \mathrm{K}) = 133.8 \pm 2.9$ kcal mol^{-1}) has a high uncertainty relative to the heats of formation for the other atoms. Schlegel and Harris, in their recent G-2 calculations,[31] used the value of 137.4 kcal mol^{-1} (298 K) reported by Storms and Mueller;[59] calculations by Ochterski et al.[21] using the complete basis set (CBS) method predict a value (136.9 ± 0.7 kcal mol^{-1}) that is in agreement with the measurements of Storms and Mueller. However, wall interactions described by Storms and Mueller may affect the accuracy of their measurement.[60] In this study, we use the value recommended by Gurvich et al. ($\Delta H_f°(298\ \mathrm{K}) = 135 \pm 1$ kcal mol^{-1}),[20] which is based on a critical evaluation of experimental data in the literature. This value is in excellent agreement with the one recommended by Nordine et al. ($\Delta H_f°(298\ \mathrm{K}) = 134.8 \pm 0.5$ kcal mol^{-1}) that is the average of experimental results obtained under conditions that eliminate wall effects.[61] It should be noted that the atomic heats of formation have no effect on calculated reaction enthalpies, since these involve energy differences. However, if thermodynamic data derived from more than one source are used to calculate reaction enthalpies, one must ensure that values of the atomic heats of formation are the same in all cases; otherwise, systematic errors will arise.

There are two major sources of uncertainty in the calculated heats of formation: uncertainties resulting from the applicability of the theoretical methods to a given molecule and systematic uncertainties resulting from lack of good reference compounds for the BACs. The magnitude of the first is estimated using an *ad hoc* method developed previously that uses the results from lower level calculations[46] and is reported in Table 4. The second

TABLE 2: Bond Additivity Corrections for the MP4(SDTQ) Level of Theory (kcal mol^{-1})

species	spin or UHF correction[a]	B−H bond length[b] (no.)[c]	BAC	B−Cl bond length (no.)	BAC	B−N bond length (no.)	BAC	N−H bond length (no.)	BAC	H−Cl or N−Cl	BAC
BH_3		1.188 (3)	2.89								
BH_2	0.14 u	1.186 (2)	2.91								
BH ($^1\Sigma$)	4.80 s	1.225	2.68								
BCl_3				1.745 (3)	4.80						
$BHCl_2$		1.175	2.97	1.746 (2)	5.02						
BH_2Cl		1.181 (2)	2.93	1.753	5.17						
BCl_2	0.25 u			1.735 (2)	5.12						
HBCl	0.20 u	1.183	2.92	1.736	5.36						
BCl				1.732	5.40						
$H_3B{:}NH_3$		1.209 (3)	2.78			1.689	3.05	1.004 (3)	9.41		
H_2BNH_2		1.193 (2)	2.87			1.389	7.16	0.996 (2)	9.57		
H_2BNH	1.16 u	1.193 (2)	2.86			1.398	6.98	0.999	9.51		
$HBNH_2$	0.32 u	1.191	2.87			1.383	7.29	0.996	9.56		
								0.998	9.52		
$B(NH_2)_2$	0.24 u					1.406 (2)	6.56	0.993 (2)	9.61		
								0.998	9.53		
HBNH		1.167	3.02			1.223	11.49	0.981	9.85		
BNH_2	3.05 s					1.383	7.30	1.000 (2)	9.48		
H_2BN	0.61 u	1.189 (2)	2.89			1.471	5.67				
BNH	2.54 u					1.228	11.32	0.982	9.83		
HBN ($^2\Pi$)	1.07 u	1.167	3.02			1.292	9.43				
BN						1.239	10.96				
$B_3N_3H_6$		1.193 (3)	2.86			1.426 (6)	6.00	0.996 (3)	9.56		
$Cl_3B{:}NH_3$				1.836 (3)	4.05	1.628	3.44	1.088 (3)	9.34		
$Cl_3B{:}NH_3 \rightarrow Cl_2BNH_2 + HCl$				2.958	0.46	1.522	4.60	1.083	7.54	1.866	2.62
				1.730 (2)	4.98			1.007 (2)	9.34		
$H_3N{:}BCl_2NH_2$				1.869 (2)	3.83	1.465	5.38	0.999 (2)	9.51		
						1.658	3.18	1.006 (3)	9.37		
$HClBNH_2$		1.183	2.92	1.786	4.65	1.382	7.01	0.996	9.55		
								0.996	9.57		
Cl_2BNH_2				1.773 (2)	4.58	1.380	6.74	0.996 (2)	9.56		
$Cl_2BNH_2 \rightarrow ClBNH + HCl$				3.236	0.27	1.291	8.79	1.130	6.80	1.757	3.22
				1.659	5.81			0.997	9.53		
$ClB(NH_2)_2$				1.806	4.32	1.403 (2)	6.37	0.994 (2)	9.60		
								0.995 (2)	9.58		
$HB(NH_2)_2$		1.195	2.85			1.412 (2)	6.45	0.995 (2)	9.57		
								0.993 (2)	9.61		
$B(NH_2)_3$						1.429 (2)	5.97	0.995 (2)	9.58		
						1.432	5.92	0.994 (4)	9.60		
Cl_2BNH	1.11 u			1.773	4.56	1.361	7.07	0.991	9.66		
				1.766	4.62						
$ClBNH_2$	0.32 u			1.772	4.78	1.379	7.06	0.998	9.52		
								0.996	9.57		
ClBNH				1.708	5.24	1.220	10.70	0.981	9.86		
Cl_2BN	0.65 u			1.745 (2)	4.85	1.473	5.26				
$BNCl_2$	3.73 s					1.415	6.07			1.694 (2)	10.38
ClBN	0.93 u			1.687	5.53	1.294	8.78				

[a] u, UHF-unstable correction; s, spin-contamination correction. [b] In angstroms. [c] Number of bonds.

source of uncertainty, lack of good reference compounds, can add a few kcal mol^{-1} to the uncertainty estimates and will scale with the number of bonds in the molecule. The use of different reference values would shift our calculated heats of formation as a group, with the consequence that calculated bond dissociation enthalpies and reaction enthalpies are affected less than the heats of formation. Overall, we believe that the uncertainties in the BAC-MP4 heats of formation lie in the 3−7 kcal mol^{-1} range.

III. Results

The results of applying the BAC-MP4 method to species in the B−N−Cl−H system are given in Tables 3−6. As in previous papers in this series, we focus the discussion of this paper on the predicted thermochemical parameters, rather than on the *ab initio* calculations themselves. Consequently, more detailed information from the calculations, including geometries from the Hartree−Fock calculations, total energies obtained from perturbation theory, and vibrational frequencies, is reserved for the Supporting Information (described in the Appendix to this paper).

