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Structural and energetic characterization of anhydrous and hemihydrated 2-mercaptoimidazole: Calorimetric, X-ray diffraction, and computational studies

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ABSTRACT

This paper reports an experimental and theoretical study on the structural and energetic characterization of the 2-mercaptoimidazole (2-MI) in the solid and in the gaseous phases. The single crystal X-ray diffraction determinations on the anhydrous and hemihydrate 2-MI forms were carried out at $T = (296 \pm 2)$ K and $T = (150 \pm 2)$ K, respectively, and suggest that in both forms the 2-MI molecule is closer to the thione conformation, albeit some single bond character is possible.

The energy of combustion of the title compound was measured by rotating-bomb combustion calorimetry, being used to derive the corresponding enthalpy of formation in the crystalline-phase. The enthalpy of sublimation of 2-MI, at $T = 298.15$ K, was obtained from high temperature Calvet microcalorimetry measurements. These two parameters yielded the gas-phase enthalpy of formation, allowing the inherent energetic analysis of the molecule. This result was discussed together with the corresponding predictions for 2-MI and its tautomer, 1,3-dihydro-2*H*-imidazole-2-thione, by the G3 method.

The dehydration reaction of 2-MI · $0.5H_2O$(cr) was also investigated and the corresponding enthalpy of dehydration was determined by Calvet microcalorimetry.

1. Introduction

The intramolecular transfer of a proton from one group to another (figure 1) represents one of the most interesting processes involved in chemical reactions, particularly those related with living systems [1,2]. The thione/thiol tautomeric equilibrium, although less studied than that for oxygen derivatives, has been attracting significant experimental and theoretical interests [3–5]. This attention has essentially been fostered by the wide range of pharmacological activity of the imidazolethiones [6], and also by their applicability in the inorganic field, as dyestuffs, catalysts, and polymerizing agents [7] or as corrosion inhibitors for a variety of metals [8].

Several studies have been reported about the effect of reaction field and hydrogen bonding on the relative energies of protomers applied to the equilibria between hydroxypyridine-pyridone and mercaptopyridine-thiopyridone [9,10] and between methyltropic isomers [11].

Abramov and Trzhtsinskaya [12] reviewed the literature data on the structure, physicochemical properties and transformations of imidazole-2-thiones and their benzo analogs, where it has been confirmed experimentally (NMR spectroscopy and X-ray diffraction analysis) that imidazolethiones present the thione form in the crystalline state and in solution. Moreover, DFT calculations on the tautomerization of 2-mercaptoimidazole led to the conclusion that the thione form is always dominant both in the gas phase and in aqueous solution [13].

Structure-energetic relationships for 2-mercaptoimidazole (2-MI) in the solid and gaseous states were investigated here (i) to evaluate the influence of condensed phase interactions in the thiol/thione tautomeric preferences and (ii) to provide key thermochemical information which is scarce for this type of compounds (enthalpies of formation and sublimation, gas-phase basicities, proton and electron affinities and adiabatic ionization enthalpies). The solid state studies involved X-ray diffraction and calorimetric experiments on anhydrous and hydrated (2-MI · $0.5H_2O$) forms. The gas phase features were probed by combining experimental thermochemical data (*e.g.* enthalpies of

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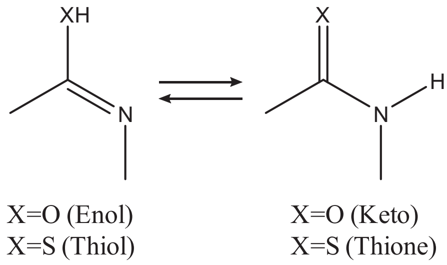

FIGURE 1. Scheme of the tautomeric equilibrium between enol/keto and thiol/thione forms.

formation and sublimation) with structural and energetic information obtained by *ab initio* molecular orbital calculations.

2. Experimental

2.1. Materials

The 2-mercaptoimidazole sample used in the thermochemical measurements (Alfa Aesar, mass fraction 0.989; CAS No. 872-35-5), was purified by repeated sublimation under reduced pressure ($T \sim 443$ K). Gas chromatography analysis indicated that the sublimed sample had a mass fraction purity 0.9999. The analysis was carried out on an Agilent 4890D gas chromatography–flame ionization detector (GC–FID) apparatus, equipped with a HP-5 column (cross-linked 5% diphenyl and 95% dimethylpolysiloxane; 15 · 0.530 mm i.d. with 1.5 μm film thickness); nitrogen was used as the carrier gas. The absence of water in all the samples was confirmed by the nonexistence of the H—O—H bending frequency at 1644 cm^{-1} in the FT-IR spectra (PerkinElmer BX spectrum, with a GladiATR diamond crystal).

2.2. Crystallization of anhydrous and hydrated, 2-mercaptoimidazole

The starting material (2-MI, Alfa Aesar, mass fraction 0.989) used in the preparation of the anhydrous and hemihydrate crystals, was purified by sublimation at $T = 393$ K and 1.33 Pa.

