



Experimental and computational study of the energetics of hydantoin and 2-thiohydantoin

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G3(MP2)//B3LYP composite method

ABSTRACT

This work reports an experimental and a theoretical study of two imidazolidine derivatives, hydantoin (CAS No. 461-72-3) and 2-thiohydantoin (CAS No. 503-87-7).

The standard ($p^\circ = 0.1$ MPa) molar energies of combustion of hydantoin and 2-thiohydantoin were measured by static and rotating bomb combustion calorimetry, respectively. The standard molar enthalpies of sublimation, at $T = 298.15$ K, were derived from the temperature dependence of the vapour pressures of these compounds, measured by the Knudsen-effusion technique, and from high temperature Calvet microcalorimetry. The conjugation of these experimental results enables the calculation of the standard molar enthalpies of formation in the gaseous state, at $T = 298.15$ K, which are discussed in terms of structural contributions.

We have also estimated the gas-phase enthalpy of formation from high-level *ab initio* molecular orbital calculations at the G3MP2B3 level of theory, being the computed values in good agreement with the experimental ones. Furthermore, this composite approach was also used to obtain information about the gas-phase basicities, proton and electron affinities and adiabatic ionization enthalpies.

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1. Introduction

The hydantoin nucleus corresponds to a five membered heterocycle, containing a reactive cyclic urea core. This imidazolidine structure is present in a wide range of biologically active compounds with important applications in medicinal fields, such as antitumor [1] and anti-arrhythmic agents [2], anti-cancer drugs [3] having also agrochemical applications (bactericides and fungicides) [4]. Therefore, the knowledge of the physico-chemical properties of this type of compounds is important, particularly those properties that are related with their reactivity.

The thermochemical data available for imidazolidine derivatives do not allow a sustained interpretation about the behaviour of such species. Experimental and computational studies for compounds with pentagonal ring cores, with two nitrogen atoms or a nitrogen and an oxygen or sulfur as heteroatoms, in the positions 1,3-, has been studied recently [5–8]. Other studies on the energetic of five-membered nitrogen heterocycles fused to a benzenic ring [9–11] have been also described in the recent literature. For hydantoin, there are studies [12] reporting the determination of the corresponding enthalpies of combustion and formation in the

crystalline phase, although the results do not match with those obtained for related compounds and those presented in this work.

We are involved in an extensive study on the energetics of compounds having a five-membered ring with one nitrogen heteroatom and a second heteroatom (nitrogen, oxygen or sulfur) on a meta-position relatively to the first nitrogen. The present work reports thermodynamic experimental results on hydantoin and 2-thiohydantoin (structural formula represented in figure 1), in order to contribute for their thermodynamic characterization. The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in crystalline phase, $\Delta_f H_m^\circ(\text{cr})$, at $T = 298.15$ K, of both compounds were derived from their standard molar energies of combustion, in oxygen, at the temperature of 298.15 K, measured by static or rotating bomb combustion calorimetry. The standard molar enthalpies of sublimation of those compounds, $\Delta_{\text{cr}}^g H_m^\circ$, at $T = 298.15$ K, were derived indirectly from the temperature dependence of the vapour pressures of these compounds, measured by the Knudsen-effusion technique, and directly using high temperature Calvet microcalorimetry. From the experimental results, the standard molar enthalpies of formation in the gaseous state, at $T = 298.15$ K, were derived and are discussed in terms of structural contributions, in order to evaluate the energetic effects associated to the replacement of a C=O group by a C=S group in the ring.

Additionally, through high level *ab initio* calculations, the gas-phase standard molar enthalpies of formation of these compounds

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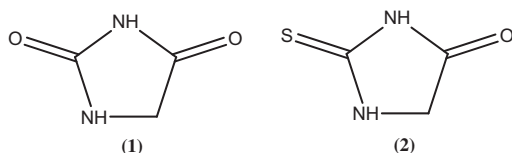


FIGURE 1. Structural formula of the two imidazolidine derivatives studied: (1) hydantoin, (2) 2-thiohydantoin.

as well as the gas-phase basicities, proton and electron affinities and adiabatic ionization enthalpies, were estimated.

2. Experimental

2.1. Materials

Hydantoin (CAS No. 461-72-3) and 2-thiohydantoin (CAS No. 503-87-7) were supplied by Alfa Aesar with lot certificated purity of 0.994 and 0.997 mass fraction, respectively. Both compounds were purified by repeated sublimation under reduced pressure. The purity of the samples was confirmed by gas chromatography, yielding molar fractions higher than 0.999. The initial and final purities of the samples are presented in [table 1](#).

The structures of both purified samples were confirmed by electrospray ionization-ion trap mass spectrometry (ESI-IT MS) and by proton (^1H -) and carbon (^{13}C -) nuclear magnetic resonance (NMR). All spectroscopic data and spectral traces are supplied in the [Supplementary Material](#).

For the calibration of the static and rotating bombs, benzoic acid NBS SRM 39j was used, while anthracene (Aldrich Chemical Co., zone-refined 99+%) was used to calibrate the Calvet microcalorimeter. Three high-purity reference materials [13]: benzoic acid (NIST Standard Reference Material 39i), tin and indium (Aldrich, mass fraction > 0.99999) were used to calibrate the temperature scale of the differential scanning calorimeter (DSC), whereas the power scale was calibrated with a highly pure indium sample.