Before proceeding to a discussion of the calculated heats of formation and bond dissociation energies, it is useful to compare the atomization energies obtained from the BAC-MP4 method with those reported by other investigators at various levels of theory (Table 3). Although these data represent basis sets of different size and a variety of approximations, it is evident that the range of values predicted by the various methods is very small for both closed and open shell molecules. Averaging the values for each compound yields standard deviations on the order of 1 kcal mol^{-1}. In the case of BH_3, if the value obtained from the lowest level of theory (266.9 kcal mol^{-1}) is discarded, the standard deviation of the BH_3 atomization energies is only 0.6 kcal mol^{-1}. This suggests that the *ab initio* methods developed over the last 10 years to predict thermochemical data, which typically employ Møller−Plesset perturbation theory, are

TABLE 3: Calculated $\Delta H_f°(0\ K)$ and $\sum D_0$ for B−N−Cl−H Compounds at Various Levels of Theory (kcal mol^{-1})

species	MP4	BAC-MP2	BAC-MP3	BAC-MP4 (SDQ)	BAC-MP4 (SDTQ)	$\sum D_0$(0 K)	$\sum D_0$, literature
BH_3	32.1	23.4	23.4	23.4	23.4	265.3	263.7[a]; 264.3[b]; 264.4[c]; 265.0[d]; 265.3[e,f]; 265.3 ± 1.7[g]; 266.9[h]
BH_2	81.5	73.7	75.0	75.5	75.6	161.4	159.2[b]; 159.4[i]; 159.7[a]; 159.8[c]; 160.1[e,f];161.1[h]
BH ($^1\Sigma$)	109.2	104.1	102.5	101.8	101.7	83.7	78.2 ± 0.9[j]; 79.6 ± 1.2[k]; 80.9[h]; 81.5[l,m]; 82.4 ± 0.1; 82.8[e]
BCl_3	−82.0	−96.5	−96.1	−96.5	−96.5	316.0	316.0[k]; 320.1[e]
$BHCl_2$	−46.9	−59.4	−59.7	−59.8	−59.9	302.5	302.1[k]; 304.9[e]
BH_2Cl	−8.2	−18.8	−19.1	−19.2	−19.3	284.9	284.1[k]; 286.1[e]
BCl_2	2.7	−8.5	−8.1	−7.9	−7.8	198.7	200.3[e]; 205.8 ± 2.9[k]
HBCl	40.7	31.3	31.9	32.2	32.2	181.8	181.9[e]; 182.8 ± 4.8[k]
BCl	48.4	46.1	44.6	43.9	43.0	119.4	121.9 ± 4.8[k]; 123.0[e]; 127[j]
$H_3B{:}NH_3$	24.1	−13.7	−14.0	−14.5	−15.5	571.6	579.3 ± 3.8[k]
H_2BNH_2	11.7	−19.6	−20.1	−20.3	−20.3	473.2	
H_2BNH	69.5	48.3	46.7	46.1	46.1	355.1	
$HBNH_2$	62.6	31.9	32.4	32.8	33.1	368.2	
$B(NH_2)_2$	57.9	4.8	4.8	5.5	6.3	559.1	
HBNH	36.1	11.0	11.8	11.8	11.8	337.8	
BNH_2	79.0	51.6	49.8	49.7	49.6	300.0	
H_2BN	116.0	106.0	104.2	103.8	103.9	245.7	
BNH	93.8	66.9	69.1	69.6	70.1	227.9	
HBN ($^2\Pi$)	108.0	95.8	94.4	94.6	94.5	203.4	
BN	150.6	148.6	173.9	154.4	139.6	106.7	112 ± 14[k]; 131[j]
$B_3N_3H_6$	−42.3	−115.6	−115.7	−115.6	−115.7	1164.4	1165.0 ± 4.8[k]
$Cl_3B{:}NH_3$	−86.4	−130.9	−128.2	−128.5	−130.0	645.5	
$Cl_3B{:}NH_3 \rightarrow Cl_2BNH_2 + HCl$	−47.6	−92.6	−91.0	−90.7	−91.5	607.1	
$H_3N{:}BCl_2NH_2$	−51.1	−115.5	−112.9	−112.8	−114.5	788.7	
$HClBNH_2$	−26.8	−60.3	−60.9	−60.8	−60.4	490.3	
Cl_2BNH_2	−62.2	−97.6	−98.3	−97.9	−97.2	504.0	
$Cl_2BNH_2 \rightarrow ClBNH + HCl$	15.5	−20.5	−20.4	−19.4	−19.0	425.8	
$ClB(NH_2)_2$	−32.3	−88.3	−89.3	−88.8	−87.7	681.6	
$HB(NH_2)_2$	5.8	−48.1	−48.9	−48.8	−48.3	665.4	
$B(NH_2)_3$	5.6	−70.4	−71.3	−70.9	−69.8	851.0	
Cl_2BNH	2.4	−23.3	−25.8	−25.8	−24.6	379.7	
$ClBNH_2$	24.7	−7.8	−7.8	−7.1	−6.5	384.7	
ClBNH	7.5	−19.1	−20.2	−19.7	−18.3	344.9	
Cl_2BN	39.4	26.0	23.9	23.5	23.8	279.7	
$BNCl_2$	136.3	109.5	107.0	105.3	105.7	197.8	
ClBN	74.8	61.3	58.6	58.9	59.5	215.4	

[a] CBS-4 calculation. See ref 21. [b] MP4/QCI calculation. See ref 22. [c] CBS-Q calculation. See ref 21. [d] MP4/6-311G++ calculation. See ref 23. [e] G-2 calculation. See ref 31. [f] G-2 calculation. See ref 24. [g] Photoionization experiment. See ref 61. [h] MP4/6-31G(d) calculation. See ref 25. [i] CCD+ST(CCD) calculation. See ref 26. [j] See ref 19. [k] See ref 20. [l] See ref 27. [m] See ref 28.

of comparable accuracy. Differences in excess of 1 kcal mol^{-1} among heats of formation predicted by these methods are likely caused by other factors, in particular the use of different values of the atomic heats of formation in the conversion of $\sum D_0$ to a heat of formation.

A. Heats of Formation and Bond Dissociation Energies. Table 3 lists $\Delta H_f°(0\ K)$ at various levels of theory and provides a measure of calculational accuracy. In almost all cases, $\Delta H_f°(0\ K)$ converges to an approximately constant value, indicating that errors in the calculation are likely to be small. The one exception to this is BN, for which the MP perturbation series did not converge, resulting in a very large uncertainty in the predicted heat of formation (Table 4). The literature values listed in Table 3 are discussed below (section III.B).

Calculated heats of formation at 298 K ($\Delta H_f°(298\ K)$) are shown in Table 4 with error estimates calculated by the *ad hoc* approach discussed above. Additional heats of formation needed to calculate bond dissociation energies and to illustrate trends are also included for reference in this table. Table 5 lists $\Delta S°(298\ K)$ and values of $\Delta G_f°$ at various temperatures. Table 4 also includes available measured and calculated values from the literature. Although comparison of these values with our BAC-MP4 results is discussed below, it is important to note here that, while a reasonable body of theoretical and experimental data exists for establishing the accuracy of the BAC-MP4 method for compounds in the B−H−Cl system, the amount of data for compounds containing B−N bonds is much smaller. This lead us to use the result of a G-2 calculation to establish the BAC for B−N multiple bonds (section II). Thus, to lend additional confidence to our predictions, we performed a G-2 calculation for the molecule H_2BNH_2. The predicted $\Delta H_f°(298\ K)$ is −21.5 kcal mol^{-1}, which is in reasonable agreement with the BAC-MP4 prediction of −23.2 kcal mol^{-1}. The somewhat more negative value obtained from the BAC-MP4 calculation is expected, since the BAC for B−N single bonds is based on $B_3N_3H_6$, resulting in a slight overcorrection for molecules with only one B−N bond.

