

Short communication

Thermodynamic studies of crystalline 2-amino-5-nitropyridine (C₅H₅N₃O₂)

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Abstract

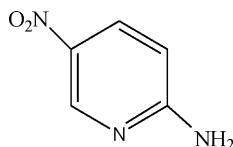
Low-temperature heat capacity $C_{p,m}$ of 2-amino-5-nitropyridine (C₅H₅N₃O₂; CAS 4214-76-0) was measured in the temperature range from 80 to 396 K with a high precision automated adiabatic calorimeter. No phase transition or thermal anomaly was observed in this range. The thermodynamic functions $[H_T - H_{298.15}]$ and $[S_T - S_{298.15}]$ were calculated in the range from 80 to 395 K based on the heat capacity data. The standard molar energy and standard molar enthalpy of combustion have been determined, $\Delta_c U$ (C₅H₅N₃O₂, s) = $-(2676.26 \pm 0.24)$ kJ mol⁻¹ and $\Delta_c H_m^\circ$ (C₅H₅N₃O₂, s) = $-(2673.16 \pm 0.24)$ kJ mol⁻¹, by means of a precision oxygen-bomb combustion calorimeter at $T = 298.15 \pm 0.001$ K. The standard molar enthalpy of formation has been derived, $\Delta_f H_m^\circ$ (C₅H₅N₃O₂, s) = $-(8.97 \pm 0.99)$ kJ mol⁻¹, from the standard molar enthalpy of combustion in combination with other auxiliary thermodynamic quantities through a Hess thermochemical cycle. The thermodynamic properties were further investigated through differential scanning calorimeter (DSC) and the thermogravimetric (TG) analysis.

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1. Introduction

2-Amino-5-nitropyridine is a necessary raw material for preparing azo-compounds, which have widely been used as coloring matter. Its molecular structure is:



2-Amino-5-nitropyridine has an interesting molecular structure, which has a nitro group as an electron donor and amino group as an electron acceptor. Further, the pyridine ring acts as a

cationic bonding site, the nitro group as a hydrogen acceptor, and the amino group as a hydrogen donor. Because of this special molecular structure, it has been commonly used as molecular building blocks of nonlinear optical materials, which have been the subject of very intensive studies in the last few years for their potential applicability in image processing and optical communications. It has also been used within hydrogen-bonded organic anionic networks, or as counterions in organic/inorganic salts [1–3]. Moreover, 2-amino-5-nitropyridine can be adsorbed on silver sols or surface to be employed in surface enhanced Raman scattering experiments or electrochemical research [4–6]. However, few data on thermodynamic properties of the organic compound have been reported till now. In order to improve the process of chemical synthesise and increase understanding of 2-amino-5-nitropyridine molecule, some of the thermodynamic properties have been studied in detail.

In this paper the low-temperature heat capacity over the temperature range (80–396 K) was measured by automated adiabatic calorimeter and the standard molar enthalpies of combustion

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of the compound at $T = 298.15$ K was determined by oxygen-bomb combustion calorimeter. In addition, the thermal stability of the compound was examined by thermogravimetry (TG) and differential scanning calorimetry (DSC).

2. Experimental

2.1. Sample

The 2-amino-5-nitropyridine is a yellow crystal. The sample for the present calorimetric study was purchased from ACROS Organics Company. The labeled purity is >0.980 mass fraction. The sample was purified by recrystallization three times using ethanol with an analytical grade prior to the calorimetric experiments. The structure of the compound was determined by IR, ^1H NMR and ^{13}C NMR, and the purity of the sample was analyzed by high-performance liquid chromatography (HPLC) to be more than 99.8 mol%.

2.2. Adiabatic calorimetry

Heat capacity measurements were carried out in a high-precision automated adiabatic system described in detail previously [7]. The sample amount used for the heat capacity measurement is 2.3269 g, which is equivalent to 16.727 mmol based on its molar mass of 139.11 g mol $^{-1}$. The heating duration and temperature increment for each experimental heat capacity point were usually controlled to be about 10 min and 1–3 K, respectively, during the whole experimental process.

Prior to the heat capacity measurements of the sample, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the reference standard material, synthetic sapphire ($\alpha\text{-Al}_2\text{O}_3$, NBS SRM 720). The sample mass used was 1.5482 g, which is equivalent to 15.1842 mmol based on its molar mass of 101.9612 g mol $^{-1}$. The deviations of our calibration results from the recommended values reported by Archer [8] of NIST are within of $\pm 0.2\%$ in the temperature range from 80 to 400 K.

