Thermochemistry of BH_mCl_n Calculated at the G-2 Level of Theory

H. Bernhard Schlegel*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Stephen J. Harris

Physical Chemistry, General Motors Research, Warren, Michigan 48090-9055

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The heats of formation of BH_mCl_n have been computed at the G-2 level of theory, which is estimated to be accurate to ±2 kcal/mol. The calculated ideal gas values in kcal/mol are $\Delta H_f°_{298}(BH) = 105.8$, $\Delta H_f°_{298}(BCl) = 42.5$, $\Delta H_f°_{298}(BH_2) = 79.4$, $\Delta H_f°_{298}(BHCl) = 34.5$, $\Delta H_f°_{298}(BCl_2) = -6.8$, $\Delta H_f°_{298}(BH_3) = 24.9$, $\Delta H_f°_{298}(BH_2Cl) = -19.0$, $\Delta H_f°_{298}(BHCl_2) = -60.7$, $\Delta H_f°_{298}(BCl_3) = -98.6$.

Introduction

After diamond, the hardest known materials are boron-rich, for example cubic boron nitride, boron carbide, and titanium diboride. Like diamond, these materials also have low densities, high melting points and considerable mechanical strength and are chemically inert. With such properties, thin films formed from these materials could provide outstanding wear- and corrosion-protection for mechanical parts.[1] However, in some cases their widespread commercial application must await better technologies for applying the coatings at higher rates, with better quality, and with lower costs. One important technique used to produce such protective coatings is chemical vapor deposition (CVD). It is generally difficult to optimize conditions in a CVD reactor because film properties depend on complex interactions involving heat and mass transport, chemical kinetics, and thermochemistry. Developing a reliable set of thermodynamic data for potential intermediates is a necessary first step for system optimization, since it provides important constraints on the possible reaction mechanisms. However, many of the intermediates are short-lived and difficult to examine experimentally.

There have been several detailed thermodynamic analyses[2] to identify the important intermediates in boron carbide chemical vapor deposition from boron trichloride, hydrogen, and methane. Boron trichloride, which is a commonly used etchant in CVD systems, is widely used as a boron precursor because of its low toxicity compared to the boranes, B_mH_n. These thermodynamic analyses depend critically on the values assumed for the heats of formation of the BH_mCl_n species present in the system. Unfortunately, there is no consistent, reliable set of thermodynamic data for these compounds. In some cases (e.g., BH_2) the quoted uncertainties in the heats of formation are so large that the data are of little use.

Fortunately, with recent advances in theoretical methods, the structures and energetics of small gas phase species can be calculated to within 1−2 kcal/mol.[3,4] In this paper, we have undertaken calculations at the G-2 level of theory to estimate the heats of formation of BH_mCl_n. Previous studies have calculated the atomization and ionization energies of BH_n at the same level of theory,[3−5] and there is a very good agreement with the energy differences obtained in recent photoionization experiments.[6] Of the remaining BH_mCl_n species, only BCl has been calculated with the G-2 method. The present high-level

TABLE 1: Geometries Optimized at the MP2/6-31G(d) Level[a]

molecule	symmetry	$R(BH)$	$R(BCl)$	∠HBH	∠HBCl	∠ClBCl
BH	$D_{∞h}$	1.2326 (1.2325)				
BCl	$D_{∞h}$		1.7140 (1.7157)			
BH_2	C_{2v}	1.1884		127.59		
BHCl	C_s	1.1900	1.7139		123.15	
BCl_2	C_{2v}		1.7203			125.34
BH_3	D_{3h}	1.1913				
BH_2Cl	C_{2v}	1.1877	1.7336	123.40	118.30	
$BHCl_2$	C_{2v}	1.1848	1.7322		119.40	121.20
BCl_3	D_{3h}		1.7354 (1.75)			

[a] Bond lengths in Å, bond angles in deg, experimental values in parentheses (cited in ref 15).

