



Chemical Engineering Thermodynamics

Enthalpy of phase transition of isonicotinic acid



Dongfang Zhao, Guanghui Liu, Jian Sun, Lisheng Wang *

School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, China

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ABSTRACT

In this work, the group contribution method of Chickos *et al.* was applied to estimate the fusion enthalpy of isonicotinic acid, and the obtained result ($29.2 \text{ kJ} \cdot \text{mol}^{-1}$) showed a large difference with the value ($135 \text{ kJ} \cdot \text{mol}^{-1}$) as reported from literatures and as determined by differential scanning calorimetry (DSC). The results of DSC/TG measurement showed that the phase transition of isonicotinic acid from 187.27°C to 277.47°C underwent a sublimation process, with a sublimation enthalpy of $128.03 \text{ kJ} \cdot \text{mol}^{-1}$. An efficient analytical technique combining pyrolysis and gas chromatography/mass spectrometry (Py-GC/MS) was used to prove this conclusion.

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1. Introduction

Chemically isonicotinic acid is pyridine-4-carboxylic acid (CAS number 55-22-1). It occurs as a fine-crystalline cream-yellow powder, and it is insoluble in water and sparingly soluble in alcohols and acetone; its molecular mass is 123.11 [1]. Isonicotinic acid is widely used as an anticorrosion reagent, plating additive, photosensitive resin stabilizer, and food additive [2,3]. Moreover, it is an important intermediate in the synthesis of anti-tuberculosis drug isoniazid (isonicotinic acid hydrazide) [1,2,4,5], against *Plasmodium gallinaceum* and *Plasmodium berghei*. This attractive compound also plays an important role in the synthesis of inabenzfide (a plant growth regulator), terefenadine (an antihistamine), nialamide (an antidepressant) and other pharmaceutically important drugs [5].

It is surprising that there are only a few thermochemical data on isonicotinic acid, even though it is an essential chemical due to its pharmaceutical and analytical applications. Its thermochemical property of fusion has received little attention in the literature. The calculation of phase change enthalpies is often necessary for the energy balances design in chemical and petrochemical processes. Furthermore, accurate predictions for the phase change enthalpy are basically for those phase change materials which are used to prevent over-heat in aerospace or high supersonic flight [6].

Generally speaking, the fusion enthalpy can be determined with convenience and accuracy via differential thermal analysis (DTA) or DSC [7–10]. The values obtained from direct calorimetry method reveal a higher reliability as the development of modern flow calorimeters in recent years. But even with today's modern instrumentation, it would

be physically impossible to measure the thermochemical properties for more than 6 million distinct known chemical substances, let alone the seemingly infinite number of possible binary, ternary and higher-order multicomponent mixtures [11]. Therefore, researchers turn to a predictive method as an approach to get desired thermochemical properties from structural information. Techniques for predicting fusion enthalpy can play several useful roles. Because they provide a numerical value that can be used in cases when there are no experimental data, and they are also useful in selecting the most probable experimental value in cases where two or more values are in significant disagreement with each other [12]. Furthermore, the predictive method can also be used to test the reliability of experimental values in the literature.

Many researchers are dedicated to the prediction of thermochemical properties of chemical compound by using different methods [13–16]. One of the most important methods is group contribution method due to its accuracy and comprehensiveness [17–29]. The group contribution method could be defined as estimation procedure for the thermochemical property of a chemical compound, where values assigned to small groups of atoms constituting the molecule are summed to estimate their contribution to the inherent physicochemical properties of the molecule [30]. Chickos *et al.* [12,31–33] have done a lot of works in this field, and it has been proved that the group values provided by him are credible.

In this study, fusion enthalpy of isonicotinic acid has been calculated via the Chickos's group contribution method. However, the result obtained was significantly lower compared with the value determined by DSC and the data published in the literature. Fusion enthalpies of other compounds, which have similar structures with isonicotinic acid, also have been calculated in the same way to prove the reliability of this method, and all of these results are in good agreement with experimental data. In addition, the thermal decomposition process of

* Corresponding author.

E-mail address: lishengwang@bit.edu.cn (L.S. Wang).

isonicotinic acid was studied by Py-GC/MS and these results were verified.

2. Experimental Section

2.1. Material

Isonicotinic acid (99%) was commercially available from Sinopharm Chemical Reagent Co., Ltd., and it was used as received without further purification.

