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Low-temperature heat capacity and standard molar enthalpy of formation of crystalline 2-pyridinealdoxime ($C_6H_6N_2O$)

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Abstract

The thermodynamic properties of 2-pyridinealdoxime were investigated through the thermogravimetric (TG) analysis and differential scanning calorimetry (DSC). Low-temperature heat capacity $C_{p,\mathrm{m}}$ of 2-pyridinealdoxime ($C_6H_6N_2O$; CAS 873-69-8) was measured in the temperature range from (80 to 373) K with a high precision automated adiabatic calorimeter. No phase transition or thermal anomaly was observed in this range. The thermodynamic functions $[H_\mathrm{T} - H_{298.15}]$ and $[S_\mathrm{T} - S_{298.15}]$ were calculated in the range from (80 to 375) K. The constant-volume energy and standard molar enthalpy of combustion have been determined, $\Delta_\mathrm{c}U$ ($C_6H_6N_2O$, cr) = $\Delta_\mathrm{c}H^\circ_\mathrm{m}$ ($C_6H_6N_2O$, cr) = – (3297.11 ± 1.53) $\mathrm{kJ \cdot mol^{-1}}$ (based on Δn being zero in reaction of the combustion), 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, $\Delta_\mathrm{f}H^\circ_\mathrm{m}$ ($C_6H_6N_2O$, cr) = (78.56 ± 2.43) $\mathrm{kJ \cdot mol^{-1}}$, from the standard molar enthalpy of combustion in combination with other auxiliary thermodynamic quantities through a Hess thermochemical cycle.

Keywords: 2-Pyridinealdoxime; Heat capacity; Thermodynamic function; Adiabatic calorimetry; Standard molar enthalpy of combustion; Standard molar enthalpy of formation; TG; DSC

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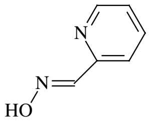
1. Introduction

2-Pyridinealdoxime is an important intermediate for preparing pralidoxime, which is worldwide used for the treatment of organophosphorus pesticide poisoning [1]. Its molecular structure is as follows:



Most of the present research carried out on 2-pyridinealdoxime was the coordination chemistry [2] because of its proper molecular structure. The structure depicted above consist of a pyridyl group attached to the oxime carbon atom, and it can act as a versatile ligand for a variety of objectives, including formation of polynuclear complexes (clusters), isolation of coordination polymers, mixed-metal chemistry, and significant magnetic characteristics [2]. For example, it has allowed the formation of a family of coordination chain compounds behaving as the so-called single-chain magnets [3,4]. Moreover, it is also an attractive synthetic reagents for allylic substitution since having both nitrogen and oxygen atoms as nucleophiles [5]. However, few data on thermodynamic properties of 2-pyridinealdoxime are reported till now. In order to

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improve the process of chemical synthesis and increase understanding of the organic compound, the study of thermodynamic properties for the substance are necessary.

In this paper, the thermal stability of 2-pyridinealdoxime was firstly examined by thermogravimetry (TG) and differential scanning calorimetry (DSC). After that the thermodynamic properties were further precisely studied. The low-temperature heat capacity over the temperature range (80 to 373) K was measured by an automated adiabatic calorimeter and the standard molar enthalpies of combustion at $T = 298.15$ K was determined by oxygen-bomb combustion calorimetry.

2. Experimental

2.1. Sample

The 2-pyridinealdoxime is a white 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 recrystallizing three times using ethanol with an analytical grade prior to the calorimetric experiments. The structure of the sample was determined by IR, ^{1}HNMR and ^{13}HNMR, and the purity was analyzed by high-performance liquid chromatography (HPLC) to be more than 99.8 mol%.

2.2. Thermal analysis

Thermogravimetric (TG) measurement was performed on Setaram setsys 16/18 apparatus. A mass of 5.68 mg was placed in a 100 μl α-alumina crucible and heated from room temperature to 500 °C with a rate of $10\ °\mathrm{C} \cdot \mathrm{min}^{-1}$ under high purity nitrogen atmosphere with a flow rate of $60\ \mathrm{mL} \cdot \mathrm{min}^{-1}$.

DSC analysis was carried out in a Setaram DSC-141 calorimeter. The sample about 3.15 mg was weighted into a closed aluminum pan, placed in the DSC cell and heated at the rate of $5\ °\mathrm{C} \cdot \mathrm{min}^{-1}$ under high purity nitrogen atmosphere with a flow rate of $50\ \mathrm{ml} \cdot \mathrm{min}^{-1}$.

