



A combined experimental and computational thermodynamic study of fluorene-9-methanol and fluorene-9-carboxylic acid

Juliana A.S.A. Oliveira^a, Maria M. Calvino^a, R. Notario^b, Manuel J.S. Monte^{a,*},
Maria D.M.C. Ribeiro da Silva^a

^a Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

^b Instituto de Química Física "Rocasolano", CSIC, Serrano 119, 28006 Madrid, Spain

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ABSTRACT

This work reports an experimental and computational thermodynamic study performed on two 9-fluorene derivatives: fluorene-9-methanol and fluorene-9-carboxylic acid. The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the crystalline phase of these compounds were derived from the standard molar energies of combustion, in oxygen, at $T = 298.15$ K, measured by static bomb combustion calorimetry. A static method, based on a capacitance diaphragm gauge, and a Knudsen effusion method were used to perform the vapour pressure study of the referred compounds, yielding accurate determination of the standard molar enthalpies and entropies of sublimation and vaporisation. For fluorene-9-carboxylic acid, the enthalpy of sublimation was also determined using Calvet microcalorimetry. The enthalpy of fusion of both compounds was derived indirectly from vapour pressure results and directly from DSC experiments. Combining the thermodynamic parameters of the compounds studied, the standard Gibbs energy of formation in crystalline and gaseous phases were derived as well as the standard molar enthalpy of formation in the gaseous phase. A theoretical study at the G3 and G4 levels has been carried out, and the calculated enthalpies of formation have been compared with the experimental values.

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1. Introduction

The use of polycyclic aromatic hydrocarbon (PAHs) derivatives with a fluorene or fluorenone core in electronic devices has suffered an impressive increase in the past decade. Some of these compounds are known to exhibit appealing optical properties [1–4] and are then suitable for being used in organic light emitting diodes (OLEDs) [5,6] and organic photovoltaic cells (OPVCs) [7–9].

Despite their important industrial applications, PAHs are well-known pollutants, harmful to both the environment and living beings. The knowledge and prediction of the behaviour of these substances in nature call for accurate and reliable information on their physical–chemical properties. This information is also of crucial importance for the optimization of industrial processes and manufacture of devices based in these compounds. However, available information is often scarce and frequently shows significant discrepancy among results published by different researchers, justifying our interest in thermodynamic studies on these compounds. Recent studies have been published for fluorene [10], fluoranthene [11], 9-fluorenone and 9-fluorenone [12]. In the

present work, we extend this study to the compounds fluorene-9-methanol and fluorene-9-carboxylic acid (in figure. 1).

Concerning fluorene-9-methanol, literature reports a result for the standard molar enthalpy of formation, in the crystalline phase, $\Delta_f H_m^\circ(\text{cr}) = -(92.36 \pm 0.97) \text{ kJ} \cdot \text{mol}^{-1}$ [13], but to the best of our knowledge no sublimation or vaporisation study was published. Fluorene-9-carboxylic acid was recently part of a vapour pressure study performed by Goldfarb and Suuberg [14] reporting the result $\Delta_{\text{cr}}^\circ H_m^\circ = (110.2 \pm 4.6) \text{ kJ} \cdot \text{mol}^{-1}$ for the standard molar enthalpy of sublimation at the temperature $T = 383.5$ K.

In order to verify the published results it was decided to perform new determinations of these properties and to extend our study aiming a reliable thermodynamic characterization of these compounds determining enthalpies of combustion, vapour pressures and calorimetric phase transition properties, as well as computational studies of gas phase thermodynamic properties.

2. Experimental

2.1. Materials and purity control

The compounds fluorene-9-methanol [CAS 24324-17-2] and fluorene-9-carboxylic acid [CAS 1989-33-9] were purchased from

* Corresponding author. Tel.: +351 220402516; fax: +351 220402659.

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

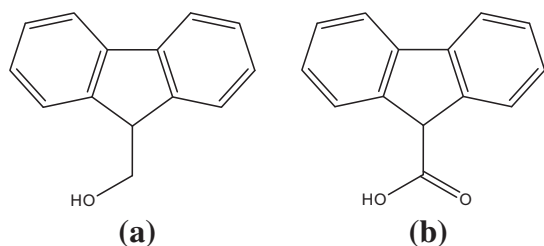


FIGURE 1. Structural formulae of fluorene-9-methanol (a) and fluorene-9-carboxylic acid (b).

TABLE 1

Source, purification and analysis details of the compounds studied.

Chemical name	Source	Minimum initial purity ^a	Purification method	Final mass fraction purity ^b
Fluorene-9-methanol	Aldrich Co.	0.993	Vacuum sublimation	0.9998
Fluorene-9-carboxylic acid	Aldrich Co.	0.986		0.9979

^a Values referred to the fraction of the HPLC area, as stated in the certificates of analysis of the manufacturer.

^b Determined in the present work using GC.

Sigma-Aldrich Chemical Co. with minimum assured mass fraction purity of, respectively, 0.99 and 0.98. Prior to the experimental study, the purification of these compounds was accomplished by successive sublimation under reduced pressure. The purity analysis of the purified samples was carried out by gas chromatography (GC), performed on an Agilent 4890D Gas Chromatograph, equipped with an HP-5 column (0.05 diphenyl and 0.95 dimethylpolysiloxane by mole fraction) and a flame ionisation detector, using nitrogen as carrier gas. These results are presented in table 1. The purity of both compounds was also confirmed by carbon dioxide mass ratios, of that recovered in the combustion experiments to that calculated from the mass of the sample pellet; the average ratio and the respective uncertainty (twice the standard deviation of the mean) are presented in tables S1 and S2.