TABLE 2: Vibrational Frequencies Computed at the HF/6-31G(d) Level[a]

molecule	ZPE	thermal	frequencies
BH	3.59	1.48	2513 (2368)
BCl	1.22	1.52	851 (844)
BH_2	9.61	1.79	1127[A_1], 2728[A_1], 2867[B_2]
BHCl	6.67	1.84	868[A'], 990[A'], 2810[A']
BCl_2	2.95	2.12	303[A_1], 743[A_1], 1016[B_2]
BH_3	17.38	1.80	1225[A_2''], 1305[E'], 2693[A_1'], 2813[E']
BH_2Cl	14.08	1.87	846[A_1], 940[B_2], 1075[B_1], 1334[A_1], 2771[A_1], 2881[B_2]
$BHCl_2$	9.93	2.17	311[A_1], 769[A_1], 846[B_1], 945[B_2], 1199[B_2], 2875[A_1]
BCl_3	5.08	2.68	276 (243)[E'], 484 (471)[A_2''], 498 (471)[A_1'], 1011 (968)[E']

[a] Zero-point energies (unscaled) and thermal corrections to the internal energy (298 K, 1 atm, ideal gas) in kcal/mol, harmonic vibrational frequencies (unscaled) in cm^{-1}, experimental values in parentheses (cited in ref 15).

calculations will form the basis of an analysis of the CVD of hard boron-containing films. They will also be useful for analyzing boron combustion chemistry,[7] which is of considerable interest because of the very high energy release possible from a small volume of fuel.

Method

Molecular orbital calculations were carried out using the GAUSSIAN 92[8] series of programs using a variety of basis sets of split valence quality or better with multiple polarization and diffuse functions.[9] Equilibrium geometries were optimized by

Thermochemistry of BH_mCl_n

J. Phys. Chem., Vol. 98, No. 43, 1994 **11179**

TABLE 3: Total Energies at the G-1 and G-2 Levels of Theory, Heats of Atomization, Heats of Formation, and Entropies[a]

| molecule | total energies | | $\Delta H_{atom}°_0$ calc | $\Delta H_f°_{298}$ | | $S°_{298}$ calc |
	G-1	G-2		calc	exp[b]	
BH	−25.234 685	−25.233 971	82.78	105.83	105.8 ± 2	41.03
BCl	−484.475 752	−484.474 621	122.95	42.52	33.8 ± 4	50.95
BH_2	−25.856 467	−25.857 212	160.12	79.43	48 ± 15	46.39
BHCl	−485.068 091	−485.068 536	181.88	34.53	27.5	57.27
BCl_2	−944.275 282	−944.274 534	200.30	−6.79	−19 ± 3	64.43
BH_3	−26.523 979	−26.524 815	265.29	24.89	24.5 ± 3	44.94
BH_2Cl	−485.734 236	−485.734 535	286.05	−18.98	−19.4	55.90
$BHCl_2$	−944.942 228	−944.941 155	304.86	−60.68	−59.3 ± 1	63.79
BCl_3	−1404.145 662	−1404.142 144	320.14	−98.63	−96.3 ± 0.5	68.67

[a] Total energies in atomic units, heats of atomization and formation in kcal/mol, entropies in cal/(mol K). [b] Reference 15, except for BHCl and BH_2Cl from ref 18.

Hartree−Fock (HF) and second-order Møller−Plesset perturbation theory (HF/6-31G(d) and MP2(full)/6-31G(d), respectively) using a quasi-Newton optimization method.[10] Vibrational frequencies and zero-point energies were calculated at the HF/6-31G(d) level using the HF optimized geometries and analytical second derivatives.[11] Correlated energies were calculated by fourth-order Møller−Plesset perturbation theory[12] (MP4SDTQ, frozen core) and by quadratic configuration interaction with a perturbative correction for triple excitations[13] (QCISD(T), frozen core) with the MP2(full)/6-31G(d) optimized geometries. In the G-1 method,[3] the energy computed at MP4/6-311G(d,p) is corrected for the effect of diffuse functions obtained at MP4/6-311+G(d,p), for the effect of higher polarization functions obtained at MP4/6-311G(2df,p), and for the effect of electron correlation beyond fourth order obtained at QCISD(T)/6-311G-(d,p). Higher level corrections for deficiencies in the wave function are estimated empirically[3] by comparing the calculated bond dissociation energy for H_2 with the exact value.