2.3. Adiabatic calorimetry

Heat capacity measurements were carried out in a high-precision automated adiabatic calorimeter described in detail previously [6]. The sample amount used for the heat capacity measurement is 2.52641 g, which is equivalent to 20.688 mmol based on its molar mass of $122.12\ \mathrm{g} \cdot \mathrm{mol}^{-1}$. The heating duration and temperature increment for each experimental heat capacity point were usually controlled to be about 10 min and (1 to 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, α-Al_2O_3. The sample mass used was 6.56257 g, which is equivalent to 64.363 mmol based on its molar mass of $101.9612\ \mathrm{g} \cdot \mathrm{mol}^{-1}$. The deviations of our calibration results from the recommended values reported by Archer [7] of NIST are within of ±0.2% in the temperature range from 80 to 380 K.

2.4. Oxygen-bomb combustion calorimetry

The constant-volume enthalpy of combustion was measured by means of a precision oxygen-bomb combustion calorimeter, which was an isoperibolic calorimeter with a static oxygen bomb. The calorimeter was set up in our thermochemistry laboratory, and the structure and principle of the calorimeter have been described previously in detail [8–10].

The sample of (0.6 to 0.7) g was pressed into pellets and put in a small sample crucible of about $0.004\ \mathrm{dm}^3$, which was suspended in the bomb of about $0.3\ \mathrm{dm}^3$, 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 real energy of combustion of the nickel fuse (Q_{Ni}) was calculated from the formula, $Q_{\mathrm{Ni}}/J = 2.929 \cdot \Delta L$, in which $\Delta L/\mathrm{cm}$ 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 $0.08684\ \mathrm{mol} \cdot \mathrm{dm}^{-3}$ of sodium hydroxide solution by using the phenolphthalein as the indicator. The enthalpy of formation of the aqueous nitric acid in the oxygen bomb can be derived from the equation, $Q_{\mathrm{HNO_3}}/J = 59.8 \cdot N \cdot V$, in which $N/\mathrm{mol} \cdot \mathrm{dm}^{-3}$ 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(aq) from N_2(g), O_2(g) and H_2O(l), $\Delta_f H_m^\circ = 59.8\ \mathrm{kJ} \cdot \mathrm{mol}^{-1}$ [11,12], for $0.1\ \mathrm{mol} \cdot \mathrm{dm}^{-3}$ of HNO_3(aq).

3. Results and discussion

3.1. The results of TG–DTG and DSC analysis

TG and DTG curves of 2-pyridinealdoxime are shown in figure 1. It can be seen that the mass loss was completed in a single step, reaching the maximum rate at $T = 489.93$ K. The weight loss is 100% when the temperature reaches 510 K. The FT-IR spectrum of the condensation product of 2-pyridinealdoxime heated to about $T = 550$ K was the same as that of the original sample. Thus, we can deduce that 2-pyridinealdoxime evaporates over the temperature range and completely changes into vapor at 510 K under the present experimental conditions.

The DSC curves are shown in figure 2. Two endothermic peak appeared during the heating process with peak temperature 388.87 K and 503.73 K, which are ascribed to melting and evaporation, respectively. The melting pointing was determined to be 386.23 K, which coincides with

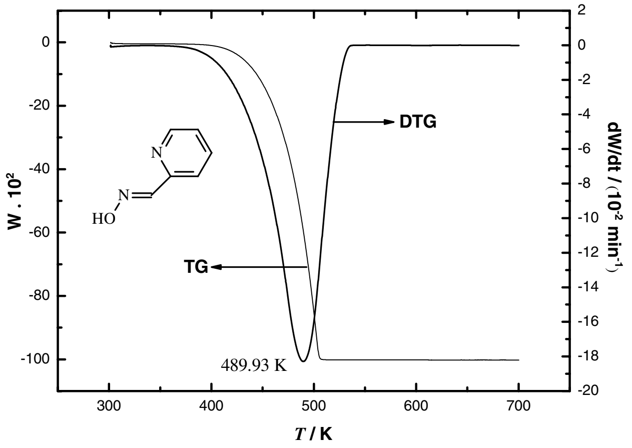

FIGURE 1. TG–DTG curves of 2-pyridinealdoxime under high purity nitrogen, W is the mass lose of the sample in percent.

