Thermodynamic properties of fluoranthene: An experimental and computational study

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ABSTRACT

Vapour pressures of both crystalline and liquid (including super-cooled liquid) phases of fluoranthene were measured using a pressure gauge (capacitance diaphragm manometer) over the temperature range (348.8 to 404.3) K yielding accurate determination of enthalpies and entropies of sublimation and vaporisation. Enthalpy of sublimation was also determined using Calvet microcalorimetry. The enthalpy of fusion was derived from vapour pressure results and from d.s.c. experiments. Static bomb calorimetry was used to determine the enthalpy of combustion of fluoranthene from which the standard enthalpy of formation in the crystalline phase was calculated. The enthalpy of formation in the gaseous phase was calculated combining the result derived for the crystalline phase with the enthalpy of sublimation determined from the vapour pressure measurements. Computational results of the enthalpies of formation of fluoranthene and fluorene were also calculated at the G3 and G4 levels, and compared with the experimental values.

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1. Introduction

Fluoranthene (figure 1) is a polycyclic aromatic hydrocarbon, PAH, that presents four fused rings, one of them a five-membered ring connecting one naphthalene and one benzene units. The presence in the fluoranthene structure of a ring other than those with six carbon atoms attributes it the classification of a non-alternant PAHs, in opposition to the compounds named as alternant PAHs, from which we highlight pyrene, a structural isomer of fluoranthene, a flat aromatic molecule with four fused benzene rings which is thermodynamically more stable due to the delocalization of the electrons throughout all the structure.

In the context of our recent interest in the thermochemical and thermophysical characterisation of fluorene [1] and related compounds with a fluorene core, we have carried out an experimental study on fluoranthene, complemented by a computational insight on these two polycyclic aromatic hydrocarbons (PAHs), with the main goal of getting reliable data to establish correlations between

energetic and structural properties, in order to improve the understanding on the reactivity of these species.

Concerning fluoranthene, the literature reports two different values for the standard enthalpy of formation in crystalline phase, at the temperature 298.15 K, $(189.9 \pm 2.1)\,kJ \cdot mol^{-1}$ [2] and $(192.5 \pm 5.8)\,kJ \cdot mol^{-1}$ [3], as well as several values, at that temperature, for the enthalpy of sublimation, scattered from $(84.6 \pm 1.8)\,kJ \cdot mol^{-1}$ [4] to $(103.6 \pm 2.2)\,kJ \cdot mol^{-1}$ [3], and for the enthalpy of vaporisation varying from $79.3\,kJ \cdot mol^{-1}$ to $(97.6 \pm 4.3)\,kJ \cdot mol^{-1}$ [5,6]. These data have been recently compiled by Roux et al. [7] in a review on the critically evaluated thermochemical properties of polycyclic aromatic hydrocarbons, where the values (190.2 ± 2.8) and $(101.2 \pm 2.8)\,kJ \cdot mol^{-1}$ have been recommended, respectively, for the enthalpy of formation in crystalline phase, and for the enthalpy of sublimation of fluoranthene, yielding the value $(291.4 \pm 4.0)\,kJ \cdot mol^{-1}$ for its enthalpy of formation in the gas phase. For the enthalpy of vaporisation the value $(87.1 \pm 3.6)\,kJ \cdot mol^{-1}$ was recommended.

In view of the differences of the literature values, we decided to reanalyse these data and so in the present work we report the redetermination of the standard ($p° = 0.1$ MPa) molar enthalpy of

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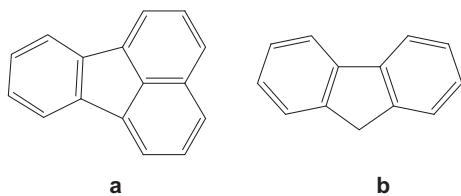 E-mail address: mjmonte@fc.up.pt (M.J.S. Monte).

FIGURE 1. Schematic formulas of fluoranthene (a) and fluorene (b).

formation of fluoranthene, at T = 298.15 K, in the crystalline phase, derived from the respective massic energy of combustion, measured by static-bomb combustion calorimetry. Vapour pressures of the crystalline and liquid phases at different temperatures were also measured using a static apparatus equipped with a capacitance manometer. These measurements enabled the determination of the enthalpies of sublimation and of vaporisation. The enthalpy of sublimation was also determined using Calvet microcalorimetry.

2. Experimental

2.1. Purification and purity control

Fluoranthene [CAS 206-44-0] was purchased from Aldrich Co., with the specification of an average molar fraction 0.99. The measurement of the purity mole fraction of the original sample, by GC (model 4890A, equipped with a FID detector), lead to the value 0.9895. The sample has been re-crystallized several times from petroleum ether and hexane until the GC analysis confirmed a purity mole fraction of at least 0.9989. These results are presented in table 1. The purity of fluoranthene was confirmed by the mass of carbon dioxide recovered in the combustion experiments to that calculated from the mass of the sample; the average ratio and the respective uncertainty (twice the standard deviation of the mean), was (0.9973 ± 0.0004). The specific density of the sample is ρ = 1.243 g · cm^{-3}[8]. The relative atomic masses used for the elements were those recommended by the IUPAC Commission in 2009 [9].

