Standard molar enthalpies of formation of some vinylfuran derivatives

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ABSTRACT

The standard (p° = 0.1 MPa) molar enthalpies of combustion, $\Delta_c H_m^\circ$, for crystalline 2-furanacrylic acid, 3-furanacrylic acid, and 3-(2-furyl)-2-propenal and for the liquid 2-furanacrylonitrile were determined, at the temperature 298.15 K, using a static bomb combustion calorimeter. For these compounds, the standard molar enthalpies of phase transition, $\Delta_{cr,l}^g H_m^\circ$, at T = 298.15 K, were determined by Calvet microcalorimetry. For the two crystalline furanacrylic acids the vapour pressures as function of temperature were measured by the Knudsen effusion technique and the standard molar enthalpies of sublimation, $\Delta_{cr}^g H_m^\circ$, at T = 298.15 K were derived by the Clausius–Clapeyron equation. The results are as follows:

	$-\Delta_c H_m^\circ(cr,l)/$ (kJ · mol^{-1})	$\Delta_{cr,l}^g H_m^\circ/$(kJ · mol^{-1})	
		Calvet	Knudsen
2-Furanacrylic acid (cr)	3149.8 ± 0.5	103.0 ± 0.7	103.3 ± 0.5
3-Furanacrylic acid (cr)	3151.5 ± 0.7	104.9 ± 1.1	106.8 ± 0.5
3-(2-Furyl)-2-propenal (cr)	3425.7 ± 1.2	82.3 ± 0.4	
2-Furanacrylonitrile (l)	3562.5 ± 1.3	65.2 ± 0.6	

These values were used to derive the standard molar enthalpies of formation of the compounds in their condensed and gaseous phases, respectively. For 2-furanacrylic acid and 3-furanacrylic acid, the standard (p° = 0.1 MPa) molar enthalpies, entropies, and Gibbs functions of sublimation, at T = 298.15 K, were derived. The derived standard molar enthalpies of formation in the gaseous state are analysed in terms of structural enthalpic increments.

1. Introduction

The particular area of furan chemistry is in itself very rich both in already acquired knowledge and in its future developments. Recently [1] catalytic methods have been developed for the preparation of substituted furans from carbohydrates and ensuing polymers. The growing interest for the preparation of nonpetroleum chemicals has naturally led to the development of the nonfood transformation of carbohydrates, the most abundant source of renewable materials on earth, into valuable chemicals [2]. This renewed interest was quite obvious with the development of the chemistry of furanic compounds, particularly for the preparation of nonpetroleum-derived polymeric materials such as polyesters, polyamides, and polyurethanes [3,4]. The 2-vinylfuran molecule is important as a synthetic reagent in polymer chemistry, being used to produce resins and polymers [5]. It belongs to a group of monomers, incorporating the furan moiety that may be produced from biomass and represents a possible alternative to petroleum-based monomers [6].

This paper reports the standard (p° = 0.1 MPa) molar enthalpies of combustion, $\Delta_c H_m^\circ$, in oxygen at T = 298.15 K, determined by static-bomb calorimetry, for 2-furanacrylic acid, 3-furanacrylic acid, 3-(2-furyl)-2-propenal, and 2-furanacrylonitrile, depicted in figure 1.

For all the compounds the enthalpies of phase transition were measured by Calvet microcalorimetry. The Knudsen mass-loss effusion technique was used to measure the vapour pressures as a function of temperature for 2-furanacrylic acid and 3-furanacrylic acid. From the temperature dependence of the vapour pressure, the molar enthalpies, and entropies of sublimation at the mean temperature of the experimental temperature range were derived. Standard molar enthalpies, entropies, and Gibbs functions of sublimation, at the temperature of 298.15 K, were calculated.

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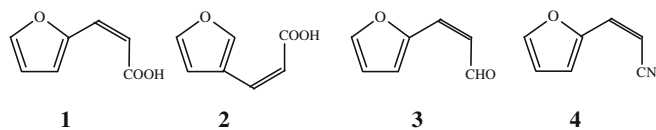*E-mail address:* risilva@fc.up.pt (M.A.V. Ribeiro da Silva).

FIGURE 1. Structural formula of 2-furanacrylic acid (**1**), 3-furanacrylic acid (**2**), 3-(2-furyl)-2-propenal (**3**), and 2-furanacrylonitrile (**4**).

2. Experimental

2.1. Compounds and purity control

All the studied compounds, commercially obtained from Aldrich Chemical Co. with the following assessed mass fractions purities: 2-furanacrylic acid [CAS 539-47-9] 0.99, 3-furanacrylic acid [CAS 81311-95-7] 0.97, 3-(2-furyl)-2-propenal [CAS 39511-08-5] 0.99+, were purified by successive sublimations, under reduced pressure; the liquid 2-furanacrylonitrile [CAS 7187-01-1] mass fraction purity 0.97, was purified by successive fractional distillation, under reduced pressure. The purities were checked by glc and by the obtained closeness to unity of the carbon dioxide recovery ratios of the combustion experiments for each compound. The average ratios of the mass of carbon dioxide recovered from combustion to that calculated from the mass of sample were: 1.00064 for 2-furanacrylic acid, 1.00059 for 3-furanacrylic acid, 0.99993 for 3-(2-furyl)-2-propenal, and 0.99968 for 2-furanacrylonitrile. The densities, at $T = 298.15$ K, were taken for the two acrylic acids as 1.375 g · cm^3 [7], for 3-(2-furyl)-2-propenal as 1.278 g · cm^3, determined from the ratio mass/volume of pellets of this compound and, for 2-furanacrylonitrile as 1.086 g · cm^3 [8].

