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Thermodynamic study of the three isomers of iodobenzoic acid

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Abstract

2-Iodo-, 3-iodo- and 4-iodobenzoic acids have been investigated by sublimation calorimetry, drop calorimetry and thermal analysis. The measurements of sublimation enthalpy of these three compounds were carried out at 363 K using a Tian–Calvet microcalorimeter equipped with a Knudsen effusion cell. The saturated vapour pressures of these acids at the sublimation temperature 363 K were also calculated. The derived values of standard molar enthalpies of sublimation at 298.15 K are 92.59 ± 0.20, 96.38 ± 0.29, and 99.32 ± 0.36 kJ mol^{-1} for 2-iodo-, 3-iodo- and 4-iodobenzoic acid, respectively.

The enthalpies of fusion, the temperatures of triple point and the mole fraction purities of these three compounds were determined using the mean temperature version DTA apparatus developed by the Centre de Thermodynamique et de Microcalorimétrie of the CNRS in Marseille. The triple point temperatures and the molar enthalpies of fusion for the 2-iodo-, 3-iodo- and 4-iodobenzoic acid have been found to be 435.02 ± 0.02 K, 21.38 ± 0.19 kJ mol^{-1}; 460.30 ± 0.01 K, 28.70 ± 0.21 kJ mol^{-1} and 543.70 ± 0.03 K, 35.24 ± 0.13 kJ mol^{-1}, respectively.

Using the contributions of benzoic acid and iodine group, determined from literature data, we have calculated the enthalpy of sublimation of 4-iodobenzoic acid and compared the calculated result with the experimental value.

It has also been possible to demonstrate and explain the existence of an intramolecular hydrogen bond in 2-iodobenzoic acid molecule.

INTRODUCTION

Iodobenzoic acids are fundamental organic compounds applied in organic analysis and synthesis; the quantitative study of chemical reacting energetics requires accurate knowledge of the thermodynamic properties

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of these compounds, such as fusion and sublimation enthalpies, which are important thermodynamic properties of their condensed phase. A variety of studies, including those which refer to the gas phase as a standard state, require accurate values for enthalpies of sublimation.

Upon consulting the literature, however, we found that such information for these compounds to be scarce. In their book Cox and Pilcher [1] gave an estimated value of the sublimation enthalpy of 4-iodobenzoic acid. In 1983, Holdiness [2] reported the fusion and sublimation enthalpies of 2-iodobenzoic acid measured by differential scanning calorimetry. For 3-iodobenzoic acid, no enthalpies of fusion and sublimation are available.

In response to the lack of such thermal data, as a part of the systematic research project performed in the laboratory of one of us (R.S.) on halogen-substituted derivatives of benzoic acids, the present work investigates the three iodobenzoic acids by differential thermal analysis as well as by sublimation calorimetry. The standard molar enthalpies of fusion and sublimation of these three compounds and their triple point temperatures have been determined accurately. We have tried to explain the difference in enthalpies of sublimation between 2-iodo- and 4-iodobenzoic acids by assuming the existence of an intramolecular hydrogen bond in the 2-iodobenzoic acid molecule.

EXPERIMENTAL

Substances

The pure commercial products of 2-iodobenzoic acid (Lancaster, purity >98%), 3-iodobenzoic acid (Fluka, purity >98%) and 4-iodobenzoic acid (Aldrich, purity >98%) were purified by vacuum sublimation under a residual pressure of about 10^{-2} Torr (1 Torr = 133.322 Pa). The temperatures of sublimation were controlled at 343, 353 and 373 K for 2-iodo-, 3-iodo- and 4-iodobenzoic acid, respectively. During the purification process the sublimation apparatus was covered by brown paper to prevent photolysis; the purified samples were also stored in brown bottles.

Apparatus, techniques and mode of operation

Differential thermal analysis

The mean temperature version of our differential thermal analyser [3, 4] was used to measure the triple point temperatures, the enthalpies of fusion and the purities of the investigated samples of the three iodobenzoic acids. The total impurity content of the sample was determined by the freezing-point method based on the Clausius–Clapeyron equation and Raoult's law as described in detail in ref. 3. About 150–200 mg of purified sample were loaded in a cleaned pyrex glass ampoule [3]. Then the ampoule was connected to the vacuum line to be evacuated under a residual pressure of 10^{-2} Torr. After cooling in liquid nitrogen the loaded ampoule was quickly sealed under evacuating condition by means of a miniature welding torch (gas and oxygen flame welder). Consequently, the pressure inside the ampoule is approximately equal to the saturated vapour pressure of the investigated substance. The mass of the sample in the ampoule was determined by differential weighings of the empty ampoule and the sealed ampoule plus sample together with the remaining glass neck of the ampoule. All weighings were performed on a Mettler M5 microbalance sensitive to 1 μg with an accuracy of ±2 μg.

