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Short communication

# Thermodynamic studies of crystalline 2-amino-5-nitropyridine ($C_5H_5N_3O_2$)

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**Abstract**

Low-temperature heat capacity $C_{p,\mathrm{m}}$ of 2-amino-5-nitropyridine ($C_5H_5N_3O_2$; 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, $\Delta_c U$ ($C_5H_5N_3O_2$, s) = −(2676.26 ± 0.24) kJ mol$^{-1}$ and $\Delta_c H_m^\circ$ ($C_5H_5N_3O_2$, s) = −(2673.16 ± 0.24) kJ mol$^{-1}$, by means of a precision oxygen-bomb combustion calorimeter at $T$ = 298.15 ± 0.001 K. The standard molar enthalpy of formation has been derived, $\Delta_f H_m^\circ$ ($C_5H_5N_3O_2$, s) = −(8.97 ± 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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*Keywords:* 2-Amino-5-nitropyridine; Heat capacity; Thermodynamic function; Adiabatic calorimetry; Standard molar enthalpy of combustion; Standard molar enthalpy of formation; TG; DSC

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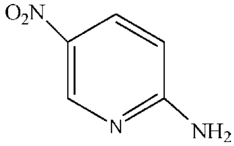
## 1. Introduction

2-Amino-5-nitropyridine is a necessary raw material for preparing azo-compounds, which have widely been used as coloring matter. It's 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 synthesize 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, $^{1}$H 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 ($\alpha$-$Al_2O_3$, 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 ±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 ($Q_{\mathrm{Ni}}$) was calculated from the formula, $Q_{\mathrm{Ni}}\ (\mathrm{J}) = 2.929\Delta L$, in which $\Delta L$ (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, $Q_{\mathrm{HNO_3}}\ (\mathrm{J}) = 59.8NV$, 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), $\Delta_f H_m^\circ = 59.8\ \mathrm{kJ\ mol^{-1}}$ [12,13], for 0.1 mol dm$^{-3}$ of $HNO_3$ (aqueous).

The calibration constant, $\varepsilon_{\mathrm{calor}}$, 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 $\Delta_c U = -(26{,}434 \pm 3)\ \mathrm{J\ g^{-1}}$ to be $\varepsilon_{\mathrm{calor}} = (13{,}572 \pm 0.98)\ \mathrm{J\ K^{-1}}$. 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 °C with a rate of 10 °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 °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.

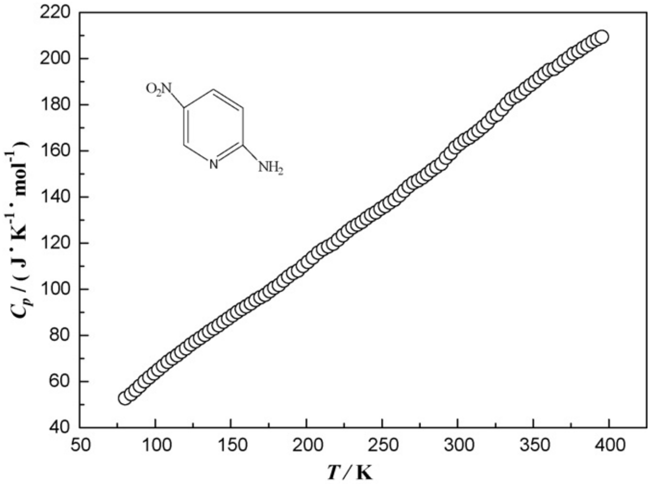

Fig. 1. Experimental molar heat capacity $C_{p,\mathrm{m}}$ of 2-amino-5-nitropyridine as a function of temperature.

Over the temperature range from 80 to 396 K:

$$C_p\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = 129.22603 + 78.78038X + 12.76753X^2 + 0.14324X^3 - 10.74162X^4$$

where $X = (T - 238)/158$ and $T$ is the absolute temperature. The correlation coefficient of the fitted curve, $R^2 = 0.99984$. The deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equation were within 0.3% except for several points around the lower and upper temperature limits. The value of 238 was obtained from half the sum of the upper limit temperature (396 K) and the lower limit temperature (80 K) in the experimental temperature range of 80–396 K, and 158 was from half the difference between the upper limit temperature (396 K) and the lower limit temperature (80 K) in the temperature range; the value $X$ is between +1 and −1.

