Computational Determination of the Energetics of Boron Ignition/Combustion Reactions

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Two computational procedures, the density functional B3PW91/6-311+G(2df,2pd) and the ab initio CBS-Q, have been used to calculate optimized geometries, energy minima at 0 K and enthalpies and free energies at 298 K for atoms and molecules involved in the ignition and/or combustion of boron. Calculated gas-phase heats of formation are presented for 58 atoms and molecules and are used to find heats of reaction for 83 possible ignition/combustion steps. The most exothermic are found to be $BO + F \rightarrow FBO$ and $BO + O \rightarrow BO_2$. It is shown that ΔH (298 K) and ΔH (2000 K) differ, on the average, by only 1.5 kcal/mol; however, ΔG can change quite considerably over the same temperature range. Relative stabilities and equilibrium constants are given for five pairs of isomers. While the geometries were obtained more accurately by the B3PW91 procedure, the CBS-Q is more reliable for heats of formation and heats of reaction.

Introduction

Due to the large and negative heats of formation of solid and liquid B_2O_3, both about −300 kcal/mol,[1] the oxidation of boron to either of these products is a highly exothermic process, releasing about 15 kcal per gram of boron. Accordingly, boron has long been of interest as a component of propellant formulations, particularly in combination with liquid hydrocarbons.[2−8] In practice, however, there are significant obstacles to achieving the potential level of performance. These include the formation of a protective oxide layer which hinders the ignition of the boron particles, the generation of boron oxyhydride intermediates which impede the combustion process, and a slow rate of condensation to the desired liquid or solid final product. It has been found that improvements in both ignition and combustion efficiency can be realized by the inclusion of fluorine in the formulation, e.g., as NF_2 functional groups on the oxidizers and/or binders.[9−13] This does not diminish the potential energy release; for example, the conversion of boron to BF_3(g) produces about 27 kcal per gram of boron.[1]

Extensive efforts are underway to quantitatively model the complex processes of boron ignition and combustion in oxygen/fluorine systems.[10−12] These modeling studies require considerable thermodynamic and kinetic data (e.g., heats of reaction, activation barriers, etc.), not all of which are currently known with sufficient accuracy.[10,12,13] In the present work, we have applied high-level computational techniques to obtain enthalpies, free energies, and heats of formation for 66 atoms and molecules that have been implicated in the oxygen/fluorine oxidation of boron. These results can be used to find heats of reaction and equilibrium constants for several hundred possible ignition and combustion steps. Some applications will be presented and discussed.

Methods

For each atom and molecule, two different computational approaches were used, the density functional B3PW91/6-311+G(2df,2pd) procedure (which combines the Becke three-parameter hybrid[14] and the Perdew−Wang correlation[15] functionals) and the ab initio CBS-Q.[16] In a recent B3PW91/6-311+G(2df) study of the decomposition of ammonium - perchlorate,[17] experimental heats of reaction were reproduced with an average absolute error of 1.6 kcal/mol, while the CBS-Q technique has been shown to give atomization energies and heats of formation to within, on the average, 1.0 kcal/mol of experiment.[16,18] In this work, all calculations were carried out with the Gaussian 94 code.[19]

With each computational method, we obtained optimized geometries, energy minima at 0 K, and enthalpies and free energies at 298 K. The enthalpies were converted to gas-phase heats of formation, using the definition of the latter as ΔH for the formation of the compound from its elements; no correction terms were introduced. Since boron and carbon are solids at 298 K, their experimental heats of sublimation (134.5 and 171.3 kcal/mol, respectively[20]) were included in finding ΔH for the formation of boron- and carbon-containing compounds.

The combustion of boron occurs at elevated temperatures, which may exceed 3000 K.[10−12] To assess the effects of temperature upon our calculated thermodynamics quantities, we also computed, for 12 molecules, the enthalpies and free energies at 2000 K and the constant volume heat capacities, C_V, at both 298 and 2000 K.

Results and Discussion

A. Structures. Experimental structures are available for 34 of the molecules included in this study.[21−25] Our optimized geometries are in good agreement with these; the B3PW91 average bond length and bond angle deviations are 0.008 Å and 1.2°, while the CBS-Q are 0.013 Å and 1.5°.

The results for the boron-containing molecules are presented in Figure 1. These structures were found to have no imaginary vibrational frequencies, confirming that they correspond to energy minima.[26] Figure 1 contains several sets of isomers; their relative stabilities and potential equilibria will be discussed in a later section. We also investigated some other possible isomers. The cyclic forms of BO_2 and B_2O_2, $\overline{B-O-B-O}$, do have B3PW91 energy minima, but they are 90.5 and 72.3 kcal/mol higher than the linear OBO and OBBO. Similarly, FOB and ClOB both have energy minima, but they are 183.5 and 126.5 kcal/mol above FBO and ClBO. These four considerably less stable structures are not included in Figure 1. For the isomeric