Bond dissociation energies (BDE) for selected compounds examined in this study are given in Table 6. The calculations show that B−H bonds for filled shell compounds are nearly unaffected by the replacement of neighboring hydrogen atoms with chlorine, in agreement with a previous discussion of the BDEs for BH_mCl_n compounds.[31] This is also the case when H is replaced by an NH_2 group, indicating that changes in electron density at boron induced by neighboring groups are not large. A comparison with other first-row hydrides shows that B−H bonds in closed shell boranes are comparable in strength to C−H bonds in alkanes, but are weaker than those formed with more electronegative atoms (e.g., BDE(BH_3) = 105.3, BDE(CH_4) = 104.9, BDE(NH_3) = 109.1 kcal mol^{-1}, BDE(H_2O) = 119.4 kcal

TABLE 4: $\Delta H_f°$(298 K) for the BAC-MP4(SDTQ) Level of Theory with Error Estimates and Literature Values for B−N−Cl−H Compounds (kcal mol^{-1})

species	$\Delta H_f°$	experiment/compilation	other theory
BH_3[a]	22.35 ± 1.00	25.5 ± 2.4[b]; 23.80[h]; 21 ± 2.4[i]	24.89[c]; 22.3 ± 3.3[d]; 11.7[g]; 19.7[j]
BH_2	75.55 ± 1.16	48.0 ± 15[b]; 45.71[h]; 76.1 ± 2.6[i]	79.43[c]; 76.5 ± [d]; 66.5[g]; 74.8[j]
BH ($^1\Sigma$)	102.39 ± 1.60	105.8 ± 2.0[b]; 108.24[h]; 106.6 ± 1.7[i]	105.83[c]; 105.1 ± 3[d]; 72.1[g]; 104.1[j]
BCl_3[a]	−96.69 ± 1.05	−96.3 ± 0.5[b]; −97.50[h]; −96.68 ± 0.31[i]	−98.63[c]; −97.0[e]
$BHCl_2$	−60.59 ± 1.02	−59.3 ± 1.0[b]; −60.52[h]; −60.2 ± [i]	−60.68[c]; −60.7[e]
BH_2Cl	−20.29 ± 1.02	−19.3 ± 4.8[i]	−18.98[c]
BCl_2	−7.53 ± 1.07	−19.0 ± 3.0[b]; −14.6 ± 2.4[h]	−6.79[c]
HBCl	32.22 ± 1.07	31.27 ± 5.0[i]	34.53[c]
BCl	43.71 ± 2.03	33.8 ± 4[b]; 36.01[h]; 41.2±6.0[i]	42.52[c]; 13.5[e]
$H_3B{:}NH_3$	−19.95 ± 2.02	−27.5 ± 3.6[i]	−21.70[f]
H_2BNH_2	−23.19 ± 1.02		−26.87[f]; −14[k]; −21.49[l]
H_2BNH	44.58 ± 1.18		
$HBNH_2$	31.18 ± 1.20		
$B(NH_2)_2$	3.29 ± 1.95		
HBNH[a]	10.95 ± 1.00		1.41[f]; 31[m]
BNH_2	48.85 ± 1.18		
H_2BN	102.93 ± 1.05		
BNH	70.03 ± 1.59		
HBN ($^2\Pi$)	94.32 ± 1.03		
BN	140.30 ± 37.35	114 ± 29.9[b]; 134.8 ± 14[i]	
$B_3N_3H_6$[a]	−121.98 ± 1.00	−121.9 ± 3.1[b]; −122.4 ± 3.1[i]	
$Cl_3B{:}NH_3$	−133.01 ± 2.49		
$Cl_3B{:}NH_3 \rightarrow Cl_2BNH_2 + HCl$	−94.72 ± 1.35		
$H_3N{:}BCl_2NH_2$	−119.09 ± 2.48		
$HClBNH_2$	−63.01 ± 1.17		
Cl_2BNH_2	−99.27 ± 1.67		
$Cl_2BNH_2 \rightarrow ClBNH + HCl$	−20.88 ± 1.83		
$ClB(NH_2)_2$	91.30 ± 2.24		
$HB(NH_2)_2$	52.44 ± 1.24		
$B(NH_2)_3$	−74.58 ± 2.08		
Cl_2BNH	−25.71 ± 1.98		
$ClBNH_2$	−8.05 ± 1.74		
ClBNH	−18.94 ± 2.57		
Cl_2BN	23.52 ± 1.06		
$BNCl_2$	105.71 ± 1.80		
ClBN	59.65 ± 1.50		
NH_3	−10.98		
NH_2	46.05		
NH	87.03		
N	112.97		
Cl	28.98		
H	52.07		
B (^{2}P)	134.93		

[a] Reference compound. [b] *JANAF Tables* (ref 19). [c] G-2 calculation (ref 31). [d] CID/6-31G*//CCD+ST(CCD/6-311+G(2df,p)B calculation (ref 26). [e] AM1 calculation (Dewar, M. J. S.; et al. *Organometallics* **1988**, *7*, 513. [f] MNDO calculation (ref 39). [g] MNDO calculation (Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231. [h] CATCH Tables (Guest, M. F.; Pedley, J. B.; Horn, M. *J. Chem. Thermodynamics* **1969**, *1*, 345. [i] Critical review of Gurvich et al. (ref 20). [j] MP4/(various basis sets yielding an approximation of 6-311G+(2df,p))//HF/6-31G(d) (ref 25). [k] HF/6-31G(d) (ref 40). [l] G-2 calculation, this work.

mol^{-1}, BDE(HF) = 136.3 kcal mol^{-1}). B−H bonds in BH_2 and HBCl are much weaker than in the closed shell boranes and point to the relative stability of the BH molecule (BDE(BH) = 84.3 kcal mol^{-1}). For similar reasons, the B−H bond in H_2BNH is extremely weak; its dissociation energy of only 18.4 kcal mol^{-1} is due to the stability of HBNH, which is an analogue of acetylene.

In contrast, boron−chlorine bonds are considerably stronger than carbon−chlorine bonds, with values ranging from 118.1 kcal mol^{-1} in BCl_3 to 124.8 kcal mol^{-1} in BH_2Cl. By comparison, the C−Cl BDE in CH_3Cl is only 84 kcal mol^{-1}. The decrease in the BDE as the number of chlorines increases has been attributed to competition for the empty p−π orbital on the boron atom by the π-bonding electrons in the 2p orbitals of the chlorine atoms.[31] BAC-MP4 predicts a BDE at 0 K for BCl of 119.4 ± 2.0 kcal mol^{-1}, which is in excellent agreement with a recent experimental measurement (121.3 ± 1.1 kcal mol^{-1}) by Hildenbrand.[62] This also agrees with previously reported G-2 calculations,[31] in which the BDE of BCl is predicted to be considerably larger than that of BH (120.3 vs 84.7 kcal mol^{-1}), due to the ability of chlorine to form π bonds. A corresponding weakness is also predicted for B−X bonds in ClBX (X = H, Cl, or NH_2) compounds due to the relative stability of BCl.

