The influence of the halogen atoms and acetyl group on vapour pressures and related properties of the *p*-haloacetophenones

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A B S T R A C T

This work reports experimental vapour pressures at different temperatures of four halogenated ace-tophenones. The liquid phase vapour pressures of *p*-fluoro and *p*-chloro acetophenones were measured, respectively, across the temperatures ranges (255.1 to 310.2) K and (271.6 to 335.0) K, using a static method based on capacitance diaphragm manometers. This experimental technique was also used to measure the vapour pressures of both (crystalline and liquid) condensed phases of *p*-bromo- and *p*-iodoacetophenones, respectively, through the temperature intervals (295.3 to 378.4) K and (313.1 to 402.0) K. The temperatures and molar enthalpies and entropies of fusion of the four *p*-halogenated ace-tophenones were determined using differential scanning calorimetry. The standard molar enthalpies, entropies and Gibbs energies of sublimation and of vaporisation, at selected reference temperatures, were derived from the experimental results. The contributions of the acetyl group and of the constituent halo-gen atoms to these thermodynamic properties were also predicted through correlation equations.

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1. Introduction

Our research group has been developing equations correlating thermodynamic properties of sublimation and vaporisation of organic compounds for a period of time [1–9]. These correlations are very useful to test the internal coherency of the experimental results and to predict results for compounds not studied experi-mentally. Some of these correlations include the temperature of fusion and describe accurately vapour pressures of several *para* substituted benzoic acids, methyl benzoates and phenols [5–7]. More recently [8], it was proposed a new method for estimating vapour pressures and enthalpies of sublimation of substituted benzenes that may be applied to 30 different substituents attached to the benzene ring in different positions. In order to extend this database to other benzene derivatives, reported results on other substituted benzenes have been currently collected but some com-mon constituent groups are still missing. One of the substituents that is lacking is the acetyl group and this work integrates four compounds selected for this study, fluoro, chloro, bromo, and iodo *p*-acetophenone. Acetophenone is an aromatic ketone occurring in several foodstuffs including some fruits (apple, apricot and banana) beef, cheese or cauliflower [10]. It is used "in perfumery as a fragrance ingredient in soaps, detergents, creams, lotions, and

perfumes; as a flavouring agent in foods, non-alcoholic beverages, and tobacco; as a specialty solvent for plastics and resins; as a catalyst for the polymerization of olefins; and in organic syntheses as a photosensitizer" [11]. It also exhibits photochemical properties [12] that have been successfully useful in investigations of biologi-cal systems [13,14]. The electrocarboxylation of aromatic ketones, namely the halogenated members of the family, "is potentially an easy way to prepare carboxylated products, some of them of indus-trial interest, particularly for the production of anti-inflammatory drugs" [15]. The selection of the halogenated derivatives of acetophenone for this study is also due to our interest in investigat-ing whether enthalpies and vapour pressures of sublimation or vaporisation of halogen substituted benzenes show a regular dependence on the volume of the halogen atom as was observed previously for *p*-halogenated benzoic acids, methyl benzoates, and phenols [6,7]. In a recent study [9] on the estimation of thermo-dynamic vaporisation properties of mono and poly halogenated benzenes it was concluded that the influence of volume in poly halogenated benzenes is not additive *per se* but a suitable combina-tion of volume and electron affinity enables good estimations of the vaporisation properties from the number of the constituent halogen atoms. This new method is also applicable to halogenated benzenes containing other groups beyond halogen atoms since results for the parent compound (acetophenone in the present study) are known and no significant intramolecular interactions exist between the halogen atoms and the other substituent groups.

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2. Experimental

2.1. Materials

Table 1 reports detailed information about the source and purification features of the four compounds studied in this work: p-fluoroacetophenone (FAc, C_8H_7FO, CASNR 403-42-9), p-chloroacetophenone (ClAc, C_8H_7ClO, CASNR 99-91-2), p-bromoacetophenone (BrAc, C_8H_7BrO, CASNR 99-90-1) and p-iodoacetophenone (IAc, C_8H_7IO, CASNR 13329-40-3). The bromo and iodo acetophenones were purified using repeated sublimation under reduced pressure, while the other two compounds were studied without prior purification taking into account their high original purity verified by gas–liquid chromatography (GC). Prior to the experimental determinations, the degree of purity of each sample studied was evaluated by GC performed using an Agilent 4890D equipped with an HP-5 column (cross-linked, 0.05 diphenyl and 0.95 dimethylpolysiloxane by mass fraction) and a FID detector, using nitrogen as the carrier gas and dimethylformamide as solvent.

2.2. Differential scanning calorimetry analysis

A power compensated Perkin Elmer calorimeter (Diamond Pyris 1) was used to detect eventual crystalline structure transitions and to determine the temperature and enthalpy of fusion of the compounds studied. The calibration of the calorimeter was performed using the following high purity materials: benzoic acid, triphenylene, naphthalene, anthracene, 1,3,5-triphenylbenzene, diphenylacetic acid, perylene, o-terphenyl and 4-methoxybenzoic acid. For each compound five fresh samples (sealed in aluminium crucibles) were scanned under a controlled nitrogen flux from $T = 298$ K (p-bromo and p-iodo acetophenones), or from $T = 263$ K (p-fluoro and p-chloro acetophenones) to a temperature $ca.$ 20 K above the fusion temperature, using a heating rate of $3.3 \cdot 10^{-2}$ K $\cdot$ s^{-1}. No cr–cr phase transition was identified between the initial and the fusion temperature. The onset temperatures of fusion, T_{fus}, as well as the enthalpies of fusion, $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\text{o}}(T_{\text{fus}})$, were taken from DSC thermograms and are reported in table 4.

