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Thermochemistry of organic azides revisited

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ABSTRACT

Highly pure samples of 4-nitro-phenyl azide, 1-octyl azide and 1 decyl-azide were prepared for thermochemical studies. Vapour pressures over the solid and the liquid sample of 4-nitro-phenyl azide have been determined by the transpiration method. The molar enthalpies of vaporization/sublimation for this compound were derived from the temperature dependencies of vapour pressures. The molar enthalpy of fusion of 4-nitro-phenyl azide was measured by DSC. The measured data set for 4-nitro-phenyl azide was successfully checked for internal consistency. Molar enthalpies of vaporization of 1-octyl azide and 1 decyl-azide were measured by transpiration. The molar enthalpies of formation of the liquid 1-octyl azide and 1 decyl-azides were derived from the combustion calorimetry. New experimental results for these organic azides have been used to derive their molar enthalpies of formation in the gas state and for comparison with results from quantum-chemical method G4.

1. Introduction

Organic azides have a broad field of application as propellants, plasticizers and pharmacy products [1]. Thermochemical data for azides are in disarray [2]. Most of enthalpies of formation and enthalpies of sublimation/vaporization available in the literature are of technical quality or reported without any sample purity information. Nowadays, the modern quantum-chemical methods allow for performing the enthalpy data evaluation, provided that sufficient amount of the experimental data with the benchmark quality are available for the methods attestation. This paper extends our previous experimental study of a series of organic azides [3]. A complex thermochemical studies (including transpiration, combustion calorimetry and DSC) on highly pure samples of 4-nitro-phenyl azide, 1-octyl azide and 1 decyl-azide. These new data are expected to help for validation of the high-level quantum-chemical calculations.

2. Experimental

2.1. Materials

Samples of 4-nitro-phenyl azide, 1-octyl azide and 1 decylazide were prepared and purified at the University of Málaga, according to the literature procedures with some modifications.

2.1.1. 4-Nitro-phenyl azide

In a round bottom flask equipped with a magnetic stirrer, a sample of 4-nitroaniline (1 g, 7.25 mmol) was dissolved in 5 mL of HCl and 5 mL of water. 10 mL of cold aqueous solution of sodium nitrite (0.5 g, 7.25 mmol) was dropped into the flask under stirring at 273 K. Then, 12 mL of aqueous solution of sodium azide (0.47 g 7.25 mmol) was dropped into the flask and the reaction was allowed to continue for 30 min. The precipitate was extracted with chloroform and washed with water. The organic layer was dried over anhydrous sodium sulphate, and the solvent was evaporated in vacuo to get 4-nitro-phenyl azide, yield 90% (1.07 g) [4], ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 9.2 Hz, 2H), 7.09 (d, J = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 144.5, 125.5, 119.3.

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2.1.2. 1-Octyl azide

NaN_3 (2.53 g, 38.86 mmol) was added to a solution of 1-bromooctane (5 g, 25.91 mmol) in dimethylformamide (10 mL). The reaction mixture was stirred at room temperature for 4 h. Water (100 mL) was added to the reaction mixture and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic phase was washed with 100 mL brine (26% of NaCl in MilliQ Water, pH 6.8), dried over anhydrous Na_2SO_4 and evaporated at reduced pressure to give azide (3.5 g, 87%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.25 (t, J = 6.9 Hz, 2H), 1.60 (quin, J = 6.7 Hz, 2H), 1.28 (br s, 10H), 0.80 (t, J = 6.4 Hz, 3H).

2.1.3. 1-Decyl azide

NaN_3 (5.25 g, 80 mmol) and 1-bromo-decane (7.08 g, 32 mmol) were dissolved in acetone: H_2O (10:1), and left stirred for 3 days under reflux at 65 °C. The extraction procedure of the azide was carried out with diethyl ether (3 × 50 mL) and dichloromethane (2 × 50 mL). To ensure the total extraction and absence of H_2O, the organic phase was washed with brine (26% of NaCl in MilliQ Water, pH 6.8), dried over anhydrous Na_2SO_4 and evaporated in vacuum. A further purification process was carried out by silica chromatography in a porous disc filter funnel, where the pure 1 decyl azide was obtained by a flow of hexane (400 mL), whereas the traces of starting 1-bromo-decane were trapped in the silica. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.25 (t, J = 7.0 Hz, 2H), 1.67–1.52 (m, 2H), 1.43–1.18 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H).