Boron−nitrogen bonds are predicted to be quite strong in both the closed shell and unsaturated species. For example, B−N BDEs in the $B(NH_2)_nH_{3-n}$ (n = 1−3) series are as high as 144.8 kcal mol^{-1} (H_2BNH_2). Boron−nitrogen bonds in the unsaturated XBNH species (X = H or Cl) are even stronger; for example, the B−N BDE in HBNH is predicted to be nearly 180 kcal mol^{-1}. The high strength of these bonds can be understood by recognizing that these compounds are analogous to stable, unsaturated hydrocarbons. For example, H_2BNH_2 is isoelectronic with C_2H_4 (C−C BDE = 173 kcal mol^{-1}), while HBNH is isoelectronic with C_2H_2 (C−C BDE = 229.7 kcal mol^{-1}). Both boron compounds have geometries that are similar to their hydrocarbon counterparts. The analogy with hydrocarbons is clearly not perfect, however; B−N bonds are considerably weaker than their C−C analogues, which is likely due to their polar nature.[63] It is unlikely, for example, that a true double bond exists in H_2BNH_2. Consistent with previous calculations,[39,40] the calculated barrier to rotation about this bond

TABLE 5: Thermochemical Parameters at Various Temperatures (K)

	ΔH_f° [a]	S° [b]	ΔG_f° [a]					
species	298	298	300	600	1000	1500	2000	2500
BH_3	22.4	45.01	23.3	24.7	27.5	31.2	35.1	39.4
BH_2	75.5	46.42	71.4	67.4	62.8	57.1	51.9	47.2
$BH\ (^1\Sigma)$	102.4	41.03	95.2	87.9	78.7	67.2	56.1	45.7
BCl_3	−96.7	69.46	−93.2	−89.8	−85.1	−79.6	−73.9	−67.7
$BHCl_2$	−60.6	64.23	−58.8	−56.9	−53.8	−50.1	−46.2	−41.8
BH_2Cl	−20.3	56.09	−19.4	−18.1	−15.6	−12.5	−9.2	−5.4
BCl_2	−7.5	64.76	−10.6	−13.7	−17.4	−22.2	−26.5	−30.3
$HBCl$	32.2	57.39	28.1	24.1	19.3	13.3	7.8	2.9
BCl	43.7	51.02	36.8	29.8	20.9	9.7	−1.0	−11.0
$H_3B{:}NH_3$	−19.9	58.30	−2.2	16.8	43.6	76.6	109.2	141.6
H_2BNH_2	−23.2	54.78	−13.7	−3.4	11.5	30.0	48.4	67.0
H_2BNH	44.6	59.99	47.9	51.2	56.3	62.2	68.3	74.6
$HBNH_2$	31.2	56.55	35.5	40.3	47.7	56.8	66.0	75.5
$B(NH_2)_2$	3.3	64.71	16.7	30.6	49.9	73.6	97.0	120.5
$HBNH$	11.0	41.62	15.1	19.4	25.9	33.9	42.3	51.1
BNH_2	48.8	53.18	49.5	50.4	52.3	54.7	57.4	60.6
H_2BN	102.9	55.26	103.0	103.3	104.4	105.7	107.1	108.9
BNH	70.0	50.14	66.9	63.9	60.2	55.5	51.1	47.3
$HBN\ (^2\Pi)$	94.3	49.91	91.3	88.4	84.9	80.3	76.0	72.2
BN	140.3	47.03	133.5	126.6	117.8	106.9	96.4	86.6
$B_3N_3H_6$	−122.0	69.64	−93.0	−62.8	−20.7	30.6	81.7	133.1
$Cl_3B{:}NH_3$	−133.0	79.63	−111.7	−90.0	−60.6	−24.8	10.5	45.5
$Cl_3B{:}NH_3 \rightarrow Cl_2BNH_2 + HCl$	−94.7	82.47	−74.3	−53.2	−24.3	11.5	47.1	82.7
$H_3N{:}BCl_2NH_2$	−119.1	83.61	−90.8	−61.7	−22.4	25.3	72.3	118.7
$HClBNH_2$	−63.0	64.43	−53.1	−42.6	−27.8	−9.6	8.5	26.9
Cl_2BNH_2	−99.3	70.61	−87.9	−76.3	−60.3	−40.8	−21.5	−2.1
$Cl_2BNH_2 \rightarrow ClBNH + HCl$	−20.9	75.02	−10.8	−0.5	14.0	31.7	49.6	67.8
$ClB(NH_2)_2$	-91.3	72.72	-72.4	-52.9	-26.5	5.8	37.8	69.6
$HB(NH_2)_2$	-52.4	63.53	-34.1	-14.8	11.8	44.5	76.7	108.8
$B(NH_2)_3$	-74.6	77.39	-48.8	-22.3	13.6	57.4	100.4	143.0
Cl_2BNH	-25.7	73.06	-19.7	-13.6	-5.0	5.6	16.6	28.0
$ClBNH_2$	-8.1	65.18	-3.0	2.3	10.1	19.6	29.1	39.0
$ClBNH$	-18.9	58.34	-16.5	-14.1	-10.8	-7.0	-3.01.3	
Cl_2BN	23.5	71.37	25.3	27.1	29.4	31.8	34.4	37.4
$BNCl_2$	105.7	70.75	107.7	109.6	112.0	114.7	117.5	120.7
$ClBN$	59.7	58.40	57.4	55.0	52.0	47.9	44.1	40.8

[a] In kcal mol^{-1}. [b] In cal mol^{-1} K^{-1}.

