Heat Capacities and Thermodynamic Properties of (3,4-Dimethoxyphenyl) Acetonitrile ($C_{10}H_{11}NO_2$)[†]

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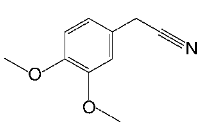
The heat capacities of (3,4-dimethoxyphenyl) acetonitrile were measured by a small sample precision automated adiabatic calorimeter over the temperature range from (78 to 399) K. A melting phase transition was observed in the experimental range. The melting temperature, the molar enthalpy, and entropy of the phase transition were determined to be (336.818 ± 0.005) K, (24.72 ± 0.14) $kJ\cdot mol^{-1}$, and (73.40 ± 0.40) $J\cdot K^{-1}\cdot mol^{-1}$. The mole fraction purity of the sample used in the adiabatic calorimetric study was determined to be 0.99602 according to the van't Hoff equation. The thermodynamic functions, $(H_T - H_{298.15\ K})$ and $(S_T - S_{298.15\ K})$, were calculated. The standard molar energy and enthalpy of combustion have been determined, $\Delta_c U_m{}^0$ ($C_{10}H_{11}NO_2$,s) = −(5297.97 ± 2.45) $kJ\cdot mol^{-1}$ and $\Delta_c H_m{}^0$ ($C_{10}H_{11}NO_2$, s) = −(5301.07 ± 2.45) $kJ\cdot mol^{-1}$, by means of a precision oxygen-bomb combustion calorimeter at T = 298.15 K. The standard molar enthalpy of formation has been derived, $\Delta_f H_m{}^0$ ($C_{10}H_{11}NO_2$, s) = −(206.10 ± 3.97) $kJ\cdot mol^{-1}$.

Introduction

Nitrile is a functional group that usually is transformed to amides or carboxylic acids under strong reaction conditions in acidic or basic media and high temperatures.[1] (3,4-Dimethoxyphenyl) acetonitrile (CAS: 93-17-4) is an important chemical raw material and intermediate in the preparation of many medicines. In the medicine industry, it can be deoxidized to (3,4-dimethoxyphenyl) ethylamine which is used in synthesizing Verapamil, narceine, and Bevantold.[2,3] The molecular formula of (3,4-dimethoxyphenyl) acetonitrile is $C_{10}H_{11}NO_2$; the molar mass is 177.1999 $g\cdot mol^{-1}$; and the molecular structure is



The heat capacity is a fundamental thermodynamic property and characteristic quantity closely related to energetics and structure of materials. From heat capacity data, many other thermodynamic properties such as enthalpy and Gibbs free energy, which are of importance to both theoretical and practical purposes, can be calculated.[4] However, up till now, the fundamental thermodynamic data of (3,4-dimethoxyphenyl) acetonitrile have not been reported in the literature. To improve the process of chemical and medicine synthesis, the study of thermodynamic properties for the substance is necessary. In this paper, the low-temperature heat capacity of this compound over the temperature range (78 to 399) K was measured by an automated adiabatic calorimeter. The standard molar enthalpy of combustion at T = 298.15 K was determined by oxygen-bomb combustion calorimetry.

Experimental

The sample used for the present calorimetric study was purchased from ACROS ORGANICS Company. The labeled chemical mass fraction purity was > 0.99.

A precision automatic adiabatic calorimeter was used to measure the heat capacity over the temperature range between T = 77 K and T = 399 K. The calorimeter was developed in our Thermochemistry Laboratory. The principle and structure of the calorimeter were described in detail elsewhere.[4–6] The temperature increment for each experimental heat capacity point was usually controlled about 3 K during the whole experimental process. The sample mass used for calorimetric measurements was 2.09943 g, which was equivalent to 0.011848 mol. Prior to the heat capacity measurements of the sample, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the synthetic sapphire (α-Al_2O_3), Standard Reference Material 720. The deviations of our calibration results from those of the smoothed curve lie within ± 0.2 %, while the uncertainty is within ± 0.3 %, as compared with the recommended values reported by Archer[7] of NIST in the temperature range from (80 to 405) K.