$$E(\text{G-1}) = E(\text{MP4/6-311G(d,p)}) + \Delta E(+) + \Delta E(\text{2df}) +$$
$$\Delta E(\text{QCI}) + \Delta E(\text{HLC}) + \text{ZPE(HF/6-31G(d))} \quad (1)$$

with

$$\Delta E(+) = E(\text{MP4/6-311+G(d,p)}) - E(\text{MP4/6-311G(d,p)}) \quad (2)$$

$$\Delta E(\text{2df}) = E(\text{MP4/6-311G(2df,p)}) - E(\text{MP4/6-311G(d,p)}) \quad (3)$$

$$\Delta E(\text{QCI}) = \text{QCISD(T)/6-311G(d,p)} - E(\text{MP4/6-311G(d,p)}) \quad (4)$$

$$\Delta E(\text{HLC}) = -0.00614 n_{paired} - 0.00019 n_{unpaired} \text{ au} \quad (5)$$

where n_{paired} and $n_{unpaired}$ are the number of electron pairs and the number of unpaired electrons, respectively. The zero-point energy computed at the HF/6-31G(d) level is scaled by 0.8929 to account for a systematic overestimation of the frequencies calculated at this level.[14] The G-2 method[4a] overcomes some limitations caused by additivity assumptions in the G-1 method by using an extra calculation at the MP2/6-311+G(2df,2p) level:

$$E(\text{G-2}) = E(\text{G-1}) + E(\text{MP2/6-311+G(3df,2p)}) -$$
$$E(\text{MP2/6-311G(2df,p)}) - E(\text{MP2/6-311+G(d,p)}) +$$
$$E(\text{MP2/6-311G(d,p)}) + 0.00114 n_{paired} \quad (6)$$

The average absolute error of the remaining additivity assumptions in the G-2 level of theory is only 0.30 kcal/mol.[4b] At the G-2 level of theory, the mean absolute error for 125 well-characterized atomization energies, ionization energies, electron

TABLE 4: B−H and B−Cl Bond Energies at the G-2 Level of Theory (kcal/mol)

molecule	B−H	B−Cl	molecule	B−H	B−Cl
BH	82.78		BH_3	105.17	
BCl		122.95	BH_2Cl	104.17	125.93
BH_2	77.33		$BHCl_2$	104.56	122.98
BHCl	58.93	99.10	BCl_3		119.84
BCl_2		77.36			

affinities, and proton affinities is 1.3 kcal/mol.[4a] A similar level of accuracy can be expected in the present study.

Results and Discussion

The geometries optimized at the MP2/6-31G(d) level are listed in Table 1. The harmonic vibrational frequencies, zero-point energies, and thermal corrections calculated at the HF/6-31G(d) level are listed in Table 2. The calculated vibrational frequencies at this level of theory are typically ca. 10% too high when compared to observed frequencies because of basis set effect, the neglect of electron correlation, and vibrational anharmonicity.[14]

The total energies at the G-1 and G-2 levels of theory[3,4] are reported in Table 3. The G-2 energies are used to calculate the atomization energies at 0 and 298 K, using the thermal corrections in Table 2. The theoretical atomization energies at 298 K are combined with the experimental heats of formation of the atoms ($\Delta H_f°_{298}(H) = 52.1$ kcal/mol,[15] $\Delta H_f°_{298}(Cl) = 28.92$ kcal/mol,[15] $\Delta H_f°_{298}(B) = 137.4$ kcal/mol[16,17]) to obtain the calculated heats of formation of BH_mCl_n. The comparison of experimental and calculated heats of formation for BH_n has been discussed previously.[3−6] The experimental $\Delta H_f°_{298}$ of BH_2 is not very well established (error bars of ±15 kcal/mol), but the theoretical value should be accurate to ±2 kcal/mol. The mean absolute error for the heats of formation of $BH_{3-n}Cl_n$ is 1.1 kcal/mol. However, the errors in $\Delta H_f°_{298}$ for BCl, BH_2, BHCl, and BCl_2 range from 7 to 31 kcal/mol. The G-2 method used to calculate the heats of formation in the present work has been shown to have a mean absolute error of 1.3 kcal/mol[4] when compared with ca. 125 accurately known experimental energy differences (atomization energies, proton affinities, ionization potentials, and electron affinities). This strongly suggests that the experimental heats of formation for BCl, BH_2, BHCl, and BCl_2 should be re-examined. In the meantime, the theoretical heats of formation listed in Table 3 form a consistent and reliable set of data that can be used in modeling CVD processes.