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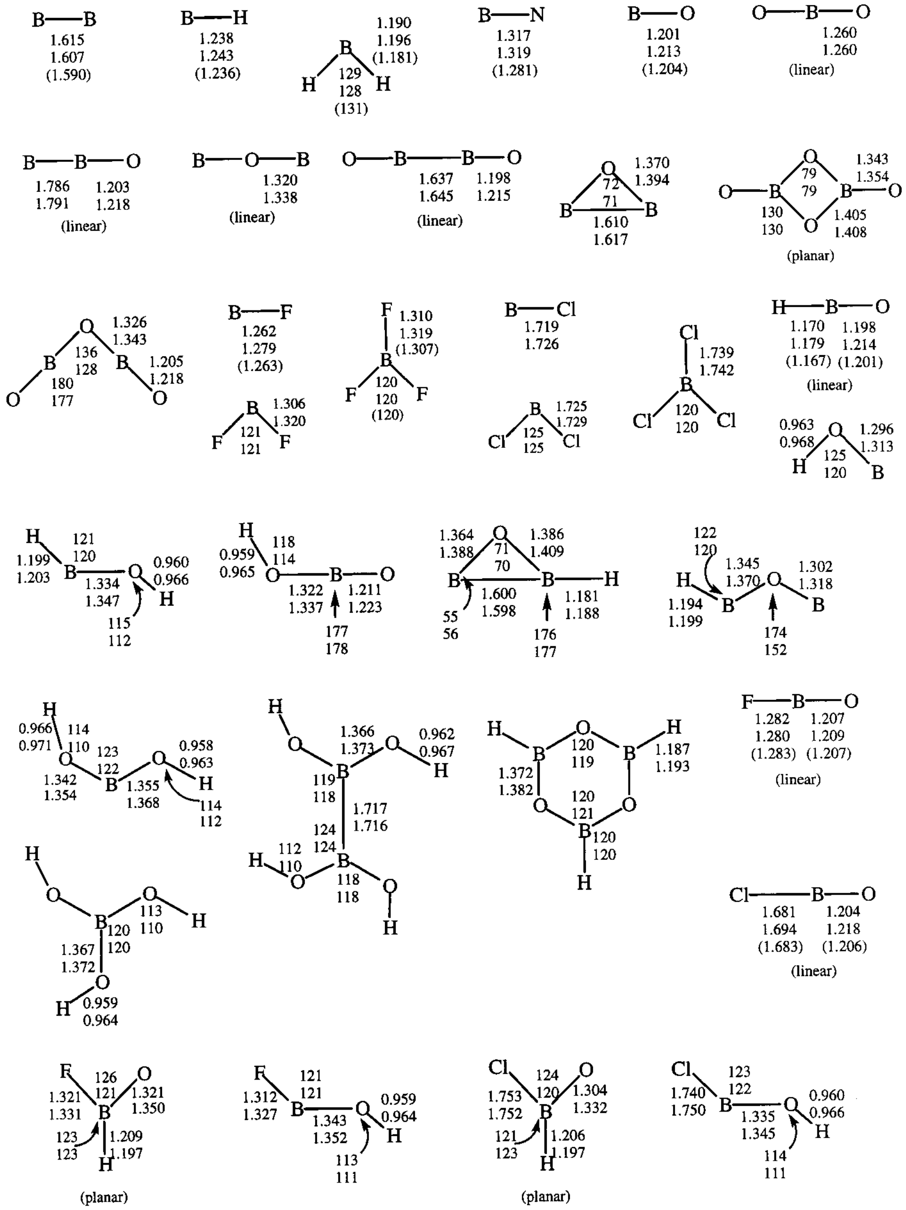

Figure 1. Bond lengths (Å) and bond angles (deg) in boron-containing molecules. The top two values in each instance are computed by the B3PW91/6-311+G(2df,2pd) and CBS-Q procedures, respectively; experimental data, when available, are given in parentheses. The latter are from ref 21, except for HBO (ref 24), FBO (ref 23), and ClBO (ref 22).

pairs, HOBF/HB(O)F and HOBCl/HB(O)Cl, we tried to optimize the geometries of HBOF and HBOCl. In each instance, the halogen atom preferentially moved to the boron, forming HB(O)F and HB(O)Cl. Finally, we were able to optimize the cyclic form of BOB only as a triplet, in contrast to its two linear isomers which are singlets.

B. Energies, Enthalpies, and Free Energies. In Table 1 are listed the computed energy minima at 0 K and the enthalpies and free energies at 298 K for 66 atoms and molecules. We have shown earlier that the quantity $\Delta H = H$ (298 K) $- E_{\mathrm{min}}$ (0 K) is nearly the same for three different density functional combinations (B3LYP, B3P86, and B3PW91) and several basis sets.[17] Table 2 confirms that this is true as well for $\Delta G = G$ (298 K) $- E_{\mathrm{min}}$ (0 K), when calculated at the B3LYP/6-311+G(2df) and B3PW91/6-311+G(2df,2pd) levels. However, this consistency does not extend to the CBS-Q results; in two instances, CO_2 and BF_3, the CBS-Q ΔH and/or ΔG is quite different from the B3LYP and B3PW91 values. This presumably reflects the fact that the former procedure uses Hartree–Fock vibrational frequencies in evaluating ΔH and ΔG.[27]

C. Heats of Formation. The enthalpies at 298 K were used to obtain the heats of formation given in Table 3. Experimental values are included when available. For the B3PW91 results, the average absolute deviation from experiment is 3.5 kcal/mol; for the CBS-Q, it is 2.5 kcal/mol. By both procedures, particularly large deviations are found for BF_2, followed by $H_3B_3O_3$. If these compounds are omitted, the B3PW91 average absolute deviation decreases to 2.9 kcal/mol and the CBS-Q to 1.7 kcal/mol. In view of the excellent overall accuracy of the computed heats of formation, particularly the CBS-Q, it seems reasonable to suggest that the experimental values be reexamined in these two cases.