The standard molar energy of combustion of the sample was measured by means of a homemade precision oxygen-bomb combustion calorimeter. It was an isoperibolic macrocalorimeter with a static oxygen bomb. The structure and principle of the calorimeter have been described previously in brief.[8,9] A sample (about 0.65 g) was pressed into a pellet and put in a small sample crucible of about 0.004 dm^3, which was suspended in the bomb of about 0.3 dm^3, and burned under an oxygen pressure of about 3 MPa. It was ignited by a nickel fuse of about 16 cm in the presence of 0.001 dm^3 of distilled water in the bomb to ensure equilibrium in the final state after the combustion. The real energy of combustion of the nickel fuse (Q_{Ni}) was calculated

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Table 1. Experimental Molar Heat Capacities of (3,4-Dimethoxyphenyl) Acetonitrile

T / K	$C_{p,\mathrm{m}}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	T / K	$C_{p,\mathrm{m}}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	T / K	$C_{p,\mathrm{m}}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
78.316	80.52	196.372	174.3	312.480	256.0
81.065	82.37	199.232	175.5	315.486	259.8
84.382	84.71	202.706	177.3	318.586	261.9
87.299	87.42	206.121	180.1	321.662	267.0
90.167	89.84	208.906	182.6	324.716	275.0
93.050	91.31	211.792	184.7	327.730	284.8
95.923	93.07	214.669	185.5	330.673	313.0
98.777	94.96	217.535	187.8	333.418	462.0
102.801	97.78	220.393	189.8	335.413	1609.6
106.788	101.8	223.237	192.6	336.283	6546.3
109.625	103.7	226.072	194.1	336.566	13531.1
112.503	106.5	228.974	196.0	336.703	21056.6
115.382	108.6	231.922	198.1	336.789	29096.0
118.251	111.0	234.864	200.2	336.823	70823.0
121.124	113.3	237.825	201.4	336.860	67651.4
123.994	115.6	240.775	203.0	336.888	57318.7
126.872	118.0	244.260	204.7	336.920	40647.3
129.708	120.3	247.725	206.0	338.201	630.6
132.551	122.1	250.620	206.7	342.040	352.0
135.400	124.9	253.504	208.8	345.022	352.7
138.257	127.8	256.375	210.7	348.083	354.6
141.121	129.7	259.238	213.1	351.142	356.8
143.944	131.8	262.095	214.8	354.195	358.7
146.778	134.2	264.938	216.4	357.244	360.1
149.623	136.7	267.886	218.3	360.284	361.3
153.269	139.5	270.928	221.1	363.322	362.6
156.884	142.9	273.960	223.6	366.351	364.4
159.692	144.6	276.980	226.3	369.378	366.3
162.545	146.5	279.994	228.9	372.400	367.9
165.365	148.6	282.996	231.4	375.418	368.7
168.161	151.4	285.983	234.1	378.429	370.1
170.931	153.9	288.954	236.8	381.437	371.6
173.775	156.3	291.892	239.8	384.440	373.0
176.627	157.8	294.782	242.2	387.437	374.5
179.459	159.5	297.684	245.2	390.427	376.1
182.268	162.3	300.708	247.1	393.410	377.4
185.060	164.3	303.675	250.1	396.394	379.4
187.827	167.4	306.624	252.2	399.376	380.9
190.652	168.8	309.559	254.2		

from the formula, $Q_{\mathrm{Ni}}/\mathrm{J} = 2.929 \cdot \Delta L$, 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 was contained in the oxygen bomb and was produced from the combustion reaction, was determined by the neutral titration with 0.05292 $\mathrm{mol \cdot dm^{-3}}$ 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, $Q_{\mathrm{HNO_3}}/\mathrm{J} = 59.831 \cdot N \cdot V$, in which $N/\mathrm{mol \cdot dm^{-3}}$ is the concentration of the sodium hydroxide solution and $V/\mathrm{cm^3}$ is the volume of the consumed sodium hydroxide solution.