2.3. Oxygen-bomb combustion calorimetry

The standard molar enthalpy of combustion was measured by means of an isoperibolic static-bomb oxygen combustion calorimeter. The structure and principle of the calorimeter have been described previously in detail [9–11].

The sample of about 0.6 g was pressed into pellets and put in a small sample crucible of about 4 cm 3 , which was suspended in the bomb of about 0.3 dm 3 , and burned under an oxygen pressure of 3.01 MPa ignited by a nickel fuse of about 16 cm. The purity of the oxygen used in the combustion was of research grade, mole fraction 0.99998. The energy of combustion of the nickel fuse (Q_{Ni}) was calculated from the formula, $Q_{\text{Ni}}(\text{J}) = 2.929\Delta L$, in which ΔL (cm) was the length of the combusted nickel wire. The energy of formation of the aqueous nitric acid produced by oxidation of a trace of nitrogen, which contained in the oxygen bomb and produced from the combustion reaction, was determined by the neutral titration with a

0.08684 mol dm $^{-3}$ of sodium hydroxide solution by using phenolphthalein as the indicator. The enthalpy of formation of the aqueous nitric acid in the oxygen bomb can be derived from the equation, $Q_{\text{HNO}_3}(\text{J}) = 59.8NV$, in which N (mol dm $^{-3}$) is the concentration of the sodium hydroxide solution and V (cm 3) is the volume of the consumed sodium hydroxide solution, based on the molar energy of formation of HNO_3 (aqueous) from N_2 (g), O_2 (g) and H_2O (l), $\Delta_f H_m^\circ = 59.8$ kJ mol $^{-1}$ [12,13], for 0.1 mol dm $^{-3}$ of HNO_3 (aqueous).

The calibration constant, $\varepsilon_{\text{calor}}$, of the calorimeter were determined by 10 combustion experiments using about 0.6 g of NIST 39i benzoic acid with certified massic energy of combustion under experimental conditions of $\Delta_c U = -(26,434 \pm 3)$ J g $^{-1}$ to be $\varepsilon_{\text{calor}} = (13,572 \pm 0.98)$ J K $^{-1}$. The uncertainty of the results was the standard deviation of mean value from the respective measurements.

2.4. Thermal analysis

Thermogravimetric (TG) measurement was performed on Setaram setsys 16/18 apparatus. A mass of 5.26 mg was placed in a 100 μl α -alumina crucible and heated from room temperature to 600 $^\circ\text{C}$ with a rate of 10 $^\circ\text{C min}^{-1}$ under high purity nitrogen atmosphere with a flow rate of 60 ml min $^{-1}$.

DSC analysis was carried out in a Setaram DSC-141 calorimeter. The sample about 3.46 mg was weighted into a closed aluminum pan, placed in the DSC cell and heated at the rate of 5 $^\circ\text{C min}^{-1}$ under high purity nitrogen atmosphere with a flow rate of 50 ml min $^{-1}$.

3. Results and discussion

3.1. Heat capacity

The experimental molar heat capacities are shown in Fig. 1 and tabulated in Table 1 of supplementary data file. The molar heat capacities were fitted to the following polynomial in reduced temperature (X), by means of least square fitting.

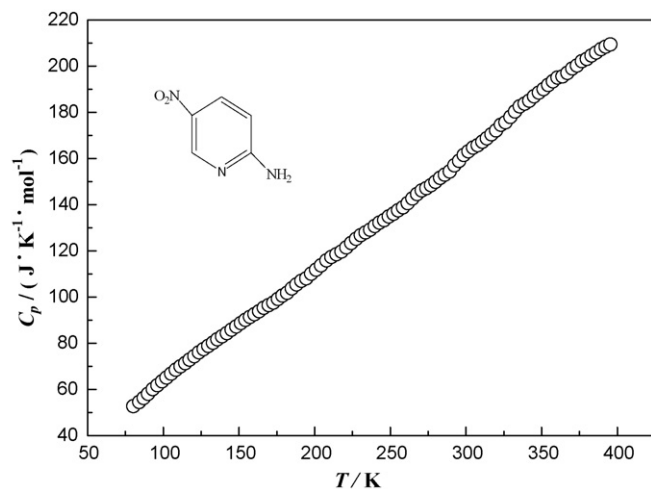


Fig. 1. Experimental molar heat capacity $C_{p,m}$ of 2-amino-5-nitropyridine as a function of temperature.

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