TABLE 6: Calculated Bond Dissociation Enthalpies (BDE) at 298 K for Selected Compounds in the B−N−Cl−H System (kcal mol^{-1})

B−N bond	BDE	N−H bond	BDE	B−H bond	BDE	B−Cl bond	BDE
$H_3B{:}NH_3$	31.3						
H_2BNH_2	144.8	H_2BNH_2	119.8	H_2BNH_2	106.4		
$HB(NH_2)_2$	129.7			$HB(NH_2)_2$	107.8		
$B(NH_2)_3$	123.9						
H_2BNH	118.0	H_2BNH	110.4	H_2BNH	18.4		
$HBNH$	178.5	$HBNH$	135.4	$HBNH$	111.2		
H_2BN	85.6			H_2BN	61.1		
BNH_2	132.2	BNH_2	73.3	HBN	98.1		
HBN	121.0						
BNH	152.0	BNH	122.3	BH_3	105.3		
BN	107.7			BH_2Cl	104.6	BH_2Cl	124.8
				$BHCl_2$	105.1	$BHCl_2$	121.8
						BCl_3	118.1
				BH_2	78.9		
				$HBCl$	63.6	$HBCl$	99.2
				BH	84.7	BCl_2	80.2
$Cl_3B{:}NH_3$	25.3					BCl	120.3
$H_3N{:}BCl_2NH_2$	8.8						
$HClBNH_2$	141.3			$HClBNH_2$	107.0	$HClBNH_2$	123.2
Cl_2BNH_2	137.8	Cl_2BNH_2	125.6			Cl_2BNH_2	120.2
$ClB(NH_2)_2$	129.3						
Cl_2BNH	105.2	Cl_2BNH	101.3			Cl_2BNH	35.8
$ClBNH_2$	97.8	$ClBNH_2$	41.2			$ClBNH_2$	85.9
$ClBNH$	149.7	$ClBNH$	130.7			$ClBNH$	118.0
Cl_2BN	81.9					Cl_2BN	65.1
$ClBN$	97.0					$ClBN$	109.6

is only 26 kcal mol^{-1}, which is considerably lower than the barrier predicted for ethylene (45 kcal mol^{-1}). Substitution of chlorine for hydrogen at the boron atom significantly weakens the B−N bond; in ClBNH, the B−N bond is 29 kcal mol^{-1} weaker than in HBNH, while in Cl_2BNH_2 it is 7 kcal mol^{-1} weaker than in H_2BNH_2. This is consistent with both the higher electronegativity of this atom relative to hydrogen and the ability of chlorine to form π bonds of its own with boron.

Boron compounds can also form donor−acceptor complexes with Lewis acids such as NH_3 and three such compounds, H_3B:NH_3, Cl_3B:NH_3, and H_3N:BCl_2NH_2, are included here. As expected for complexes of this type,[3] the B−N bonds in these three compounds are predicted to be rather weak: 31.3, 25.3, and 8.8 kcal mol^{-1} for H_3B:NH_3, Cl_3B:NH_3, and H_3N:BCl_2NH_2, respectively. This weakness is reflected in the B−N bond length, which is significantly longer than in the closed shell or unsaturated compounds. In the series H_3B:NH_3, H_2BNH_2, HBNH, the B−N bond lengths are 1.689, 1.389, and 1.223 Å, respectively. We also note that the B−N distance predicted for Cl_3B:NH_3 is 1.628 Å, which is shorter than the same bond in H_3B:NH_3, even though the bond in Cl_3B:NH_3 is predicted to be almost 6 kcal mol^{-1} weaker. Previously reported calculations at the MP2/TZ2P level[1] yield similar results. Substitution of an NH_2 group for a chlorine atom in H_3N:BCl_3 yields the complex H_3N:BCl_2NH_2, whose B−N bond is much weaker (8.3 kcal mol^{-1}) than that of H_3N:BCl_3. Evidently, BCl_2NH_2 is a much weaker Lewis acid than BCl_3, leading us to predict that the B−N bonds in complexes with even more highly amine-substituted boron compounds ($BCl(NH_2)_2$ or $B(NH_2)_3$) are probably too weak to exist at room temperature.

It is also interesting to note that the predicted B−N BDE in H_3B:NH_3 is 6 kcal mol^{-1} larger than in Cl_3B:NH_3. This appears to contradict the suggestion by Brinck et al. that complexation energies (which are the negative of the B−N bond energy) in X_3B:NH_3 species should increase with increasing ability to accept charge.[36] In the case of the halogens, they predict this order to be $BF_3 < BCl_3 < BBr_3$, which is consistent with the observed Lewis acidities of these molecules. Based on this argument, one would expect a weaker B−N bond in H_3B:NH_3 than in Cl_3B:NH_3. However, a detailed theoretical analysis of the bonding in complexes of this type by Jonas et al. indicates that the B−N bond strength includes contributions from both covalent and electrostatic interactions,[1] making trends in bond energies very difficult to predict *a priori*.

Bonds between nitrogen and hydrogen are strengthened by bonding to boron-containing groups, making the N−H bonds in H_2BNH_2 (119.8 kcal mol^{-1}) and HBNH (135 kcal mol^{-1}) stronger than either their hydrocarbon analogues, C_2H_4 (110.8 kcal mol^{-1}) and C_2H_2 (132 kcal mol^{-1}), or NH_3 (109.1 kcal mol^{-1}). The N−H bond is further strengthened in X_2BNH_2 species by increasing the electronegativity of the boron-containing moiety; for example, the N−H BDE in Cl_2BNH_2 is 125.6 kcal mol^{-1}. This is consistent with trends predicted for other amines; for example, the N−H BDEs in the series NH_3, H_2NSiH_3, H_2NSiF_3[49] are 109, 115, and 120 kcal mol^{-1}.

B. Comparison of Calculated Heats of Formation with Literature Values. A substantial body of literature exists concerning the thermochemistry of boron-containing species, consisting of both experimental and theoretical investigations. Experimental measurements leading to heats of formation are available for compounds containing B−H, B−Cl, and B−N bonds, allowing a direct comparison between theory and experiment. Unfortunately, in very few cases can the values recommended in compilations of thermodynamic data be considered well established. The most recent critical review, published by Gurvich et al.,[20] recommends heats of formation and other thermodynamic data based on a thorough evaluation of the available experimental data, combined with updated spectroscopic constants. This compilation includes 12 of the compounds in this study. In cases where the experimental data are insufficient to provide reliable values for heats of formation, Gurvich et al. make use of atomization energies predicted by *ab initio* calculations coupled with measured spectroscopic data to determine a heat of formation. The *JANAF Tables*[19] also include data for a number of boron-containing compounds; however, some of these tables have not been revised since the mid-1960s. A corresponding review of the theoretical work has not been published, so these results are summarized in Table 4 along with the values recommended by *JANAF* and Gurvich et al. Heats of formation obtained by individual experimental investigations are not listed, except where they are not included in the review of Gurvich et al. Atomization energies referred to in the discussion below are given in Table 3.

Heats of formation for the boron hydrides (BH_n, ($n = 1-3$) have not been firmly established. There is wide scatter in the experimental values reported for BH_3, and the uncertainty quoted by both the *JANAF Tables*[19] and Gurvich et al.[20] is relatively high (±2.4 kcal mol^{-1}). As noted by Gurvich et al., the experimental data for BH_3 are contradictory, with results from kinetic investigations in the range 18−23 kcal mol^{-1}, while predictions based on electron impact and photoionization studies range from 14 to 35 kcal mol^{-1}. The BAC-MP4 value (22.4 ± 1.0 kcal mol^{-1}) is based on a G-2 calculation and thus does not constitute a new prediction. However, it is consistent with the value recommend by Gurvich et al. (21 ± 2.4 kcal mol^{-1}) and thus supports the values measured by the kinetic studies. Recent *ab initio* calculations of the BH_3 atomization energy, typically performed at the MP4 level of theory or above, are generally in good agreement with each other, with values varying by only ±1 kcal mol^{-1}. In addition, these values agree well with the experimental measurement of this quantity by Ruscic et al. (265.3 ± 1.7 kcal mol^{-1}).[64]

Reliable measurements of thermodynamic and spectroscopic constants for BH_2 are unavailable. Gurvich et al.[20] base their recommendation (76.1 ± 2.6 kcal mol^{-1}) on an atomization energy predicted by Pople et al. at the MP4/6-31G(d) level.[25] The heat of formation predicted by BAC-MP4 (75.6 ± 1.2 kcal mol^{-1}) is consistent with this recommendation, as well as with the results of calculations at various levels of theory. The *JANAF* value (48 ± 15 kcal mol^{-1})[19] is based on appearance-potential measurements that have been shown to be spurious.[64] As noted above, differences in heats of formation predicted by various investigators are in part due to the different values of the boron atom heat of formation used to convert predicted atomization energies into heats of formation. However, the atomization energy for BH_2 predicted by the BAC-MP4 method is in good agreement with other calculated values, which vary by only ±1.1 kcal mol^{-1}.