Results and Discussion

Heat Capacity. The experimental molar heat capacities of (3,4-dimethoxyphenyl) acetonitrile are tabulated in Table 1 and shown in Figure 1. The molar heat capacities were fitted to the two following polynomial equations by the least-squares fitting. For the solid phase over the temperature range (78 to 320) K

$$C_{p,\mathrm{m}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 174.86374 + 85.18846X - 19.79301X^2 + 7.15223X^3 + 18.19188X^4 \quad (1)$$

where X is the reduced temperature, and $X = [T - (T_{\max} + T_{\min})/2]/[(T_{\max} - T_{\min})/2]$, where T is the experimental temperature. In this equations, $T_{\max}$ is the upper limit (320 K), and $T_{\min}$ is the lower limit (78 K). So $X = [(T/\mathrm{K} - 199)/121]$. Thus, it could be made the value of X between +1 and −1. The correlation coefficient of the fitted curve $R^2 = 0.9997$.

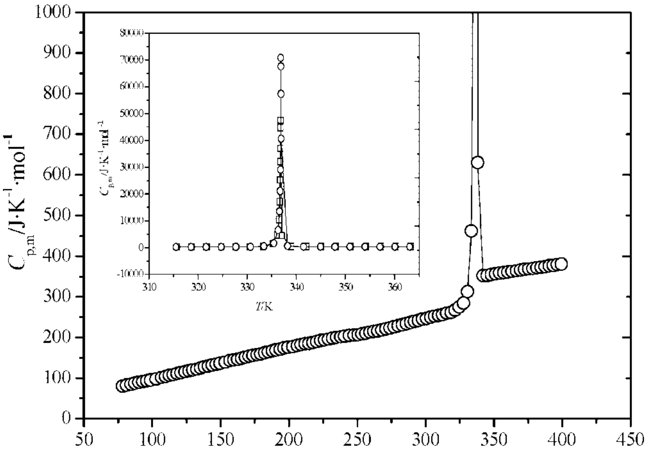

Figure 1. Experimental molar heat capacity $C_{p,\mathrm{m}}$ of (3,4-dimethoxyphenyl) acetonitrile as a function of temperature.

For the liquid phase over the temperature range (340 to 400) K

$$C_{p,\mathrm{m}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 366.3341 + 366.3341X - 1.69161X^2 + 1.06215X^3 + 1.35034X^4 \quad (2)$$

where $X = [(T/\mathrm{K} - 370)/30]$, and $R^2 = 0.9990$.

Thermodynamic Functions. The thermodynamic functions relative to the reference temperature of 298.15 K were calculated in the temperature range (80 to 320) K and (340 to 400) K with an interval of 5 K, using the polynomial equations of heat capacity and thermodynamic relationships as follows

Before the melting of the sample

$$H_T - H_{298.15\mathrm{K}} = \int_{298.15\mathrm{K}}^{T} C_{p,\mathrm{m}}(\mathrm{s})\mathrm{d}T \quad (3)$$

$$S_T - S_{298.15\mathrm{K}} = \int_{298.15\mathrm{K}}^{T} C_{p,\mathrm{m}}(\mathrm{s})T^{-1}\mathrm{d}T \quad (4)$$

After the melting of the sample

$$H_T - H_{298.15\mathrm{K}} = \int_{298.15\mathrm{K}}^{T_\mathrm{i}} C_{p,\mathrm{m}}(\mathrm{s})\mathrm{d}T + \Delta_{\mathrm{fus}}H_\mathrm{m} + \int_{T_\mathrm{f}}^{T} C_{p,\mathrm{m}}(\mathrm{l})\mathrm{d}T \quad (5)$$

$$S_T - S_{298.15\mathrm{K}} = \int_{298.15\mathrm{K}}^{T_\mathrm{i}} [C_{p,\mathrm{m}}(\mathrm{s})T^{-1}]\mathrm{d}T + \Delta_{\mathrm{fus}}H_\mathrm{m} \cdot T_\mathrm{m}^{-1} + \int_{T_\mathrm{f}}^{T} [C_{p,\mathrm{m}}(\mathrm{l})T^{-1}]\mathrm{d}T \quad (6)$$

The values of thermodynamic function $[H_T - H_{298.15\mathrm{K}}]$ and $[S_T - S_{298.15\mathrm{K}}]$ are listed in Table 2.