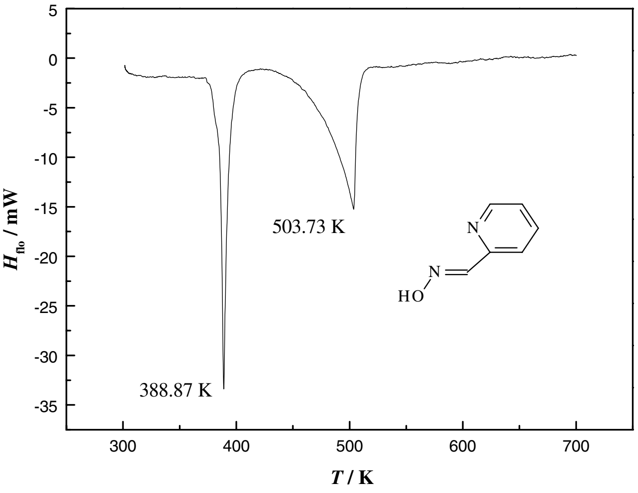

FIGURE 2. DSC curve of 2-pyridinealdoxime under high purity nitrogen, H_{flo} is the heat flow.

the literature value [15]. The molar enthalpy of fusion was determined to be 19.98 kJ · mol^{-1} by integration of the area of the first peak. The molar entropy of fusion was derived to be 51.73 J · K^{-1} · mol^{-1}.

3.2. Heat capacity

The experimental molar heat capacities of 2-pyridinealdoxime are shown in figure 3 and tabulated in table 1. The molar heat capacities were fitted to the following polynomial in reduced temperature (X), by means of least square fitting.

Over the temperature range from (80 to 373) K,

$$C_p(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 117.80909 + 67.31264X + 7.28686X^2 - 1.2219X^3 - 7.0761X^4$$

where $X = (T - 226.5)/146.5$, and T is the absolute temperature. The correlation coefficient of the fitted curve, $R^2 = 0.99991$. 226.5 was obtained from half the sum of

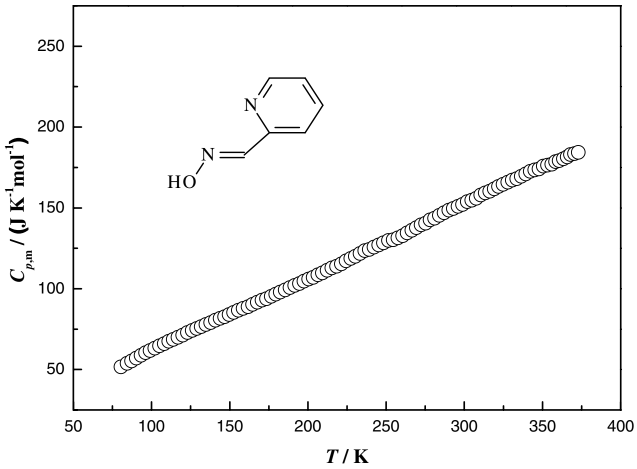

FIGURE 3. Experimental molar heat capacity $C_{p,\text{m}}$ of 2-pyridinealdoxime as a function of temperature.

the upper limit temperature (373 K) and the lower limit temperature (80 K) in the experimental temperature range of (80 to 373) K, and 146.5 was from half the difference

TABLE 1
The experimental molar heat capacity data of 2-pyridinealdoxime (molar mass $M = 122.12$ g · mol^{-1})

T/K	C_p (J · K^{-1} · mol^{-1})	T/K	C_p (J · K^{-1} · mol^{-1})	T/K	C_p (J · K^{-1} · mol^{-1})
80.459	51.676	182.381	97.915	284.009	145.454
84.395	53.782	185.453	99.230	287.035	147.062
87.269	55.385	188.500	100.673	290.037	148.677
90.224	57.071	191.524	101.974	293.009	149.589
93.263	58.782	194.525	103.155	295.976	150.985
96.219	60.423	197.504	104.640	298.931	152.097
99.102	61.803	200.466	106.057	301.865	153.857
102.071	63.155	203.408	107.000	304.784	154.721
105.127	64.653	206.328	108.590	307.687	155.908
108.120	65.953	209.234	109.824	310.570	157.909
111.052	67.399	212.222	111.347	313.438	159.333
113.933	68.687	215.294	112.899	316.285	160.277
116.902	69.935	218.346	113.966	319.112	161.830
119.961	71.329	221.376	115.374	321.922	163.285
122.969	72.927	224.384	117.315	324.797	164.636
125.935	74.138	227.368	118.697	327.740	165.878
128.855	75.406	230.298	120.004	330.664	167.182
131.738	76.558	233.323	121.772	333.568	168.109
134.710	77.885	236.347	123.515	336.450	169.621
137.773	79.053	239.262	124.251	339.314	171.009
140.797	80.490	242.248	125.830	342.158	172.573
143.787	81.654	245.318	127.093	344.982	173.513
146.741	82.724	248.389	128.401	347.783	174.141
149.664	83.990	251.438	129.847	350.554	175.824
152.558	85.274	254.474	130.364	353.292	176.471
155.540	86.711	257.497	131.522	355.961	177.079
158.614	87.834	260.500	132.739	358.396	178.592
161.656	88.910	263.487	134.492	360.605	179.152
164.672	90.296	266.458	136.140	363.305	180.384
167.664	91.696	269.411	137.724	365.844	181.564
170.634	92.907	272.346	139.497	367.878	182.966
173.579	93.875	275.265	140.579	370.494	183.669
176.498	95.229	278.165	142.551	372.973	184.416
179.396	96.674	281.055	143.696		