The experimental heats of formation of BH_2 (48 ± 15 kcal/mol) and BCl_2 (−20 ± 15 kcal/mol) are not included in Table 3 because of the very large estimated uncertainties.[20] It is notable, however, that a recent very thorough ab initio UCCSD(T)/CBS calculation predicts the heat of formation of BH_2 to

TABLE 1: Computed Energy Minima, Enthalpies, and Free Energies at 298 K, in Hartrees

atom or molecule	B3PW91/6-311+G(2df,2pd)			CBS-Q		
	E_{min} (0 K)	H (298 K)	G (298 K)	E_{min}	H (298 K)	G (298 K)
H	−0.50398	−0.50162	−0.51463	−0.49982	−0.49746	−0.51047
B	−24.64354	−24.64118	−24.65758	−24.60161	−24.59925	−24.61565
C	−37.83546	−37.83310	−37.85001	−37.78515	−37.78279	−37.79970
N	−54.57895	−54.57659	−55.59398	−54.52026	−54.51790	−54.53529
O	−75.05961	−75.05725	−75.07456	−74.98704	−74.98468	−75.00200
F	−99.72343	−99.72107	−99.73824	−99.64217	−99.63981	−99.65699
Cl	−460.11123	−460.10887	−460.12691	−459.68285	−459.68049	−459.69853
H_2	−1.17895	−1.16559	−1.18039	−1.17581	−1.16277	−1.17753
B_2	−49.39104	−49.38539	−49.40837	−49.30560	−49.30021	−49.32325
N_2	−109.51673	−109.50782	−109.52956	−109.40175	−109.39265	−109.41435
O_2	−150.31826	−150.31113	−150.33439	−150.16693	−150.15942	−150.18261
F_2	−199.50459	−199.49882	−199.52177	−199.34671	−199.34092	−199.36379
Cl_2	−920.31493	−920.31017	−920.33545	−919.46087	−919.45612	−919.48140
BH	−25.27798	−25.26937	−25.28888	−25.23709	−25.22858	−25.24809
BH_2	−25.92821	−25.91003	−25.93207	−25.86980	−25.85208	−25.87415
NH	−55.21982	−55.20903	−55.22957	−55.15127	−55.14056	−55.16108
OH	−75.73390	−75.72207	−75.74230	−75.65726	−75.64557	−75.66576
H_2O	−76.43319	−76.40796	−76.42938	−76.35766	−76.33269	−76.35404
HO_2	−150.90608	150.88801	−150.91400	−150.75266	−150.73435	−150.76025
H_2O_2	−151.55072	−151.51965	−151.54537	−151.40313	−151.37197	−151.39773
HF	−100.44856	−100.43584	−100.45555	−100.36810	−100.35576	−100.37543
HCl	−460.78355	−460.77346	−460.79464	−460.35374	−460.34377	−460.36493
BN	−79.39970	−79.39278	−79.41628	−79.28645	−79.27945	−79.30291
BO	−100.01583	−100.00814	−100.03124	−99.89797	−99.89030	−99.91337
BO_2	−175.28792	−175.27617	−175.30161	−175.09464	−175.08735	−175.10935
BOB	−124.80723	−124.79670	−124.81863	−124.65579	−124.64549	−124.66932
BBO	−124.78399	−124.77252	−124.79923	−124.63104	−124.61949	−124.64579
BOB[a,b]	−124.76567	−124.75440	−124.78186	−124.59033	−124.57917	−124.60661
B_2O_2	−200.21462	−200.19623	−200.22317	−199.98572	−199.96741	−199.99416
B_2O_3	−275.51460	−275.49010	−275.52315	−275.21283	−275.18864	−275.22164
B_2O_4	−350.65287	−350.62533	−350.65948	−350.27038	−350.24258	−350.27659
BF	−124.65294	−124.64643	−124.66919	−124.53412	−124.52784	−124.55061
BF_2	−224.56499	−224.55394	−224.51894	−224.35519	−224.34441	−224.37243
BF_3	−324.55576	−324.53889	−324.56948	−324.27559	−324.25900	−324.28791
BCl	−484.94879	−484.94351	−484.96771	−484.48147	−484.47632	−484.50057
BCl_2	−945.19839	−945.18958	−945.22026	−944.29303	−944.28436	−944.31512
BCl_3	−1405.49500	−1405.48206	−1405.51490	−1404.17086	−1404.15812	−1404.19109
CN	−92.69915	−92.69092	−92.71390	−92.59042	−92.58295	−92.60592
CO	−113.30216	−113.29379	−113.31621	−113.18659	−113.17818	−113.20058
CO_2	−188.57886	−188.56350	−188.58773	−188.38316	−188.36963	−188.38973
CF_4	−437.48532	−437.46351	−437.49453	−437.11918	−437.09673	−437.12632
NO	−129.88330	−129.87543	−129.89872	−129.75172	−129.74371	−129.76696
NO_2	−205.07195	−205.05915	−205.08636	−204.86079	−204.84777	−204.87553
N_2O	−184.65730	−184.64240	−184.66731	−184.45881	−184.44390	−184.46876
ClO	−535.27663	−535.27122	−535.29629	−534.77212	−534.76700	−534.79217
ClO_2	−610.42863	−610.41871	−610.44785	−609.85961	−609.84964	−609.87938
HBO	−100.70148	−100.68361	−100.70662	−100.58459	−100.56696	−100.58993
HOB	−100.62657	−100.60931	−100.63425	−100.51095	−100.49403	−100.51894
HBOH	−101.23385	−101.20594	−101.23222	−101.10484	−101.07750	−101.10379
HOBO	−175.97870	−175.95401	−175.98156	−175.78942	−175.76521	−175.79276
HBOB[a]	−125.44008	−125.41881	−125.44699	−125.26455	−125.24380	−125.27198
HBOB	−125.41766	−125.39786	−125.42762	−125.24886	−125.22948	−125.25966
$B(OH)_2$	−176.52754	−176.49173	−176.52123	−176.32866	−176.29321	−176.32266
$B(OH)_3$	−252.49508	−252.44062	−252.47132	−252.23214	−252.17848	−252.20916
$H_4B_2O_4$	−353.21491	−353.13820	−353.17706	−352.83179	−352.75608	−352.79418
$H_3B_3O_3$	−302.28491	−302.22411	−302.25841	−301.92985	−301.87058	−301.90492
HCO	−113.84715	−113.83026	−113.85571	−113.71731	−113.70038	−113.72577
HNO	−130.46830	−130.45049	−130.47552	−130.33596	−130.31739	−130.34235
HONO	−205.70116	−205.67654	−205.70467	−205.49448	−205.46909	−205.49705
FBO	−199.99530	−199.98201	−200.00749	−199.80221	−199.79024	−199.81047
F_2CO	−313.01220	−312.99394	−313.02398	−312.72874	−312.71000	−312.73995
ClBO	−560.31949	−560.30739	−560.33422	−559.77710	−559.76591	−559.78922
HB(O)F	−200.53291	−200.51239	−200.54161	−200.32736	−200.30640	−200.33546
HOBF	−200.54855	−200.52494	−200.55395	−200.34448	−200.32130	−200.35031
HB(O)Cl	−560.85507	−560.83580	−560.86666	−560.30083	−560.28115	−560.31161
HOBCl	−560.86546	−560.84297	−560.87332	−560.31346	−560.29138	−560.32179

