



Experimental and computational energetic study of two halogenated 2-acetylpyrrole derivatives: 2-Trichloroacetylpyrrole and 2-trifluoroacetylpyrrole

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ABSTRACT

The present work reports the values of the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the crystalline phase, of 2-trichloroacetylpyrrole and 2-trifluoroacetylpyrrole, which were derived from the standard molar energies of combustion, in oxygen, to yield $\text{HCl}\cdot 600\text{H}_2\text{O}(\text{l})$ and $\text{HF}\cdot 10\text{H}_2\text{O}(\text{l})$, respectively, as well as $\text{CO}_2(\text{g})$ and $\text{N}_2(\text{g})$, at $T = 298.15$ K, measured by rotating bomb combustion calorimetry. The values of the standard molar enthalpies of sublimation, at $T = 298.15$ K, derived from the Knudsen mass-loss effusion technique are also presented. From the above mentioned experimental quantities, the standard molar enthalpies of formation, in the gaseous phase, were derived: $\Delta_f H_m^\circ(2\text{-trichloroacetylpyrrole, g}) = -(102.5 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H_m^\circ(2\text{-trifluoroacetylpyrrole, g}) = -(704.7 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$. These experimental values are compared with estimates based on high-level *ab initio* molecular orbital calculations at the G3(MP2)//B3LYP level, which have also been extended to the calculation of other thermodynamic properties namely N–H bond dissociation enthalpies, gas-phase acidities and basicities, proton affinities, and adiabatic ionization enthalpies.

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1. Introduction

The pyrrole ring is the basic chemical structure of many pharmacologically active molecules and biologically relevant natural products. Thus, a wide range of synthetic drugs with high therapeutic potential incorporates this heterocyclic moiety [1,2]. Porphyrin is an important cyclic tetrapyrrole that is the core structure of heme and chlorophyll. Moreover, polymers incorporating pyrrole units have interesting chemical, thermal, and electrical properties, and are promising candidates for use as battery materials and catalysts [3]. Both halogenated title compounds are widely used in synthetic organic chemistry. The 2-trichloroacetylpyrrole is used in the synthesis of naturally occurring pyrrole alkaloids, extracted from marine sponges [4–6]; these alkaloids have found applications in the treatment of neurodegenerative disorders, diabetes, cancer, inflammatory pathologies, and ocular diseases. Furthermore, 2-trichloroacetylpyrrole is used as starting material in the preparation of antibacterial agents of potential interest in human chemotherapy [7]. 2-Trifluoroacetylpyrrole is employed in the synthesis of trifluoromethylamines, which are precursors of biological molecules [8].

Thermochemical data, namely enthalpies of formation and bond dissociation enthalpies, are of crucial importance in establishing energetics–structure–reactivity relationships. These ther-

mochemical parameters are fundamental to several fields ranging from chemistry, medicine, pharmaceutical sciences, biology, environmental, and industrial chemistry. They provide information concerning stability, reactivity, and biodegradability of chemical compounds in the environment, helpful in choosing the most appropriate method for their elimination. Despite the large number of important applications of pyrrole derivatives, information on their energetic properties is still scarce.

In order to improve this situation, we are presently involved in a study of thermodynamic and thermochemical properties of pyrrole derivatives, in which the main goal is to analyze and evaluate the enthalpic effects produced by different substituent groups in this family of compounds. In recent work we reported experimental and theoretical thermochemical studies of some pyrrole derivatives, in particular 2- and 3-acetylpyrroles [9], 2-pyrrolecarboxylic acid and 1-methyl-2-pyrrolecarboxylic acid [10], 2- and 3-acetyl-1-methylpyrroles [11], 1-phenylpyrrole and 1-(4-methylphenyl)pyrrole [12]. In this work, we have carried out the experimental determination of the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the gaseous phase, at $T = 298.15$ K, of two halogenated 2-acetylpyrrole derivatives: 2-trichloroacetylpyrrole and 2-trifluoroacetylpyrrole (figure 1). The standard molar enthalpies of formation, in the crystalline phase, of both compounds, were obtained by rotating bomb combustion calorimetry and their standard molar enthalpies of sublimation were determined using the Knudsen mass-loss effusion technique, by means of the Clausius–Clapeyron equation. Furthermore, we have also