The BH heats of formation recommended by Gurvich et al.[20] and the *JANAF Tables*[19] are based on experimental estimates of the molecular dissociation energy (D_0(BH)), which were determined from the observation of molecular predissociation in the A $^1\Pi$ excited state. Unfortunately, these data yield only an upper limit for D_0(BH) (≤82.5 kcal mol^{-1}), since there is a barrier to dissociation in the A $^1\Pi$ state.[65] The magnitude of this barrier has not been measured, although there are several predictions from theory, most of which range from 1.8 to 3.7 kcal mol^{-1}.[20] However, a CCD+ST(CCD) calculation reported by Martin et al. suggests that the barrier is quite small (∼0.2 kcal mol^{-1}), resulting in a predicted D_0(BH) of 82.4 ± 0.2 kcal mol^{-1}.[29] The value assumed by Gurvich et al. (3.0 kcal mol^{-1}) yields D_0(BH) of 79.6 ± 1.2 kcal mol^{-1}.[20] In contrast, the values of D_0(BH) predicted by G-2[31] (82.8 kcal mol^{-1}) and BAC-MP4 (83.7 kcal mol^{-1}) both exceed the experimental upper limit. In the case of the BAC-MP4 prediction, we believe that the inconsistency is caused by the inability of the theoretical method to completely correct for electron correlation effects (i.e., the UHF instability) associated with the empty p orbitals on the boron atom. For this reason, we consider the heat of formation recommended by Gurvich et al. (106.6 ± 1.7 kcal mol^{-1}) to be more reliable than the BAC-MP4 prediction (102.4 ± 1.6 kcal mol^{-1}).

The boron chlorides provide the only example of a well-established heat of formation for a boron-containing compound: boron trichloride. The results of nine experimental studies of BCl_3 (summarized by Gurvich et al.[20]) employing a range of methods are largely in agreement and lead to a recommended heat of formation[20] of −96.68 ± 0.31 kcal mol^{-1}. We use this value as a reference to establish the B−Cl BAC (see discussion above). This assumption yields predicted heats of formation for two other closed shell boron chlorides that agree well with recommended values:[20] $BHCl_2$ (-60.6 ± 1.0 kcal mol^{-1} predicted, −60.2 ± 1.2 kcal mol^{-1} recommended[20]) and BH_2Cl (-20.3 ± 1.0 kcal mol^{-1} predicted, −19.3 ± 4.8 kcal mol^{-1} recommended[20]). The BAC-MP4 heats of formation are derived from the predicted heats of atomization 316.0, 302.5, and 284.9 kcal mol^{-1} for BCl_3, $BHCl_2$, and BH_2Cl, respectively; the latter two values are in excellent agreement with those used by Gurvich et al.[20] In contrast, G-2 predicts significantly higher values: 320.1, 304.9, and 286.1 kcal mol^{-1},[31] two of which (for BCl_3 and $BHCl_2$) are outside the uncertainty limits quoted by Gurvich et al. The source of this difference between the two methods is unclear at this time.

Experimental data for the open shell boron chlorides BCl_2 and HBCl are more limited. The heat of formation for BCl_2 recommended by Gurvich et al.[20] (−14.6 ± 2.4 kcal mol^{-1}) is based on an atomization energy of 205.8 ± 2.9 kcal mol^{-1}, which disagrees significantly with predictions of both BAC-MP4 (198.7 kcal mol^{-1}) and G-2[31] (200.3 kcal mol^{-1}). The *JANAF Tables*[19] recommend a different value (-19.0 ± 3.0 kcal mol^{-1}), derived from another experimental study. Thus, a serious disagreement exists among the heats of formation predicted by BAC-MP4 (−7.5 ± 1.1 kcal mol^{-1}), G-2 (−6.8 kcal mol^{-1}), and those based on experiment. In contrast, the atomization energies for HBCl predicted by BAC-MP4 (181.8 kcal mol^{-1}) and G-2 (181.9 kcal mol^{-1}) are in good agreement with the value used by Gurvich et al. (182.8 ± 4.8 kcal mol^{-1}), leading to consistency among the resulting heats of formation (Table 4). However, this agreement may be fortuitous, since $\sum D_0$(HBCl) used by Gurvich et al. is not based on experimental data, but was estimated by assuming that the average bond energies in BHCl, BH_2, and BCl_2 are the same.

The relatively large uncertainties associated with experimental measurements of D_0(BCl) make it difficult to establish the accuracy of the BAC-MP4 heats of formation for BCl. D_0(BCl) predicted by BAC-MP4 (119.4 kcal mol^{-1}) is 3.6 kcal mol^{-1} smaller than the G-2 prediction[31] (123.0 kcal mol^{-1}). Although the latter value agrees somewhat better with the one used by Gurvich et al.[20] (121.9 ± 4.8 kcal mol^{-1}, based on mass-spectrometric measurements), the wide range of experimental values (100−139 kcal mol^{-1})[20] and the relatively high uncertainty quoted by Gurvich et al. make it unclear which of the predicted values is the more accurate. The BCl heat of formation predicted by BAC-MP4 (43.7 kcal mol^{-1}) does, however, agree with the recommended value[20] (41.2 ± 6.0 kcal mol^{-1}) within the quoted uncertainty. As is the case for BCl_2, the *JANAF Tables*,[19] using a different value of D_0(BCl) than the one employed by Gurvich et al., recommend a substantially lower heat of formation. However, since the analysis of Gurvich et al. accounts for the presence of low-lying excited electronic states, while the *JANAF* analysis does not, we expect that the number recommended by Gurvich et al. is more accurate.

