Note

A DSC STUDY OF BENZOIC ACID: A SUGGESTED CALIBRANT COMPOUND

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The sublimation enthalpy of a compound in the solid state is usually derived using an isoteniscope [1], a spoon gauge [2], a Knudsen effusion cell [3,4], the sublimation bulb method [5,6] or a transpiration method [7]. Ashcroft [8] has reported a novel thermogravimetric method for obtaining sublimation enthalpies using the Langmuir equation to relate mass loss to vapour pressure. All of these methods, with the exception of the thermogravimetric method are experimentally tedious and appear to be less precise than the relatively new differential scanning calorimetric method. DSC has been employed successfully for the measurement of enthalpies of phase transformations and decomposition reactions [9]. It has also been employed with limited success for the measurement of heats of vaporisation of liquids [10]. Beech and Lintonbon [11] have recently published fusion and vaporisation enthalpies for several metal acetylacetonate complexes as derived from DSC data using nitrogen as the inert atmosphere for thermal analysis. Many metal complexes decompose when heated in an inert atmosphere [11], whereas sublimation may occur when the same complex is heated in vacuum: thus the vacuum DSC technique appears ideally suited for the direct measurement of sublimation enthalpies of metal complexes. The DSC instrument constant is usually determined using indium metal as calibrant; the standard reference process is the melting of indium [12]. Hepler and co-workers [12] have recently suggested that the fusion of sodium nitrate (ΔH_{fus} = 15.13 kJ mole^{-1}) be used for DSC calibration. However, the variation of instrument constant according to the nature of the phase transformation under study has not been investigated. The present study assumes that the instrument constant for a fusion process is not identical to that for a sublimation process and a recommendation is proposed: that indium be used as a DSC calibrant for the determination of fusion enthalpies and that benzoic acid be used as calibrant for the determination of sublimation enthalpies.

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EXPERIMENTAL

A Rigaku—Denki differential scanning calorimeter (Thermoflex 8085) was employed. The associated modular atmosphere control unit allowed thermal analysis to proceed in an atmosphere of nitrogen or under vacuum. All samples, including the alumina reference, were crimped in aluminium crucibles and in the case of vaporisation and sublimation studies, a 0.1 mm diameter hole in the lid of the sample crucible allowed spontaneous escape of volatile sample. This sample preparation technique minimises temperature gradients within the sample crucible such that recondensation of the sample is eliminated. Sample and alumina reference masses ranged from 3—10 mg and heating rates of 5, 10 and 20°C min^{-1} were employed. For thermal analysis in a dry nitrogen atmosphere, a flow rate of 0.1 dm^3 min^{-1} was employed. For vacuum DSC studies, the sample chamber was maintained at 5 × 10^{-3} τ. In the case of sublimation enthalpy determination, all samples were sublimed under DSC conditions several times prior to the nominated DSC run, to remove moisture and occluded gas. These pre-run sublimations resulted in improved precision. DSC peak areas were computed by an "on-line" integrator (Rikadenki—Padac 1 programmable and digital analogue computer). Phase transformation enthalpies were derived using the equations

$$E_{PT} = 0.48Aab^{-1} \qquad (1)$$

and

$$\Delta H_{PT} = kE_{PT} \qquad (2)$$

where E_{PT} is the measured energy of the phase transformation (kJ mole^{-1}); A is the peak area (cm^2); a is the DSC range (m cal sec^{-1}) and b is the chart speed (mm min^{-1}); k is known as the "instrument constant". In the present study it is assumed that the value of k is dependent upon the "nature" of the process under study. For the determination of enthalpy of fusion, k is determined using indium metal as calibrant (ΔH_{fus} In = 3.29 ± 0.01 kJ mole^{-1} [12]; for the determination of enthalpy of sublimation, k is determined using benzoic acid as calibrant (ΔH_{sub} = 89.7 ± 0.5 kJ mole^{-1}). The following samples were sublimed three times prior to vacuum DSC study: benzoic acid (BDH, analar grade): m.p. 122.5, lit. 122.4 [14]; ferrocene (Merck, SP grade): m.p. 173°C, lit. 172.5—173.0 [15]; naphthalene (Merck, scintillation grade): m.p. 80.5°C, lit. 80.55 [15]. The quoted melting points were derived directly from DSC data using a nitrogen atmosphere for thermal analysis.

RESULTS AND DISCUSSION

It is relevant to review the available sublimation enthalpy data for benzoic acid. Davies and Jones [14] derived 91.4 ± 1.4 kJ mole^{-1} for the enthalpy of sublimation at 363 K, from measurements of the saturated vapour pressure of crystalline benzoic acid in the temperature range 343—387 K. Colomina

et al. [16] measured the vapour pressure of the crystalline acid at near-ambient temperatures by an improved Knudsen method, and calculated 90.0 ± 0.3 kJ mole^{-1} (298 K). Morawetz [17] obtained 89.5 ± 0.2 kJ mole^{-1} from calorimetric measurements at 298 K. Malaspina et al. [18] used a combined effusion—microcalorimetry apparatus to study the vaporisation of crystalline benzoic acid (338—383 K) and report the following mean values for the enthalpy of sublimation at 298 K : 89.3 ± 0.4 kJ mole^{-1} by microcalorimetry; 89.0 ± 0.4 kJ mole^{-1} by second-law treatment of effusion data; 94.5 ± 0.3 kJ mole^{-1} by third-law treatment of effusion data. More recently, Ashcroft [8] has obtained ΔH_{sub}(benzoic acid) = 89.1 kJ mole^{-1} (299—312 K) using the thermogravimetric method. Cox [13] has selected ΔH_{sub}(benzoic acid) = 89.7 ± 0.5 kJ mole^{-1} and this value is adopted in the present study.