between the upper limit temperature (373 K) and the lower limit temperature (80 K) in the temperature range; the value X is between +1 and −1.

It can be seen from figure 3 that the heat capacities of the sample increases with temperature in a smooth and continuous manner from 80 to 373 K. No phase transition or thermal anomaly was observed in this range. Therefore, the sample is structurally stable in the temperature range from 80 to 373 K.

3.3. Thermodynamic functions

The thermodynamic functions relative to the reference temperature 298.15 K were calculated in the temperature range (80 to 375) K with an interval of 5 K, using the polynomial equation for heat capacity and thermodynamic relationships as follows:

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

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

The values of thermodynamic function $H_T - H_{298.15}$, $S_T - S_{298.15}$ are listed in table 2.

3.4. Constant-volume combustion energy, standard molar enthalpy of combustion and standard enthalpy of formation

The constant-volume combustion energy can be calculated from the equation:

$$\Delta_c U/\mathrm{J\cdot mol^{-1}} = (\varepsilon_{\mathrm{calor}} \cdot \Delta T - Q_{\mathrm{Ni}} - Q_{\mathrm{HNO_3}}) \cdot M/W$$

in which $\varepsilon_{\mathrm{calor}}/\mathrm{J\cdot K^{-1}}$ was the energy equivalent of the oxygen bomb calorimeter; ΔT/K, the corrected temperature rise; $M/\mathrm{g\cdot mol^{-1}}$, the molar mass of the sample; W/g, the mass of the sample. The results calculated by the equation were listed in table 3.

The standard molar enthalpy of combustion, $\Delta_c H^\circ_m$, referred to the combustion enthalpy change of the following reaction at $T = 298.15$ K and $P^\circ = 100$ kPa based on the definition of the combustion enthalpy:

$$C_6H_6N_2O(\mathrm{cr}) + 7O_2(\mathrm{g}) = 6CO_2(\mathrm{g}) + 3H_2O(\mathrm{l}) + N_2(\mathrm{g}) \qquad (3)$$

The standard molar enthalpies of combustion can be derived from the constant-volume combustion energy by means of the following formula:

$$\Delta_c H^\circ_m = \Delta_c U_m + \Delta n \cdot RT,$$
$$\Delta n = \Sigma n_i\ (\text{products, g}) - \Sigma n_i\ (\text{reactants, g}),$$

where Σn_i was the total molar amount of the gases in products or reactants. The calculated standard molar enthalpy of combustion was: $\Delta_c H^\circ_m = -(3297.11 \pm 1.53)\ \mathrm{kJ\cdot mol^{-1}}$.

The standard molar enthalpy of formation, $\Delta_f H^\circ_m$, was calculated by a designed Hess thermochemical cycle according to the reaction (3) as follows:

