Research Article

Enthalpy of combustion and enthalpies of formation of solid, liquid and gaseous aspirin by quantum chemistry composite method

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Abstract In the present work, a computational study (quantum chemistry composite method) of the thermodynamic properties of aspirin is performed, and the obtained results compared with those from literature. The calculated values for $\Delta_c H_m^0$ (s), $\Delta_f H_m^0$ (s), $\Delta_f H_m^0$ (l) and $\Delta_f H_m^0$ (g) (kJ mol^{-1}), are -4035.35, -775.24, -755.96 and -649.56, respectively, in very good agreement (3%) with experimental values (from literature) obtained by combustion calorimetry.

Keywords Aspirin; Enthalpy of formation; Combustion enthalpy; Quantum chemistry

Introduction

Due to its pharmacological properties [1], as well as its properties of interest to materials chemistry, such as a polymer formation under thermal degradation [2] the 2-(acetyloxy)benzoic acid (aspirin) is a largely studied substance, including in the preparation of complexes [3].

From the point of view of thermochemistry, there are a few works [4-5] dedicated to investigate its combustion and formation enthalpies, as well as its calorific capacity.

In the present work, a computational study of the thermodynamic properties of aspirin is performed, and the obtained results compared with those from literature.

Experimental

Combustion and formation enthalpies for aspirin were found by computational modelling of the molecule by using Spartan´14 (version 1.1.8) [6]. The enthalpy of formation in gaseous phase was provided by the T1 recipe.

The main characteristic of T1 is that it follows the G3(MP2) recipe, substituting an <u>HF</u>/6-31G* for the MP2/6-31G* geometry, eliminating both the HF/6-31G* frequency and QCISD(T)/6-31G* energy and approximating the MP2/G3MP2 large energy using dual basis set RI-MP2 techniques [7].

The calculated results are compared with experimental ones, obtained by combustion calorimetry [4-5]. In order to obtain the $\Delta_f H_m^0$ (l) and $\Delta_f H_m^0$ (g) values, the melting and vaporization enthalpy values of 29.80 and 106.40 kJ mol^{-1}, respectively [4] were employed.

The combustion enthalpy for aspirin was calculated as $\Delta_c H_m^0$ (s) = [(9 x $\Delta_f H_m^0$, CO$_2$ (g) + 4 x $\Delta_f H_m^0$ H$_2$O (l)] – [$\Delta_f H_m^0$, Aspirin (s)]. $\Delta_f H_m^0$, CO$_2$ (g) = 393.51 kJmol^{-1} [8] and $\Delta_f H_m^0$ H$_2$O (l) = -285.83 kJmol^{-1} [8].

Results and discussion

The obtained results are summarized in Table 1. As can be verified, the calculated values are in very good agreement with the experimental ones [4-5] (3% range) obtained by combustion calorimetry.

Table 1: Calculated and experimental values to combustion and formation enthalpies (kJ/mol^{-1}) for aspirin.

	$\Delta_c H_m^0$ (s)	$\Delta_f H_m^0$ (s)	$\Delta_f H_m^0$ (l)	$\Delta_f H_m^0$ (g)
Calculated	-4035.35	-775.24	-755.96	-649.56
Exp. [Ref. 4]	-3926.71 ± 0.34	-758.19 ± 0.52	-738.91 ± 0.56	-632.50 ± 2.1
Exp. [Ref. 5]	-3945.26 ± 2.36	-736.41 ± 1.30	-715.38*	-

*The authors [Ref. 5] reported that aspirin exhibited a melting point of 409.2 K. However, the obtained Cp values (by using a precision automated adiabatic calorimeter) were obtained from 78 to 383 K. To obtain the valueof $\Delta_f H_m^0$ (l) shown here,it was employed the H_{382}-$H_{298.15}$ value = 21.03 kJmol^{-1}, as the melting enthalpy.

It is worthnoting that the formation enthalpy calculated in the present work, and in very good agreement with experimental data, is well above previous calculated values employing semi-empirical (AM1) heats of formation [9] (about -140 kJ mol^{-1}) for aspirin. Furthermore, in the present work it was not considered any possible polymorph of aspirin [9].

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