Temperature, Molar Enthalpy and Entropy of Fusion. The molar enthalpy $\Delta_{\mathrm{fus}}H_\mathrm{m}$ and entropy $\Delta_{\mathrm{fus}}S_\mathrm{m}$ of fusion of the compound were calculated from the following equations

$$\Delta_{\mathrm{fus}}H_\mathrm{m} = \left[Q - n\int_{T_\mathrm{i}}^{T_\mathrm{m}} C_p(\mathrm{s})\mathrm{d}T - n\int_{T_\mathrm{m}}^{T_\mathrm{f}} C_p(\mathrm{l})\mathrm{d}T - \int_{T_\mathrm{i}}^{T_\mathrm{f}} \bar{H}_0\mathrm{d}T\right]/n \quad (7)$$

$$\Delta_{\mathrm{fus}}S_\mathrm{m} = \Delta_{\mathrm{fus}}H_\mathrm{m}/T_\mathrm{m} \quad (8)$$

where T_i is the temperature slightly lower than the initial melting temperature; T_f is the temperature slightly higher than the final melting temperature; Q is the total energy introduced to the sample cell from T_i to T_f; $C_p(\mathrm{s})$ is the heat capacity of the sample in the solid phase from T_i to T_m; $C_p(\mathrm{l})$ is the heat capacity of

Table 2. Smoothed Heat Capacities and Thermodynamic Functions of (3,4-Dimethoxyphenyl) Acetonitrile

T / K	$C_{p,\mathrm{m}}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$H_T - H_{298.15\ \mathrm{K}}$ / $\mathrm{kJ \cdot mol^{-1}}$	$S_T - S_{298.15\ \mathrm{K}}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
80	82.15	−35.86	−193.5
85	85.39	−35.45	−188.4
90	88.81	−35.01	−183.4
95	92.41	−34.56	−178.5
100	96.15	−34.09	−173.7
105	100.0	−33.60	−168.9
110	104.0	−33.09	−164.2
115	108.0	−32.56	−159.5
120	112.1	−32.01	−154.8
125	116.3	−31.44	−150.1
130	120.4	−30.84	−145.5
135	124.6	−30.23	−140.9
140	128.8	−29.60	−136.2
145	133.0	−28.94	−131.7
150	137.1	−28.27	−127.1
155	141.2	−27.57	−122.5
160	145.3	−26.86	−118.0
165	149.3	−26.12	−113.4
170	153.3	−25.36	−108.9
175	157.2	−24.59	−104.4
180	161.0	−23.79	−99.95
185	164.7	−22.98	−95.49
190	168.4	−22.15	−91.05
195	172.0	−21.30	−86.63
200	175.6	−20.43	−82.23
205	179.0	−19.54	−77.86
210	182.5	−18.64	−73.50
215	185.8	−17.72	−69.17
220	189.1	−16.78	−64.87
225	192.4	−15.83	−60.58
230	195.6	−14.86	−56.32
235	198.8	−13.87	−52.09
240	202.0	−12.87	−47.87
245	205.2	−11.86	−43.68
250	208.4	−10.82	−39.50
255	211.6	−9.774	−35.35
260	214.9	−8.709	−31.21
265	218.2	−7.627	−27.09
270	221.6	−6.529	−22.98
275	225.2	−5.413	−18.89
280	228.8	−4.279	−14.80
285	232.6	−3.126	−10.72
290	236.6	−1.954	−6.645
295	240.8	−0.762	−2.569
298.15	243.5	0.000	0.000
300	245.2	0.452	1.510
305	249.8	1.688	5.597
310	254.8	2.948	9.694
315	260.0	4.233	13.81
320	265.6	5.546	17.94
325	phase transition		
330	phase transition		
335	phase transition		
340	350.5	44.36	135.5
345	353.2	46.12	140.6
350	356.0	47.90	145.7
355	358.7	49.69	150.8
360	361.4	51.49	155.8
365	363.9	53.31	160.9
370	366.3	55.13	165.8
375	368.7	56.97	170.8
380	371.0	58.82	175.7
385	373.3	60.69	180.5
390	375.7	62.56	185.4
395	378.4	64.45	190.2
400	381.5	66.35	195.0

the sample in the liquid phase from T_m to T_f, $\bar{H}_0$ is the heat capacity of the empty sample cell at temperature $(T_\mathrm{i} + T_\mathrm{f})/2$.