2.3. Vapour pressure measurements

The vapour pressures of the liquid phases of p-fluoro and p-chloro acetophenones and of both the condensed phases (crystalline and liquid) of the other two compounds studied were measured at different temperatures using a static apparatus based on a capacitance diaphragm manometer that was previously tested and described [16]. The measurements were performed using two different Baratron gauges which operate at self-controlled temperatures: gauge I, Baratron 631A01TBEH ($T_{\text{gauge}} = 423$ K), for pressures in the range (0.5 to 130) Pa and gauge II, Baratron 631A11TBFP ($T_{\text{gauge}} = 473$ K) for pressures in the range (3 to 1300) Pa [17]. The expressions $u(p/\text{Pa}) = 0.01 + 0.0025$ (p/Pa) and $u(p/\text{Pa}) = 0.1 + 0.0025$ (p/Pa) describe the standard

uncertainties of the pressure measurements related to gauges I and II, respectively. The standard uncertainty of the temperature measurements was estimated to be $u(T/\text{K}) = 0.01$. In order to assure that the sample is adequately outgassed and that eventual traces of volatile substances are eliminated, upward and downward temperature cycles are performed during the vapour pressure measurements until coherent results of the measured vapour pressures are obtained.

3. Results and discussion

3.1. Thermodynamic properties of sublimation and vaporisation

Table 2 reports vapour pressures of the liquid phase of p-fluoro and p-chloro acetophenones and also the vapour pressures of the crystalline and liquid (including supercooled liquid) p-bromo and p-iodo acetophenones. Experimental (p, T) results were individually fit by the truncated form of the Clarke and Glew equation [18], equation (1):

$$R \ln\left(\frac{p}{p^{\text{o}}}\right) = -\frac{\Delta_{\text{cr,l}}^{\text{g}} G_{\text{m}}^{\text{o}}(\theta)}{\theta} + \Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\text{o}}(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{\text{cr,l}}^{\text{g}} C_{p,\text{m}}^{\text{o}}(\theta)\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{T}{\theta}\right)\right]. \quad (1)$$

In this equation, p is the vapour pressure at the temperature T, $p^{\text{o}} = 10^5$ Pa, θ is a selected reference temperature, $R = 8.3144621$ J $\cdot$ K^{-1} $\cdot$ mol^{-1} [19], and the thermodynamic properties of phase transition (sublimation or vaporisation) $\Delta_{\text{cr,l}}^{\text{g}} G_{\text{m}}^{\text{o}}(\theta)$, $\Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\text{o}}(\theta)$ and $\Delta_{\text{cr,l}}^{\text{g}} C_{p,\text{m}}^{\text{o}}(\theta)$ are adjustable parameters. The derived values of these properties are reported in table 3 for the following reference temperatures, $viz.$ 298.15 K, the mean temperature of the experiments, and also the temperature of the triple point for the two compounds studied in both condensed phases (p-bromo and p-iodo acetophenones). The corresponding uncertainties are standard deviations of the least squares regressions of the fittings and the standard molar entropies of those phase transitions, also reported in table 3, were calculated using equation (2):

$$\Delta_{\text{cr,l}}^{\text{g}} S_{\text{m}}^{\text{o}}(\theta) = \frac{\Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\text{o}}(\theta) - \Delta_{\text{cr,l}}^{\text{g}} G_{\text{m}}^{\text{o}}(\theta)}{\theta}. \quad (2)$$

For accurate vapour pressure measurements performed over wide temperature intervals ($ca.$ 50 K), the fit of equation (1) to the experimental (p, T) values often produces reliable values of the isobaric molar heat capacity differences between gaseous and condensed phases, $\Delta_{\text{cr,l}}^{\text{g}} C_{p,\text{m}}^{\text{o}}$. This was the case for the vaporisation results allowing the determination of $\Delta_{\text{l}}^{\text{g}} C_{p,\text{m}}^{\text{o}}$ from the fittings of equation (1) to the liquid vapour pressure–temperature values of the four compounds studied. The values of $\Delta_{\text{cr}}^{\text{g}} C_{p,\text{m}}^{\text{o}}$ (also reported in table 3), were inserted in equation (1) after being estimated using equation (3), proposed by Monte et $al.$ [20], that is a rearrangement of equation (4) proposed by Chickos et $al.$ [21]. The

TABLE 1

Provenance and purity details of the four substituted acetophenones studied in this work.

Chemical name	Source	Minimum initial purity[a]	Purification method	Final mass fraction purity[b]	Analysis method[c]
p-Fluoroacetophenone	Alfa-aesar	0.99		0.9923	GC
p-Chloroacetophenone	Alfa-aesar	0.98		0.9990	GC
p-Bromoacetophenone	Sigma–Aldrich	0.98	Sublimation[d]	0.9998	GC
p-Iodoacetophenone	Sigma–Aldrich	0.98	Sublimation[d]	0.9977	GC

[a] As stated by the supplier.
[b] The analysis method is not sensitive to water content.
[c] Gas–liquid chromatography (Flame Ionisation Detector).
[d] Under reduced pressure (p = 1 Pa).