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Accurate Borane Sequential Bond Dissociation Energies by High-Level ab Initio Computational Methods

Paul R. Rablen* and John F. Hartwig

Contribution from the Department of Chemistry, Swarthmore College, 500 College Ave., Swarthmore, Pennsylvania 19081-1397, and Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

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Abstract: Ab initio molecular orbital calculations at the G-2 and CBS-4 compound levels of theory were used to determine the sequential homolytic bond dissociation energies (BDE's) for a series of B−H, B−C, and B−F bonds in a variety of cyclic and acyclic boranes. The calculated *average* BDE's agreed very well with the limited experimental data available. However, the first sequential BDE's, which are the most relevant for understanding borane reactivity, were substantially higher than the average BDE's. In general, first BDE's were found to be larger for B−C and B−H bonds in organoboranes than for C−C and C−H bonds in hydrocarbons, even though *average* B−H and B−C BDE's are lower than average C−H and C−C BDE's. In all the boron substitution patterns examined, B−H and B−C bonds were found to be of almost identical strength, while B−F bonds were found to be much stronger. Moreover, the strengths of B−H and B−C bonds were found to be essentially independent of the electronegativity, π-donating ability, and conjugative ability of the other substituents on boron. Thus, for instance, a phenyl group was found not to stabilize the odd electron of borane radicals and hence not to lead to reduced B−H or B−C bond strengths. However, B−H bonds of four-coordinate boron were slightly weaker than those of three-coordinate boron.

Introduction

Boranes are important synthetic intermediates and serve as Lewis acids in many useful synthetic applications.[1−3] Further, the chemistry of metal-substituted three-coordinate boranes and transition metal−boryl complexes has recently been the subject of intensive study.[4−17] In many cases a knowledge of borane bond energies would be helpful in gaining an understanding of metalloborane, organoborane, and purely inorganic borane chemistry. However, the available experimental data are limited, and are usually average bond energies derived from heats of formation.[18] Even here, bomb calorimetry is plagued by the formation of multiple products,[19−24] and determinations derived from the heats of hydroboration reactions must correct for products with differing regiochemistry.[25,26] The values that are most relevant to reaction chemistry are individual, sequential bond energies. These values correspond to the average bond energies derived from heats of formation only if each, sequential bond energy is similar. It is well-known that sequential bond energies can differ substantially, and so there is no *a priori* justification for making such an assumption in the case of boranes.

Theoretical methods have been developed that provide molecular energies, and from them sequential bond dissociation energies, with exceptional accuracy.[27] Pople has recently reported the G-2 method that reproduces atomization energies to an accuracy of within 1 kcal/mol for small molecules.[28] G-2 is a compound ab initio molecular orbital procedure consisting of seven individual calculations using varying basis sets and techniques for treating electron correlation. Reliable sequential BDE's, more important for thermodynamic analysis of reaction chemistry than average BDE's, can be determined in this manner. MP2 and MP4 calculations have been used previously to determine ΔH_f and average bond energies for a series of small electrophilic molecules including small boranes.[29,30] In contrast

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to simple MP2 and MP4 calculations, however, G-2 allows direct determination of BDE's by calculation of both closed shell molecules and the open shell species formed by bond scission in a manner that allows accurate, direct comparison of the total energies. Consequently, reliable *sequential* BDE's can be computed in a straightforward fashion using the G-2 method.

However, G-2 is very demanding of computational resources, and an alternative approach is necessary to obtain similarly accurate bond energies for larger molecules. The CBS-4 method recently developed by Petersson and Ochterski is much less intensive computationally, but demonstrates an accuracy only modestly diminished from G-2 theory.[31] A single-point Hartree−Fock calculation with a very large basis set (6-311+G(3d2f,2df,p)) at the HF/3-21G* optimized geometry followed by correction for electron correlation using MP2 and MP4(SDQ) calculations with much smaller basis sets and an extrapolation to the complete basis set limit serves as the foundation of the CBS-4 calculation.[32,33]