[a] Three-membered ring. [b] This is a triplet, in contrast to its two isomers which are singlets.

be 78.4 ± 0.4 kcal/mol,[28] in remarkable agreement with our CBS-Q value.

D. Effects of Temperature Upon Δ*H* and Δ*G*. In Table 4, are presented the enthalpies, free energies, and constant volume heat capacities for 12 molecules, computed at both 298 and 2000 K. The latter was selected as representative of the elevated temperatures associated with boron combustion.

While the values of all of these properties for any individual molecule change significantly over this temperature range, the changes in enthalpies largely cancel in calculating Δ*H* for a

TABLE 2: Computed Changes in Enthalpy and Free Energy between 0 and 298 K, in kcal/mol[a]

molecule		B3LYP/ 6-311+G(2df)	B3PW91/ 6-311+G(2df, 2pd)	CSB-Q
H_2O				
	ΔH	15.7	15.8	15.7
	ΔG	2.3	2.4	2.3
CO_2				
	ΔH	9.6	9.6	8.5
	ΔG	−5.6	−5.6	−4.1
BF_3				
	ΔH	10.5	10.6	10.4
	ΔG	−8.7	−8.6	−7.7
B_2O_3				
	ΔH	15.3	15.4	15.2
	ΔG	−5.4	−5.4	−5.5
HOBO				
	ΔH	15.4	15.5	15.2
	ΔG	−1.9	−1.8	−2.1
HCO				
	ΔH	10.5	10.6	10.6
	ΔG	−5.5	−5.4	−5.3

[a] Zero-point energy is included.

reaction. Thus, Table 5 shows, for a group of seven reactions, that ΔH (2000 K), when obtained directly from the enthalpies at 2000 K, differs by an average of only 1.5 kcal/mol from ΔH (298 K). (The same point has been demonstrated earlier for a different set of reactions and a range of 298−800 K,[17] and it is also fully consistent with experimental data.[29]) ΔH (2000 K) can also be determined with the Kirchhoff equation,[29]

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_P \, dT \tag{1}$$

where ΔC_P is the change in the sum of the constant pressure heat capacities in going from reactants to products. Taking ΔC_P to be temperature-independent (an approximation) and since $C_P = C_V + R$ (for an ideal gas, R being the gas constant), ΔH (2000 K) was evaluated for the reactions in Table 5, first using C_V (298 K) and then the average of C_V (298 K) and C_V (2000 K). While the second approach gives better results, overall the best estimates of ΔH (2000 K) for these reactions actually are provided by ΔH (298 K).