Heats of formation derived from experimental data for species containing B−N bonds are only available for $B_3N_3H_6$ (borazole), $H_3B{:}NH_3$, and BN (Table 4). As discussed above, the $B_3N_3H_6$ heat of formation is used in this investigation as a reference compound to establish the BAC for B−N bonds and consequently cannot be used to test the accuracy of the BAC-MP4 predictions. However, the Lewis acid−base complex $H_3B{:}NH_3$ has been studied extensively by theoretical methods,[2] yielding several predictions of the B−N bond energy. In addition, four experimental studies (reviewed by Gurvich et al.[20]) provide a heat of formation for comparison with BAC-MP4 results. Gurvich et al. recommend a heat of formation for $H_3B{:}NH_3$ of −27.5 ± 3.6 kcal mol^{-1}, which is somewhat more negative than the BAC-MP4 prediction of −20.0 ± 2.0 kcal mol^{-1}. The BAC-MP4 prediction of 31.3 kcal mol^{-1} for the B−N bond energy is in reasonable agreement with other predictions: 34.7 kcal mol^{-1} (MP4(SDTQ)/6-311G**),[38] 30.7 kcal mol^{-1} (MP2/TZ2P),[1] 27.6 kcal mol^{-1} (CEPA-2),[66] 27 kcal mol^{-1} (CEPA),[37] and 21 kcal mol^{-1} (6-31G*).[40] Haaland also estimated the B−N BDE (31.1 kcal mol^{-1}) by making comparisons with related methylated aminoboranes.[3] The heats of formation recommend by Gurvich et al. yield a B−N bond energy of 37.5 kcal mol^{-1}, which is significantly higher than any of the predicted values, as well as Haaland's estimate. Bearing in mind that the B−N reference heat of formation is based on a single experimental study and is thus not firmly established, these comparisons suggest that the heat of formation determined by Gurvich et al. is too negative by 3−7 kcal mol^{-1}.

The only thermodynamic information in the literature for the complex $Cl_3B{:}NH_3$ is a calculation of its complexation energy carried out by Brinck et al. at the MP2/6-31+G(2d,p) level of theory.[36] The B−N bond energy obtained by these authors is 24.08 kcal mol^{-1} (at 0 K), in excellent agreement with the BAC-MP4 prediction of 24.27 kcal mol^{-1}. Jonas et al. also predicted the B−N energy for this compound at a similar level of theory (MP2/TZ2P), but predicted a somewhat larger bond energy (29.7 kcal mol^{-1} at 298 K).[1] Unfortunately, there are no experimental data for comparison.

Uncertainties in the recommended heats of formation for BN are high; the *JANAF Tables* quote a value of 114 ± 30 kcal mol^{-1}, while Gurvich et al. recommend 135 ± 14 kcal mol^{-1}. Neither value is based on a direct measurement of D_0(BN). The uncertainties in these values encompass the BAC-MP4 prediction of 140.3 ± 37 kcal mol^{-1}, which itself has a large uncertainty due to the poor convergence behavior of the MP perturbation series (Table 3). Reddy et al. obtained a value for D_0(BN) of 77.5 kcal mol^{-1} by fitting an empirical potential function;[32] the corresponding value predicted by BAC-MP4 is 108 ± 38 kcal mol^{-1}. Clearly, additional experimental and theoretical work is necessary to achieve a useful understanding of the energetics of this molecule.

C. Gas-Phase Reactions Relevant to the CVD of Boron Nitride. As discussed in the Introduction, reactions between boron halides and ammonia are used in CVD processes to deposit films or coatings of boron nitride. In particular, boron trichloride and ammonia are commonly used as reactants. The potential for gas-phase reactions between these species is thus of some practical interest, not only for the purpose of developing quantitative process models but for avoiding reactor conditions that may lead to homogeneous nucleation of particulates. We calculated the transition-state energetics for two reactions that are likely to be important under typical CVD conditions. (The calculated heats of formation discussed in section A may also

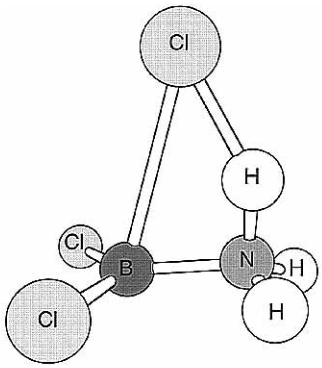

Figure 1. Transition state for the reaction $BCl_3 + NH_3 \rightarrow Cl_2BNH_2 + HCl$. Bond distances are given in Table 2.

be used to calculate enthalpies for other potentially important reactions not discussed here, since numerous species that may be present at high temperatures are included.) Before proceeding we note that predictions of transition-state energies are very dependent upon the molecular geometry used; since the BAC-MP4 method uses a relatively low level of theory (HF) to predict these geometries, the energies discussed below should be interpreted with some caution. Previous investigations using the BAC-MP4 method indicate that activation energies may be overpredicted by several kcal mol^{-1} in some cases.[48] However, BAC-MP4 predictions are still sufficiently accurate to provide a basis for evaluating the relative importance of various gas-phase pathways, particularly for reaction systems such as BCl_3/NH_3 that are very poorly characterized. We also note that the good convergence behavior of the calculated transition-state energies (Table 3) and consequently small error estimates (Table 4) suggest that large changes in these energies are not likely to result further refinement of the geometry.

At room temperature, BCl_3 and NH_3 form a stable gas-phase complex:

$$BCl_3 + NH_3 \leftrightarrow Cl_3B{:}NH_3 \qquad (1)$$

This reaction is predicted to be exothermic by 25 kcal mol^{-1}. At the temperatures employed in CVD reactors (1000−2000 K), a second reaction can occur in which HCl is eliminated from a transition state formed by the collision of the two reactants:

$$BCl_3 + NH_3 \leftrightarrow [Cl_3BNH_3]^{\dagger} \leftrightarrow Cl_2BNH_2 + HCl \qquad (2)$$

The barrier for this reaction, as determined from the calculated heats of formation (Table 4) for BCl_3 and the transition state $[Cl_3BNH_3]^{\dagger}$, is a relatively modest 13 kcal mol^{-1}. The overall reaction is predicted to be exothermic by about 14 kcal mol^{-1}. The transition state for reaction 2 is shown in Figure 1 and can be described crudely as a four-center elimination pathway. However, the inequality of the N−H and B-Cl bond lengths (1.083 vs 2.958 Å, respectively) suggests that the reaction is more accurately described either by a sequential loss of a chlorine atom followed by hydrogen-atom abstraction, or by formation of a charge-stabilized adduct in which the chlorine atom is negatively charged and the hydrogen atom positively charged. The latter mechanism appears to be more likely, since the activation energy for reaction 2 is so much smaller than the B−Cl BDE (120 kcal mol^{-1}). This is also supported by the absence of UHF instability in the transition state (Table 2), which indicates a lack of biradical (multireference state) character. The sequential nature of the process is supported by the fact that the B−Cl bond in the transition state is nearly twice as long as in BCl_3 (2.958 vs 1.511 Å), while the N−H bond is only slightly elongated from its length in NH_3 (1.083 vs 1.003 Å). Both products of reaction 2 have been detected at temperatures similar to those used in CVD reactors,[16,17] indicating that this reaction probably occurs under CVD conditions. However, kinetic measurements suggest that the actual barrier is smaller than is predicted here; in experiments by Kapralova et al.,[16] a rate near the collision limit was measured at 343 K, while a limited flow-reactor study indicates that the rate may be 500−1000 times faster than that based on the BAC-MP4 prediction at 725 K.[17] If the flow-reactor data are accurate, and all of the error in the BAC-MP4 prediction is contained in the activation energy, then the BAC-MP4 prediction is 8−10 kcal mol^{-1} too high. An error of this size is somewhat larger than we expect on the basis of application of the BAC-MP4 method to other first-row systems.[48] Thus, additional experiments are required to fully resolve this question.