Table 3. Results of Phase Transition of the Compound Obtained from Two Series of Heat Capacity Measurements

thermodynamic properties	series 1, x_1	series 2, x_2	$(\bar{x} \pm \sigma_\mathrm{a})^a$
T_m/K	336.823	336.812	(336.818 ± 0.005)
$\Delta_\mathrm{trans}H_\mathrm{m}/(\mathrm{kJ \cdot mol^{-1}})$	24.86	24.59	(24.72 ± 0.14)
$\Delta_\mathrm{trans}S_\mathrm{m}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	73.80	72.99	(73.40 ± 0.40)

[a] $\sigma_a = \sqrt{\sum_{i=l}^{2} (x_1 - \bar{x})^2 / n(n-1)}$, in which n is the experimental number; x_i is a single value in a set of measurements; and $\bar{x}$ is the mean value of a set of measurement results.

Table 4. Experimental Results of Melting Fractions and Equilibrium Temperatures of (3,4-Dimethoxyphenyl) Acetonitrile

q/J	F	$1/F$	T/K
144.425	0.4930	2.0282	336.703
178.064	0.6079	1.6451	336.789
211.687	0.7227	1.3838	336.823
245.377	0.8377	1.1938	336.860
279.044	0.9526	1.0497	336.888

Two series of heat capacity measurements of the sample in the fusion region were carried out so that the reversibility and repeatability of the fusion process were verified. The results of the melting point, molar enthalpy, and entropy of fusion obtained from the two series of heat-capacity measurements are listed in Table 3.

Purity Determination. The purity of the sample was determined by a set of equilibrium melting temperatures and melting fractions corresponding to these temperatures. The principium was described in detail in the literature.[10,11] The experimental equilibrium melting temperature T and melting fraction F corresponding to the temperature are listed in Table 4. The equilibrium melting temperature T is plotted against the reciprocal of the melting fractions $1/F$ as shown in Figure 2. The melting points of the absolute pure sample, $T_0 = 337.082$ K, and that of the sample, $T_1 = 336.897$ K, can be obtained at $1/F = 0$ and $1/F = 1$, respectively. The mass fraction purity of the sample was determined to be 0.99602 (mol fraction).

Standard Molar Energy and Enthalpy of Combustion and Standard Molar Enthalpy of Formation. The standard molar energy of combustion of the compound can be calculated from the equation

$$\Delta_\mathrm{c}U^0 = (\varepsilon_\mathrm{calor} \cdot \Delta T - Q_\mathrm{Ni} - Q_{\mathrm{HNo}_3}) \cdot M/W \qquad (9)$$

where $\varepsilon_\mathrm{calor}/\mathrm{J \cdot K^{-1}}$ is the energy equivalent of the oxygen bomb calorimeter; ΔT is the corrected temperature rise; M is the molar mass of the sample; and W is the mass of the sample. The results calculated by the equation were listed in Table 5.

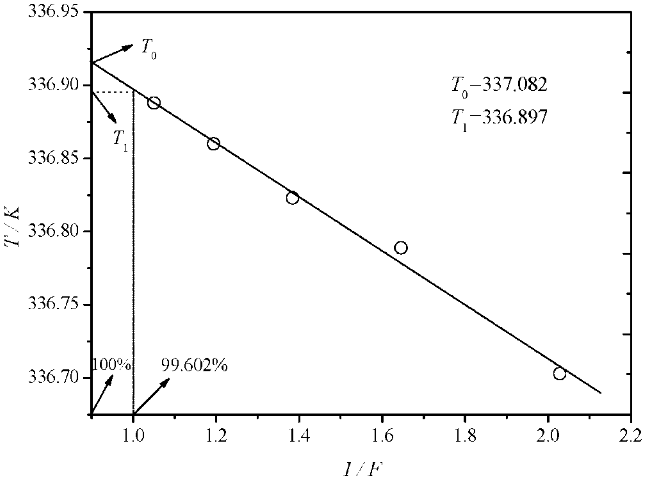

Figure 2. Melting curve (T vs $1/F$) of (3,4-dimethoxyphenyl) acetonitrile during fusion.