TABLE 2
Calculated thermodynamic function data of 2-pyridinealdoxime

T/K	C_p ($\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$)	$H_T - H_{298.15}$ ($\mathrm{kJ\cdot mol^{-1}}$)	$S_T - S_{298.15}$ ($\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$)
80	51.929	−22.175	−120.019
85	54.534	−21.909	−116.792
90	57.073	−21.630	−113.603
95	59.550	−21.339	−110.450
100	61.972	−21.035	−107.334
105	64.345	−20.719	−104.253
110	66.673	−20.391	−101.206
115	68.963	−20.052	−98.191
120	71.219	−19.702	−95.208
125	73.446	−19.340	−92.256
130	75.649	−18.967	−89.332
135	77.831	−18.584	−86.436
140	79.997	−18.189	−83.567
145	82.150	−17.784	−80.722
150	84.294	−17.368	−77.901
155	86.433	−16.941	−75.102
160	88.570	−16.503	−72.324
165	90.706	−16.055	−69.566
170	92.846	−15.596	−66.826
175	94.992	−15.127	−64.104
180	97.145	−14.646	−61.398
185	99.308	−14.155	−58.707
190	101.482	−13.653	−56.029
195	103.670	−13.140	−53.365
200	105.871	−12.616	−50.713
205	108.088	−12.082	−48.071
210	110.321	−11.536	−45.440
215	112.570	−10.978	−42.817
220	114.837	−10.410	−40.204
225	117.121	−9.830	−37.597
230	119.421	−9.239	−34.998
235	121.739	−8.636	−32.405
240	124.072	−8.021	−29.817
245	126.421	−7.395	−27.235
250	128.784	−6.757	−24.657
255	131.161	−6.107	−22.084
260	133.548	−5.445	−19.514
265	135.946	−4.772	−16.947
270	138.352	−4.086	−14.383
275	140.763	−3.388	−11.823
280	143.177	−2.678	−9.265
285	145.592	−1.956	−6.709
290	148.005	−1.222	−4.156
295	150.413	−0.476	−1.606
298.15	151.925	0.000	0.000
300	152.812	0.282	0.943
305	155.199	1.052	3.488
310	157.569	1.834	6.031
315	159.920	2.628	8.571
320	162.246	3.433	11.108
325	164.544	4.250	13.641
330	166.808	5.078	16.170
335	169.033	5.918	18.696
340	171.215	6.769	21.216
345	173.348	7.630	23.731
350	175.427	8.502	26.240
355	177.444	9.384	28.743
360	179.396	10.276	31.239
365	181.274	11.178	33.726
370	183.072	12.089	36.205
375	184.785	13.009	37.674

TABLE 3
The experimental results of the combustion energies of 2-pyridinealdoxime obtained from the oxygen-bomb combustion calorimetry at $T = 298.15$ K

No.	Sample mass (m/g)	Heat value of nickel wire (Q_{Ni}/J)	Heat value of nitric acid (Q_{N}/J)	Corrected temperature rise ΔT/K	Combustion energies ΔU_{c} / ($\mathrm{kJ \cdot mol^{-1}}$)
1	0.63349	41.003	50.889	1.22898	3299.41
2	0.62331	39.832	52.343	1.20962	3300.14
3	0.61522	39.932	52.187	1.19345	3298.60
4	0.61795	39.334	52.135	1.19611	3291.52
5	0.62658	38.702	51.979	1.2157	3299.80
6	0.62207	39.832	52.264	1.20469	3293.18
Avg. $\Delta U_{\mathrm{c}} = (\overline{\Delta U_{\mathrm{c}}} \pm \sigma_{\mathrm{a}})^{a} = -(3297.11 \pm 1.53)\ \mathrm{kJ \cdot mol^{-1}}$					

[a] $\sigma_{\mathrm{a}} = \left(\sum_{i=1}^{n}(x_i - \bar{x})^2/n(n-1)\right)^{1/2}$, in which n is the experimental number; x_i, a single value of combustion energies; $\bar{x}$, the mean value of combustion energies.

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{C_6H_6N_2O, cr}) = [6\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{CO_2, g}) + 3\Delta_{\mathrm{f}}\mathrm{H}^{\circ}_{\mathrm{m}}(\mathrm{H_2O, l})] - \Delta_{\mathrm{c}}H^{\circ}_{\mathrm{m}}(\mathrm{C_6H_6N_2O,\ cr}).$$

In the above formula, the standard molar enthalpies of formation of CO_2(g) and H_2O (l), recommended by *CODATA* [13,14], $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (CO_2, g) $= -(393.51 \pm 0.13)$ $\mathrm{kJ \cdot mol^{-1}}$ and $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (H_2O, l) $= -(285.83 \pm 0.04)$ $\mathrm{kJ \cdot mol^{-1}}$, were employed in the calculation of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($C_6H_6N_2O$, cr) values. Based on these values and the standard molar enthalpy of combustion, the standard molar enthalpy of formation can be calculated to be: $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($C_6H_6N_2O$, cr) $= (78.56 \pm 2.43)\ \mathrm{kJ \cdot mol^{-1}}$.

Acknowledgements

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