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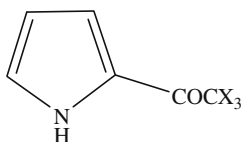


FIGURE 1. Structural formula of 2-trichloroacetylpyrrole ($X = \text{Cl}$) and 2-trifluoroacetylpyrrole ($X = \text{F}$).

performed high-level *ab initio* molecular orbital calculations at the G3(MP2)//B3LYP level, from which the gas-phase standard molar enthalpies of formation were estimated, as well as N–H bond dissociation enthalpies, gas-phase acidities and basicities, proton affinities and adiabatic ionization enthalpies.

2. Experimental

2.1. Materials and purity control

The 2-trichloroacetylpyrrole [CAS 35302-72-8] and 2-trifluoroacetylpyrrole [CAS 2557-70-2] were supplied from Sigma–Aldrich Chemical Co., with a minimum mass fraction purity of 0.99. The two crystalline compounds were purified by repeated vacuum sublimations and the final purity of each one was checked by gas–liquid chromatography. No impurities greater than 10^{-3} in mass fraction were found in each respective sample.

The specific densities for 2-trichloroacetylpyrrole and 2-trifluoroacetylpyrrole were taken as, $\rho = (1.602 \text{ and } 1.488) \text{ g} \cdot \text{cm}^{-3}$, respectively, determined from the ratio mass/volume of a pellet of the compound (made in vacuum, with an applied pressure of $10^5 \text{ kg} \cdot \text{cm}^{-2}$).

2.2. Combustion calorimetry

The standard ($p^\circ = 0.1 \text{ MPa}$) molar energies of combustion of 2-trichloroacetylpyrrole and 2-trifluoroacetylpyrrole were measured in two different isoperibol rotating bomb calorimetric systems:

(i) The calorimetric study of 2-trichloroacetylpyrrole was carried out in an isoperibol rotating bomb combustion calorimeter, previously described in the literature [13,14], equipped with a twin valve bomb lined with tantalum, with an internal volume of 0.329 dm^3 . This system was calibrated with benzoic acid NIST Thermochemical Standard 39i, with a certified massic energy of combustion, under bomb conditions of $-(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$ [15]. The value of the energy equivalent of the calorimeter was found to be $\varepsilon(\text{calor}) = (20369.0 \pm 2.3) \text{ J} \cdot \text{K}^{-1}$, for an average mass of water added to the calorimeter of 3969.2 g, where the quoted uncertainty refers to the standard deviation of the mean. The crystalline samples of 2-trichloroacetylpyrrole were ignited in pellet form at a pressure $p = 3.04 \text{ MPa}$ of oxygen and in the presence of 25.00 cm^3 of aqueous solution of $\text{As}_2\text{O}_3(\text{aq})$ $0.09073 \text{ mol} \cdot \text{dm}^{-3}$, which reduces all the free chlorine produced in the combustion to hydrochloric acid. The *n*-hexadecane (Aldrich, mass fraction >0.999), stored under nitrogen, was used as a combustion auxiliary, for the purpose of avoiding carbon soot residue formation. Its mass-related energy of combustion was found to be $\Delta_c u^\circ = -(47132.7 \pm 2.6) \text{ J} \cdot \text{g}^{-1}$.

After the combustion experiment, the remaining quantity of $\text{As}_2\text{O}_3(\text{aq})$ was determined by titration with a standardized iodine solution and the nitric acid formed was analysed by the Devarda's alloy method [16]. The energy of oxidation of aqueous As_2O_3 to As_2O_5 , $\Delta U(\text{As}_2\text{O}_3)$, was calculated following the procedure described by Hu *et al.* [17] using the value of the enthalpy of oxidation of $\text{As}_2\text{O}_3(\text{aq})$ by Cl_2 , determined by Sunner and Thorén [18] and the thermal effects of mixing $\text{As}_2\text{O}_5(\text{aq})$ with strong acids