2.2. Estimation of fusion enthalpy of isonicotinic acid

Fusion enthalpy ($\Delta_{\text{fus}}H_m$) and fusion entropy ($\Delta_{\text{fus}}S_m$) are related to each other through the following equation:

$$\Delta_{\text{fus}}H_m(T_{\text{fus}}) = T_{\text{fus}} \cdot \Delta_{\text{fus}}S_m(T_{\text{fus}}) \quad (1)$$

The total phase change entropy ($\Delta_0^{T_{\text{fus}}}S_{\text{tpce}}$) has been defined as the sum of the entropy associated with all the phase changes occurring in the condensed phase prior to and including melting. The $\Delta_0^{T_{\text{fus}}}S_{\text{tpce}}$ in most cases provides a good estimate of the $\Delta_{\text{fus}}S_m(T_{\text{fus}})$. If there are no additional solid phase transitions then $\Delta_0^{T_{\text{fus}}}S_{\text{tpce}}$ becomes numerically equal to $\Delta_{\text{fus}}S_m(T_{\text{fus}})$. The estimation of $\Delta_0^{T_{\text{fus}}}S_{\text{tpce}}$ can be achieved by summing the group values consistent with the structure of the molecule as illustrated by Eq. (2) for acyclic and aromatic hydrocarbons.

$$\Delta_0^{T_{\text{fus}}}S_{\text{tpce}} = \sum_i n_i G_i + n_{\text{CH}_2} C_{\text{CH}_2} G_{\text{CH}_2}; \quad C_{\text{CH}_2} = 1.31 \text{ when } n_{\text{CH}_2} \geq \sum n_i, i \neq \text{CH}_2$$

otherwise $C_{\text{CH}_2} = 1.0$

(2)

where n_i refers to the number of i type group defined in Table 1; G_i the group value of i type group defined in Table 1; n_{CH_2} the number of methylene groups in the molecule; and G_{CH_2} the group value associated with a CH_2 group.

The parameters used for estimating $\Delta_0^{T_{\text{fus}}}S_{\text{tpce}}$ of isonicotinic acid and its analogs are listed in Table 1, and the group coefficients are used to modify group values whenever a functional group is attached to the carbon in question. Once $\Delta_0^{T_{\text{fus}}}S_{\text{tpce}}$ of isonicotinic acid and its analogs are calculated and the fusion temperature are measured, the fusion enthalpy ($\Delta_{\text{fus}}H_m$) can be calculated via Eq. (1).

2.3. TGA and DSC analysis

Thermogravimetric analysis (TGA) was implemented using a SDT Q600 (TA Instruments, USA) thermogravimetric analyzer at a heating

rate of $10 \text{ K} \cdot \text{min}^{-1}$. Isonicotinic acid was analyzed in an atmosphere of dry nitrogen at a flow rate of $100 \text{ ml} \cdot \text{min}^{-1}$.

DSC was implemented using a DSC-60 (Shimadzu, Japan) differential scanning calorimetry analyzer at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$. Isonicotinic acid was analyzed under dry nitrogen atmosphere with a flow rate of $50 \text{ ml} \cdot \text{min}^{-1}$.

2.4. Py-GC/MS analysis

Py-GC/MS was carried out using a GCMS-QP2010SE (Shimadzu, Japan) equipped with a microfurnace pyrolyzer (Model EGA/PY-3030D, Frontier Lab, Japan). About 1 mg of isonicotinic acid sample was loaded into the pyrolysis cup and then introduced into the heat center of pyrolyzer. The pyrolysis was performed at 600°C for 60 s, using $1 \text{ ml} \cdot \text{min}^{-1}$ Helium (He) carrier gas. The GC/MS instrument, fitted with an Ultra alloy-5 column ($30 \text{ m} \times 0.25 \text{ mm i.d.}$, $0.25 \mu\text{m}$ in film thickness) and a mass selective detector, was used to separate and detect the compounds from pyrolysis gases and vapors. The GC/MS conditions were the following: inlet temperature at 280°C , split ratio 50:1. The GC oven temperature was programmed from 50°C (hold for 1 min) to 180°C at $5^\circ\text{C} \cdot \text{min}^{-1}$ and then to 280°C (hold for 10 min) at $10^\circ\text{C} \cdot \text{min}^{-1}$. The mass spectrometer conditions: ion source temperature 250°C and electron impact ionization at 70 eV. Electro ionization (EI) mass spectra were obtained from m/z 33 to 600 every 0.2 s. Finally, the compounds from pyrolysis gases and vapors were identified by comparing their mass spectra with stored data (F-Search System, Frontier Lab, Japan) which include a National Institute of Standards and Technology (NIST) library and previously published mass spectra.