We have used the CBS-4 method to compute a range of borane bond energies and where possible have compared them to BDE's obtained at the more detailed G-2 level to demonstrate the applicability of the former to electrophilic main group molecules. While remarkably economical, the CBS-4 procedure still reproduces the atomization energies of the 55 molecules in the G-2 test set with an average absolute error of only 1.9 kcal/mol.[31] On this basis, one would expect reproduction of experimental BDE's with similar accuracy. An examination of Table 2 shows that the G-2 and CBS-4 BDE's agree very closely for the 36 cases where both methods were feasible, yielding a root mean square (RMS) difference of 1.5 kcal/mol. The agreement lends credence to the CBS-4 derived BDE's of the larger species for which G-2 calculations were impossible. Both the G-2 and the CBS-4 BDE's are given as enthalpies at 0 K and also at 298 K. Selected examples from this list have been published in communication form and we have used one of these values in combination with solution calorimetry to provide the first transition metal−boryl bond energy.[5] We report here our full results for BDE calculations of a large series of boranes.

Results and Discussion

Table 1 provides the total energies calculated for a number of boranes and boron-containing fragments. Table 2 provides sequential bond dissociation energies for a number of B−X bonds for 1-, 2-, 3-, and 4-coordinate boron compounds, including B−H, B−Me, B−F, and B−O bonds. The first B−H and B−C bond energies were found to be similar to or stronger than their C−H and C−C counterparts and much greater than the second or third B−H or B−C BDE. The B−C dissociation energies were similar to the corresponding B−H bond energies, generally differing by no more than 2 kcal/mol for any given case. In addition, the B−H bonds in sp^3-hybridized diborane and in the borane−ammonia complex were weaker than in the sp^2-hybridized base free BH_3. Concerning ancillary groups, heteroatom substitution at 3-coordinate boron led to little change in the dissociation energies of the accompanying B−X bonds, and no resonance stabilization was observed that would lead to weak B−H bonds in $PhBH_2$.

Differences in Sequential Bond Energies. The first B−H BDE's were found to range from 103.4 to 109.9 kcal/mol at the CBS-4 level of theory, while the B−C bonds ranged from 103.1 to 111.8 kcal/mol. These values are similar to or stronger than their C−H and C−C counterparts. Further, these first bond energies are much stronger than the corresponding second and third B−H or B−C BDE's such as FB−H (45.2 kcal/mol), HB−H (78.9 kcal/mol), MeB−H (71.4 kcal/mol), HB−Me (79.3 kcal/mol), and MeB−Me (72.1 kcal/mol) or those in B−H (80.7 kcal/mol) and B−Me (88.6 kcal/mol). These high first BDE's contrast the average B−C and B−H bond energies that have been obtained experimentally from values for ΔH_f and which are lower than typical C−H and C−C bond energies. This difference results from a phenomenon similar to the divalent state stabilization that occurs with silicon compounds.[34] Specifically, the second B−X bond is dramatically weaker than the first, since the singlet B−X molecule is unusually stable. This effect is shown in a graphical format in Figure 1, which depicts the sequential homolysis of monomeric BH_3 and BMe_3 versus that of CH_4.

The average of the three BDE's for BMe_3 (87.7 kcal/mol) and BH_3 (88.0 kcal/mol) compare favorably with the average BDE's determined from experimental ΔH_f values, confirming the accuracy of the computed dissociation energies. BMe_3 has a well-accepted experimental ΔH_f that gives an average BDE of 86.8 kcal/mol. The ΔH_f of diborane and the dimerization energy of BH_3 suffer from large errors and are subject to debate.[21,24,35] However, our average BDE is similar to that derived from the JANAF tables (89 kcal/mol),[36] and considering experimental difficulties, the G-2 level of theory is likely to provide a dimerization energy (36.4 kcal/mol) that is closest to the actual value.

Effect of Coordination Number and Heteroatoms on B−H and B−C BDE's. The B−H bond energies in diborane and in a Lewis base adduct of BH_3 are more relevant to solution chemistry than are the values for monomeric, base-free BH_3. The first bond dissociation energy for diborane was found to be 100.2 kcal/mol at the G-2 level of theory and 98.7 kcal/mol at the CBS-4 level, weaker than that in BH_3. The first bond dissociation energy in $BH_3{\cdot}NH_3$ was also found to be weaker than that in BH_3 (102.1 kcal/mol by G-2 and 101.1 kcal/mol by CBS-4). This effect is similar to the weaker bond energy for sp^3-hybridized C−H bonds of alkanes relative to the sp^2-hybridized C−H bonds of alkenes.