Table 5. Experimental Results of the Combustion Energies of the Compound Obtained from the Oxygen-Bomb Combustion Calorimetry at $T = 298.15$ K

	sample mass	heat value of nickel wire	heat value of nitric acid	corrected temperature rise	combustion energies
no.	m/g	Q_{Ni}/J	Q_N/J	ΔT/K	$\Delta U_c{}^0$/kJ·mol^{-1}
1	0.64899	35.731	45.277	1.3776	5290.15
2	0.64979	36.610	48.349	1.3822	5300.01
3	0.64107	33.974	48.855	1.3648	5304.73
4	0.65459	36.610	43.061	1.3869	5302.52
5	0.65396	36.610	41.351	1.3892	5295.22
6	0.65092	37.196	42.681	1.3829	5295.20

Average $\Delta U_c{}^0(s) = (\Delta \bar{U}_c^0 \pm \sigma_a)^a = -(5297.97 \pm 2.45)$ kJ·mol^{-1}

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

The standard molar enthalpy of combustion of the compound, $\Delta_c H_m^0$, referred to the combustion enthalpy change of the following reaction at $T = 298.15$ K and $P^0 = 100$ kPa based on the definition of the combustion enthalpy about the organic compound

$$C_{10}H_{11}NO_2(s) + 47/4O_2(g) = 10CO_2(g) + 11/2H_2O(l) + 1/2N_2(g) \quad (10)$$

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

$$\Delta_c H_m^0 = \Delta_c U_m^0 + \Delta n \cdot RT \quad (11)$$

$$\Delta n = \sum n_i(\text{products, g}) - \sum n_i(\text{reactants, g}) \quad (12)$$

where $\sum n_i$ was the total molar amount of the gases in products or reactants. The calculated standard molar enthalpy of combustion of the organic compound was

$$\Delta_c H_m^0 = -(5301.07 \pm 2.45)\ \text{kJ} \cdot \text{mol}^{-1}$$

The standard molar enthalpy of formation of the organic compound, $\Delta_f H_m^0$, was calculated by a designed Hess thermochemical cycle according to the following reaction

$$\Delta_f H_m^0(C_{10}H_{11}NO_2, s) = [10\Delta_f H_m^0(CO_2, g) + 11/2\Delta_f H_m^0(H_2O, l) - \Delta_c H_m^0(C_{10}H_{11}NO_2, s) \quad (13)$$

In the above formula, the standard molar enthalpies of formation of CO_2(g) and H_2O(l), recommended by CODATA,[12,13] $\Delta_f H_m^0(CO_2,g) = -(393.51 \pm 0.13)$ kJ·mol^{-1} and $\Delta_f H_m^0(H_2O,l) = -(285.83 \pm 0.04)$ kJ·mol^{-1}, were employed in the calculation of $\Delta_f H_m^0(C_{10}H_{11}NO_2,s)$ values. On the basis of these values and the standard molar enthalpy of combustion, the standard molar enthalpy of formation of the substance can be calculated to be: $\Delta_f H_m^0(C_{10}H_{11}NO_2,s) = -(206.10 \pm 3.97)$ kJ·mol^{-1}.

Conclusion

The heat capacities of (3,4-dimethoxyphenyl) acetonitrile were measured in the temperature range from (78 to 399) K by a high-precision automated adiabatic calorimeter. From the results of heat capacity experiments, the thermodynamic properties of fusion were completely studied, and the thermodynamic functions $(H_T - H_{298.15K})$ and $(S_T - S_{298.15K})$ were derived in the range from (80 to 400) K with temperature intervals of 5 K. The melting temperature T_m, the standard molar enthalpy $\Delta_{fus} H_m^0$, and the entropy $\Delta_{fus} S_m^0$ of fusion were determined to be (336.818 ± 0.005) K, (24.72 ± 0.14) kJ·mol^{-1}, and (73.40 ± 0.40) J·K^{-1}·mol^{-1}, respectively. The mole fraction purity was calculated to be 0.99602 according to the van't Hoff equation. The standard molar enthalpy of formation of (3,4-dimethoxyphenyl) acetonitrile was derived to be $-(206.10 \pm 3.97)$ kJ·mol^{-1} with a precision oxygen-bomb combustion calorimeter.

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