The anhydrous 2-MI crystals were obtained as follows. Ethanol (Fisher Scientific, mass fraction 0.9999) was pre-dried with CaH (Acrös, mass fraction ~0.93) and distilled over metallic sodium under N_2 atmosphere. 2-MI (~0.7 g) was added to 15 cm^3 of ethanol inside a Schlenk tube under N_2 atmosphere. The mixture was magnetically stirred for 1 h at room temperature (291 K). The saturated solution was filtered into another Schlenk tube, under N_2 atmosphere, and left to crystallize in a freezer, at $T = 253$ K. Colorless crystals suitable for single crystal X-ray diffraction analysis were typically formed within three days.

In the case of the 2-mercaptoimidazole hemihydrate, 2-MI · $0.5H_2O$, ~1 g of 2-MI was dissolved in 10 cm^3 of ethanol (Fisher Scientific, mass fraction 0.995, water mass fraction 0.002), at $T = 323$ K, under magnetic stirring. The solution was left to evaporate in air (relative humidity $\Phi \sim 50\%$) at $T = 291$ K during ~1 week. The colorless crystals obtained were stored in a flask, under air, at room temperature.

Table 1 summarizes the provenance, method of purification and type of samples used in experimental measurements.

2.3. X-ray diffraction

X-ray powder diffraction experiments were carried out on a Philips PW1730 diffractometer with automatic data acquisition (APD Philips v.35B), operating in the $\theta - 2\theta$ mode. The apparatus had a vertical goniometer (PW1820), a proportional xenon detector (PW1711), and a graphite monocromator (PW1752). A Cu Kα radiation source was used. The tube amperage was 30 mA and the tube voltage 40 kV. The diffractograms were recorded at room temperature in the range $10° \leqslant 2\theta \leqslant 35°$. Data were collected in the continuous mode, with a step size of 0.015° (2θ) and an acquisition time of 1.5 s per step. The samples were mounted on an aluminum sample holder.

The single crystal X-ray diffraction determinations on the anhydrous and hemihydrate 2-mercaptoimidazole forms were carried out at $T = (296 \pm 2)$ K and $T = 150 \pm 2$ K, respectively, on a Bruker AXS-KAPPA APEX II area detector diffractometer, using graphite-monochromated MoKα ($\lambda = 71.073$ pm) radiation. The X-ray generator was operated at 50 kV and 30 mA and the X-ray data collection was monitored by using the APEX2 program [14]. All data were corrected for Lorentzian, polarization, and absorption effects using the SAINT [14] and SADABS [14] programs. The structures were solved by direct methods with SHELXS-97 [15], and refined by full-matrix least-squares on F^2 with SHELXL-97 [16], both included in WINGX-Version 1.80.05 [17]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located in a Fourier map and their positions and isotropic displacement parameters, Uiso(H), were refined freely. Graphical representations were prepared using Mercury 3.1.1 [18]. PLATON [19] was used for hydrogen bond interactions. A summary of the crystal data, structure solution, and refinement parameters is given in table 2.

2.4. Rotating-bomb combustion calorimetry

The standard ($p° = 0.1$ MPa) massic energy of combustion of the 2-mercaptoimidazole anhydrous was measured in an isoperibol rotating-bomb calorimeter, originally developed at Lund University [20] and installed in the Porto laboratory. The apparatus and procedure were already described and only the most relevant aspects are presented here [21]. The calorimetric system was equipped with a platinum lined stainless steel twin valve bomb of 0.258 dm^3 internal volume. Calorimeter temperatures were measured to ±0.1 mK, at time intervals of 10 s, using a quartz thermometer (Hewlett–Packard, HP-2804A). The final temperature was close to 298.15 K and the bomb rotation was started when the temperature rise in the main-period reached about 0.63 of its total value [22].

The energy equivalent of the calorimeter was determined using benzoic acid (NIST SRM 39j), with a certified massic energy of combustion, under standard bomb conditions, of $-(26434 \pm 3)\ \text{J} \cdot \text{g}^{-1}$. Calibration experiments were made in oxygen at 3.04 MPa, with 1.00 cm^3 of water added to the bomb, without bomb rotation. The energy equivalent of the calorimeter was $\varepsilon_{\text{cal}} = (25146.4 \pm 1.3)\ \text{J} \cdot \text{K}^{-1}$, where the assigned uncertainty is the standard error of the mean of six independent experiments. The ε_{cal} value refers to an average mass of water added to the calorimeter of 5222.5 g.

The solid samples were burnt in pellet form, under an oxygen pressure of 3.04 MPa, in the presence of 15.00 cm^3 of deionized water, to ensure the formation of $H_2SO_4 \cdot 115H_2O(l)$. *n*-Hexadecane (Aldrich, Gold Label), with a massic energy of combustion $\Delta_c u° = -(47126.0 \pm 4.1)\ \text{J} \cdot \text{g}^{-1}$, was used as combustion aid to produce an appropriate temperature rise and to ensure a complete reaction. The cotton thread fuse, of empirical formula $CH_{1.686}O_{0.843}$, had a standard massic energy of combustion $\Delta_c u° = -16240\ \text{J} \cdot \text{g}^{-1}$ [23]. The ignition energy was determined from the change in potential difference on discharge of a 1400 μF condenser across a platinum wire.

The standard massic energy of combustion, $\Delta_c u°$, of 2-MI was calculated by a similar procedure to that developed by Hubbard et al. [24] for compounds with general formula $C_aH_bO_cN_d$, and extended by Good et al. [25] to sulfur compounds. The following auxiliary data at $T = 298.15$ K were used: specific density,