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Experimental and computational study of the thermodynamic properties of 2-nitrofluorene and 2-aminofluorene

Juliana A.S.A. Oliveira [a], Manuel J.S. Monte [a,*], R. Notario [b], Maria D.M.C. Ribeiro da Silva [a]

[a] *Centro de Investigação em Química, Department of Chemistry and Biochemistry, Faculty of Science, University of 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 report presents a comprehensive experimental and computational study of the thermodynamic properties of two fluorene derivatives: 2-aminofluorene and 2-nitrofluorene. 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 Knudsen effusion method was used to perform the vapour pressure study of the referred compounds, yielding an accurate determination of the standard molar enthalpies and entropies of sublimation. The enthalpies of sublimation were also determined using Calvet microcalorimetry and the enthalpy and temperature of fusion were derived from DSC experiments. Derived results of standard enthalpy and Gibbs energy of formation in both gaseous and crystalline phases were compared with the ones reported in literature for fluorene. A theoretical study at the G3 and G4 levels has been carried out, and the calculated enthalpies of formation have been compared to the experimental values.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are well-known pollutants, harmful to both the environment and living beings. PAHs may react with nitrogen oxides originating nitro aromatics (nitro-PAHs) from incomplete combustion of carbon-containing fuels and atmospheric pollution [1,2]. These nitro aromatic compounds, including nitrofluorenes, are commonly present in nature, and are detected in a variety of environmental pollution sources: cigarette smoke, coal fly ash, emissions from kerosene, diesel, and gasoline heaters and engines [3–6].

As early as the 1950s, nitro-PAHs were reported to be potentially carcinogenic and mutagenic to humans through inhalation, ingestion, and skin contact [7,8]. Among the nitro-PAHs listed as "possibly carcinogenic to humans" by the International Agency for Research on Cancer is 2-nitrofluorene (2-NF) [4].

Carcinogenic activity in nitro-aromatic compounds was thought to be initiated by nitro-reduction [9–11]. 2-NF, used in several studies as a model substance for nitro-PAHs, is mainly metabolised to the corresponding amine, under anaerobic conditions, by enzyme-catalysed reactions [12,13]. When metabolised, these types of aromatic amines selectively react with guanine bases in DNA causing damage and increasing the probability for tumours or cancers [14]. 2-Aminofluorene (2-AF), the fully reduced form of 2-NF, can be converted by biological systems to another well-known animal carcinogen, 2-acetylaminofluorene (2-AAF) through acetylation, both of which are among the most intensively studied of all chemical mutagens and carcinogens [14–16]. 2-NF can also be formed by photo-oxidation of 2-AF, which is used in synthetic petroleum, dye and rubber industries [17,18].

The common presence of nitro-PAHs in nature and the knowledge and prediction of their behaviour call for accurate and reliable information on their physical–chemical properties. However, available information is often scarce and frequently shows significant discrepancy among published results, hence our interest in thermodynamic studies on these compounds.

Recent thermodynamic studies have been reported for fluorene [19], fluoranthene [20], and several fluorene derivatives [21,22]. In

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* Corresponding author. Tel.: +351 22 0402516; fax: +351 22 0402659.
E-mail address: mjmonte@fc.up.pt (M.J.S. Monte).

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the present work, we extend this study to the above mentioned compounds 2-AF and 2-NF (figure 1).

The compound 2-NF was recently part of a vapour pressure study performed by Goldfarb and Suuberg [23], reporting the result $\Delta_{cr}^{g}H_m^o = (114.2 \pm 3.0)$ kJ · mol^{-1} for the standard molar enthalpy of sublimation at the temperature $T = 366.5$ K. With respect to 2-AF to the best of our knowledge, no thermodynamic study has been published.

2. Experimental

2.1. Materials and purity control

The compounds 2-aminofluorene [CAS 153-78-6] and 2-nitrofluorene [CAS 607-57-8] were purchased from Sigma–Aldrich Chemical Co., with minimum assured purity of 0.98. In order to proceed with the experimental study of these compounds, the minimum mass fraction purity requirement of 0.999 was achieved by submitting them to successive sublimation under reduced pressure. In the case of 2-NF, it was necessary further re-crystallisation using ethanol as solvent. During the purification process, the purity control of the 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 (results presented in table 1). As part of the experimental procedure, the purity of the samples 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 supporting information, tables S1 and S2.

