



Experimental and computational thermochemical studies of benzoxazole and two chlorobenzoxazole derivatives

Ana L.R. Silva, Álvaro Cimas, Maria D.M.C. Ribeiro da Silva *

Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

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ABSTRACT

The energetic study of benzoxazole, 5-chloro-2-methylbenzoxazole, and 2-chlorobenzoxazole, in condensed and gaseous states, has been developed using experimental techniques and computational approaches. The values of the standard ($p^\circ = 0.1$ MPa) molar enthalpy of formation, at $T = 298.15$ K, of crystalline benzoxazole (36.0 ± 2.0) $\text{kJ} \cdot \text{mol}^{-1}$ and 5-chloro-2-methylbenzoxazole (145.6 ± 2.2) $\text{kJ} \cdot \text{mol}^{-1}$ and liquid 2-chlorobenzoxazole (52.5 ± 3.0) $\text{kJ} \cdot \text{mol}^{-1}$ were determined from the corresponding experimental standard molar energy of combustion in oxygen, $-(3432.1 \pm 1.7)$ $\text{kJ} \cdot \text{mol}^{-1}$, $-(3883.0 \pm 2.0)$ $\text{kJ} \cdot \text{mol}^{-1}$, and $-(3298.0 \pm 2.8)$ $\text{kJ} \cdot \text{mol}^{-1}$, respectively, measured by static or rotating-bomb combustion calorimetry. At $T = 298.15$ K, the standard ($p^\circ = 0.1$ MPa) molar enthalpy of sublimation of benzoxazole and 5-chloro-2-methylbenzoxazole and of vaporization of 2-chlorobenzoxazole, (69.2 ± 0.8) $\text{kJ} \cdot \text{mol}^{-1}$, (82.4 ± 2.2) $\text{kJ} \cdot \text{mol}^{-1}$, and (56.3 ± 1.6) $\text{kJ} \cdot \text{mol}^{-1}$ respectively, were determined by a direct method, using the vacuum drop microcalorimetric technique. From the latter values and from the enthalpies of formation of the condensed compounds, the standard ($p^\circ = 0.1$ MPa) enthalpies of formation of the gaseous compounds have been calculated. Standard *ab initio* molecular orbital calculations were performed using the G3(MP2)//B3LYP composite procedure and several working reactions in order to derive the standard molar enthalpy of formation of the three compounds. There exists a good agreement between the experimental and the computational data.

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1. Introduction

Benzoxazoles are well known medical relevant organic compounds due to their recognized biological and therapeutic properties [1–3], related with the inherent antiviral, antimicrobial, or antibiotic activities. These heterocyclic derivatives constitute basic structural fragments in a wide range of natural products which makes them attractive targets in drug synthesis [4]. On the other hand, this kind of molecule constitutes interesting systems for the design and synthesis of liquid crystals compounds [5] with classical rod-like structures: for example, 2-arylbenzoxazole derivatives are well known for their anisotropic molecular shape with an efficient π -electron conjugation along the molecular long axis. The efficiency in π -electron conjugation and the high yielding photoluminescence properties presented by 2-arylbenzoxazole derivatives, assign them as well known fluorescent materials and laser dyes, being also considered core advanced materials for organic light-emitting diodes (OLED) [6] and non-linear optics (NLO) [7].

These compounds participate in many different reaction mechanisms and, consequently, the understanding of their reactivity on

the chemical and/or biochemical processes, in which these species are involved, benefits with the knowledge of the thermochemical parameters for the isolated species. In the literature, there exist scattered data for some heterocyclic compounds containing the oxygen and nitrogen heteroatoms in a pentagonal ring, from which we highlight those reported by McCormick *et al.* [8] and Steele *et al.* [9], respectively, for the enthalpies of formation of oxazole and benzoxazole, in the gaseous state. Hilal *et al.* [10] have computed the proton affinities of benzoxazole and benzothiazole. More recently, several other experimental and computational studies have also been described in the literature for 2-benzoxazolinone and 2-benzimidazolinone [11], 1,3-oxazolidine-2-thione [12] and 3H-1,3-benzoxazole-2-thione [13]. Gomes *et al.* [14] estimated the enthalpy of formation of benzoxazole from B3LYP calculations and presented a value more than 10 $\text{kJ} \cdot \text{mol}^{-1}$ lower than that from the experiments [9].

The present work is part of an extensive and systematic study on the thermochemical properties of 1,3-azoles compounds, containing the pentagonal heterocyclic ring fused to a benzenic ring, in order to evaluate the energetic effect of different substituents on the rings [15,16]. We report new experimental results for the energies of combustion and the enthalpies of phase transition of benzoxazole and two benzoxazole chlorinated derivatives (figure 1), measured by static or rotating bomb calorimetry, at

* Corresponding author. Tel.: +351 220 402 538; fax: +351 220 402 522.

E-mail address: mdsilva@fc.up.pt (M.D.M.C. Ribeiro da Silva).

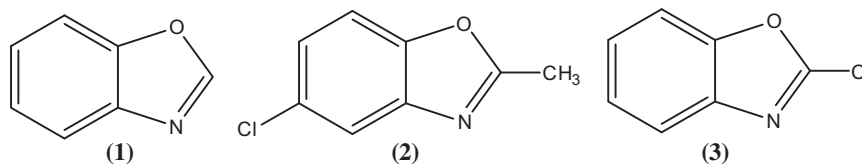


FIGURE 1. Structures of (1) benzoxazole, (2) 5-chloro-2-methylbenzoxazole, and (3) 2-chlorobenzoxazole.

$T = 298.15$ K, and high temperature Calvet microcalorimetry, respectively. From these results, the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation of the three benzoxazole derivatives, in condensed and gaseous states, were derived.