The group electronegativities of the boron-containing fragments formed by bond scission of heteroatom-substituted boranes are different from the group electronegativities of boron-containing fragments formed by bond scission of pure organoboranes. Moreover, the electron pairs of heteroatoms bound to boron overlap with the unoccupied p-orbital, while similar π-interactions in purely organoboranes are much weaker. Nevertheless, the presence of groups bound to boron through electronegative heteroatoms perturbed accompanying B−X bond energies only slightly relative to analogous B−X bond energies of boranes with ancillary alkyl groups or hydrides. For example, the values obtained for BF_2−H were 108.8 (G-2) or 107.1 kcal/mol (CBS-4), the values for BFH−H were 104.8 (G-2) or 103.4 kcal/mol (CBS-4), the values for BH_2−H were 105.2 (G-2) or 104.0 kcal/mol (CBS-4), and the values for $B(OH)_2$−H were 107.4 (G-2) or 105.7 kcal/mol (CBS-4).

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Table 1. G-2 and CBS-4 Total Enthalpies (Hartrees)

structure	symmetry	state	0 K[a]		0 to 298 K increment[b]	
			G-2	CBS-4	G-2	CBS-4
H	K_h	2	−0.500 00[c]	−0.503 35[d]	0.002 36	0.002 36
B	K_h	2	−24.602 05[c]	−24.606 34[d]	0.002 36	0.002 36
F	K_h	2	−99.632 82[c]	−99.650 77[d]	0.002 36	0.002 36
BH	$C_{\infty v}$	1	−25.233 99[c]	−25.238 30	0.003 30	0.003 30
BH	$C_{\infty v}$	3	−25.180 30	−25.189 22	0.003 30	0.003 30
BH_2	C_{2v}	2	−25.857 26[c]	−25.867 44	0.003 81	0.003 81
BH_3	D_{3h}	1	−26.524 86[c]	−26.536 60	0.003 84	0.003 84
B_2H_5	C_{2v}	2	−52.447 82	−52.471 17	0.004 82	0.004 76
B_2H_6	D_{2h}	1	−53.107 51	−53.131 82	0.004 56	0.004 51
BF	$C_{\infty v}$	1	−124.523 02	−124.542 03	0.003 32	0.003 31
BF	$C_{\infty v}$	3	−124.386 20	−124.409 78	0.003 32	0.003 32
BF_2	C_{2v}	2	−224.330 59	−224.368 44	0.004 04	0.004 03
BF_3	D_{3h}	1	−324.237 44	−324.291 77	0.004 51	0.004 51
BFH	C_s	2	−125.093 89	−125.117 40	0.003 83	0.003 82
BH_2F	C_{2v}	1	−125.760 86	−125.785 54	0.003 88	0.003 86
BF_2H	C_{2v}	1	−225.004 00	−225.042 54	0.004 11	0.004 08
CH_3	D_{3h}	2	−39.745 09[c]	−39.759 73[d]	0.004 24	0.004 11
CH_3CH_2	C_s	2	−78.970 34[c]	−78.998 70	0.004 94	0.004 97
CH_3CH_3	D_{3d}	1	−79.630 90[c]	−79.661 16	0.004 48	0.004 45
CH_3B	C_s	1	−64.491 11	−64.507 20	0.004 19	0.004 09
CH_3B	C_s	3	−64.421 63	−64.443 01	0.004 07	0.004 04
CH_3BH	C_s	2	−65.102 24	−65.124 41	0.004 16	0.004 89
CH_2BH_2	C_{2v}	2	−65.117 85	−65.138 91	0.004 54	0.004 54
CH_3BH_2	C_s	1	−65.768 37[e]	−65.792 06	0.004 97	0.004 93
$(CH_3)_2B$	C_2	2	−104.346 79	−104.381 82	0.006 29	0.006 25
$(CH_3)_2BH$	C_2	1	−105.012 59	−105.048 42	0.006 47	0.006 41
$(CH_3)_3B$	C_{3h}	1		−144.304 81		0.008 05
CH_3BF_2	C_s	1	−264.250 47	−264.301 62	0.005 90	0.005 79
BH_2NH_3	C_s	1	−82.362 31	−82.388 43	0.004 92	0.004 86
BH_3NH_3	C_{3v}	1	−83.025 05	−83.052 93	0.004 95	0.004 86
$(HO)_2B$	C_s	2	−176.288 64	−176.318 53	0.004 61	0.004 61
$(HO)_2BH$	C_s	1	−176.959 77	−176.990 40	0.004 62	0.004 61
$(CH_3O)(HO)B$	C_s	2		−215.534 93		0.006 35
$(CH_3O)(HO)BH$	C_s	1		−216.207 05		0.006 31
$(CH_3O)_2B$	C_s	2		−254.752 54		0.008 20
$(CH_3O)_2BH$	C_s	1		−255.421 04		0.008 12
cyclo(−OCH_2CH_2OB−)	C_{2v}	2		−253.559 80		0.005 40
cyclo(−OCH_2CH_2OBH−)	C_{2v}	1		−254.237 47		0.005 52
cyclo(−$OCH_2CH_2OBCH_3$−)	C_s	1		−293.495 45		0.007 51
cyclo(−OCHCHOB−)	C_{2v}	2		−252.351 44		0.004 59
cyclo(−OCHCHOBH−)	C_{2v}	1		−253.030 76		0.004 72
cyclo(−$OCHCHOBCH_3$−)	C_s	1		−292.288 63		0.006 70
catecholborane radical	C_{2v}	2		−405.831 81		0.006 69
catecholborane	C_{2v}	1		−406.510 36		0.006 85
methylcatecholborane	C_s	1		−445.769 70		0.008 95
methoxycatecholborane	C_s	1		−520.944 53		0.010 02
MeO	C_s	2		−114.888 26		0.003 99
cyclo(−$(CH)_4B$−)	C_s	2		−179.181 12[f]		0.005 04
cyclo(−$(CH)_4BH$−)	C_{2v}	1		−179.886 60		0.005 30
cyclo(−$(CH)_4BCH_3$−)	C_s	1		−219.145 34		0.007 24
cyclo(−$(CH)_6B$−)	C_{2v}	2		−256.531 42		0.006 61
cyclo(−$(CH)_6BH$−)	C_{2v}	1		−257.201 18		0.006 73
cyclo(−$(CH)_6BCH_3$−)	C_s	1		−296.456 38		0.008 71
PhBH	C_s	2		−256.556 92		0.006 60
$PhBH_2$	C_{2v}	1		−257.227 65		0.006 77
$PhBCH_3$	C_s	2		−295.815 20		0.008 53
$PhBHCH_3$	C_s	1		−296.484 22		0.008 54
$PhB(CH_3)_2$	C_s	1		−335.740 23		0.010 34

