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Enthalpies of combustion and formation of 3-formylchromones

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Abstract

The enthalpies of combustion of 3-formylchromone (3F), 3-formyl-6-methylchromone (3F6M) and 3-formyl-6-isopropylchromone (3F6I) were determined by combustion calorimetry. The molar combustion energies ($\Delta_c U_m^0$ (cr, 298.15 K)) of the 3F, 3F6M and 3F6I are: $-(4452.4 \pm 1.8)$, $-(5115.6 \pm 2.7)$ and $-(6411.4 \pm 2.5)$ kJ mol^{-1}, respectively. The formation enthalpies in the crystalline state ($\Delta_f H_m^\circ$ (cr, 298.15 K)) are: $-(340.2 \pm 2.2)$, $-(355.1 \pm 3.1)$ and $-(415.5 \pm 3.0)$ kJ mol^{-1}, respectively.s

Keywords: Micro-combustion calorimeter; 3-Formylchromones; Enthalpies of formation

1. Introduction

Micro-combustion calorimetry, which works with samples of 5–300 mg, has been developed and improved since the first half of 20th century to the present time [1–4], leading to results with a precision similar to those obtained from macro combustion calorimetry. In the present work, a micro-combustion calorimeter designed, calibrated and tested recently [5] was used to determine the combustion energies in solid phase of 3-formyl chromone (3F), 3-formyl-6-methylchromone (3F6M) and 3-formyl-6-isopropylchromone (3F6I). The molecular structures of the 3-formylchromones studied in the present work are shown in Fig. 1.

The 3-formylchromones have many applications. They are used as versatile synthons in heterocyclic chemistry; for example, in the reaction with heterocyclic primary amines to obtain the correspondent Schiff base [6], in cyclic additions with three phenyl phosphine derivatives [7], in the synthesis of 3-styryl chromones [8], in the synthesis of biologically novel systems [9], in reactions with 1,3-bis-silyl enol ethers [10] and in the synthesis of benzo[*b*]xanthones [11]. In the pharmaceutical area, the potency and selectivity of derivates of 3-formylchromones, provides a novel pharmacophore for the design of drugs for the treatment of type 2 diabetes and obesity [12]. In industry, the compounds are used as photosensitive agents in photography [13]. Despite the different uses of 3-formylchromones in organic synthesis and chemical industry, no thermochemical information is available.

2. Experimental

The 3-formylchromones were supplied by Aldrich, two of them with a mass fraction better than 0.99 and 3F with a mass fraction of 0.97. 3F was purified by repeated recrystallization from ethanol. The purities of the compounds were determined with a TA Instrument 2010 differential scanning calorimeter with aluminum non-hermetic cells under constant flow of dry nitrogen. The heating rates were of 1 K min^{-1} and the masses of the samples were approximately 2 mg. Calibration and the correction of temperature were obtained by the fusion of high-purity indium [14]. From the analysis of the melting curve, the mole fraction purities for 3F, 3F6M and 3F6I were 0.9998, 0.9998 and 0.9984, respectively. The molar heat capacities of the samples were obtained by comparison with synthetic sapphire as Refs. [15,16].

The densities of the compounds were determined with a 5 cm^3 volume picnometer and paraffin oil as solvent. Table 1 shows the auxiliary quantities used in calculations and those obtained by DSC.

Benzoic acid used in the calibration of the combustion calorimeter (with a combustion bomb Parr 1107) was supplied by NIST as reference material (SRM 39j), which has a massic energy of $\Delta_c u = -(26.434 \pm 3)$ kJ g^{-1}.

Calibration and combustion of 3-formylchromones were carried out under the same conditions. Inside the bomb of 22 cm^3 volume, with 0.1 cm^3 of demineralized water at the bottom, the

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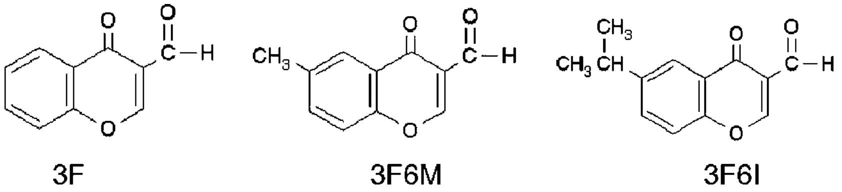

Fig. 1. Molecular structures of 3-formylchromones.