The D_0 values for various B−H and B−Cl bonds in BH_mCl_n are listed in Table 4 and are obtained from the calculated heats of atomization at 0 K. The B−H bond energies in BH_nCl_{3-n} are fairly constant. However, the B−Cl bond energies show a 3 kcal/mol decrease per Cl. This is probably due to increased competition in π bonding between the chlorines and the empty

boron p orbital. Except for BCl, the bonds in the remaining compounds are much weaker than in BH_nCl_{3-n}. In particular, the B—X bond in BXCl is much weaker than in BXH for both X = H and X = Cl. For B—X bond dissociation in BXCl, the product is BCl, which is strongly stabilized by B—Cl π bonding. By contrast, there is no opportunity for π bonding in BH. This is supported by the geometries in Table 1. The B—Cl bond in BCl is 0.02 Å shorter than that in BH_nCl_{3-n} whereas the B—H bond in BH is 0.02 Å longer than that in BH_nCl_{3-n}. A similar shortening and strengthening of the B—F bond is seen when BF is compared to BF_3.[15]

References and Notes

(1) Olsson, M.; Stridh, B.; Jansson, U.; Carlsson, J.; Soderberg, S. *Mater. Sci. Eng.* **1988**, *A105*, 453. Gafri, O.; Grill, A.; Itzhak, D.; Inspektor, A.; Avni, R. *Thin Solid Films* **1980**, *72*, 523. Friesen, T.; Haupt, J.; Gissler, W.; Barna, A.; Barna, P. B. *Surf. Coat. Technol.* **1991**, *48*, 169.

(2) Vandenbulcke, L. G. *Ind. Eng. Chem. Prod. Res. Dev.* **1985**, *24*, 568. Rebenne, H.; Pollard, R. *J. Am. Ceram. Soc.* **1987**, *70*, 907. Ducarroir, M.; Bernard, C. *J. Electrochem. Soc.* **1976**, *123*, 136.

(3) Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1990**, *93*, 2537.

(4) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. Curtiss, L. A.; Carpenter, J. E.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1992**, *96*, 9030.

(5) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1988**, *89*, 615.

(6) Ruscic, B.; Mayhew, C. A.; Berkowitz, J. *J. Chem. Phys.* **1988**, *88*, 5580.

(7) Rice, J. K.; Caldwell, N. J.; Nelson, H. H. *J. Phys. Chem.* **1989**, *93*, 3600.

(8) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(9) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213 and references cited therein. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265 and references cited therein. The 6-31G(d) and 6-31G-(d,p) basis sets are the same as 6-31G* and 6-31G**, respectively.

(10) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(11) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 225.

(12) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. For a review: Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.

(13) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(14) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; Defrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum. Chem., Quantum Chem. Symp.* **1981**, *15*, 269.

(15) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Szverud, A. N. *JANAF Thermochemical Tables, 3rd ed.*, *J. Phys. Chem. Ref. Data* **1985**, 14.

(16) Storms, E.; Mueller, B. *J. Phys. Chem.* **1977**, *81*, 318.

(17) The photoionization studies of Berkowitz and co-workers[6] support this more recent, higher value for the heat of formation of gas phase elemental boron.

(18) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*; Hemisphere Publishing Corp.: New York, 1990.