[a] Enthalpies at 0 K, in hartrees. [b] Increments in enthalpies on going from 0 to 298 K, in hartrees. [c] These values are taken from Curtis et al. (Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221) and are reproduced here only for the reader's convenience. [d] These values are taken from: Ochterski, J. W.; Petersson, G. A. submitted to *J. Chem. Phys.* [e] Taken from: Wiberg, K. B.; Nakaji, D. Y. *J. Am. Chem. Soc.* **1993**, *115*, 10658. [f] The expectation value for s^2 was 0.9070 (versus an expected value of 0.7500) for this calculation; the energy probably is not as accurate as the others as a result of this spin contamination.

Changing hydroxy groups to methoxy led to slightly weaker B−H bonds, but an ancillary catecholate provided slightly stronger B−H bonds. This greater bond energy for the catecholate-substituted system may be attributed to the five-membered ring system, since both saturated and unsaturated diolate groups gave similar high B−H BDE's. Five-membered rings with only methylene groups and boron in the ring gave even higher BDE's, but unusually large spin contamination observed in the Hartree−Fock calculation makes these values potentially unreliable.

The strengths of the B−F bonds in fluoroboranes (BH_2F, BHF_2, and BF_3) are remarkably constant. For example, the B−F bond in BH_2F was found to be 169.9 kcal/mol by G-2 or 167.8 kcal/mol by CBS-4, while the first B−F bond in BF_3 was found to be 172.0 kcal/mol by G-2 and 171.0 kcal/mol by CBS-4. Although one might expect little effect of π-donating groups

Table 2. G-2 and CBS-4 Bond Dissociation Enthalpies (kcal/mol)