Table 5 also gives ΔG (298 K) and ΔG (2000 K), obtained from the calculated free energies at those temperatures. Unlike ΔH, ΔG can change considerably in going from 298 to 2000 K. This can also be treated by means of the Gibbs−Helmholtz equation,[29]

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = -\frac{\Delta H}{T^2} \tag{2}$$

If ΔH is taken to be temperature-independent, then eq 2 can be integrated to give

$$\Delta G\ (2000\ \mathrm{K}) = 6.7080\Delta G\ (298\ \mathrm{K}) - 5.7080\Delta H \tag{3}$$

Table 5 shows the results of using either ΔH (298 K) or the average of ΔH (298 K) and ΔH (2000 K) in eq 3. (The ΔG (2000 K) obtained by these two approaches differ by an average 4.1 kcal/mol, showing how sensitive they are to the exact value used for ΔH.) The average absolute differences from the directly evaluated ΔG (2000 K) are 4.4 and 4.5 kcal/mol, respectively.

TABLE 3: Calculated and Experimental Gas-Phase Heats of Formation, in kcal/mol

molecule	B3PW91	CBS-Q	expt[a]
H	50.9	52.7	52.10
B			134.5
C			171.3
N	111.3	112.0	113.0
O	61.7	59.6	59.6
F	17.8	19.2	19.0 ± 0.1
Cl	29.0	29.9	29.0
B_2	204.3	205.2	
BH	106.0	104.4	105.8 ± 2
BH_2	69.7	78.0	
NH	80.1	86.1	90.0 ± 4.0
OH	10.2	9.7	9.3 ± 0.3
HO_2	3.7	4.1	2.5
H_2O	−54.5	−56.6	−57.80
H_2O_2	−27.0	−31.2	−32.6
HF	−65.0	−65.2	−65.1 ± 0.2
HCl	−22.3	−21.5	−22.1 ± 0.04
BN	135.9	144.6	
BO	1.8	1.9	0
BO_2	−68.7	−71.7	−72
BOB	43.9	38.5	
BBO	59.0	54.8	
BOB[b]	70.4	80.1	
B_2O_2	−109.2	−113.5	−109 ± 2
B_2O_3	−196.0	−202.3	−201.3
B_2O_4	−183.2	−186.1	
BF	−26.0	−27.5	−27.7
BF_2	−125.2	−119.2	−141.0 ± 3
BF_3	−273.0	−272.4	−271.7
BCl	42.1	41.0	33.8
BCl_2	−15.0	−9.2	
BCl_3	−101.2	−100.6	−96
CN	106.1	106.1	104.0 ± 2
CO	−20.2	−26.8	−26.42
CO_2	−91.8	−96.9	−94.05
NO	21.4	20.3	21.82
NO_2	3.7	5.0	7.9
N_2O	13.2	17.9	19.6
ClO	24.7	25.6	24.4
ClO_2	29.8	23.7	23 ± 2
HBO	−56.3	−57.9	
BOH	−9.7	−12.1	
HOBO	−128.4	−132.3	−134
HBOB[b]	19.2	27.9	
HBOB	32.3	36.9	
HBOH	−18.4	−13.4	
$B(OH)_2$	−100.1	−98.8	
$B(OH)_3$	−232.2	−239.5	
$H_4B_2O_4$	−297.3	−304.0	
$H_3B_3O_3$	−277.6	−280.2	−291
$H_3B_3O_6$	−523.6		
HCO	8.9	10.3	10.7
HNO	26.2	25.1	24
HONO	−18.0	−20.1	−19
FBO	−139.0	−142.1	
HB(O)F	−106.1	−101.2	
HOBF	−114.0	−110.5	
ClBO	−88.6	−90.7	
HB(O)Cl	−54.5	−49.2	
HOBCl	−59.0	−55.6	

[a] Reference 20. The cited values for BH_2 and BCl_2 are not included because the error ranges are both ±15 kcal/mol. [b] Three-membered ring.

E. Relative Stabilities of Isomers. Table 1 contains five pairs of isomers. (Only the singlet forms of B_2O will be compared.) As mentioned earlier, we did also find energy minima for the molecules FOB, ClOB, and a cyclic form of B_2O_2; however, these minima are so much higher than the energies of FBO, ClBO, and O═B−B═O that the former three molecules are not included in Table 1 and Figure 1.

TABLE 4: Computed[a] Thermochemical Properties at 298 and 2000 K

molecule	*T*, K	*H*, hartrees	*G*, hartrees	C_V, cal/deg mol
H_2	298	−1.16559	−1.18039	4.97
	2000	−1.14671	−1.28968	6.06
O_2	298	−150.31113	−150.33439	5.01
	2000	−150.28916	−150.49352	6.77
F_2	298	−199.49882	−199.52177	5.28
	2000	−199.47577	−199.68072	6.88
BH	298	−25.26937	−25.28888	4.97
	2000	−25.24836	−25.42588	6.63
BO_2	298	−175.27617	−175.30161	7.98
	2000	−175.23962	−175.49116	12.67
BF	298	−124.64643	−124.66919	5.07
	2000	−124.62402	−124.82603	6.83
BF_3	298	−324.53889	−324.56948	10.11
	2000	−324.49114	−324.79035	17.49
CO	298	−113.29379	−113.31621	4.97
	2000	−113.27262	−113.46980	6.63
HBO	298	−100.68361	−100.70662	6.36
	2000	−100.65053	−100.87584	12.13
HCO	298	−113.83026	−113.85571	6.26
	2000	−113.80024	−114.03653	11.17
FBO	298	−199.98201	−200.00749	7.75
	2000	−199.94650	−200.19603	12.53
HB(O)F	298	−200.51239	−200.54161	9.00
	2000	−200.46721	−200.76217	17.18

[a] B3PW91/6-311+G(2df,2pd).

