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Direct Calculation of the Heats of Formation of some Boron Hydrides

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The heats of formation of some boron hydrides are calculated by the molecular orbital-bond index method. A satisfactory correlation with known data is obtained and this indicates the value of the method for predicting heats of formation where these are not known. A few sample species are evaluated. There is a significant discrepancy between the experimental and calculated heats of formation for decaborane and we believe this indicates the need for revision of the experimental value. The trend in B–B bond energies over the series of compounds is in accord with earlier work.

Introduction

The molecular orbital-bond index method (MOBI) has previously been shown to be successful in predicting the heats of formation of hydrocarbons, alkyl halides, and silicon compounds [1–4]. Very good agreement with reliable experimental data may be obtained and it has been possible, in some instances [4], both to correct experimental results and to predict new heats of formation.

All the above examples, however, have been drawn from the 'classical' series of compounds and we now wish to find how applicable the method is to a 'non-classical' series. In order to do this we have chosen a group of boranes in which there exists also both hydrogen bridging and intracage B–B bonding.

Previous attempts [5, 6] to predict the heats of atomisation in neutral boranes have been based on estimation of the B–B and B–H bond enthalpy contributions generally using the two- and three-centre electron pair approach. This also assumed transferability of energy terms between similar bonds in a series of compounds. The latter assumption seems a perfectly reasonable one but such treatments tend to neglect the changes in bond energy induced by changes in bond length and it has to be assumed that the errors incurred are self-cancelling. The most recent study of the problem attempts to allow for the variation in bond energy with bond length using relationships of the form [7],

$$E(B{-}B) = 1.766 \times 10^{11}\ [d(B{-}B)]^{-4.0}$$

and

$$E(B{-}H) = 4.476 \times 10^{11}\ [d(B{-}H)]^{-4.4}$$

constants are deduced which yield the best fit to observed results. Many revealing trends are found but, overall, such methods lead to values for the enthalpy of atomisation of boranes which are not sufficiently accurate to afford reliable heats of formation for the compound in the standard state.

In order to obtain reasonably reliable values for the standard enthalpies of formation, very accurate values of heats of atomisation are required as any error in the heat of atomisation is carried directly over to the heat of formation where it necessarily constitutes a larger percentage error.

The molecular orbital-bond index method starts from an INDO calculation of the molecular electronic structure. From the density matrix afforded by such a calculation, *bond indices* can be constructed via the equations of Armstrong, Perkins and Stewart [8]. Bond indices between all pairs of atoms are included in the scheme. The heat of atomisation may then be expressed as a weighted sum of bond indices for all atom pairs.

Method and Results

The structures of many neutral *nido*- and *arachno*-boranes, B_nH_{n+4} and B_nH_{n+6}, have been determined by X-ray and electron diffraction investigations and detailed structural data are available for B_2H_6 [9] and B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10} and $B_{10}H_{14}$ [10]. Thermochemical data is only, however, available for diborane (B_2H_6), tetraborane (B_4H_{10}), pentaborane-9 (B_5H_9), pentaborane-11 (B_5H_{11}), hexaborane-10 (B_6H_{10}), and decaborane-14 ($B_{10}H_{14}$)

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TABLE I. Standard Enthalpies of Formation and Atomisation of Gaseous Boranes (kJ mol^{-1}).

B_2H_6	35.6	2392
B_4H_{10}	66.1	4354
B_5H_9	73.2	4689
B_5H_{11}	103.3	5092
B_6H_{10}	94.6	5445
$B_{10}H_{14}$	31.5	8620

[11]. Standard enthalpies of formation and atomisation for these compounds are listed in Table I.

The enthalpy of atomisation of gaseous B_nH_{n+x} into boron atoms and hydrogen atoms will have contributory energy terms $\Sigma E(B-B)$ and $\Sigma E(B-H)$, where $\Sigma E(B-B)$ is the total bonding energy between boron atoms, $\Sigma E(B-H)$ the total bonding energy between all boron atoms and all hydrogen atoms. We assume that these bonding energies are directly proportional to the sum of the relevant bond indices and that, overall, the bond energies are additive. The heat of atomisation for a borane is then given by,

$$\Delta H^\circ_{atom} = A\Sigma(\text{B–B bond indices}) + C\Sigma(\text{B–H bond indices})$$

where A = bond enthalpy (kJ mol^{-1}) of a B–B bond of unit index and C = the bond enthalpy of a B–H bond of unit index: ΔH°_{atom} is the standard heat of atomisation for the borane.

The quantum mechanical method used for such calculations is not critical and, in the present case, we used a method at the INDO level of approximation [12]. It is necessary to calibrate the method by reference to compounds with known heats of formation. In the present case, we need bond energy parameters for the B–B and B–H bonds and this requires a knowledge of the standard heats of atomisation for two compounds. The standard heat of atomisation of a borane demands a knowledge of the heat of sublimation of boron and the heat of dissociation of a hydrogen molecule. The latter is accurately known (436 kJ mol^{-1}) but the former is subject to somewhat more uncertainty. We adopted the value used by Wade *et al.* (560 ± 12 kJ mol^{-1}, Ref. [7] *op. cit.*). From the quantum mechanical calculations for B_4H_{10} and B_5H_9 and the bond indices therefrom, we obtained the B–B bonding parameter as 297.9 kJ mol^{-1} and for B–H the bonding parameter was 374.8 kJ mol^{-1}. This pair of molecules gave the best fit to the known experimental data. We attempted to improve the agreement by calibrating the bond indices using three bond energy parameters corresponding to the B–B, B–H (terminal), and B–H (bridge) interactions. No improvement of the fit was obtained, however, and it can be concluded, therefore, that the B–H bond index fully describes the energy contributions made by both bridge and terminal hydrogen atoms.