	0 K		298 K		
bond	G-2	CBS-4	G-2	CBS-4	comment
B−H	82.8	80.7	83.7	81.6	singlet BH
B−H	49.1	49.9	50.0	50.8	triplet BH
BH−H	77.4	78.9	78.5	80.1	singlet BH
BH−H	111.0	109.7	112.2	110.9	triplet BH
BH_2−H	105.2	104.0	106.6	105.5	
B_2H_5−H	100.2	98.7	101.9	100.3	
B−F	180.8	178.8	181.7	179.7	singlet BF
B−F	95.0	95.8	95.8	96.7	triplet BF
BF−F	109.7	110.2	110.7	111.2	singlet BF
BF−F	195.5	193.2	196.5	194.2	triplet BF
BF_2−F	172.0	171.0	173.1	172.2	
BF_2−H	108.8	107.1	110.3	108.6	
BF−H	44.5	45.2	45.6	46.4	singlet BF
BF−H	130.3	128.2	131.5	129.3	triplet BF
BH−F	142.5	143.3	143.6	144.4	singlet BH
BH−F	176.2	174.1	177.3	175.2	triplet BH
BH_2−F	169.9	167.8	171.4	169.2	
BFH−H	104.8	103.4	106.2	104.9	
BFH−F	174.0	172.2	175.3	173.5	
CH_3CH_2−H	100.8	99.8	102.5	101.7	
B−CH_3	90.3	88.6	91.9	90.1	singlet BCH_3
B−CH_3	46.7	48.3	48.3	49.8	triplet BCH_3
BH−CH_3	77.3	79.3	79.4	80.9	singlet BH
BH−CH_3	111.0	110.1	113.1	111.7	triplet BH
BH_2−CH_3	104.2	103.5	106.1	105.3	
BH_2CH_2−H	94.5	94.0	95.7	95.2	
BCH_3−CH_3	69.4	72.1	70.7	73.3	singlet BCH_3
BCH_3−CH_3	113.0	112.4	114.3	113.6	triplet BCH_3
$BHCH_3$−CH_3	103.7	103.1	104.9	104.7	
$B(CH_3)_2$−CH_3		102.4		103.9	
BCH_3−H	69.7	71.4	71.2	72.4	singlet BCH_3
BCH_3−H	113.3	111.7	114.8	112.7	triplet BCH_3
$BHCH_3$−H	104.2	103.1	105.2	104.6	
$B(CH_3)_2$−H	104.0	102.4	105.4	103.8	
BF_2−CH_3	109.7	108.8	111.2	110.3	
NH_3BH_2−H	102.1	101.1	103.6	102.6	
$(HO)_2B$−H	107.4	105.7	108.9	107.2	
$(HO)(CH_3O)B$−H		105.9		107.4	
$(CH_3O)_2B$−H		103.6		105.2	
cyclo(−OCH_2CH_2OB−)−H		109.4		110.8	
cyclo(−OCH_2CH_2OB−)−CH_3		110.4		111.6	
cyclo(−OCHCHOB−)−H		110.4		111.8	
cyclo(−OCHCHOB−)−CH_3		111.4		112.6	
catecholborane−H		109.9		111.3	
catecholborane−CH_3		111.8		113.0	
catecholborane−OMe		140.9		141.3	
cyclo(−$(CH)_4B$−)−H		[126.8][a]		[128.2][a]	
cyclo(−$(CH)_4B$−)−CH_3		[128.3][a]		[129.5][a]	
cyclo(−$(CH)_6B$−)−H		104.4		105.8	
cyclo(−$(CH)_6B$−)−CH_3		103.7		104.9	
PhBH−H		105.0		106.4	
PhBH−CH_3		105.2		106.5	
$PhBCH_3$−H		104.0		105.4	
$PhBCH_3$−CH_3		103.7		105.2	

[a] These numbers are based on the CBS-4 energy for cyclo(−$(CH)_4B$−), which showed unusually large spin contamination observed in the Hartree−Fock calculation for this species (0.157). As a result, these two bond dissociation energies are probably much less accurate than the others.

on the bond energies of purely σ-bonding groups such as hydrogen (as is observed), one might predict a significant effect of π-donating groups on the bond energies of other π-donating X-groups. Back-bonding would be expected to strengthen B−X bonds to π-donors such as fluorine. However, an increase in the number of fluorine atoms bound to a single boron atom would be expected to decrease the strength of each B−F π-bond, and therefore weaken the overall B−F bond relative to H_2BF or Me_2BF. On the other hand, it has been shown that an increase in the number of fluorine atoms at a single carbon center, as in the series CH_3F, CH_2F_2, CHF_3, and CF_4, leads to increasing C−F bond strengths, due to mutual reinforcement of the ionic components of the bonds.[37] Apparently, these two opposing trends cancel each other. Little increase or decrease in the B−F bond energy is observed as the other substituents on boron are changed from hydrogen to fluorine.