The relative atomic masses used for the elements in the calculation of all molar quantities throughout this paper were based on the atomic weights recommended by the IUPAC Commission in 2011 [24], yielding (181.2331 and 211.2161) g · mol^{-1} for the molar masses of 2-AF and 2-NF, respectively. The specific densities used to calculate the true mass from the apparent mass in air were $\rho = 1.0458$ g · cm^{-3} and $\rho = 1.1685$ g · cm^{-3} for 2-AF and 2-NF, respectively [25].

2.2. Static bomb combustion calorimetry

The standard molar enthalpies of combustion of the studied compounds were derived from the respective energy of combustion determined by static bomb combustion calorimetry. The combustion reaction takes place in a stainless steel twin valve combustion bomb with an internal volume 0.290 dm^3 [26–28]. 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), with a massic energy of combustion, under bomb conditions, of $-(26434 \pm 3)$ J · g^{-1}. The energy equivalent of the calorimeter ε(calor) = (15551.7 ± 1.6) J · 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 combustion experiments of both the calibration and compound samples were carried under identical conditions: burnt in pellet form, ignited at $T = (298.150 \pm 0.001)$ K, in the presence of oxygen (minimum purity molar fraction 0.99999) at $p = 3.04$ MPa and 1.00 cm^3 of deionised water. The energetic contribution for the electrical ignition of the sample, ΔU(ign), was determined from the change in potential difference across a 1400 μF capacitor when discharged through a platinum wire ($\phi = 0.05$ mm, Goodfellow, mass fraction 0.9999). The necessary correction for the cotton thread, of empirical formula $CH_{1.686}O_{0.843}$, used as an ignition fuse was based on $\Delta_c u^o = -16240$ J · g^{-1} [29], which has been confirmed in our laboratory. The corrections for nitric acid formation, $\Delta U(HNO_3)$, were based on the value -59.7 kJ · mol^{-1} [30], 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 [31], a typical value for most organic compounds, was assumed. 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. Calorimeter temperatures were automatically collected at regular intervals. For each compound, the standard massic energy of combustion, $\Delta_c u^o$, was calculated by the procedure given by Hubbard et al. [32].

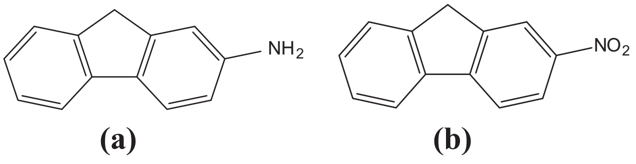

FIGURE 1. Structural formulae of 2-aminofluorene (a) and 2-nitrofluorene (b).

2.3. Phase transitions

2.3.1. Differential scanning calorimetry

The temperatures and enthalpies of fusion of the referred compounds were determined calorimetrically, using a power compensated differential scanning calorimeter (Setaram 141). The power scale of the calorimeter was calibrated 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 [33]: naphthalene, benzoic acid and indium. For each compound, five or six independent scans were performed on fresh samples sealed in aluminium pans using a heating rate of $3.3 \cdot 10^{-2}$ K · s^{-1} under nitrogen atmosphere. No crystalline transitions were detected above the temperature 298 K.

2.3.2. Vapour pressure measurements

The vapour pressure study of the two fluorene derivatives was performed using the Knudsen mass-loss effusion method, which allowed the determination of the enthalpy of sublimation from the dependency of the vapour pressure with temperature. This method was used to measure the vapour pressures from $T = (345.16 - 365.09)$ K for 2-AF and from $T = (357.16 - 379.12)$ K for 2-NF. The experimental apparatus, previously described in detail [34], enables the simultaneous operation of nine effusion cells. During an effusion experiment, the effusion cells are contained in cylindrical holes inside three aluminium blocks, each kept at a controlled temperature and different from the other two blocks. Each block contains three effusion cells with different areas of the effusion orifices: one "small" ($A_o \approx 0.5$ mm^2: series A), one "medium" ($A_o \approx 0.8$ mm^2: series B) and one "large" ($A_o \approx 1.1$ mm^2: series C). The exact areas and the transmission probability factors of each effusion orifice, made in platinum foil of 0.0125 mm thickness, are presented in the supporting information, table S3. The temperature of each block is measured using a platinum resistance thermometer Pt100 class 1/10 (in a four wire connexion) previously calibrated by comparison with an SPRT (25 X; Tinsley, 5187 A). For each effusion experiment, the mass loss of the crystalline sample, Δm, was measured by weighing the cells, within ±0.01 mg, be-