Additionally, the gas-phase standard molar enthalpies of formation of these compounds were estimated computationally as well as their gas-phase basicity, proton and electron affinity and adiabatic ionization enthalpy.

The new measurements for the enthalpies of formation and sublimation of crystalline benzoxazole, at $T = 298.15$ K, have been performed experimentally in the sequence of the disagreement obtained between the experimental and computational studies, for which the value of enthalpy of formation of benzoxazole in the gaseous phase is a key value.

The results obtained allow determination of both the general behavior and the individual difference of correlations between energetic parameters and structural characteristics, which are important to evaluate the reactivity of the species.

2. Experimental

2.1. Materials and purity control

The benzoxazole (CAS No. 273-53-0) was supplied by Sigma-Aldrich with a purity of 0.975 mole fraction and purified by sublimation under reduced pressure. The 5-chloro-2-methylbenzoxazole (CAS No. 19219-99-9) was obtained commercially from TCI Europe with a purity of 0.994 mole fraction and purified by sublimation under reduced pressure. The 2-chlorobenzoxazole (CAS No. 615-18-9) was supplied by Alfa Aesar with a purity of 0.996 mole fraction and purified by fraction distillation under reduced pressure ($T = 363$ K and $p = 3000$ Pa). The purity of each compound was confirmed by gas chromatography, yielding mole fraction greater than 0.999. The provenance and purity of the compounds used are listed in table 1. The benzoic acid used in the calibration of the static and rotating bombs was the NIST Standard Reference Material (SRM 39j), while naphthalene and *n*-undecane, both supplied by Aldrich Chemical Co. with mass fraction purity 0.99+, were used to calibrate the Calvet microcalorimeter.

The literature values of the specific densities used were $\rho = 1.1754$ g · cm⁻³ for benzoxazole [17], $\rho = 1.2191$ g · cm⁻³ for 5-chloro-2-methylbenzoxazole [17], and $\rho = 1.390$ g · cm⁻³ for 2-chlorobenzoxazole [18], and the relative atomic masses used for the elements were the ones recommended by the IUPAC Commission in 2009 [19].

The temperature and the enthalpy of fusion for the 5-chloro-2-methylbenzoxazole, respectively, $T_{\text{fus}} = (328.8 \pm 0.1)$ K and

$\Delta_{\text{cr}}^1 H_{\text{m}}^\circ(T_{\text{fus}}) = (20.2 \pm 0.2)$ kJ · mol⁻¹, were determined by differential scanning calorimetry (DSC, Setaram DSC 141). No phase transitions were detected in the crystalline phase, between $T = 298$ K and the temperature of fusion of the compound.

2.2. Static-bomb calorimetry

The standard ($p^\circ = 0.1$ MPa) massic energy of combustion of benzoxazole was measured in an isoperibol static-bomb combustion calorimeter, with a twin valve bomb of an internal volume of 0.290 dm³, that has been used formerly at the National Physical Laboratory, in Teddington [20], and in Manchester [21]. This calorimeter has been transferred to Porto, where it has undergone a few changes. Only a brief description is made, since the apparatus and the technique have been already described [22].

The calorimeter temperatures were measured at $\pm 10^{-4}$ K, with a S10 four wire calibrated ultra-stable thermistor probe (Thermometrics, standard serial No. 1030) and recorded by a high sensitivity nanovolt/microohm meter (Hewlett-Packard, HP 34420 A) interfaced to a PC, which registers changes in adiabatic temperature. Temperature measurements were automatically collected every 10 s and the initial temperature was as close as possible to $T = 298.15$ K.

The calorimetric system was calibrated using benzoic acid (NBS 39j) having a massic energy of combustion, under standard bomb conditions, of $-(26434 \pm 3)$ J · g⁻¹. The calibration results were corrected to an energy equivalent, ϵ_{cal} , corresponding to an average mass of water added to the calorimeter of 2900.0 g. Six calibration experiments were made in an oxygen atmosphere at $p = 3.04$ MPa, with 1.00 cm³ of deionised water added to the bomb, leading to an energy equivalent of the calorimeter of $\epsilon_{\text{cal}} = (15551.2 \pm 1.6)$ J · K⁻¹, where the uncertainty quoted is the standard deviation of the mean.

The samples of benzoxazole, enclosed in Melinex bags, were ignited in an oxygen atmosphere at $p = 3.04$ MPa, at $T = 298.15$ K, with 1.00 cm³ of deionised water added to the bomb. The Melinex bags, with the specific energy of combustion of dry Melinex $-(22902 \pm 5)$ J · g⁻¹, were made according to the technique described by Skinner *et al.* [23] and for the cotton thread fuse (empirical formula CH_{1.686}O_{0.843}), $\Delta_{\text{c}} u^\circ = -16240$ J · g⁻¹ [24]; both values have been previously confirmed in our laboratory. The electric energy for ignition was determined from the change in potential difference on discharge of a 1400 μ F condenser across a platinum wire. A value for the pressure coefficient of specific energy $(\partial u/\partial p)_T = -0.2$ J · g⁻¹ · MPa⁻¹ at $T = 298.15$ K, a typical value for organic compounds was assumed. The amount of the compound burnt in each experiment was determined from the total mass of

TABLE 1

Source, purification, and analysis details of the studied samples.

Chemical name	Provenance	Minimum initial mole fraction purity	Purification method	Final mole fraction purity	Analytical method
Benzoxazole	Sigma-Aldrich	0.98	Sublimation	0.9999	GC ^a
5-Chloro-2-methyl-benzoxazole	TCI Europe	0.98	Sublimation	0.9997	GC ^a
2-Chlorobenzoxazole	Alfa-Aesar	0.99	Distillation	0.9991	GC ^a

^a GC – Gas-liquid chromatography.

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