Absence of Resonance Stabilization. An interesting set of B−H and B−C BDE's were observed in monomeric base-free aryl-substituted boranes. It is well-known that the methyl C−H bonds in toluene are much weaker than those in methane or ethane. However, the B−H bond energy in phenylborane was 105.0 kcal/mol, essentially identical, and even slightly stronger, than the 104.0-kcal/mol B−H bond in monomeric, base-free

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(37) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 614.

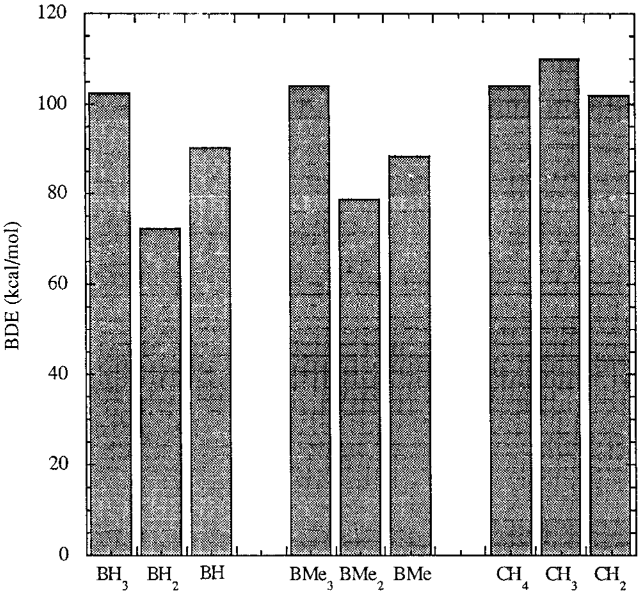


Figure 1. A graphical representation of the sequential BDE's of BH_3, BMe_3, and CH_4. The values are for dissociation of a hydrogen or methyl radical from the fragments written below each bar.

Table 3. Calculated Bond Orders[a] (MP2/6-31+G*)

compd	B−H	B−C	B−F
BH_3	0.582		
CH_3BH_2	0.542	0.503	
$(CH_3)_2BH$	0.506	0.470	
$(CH_3)_3B$		0.438	
BH_2F	0.531		0.419
BHF_2	0.504		0.362
BF_3			0.310

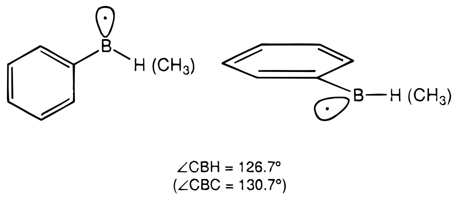
[a] Bond orders were calculated using a modified version of the program BONDER: Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142.

Table 4. AIM Calculated Atomic Charges[a] (MP2/6-31+G*)

compd	B	H	CH_3	F	sum[b]
BH_3	1.906	−0.635			0.001
CH_3BH_2	2.000	−0.648	−0.706		−0.003
$(CH_3)_2BH$	2.083	−0.657	−0.713		0.001
$(CH_3)_3B$	2.160		−0.719		0.004
BH_2F	2.117	−0.638		−0.842	−0.001
BHF_2	2.303	−0.614		−0.844	0.001
BF_3	2.506			−0.833	0.008

[a] Atomic charges were calculated using the program PROAIM: Biegler-König, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *3*, 317. Bader, R. F. W.; Tang, T.-H.; Tal, Y.; Biegler-König, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 946. [b] The sum represents the summation of atomic charge over all atoms in the molecule, and ideally should equal zero. It is included as a rough estimate of the error incurred in the numerical integration of charge density required to obtain atomic charges in the AIM formalism.

BH_3. Similarly, the B−Me bond energy in PhHB−Me was found to be 105.2 kcal/mol and was slightly greater than the 103.1-kcal/mol BDE for MeHB−Me or the 103.5-kcal/mol BDE for H_2B−Me. The absence of an effect similar to benzylic radical stabilization results from a lack of π delocalization of the radical electron on boron into the aromatic ring. The minimum energy geometry, shown below schematically in two different perspectives, places the odd electron on boron in an orbital orthogonal to the π system of the aromatic ring and therefore incapable of stabilization by resonance. As a result, the B−H BDE is essentially identical to all other B−H bond energies.