The relative enthalpies and free energies at 298 K within the five sets of isomers are in Table 6. The results for the two computational procedures are in generally good agreement, the largest differences being for the HBOB pair. The table also shows the equilibrium constants *K* for the conversions of the more stable into the less stable forms, calculated using the equation[29]

$$K = \exp(-\Delta G/RT) \tag{4}$$

which shows *K* to be very sensitive to the magnitude of Δ*G*. It can be seen that the presence of the less stable isomer is expected to be most significant for the HOBCl/HB(O)Cl pair.

It is particularly relevant to note the difference in stability between HBO and HOB, since a possible role for the latter has been mentioned on several occasions.[4,5,7,13] The data in Table 6 indicate that this is likely to be minimal.

F. Heats of Reaction. Table 7 lists 83 reactions that have been implicated or suggested as being involved, in either the forward or reverse direction, in the ignition and/or combustion of boron.[4,5,7,8,10,12,13,30,31]

We have used the heats of formation in Table 3 to compute the B3PW91 and CBS-Q heats of reaction for these processes, Δ*H* (298 K). Experimental values are included when possible, although not for reactions involving BH_2, BF_2, and BCl_2, for which the heats of formation are unreliable or suspect, as discussed earlier. The data in Table 3 could similarly be used to find Δ*H* (298 K) for many other possible processes.

The B3PW91 and CBS-Q results in Table 7 are in overall good agreement with each other and with experiment. The average absolute deviations from the latter are 2.6 kcal/mol (B3PW91) and 2.5 kcal/mol (CBS-Q). The average absolute deviation between the two sets of calculated heats of reaction is 2.8 kcal/mol. In view of the greater accuracy of the CBS-Q heats of formation, it seems reasonable to prefer the CBS-Q heats of reaction to the B3PW91 when the two differ significantly.

By far the most exothermic process in Table 7 is

$$\mathrm{BO} + \mathrm{F} \rightarrow \mathrm{FBO} \qquad \Delta H\ (298\ \mathrm{K}),\ \mathrm{CBS\text{-}Q} = -163.2\ \mathrm{kcal/mol}$$

followed by

$$\mathrm{BO} + \mathrm{O} \rightarrow \mathrm{BO_2} \qquad \Delta H\ (298\ \mathrm{K}),\ \mathrm{CBS\text{-}Q} = -133.2\ \mathrm{kcal/mol}$$

Four other highly energy releasing reactions are $2BO \rightarrow B_2O_2$, $2B(s) + O_2 \rightarrow B_2O_2$, $BO_2 + H \rightarrow HOBO$, and $BO + H \rightarrow HBO$. All of them have Δ*H*(298 K), CBS-Q between −112 and −118 kcal/mol.

TABLE 5: Comparisons of Δ*H* and Δ*G*, in kcal/mol, at 298 and 2000 K

		Δ*H* (2000 K)				Δ *G* (2000 K)		
reaction	Δ*H* (298 K)	*H* (2000 K)	eq 1, C_V (298 K)	eq 1, C_V(avg)	Δ*G* (298 K)	*G* (2000 K)	eq 3, Δ*H* (298 K)	eq 3, Δ*H* (avg)
$2BH + O_2 \rightarrow 2HBO$	−324.6	−323.3	−331.8	−326.3	−314.4	−255.0	−256.2	−259.8
$2CO + H_2 \rightarrow 2HCO$	58.1	57.4	50.6	55.3	63.6	98.0	95.0	96.9
$2HBO + O_2 \rightarrow H_2 + 2BO_2$	−24.8	−22.4	−19.3	−21.7	−22.6	−16.8	−10.6	−16.7
$2BF + H_2 \rightarrow 2BH + F_2$	264.1	265.0	264.3	264.5	263.1	256.8	257.4	254.9
$2HBO + F_2 \rightarrow 2FBO + H_2$	−165.4	−165.0	−161.2	−163.3	−163.4	−156.5	−152.0	−153.2
$2BH + 3F_2 \rightarrow 2BF_3 + H_2$	−758.1	−756.1	−765.9	−759.3	−738.1	−612.7	−623.9	−629.5
$HBO + BF + O_2 \rightarrow HB(O)F + BO_2$	−92.5	−89.8	−95.0	−95.9	−83.5	−36.4	−32.1	−39.8

TABLE 6: Relative Stabilities of Isomers

	relative *H* (298 K), kcal/mol		relative *G* (298 K), kcal/mol		equilibrium constant, more stable ⟺ less stable	
isomer	B3PW91	CBS-Q	B3PW91	CBS-Q	B3PW91	CBS-Q
BBO[a]	15.2	16.3	12.2	14.8		
BOB[a]	0	0	0	0	1.2×10^{-9}	1.5×10^{-11}
HOB	46.6	45.8	45.4	44.5		
HBO	0	0	0	0	5.1×10^{-34}	2.2×10^{-33}
HBOB	13.1	9.0	12.2	7.7		
HBOB[b]	0	0	0	0	1.2×10^{-9}	2.2×10^{-6}
HB(O)F	7.9	9.3	7.7	9.3		
HOBF	0	0	0	0	2.1×10^{-6}	1.5×10^{-7}
HB(O)Cl	4.5	6.4	4.2	6.4		
HOBCl	0	0	0	0	8.6×10^{-4}	2.1×10^{-5}

[a] The triplet three-membered ring isomer of B_2O is not included. [b] Three-membered ring.