The ampoule filled with sample was dropped into the sample cell of the DTA furnace held at about 293 K. The sample was heated with a rate of about 2 K min^{-1} up to a temperature approximately 10 K below the triple point temperature of the sample. When temperature equilibrium was reached, the sample was allowed to heat at a rate of 0.2 K min^{-1} up to about 2 K higher than its melting point, so as to allow the accurate determination of the enthalpy of fusion, the triple point temperature and the purity of the sample.

Sublimation calorimetry

A differential Tian–Calvet microcalorimetric system equipped with specially designed Knudsen effusion cells was used to determine the sublimation enthalpies of the investigated three iodobenzoic acids. The construction of the device and the procedure of its operation has been described in detail elsewhere [5]. The effusion apparatus was completely metallic, easily dismountable and the possibility of vacuum leakages during the process of effusion was minimized. The effusion cell, made of AU4G alloy (96% Al, 4% Cu) with a capacity of 1.45 cm^3 and a mass of 2.01 g was kept in excellent thermal contact with the calorimetric cylinder. The effusion orifice was bored in a 0.2 mm thick teflon joint. The working temperature of the calorimeter and the diameter of the effusion cell orifice were chosen in dependence of the volatility of the investigated compounds. The saturated vapour pressures of iodobenzoic acids are relatively low, so the sublimation could not be carried out at 298.15 K. For all three iodobenzoic acids, the sublimation was performed at 363 K. The effusion cell orifice selected was 0.5 mm for 2-iodo-, 0.7 mm for 3-iodo- and 1.0 mm for 4-iodobenzoic acid.

About 15–20 mg sample of the investigated substance was introduced into the effusion cell. The mass of the sample loaded in the cell was determined by differential weighings using a microbalance Mettler UM3 sensitive to 0.1 μg with an accuracy ±0.2 μg. The weighed samples were completely evaporated during a period of about 10 h in the effusion experiments.

The calorimeter was electrically calibrated using the Joule effect. The electrical energy input into the calorimeter was adjusted to be as nearly as possible identical to the sublimation energy. The energy calibration coefficient of the calorimeter varies with temperature. For each temperature it is necessary to carry out at least six calibration experimental runs so as to yield high accuracy calibration results. The energy calibration coefficient of the calorimeter at our experimental temperature (363 K) was found to be (59.81 ± 0.03) $\mathrm{J\,V^{-1}\,s^{-1}}$ under the corresponding experimental conditions (the sensitivity range of the amplifier for e.m.f. signal of the differential thermopile in the calorimeter is 30 μV and the chart speed of the recorder 1 mm $\mathrm{min^{-1}}$).

Drop calorimetry

The observed enthalpies of sublimation at experimental temperature T were corrected to 298.15 K. The correction to the standard temperature requires the knowledge of the molar heat capacities of the investigated substances in the gaseous and condensed phases

$$\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\ominus}(298.15\ \mathrm{K}) = \Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\ominus}(T/\mathrm{K}) + \int_{T/\mathrm{K}}^{298.15\ \mathrm{K}} [C_{p,\mathrm{m}}^{\ominus}(\mathrm{g}) - C_{p,\mathrm{m}}^{\ominus}(\mathrm{s})]\,\mathrm{d}T \qquad (1)$$

The heat capacities in the gaseous phase, $C_{p,\mathrm{m}}^{\ominus}(\mathrm{g})$ may be calculated by a group contribution approach. The condensed phase heat capacities, $C_{p,\mathrm{m}}^{\ominus}(\mathrm{s})$ can be determined by different experimental techniques, including precision adiabatic calorimetry, drop calorimetry, differential scanning calorimetry, etc. In the present work, we have used the drop method to directly measure the enthalpy differences $H(T/\mathrm{K}) - H(298.15\ \mathrm{K})$ for the condensed phase of iodobenzoic acids.

