

Note

MEASUREMENT OF HEATS OF SUBLIMATION OF SOME *ORTHO*-SUBSTITUTED BENZOIC ACIDS BY DIFFERENTIAL SCANNING CALORIMETRY

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The quantitative study of chemical reaction energetics requires accurate knowledge of the thermochemical properties of reacting compounds; however, the extent of such data is still limited. Various techniques have been applied for obtaining thermochemical data such as heats of vaporisation and sublimation but most are time-consuming and have various sources of errors [1]. Differential scanning calorimetry (DSC) has been applied to the measurement of such chemical data with good accuracy and rapidity [2]. Values of the heats of sublimation for nine *ortho*-substituted benzoic acids and related compounds are reported in this paper.

EXPERIMENTAL

High purity grades of commercial samples of 1-naphthoic acid, 2-naphthoic acid, naphthalene, 2-bromobenzoic acid, 2-chlorobenzoic acid, 2-iodobenzoic acid, 2-methylbenzoic acid and 2-methoxybenzoic acid were purchased from Aldrich Chemical Company. Benzoic acid was obtained from the National Bureau of Standards. All compounds were purified by zone refining and the purity was checked by C, H, O and halogen analysis and high-pressure liquid chromatography as described previously [3]. A Perkin-Elmer DSC-1B was used for all thermochemical measurements and the method used for analysis has been described previously [2]. A heating rate of 8 K min⁻¹ was chosen for all samples.

RESULTS AND DISCUSSION

Table 1 gives values for the heats of fusion (ΔH_{fus}), vaporisation (ΔH_{vap}), and sublimation (ΔH_{sub}) and compares these with any previously determined values from the literature. The results obtained are within $\pm 5\%$ of any literature values for the compounds observed. Intrasample variation for ΔH_{fus} , ΔH_{vap} and ΔH_{sub} for each compound tested ($n = 7$) was $< 1.0\%$ (C.V.) and intersample variation ($n = 7$) was $< 1.3\%$ (C.V.). This technique

TABLE 1
Heats of fusion, vaporisation and sublimation
Values in kcal mole⁻¹.

Compound	Experimentally determined values			Literature values (ref. 4)		
	ΔH_{fus}	ΔH_{vap}	ΔH_{sub}	ΔH_{fus}	ΔH_{vap}	ΔH_{sub}
Benzoic acid	4.33 ± 0.06	17.07 ± 0.07	21.40 ± 0.10	4.13	16.29	21.85
2-Methylbenzoic acid	4.79 ± 0.10	28.11 ± 0.05	32.90 ± 0.12	4.82		
2-Methoxybenzoic acid	5.53 ± 0.07	16.37 ± 0.10	21.90 ± 0.10			21.71
2-Bromobenzoic acid	5.50 ± 0.06	14.42 ± 0.09	19.92 ± 0.10			
2-Chlorobenzoic acid	6.10 ± 0.04	21.67 ± 0.12	27.77 ± 0.15	6.15		
2-Iodobenzoic acid	6.27 ± 0.05	18.34 ± 0.10	24.61 ± 0.10			
Naphthalene	4.40 ± 0.03	12.95 ± 0.10	17.35 ± 0.10	4.49	12.31	17.31
1-Naphthoic acid	5.42 ± 0.07	22.68 ± 0.07	28.10 ± 0.10		22.58	
2-Naphthoic acid	5.75 ± 0.08	22.80 ± 0.13	28.55 ± 0.14		22.63	

has provided rapid and accurate analysis of some previously unknown thermochemical data for the compounds studied.

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