TABLE 7: Calculated and Experimental Heats of Reaction at 298 K, in kcal/mole[a]

reaction	B3PW91	CBS-Q	expt[b]
$B(s) + H \rightarrow BH$	55.1	51.7	53.7
$B(s) + O \rightarrow BO$	−59.9	−57.7	−60
$B(s) + F \rightarrow BF$	−43.8	−46.7	−46.7
$B(s) + O_2 \rightarrow BO_2$	−68.7	−71.7	−72
$B(s) + O_2 \rightarrow BO + O$	63.5	61.5	60
$2B(s) + O_2 \rightarrow 2BO$	3.6	3.8	0
$2B(s) + O_2 \rightarrow B_2O_2$	−109.2	−113.5	−109
$B(s) + OH \rightarrow HBO$	−66.5	−67.6	
$B(s) + OH \rightarrow BO + H$	42.5	44.9	43
$2B(s) + OH \rightarrow BH + BO$	97.6	96.6	97
$B(s) + HF \rightarrow BF + H$	89.9	90.4	89.5
$2B(s) + HF \rightarrow BH + BF$	145.0	142.1	143.2
$B(s) + H_2O \rightarrow HBO + H$	49.1	51.4	
$2B(s) + H_2O \rightarrow BH + HBO$	104.2	103.1	
$B(s) + CO_2 \rightarrow BO + CO$	73.4	72.0	68
$B(s) + BO_2 \rightarrow B_2O_2$	−40.5	−41.8	−37
$B(s) + BO_2 \rightarrow 2BO$	72.3	75.5	72
$B(s) + BF_2 \rightarrow 2BF$	73.2	64.2	
$B(s) + B_2O_3 \rightarrow B_2O_2 + BO$	88.6	90.7	92
$B(s) + BF_3 \rightarrow BF + BF_2$	121.8	125.7	
$B(s) + HOBO \rightarrow B_2O_2 + H$	70.1	71.5	77
$B(s) + HOBO \rightarrow BO + HBO$	73.9	76.3	
$2B(s) + HOBO \rightarrow B_2O_2 + BH$	125.2	123.2	131
$B(s) + FBO \rightarrow BO + BF$	114.8	116.5	
$B + O_2 \rightarrow BO + O$	−71.0	−73.0	−75
$B + H_2O \rightarrow HBO + H$	−85.4	−83.1	
$B + CO_2 \rightarrow BO + CO$	−61.1	−62.5	−67
$BO + H \rightarrow HBO$	−109.0	−112.5	
$BO + O \rightarrow BO_2$	−132.2	−133.2	−132
$BO + F \rightarrow FBO$	−158.6	−163.2	
$BO + F \rightarrow BF + O$	16.1	11.0	13
$BO + H_2 \rightarrow HBO + H$	−7.2	−7.1	
$BO + O_2 \rightarrow BO_2 + O$	−8.8	−14.0	−12
$BO + OH \rightarrow HBO + O$	−6.6	−9.9	
$BO + OH \rightarrow BO_2 + H$	−29.8	−30.6	−29
$BO + HF \rightarrow HBO + F$	24.7	24.6	
$BO + HF \rightarrow HOBF$	−50.8	−47.2	
$BO + HF \rightarrow HB(O)F$	−42.9	−37.9	
$BO + HCl \rightarrow HBO + Cl$	−6.8	−8.4	
$BO + HCl \rightarrow HOBCl$	−38.5	−36.0	
$BO + HCl \rightarrow HB(O)Cl$	−34.0	−29.6	
$BO + H_2O \rightarrow HBO + OH$	6.6	6.5	
$2BO \rightarrow B_2O_2$	−112.8	−117.3	−109
$BO + BO_2 \rightarrow B_2O_2 + O$	19.4	15.9	23
$BO + CO_2 \rightarrow BO_2 + CO$	1.1	−3.5	−4
$BO + HBO \rightarrow B_2O_2 + H$	−3.8	−4.8	
$BO + BF_2 \rightarrow FBO + BF$	−41.6	−52.3	
$BO + BF_3 \rightarrow FBO + BF_2$	7.0	9.2	
$BO + HOBO \rightarrow B_2O_3 + H$	−18.5	−19.2	−15.2
$BO + HOBO \rightarrow B_2O_2 + OH$	27.6	26.6	34
$BO + FBO \rightarrow B_2O_2 + F$	45.8	45.9	
$BO + FBO \rightarrow BO_2 + BF$	42.5	41.0	
$BO_2 + H \rightarrow HOBO$	−110.6	−113.3	−114
$BO_2 + H \rightarrow HBO + O$	23.2	20.7	
$BO_2 + F \rightarrow FBO + O$	−26.4	−30.0	
$BO_2 + H_2 \rightarrow HOBO + H$	−8.8	−7.9	−9.9
$BO_2 + OH \rightarrow HOBO + O$	−8.2	−10.7	−12
$BO_2 + HF \rightarrow HOBO + F$	23.1	23.8	22
$BO_2 + H_2O \rightarrow HOBO + OH$	5.0	5.7	5.1
$2BO_2 \rightarrow B_2O_3 + O$	3.1	0.7	2.3
$HBO + F \rightarrow HB(O)F$	−67.6	−62.5	
$HBO + F \rightarrow FBO + H$	−49.6	−50.7	
$HBO + Cl \rightarrow HB(O)Cl$	−27.2	−21.2	
$HBO + Cl \rightarrow ClBO + H$	−10.4	−10.0	
$HBO + O_2 \rightarrow HOBO + O$	−10.4	−14.8	
$HBO + OH \rightarrow HOBO + H$	−31.4	−31.4	
$HOBO + F \rightarrow FBO + OH$	−18.2	−19.3	
$2HOBO \rightarrow B_2O_3 + H_2O$	6.3	5.7	9
$BF + O_2 \rightarrow FBO + O$	−51.3	−55.0	
$BF + OH \rightarrow FBO + H$	−72.3	−71.6	
$BF + HF \rightarrow BF_2 + H$	16.7	26.2	
$BF + BF_3 \rightarrow 2BF_2$	48.6	61.5	
$BF_2 + O \rightarrow FBO + F$	−57.7	−63.3	
$BF_2 + HF \rightarrow BF_3 + H$	−31.9	−35.3	
$FBO + H \rightarrow HOBF$	−25.9	−21.1	
$FBO + H \rightarrow HB(O)F$	−18.0	−11.8	
$ClBO + H \rightarrow HOBCl$	−21.3	−17.6	
$ClBO + H \rightarrow HB(O)Cl$	−16.8	−11.2	
$H + O_2 \rightarrow OH + O$	21.0	16.6	16.8
$H + H_2O \rightarrow OH + H_2$	13.8	13.6	15.0
$O + H_2 \rightarrow OH + H$	−0.6	2.8	1.8
$F + H_2 \rightarrow HF + H$	−31.9	−31.7	−32.0
$F + H_2O \rightarrow OH + HF$	−18.1	−18.1	−17.0