2.2. Static bomb combustion calorimetry

The energy of combustion of fluoranthene was determined from static bomb calorimetry, using a calorimeter with a twin valve bomb of internal volume 0.290 dm^3 [10–12]. The samples were ignited at T = (298.150 ± 0.001) K, in oxygen at p = 3.04 MPa, with 1.00 cm^3 of deionised water previously added to the bomb; the mass of compound, m(cpd), used in each experiment was determined from the total mass of carbon dioxide, m(CO_2, total), produced after allowance for that formed from the combustion of the cotton thread.

The energy equivalent of the calorimeter ε(calor) was determined using benzoic acid [CAS 65-85-0], Standard Reference Material (SRM 39j) supplied by the National Institute of Standards and Technology (NIST), having a massic energy of combustion, under bomb conditions, of –(26,434 ± 3) J · g^{-1}. The energy equivalent of

the calorimeter, ε(calor) = (15551.7 ± 1.2) J · K^{-1}, where the uncertainty quoted is the standard deviation of the mean, was determined from eight calibration experiments (under oxygen at p = 3.04 MPa and using 1.00 cm^3 of water added to the bomb) and corresponds to an average mass of 2900.0 g of water added to the calorimeter. The electrical energy for ignition ΔU(ign.) was determined from the change in potential difference across a 1400 μF capacitor when discharged through the platinum ignition wire. For the cotton thread fuse, of empirical formula $CH_{1.686}O_{0.843}$, the massic energy of combustion is $\Delta_c u$ = −16,240 J · g^{-1} [13]. The corrections for nitric acid formation, ΔU(HNO_3), were based on the value −59.7 kJ · mol^{-1} [14], for the molar energy of formation of 0.1 mol · dm^{-3} HNO_3(aq) from N_2 (g), O_2 (g), and H_2O (l). 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 standard massic energy of combustion, $\Delta_c u°$, was calculated by the procedure given by Hubbard et al. [16].

2.3. Phase transitions

2.3.1. Measurements

The temperature and enthalpy of fusion of fluoranthene was determined using a power compensated differential scanning calorimeter (Setaram 141). The calibration of the power scale of the calorimeter was performed using high-purity indium (mass fraction > 0.99999) and the temperature scale was calibrated by measuring the melting temperature of the following high purity reference materials [17]: naphthalene, benzoic acid, and indium. Six independent scans were performed under a nitrogen atmosphere using a heating rate of $3.3 \cdot 10^{-2}$ K · s^{-1}. No crystalline transitions were detected above the temperature 298 K.

2.3.2. Vapour pressure measurements

The vapour pressure of fluoranthene was measured at different temperatures using a pressure gauge static method [18] for both crystalline and liquid phases. The vapour pressures of the crystalline phase were measured from T = (348.83 to 375.59) K and the vapour pressures of the liquid phase (including super cooled liquid) were measured from T = (354.78 to 404.30) K. The results enabled the indirect determination of enthalpies and entropies of sublimation, vaporisation and fusion.

The used static apparatus is based on capacitance diaphragm gauges and was previously described in detail [18]. This method has been used for measuring vapour pressures of several organic compounds yielding reliable results when compared with those obtained on the same compounds using the Knudsen effusion method [1,19,20]. The two capacitance diaphragm absolute gauges available in this apparatus were obtained from MKS Instruments, Inc. They operate at self-controlled constant temperatures: gauge 1, Baratron 631A01TBEH (Tgauge = 423 K) for measuring pressures in the range (0.4 to 133) Pa and in the temperature range (253 to 413) K was the only gauge used in the present work. Gauge 2, Baratron 631A11TBFP (Tgauge = 473 K) is capable of measuring pressures in the range (3 to 1330) Pa and in the temperature range (253 to 463) K. A platinum resistance thermometer Pt100 class 1/10 DIN (in a four wire connection) measures the temperature of the condensed sample. This thermometer was calibrated by comparison with a SPRT (25 Ω; Tinsley, 5187A). The metal tubing between the cell containing the condensed sample and the pressure gauge is kept at a temperature higher than the temperature of the sample and lower than the temperature of the gauge. The uncertainty of the temperature measurements is estimated to be better than ±0.01 K and the uncertainty in the pressure measurements is adequately described by the expression $\sigma(p/Pa) = 0.01 + 0.0025 (p/Pa)$.

TABLE 1
Source, purification and analysis details of the fluoranthene sample.

Chemical name	Source	Initial mole fraction purity	Purification method	Final mole fraction purity	Analysis method
Fluoranthene	Aldrich Co.	0.9895	Re-crystallization[a]	0.9989	GC[b]

[a] A mixture of hexane and petroleum ether was used as solvent.
[b] Gas–liquid chromatography.