3. Results and Discussion

3.1. Fusion enthalpy of isonicotinic acid calculated by group contribution method

The estimation of $\Delta_0^{T_{\text{fus}}}S_{\text{tpce}}$ for isonicotinic acid follows directly from Eq. (2). The molecule contains four kinds of groups: four tertiary benzenoid $\text{sp}^2 \text{C}$ ($=\text{CH}-$), one quaternary benzenoid $\text{sp}^2 \text{C}$ adjacent to an sp^2 atom ($=\text{C}(\text{R})-$), one carboxylic acid ($\text{R}-\text{C}(=\text{O})\text{OH}$), and one aromatic heterocyclic nitrogen ($=\text{N}-$). Group coefficient identified as B36 in Table 1 is used for the carboxylic acid since isonicotinic acid would be considered to contain only two functional groups. Additionally, there are no methylene groups, resulting in the absence of $n_{\text{CH}_2} C_{\text{CH}_2} G_{\text{CH}_2}$ in Eq. (2). $\Delta_0^{T_{\text{fus}}}S_{\text{tpce}}$ for isonicotinic acid was calculated by summing these group values listed in Table 1 ($4 \times \text{A10} + \text{A12} + \text{A41} + \text{A36} \times \text{B36} = 49.2 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$). $\Delta_{\text{fus}}S_m$ for isonicotinic acid is numerically equal to $\Delta_0^{T_{\text{fus}}}S_{\text{tpce}}$ since no extra solid phase transitions can be observed from the DSC curve in Fig. 1. In consideration of the melting point of

Table 1

Contributions of the hydrocarbon and the functional group portions of isonicotinic acid molecule and its analogues^①

Functional groups	Group value(G_i) ^② / $\text{J} \cdot \text{mol}^{-1} \text{ K}^{-1}$	Group coefficient(C_k) ^③ /K		
		2	3	k_n ^④
Total number of functional groups				
Primary $\text{sp}^3 \text{C}$	CH_3-R	17.6 (A1)		
Tertiary benzenoid $\text{sp}^2 \text{C}$	$=\text{CH}-$	7.4 (A10)		
Quaternary benzenoid $\text{sp}^2 \text{C}$ adjacent to sp^3 atom ^⑤	$=\text{C}(\text{R})-$	-9.6(A11)		
Quaternary benzenoid $\text{sp}^2 \text{C}$ adjacent to an sp^2 atom ^⑤	$=\text{C}(\text{R})-$	-7.5(A12)		
Carboxylic acid	$\text{R}-\text{C}(=\text{O})\text{OH}$	13.4 (A36)	1.21 (B36)	2.25(D36)
Aromatic heterocyclic nitrogen	$=\text{N}-$	10.9(A41)		
Primary amine	$\text{R}-\text{NH}_2$	21.4(A45)		
Nitro group	$\text{R}-\text{NO}_2$	17.7 (A50)		

^① Data from Ref. [12].

^② The alphanumeric terms, A1, A2, B2, ... are a device used to identify each group value in the estimation process; the group value refers to the atoms in bold; the group coefficient refers to the total number of functional groups; R refers to any organic fragment including other functional groups or heteroatom.

^③ To be used in all cases of multiple substitutions unless noted otherwise in the preceding two columns.

^④ This group applies to any quaternary benzenoid carbon adjacent to an sp^3 hybridized atom with no lone pair of electrons.

^⑤ This group applies to any quaternary benzenoid carbon adjacent to any sp^2 hybridized atom and to sp^3 hybridized atoms with non-bonding electrons with the exception of internal quaternary carbon atoms.

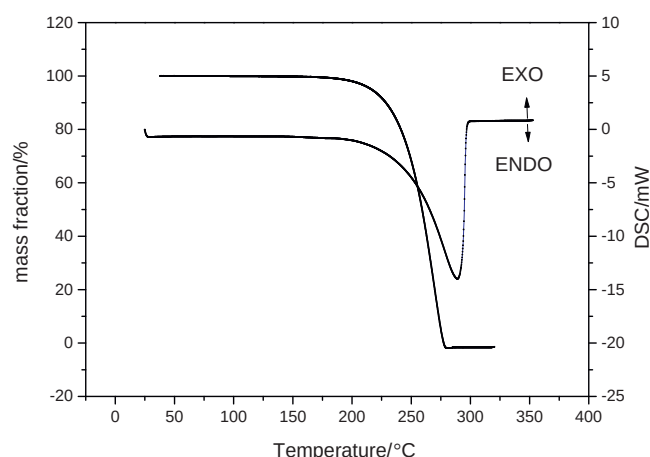


Fig. 1. TG-DSC plot of isonicotinic acid.

isonicotinic acid (593 K), a numerical value of $29.2 \text{ kJ} \cdot \text{mol}^{-1}$ was calculated for the fusion enthalpy of isonicotinic acid using Eq. (1).

