Thermodynamic study of phase transitions in methyl esters of *ortho- meta-* and *para*-aminobenzoic acids

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ABSTRACT

A static method based on capacitance gauges was used to measure the vapor pressures of the condensed phases of the methyl esters of the three aminobenzoic acids. For methyl *o*-aminobenzoate the vapor pressures of the liquid phase were measured in the range (285.4 to 369.5) K. For the *meta* and *para* isomers vapor pressures of both crystalline and liquid phases were measured in the ranges (308.9 to 376.6) K, and (332.9 to 428.0) K, respectively. Vapor pressures of the latter compound were also measured using the Knudsen effusion method in the temperature range (319.1 to 341.2) K.

From the dependence of the vapor pressures on the temperature, the standard molar enthalpies and entropies of sublimation and of vaporization were derived. Differential scanning calorimetry was used to measure the temperatures and molar enthalpies of fusion of the three isomers. The results enabled the estimation of the enthalpy of the intermolecular (N–H···O) hydrogen bond in the crystalline methyl *p*-aminobenzoate. A correlation relating the temperature of fusion and the enthalpy and Gibbs energy of sublimation of benzene, methyl benzoates and benzoic acids was derived.

1. Introduction

The current study is an extension of a recent work [1] in which the vapor pressure of methyl *p*-methylbenzoate and methyl *p*-(dimethylamino)benzoate were measured in both crystalline and liquid phases. Those results enabled the determination of the enthalpy of the intermolecular OH···O hydrogen bonds formed in the crystalline packing of the parent benzoic acids. The present study aimed the determination of the enthalpy of the intermolecular NH···O hydrogen bonds formed in the crystalline packing of methyl *p*-aminobenzoate in order to compare this result with the one derived for similar hydrogen bond occurring in the crystals of *N*-methylbenzamide [2]. Furthermore we decided also to measure the vapor pressures of the other two isomers of methyl aminobenzoate with the purpose of comparing their thermodynamic parameters of sublimation with published values of these properties for the related benzoic acids.

Methyl *o*-aminobenzoate (*o*-MAB) naturally occurs in the Concord grapes and other Vitis labrusca grapes [3]. It is an effective, non-toxic bird repellent with application for protecting crops, seeds, turf and fish stocks from bird damage [4]. It is also used

for flavoring of candy, gums, ice creams, soft drinks, gelatins, drugs [5] as well as perfumes [6]. Methyl *m*-aminobenzoate (*m*-MAB) is used in the process of preparation of urea-substituted benzoylguanidines [7], as leukotriene antagonistic [8], as receptor ligands with pharmacologic properties [9] and for dyeing cellulose fibers with water-insoluble azo dyestuffs [10]. Methyl *p*-aminobenzoate (*p*-MAB) is a member of *p*-aminobenzoic acid family, a well known bacterial grower group of compounds [11].

2. Experimental

2.1. Compounds and purity control

Methyl *m*-aminobenzoate (CAS Registry No. 4518-10-9) and methyl *p*-aminobenzoate (CAS Registry No. 619-45-4) were purified by repeated sublimation under reduced pressure prior to the experimental measurements. Their final purities were checked by gas chromatography (GC) using an Agilent 4890D gas chromatograph equipped with HP-5 column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane (15 m × 0.530 mm i.d. × 1.5 μm film thickness) and a flame ionization detector, using nitrogen as carrier gas. The initial and final purities of the samples are presented in table 1. Methyl *o*-aminobenzoate (CAS Registry No. 134-20-3) was

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supplied with a mole fraction purity of 0.9990 and was studied without further purification.

2.2. Differential scanning calorimetry

D.S.C. was used to determine the temperature and enthalpy of fusion of the compounds studied and to detect possible phase transitions in the crystalline phase. The measurements were made in sealed aluminum crucibles under nitrogen atmosphere, using a power compensated differential scanning calorimeter, Setaram DSC 141. The calibration of the power scale of the calorimeter was performed using high purity indium (mass fraction > 0.99999). The temperature scale of the calorimeter was calibrated by measuring the temperature of fusion of the following high purity reference materials: naphthalene, benzoic acid, tin and indium [12]. For each compound at least four independent runs were performed using a heating rate of $3.3 \cdot 10^{-2}$ K·s^{-1}. No crystalline transitions were detected between the temperatures 298 K (m-MAB and p-MAB) or 281 K (o-MAB) and the melting temperature of the compounds studied.

The onset temperature of fusion, T_{fus}, and the enthalpy of fusion, $\Delta_{cr}^{l}H_m^o(T_{fus})$, were computed from the d.s.c. thermograms and are presented in table 6 together with the fusion results derived indirectly from vapor pressure measurements.