The heat capacities increase with temperature in a smooth and continuous manner from 80 to 396 K. No phase transition or thermal anomaly was observed in this range.

### 3.2. Thermodynamic functions

The thermodynamic functions relative to the reference temperature (298.15 K) were calculated in the temperature range of 80–395 K with an interval of 5 K, using the polynomial equation for heat capacity and thermodynamic relationships as follows:

$$H_T - H_{298.15} = \int_{298.15}^{T} C_{p,\mathrm{m}}\,\mathrm{d}T \qquad (1)$$

$$S_T - S_{298.15} = \int_{298.15}^{T} \frac{C_{p,\mathrm{m}}}{T}\,\mathrm{d}T \qquad (2)$$

The values of thermodynamic function $H_T - H_{298.15}$, $S_\mathrm{T} - S_{298.15}$ are listed in Table 2 of supplementary data file.

### 3.3. Standard molar combustion energy, standard molar enthalpy of combustion and standard enthalpy of formation

The standard molar combustion energy can be calculated from the following equation:

$$\Delta_\mathrm{c}U\,(\mathrm{J\,mol^{-1}}) = \frac{(\varepsilon_\mathrm{calor}\,\Delta T - Q_\mathrm{Ni} - Q_{\mathrm{HNO_3}})M}{W} \qquad (3)$$

in which $\varepsilon_\mathrm{calor}$ ($\mathrm{J\,K^{-1}}$) is the energy equivalent of the oxygen bomb calorimeter, $\Delta T$ (K) the corrected temperature rise, $M$ ($\mathrm{g\,mol^{-1}}$) the molar mass of the sample and $W$ (g) is the mass of the sample. The results are $\Delta U_\mathrm{c} = (\overline{\Delta U_\mathrm{c}} \pm \sigma_\mathrm{a}, n = 6) = -(2676.26 \pm 0.24)\,\mathrm{kJ\,mol^{-1}}$.

The standard molar enthalpy of combustion, $\Delta_\mathrm{c}H_\mathrm{m}^\circ$, at $T = 298.15$ K and $P^0 = 100$ kPa can be derived from the standard molar combustion energy by means of the following formula:

$$\mathrm{C_5H_5N_3O_2\,(s)} + (21/4)\mathrm{O_2\,(g)} = 5\mathrm{CO_2\,(g)} + (5/2)\mathrm{H_2O\,(l)} + (3/2)\mathrm{N_2\,(g)} \qquad (4)$$

$$\Delta_\mathrm{c}H_\mathrm{m}^\circ = \Delta_\mathrm{c}U_\mathrm{m} + \Delta nRT \qquad (5)$$

$$\Delta n = \sum n_i(\text{products, g}) - \sum n_i(\text{reactants, g}) \qquad (6)$$

where $\Sigma n_i$ was the total molar amount of the gases in products or reactants. The calculated standard molar enthalpy of combustion of the organic compound was $\Delta_\mathrm{c}H_\mathrm{m}^\circ = -(2673.16 \pm 0.24)\,\mathrm{kJ\,mol^{-1}}$.

The standard molar enthalpy of formation, $\Delta_\mathrm{f}H_\mathrm{m}^\circ$, was calculated by a thermochemical cycle according to the reaction (4) as follows:

$$\Delta_\mathrm{f}H_\mathrm{m}^\circ\,(\mathrm{C_5H_5N_3O_4, s}) = [5\,\Delta_\mathrm{f}H_\mathrm{m}^\circ\,(\mathrm{CO_2, g}) + (5/2)\Delta_\mathrm{f}H_\mathrm{m}^\circ\,(\mathrm{H_2O, l})] - \Delta_\mathrm{c}H_\mathrm{m}^\circ\,(\mathrm{C_5H_5N_3O_4, s}) \qquad (7)$$