To demonstrate the validity of this group contribution method, fusion enthalpies of several compounds were calculated by using the method mentioned above. Calculated results are compared with data described in the literature, and the percent of error $[(\text{calculated} - \text{experimental}) / \text{experimental}] \times 100$, are listed in Table 2. As indicated in Table 2, the results of group contribution method are in good agreement with experimental data. These calculated compounds are similar in structure with isonicotinic acid. In view of this, we consider that the fusion enthalpy of isonicotinic acid obtained by group contribution

method is credible, even though the obtained result shows a large difference with the value described in the literature.

3.2. Fusion enthalpy of isonicotinic acid by DSC

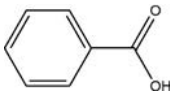
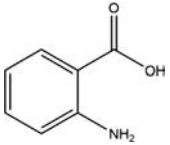
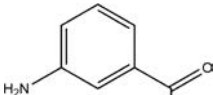
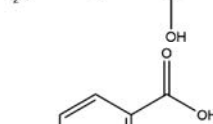
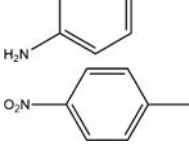
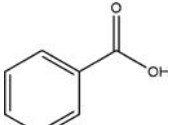
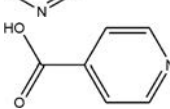
Fig. 1 shows the TG and DSC curves of isonicotinic acid. The TG curve elucidates that isonicotinic acid undergoes a single mass loss step from 187.27°C to 277.47°C with total elimination of the sample. The DSC curve shows an endothermic peak at 288.9°C , and the endothermic process is observed in the range $188\text{--}298^\circ\text{C}$. In this case, the enthalpy was determined by using a straight baseline for integration, and the value of the phase transition enthalpy is $128.03 \text{ kJ} \cdot \text{mol}^{-1}$.

The thermal analysis studies of isonicotinic acid were done by Allan [38], and a similar value of $135 \text{ kJ} \cdot \text{mol}^{-1}$ was obtained for the fusion enthalpy of isonicotinic acid *via* DTA. In addition, this value was extracted as the data on enthalpy of phase transition from solid to liquid by Domalski [39], and the data was evaluated as A (high quality) based upon the method used, purity of the sample, the number of measurements, the details of the measurements as reported, calibrations, and corrections applied to the data.

Although the two values mentioned above are similar to each other, neither of the two values determined by DSC and DTA could be considered as the correct data on fusion enthalpy of isonicotinic acid. Both of the two values show a large difference with the value estimated by the group contribution method, and the group contribution method was demonstrated to be validity in a preceding part of this paper. Moreover, the pyrolytic decomposition ought to be accompanied by significant exothermic or endothermic peaks, but no extra exothermic or endothermic peaks can be observed except that caused by phase transition at 288.9°C from the DSC curve in Fig. 1. Therefore, we have every

Table 2

Experimental and calculated fusion enthalpy of isonicotinic acid and its analogs

Compound	T_m/K	$\Delta_f^{\text{fus}} S_{\text{tpce}}$	$\Delta_{\text{fus}} H_m / \text{kJ} \cdot \text{mol}^{-1}$		Dev/%
			Calculated	Experimental	
	395.4 [34]	$5 \times A10 + A12 + A36$	17.0	17.1 [34]	0.58
	417.8 [35]	$4 \times A10 + 2 \times A12 + A36 \times B36 + A45$	21.8	20.5 [35]	6.3
	452.9 [35]	$4 \times A10 + 2 \times A12 + A36 \times B36 + A45$	23.6	21.84 [35]	8.0
	452.9 [36]	$4 \times A10 + 2 \times A12 + A36 \times B36 + A45$	24.0	24.5 [36]	6.1
	324.8 [35]	$4 \times A10 + A12 + A11 + A1 + A50$	15.5	16.81 [35]	−7.8
	510 [37]	$4 \times A10 + A12 + A41 + A36 \times B36$	25.1	26.7 [37]	−6.0
	593 [38]	$4 \times A10 + A12 + A41 + A36 \times B36$	29.2	135 [38]	−78.4

