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Reprint of: Energetics and molecular structure of alkyl 1-methylpyrrolecarboxylates (alkyl = methyl or ethyl)

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Methyl 1-methyl-3-pyrrolecarboxylate
Ethyl 1-methyl-2-pyrrolecarboxylate
Ethyl 1-methyl-3-pyrrolecarboxylate

ABSTRACT

Calorimetric techniques, namely static bomb calorimetry and high temperature Calvet microcalorimetry were used to derive, respectively, the standard ($p^o = 0.1$ MPa) molar enthalpy of formation, in the liquid phase, $\Delta_f H_m^o$ (l), and the standard molar enthalpy of vaporization, at $T = 298.15$ K, $\Delta_l^g H_m^o$, of the methyl 1-methyl-2-pyrrolecarboxylate (M1M2PC). These experiments allowed the determination of its standard ($p^o = 0.1$ MPa) molar enthalpy of formation, in the gaseous phase, $\Delta_f H_m^o$ (g) = $-(270.3 \pm 2.2)$ kJ · mol^{-1}, at $T = 298.15$ K.

Additionally, the standard molar enthalpy of formation of M1M2PC was estimated by computations based on standard *ab initio* molecular calculations at the G3(MP2)//B3LYP level. The estimated values are in very good agreement with experimental one, giving us support to estimate the gas-phase enthalpies of formation of the methyl 1-methyl-3-pyrrolecarboxylate (M1M3PC), ethyl 1-methyl-2-pyrrolecarboxylate (E1M2PC) and ethyl 1-methyl-3-pyrrolecarboxylate (E1M3PC), that were not studied experimentally. The molecular structures of the four molecules were established and the structural parameters were determined at the B3LYP/6-31G(d) level of theory. Furthermore, all the results were interpreted in terms of enthalpic increments.

1. Introduction

Experimental and computational thermodynamic studies of pyrrole derivatives, with different substituent groups [1–13], have been developed in our Research Group during the last few years, with the main goal to correlate the effects of the corresponding molecular structures on the energetic characteristics of the compounds. Pyrrole moiety is the structural core of the naturally-occurring porphyrins, the tetrapyrrolic "pigments of life", which include the hemoglobin, porphyrins, corrins, vitamin B_{12}, the bile pigments and chlorophyll, playing an important role in respiration and photosynthesis processes [14–18]. Moreover, pyrrole and derivatives scaffolds are widely used as precursors in the synthesis of drugs with high therapeutical potential [19–30], polymers and new materials [31–37]. In this context, the knowledge of the molecular energetics of the core units is of great importance to understand the activity and the chemical behaviour of larger molecules involving them.

Following the same line of research, in the present work, we report an experimental and computational study on the energetic and structural properties of several alkyl 1-methylpyrrolecarboxylates (alkyl = methyl or ethyl), which are intended to be used as a building blocks of porphyrins, polypyrroles and medicines. An extensive characterization of molecules, in particular their energetic properties, is of high relevance, to a better knowledge about their reactivity and it is essential for studies of chemical equilibrium, kinetics and stability.

In this context, we report both the experimental standard ($p° = 0.1$ MPa) molar enthalpy of formation, in the liquid phase, and the standard molar enthalpy of vaporization, at $T = 298.15$ K, of the methyl 1-methyl-2-pyrrolecarboxylate (M1M2PC – figure 1) obtained, respectively, by static bomb combustion calorimetry and high temperature Calvet microcalorimetry. From these results, the standard ($p° = 0.1$ MPa) molar enthalpy of formation of the compound, in the gaseous phase, was derived. The G3(MP2)//B3LYP approach allowed the estimation of the gas-phase standard molar enthalpy of formation of M1M2PC, which was compared with the experimental value. These calculations were further extended to other alkyl 1-methylpyrrolecarboxylates, namely M1M3PC, E1M2PC and E1M3PC, whose study was not performed experimentally. Computationally, the molecular structures of the four molecules were established and the geometrical parameters were determined at the B3LYP/6-31G(d) level of theory.

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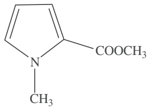


FIGURE 1. Structural formula for the methyl 1-methyl-2-pyrrolecarboxylate (M1M2PC).

2. Experimental

2.1. Compounds and purity control

The origin and purification details of the sample of M1M2PC used in this work are summarized in table 1. Its final purity was also checked by the percentage of carbon dioxide recovered during the combustion experiments; the average ratio of the mass of carbon dioxide recovered to those calculated from the mass of samples used in each experiment, together with the uncertainty (twice the standard deviation of the mean) was (1.0009 ± 0.0001).

The specific density of M1M2PC, used to calculate the true mass from apparent mass in air, was $\rho = 1.07\ \mathrm{g \cdot cm^{-3}}$ [38]. The atomic weights used in this paper were those recommended by the IUPAC Commission in 2009 [39].