The relative atomic masses used for the elements in the calculation of all molar quantities throughout this paper were those recommended by the IUPAC Commission in 2009 [15], yielding $196.2440 \text{ g} \cdot \text{mol}^{-1}$ and $210.2276 \text{ g} \cdot \text{mol}^{-1}$ for the molar masses of fluorene-9-methanol and fluorene-9-carboxylic acid, respectively. The specific densities used to calculate the true mass from the apparent mass in air, calculated from the ratio mass/volume of a pellet of the compounds, were $\rho = 1.084 \text{ g} \cdot \text{cm}^{-3}$ and $\rho = 1.164 \text{ g} \cdot \text{cm}^{-3}$ for fluorene-9-methanol and fluorene-9-carboxylic acid, respectively.

2.2. Static bomb combustion calorimetry

The energy of combustion of the studied compounds, from which the standard molar enthalpies of combustion were derived, was measured in a static bomb calorimeter. The combustion reaction takes place in a stainless steel twin valve platinum lined combustion bomb, whose internal fittings are also constructed in platinum, presenting an internal volume 0.290 dm^3 [16–18]. The energy equivalent of the calorimeter $\varepsilon(\text{calor})$ 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 $-(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$. The energy equivalent of the calorimeter $\varepsilon(\text{calor}) = (15551.7 \pm 1.2) \text{ J} \cdot \text{K}^{-1}$, where the uncertainty quoted

is the standard deviation of the mean, was determined from eight calibration experiments, corresponding to an average mass of 2900.0 g of water used as calorimetric fluid. The compounds were burnt in pellet form, however in some of the fluorene-9-carboxylic acid combustion experiments it was necessary to inclose the sample in Melinex[®] bags, $\Delta_c u^0 = -(22902 \pm 5) \text{ J} \cdot \text{g}^{-1}$, using the technique described by Skinner and Snelson [19] given the brittle nature of the pressed compound. This last value was confirmed by combustion of melinex samples in our laboratory. All the samples of both the calibration and compound experiments were ignited at $T = (298.150 \pm 0.001) \text{ K}$, in oxygen at $p = 3.04 \text{ MPa}$, with 1.00 cm^3 of deionised water previously added to the bomb. The electrical energy for ignition $\Delta U(\text{ign})$ was determined from the change in potential difference across a $1400 \mu\text{F}$ capacitor when discharged through a platinum wire ($\phi = 0.05 \text{ mm}$, Goodfellow, mass fraction 0.9999). The necessary correction for the cotton thread, of empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$, used as an ignition fuse was based on $\Delta_c u^0 = -16240 \text{ J} \cdot \text{g}^{-1}$ [20], which has been confirmed in our laboratory. The corrections for nitric acid formation, $\Delta U(\text{HNO}_3)$, were based on the value $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$ [21], for the molar energy of formation of $0.1 \text{ mol} \cdot \text{dm}^{-3}$ HNO_3 (aq) from N_2 (g), O_2 (g) and H_2O (l). An estimated pressure coefficient of specific energy: $(\partial u/\partial p)_T = -0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$ at $T = 298.15 \text{ K}$ [22], a typical value for most organic compounds, was assumed. The mass of compound, $m(\text{cpd})$, used in each experiment was determined from the total mass of carbon dioxide, $m(\text{CO}_2, \text{total})$, produced after allowance for that formed from the combustion of the cotton thread and melinex. Calorimeter temperatures were automatically collected at regular intervals. For each compound, the standard massic energy of combustion, $\Delta_c u^0$, was calculated by the procedure given by Hubbard *et al.* [23].

2.3. Phase transitions

2.3.1. Differential scanning calorimetry

A power compensated differential scanning calorimeter (Setaram 141) was used to determine the temperatures and enthalpies of fusion of the fluorene derivatives. The calibration of the power scale of the calorimeter was performed using high-purity indium (mass fraction purity > 0.99999). The temperature scale of the calorimeter was calibrated by measuring the melting temperature of the following high purity reference materials [24]: naphthalene, benzoic acid and indium. Five independent scans were performed under nitrogen atmosphere using a heating rate of $3.3 \cdot 10^{-2} \text{ K} \cdot \text{s}^{-1}$. No crystalline transitions were detected above the temperature 298 K .

2.3.2. Vapour pressure measurements

A static method was employed to determine the vapour pressures of fluorene-9-methanol in the liquid phase, enabling the indirect determination of the enthalpy and entropy of vaporisation. The used apparatus is based on capacitance diaphragm gauges, previously tested and described in detail [25]. 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 ($T_{\text{gauge}} = 423 \text{ K}$) for measuring pressures over the range (0.4 to 133) Pa and temperature of the condensed sample from (253 to 413) K; gauge 2, Baratron 631A11TBFP ($T_{\text{gauge}} = 473 \text{ K}$) capable of measuring pressures over the range (3 to 1330) Pa and temperature of the condensed sample from (253 to 463) K. A platinum resistance thermometer Pt100 class 1/10 (in a four wire connection) was used to measure the temperature of the condensed samples. This thermometer was calibrated by comparison with a SPRT (25 X; Tinsley, 5187 A). To avoid condensation of the vapour, the tubing between the condensed sample and the pressure gauge is kept at

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