reason to believe that the sample undergoes a sublimation step instead of a decomposition one from 187.27 °C to 277.47 °C, as shown in Fig. 1. DSC and DTA are the most widely used thermal analytical technique, but are used almost exclusively under ambient conditions. The isonicotinic acid sample undergoes a sublimation step under the test conditions. Therefore, the value determined by DSC or DTA is not the fusion enthalpy of isonicotinic acid. That is to say, the fusion enthalpy of isonicotinic acid cannot be determined by DSC or DTA. The fusion enthalpy of isonicotinic acid determined by DSC or DTA is thus not credible. In practice, the fusion enthalpy of a compound is not easily determined by the experiment, especially for the compound that will be sublimed before melting point temperature. We have already searched extensive literature and unfortunately we could not find any other experimental methods to determine the fusion enthalpy of isonicotinic acid.

Very few general techniques have been developed for directly estimating fusion enthalpy, in part, as a consequence of the complex phase behavior exhibited by some compounds. By contrast, the group contribution method provides a numerical value for fusion enthalpy of isonicotinic acid in cases when there are no experimental data. The reliability of this group contribution method has been proved in a preceding part of this paper. The same conclusion also has been drawn in other literatures. [17–29] In view of this, we consider that the fusion enthalpy of isonicotinic acid obtained by group contribution method is credible.

3.3. Py-GC/MS Analysis

The Py-GC/MS pyrogram for isonicotinic acid is presented in Figs. 2–5. As shown in Fig. 2, three main peaks are observed at 1.705 min, 3.075 min and 18.770 min respectively. The three compounds were clearly identified by comparing these mass spectra with stored data (F-Search System, Frontier Lab, Japan).

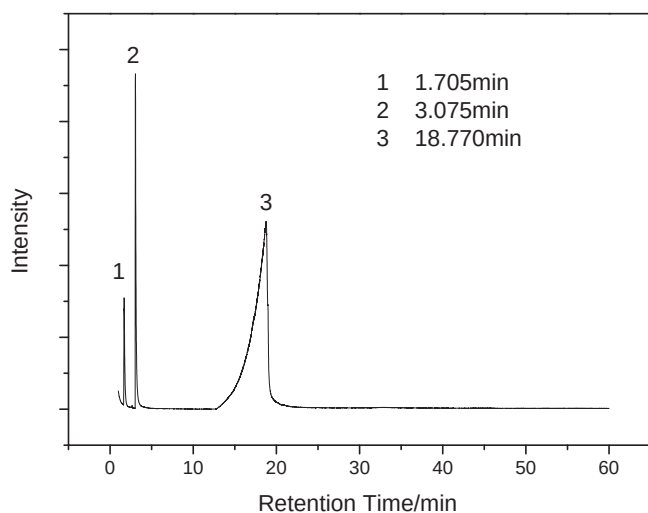


Fig. 2. Mass chromatogram resulting from the pyrolysis of isonicotinic acid at 600 °C for 60 s.

As shown in Figs. 3–5, both of detected mass spectra (a) and mass spectra published by NIST (b) are presented. The mass spectrum at retention time 1.705 min, Fig. 3(a), shows a diagnostic peak at m/z 44, and it is in good agreement with the value for carbon dioxide published by NIST, Fig. 3(b). The mass spectrum at retention time 3.075 min, Fig. 4(a), shows a diagnostic peak at m/z 79, and it is in good agreement with the value for pyridine published by NIST, Fig. 4(b). The mass spectrum at retention time 18.770 min, Fig. 5(a), shows a diagnostic peak at m/z 123, and it is in good agreement with the value for isonicotinic acid published by NIST, Fig. 5(b). As indicated above, the characteristic peaks

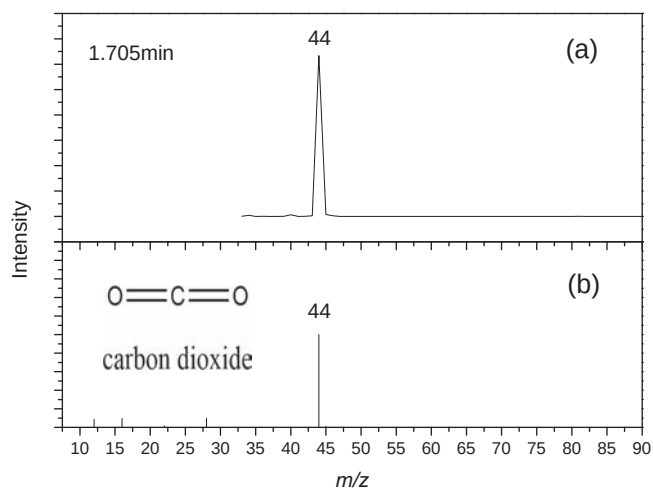


Fig. 3. Mass spectrum of peak number 1 from the pyrogram shown in Fig. 2, identified as carbon dioxide.