The specific densities of the compounds studied were taken from literature, as $\rho = 1.3105 \text{ g} \cdot \text{cm}^{-3}$ for hydantoin [14] and $\rho = 1.3456 \text{ g} \cdot \text{cm}^{-3}$ for 2-thiohydantoin [14], and the relative atomic masses used for the elements were the ones recommended by the IUPAC commission in 2009 [15].

2.2. Enthalpies and temperatures of fusion

The temperatures and the enthalpies of fusion of the two compounds were determined using a differential scanning calorimetry (DSC, Setaram DSC 141). The samples were sealed in aluminium crucibles and five runs were done for each compound, under nitrogen atmosphere, using a heating rate of $3.3 \times 10^{-2} \text{ K} \cdot \text{s}^{-1}$. The temperature and power scales of the calorimeter were calibrated under the same conditions as the experimental determinations.

The temperature and the enthalpy of fusion obtained for hydantoin were $T_{\text{fus}} = (495.8 \pm 0.2) \text{ K}$ and $\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ}(T_{\text{fus}}) = (24.8 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$. For 2-thiohydantoin, the results $T_{\text{fus}} = (506.1 \pm 0.5) \text{ K}$ and $\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ}(T_{\text{fus}}) = (27.1 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$ were obtained. No phase transitions were

detected in the crystalline phase, between $T = 298 \text{ K}$ and the temperature of fusion of each compound.

2.3. Combustion calorimetry

The standard ($p^{\circ} = 0.1 \text{ MPa}$) massic energy of combustion of hydantoin and 2-thiohydantoin were determined using two different isoperibol bomb combustion calorimeters:

- (i) Static-bomb calorimeter with a twin valve bomb and an internal volume of 0.290 dm^3 , with a detailed description in the literature [16]. The calorimeter temperatures were measured to $\pm (1 \times 10^{-4}) \text{ K}$, at time intervals of 10 s, 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. The initial temperature was close to $T = 298.15 \text{ K}$.
- (ii) Rotating-bomb calorimeter with a stainless steel twin valve bomb, lined with platinum, whose internal volume is 0.258 dm^3 , previously described in the literature [17]. The calorimeter temperatures were measured to $\pm (1 \times 10^{-4}) \text{ K}$, at time intervals of 10 s, using a Hewlett-Packard (HP-2804 A) quartz thermometer, interfaced to a PC. The final temperature was close to $T = 298.15 \text{ K}$ and the bomb rotation was started when the temperature rise in the main-period reached about 0.63 of its total value, and continued until the end of each experiment.

The two calorimetric systems were calibrated using benzoic acid having a massic energy of combustion, under standard bomb conditions, of $-(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$. The calibration results were corrected to give an energy equivalent, ε_{cal} , corresponding to an average mass of water added to the static-bomb or rotating-bomb calorimeters of 2900.0 g or 5222.5 g, respectively. For the static calorimeter system, six calibration experiments were made in an oxygen atmosphere at $p = 3.04 \text{ MPa}$, with 1.00 cm^3 of deionised water added to the bomb, leading to an energy equivalent of the calorimeter of $\varepsilon_{\text{cal}} = (15551.7 \pm 1.2) \text{ J} \cdot \text{K}^{-1}$. For the rotating calorimeter system, six calibration experiments were made in the conditions above referred and without rotation, yielding an energy equivalent of the calorimeter of $\varepsilon_{\text{cal}} = (25157.4 \pm 1.1) \text{ J} \cdot \text{K}^{-1}$. The uncertainties mentioned are the standard deviations of the means.

The samples of the two compounds, in pellet form, were ignited in an oxygen atmosphere ($p = 3.04 \text{ MPa}$), with 1.00 cm^3 and 20.00 cm^3 of deionised water added to the bomb, for hydantoin and 2-thiohydantoin, respectively. *n*-Hexadecane (Aldrich, Gold Label), with a massic energy of combustion of $\Delta_{\text{c}} u^{\circ} = -(47126.0 \pm 4.1) \text{ J} \cdot \text{g}^{-1}$, was used as auxiliary of combustion to produce an appropriate temperature rise. For the cotton thread fuse (empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$), $\Delta_{\text{c}} u^{\circ} = -16240 \text{ J} \cdot \text{g}^{-1}$ [18]; 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 $1400 \mu\text{F}$ condenser across a platinum wire. A value for the pressure coefficient of specific energy $(\partial u / \partial p)_{\text{T}} = -0.2 \text{ J} \cdot \text{g}^{-1} \text{ MPa}^{-1}$ at $T = 298.15 \text{ K}$, a typical value for organic compounds was assumed [19]. For the static-bomb, the amount of

TABLE 1

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

Chemical name	Source	Lot certificate purity	Purification method	Final molar purity	Analysis method
Hydantoin	Alfa-Aesar	0.994	Sublimation	0.9993	GC ^a
2-Thiohydantoin	Alfa-Aesar	0.997	Sublimation	0.9995	GC ^a

^a GC – gas-liquid chromatography.

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