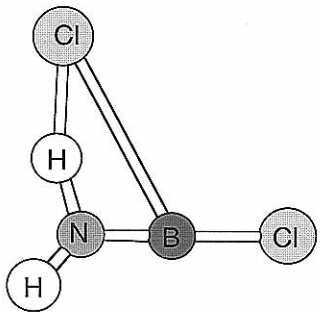

Figure 2. Transition state for the reaction $Cl_2BNH_2 \rightarrow ClBNH + HCl$. Bond distances are given in Table 2.

The calculations also predict that Cl_2BNH_2 can lose HCl via a 1,2-elimination process:

$$Cl_2BNH_2 \leftrightarrow ClBNH + HCl \qquad (3)$$

The transition state for this reaction (Figure 2) is very similar to that for reaction 2, i.e., a distorted, four-center complex in which the B−Cl bond is stretched to nearly twice its equilibrium value (1.773 Å), while the N−H bond is extended by only about 13% from its equilibrium value. In this case, however, the reaction is endothermic by 58 kcal mol^{-1} and a substantial activation barrier of 78 kcal mol^{-1} must be surmounted in order for reaction to occur. It seems likely that reaction 3 will not be very important except at high temperatures, since the preexponential factor for this reaction will be relatively small due to the tight transition state, and falloff effects at the low pressures used in CVD processing (2−60 Torr) will further reduce the rate.

Two other possible reaction pathways involve the continued amination of the boron halide via processes analogous to reaction 2. Since BN CVD normally occurs in an excess of ammonia, the possibility exists for NH_3 to react further with the initially formed Cl_2BNH_2 product:

$$Cl_2BNH_2 + NH_3 \leftrightarrow ClB(NH_2)_2 + HCl \qquad (4)$$

$$ClB(NH_2)_2 + NH_3 \leftrightarrow B(NH_2)_3 + HCl \qquad (5)$$

Reaction 4 is slightly exothermic ($\Delta H^{\circ}_{R4}(298\ K) = -3.1$ kcal mol^{-1}), while reaction 5 is endothermic ($\Delta H^{\circ}_{R5}(298\ K) = 5.6$ kcal mol^{-1}). We did not determine the energies of the transition states for these two reactions as part of this study. However, on the current understanding of the factors affecting Lewis acid−base reactions, it is reasonable to conclude that the activation barriers for both reactions will be higher than for reaction 2. In a theoretical study of the factors affecting the bonding in complexes of BCl_3 and BF_3 with NH_3, Brinck et al.[36] concluded that the B−N bond energies of $X_3B{:}NH_3$ (X = F, Cl, or Br) complexes are strongly affected by the electron affinity and ability to accept charge of the BX_3 moiety. Thus, although the trend in the halogen electronegativities is F > Cl > Br, the trends in electron affinity and charge capacity are the opposite, leading to B−N bond energies that increase in the order $F_3B{:}NH_3 < Cl_3B{:}NH_3 < Br_3B{:}NH_3$. If the transition states of reactions 2, 4, and 5 can be assumed to form by attack of the filled NH_3-2p orbital on the unfilled boron 2p orbital, creating a donor−acceptor complex (e.g., for reaction 4, $[Cl_2(NH_2)B{:}NH_3]^{\dagger}$) that rearranges to yield the four-center transition state, then one would predict that the activation energy would increase as the Lewis acidity of the boron-containing reactant decreased. Substitution of an NH_2 group for Cl should reduce the Lewis acidity based on the arguments of Brinck et al., since the electron affinity of nitrogen is considerably lower than that of chlorine,[67] and we expect the charge capacity of NH_2 also to be less than that of Cl. There are no direct experimental data to confirm this speculation at the present time, although neither $ClB(NH_2)_2$ nor $B(NH_2)_3$ was detected in flow-reactor measurements at temperatures up to 963 K[17] or in analysis of the gases produced by a BN CVD reactor,[12] suggesting that reactions 4 and 5 are indeed slower than reaction 2.

Reactions 3−5 are an illustration of the general phenomenon that electron-deficient elements such as boron can undergo addition−elimination reaction cycles by taking advantage of empty orbitals (p-type, in the case of boron) to stabilize an adduct and then eliminate a stable (i.e., nonradical) product. This provides a low-energy pathway for ligand substitution and allows strongly bound ligands such as chlorine to be exchanged without the energy necessary to break a bond unimolecularly. In contrast, such one-step ligand substitution reactions cannot occur in closed shell compounds of carbon or silicon, but must involve high-energy pathways in which a radical is formed first.

IV. Summary and Conclusions

We have used *ab initio* calculations coupled with empirical bond-additivity corrections to arrive at a set of thermodynamic data for species in the B−N−Cl−H system. Predicted heats of formation for compounds in the B−H−Cl series are generally in good agreement with the most recent critical review of the available experimental data,[20] although there is a discrepancy between the predicted and experimental values for BCl_2 that will ultimately have to be resolved by further experiments. Since experimental data for compounds containing B−N bonds are so sparse and generally have high uncertainties, we cannot determine the accuracy of the BAC-MP4 method for predicting thermodynamic properties for these compounds at this time. However, for ($H_3B{:}NH_3$), for which there are both experimental data as well as other theoretical predictions, the BAC-MP4 results are in good agreement with both. Thus, we expect that the self-consistent set of thermochemical data provided by these calculations will lead to valuable insights into the high-temperature reactions occuring in CVD processes involving boron. In particular, rate constants derived from the predicted transition-state energies for reactions between BCl_3 and NH_3 represent the first quantitative estimates of these rates.[17] Experiments currently underway in our laboratories will provide additional experimental evidence that can be used to test the validity of these predictions.

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Appendix

Data contained in the Supporting Information are as follows: Table 7 presents atomic coordinates for each of the molecular species obtained from the HF/6-31G* geometry optimization calculations. Table 8 gives moments of inertia in atomic units (amu bohr^2), while Table 9 lists scaled vibrational frequencies obtained at the same level of theory. Table 10 presents electronic energies resulting from various perturbation-theory calculations using the 6-31G** basis set. The projected UHF (PUHF) and projected UMP2 (PUMP2) energies are given for reference, although they are not used in the derivation of the BACs.

Table 11 gives polynomial coefficients for C_p, H, and S as a function of temperature for the species considered in this paper. These fits can be used with the CHEMKIN software package[68] and are defined by

$$C_p/R = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

$$\frac{H}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 \frac{a_6}{T}$$

$$\frac{S}{R} = a_1 \ln T + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7$$

Supporting Information Available: Tables as described in the Appendix (18 pages). Ordering information is given on any current masthead page.

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