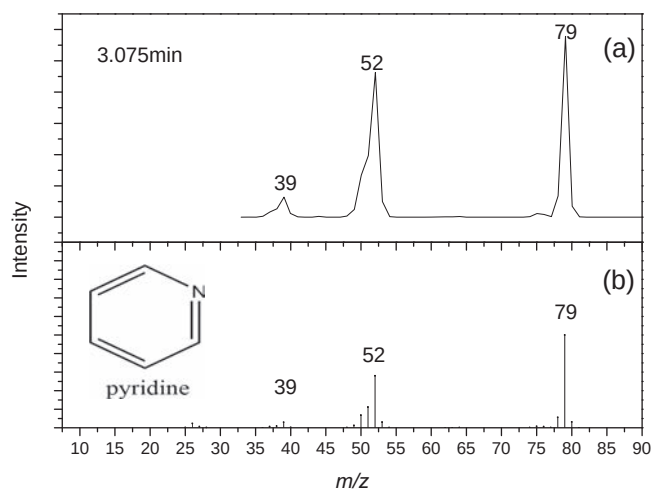


Fig. 4. Mass spectrum of peak number 2 from the pyrogram shown in Fig. 2, identified as pyridine.

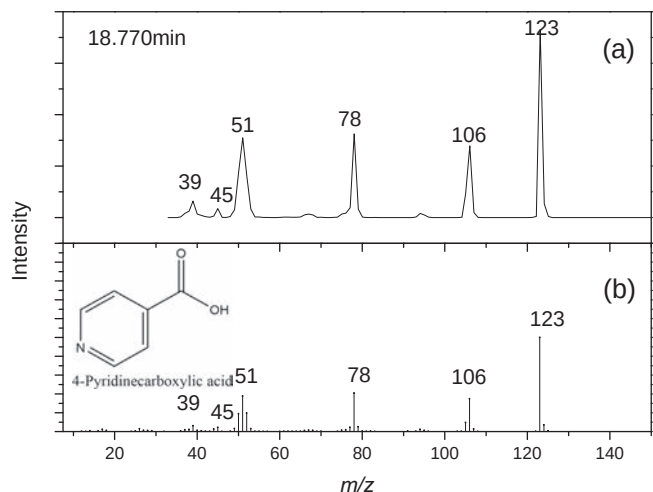


Fig. 5. Mass spectrum of peak number 3 from the pyrogram shown in Fig. 2, identified as isonicotinic acid.

were assigned as follows: retention time 1.705 min, carbon dioxide; 3.075 min, pyridine; 18.770 min, isonicotinic acid.

Peak area is an indication of the quantities of the pyrolyzed products. As shown in Fig. 2, carbon dioxide and pyridine occur in minute amounts in all pyrolysis products, and meanwhile almost all of the pyrolysis products are isonicotinic acid, elucidating that pyrolytic decomposition of isonicotinic acid sample does not occur at 600 °C. Moreover, this result reinforces our view that the isonicotinic acid sample undergoes a sublimation step under the test conditions. Therefore, the fusion enthalpy of isonicotinic acid determined by DSC or DTA is simply not credible. By contrast, the group contribution method provides a reliable value for the fusion enthalpy of isonicotinic acid.

4. Conclusions

In this study, the value for the fusion enthalpy of isonicotinic acid determined by using DTA or DSC was proved incorrect. The DSC/TG measurement and Py-GC/MS measurement were done to show this conclusion. A numerical value of $29.2 \text{ kJ} \cdot \text{mol}^{-1}$ was calculated for the fusion enthalpy of isonicotinic acid by using group contribution method. The value and this group contribution method were proved credible. Phase transition of isonicotinic acid from solid to gas occurred at 187.27 °C, and the sample underwent a sublimation process from 187.27 °C to 277.47 °C with a sublimation enthalpy of $128.03 \text{ kJ} \cdot \text{mol}^{-1}$.

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