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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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