2.2. Combustion calorimetry

The combustion experiments were performed with an isoperibol calorimetric system. The bomb calorimeter, subsidiary apparatus, and technique have been described previously in the literature [9,10].

Combustion of NBS Reference Material 39j Thermochemical Standard benzoic acid was used for calibration of this bomb. Its massic energy of combustion is $-(26\,434 \pm 3)$ J · g^{-1}, under certificate conditions [11]. The calibration results were corrected to give the energy equivalent of the calorimeter, ε(calor), corresponding to the average mass of 3119.6 g of water added to the calorimeter. From seven calibration experiments, ε(calor) was found to be (15907.1 ± 0.7) J · K^{-1}.

In all combustion experiments, 1.00 cm^3 of water was introduced into the bomb, a twin-valve static combustion bomb Type 1105, Parr Instrument Company, made of stainless steel, with an internal volume of 0.340 cm^3. The bomb was purged twice to remove air, before being charged with 3.04 MPa of oxygen.

For all experiments, the calorimeter temperatures were measured to $\pm(1 \cdot 10^{-4})$ K, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett Packard HP 2804A), interfaced to a PC. At least 100 readings of the temperature, at time intervals of 10 s, were taken before the ignition of the samples which was made at $T = (298.150 \pm 0.001)$ K by the discharge of a 1400 μF capacitor through the platinum ignition wire ($\varphi = 0.05$ mm, Goodfellows). After ignition, 100 readings were taken for each the main and after periods.

The crystalline samples were ignited in the pellet form, whereas the liquid samples of 2-furanacrylonitrile were contained in sealed polyester bags made of melinex (0.025 mm of thickness) with massic energy of combustion $\Delta_c u^\circ = -(22\,902 \pm 5)$ J · g^{-1} [12] The mass of melinex used in each experiment was corrected for the mass

fraction of water ($w = 0.0032$) and the mass of carbon dioxide produced from its combustion was calculated using the factor previously reported [12]. For the cotton thread fuse of empirical formula $CH_{1.686}O_{0.843}$, the massic energy of combustion was assigned to $-\Delta_c u^\circ = 16\,240$ J · g^{-1} [13]. The values of the massic energies of combustion of the melinex and of the cotton thread fuse have been previously confirmed in our laboratory. In the experiments with a residue carbon soot formation inside the crucible, during the combustion, the necessary energetic correction for its formation was based on $\Delta_c u^\circ = -33$ J · g^{-1} [13]. If the soot residue were formed outside the crucible, the experiment was discarded.

The electrical energy for ignition was determined from the change in potential difference across the capacitor when discharged through the platinum ignition wire. The corrections for nitric acid formation were based on 59.7 kJ · mol^{-1} [14], for the molar energy of formation of 0.1 mol · dm^{-3} HNO_3(aq) from N_2, O_2, and H_2O(l). All the necessary weightings were made in a Mettler AE 240 microbalance, with sensitivity $\pm(1 \cdot 10^{-6})$ g; corrections from apparent mass to true mass were made. An estimated 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 most organic compounds [15] was assumed. For each compound, the massic energy of combustion, $\Delta_c u^\circ$, was calculated by the procedure given by Hubbard *et al.* [16]. The amounts of the compounds used in each experiment were determined from the total mass of carbon dioxide (Mettler Toledo AT 201 balance, sensitivity $\pm(1 \cdot 10^{-5})$ g), produced during the experiments, taking into account that formed from the combustion of the cotton-thread fuse and of the melinex.

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2005 [17].

2.3. Microcalorimetry Calvet

The standard molar enthalpies of phase transition of the four compounds studied in this work were measured using the vacuum sublimation drop-microcalorimetric technique [18,19]. The apparatus and technique have been recently described [19]. Samples of about (3 to 8) mg of the compounds, contained in a small thin glass capillary tube sealed at one end, and a blank capillary with similar mass, were simultaneously dropped at room temperature into the hot reaction vessel in the Calvet high-temperature microcalorimeter (Setaram HT 1000), held at a convenient temperature T, and were removed from the hot zone by vacuum sublimation/vaporization. The thermal corrections for the glass capillary tubes were determined in separate experiments, and were minimized, as far as possible, by dropping tubes of nearly equal mass, to within ±10 μg, into each of the twin calorimeter cells. The observed enthalpies of phase transition, $\Delta_{cr,l,298.15\,K}^{g,T} H_m$, were corrected to $T = 298.15$ K using values of $\Delta_{298.15\,K}^T H_m^\circ$(g) estimated by a group method, based on the data of Stull *et al.* [20], where T is the temperature of the hot reaction vessel. For these measurements, the microcalorimeter was calibrated *in situ* using the reported standard molar enthalpies of sublimation of naphthalene [21] for the experiments with crystalline 2-furanacrylic acid, 3-furanacrylic acid, and 3-(2-furyl)-2-propenal and of the enthalpy of vaporization of *n*-undecane [21] for the experiments with liquid 2-furanacrylonitrile.

2.4. Vapour pressures measurements

The vapour pressures of the crystalline acrylic acids were measured, at several temperatures, by the mass-loss Knudsen-effusion technique. A detailed description of the apparatus, procedure, and technique, and the results obtained with two test substances (benzoic acid and ferrocene) have been reported before [22]. For each compound, the measurements were extended through a chosen temperature interval corresponding to measured vapour pressures