[a] All reactants and products are in the gaseous phase except where otherwise indicated. For reactions involving B(g), calculated results were obtained using experimental heat of formation of B(g). [b] Reference 20. Experimental values for BH_2, BF_2, and BCl_2 were not used, due to uncertain accuracy (see text).

G. B_2O_4. Archibong and St-Amant have recently reviewed earlier experimental and theoretical studies relating to the Al_2O_4 system[32] and have computationally characterized several stationary points on its singlet and triplet potential energy surfaces. They found the most stable to correspond to a triplet with D_{2h} symmetry. We have accordingly investigated the analogous structure for B_2O_4 and found that it does give an energy minimum. The optimized geometry is shown in Figure 1. Our computed heat of formation for this compound in the gas phase is −186.1 kcal/mol (Table 3) so that the oxidation of boron to B_2O_4 would release 9.3 kcal per gram of boron, compared to 10 kcal when producing gaseous B_2O_3.

Summary

(1) Optimized B3PW91/6-311+G(2df,2pd) and CBS-Q geometries are presented for 34 boron-containing molecules, for most of which these experimental data are not available. Two structures that were investigated (HBOF and HBOCl) do not correspond to energy minima.

(2) Energy minima at 0 K and enthalpies and free energies at 298 K have been computed by both procedures for 66 atoms and molecules relevant to the oxygen/fluorine oxidation of boron. These permit the evaluation of ΔH (298 K), ΔG (298 K), and the equlibrium constants for several hundred possible ignition and combustion reactions.

(3) The enthalpies at 298 K were used to find heats of formation for 58 atoms and molecules, for many of which they are not known experimentally. Four instances are noted in which the experimental values are unreliable or suspect.

(4) It is shown, for a representative group of seven reactions, that ΔH (298 K) and ΔH (2000 K) differ, on the average, by only 1.5 kcal/mol. On the other hand, ΔG can change considerably between these temperatures. Its value at a higher temperature can be estimated using ΔH (298 K).

(5) Among the five sets of isomers included in this study, the most similar in stability are the pair HOBCl/HB(O)Cl; the greatest difference is between HBO and HOB, with the latter being much less stable.

(6) Calculated heats of reaction are presented for 83 processes that are known or possible steps in the ignition and/or combustion of boron. The two most exothermic are $BO + F \rightarrow FBO$ and $BO + O \rightarrow BO_2$.

(7) It has been shown that a triplet B_2O_4 structure with D_{2h} symmetry corresponds to an energy minimum and is thus another possible oxidation product of boron.

(8) Both of the computational procedures used in this work achieved good levels of accuracy. Comparisons with experimental data indicate that the B3PW91 is better for geometries while the CBS-Q is more reliable for heats of formation and heats of reaction, for which the average absolute deviations are, respectively, 1.7 kcal/mol (omitting BF_2 and $H_3B_3O_3$) and 2.5 kcal/mol.

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