2.3. Vapor pressures measurements

A static apparatus based on capacitance diaphragm gauges [13] was used to measure the vapor pressures at different temperatures of liquid phase of o-MAB and of both condensed phases of the *meta* and *para* isomers. The equipment includes two capacitance diaphragm absolute gauges (available from MKS Instruments, Inc.) working at self-controlled constant temperatures: gauge I – Baratron 631A01TBEH (T_{gauge} = 423 K) that allows measuring pressures in the range (0.4 to 133) Pa and in the temperature range (253 to 413) K and gauge II – Baratron 631A11TBFP (T_{gauge} = 473 K) capable of measuring pressures in the range (3 to 1330) Pa and in the temperature range (253 to 463) K. A platinum resistance thermometer (PRT) Pt100 class 1/10 DIN (in a four-wire connection) was used to measure the temperatures of the condensed samples. This thermometer was calibrated by comparison with a standard PRT (25 Ω; Tinsley, 5187A). The tubing between the cell containing the condensed sample and the pressure gauge is kept at a temperature higher than the temperature of the sample and lower than the temperature of the gauge. The uncertainty of the temperature measurements is estimated to be better than ±0.01 K and the uncertainty of the vapor pressure measurements is adequately described by the expression $\sigma(p/Pa) = 0.01 + 0.0025 (p/Pa)$ for gauge 1 and $\sigma(p/Pa) = 0.1 + 0.0025 (p/Pa)$ for gauge 2 [1,13].

A mass-loss Knudsen effusion apparatus [14] enabling the simultaneous operation of nine effusion cells, contained in cylindrical holes inside three temperature-controlled aluminum blocks, was used to measure the vapor pressures of the purified crystalline sample of p-MAB in the pressure range (319.10 to 341.17) K. Each aluminium block is kept at a constant temperature, different from the other two blocks, where three effusion cells with orifices of

different areas are inserted: one "*small*" ($A_o \approx 0.5$ mm^2: series A), one "*medium*" ($A_o \approx 0.8$ mm^2: series B) and one "*large*" ($A_o \approx 1.1$ mm^2: series C). The exact areas and Clausing factors of each used effusion orifice in platinum foil of 0.0125 mm thickness are presented in the supporting information, table S1. The temperature of each block is measured using platinum resistance thermometers Pt100 calibrated as referred above. For each effusion experiment, the loss of mass of the samples during a convenient effusion period of time is determined by weighing the effusion cells to ±0.01 mg before and after the effusion period. For the temperature T, measured with an uncertainty better than ±0.01 K, the vapor pressure p of the crystalline sample contained in each effusion cell is calculated by equation (1), where m is the sublimed mass during the effusion time period t, M is the molar mass of the effusing vapor, R is the gas constant, ($R = 8.3145$ J·K^{-1}·mol^{-1}), A_o is the area of the effusion orifice, and w_o is the respective Clausing factor. The accuracy of the measured pressures is estimated to be better than ±0.01 (p/Pa).

$$p = (m/A_o w_o t)(2\pi RT/M)^{0.5}. \tag{1}$$

3. Results and discussion

3.1. Vapor pressures

Tables 2–4 present the vapor pressure results measured using the static apparatus for liquid phase of o-MAB and for both condensed phases (including metastable supercooled liquid) of m-MAB and p-MAB, respectively. Table 4 also includes the effusion sublimation vapor pressures of p-MAB, calculated for each temperature as the mean of the vapor pressures derived from each Knudsen-effusion cell. The detailed experimental data obtained from each effusion cell, summarized in table S2 (supporting information), show the nonexistence of any relevant effect of the size of the effusion orifices on the measured pressures. The experimental results of crystalline and liquid vapor pressures were fitted (independently) by the truncated form of Clarke and Glew equation (2) [15].

$$R \ln \left(\frac{p}{p^o} \right) = -\frac{\Delta_{cd}^g G_m^o(\theta)}{\theta} + \Delta_{cd}^g H_m^o(\theta) \left(\frac{1}{\theta} - \frac{1}{T} \right)$$
$$+ \Delta_{cd}^g C_{p,m}^o(\theta) \left[\left(\frac{\theta}{T} \right) - 1 + \ln \left(\frac{T}{\theta} \right) \right], \tag{2}$$

where p is the vapor pressure at the temperature T, p^o is a selected reference pressure ($p^o = 10^5$ Pa in this work), θ is a selected reference temperature, R is the molar gas constant (8.3145 J·K^{-1}·mol^{-1}), $\Delta_{cd}^g G_m^o(\theta)$ is the difference in molar Gibbs energy between the gaseous and the crystalline or liquid phases (condensed phases) at the selected reference pressure. $\Delta_{cd}^g H_m^o(\theta)$ is the difference in molar enthalpy between the gas and the condensed phases and $\Delta_{cd}^g C_{p,m}^o(\theta)$ is the difference in molar heat capacity at constant pressure between the gaseous and the condensed phase. The thermodynamic parameters ($\Delta_{cd}^g H_m^o, \Delta_{cd}^g G_m^o$, and $\Delta_{l}^g C_{p,m}^o$) derived from the fittings are presented in table 5. The values of $\Delta_{cr,l}^g S_m^o(\theta)$ were calculated as $\{[\Delta_{cr,l}^g H_m^o(\theta) - \Delta_{cr,l}^g G_m^o]/\theta\}$ and $p(\theta)$ may be easily calculated from the equation $[\Delta_{cr,l}^g G_m^o(\theta) = -R\theta \ln(p/p^o)]$. The values

TABLE 1
Source, purification and analysis details of the samples.

Chemical name	Acronym	Source	Initial mole fraction purity	Purification method	Final mole fraction purity	Analysis method
Methyl o-aminobenzoate	o-MAB	Sigma–Aldrich	0.999		0.9990	GC[a]
Methyl m-aminobenzoate	m-MAB	Alfa–Aesar	0.980	sublimation	0.9979	GC[a]
Methyl p-aminobenzoate	p-MAB	Alfa–Aesar	0.996	sublimation	0.9986	GC[a]

[a] GC – Gas–liquid chromatography.