The bent (rather than linear) geometry also indicates that the lone electron is in an approximately sp^2-hybridized orbital rather than a p orbital. This geometry and hybridization can be rationalized by the preference for the electron to occupy the nonbonding orbital with the most s-character. In addition, this geometry is consistent with the tendency of boron to have high p-character in its bonds to carbon and hydrogen. The latter observation is in accordance with Bent's rule, considering that carbon and hydrogen are electronegative elements with respect to boron.[38]

Comparison of B−C and B−H BDE's. In addition to the constancy of the B−H and B−C bond strengths upon various substitution patterns, the similarity between the B−C and the B−H bond strengths is unusual, although experimental ΔH_f data already suggested that this might be the case.[21,39] It is known experimentally that for electronegative elements X, X−H bonds tend to be stronger than the corresponding X−C bonds, as discussed recently.[40] However, as electronegativity decreases, the X−Me bond strength becomes more similar to that of the X−H bond and can even surpass the strength of the X−H bond. Since boron is even less electronegative than carbon, the similarity of B−C and B−H bond strengths is consistent with this pattern.

The smaller difference between B−C and B−H bond energies than that between C−X and H−X bonds of more electronegative elements can be rationalized in terms of polarities and hybridization. The polarity of B−C bonds is likely to be greater than that of B−H bonds, since the electronegativity difference between boron and carbon is greater than that between boron and hydrogen. This difference in polarity might lead to preferential stabilization of the B−C bonds that compensates for the greater intrinsic (covalent) strength of bonds to hydrogen. One way to assess the degree of covalency and polarity of bonds is by calculating covalent bond orders according to the procedure of Cioslowski and Mixon.[41] As the covalent bond order decreases, the fraction of ionic bonding increases, as does the polarity of the bond. As can be seen from Table 3, B−C bonds are consistently somewhat more polar than B−H bonds, despite the similar electronegativities of carbon and hydrogen. For instance, the B−C bond of methylborane has a covalent bond order of 0.50, while the B−H bonds have covalent bond orders of 0.54. Long ago, Pauling noted that bond strength correlates with increasing polarity,[42] and so this factor tends to increase the strength of B−C bonds relative to B−H bonds.[40] The B−F bonds in Table 2 are the most polar of all, as indicated by their especially small covalent bond indices, and they are also by far the strongest. The atomic charges in Table 4, calculated by the integration of the charge density in appropriately defined

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(38) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.
(39) Skinner, H. *Adv. Organomet. Chem.* **1964**, *2*, 49.
(40) Benson, S. W.; Francis, J. T.; Tsotsis, T. T. *J. Phys. Chem.* **1988**, *92*, 4515.
(41) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142.
(42) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

atomic basins according to the method of Bader,[43,44] also illustrate the polarity of the B−H, B−C, and B−F bonds.

A hybridization effect is also likely to strengthen B−C bonds relative to B−H bonds. The hydrogen atom has no opportunity to rehybridize, and uses a 1s orbital in bonding to either carbon or boron. However, the carbon atom of a methyl group can rehybridize. The electronegativity difference between carbon and hydrogen is small, and so the methyl carbon will use close to sp^3 hybrids for all four bonds. However, the electronegativity difference between carbon and boron is greater, and will lead to increased s-character in the C−B bond. The increased s-character in the C−B bond must be accompanied by decreased s-character in the bonds from carbon to hydrogen, since the total s-character at carbon must be conserved.[38] This effect will strengthen the B−C bond at the expense of the C−H bonds. This hypothesis predicts that boron substitution on a methyl group will weaken the C−H bonds, and the data in Table 2 support this analysis. For example, the C−H bond energy of ethane is 101.8 kcal/mol, while the C−H bond energy of methylborane is 94.5 kcal/mol. Changes in both hybridization and polarity, then, strengthen the B−C bond relative to the B−H bond and counteract factors that lead to stronger H−X than C−X bonds.