About 150–200 mg sample were filled tightly in an AU4G sample cell (diameter 5 mm, height 8 mm) and then were heated in a furnace to the temperature T at which the sublimation experiment was carried out. When thermal equilibrium was reached, the loaded sample heated up to temperature T was dropped into the Tian–Calvet microcalorimeter held at 298.15 K. The enthalpy difference $H(T/\mathrm{K}) - H(298.15\ \mathrm{K})$ of the sample plus the cell can be determined from

$$H(T/\mathrm{K}) - H(298.15\ \mathrm{K}) = k \cdot S \qquad (2)$$

where S is the peak area due to the heat issued from the dropped sample, and k is the calibration coefficient of the calorimeter. Under the same condition, the enthalpy difference $H(T/\mathrm{K}) - H(298.15\ \mathrm{K})$ of the empty cell is measured. The enthalpy difference of the sample can be obtained from the total enthalpy difference by substracting the value of empty cell. The calorimeter was previously calibrated with a standard reference material, α-alumina sample (SRM-720) from the National Institute of Standards and Technology; the enthalpy difference $H(T/\mathrm{K}) - H(298.15\ \mathrm{K})$ for this standard material has been well established [6].

In all our experiments, the data acquisition and processing and the determination of thermodynamic quantities were performed automatically using computer programs.

RESULTS

The uncertainties associated with the experimental results in this work are reported as standard deviations of the mean, usually of eight experimental runs. The temperatures reported in the present research are in terms of the ITS-90 [7]. The molar masses of the investigated substances are calculated based on the standard atomic masses of the elements of 1991 [8] and the value of the gas constant ($R = 8.314\,510\ \mathrm{J\,K^{-1}\,mol^{-1}}$), adopted by IUPAC [9], is used.

Enthalpy of fusion and triple point temperature

The experimental values of the molar fusion enthalpy, the triple point temperature and the mole fraction purity of the samples used for the three iodobenzoic acids determined by differential thermal analysis are summarized in Table 1. We have carefully analysed the thermal behaviour of the tested samples according to the recorded thermograms of DTA obtained with a heating rate of $2\ \mathrm{K\,min^{-1}}$ in the temperature range from 298 K to their triple point; no phase transition has been observed in the above range for all samples of the three compounds.

TABLE 1

Experimental values of purity, triple point temperature and enthalpy of fusion of the three iodobenzoic acids [a]

Substance	m/g	Number of experiments	Purity/mol%	T_{tp}/K	$\Delta_{fus}H_m$/kJ mol^{-1}
2-Iodobenzoic acid	0.190109	6	99.75 ± 0.01	435.02 ± 0.02	21.38 ± 0.19
3-Iodobenzoic acid	0.164025	8	99.80 ± 0.01	460.30 ± 0.01	28.70 ± 0.21
4-Iodobenzoic acid	0.195630 [b]	6	99.65 ± 0.01	543.70 ± 0.03	35.24 ± 0.13

[a] Molar mass = 248.01997 g mol^{-1}. [b] Because of thermal decomposition during its melting, five other samples of this substance with the following masses were used for the measurements: m = 0.197520, 0.185830, 0.169140, 0.163075 and 0.157520 g.

Enthalpy of sublimation

The experimental molar enthalpies of sublimation of the iodobenzoic acids and their saturated vapour pressures at the corresponding experimental temperature are presented in Table 2. Since the saturated vapour pressures of the iodobenzoic acids are relatively low, the identity

TABLE 2

Experimental values of sublimation enthalpy and saturated vapour pressure of the three iodobenzoic acids

Substance	T/K	m/mg	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\ominus}(T/\mathrm{K})$/ kJ mol^{-1}	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\ominus}(T/\mathrm{K})$/ kJ mol^{-1}	$\Delta_{298.15\,\mathrm{K}}^{T/\mathrm{K}}H_{\mathrm{m}}^{\ominus}(\mathrm{s})$/ kJ mol^{-1}	$\Delta_{298.15\,\mathrm{K}}^{T/\mathrm{K}}H_{\mathrm{m}}^{\ominus}(\mathrm{g})$/ kJ mol^{-1}	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\ominus}(298.15\,\mathrm{K})$/ kJ mol^{-1}	$P(T/\mathrm{K})$/ Torr
2-Iodobenzoic acid	363	16.7432	89.78	89.97 ± 0.18 [a]	11.70 ± 0.03 [a]	9.08 ± 0.07	92.59 ± 0.20	1.2×10^{-2}
		17.9557	90.37					
		17.7746	90.07					
		16.3375	90.23					
		17.4415	89.90					
		16.3807	89.39					
		17.2357	89.24					
		16.9445	90.81					
3-Iodobenzoic acid	363	17.4525	94.81	94.24 ± 0.16[a]	11.22 ± 0.23 [a]	9.08 ± 0.07	96.38 ± 0.29	4.0×10^{-3}
		16.2820	93.88					
		17.0275	93.82					
		17.1762	94.49					
		17.4818	93.66					
		18.8772	94.84					
		17.1255	94.08					
		17.9280	94.84					
		18.6058	94.43					
		17.0008	93.54					
4-Iodobenzoic acid	363	12.6754	98.65	97.69 ± 0.29 [a]	10.71 ± 0.20 [a]	9.08 ± 0.07	99.32 ± 0.36	1.4 ± 10^{-3}
		20.7683	97.94					
		21.5774	97.85					
		21.3940	98.53					
		21.3668	97.13					
		21.5249	96.82					
		19.6803	97.27					
		21.3415	96.30					
		21.4758	98.72					