Table 1
Auxiliary quantities and values obtained from DSC measurements

Substance	Molecular formula	M^a (g mol^{-1})	ρ (g cm^{-3})	$-(\partial u/\partial p)_T$ (J g^{-1} MPa^{-1})	C_p (J K^{-1} g^{-1})	$\Delta_{fus}H^b$ (kJ mol^{-1})	$T_{fus}{}^b$ (K)
3F	$C_{10}H_6O_3$	174.153	1.70[b]	0.100[c]	0.695[b]	25.37 ± 0.23	424.89 ± 0.01
3F6M	$C_{11}H_8O_3$	188.179	1.47[b]	0.100[c]	0.951[b]	26.80 ± 0.57	444.45 ± 0.02
3F6I	$C_{13}H_{12}O_3$	216.233	1.17[b]	0.100[c]	1.029[b]	24.08 ± 0.66	371.47 ± 0.03
Cotton	$C_1H_{1.742}\,O_{0.921}$	28.502	1.50 [18]	0.289 [18]	1.647 [18]		
Benzoic acid	$C_7H_6O_2$	122.122	1.32 [18]	0.115 [18]	1.209 [18]		

[a] Molar masses are based on 2001 IUPAC recommendations [17].
[b] Experimental values.
[c] Estimated values as in Ref. [18].

sample was burnt in pellets in a platinum crucible of 0.75 cm diameter and 3.04 MPa of high-purity oxygen (Air Liquide Corp., mass fraction of 0.99999). To remove atmospheric nitrogen from the bomb, it was flushed by charging the bomb with oxygen to 0.1 MPa and then reducing the pressure to atmospheric at least 10 times. The masses of all substances were measured with an ME 215 S Sartorius balance.

The necessary energy to begin the combustion was supplied by a Parr 2901 ignition unit and the circuit was closed with a platinum wire of 0.05 cm of diameter and 1.5 cm long. The connection between the platinum wire and the sample was made through a cotton thread, with a massic energy of combustion of $\Delta_c u^\circ = -(16945.2 \pm 4.2)$ J g^{-1} [18].

The combustion bomb and 250 g of distilled water, weighed with a BP 12000-S Sartorius balance, were placed into the calorimetric vessel which was hermetically closed.

The temperature rise of the combustion experiments was measured with a 5610 Hart Scientific thermistor calibrated over a 273.15–373.15 K temperature range. The resistances were measured with an HP 34420A digital multimeter connected to a PC to get automatic recording of data.

The corrected temperature rise, the correction of apparent mass to mass and the Washburn corrections were obtained by computational programs created in the laboratory based on literature information [19,20,21].

3. Results and discussion

Since there are deviations from the certification conditions, it was necessary to use the standard energy of combustion of benzoic acid, as $\Delta_c u^\circ = -(26.414 \pm 3)$ kJ g^{-1} [22] and corrections to standard states. From 12 combustion experiments the calibration constant was determined as ε (calor) = (1.2775 ± 0.0004) kJ K^{-1}, with the Eq. (1):

$$\varepsilon\,(\text{calor}) = \left[\frac{(-m(\text{ba}) \cdot \Delta_c u^\circ(\text{ba}) - m(\text{cott}) \cdot \Delta_c u^\circ(\text{cott}) + \Delta U_{\text{ign}} + \Delta U_{\Sigma})}{\Delta T_c}\right] - \varepsilon\,(\text{cont}) \qquad (1)$$

Table 2
Molar standard values for 3-formylchromones at T = 298.15 K and p = 0.1 MPa

Compound	$-\Delta_c U^\circ$ (kJ mol^{-1})	$-\Delta_c H^\circ$ (kJ mol^{-1})	$-\Delta_f H^\circ$ (kJ mol^{-1})
3F	4452.4 ± 1.8	4452.4 ± 1.8	340.2 ± 2.2
3F6M	5115.6 ± 2.7	5116.8 ± 2.7	355.1 ± 3.1
3F6I	6411.4 ± 2.5	6415.1 ± 2.5	415.5 ± 3.0

Uncertainties represent the overall standard deviation.

From combustion experiments, the standard combustion energies of 3F, 3F6M and 3F6I were determined as $\Delta_c u^\circ = -(25.57 \pm 0.01)$, $-(27.19 \pm 0.01)$ and $-(29.65 \pm 0.01)$ kJ g^{-1}, respectively. Table A (in supplementary data file) shows typical experimental results from the combustion of benzoic acid and 3-formylchromones.

The individual results of the calibration experiments and the combustion experiments, together with the mean value and its standard deviation for each compound are given in Table B (in supplementary data file).

The derived values of standard molar energies and enthalpies of combustion, $\Delta_c U^\circ$ and $\Delta_c H^\circ$, and the standard molar enthalpies of formation in condensate phase, $\Delta_f H^\circ$ are listed in Table 2. The uncertainties assigned to the standard molar enthalpies of combustion and formation are the overall standard deviation of the mean, which includes the uncertainties in calibration and in the auxiliary quantities [23].

The values for the standard molar enthalpies of formation of H_2O (l), $-(285.830 \pm 0.042)$ kJ mol^{-1} and CO_2 (g), $-(393.51 \pm 0.13)$ kJ mol^{-1} at T = 298.15 K were taken from CODATA [24].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.07.010.

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