

On the trustability of semi-empirical methods to the calculation of gas phase formation enthalpies of inorganic compounds containing heavy metals: tin borates

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Abstract

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Received 10 June 2017,

Revised 14 Nov 2017,

Accepted 01 Feb 2018

In the present work, are calculated the gas formation enthalpies (SE; PM3 and PM6) for tin borates: SnB_2O_4 and $\text{Sn}_2\text{B}_2\text{O}_5$. The calculated values are compared with experimental ones, obtained by Knudsen effusion mass spectrometry [3]. It is shown that SE methods, besides their lower computational time consuming can, indeed, provide reliable gas phase formation enthalpy values for inorganic compounds containing heavy metals.

Keywords: ; Tin; Borates; Formation enthalpy; Semi-Empirical

1.Introduction

As is well known, the principal disadvantage of Hartree-Fock, density functional and MP2 models is their computational cost. The Semi-Empirical methods, with their approximations (elimination of the overlap between functions on different atoms; minimal valence basis set, etc.), reduces, very much, the computational cost. With the advancements in computers, *ab initio* and DFT methods (specially the last ones) have been preferred to perform calculations involving coordination compounds and related species, with semi-empirical methods been seen, by many researchers, as “second class” and “not up-to-date” approach. However, as recently shown [1], a semi-empirical method can provide reliable gas phase formation enthalpy values even for a salt with a non-regular gas phase transient structure, for which relativistic contributions matters, such as PtF_6 [1]. The so-called gaseous salts of oxygen-containing acids (which includes borates, tungstates, molybdates, etc.), are a very important class of compounds, due to its presence in many technological systems, such as high-temperature coatings, glasses, cements, etc. [2]. The study of such salts formed on oxides under vaporization is important from a theoretical point of view, since in such systems so many thermal dissociation reactions can take place, producing compounds with monomeric or polymeric structures which, frequently, contains gaseous oxides not existing in condensed phase [2]. The thermochemical study of such gaseous salts of oxygen-containing acids are not so easy, and are made by using Knudsen effusion technique combined with high-temperature mass spectrometry [2,3]. In the present work, are calculated, by Semi-Empirical (PM3 and PM6) method, the gas formation enthalpies for tin borates: SnB_2O_4 and $\text{Sn}_2\text{B}_2\text{O}_5$. The calculated values are compared with experimental ones, obtained by Knudsen effusion mass spectrometry [3].

2.Methodology

All computation were performed by using Spartan '16 [4], Semi-Empirical (PM3 and PM6) approach. The modelled structures (for which the gaseous phase formation enthalpy values were calculated), were those previously considered as the most stable ones [3].

3.Results and discussion

The obtained results are summarized in Table 1. The modelled structures are shown in Figures 1 and 2. Must be pointed out that in the investigated compounds only main group elements are present and, for Sn ($Z=50$), relativistic effects are not so considerable. As is well known, to choose an appropriate method/theory level for the computations is, of course, of paramount importance since that predict structures and energetics are the main uses of computational chemistry today and that to know how good is the calculated numbers is an absolute requirement [5].

Table 1. Calculated and experimental standard gaseous phase formation enthalpies ($\Delta_f H_g^\circ$; kJ mol⁻¹) for tin borates.

Method/Compound	SnB_2O_4 ^c	$\text{Sn}_2\text{B}_2\text{O}_5$ ^d
Exp.(Ref. 3)	-1168 ± 17 ^a	-1474 ± 13 ^c
Exp.(Ref. 3)	-1164 ± 22 ^b	-1479 ± 28 ^c
SE/PM3	-1124.00	-1430.95
SE/PM6	-964.53	-1043.19

^aBy the reaction: $\text{SnO} + \text{B}_2\text{O}_3 \rightarrow \text{SnB}_2\text{O}_4$; ^bBy the reaction: $\frac{1}{2} \text{Sn}_2\text{O}_2 + \text{B}_2\text{O}_3 \rightarrow \text{SnB}_2\text{O}_4$; ^cBy the reaction $2\text{SnO} + \text{B}_2\text{O}_3 \rightarrow \text{Sn}_2\text{B}_2\text{O}_5$; ^dBy the reaction $\text{Sn}_2\text{O}_2 + \text{B}_2\text{O}_3 \rightarrow \text{Sn}_2\text{B}_2\text{O}_5$; ^cC2v point group; ^dC2 point group;

The Semi-Empirical (PM3) approach was those whose provided better results, with calculated values in really very good ($\approx 3.5\%$) with the experimental ones. As is well known, density-functional approximations can be used for calculation of accurate structural and spectroscopic properties, but they are most widely used for thermochemical predictions [6].

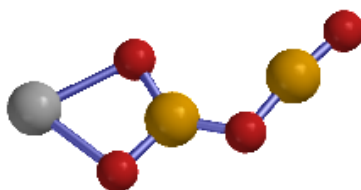


Figure 1. Modelled structure for SnB_2O_4

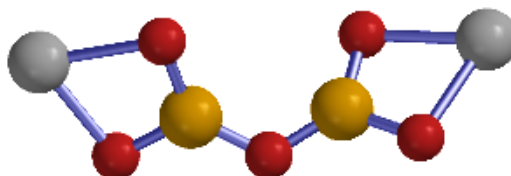


Figure 2. Modelled structure for $\text{Sn}_2\text{B}_2\text{O}_5$.

For years, DFT development focused on energies, implicitly assuming that functionals producing better energies become better approximations of the exact functional. However, as have been recently pointed out [6], developments in DFT have improved the energies while not always concurrently improving the electron densities, suggesting a departure from the theoretical principles underlying DFT [7]. As shown in the present study, as well as previously, for platinum fluorides [1,8] SE methods besides their lower computational time consuming, can, indeed, provide reliable gas phase formation enthalpy values for inorganic compounds with heavy metals. In worth nothing that even in the Spartan'16 tutorial [4], PM3 model is classified as a “poor” approach for both “easy” and “difficult” thermochemistry.

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