[a] Mean value and standard deviation of the mean.

$\Delta_{\mathrm{sub}}H_{\mathrm{m}}(T) \equiv \Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\ominus}(T)$ is assumed. We utilize the relationship (1) mentioned above to calculate the molar enthalpies of sublimation at the standard temperature 298.15 K, ($\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\ominus}$(298.15 K)) from the values at the experimental temperature 363 K ($\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\ominus}$(363 K)).

As mentioned above, the validity of the relationship (1) for the three iodobenzoic acids have been confirmed by corresponding differential thermal analysis experiments.

The enthalpy differences $\Delta_{298.15\,\mathrm{K}}^{363\,\mathrm{K}}H_{\mathrm{m}}^{\ominus}(\mathrm{s})$ for iodobenzoic acids in the condensed phase were determined by drop calorimetry (see Table 2). The enthalpy difference $\Delta_{298.15\,\mathrm{K}}^{363\,\mathrm{K}}H_{\mathrm{m}}^{\ominus}(\mathrm{g})$ for iodobenzoic acids in the gaseous phase was calculated by a group contribution method, (i.e. iodobenzoic acid = iodobenzene-benzene + benzoic acid), based on the data from the compilation of Stull et al. [10] (see Table 2). The standard molar enthalpies of sublimation at 298.15 K are given in Table 2.

Saturated vapour pressure

The saturated vapour pressure P of the investigated iodobenzoic acids can be evaluated in sublimation experiments according to the eqn. (3) if Knudsen effusion conditions are fulfilled during the sublimation experiments

$$P \approx \Delta P = \frac{\mathrm{d}m}{aF\,\mathrm{d}t}\left[\frac{2\pi RT}{M}\right]^{1/2} \tag{3}$$

where ΔP is the difference of pressure between the inside and the outside of the effusion cell, nearly equal to the saturated vapour pressure P of the tested substance; $\mathrm{d}m/\mathrm{d}t$ is the effusion rate, a is the orifice area, F is the Clausing factor [11], R is the gas constant, T the absolute sublimation temperature, and M the molar mass of the substance. The calculated values of the saturated vapour pressure at the experimental temperature 363 K are listed in Table 2.

DISCUSSION

Comparison of our results with literature values

First of all we have compared our experimental results with any previously determined values from the literature. For the convenience of this comparison, our final results of enthalpies of fusion and sublimation and triple point temperatures for the investigated substances are summarized in Table 3 together with corresponding literature values. From Table 3 it can be seen that, for the enthalpy of sublimation, our result for 2-iodobenzoic acid is 10% lower than the value determined by Holdiness [2] based on the differential scanning calorimetric technique. The author

TABLE 3

Triple point temperatures (T_{tp}), molar enthalpies of sublimation ($\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\ominus}$) and of fusion ($\Delta_{\mathrm{fus}}H_{\mathrm{m}}$) of the three iodobenzoic acids and comparison with literature values

Substance	T_{tp}/K		$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/kJ mol^{-1}		$\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\ominus}$(298.15 K)/kJ mol^{-1}	
	This work	Literature	This work	Literature	This work	Literature
2-Iodobenzoic acid	435.02 ± 0.02	436 [a] [12]	21.38 ± 0.19	26.23 ± 0.21 [2]	92.59 ± 0.20	102.97 ± 0.42 [b] [2]
3-Iodobenzoic acid	460.30 ± 0.01	460.9 [a] [12]	28.70 ± 0.21		96.38 ± 0.29	
4-Iodobenzoic acid	543.70 ± 0.03	544.74 [4], 543 [a] [12]	35.24 ± 0.13		99.32 ± 0.36	87.9 ± 4.2 [1]