2.2. Combustion calorimetry

An isoperibol static bomb calorimeter, equipped with a twin valve bomb made of stainless steel and with an internal volume of $0.342\ \mathrm{dm^3}$, was used to measure the enthalpy of combustion of M1M2PC. Both the apparatus and the operating technique have been previously described [11,40,41].

The calorimetric system was calibrated following the procedure of Coops *et al.* [42] with benzoic acid NIST Standard Reference Material, sample 39j, [43]. The energy equivalent of the calorimeter was found to be $\varepsilon(\mathrm{calor}) = (15995.3 \pm 2.0)\ \mathrm{J \cdot K^{-1}}$, as a mean of six calibration experiments, for an average mass of water added to the calorimeter of 3119.6 g; the quoted uncertainty refers the standard deviation of the mean.

The liquid M1M2PC was burnt contained in previously weighed polyester bags made of melinex, 0.025 mm of thickness, $\Delta_c u^o(\mathrm{melinex}) = -(22902 \pm 5)\ \mathrm{J \cdot g^{-1}}$ [44]. The energetic effect for the amount of nitric acid produced in the combustion has been determined as it is reported in previous studies [11]. The amount of compound, $m(\mathrm{cpd})$, used in each experiment and on which the energy of combustion was based, was determined from the mass of CO_2 produced, taking into account that formed from the combustion of the cotton thread fuse and of the melinex. The corrections to the standard state, ΔU_Σ, and the calculation of the standard massic energies of combustion of both compounds, $\Delta_c u^o$, were made following the procedure given by Hubbard *et al.* [45].

2.3. High temperature Calvet microcalorimetry

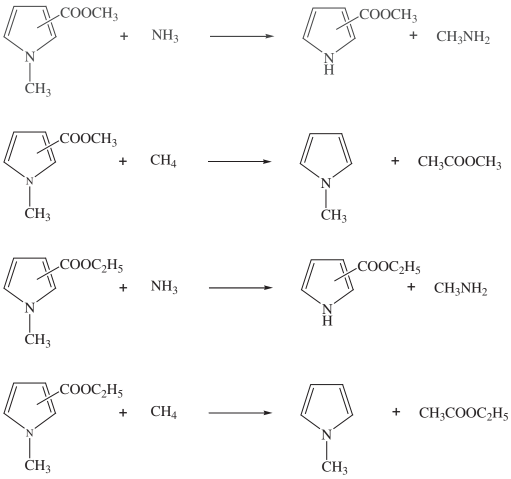
A high temperature Calvet microcalorimeter (Setaram HT 1000) was used, in this work, to measure the standard molar enthalpy of vaporization of the M1M2PC, through the drop-microcalorimetric technique for vacuum sublimation, described by Skinner *et al.* [46], for the sublimation of solid compounds and adapted, in our Laboratory, for liquid vaporizations [47]. The measuring procedure and a detailed description of the technique have been previously reported [48].

The microcalorimeter was calibrated making use of the standard molar enthalpy of vaporization of *n*-undecane (Aldrich, mass fraction purity > 0.99), $\Delta_l^g H_m^o\ (298.15\ \mathrm{K}) = (56.580 \pm 0.566)\ \mathrm{kJ \cdot mol^{-1}}$ [49]. The calibration constant, *k*, of the calorimeter was obtained as the average of six independent experiments for the predefined temperature, $k(T = 360\ \mathrm{K}) = (1.0437 \pm 0.0012)$; the uncertainty presented is the standard deviation of the mean.

3. Computational thermochemistry

Standard *ab initio* molecular orbital calculations, [50], were performed with the Gaussian 03 computer code [51], and the composite G3(MP2)//B3LYP approach was the methodology employed to compute the gas-phase enthalpies of all species considered [52].

The absolute enthalpies, at $T = 298.15$ K, were then used to estimate the enthalpy of formation of the compound studied experimentally (M1M2PC), by combining the enthalpy of the gas-phase working reactions (1) and (2) and the experimental enthalpies of formation of the molecules there included. The calculations were also extended to the M1M3PC (reactions (1) and (2)), E1M2PC (reactions (3) and (4)) and E1M3PC (reactions (3) and (4)), molecules that were not studied experimentally. The enthalpies of formation of the four referred compounds have also been estimated from the respective computed enthalpy of atomization reaction, at $T = 298.15$ K:



(1)

(2)

(3)

(4)

TABLE 1
Provenance and purity details of the compound studied.

Chemical name	CAS	Provenance	Initial molar fraction purity	Purification method	Final molar fraction purity	Analysis method
Methyl 1-methyl-2-pyrrolecarboxylate (l)	37619-24-2	Alfa-Aesar	0.99	Distillation	0.9997	GC[a]

[a] Gas–liquid chromatography.