Vacuum DSC data for benzoic acid are summarised in Table 1. The mean E_{sub} is 133.48 ± 3.37 kJ mole^{-1} for the measured temperature range of sublimation, 328—398 K. The excellent reproducibility of E_{sub} for a wide range of sample masses suggests that benzoic acid is an excellent calibrant for the direct measurement of enthalpies of sublimation by DSC.

To test the validity of this proposal, the sublimation enthalpies of naphthalene and ferrocene were determined by vacuum DSC, using benzoic

TABLE 1

DSC data for benzoic acid

Sample no.	Sample mass (mg)	DSC range (m cal sec^{-1})	E_{sub} (kJ mole^{-1})
1	6.09	±4	132.1
2	7.33	±4	132.9
3	5.22	±4	132.3
4	6.57	±4	127.2
5	5.88	±4	134.0
6	9.29	±4	134.6
7	7.13	±4	130.4
8	7.05	±4	132.5
9	8.04	±4	133.6
10	5.54	±4	141.5
11	7.05	±4	131.2
12	5.46	±4	133.4
13	8.15	±4	138.1
14	6.60	±4	133.1
15	9.44	±4	134.2
16	9.30	±8	136.1
17	8.00	±8	139.7
18	3.39	±4	134.0
19	6.09	±4	132.4
20	5.85	±4	132.5
21	8.74	±4	129.4
22	9.99	±8	135.5
23	5.81	±8	137.4
24	7.86	±4	131.7
25	8.95	±8	127.3

acid as a calibrant for the determination of the instrument constant k. The sublimation enthalpy values obtained, based on five determinations, were 76 ± 2 and 70 ± 2 kJ mole^{-1}, respectively. Significantly lower ΔH_{sub} values are consistently obtained for both compounds if k is calculated using indium metal as calibrant; ΔH_{sub}(naphthalene) = 73 ± 2 kJ mole^{-1} and ΔH_{sub} (ferrocene) = 67 ± 2 kJ mole^{-1}. The following ΔH_{sub} (298 K) data for naphthalene have been published: 72.68 ± 0.33 [19]; 72.05 ± 0.25 [17]; and 73.00 ± 0.25 kJ mole^{-1} [20]. Beech and Lintonbon [21] have published ΔH_{sub}-(naphthalene) = 78 ± 2 (355—490 K) based on DSC derivation of ΔH_{fus} and ΔH_{vap}(naphthalene): 18.9 ± 0.2 and 59 ± 2 kJ mole^{-1}, respectively. The calibrant used is not stated. The "best" available ΔH_{sub}(naphthalene) appears to be 76.7 kJ mole^{-1}, based on Knudsen effusion, vapour pressure/temperature data [19]. Edwards and Kington [22] have determined the enthalpy of sublimation of ferrocene by the Knudsen effusion method, ΔH_{sub} = 73.4 ± 0.4 kJ mole^{-1} and Beech and Lintonbon [21] have published DSC data yielding ΔH_{fus} and ΔH_{vap}(ferrocene) as 18.5 ± 0.1 and 65.5 ± 2 kJ mole^{-1}, respectively. Due to the uncertainties associated with the latter data, the "best" available ΔH_{sub}(ferrocene) appears to be 73.4 ± 0.4 kJ mole^{-1} [22]. Our DSC ΔH_{sub} values for naphthalene and ferrocene derived using benzoic acid as calibrant are in excellent agreement with the corresponding "best" literature values and hence the following procedural recommendation is proposed. For the direct measurement of enthalpy of sublimation by vacuum DSC, benzoic acid may be used as calibrant for the determination of the instrument constant: the corresponding enthalpy of fusion may be derived using a nitrogen atmosphere and indium metal as calibrant. Since no calibrant has been suggested for the determination of enthalpy of vaporisation by DSC, this is best obtained by subtraction of the fusion enthalpy from the sublimation enthalpy. This procedural recommendation follows the accepted principle for the calibration of calorimeters generally — the calibration process parallels the process under study with respect to the phase changes occurring. For completeness, the enthalpies of fusion of benzoic acid, naphthalene and ferrocene have been derived using DSC and employing the calibration procedure herein recommended. The data are reported in Table 2 and the calculated corresponding ΔH_{vap} values are included. Uncertainty intervals are quoted as the standard deviation of the mean of five determinations.

TABLE 2

Thermodynamic data for benzoic acid, naphthalene and ferrocene

Compound	ΔH_{sub} (kJ mole^{-1})	ΔH_{fus} (kJ mole^{-1})	ΔH_{vap} (kJ mole^{-1})
Benzoic acid	89.7 ± 3 [13]	18.7 ± 0.3	71.0 ± 3.0
Naphthalene	76.0 ± 2	19.4 ± 0.3	56.6 ± 2.0
Ferrocene	70.0 ± 2	18.3 ± 0.2	51.7 ± 2.0

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