The solid sample of 4-nitrophenyl azide was purified by recrystallization from ethanol and then by fractional sublimation in vacuum. The liquid samples of 1-octyl azide and 1 decyl azide were purified by a repeated fractional distillation at reduced pressure. Purities of samples were determined by a Hewlett Packard gas chromatograph 5890 Series II equipped with a flame ionization detector. We used a 25 m capillary column HP-5 with inside diameter of 0.32 mm and a film thickness of 0.25 mm. The standard temperature program of the GC was T = 333 K for 180 s followed by a heating rate of 0.167 K s^{-1} to T = 523 K. No impurities (greater than mass fraction 0.001) for both samples could be detected in the samples used for the thermochemical measurements.

Provenance and purity of the compounds prepared for thermochemical studies in this work are given in Table 1.

Cautions should be taken during the manipulation and storage of azides. These compounds must be handled in a powerful fume hood. They should be handled only on a small scale with appropriate safety precautions (face shields, leather gloves and protective clothing).

2.2. Vapour pressure measurements

Vapour pressures of organic azides were determined using the method of transpiration [5,6] in a saturated nitrogen stream. About 0.5 g of the sample was mixed with small glass beads and placed in a thermostated U-shaped saturator. A well defined nitrogen stream was passed through the saturator at a constant temperature (±0.1 K), and the transported material was collected in a cold trap. The amount of condensed sample of 1-octyl azide and 1 decyl-azide was determined by GC analysis using an external standard (n-C_8H_{18} and n-$C_{11}H_{24}$). The amount of condensed sample of 4-nitro-phenyl azide was determined by weighing of the trap (±0.0001 g). The absolute vapour pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period of time. Assuming validity of the Dalton's law applied to the nitrogen stream saturated with the substance i, values of p_i were calculated with equation:

$$p_i = \frac{m_i \times R \times T_a}{V \times M_i}; V = V_{N2} + V_i; V_{N2} \gg V_i \quad (1)$$

where R = 8.314472 J K^{-1} mol^{-1}; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i; its volume contribution to the gaseous phase. V_{N2} is the volume of the carrier gas and T_a is the temperature of the soap bubble meter used for measurement of the gas flow. The volume of the carrier gas V_{N2} was determined from the flow rate and the time measurement. Experimental results are given in Tables 2 and 3.

2.3. Combustion calorimetry

The molar enthalpies of combustion of 1-octyl azide and 1 decyl-azide were measured with an isoperibolic calorimeter with a static bomb and a stirred water bath. The sample was placed (under an inert atmosphere in a glove-box) in a polythene ampoule and burned in oxygen at 3.04 MPa pressure. The detailed procedure has been described previously [7]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither was detected. The energy equivalent of the calorimeter ε_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). For the reduction of the data to standard conditions, conventional procedures [8] were used. Auxiliary data are collected in Table 4. Correction for nitric acid formation was based on titration with 0.1 mol dm^{-3} NaOH (aq). The residual water concentration in the liquid samples was determined by Karl Fischer titration before starting experiments and appropriate corrections have been made for combustion results.

2.4. Phase transitions in the solid state. DSC-measurements

The thermal behaviour of 4-nitro-phenyl azide including melting temperature and enthalpy of fusion was determined with a PerkinElmer DSC-2. The fusion temperature and enthalpies were determined as the peak onset temperature and by using a straight baseline for integration, respectively. The temperature and heat flow rate scale of the DSC was calibrated by measuring high-purity indium. The thermal behaviour of the specimen was investigated during heating the sample at a cooling rate of 10 K min^{-1}. The DSC measurements were repeated in triplicate and values agreed within the experimental uncertainties $u(\Delta_{cr}^{g}H_m)$ = 0.2 kJ mol^{-1} for the enthalpy of fusion and $u(T)$ = 0.5 K for the melting temperature.

Table 1
Provenance and purity of the synthesis materials.

Material	4-Nitro-phenyl azide	1-Octyl azide	1-Decyl azide
CASRN	1516-60-5	7438-05-3	62103-13-3
Origin	Synthesis in this work	Synthesis in this work	Synthesis in this work
Method of purification	Fractional sublimation	Fractional distillation	Fractional distillation
GC purity (mass fraction)	0.999[a]	0.999	0.999
Water content after drying		306.42 ppm	266.02 ppm

[a] The same result was measured by DSC.