Table II presents the results obtained for the series of boranes for which experimental data are available. The only borane for which there is a serious discrepancy between calculated and experimental results is $B_{10}H_{14}$. The others in the group show a steady increase in the absolute value of the standard heat of formation (both calculated and experimental) as the number of boron atoms in the skeleton increases. At $B_{10}H_{14}$ the experimental value shows a dramatic decrease whilst the calculated quantity follows the upward trend. We believe there is a good case for the revision of the currently accepted value for decaborane and, accordingly, propose a value of ΔH°_f = 115.5 ± 10 kJ mol^{-1}. The RMS difference between calculated and experimental value for the rest of the molecules is 9.9 kJ mol^{-1}.

TABLE II. Total Calculated Bond Indices with Experimental and Calculated Thermochemical Values of Some Boranes.

Compound	Total Bond Indices		Experimental Values ΔH°_f (298) kJ mol^{-1}	Calculated Values ΔH°_f kJ mol^{-1}
	B–B	B–H		
BH_3	–	2.990	100.0	93.3
B_2H_6	0.655	5.892	35.6	23.6
B_4H_{10}*	2.425	9.688	66.1	66.1
B_5H_9*	4.715	8.762	73.2	73.2
B_5H_{11}	3.857	10.578	103.3	86.3
B_6H_{10}	6.042	9.727	94.6	93.6
$B_{10}H_{14}$	11.446	13.675	31.5	115.5

*Calibration molecules.

TABLE III. Thermochemical Data for Some Higher Boranes and Borane Anions (kJ mol^{-1}).

	Total Bond Indices		Calculated Values	
	B–B	B–H	ΔH°_{atom}	ΔH°_f
B_8H_{12}	8.774	11.710	7003	92.7
$B_{18}H_{22}$	22.187	21.523	14676	200.3
$B_6H_6^{2-}$	8.308	5.727	4622	45.4
$B_{10}H_{10}^{2-}$	13.662	9.686	7701	78.2
$B_{12}H_{12}^{2-}$	16.389	11.684	9263	71.4

TABLE IV. Average B–B Bond Energies per Skeleton Edge, per Skeletal Electron Pair and per Boron Atom (kJ mol^{-1}); *closo* Species.

	$\Sigma E(B-B)/3n-6$		$\Sigma E(B-B)/n+1$		$\Sigma E(B-B)/n$	
	a	b	a	b	a	b
$B_6H_6^{2-}$	206.3	217	353.6	371	412.6	433
$B_{10}H_{10}^{2-}$	169.6	184	370.0	401	407.0	441
$B_{12}H_{12}^{2-}$	162.8	178	375.6	410	406.9	445

[a]Present work. [b]Wade *et al.* [7].

The Enthalpies of Atomisation of Some Higher Boranes and Borane Anions

There are a number of higher boranes, the structures of which have been determined [10] but of which the thermochemistry is, as yet, unexplored. Values for the enthalpies of formation can be predicted, as before, and in this section we investigate the *nido*-boranes, B_8H_{12}, $B_{18}H_{22}$ and borane anions, $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{12}H_{12}^{2-}$. The calculated standard enthalpies of formation for these systems are listed in Table III.

The values of the enthalpy of formation calculated for B_8H_{12} and $B_{18}H_{22}$ are consistent with the value calculated for the *nido*-borane $B_{10}H_{14}$. We believe this is further evidence for our view that the calculated value for $B_{10}H_{14}$ is more reliable than the current experimental value.

Our results may be compared with those previously reported by Wade *et al.* Since we do not, in m.o. theory, assign an integral number of electrons to any particular bond, we cannot, in principle, adopt electron counting procedures for isolating B–B and B–H bonding electrons. However, in those cases (the *closo* series) where we have only terminal B–H bonds, the B–H bond indices are close enough to unity that we can consider them as two-electron B–H bonds for comparison purposes. Table IV lists the average B–B bond energy per primary skeletal bond, per skeleton pair and per boron atom in the molecule. For the first two, our trends are identical with those deduced by Wade, the absolute energies coinciding fairly well also. However, we find that the B–B energy per boron atom remains essentially constant whilst Wade suggests that this trends slightly upwards as n increases.

TABLE V. Average B–B Bond Energy per Boron Atom and per Skeletal Electron Pair for *nido* and *arachno* Species (kJ mol^{-1}).

	E(B–B)/n	E(B–B)/electron pair
B_2H_6	98.3	–
B_4H_{10}	181.7	103.2
B_5H_9	280.1	200.7
B_5H_{11}	229.4	143.6
B_6H_{10}	300.9	225.0
B_8H_{12}	324.8	261.4
$B_{10}H_{14}$	339.7	284.2
$B_{18}H_{22}$	366.5	330.5

When we consider the *nido* and *arachno* series, the presence of bridge hydrogens complicates comparisons and we quote only the B–B energy per boron atom here. From Table V we find that the average intrinsic B–B bond energy rises as the number of boron atoms increases. This is, essentially, the outcome of an increased number of secondary

B–B interactions. It is also interesting that the 'double basket' $B_{18}H_{22}$ shows enhanced B–B energy per boron over $B_{10}H_{14}$. The difference between the 'stable' and 'unstable' pentaboranes (B_5H_9 and B_5H_{11}) is well brought out by the calculations. The total energy devoted to cage bonding in the latter is only 80% of that in the former and, hence, the stability of the cage is clearly lessened.

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