

Thermochemistry of nitronaphthalenes and nitroanthracenes

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Abstract

The standard ($p^\circ = 0.1$ MPa) molar energies of combustion, $\Delta_c U_m^\circ$, for crystalline 1-nitronaphthalene and 9-nitroanthracene were determined, at the temperature 298.15 K, using a static bomb combustion calorimeter. For these compounds, the standard molar enthalpies of sublimation, $\Delta_{cr}^\circ H_m^\circ$, at $T = 298.15$ K, were derived by the Clausius–Clapeyron equation, from the temperature dependence of the vapour pressures of these compounds, measured by the Knudsen effusion technique. The results were as follows:

	$-\Delta_c U_m^\circ(\text{cr})$ kJ · mol ⁻¹	$\Delta_{cr}^\circ H_m^\circ$ kJ · mol ⁻¹
1-Nitronaphthalene	4984.8 ± 1.4	95.1 ± 0.4
9-Nitroanthracene	6905.0 ± 2.8	111.4 ± 0.6

These values were used to derive the standard molar enthalpies of formation of the compounds in their crystalline and gaseous phases, respectively. The derived standard molar enthalpies of formation, in the gaseous state, are analysed in terms of enthalpic increments and interpreted in terms of molecular structure. Using estimated values for the heat capacity differences between the gas and the crystal phases of the studied compounds, the standard ($p^\circ = 0.1$ MPa) molar enthalpies, entropies and Gibbs energies of sublimation, at $T = 298.15$ K, were derived.

Additionally, standard enthalpies of formation for these two compounds were estimated by computations based on density functional theory. The estimated values are in excellent agreement with experimental data, which gives support to the estimates based on computational thermochemistry for the gas-phase enthalpies of formation of 2-nitronaphthalene, 1-nitroanthracene and 2-nitroanthracene.

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1. Introduction

For over a decade, we have been focusing deep attention on the thermochemistry of aromatic compounds, where some polycyclic aromatic hydrocarbons are included, and with results already reported in the literature [1–3]. In the

present work, the thermochemistry of two crystalline nitro derivatives of naphthalene and anthracene, namely, 1-nitronaphthalene [CAS 86-57-7] and 9-nitroanthracene [CAS 602-60-8] whose formulae are represented in figure 1, has been studied by means of experimental and computational techniques.

This paper reports the standard ($p^\circ = 0.1$ MPa) molar enthalpies of combustion, $\Delta_c H_m^\circ$, in oxygen at $T = 298.15$ K, determined by static-bomb calorimetry, for these two compounds.

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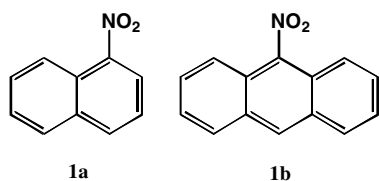


FIGURE 1. Structural formula of 1-nitronaphthalene (**1a**) and 9-nitroanthracene (**1b**).

The Knudsen mass-loss effusion technique was used to measure the vapour pressures as a function of temperature of the two crystalline compounds. 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 energies of sublimation, at the temperature of 298.15 K, were calculated estimating the heat capacity differences between the gas and the crystal phases of each studied compound.

Combined with this experimental work, density functional theory based calculations have been performed for comparison purposes and also to estimate the gas-phase enthalpies of formation of 2-nitronaphthalene and of the other two nitroanthracene isomers, *i.e.*, of 1-nitroanthracene and 2-nitroanthracene.

The 1-nitronaphthalene and 9-nitroanthracene compounds have several important applications both in industry and in academic research. The former compound is used as an intermediate in the preparation of dyes, as a component in the formulation of nitrate explosives and as a deblooming agent for petroleum and oils [4] while, the latter compound, is used as a matrix for MALDI-TOF-MS (matrix laser desorption ionization time of flight – mass spectrometry) analysis of fluorinated fullerenes [5] and for the characterization of PAHs (polycyclic aromatic hydrocarbons) [6].

2. Experimental

2.1. Compounds and purity control

All the studied compounds were commercially obtained from Aldrich with the following assessed purity: 1-nitronaphthalene, mass fraction 0.99 and 9-nitroanthracene, mass fraction 0.97, and were purified by vacuum sublimation.

Purity was checked by the consistent results obtained from the combustion experiments, as well as by the closeness to unity of the carbon dioxide recovery ratios for each compound.

2.2. Combustion calorimetry

The standard molar energies of combustion of 1-nitronaphthalene and 9-nitroanthracene were determined in two isoperibol static calorimeters:

- (i) The bomb calorimeter used for 1-nitronaphthalene is a twin valve bomb, type 1105, Parr Instrument Company; this apparatus was carefully described elsewhere [7,8]. Combustion of NBS 39j Thermochemical Standard benzoic acid was used for calibration of this bomb. Its massic energy of combustion is $-(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$, under certificate conditions. The calibration results were corrected to give the energy equivalent of the calorimeter, $\varepsilon(\text{calor})$, corresponding to the average mass of 3119.6 g of water added to the calorimeter. From seven calibration experiments, $\varepsilon(\text{calor})$ was found to be $(15905.7 \pm 1.0) \text{ J} \cdot \text{K}^{-1}$.
- (ii) The bomb calorimeter, subsidiary apparatus and technique used to measure the enthalpy of combustion of 9-nitroanthracene have been described previously in the literature [9,10]. The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, Batch No. 693916/01) having a massic energy of combustion, under standard bomb conditions, of $-(26435.1 \pm 3.5) \text{ J} \cdot \text{g}^{-1}$ [11]. From nine calibration experiments $\varepsilon(\text{calor}) = (15551.7 \pm 2.6) \text{ J} \cdot \text{K}^{-1}$, for an average mass of water added to the calorimeter of 2900.0 g.

Samples in pellet form were ignited at $T = (298.150 \pm 0.001) \text{ K}$ in oxygen at a pressure $p = 3.04 \text{ MPa}$, with a volume of 1.00 cm^3 of water added to the bomb. The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton thread fuse used, empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$, $-\Delta_c u^\circ = 16250 \text{ J} \cdot \text{g}^{-1}$ [12]; this value has been previously confirmed in our laboratory. Corrections for nitric acid formation were based on $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$ for the molar energy of formation of $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3(\text{aq})$ from N_2 , O_2 and $\text{H}_2\text{O}(\text{l})$ [13]. At temperature $T = 298.15 \text{ K}$, a pressure coefficient of specific energy, $(\partial u/\partial p)_T$, for these solids was assumed to be $-0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$, a typical value for organic solids [14]. The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that formed from the cotton thread fuse. All the necessary weighing was made in a Mettler Toledo AT201 balance, sensitivity $(1 \cdot 10^{-5} \text{ g})$ and corrections from apparent mass to true mass were made. For each compound, $-\Delta_c u^\circ$ was calculated by the procedure given by Hubbard *et al.* [12]. The relative atomic masses used were those recommended by the IUPAC Commission in 2001 [15].

2.3. Vapour pressures measurements

The vapour pressures of the crystals of the studied compounds were measured, at several temperatures, by the mass-loss Knudsen-effusion technique. For the 1-nitronaphthalene, due to the limited amounts available for this compound, the apparatus enabling the simultaneous

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