In the above formula, the standard molar enthalpies of formation of $\mathrm{CO_2}$ (g) and $\mathrm{H_2O}$ (l), recommended by CODATA [14,15], $\Delta_\mathrm{f}H_\mathrm{m}^\circ$ ($\mathrm{CO_2}$, g) = $-(393.51 \pm 0.13)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_\mathrm{f}H_\mathrm{m}^\circ$ ($\mathrm{H_2O}$, l) = $-(285.83 \pm 0.04)\,\mathrm{kJ\,mol^{-1}}$, were employed in the calculation of $\Delta_\mathrm{f}H_\mathrm{m}^\circ$ ($\mathrm{C_5H_5N_3O_4}$, s) values. Based on these values and the standard molar enthalpy of combustion, the standard molar enthalpy of formation of the organic compound can be calculated to be: $\Delta_\mathrm{f}H_\mathrm{m}^\circ$ ($\mathrm{C_5H_5N_3O_4}$, s) = $-(8.97 \pm 0.99)\,\mathrm{kJ\,mol^{-1}}$.

### 3.4. The results of TG–DTG and DSC analysis

TG and DTG curves of 2-amino-5-nitropyridine are shown in Fig. 2. The mass loss was completed in a single step, reaching the maximum rate at $T = 554.5$ K. The weight loss is 100% when the temperature reaches 560 K. The FT-IR spectrum of the condensation product of 2-amino-5-nitropyridine heated to about $T = 580$ K was the same as that of the original sample. Thus we can deduce that 2-amino-5-nitropyridine evaporates over the temperature range and completely changes into vapor at 560 K under the present experimental conditions.

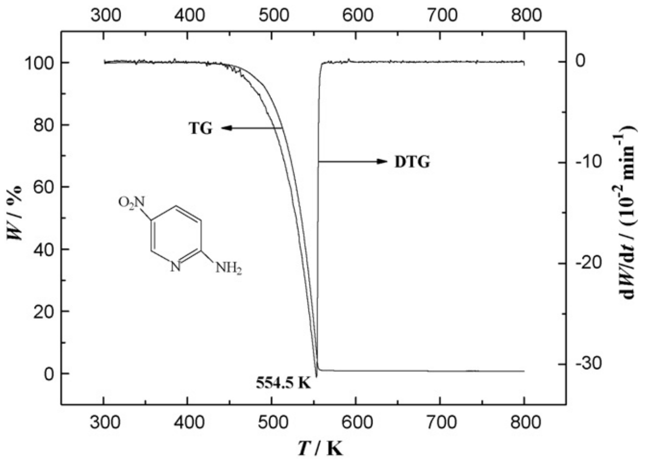

Fig. 2. TG–DTG curves of 2-amino-5-nitropyridine under high purity nitrogen. $W$ is the mass loss of the sample in percent.

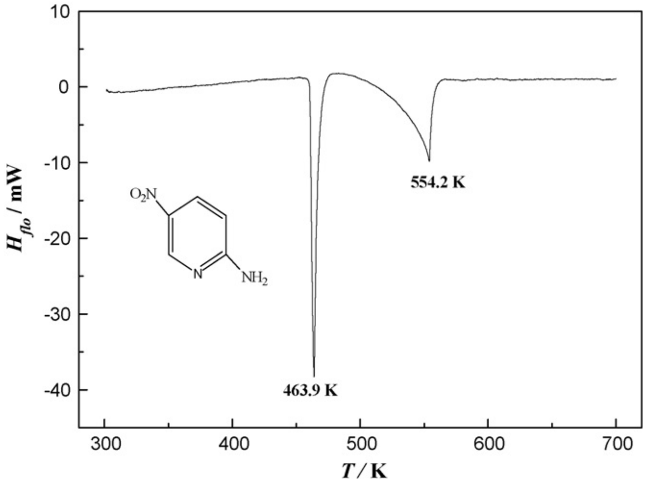

Fig. 3. DSC curve of 2-amino-5-nitropyridine under high purity nitrogen. $H_{\mathrm{flo}}$ is the heat flow.

The DSC curves are shown in Fig. 3. Two endothermic peaks appeared during the heating process with peak temperature 463.9 and 554.2 K, which are ascribed to melting and evaporation, respectively. The melting pointing is determined to be (461.4 ± 0.1 K), which coincides with the literature value [16]. The molar enthalpy of fusion was determined to be 29.2 kJ $\mathrm{mol}^{-1}$ through the integration of the area of the first peak. The molar entropy of fusion was derived to be 63.3 J $\mathrm{K}^{-1}$ $\mathrm{mol}^{-1}$.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2007.04.006.

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