Absence of Radical Chemistry of Two-Coordinate Boranes. The modest magnitudes of average bond energies for three-coordinate boranes imply that radical chemistry involving the two-coordinate boranes that would result from H-atom abstraction should be readily accessible. However, the data in Table 2 show that the first bond energy is considerably higher than the average bond energy. This explains the difficulty in inducing such homolytic bond cleavage and the consequent dearth of two-coordinate borane radical chemistry.

Summary

We have provided a large range of B−X bond dissociation energies. The values of a type of B−X bond are essentially invariant to the accompanying group's electronegativity, π-donating ability, and conjugative ability. B−H bond energies of four-coordinate boron are slightly weaker than those of three-coordinate boron, and the first bond dissociation energies of boranes are vastly different from average bond dissociation energies, due to a divalent state stabilization energy. In general, the first B−C and B−H bond energies are stronger than those for C−C and C−H bonds, while average B−H and B−C bonds for organoboranes are lower than those for hydrocarbons. The large first bond dissociation energies of boranes explain the dearth of two-coordinate borane radical chemistry.

Methods

All ab initio calculations were performed using a development version of the Gaussian 93 package or the Gaussian 94 package.[45] The G-2 energies were obtained using a c-shell script written at Wesleyan University[31] which interfaces to Gaussian 93. All structures for which G-2 energies are listed in Table 1 were verified as minima by calculation of the vibrational frequencies at the HF/6-31G* level of theory in the course of the G-2 procedure, i.e., no imaginary frequencies were found.

The CBS-4 method developed recently by Ochterski and Petersson provides a much less computationally intensive alternative having a demonstrated accuracy only slightly diminished from G-2 theory. A single-point Hartree−Fock calculation with a very large basis set (6-311+G(3d2f,2df,p)) at the HF/3-21G* optimized geometry serves as the starting point. Corrections for electron correlation are added using MP2 and MP4(SDQ) calculations with much smaller basis sets. An extrapolation is then performed to the complete basis set limit.[32,33] Zero-point vibrational energies are also included, along with a higher level correction analogous to the one used in the G-2 method. With a single exception, no spin contamination greater than 0.013 was found for the open-shell species in this study.[46] All structures for which CBS-4 energies are listed in Table 1 were verified as minima by calculation of the vibrational frequencies at the HF/3-21G* level of theory in the course of the CBS-4 procedure, i.e., no imaginary frequencies were found.

The G-2 and CBS-4 methods by themselves give enthalpies at 0 K. The thermodynamic corrections necessary to convert these to enthalpies at 298 K were carried out by treating the translational, rotational, and vibrational components in the standard manner.[47] HF/3-21G* frequencies scaled by 0.9167 were used to make corrections for the CBS-4 energies, while HF/6-31G* frequencies scaled by 0.8934 were used to make corrections to the G-2 energies. These are the same levels at which the zero-point vibrational energies are computed.[28,31] All vibrational modes were treated as harmonic, and no attempt was made to treat torsional modes in a more appropriate manner, but the errors introduced by these approximations are expected to lie well below the inherent error limits of the electronic structure calculations.

Atomic charges and atomic overlap matrices (required for calculating the covalent bond orders) were computed using PROAIM,[43,44] and the covalent bond orders were calculated using a modified version of the program BONDER.[41]

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Supporting Information Available: Optimized geometries in Z-matrix form, of all species for which calculated energies are reported in Table 1 (61 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS; and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(43) Bader, R. F. W.; Tang, T.-H.; Tal, Y.; Biegler-König, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 946.

(44) Biegler-König, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *3*, 317.

(45) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Foresman, J. B.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Ayala, P. Y.; Wong, M. W.; 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. P.; Pople, J. A. *Gaussian 93*; Development Version (Revision E.2); Gaussian, Inc.: Pittsburgh, PA, 1993. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94;* Revision C.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(46) With one exception, the worst case of spin contamination was observed for the ethyl radical, in which the s^2 expectation value of the UHF wave function was 0.7630 instead of the desired 0.7500. The next worst case was the boron atom (doublet state), in which the s^2 expectation value was 0.7610. In all other cases, the spin contamination was 0.0080 or less. The exception was for the cyclic $BCH_2CH_2CH_2CH_2$, for which $s^2 = 0.9070$.

(47) Janz, G. J. *Thermodynamic Properties of Organic Compounds: Estimation Methods, Principles and Practice,* revised edition; Academic Press: New York, 1967.