[19]. The amount of $\text{H}_2\text{PtCl}_6(\text{aq})$ was determined from the loss of mass of the platinum crucible, and the energy correction was based on $\Delta_f H_m^\circ(\text{H}_2\text{PtCl}_6, \text{aq}) = -(676 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$ [20]. In the cases where a small amount of carbon residue soot was formed in the platinum crucible, the necessary energetic correction for its formation was based on $\Delta_c u^\circ = -33 \text{ kJ} \cdot \text{g}^{-1}$ [21]. The standard state corrections, ΔU_S , were calculated following the method given by Hubbard *et al.* [22] using the solubility constants and energies of solution of CO_2 and O_2 as given by Hu *et al.* [17].

(ii) The enthalpy of combustion of 2-trifluoroacetylpyrrole was measured in another calorimeter using an isoperibol rotating bomb calorimeter, developed in Lund, Sweden, by Sunner [23]. This system, already described in the literature [24], is equipped with a twin valve platinum lined bomb, whose internal volume is 0.258 cm^3 .

Benzoic acid NIST Thermochemical Standard 39j [25] was also used for calibration of this bomb. From seven calibration experiments the value of the energy equivalent of the calorimeter was determined as $\varepsilon(\text{calor}) = (25157.4 \pm 1.1) \text{ J} \cdot \text{K}^{-1}$, for an average mass of water added to the calorimeter of 5222.5 g; the quoted uncertainty is the standard deviation of the mean.

The 2-trifluoroacetylpyrrole was burnt in pellet form enclosed in previously weighed polyethylene bags, $\{\Delta_c u^\circ = -(46282.4 \pm 4.8) \text{ J} \cdot \text{g}^{-1}$, a value determined in our laboratory}, under oxygen at $p = 3.04 \text{ MPa}$ and with 10.00 cm^3 of deionised water placed in the bomb, to yield an acid of uniform and well-defined concentration.

In 2-trifluoroacetylpyrrole, the atomic ratio of hydrogen to fluorine is very close to the unity; the combustion reaction can yield a mixture of hydrogen fluoride and carbon tetrafluoride as fluorine combustion products. To prevent and avoid the formation of carbon tetrafluoride, a rich hydrogen containing compound was used to ensure that the hydrogen to fluorine atomic ratio is greater than the unity. Therefore, in the combustion experiments of 2-trifluoroacetylpyrrole, the polyethylene was used with a double purpose: to enclose this fluorine compound due to its high volatility and to increase the atomic ratio of hydrogen to fluorine. The nitric acid formed in the combustion experiments of this fluorine compound was also determined using the Devarda's alloy method [16]. The corrections to the standard state to calculate the standard massic energy of combustion, $\Delta_c u^\circ$, were made by the procedure given by Good and Scott [26] for fluorine containing compounds. The corrections were based on the method implemented by Hubbard *et al.* [22] and included the values of the solubility of CO_2 in HF solutions, as recommended by Cox *et al.* [27].

For both halogenated compounds, the calibration experiments were carried out in oxygen, at a pressure of 3.04 MPa, with 1.00 cm^3 of deionised water introduced into the bomb, according to the procedure suggested by Coops *et al.* [21], without bomb rotation.

The calorimeter temperature readings were collected at time intervals of 10 s, with a precision of $\pm(1 \cdot 10^{-4}) \text{ K}$, with a quartz crystal thermometer (Hewlett Packard HP 2804 A), interfaced to a PC programmed to compute the adiabatic temperature change, through the LABTERMO program [28]. In all experiments, the ignition temperature was chosen so that the final temperature was as close as possible to 298.15 K and the rotation of the bomb was started when the temperature rise in the main period reached about 63% of its final value and continued throughout the experiment, according to the procedure recommended by Good *et al.* [29]. In this way, the frictional work produced by the bomb rotation is included in the correction for heat exchange and work of stirring. The electrical energy for the ignition was determined from the change in potential across a condenser when *ca.* 40 V were discharged through a platinum wire of diameter 0.05 mm. The empirical formula and the massic energy of combustion of the cotton

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