[a] Melting point temperature. [b] Author did not mention sublimation temperature.

did not mention the experimental conditions in which the sublimation was carried out; in particular he did not point out the sublimation temperature. Concerning the 4-iodobenzoic acid, our value of sublimation enthalpy is 13% higher than that estimated by Cox and Pilcher [1]. The significant discrepancy between our values and the literature ones may be due to the different experimental techniques used. With respect to the reliability of the data, it is generally admitted that the results of sublimation enthalpy determined by calorimetry are more accurate than those obtained by vapour pressure measurements and by the DSC technique. For the time being, no literature data is available for 3-iodobenzoic acid. Nevertheless, the value of sublimation enthalpy of this compound seems to be reasonably reliable when compared with the values for 2-iodo- and 4-iodobenzoic acids, the value being just between the two others.

For the enthalpy of fusion, our result for 2-iodobenzoic acid is 19% lower than the value reported by Holdiness [2]. The disaccord between our value and Holdiness result is probably due to the large difference in heating rate between our experiments and those of Holdiness (the heating rate used by Holdiness is $8\,\mathrm{K\,min^{-1}}$, while in our experiments it is $0.2\,\mathrm{K\,min^{-1}}$). Concerning the enthalpy of fusion of 4-iodobenzoic acid one of us (R.S.) previously observed the decomposition of this compound during its melting process [4]. In the present study, we have further carefully observed the decomposition phenomenon and found that the sample of 4-iodobenzoic acid undergoes a slight decomposition about 2 K above its triple point temperature. Consequently, the results of the enthalpy of fusion for our sample are not very reproducible and the value reported in Table 3 must be used with caution. For 3-iodobenzoic acid, no comparison is made, since no literature data has been published.

Concerning the triple point temperature, all our results for the investigated three iodobenzoic acids are in agreement within ±1 K with corresponding literature values [4, 12] (see Table 3).

The existence of an intramolecular hydrogen bond in the 2-iodobenzoic acid molecule

The enthalpy of sublimation of an organic substance is associated with the intermolecular interactions which include the energies corresponding to the van der Waals' forces and, in some cases, to the hydrogen bonds. In order to elucidate more clearly this kind of intermolecular interaction, the knowledge of crystal structure data of the investigated compounds is often required. However this kind of data reported in the literature on iodosubstituted derivatives of benzoic acid are less numerous. Gougoutas [13] studied the crystal structure of 2-iodobenzoic acid; Baughman and Nelson [14] investigated the molecular structure of 4-iodobenzoic acid. They provided evidence of the existence of intermolecular hydrogen bonding in crystals of iodobenzoic acids arising from the hydrogen atom of the carboxyl group.

In the present case, the enthalpy of sublimation of 2-iodobenzoic acid is 3.78 and 6.73 kJ mol^{-1} lower than 3-iodo- and 4-iodobenzoic acids, respectively. This difference should be attributed to the fact that the 2-iodobenzoic acid molecule possesses fewer intermolecular hydrogen bonds than the two other isomers. In fact, it is only 2-iodobenzoic acid among the three isomers that can form an intramolecular hydrogen bond between the iodine atom and the hydrogen atom of the carboxyl function group.

In a previous work on the study of sublimation of the three aminobenzoic acids [15], one of us (R.S.) demonstrated that the enthalpy of sublimation of the ortho isomer is 11.2 kJ mol^{-1} lower than the para isomer. This is the same for hydroxybenzoic acids for which a recent study carried out in the laboratory of one of us (R.S.) [16] shows that the ortho derivative has an enthalpy of sublimation 17.78 kJ mol^{-1} lower than the para one. This result is in accordance with that of Davies and Jones [17]. In consequence, the chelation due to intramolecular hydrogen bonding is weakened gradually in the order hydroxy-, amino- and iodobenzoic acids.

In addition to the above experimental results for sublimation enthalpy, we tried to verify the existence of intramolecular hydrogen bonding in the 2-iodobenzoic acid molecule by observing some physiochemical properties of iodobenzoic acids. According to our sublimation experiments, the saturated vapour pressure of the ortho isomer is higher than that of the para isomer at the same temperature (see Table 2), which means that intermolecular hydrogen bonding in 2-iodobenzoic acid molecules is less than in 4-iodobenzoic acid molecules. However, for the same reason, the enthalpy of fusion and the triple point temperature are higher in the case of 4-iodobenzoic acid than in that of 2-iodobenzoic acid (see Table 1). Besides, in the liquid state 4-iodobenzoic acid possesses more intermolecular association arising from hydrogen bonding than 2-iodobenzoic acid. In consequence, it is insoluble in a liquid which is not associative (for instance, ether), whereas 2-iodobenzoic acid is soluble in ether [12].

Evaluation of the enthalpy of sublimation of 4-iodobenzoic acid

As has been done previously by several researchers, we have tried to calculate the enthalpy of sublimation of 4-iodobenzoic acid from the contributions of benzoic acid and the iodine functional group. In the net of crystalline lattice, this acid has been found to exist in the molecular state without intramolecular hydrogen bonding [14]. In order to take good account of the interaction between the benzene ring and the functional groups of acid and iodine in the 4-iodobenzoic acid molecule, we intended to calculate these contributions from benzoic acid and molecules such as benzene and iodobenzene. The standard enthalpy of sublimation at 298.15 K of benzoic acid is (89.7 ± 0.5) kJ mol^{-1} [18]. Adding the contribution of the iodine group only to this value we can obtain the enthalpy of sublimation of 4-iodobenzoic acid.

We have determined the contribution of the iodine group from results for benzene and iodobenzene. From literature data, we have been able to calculate their standard enthalpy of sublimation at 298.15 K. For benzene we have calculated the enthalpy of sublimation from the quantities of $\Delta_{\text{vap}}H_{\text{m}}^{\ominus}$(298.15 K) and $\Delta_{\text{fus}}H_{\text{m}}$(298.15 K). The former is taken directly from ref. 19, $\Delta_{\text{vap}}H_{\text{m}}^{\ominus}$(298.15 K) being 33.92 kJ mol^{-1}. The latter is calculated from the value $\Delta_{\text{fus}}H_{\text{m}}$(278.68 K) = 9.84 kJ mol^{-1} [10] by using Sidgwick's rule [20]

$$\Delta_{\text{fus}}H_{\text{m}}(298.15\ \text{K}) = \Delta_{\text{fus}}H_{\text{m}}(T/\text{K}) + k(298.15 - T) \tag{4}$$

with $k = 0.0544$ kJ mol^{-1} K^{-1}. It has been found that $\Delta_{\text{fus}}H_{\text{m}}$(298.15 K) is equal to 10.91 kJ mol^{-1}, so $\Delta_{\text{sub}}H_{\text{m}}^{\ominus}$(298.15 K) = $\Delta_{\text{fus}}H_{\text{m}}$(298.15 K) + $\Delta_{\text{vap}}H_{\text{m}}^{\ominus}$(198.15 K) = 44.83 kJ mol^{-1}.

We have further calculated the enthalpy of sublimation of iodobenzene at 298.15 K by using the same scheme as for benzene and the corresponding data. For iodobenzene, $\Delta_{\text{fus}}H_{\text{m}}$(241.83 K) = 9.75 kJ mol^{-1} [10], from which we have calculated $\Delta_{\text{fus}}H_{\text{m}}$(298.15 K) = 12.84 kJ mol^{-1}. The enthalpy of vaporization of iodobenzene $\Delta_{\text{vap}}H_{\text{m}}^{\ominus}$(298.15 K) = (47.7 ± 4.2) kJ mol^{-1} [1]; accordingly its enthalpy of sublimation $\Delta_{\text{sub}}H_{\text{m}}^{\ominus}$(298.15 K) = $\Delta_{\text{vap}}H_{\text{m}}^{\ominus}$(298.15 K) + $\Delta_{\text{fus}}H_{\text{m}}$(298.15 K) = 60.54 kJ mol^{-1}. The contribution of the iodine group can be calculated from the difference in enthalpy of sublimation between iodobenzene and benzene. For this contribution we have found the value of 15.71 kJ mol^{-1}.

From the enthalpy of sublimation of benzoic acid and the contribution of the iodine group, the standard molar enthalpy of sublimation of 4-iodobenzoic acid has been evaluated to be 105.4 kJ mol^{-1} which is in about 6% agreement with our experimental value. This discrepancy is mainly due to the significant uncertainty in the value of enthalpy of vaporization of iodobenzene which was used for the calculation.

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