



# Vapour pressures and phase transition properties of four substituted acetophenones



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## ABSTRACT

This paper reports experimental vapour pressures at different temperatures of four substituted acetophenones. Using the diaphragm manometer static method, the vapour pressures of both (crystalline and liquid) condensed phases of *ortho* and *para* acetoxyacetophenones and also of *para*-methoxyacetophenone were measured in the following temperature ranges  $T = (313.0\text{--}398.0)$  K,  $(315.0\text{--}378.3)$  K and  $(296.2\text{--}355.7)$  K, respectively. This experimental technique was also used to measure the vapour pressures of the liquid phase of *meta*-acetoxyacetophenone through the temperature interval  $T = (305.1\text{--}368.5)$  K. The vapour pressures of the crystalline phase of *meta*-acetoxyacetophenone were measured using the Knudsen effusion technique over the temperature ranges,  $T = (297.7\text{--}307.3)$  K. This technique was also used for complementing the range of the vapour pressure measurements of the *ortho* and *para* acetoxyacetophenone isomers between  $T = (298.0\text{--}321.3)$  K and  $(298.1\text{--}309.3)$  K, respectively. The standard molar enthalpies, entropies and Gibbs energies of sublimation and of vaporization, at reference temperatures, were derived from the experimental results. Differential scanning calorimetry was used to determine the temperatures and molar enthalpies of fusion and of the observed crystalline transitions. The contributions of the acetoxy and acetyl groups to the sublimation properties of the compounds studied were calculated.

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## 1. Introduction

A straightforward method for predicting vapour pressures and enthalpies of sublimation of substituted benzenes taking into account their temperatures of fusion and the contribution of several different substituents of benzene derivatives was presented in a previous work [1]. To enlarge the database that supports this method, literature results of other substituted benzenes have been collected but some constituent groups were still missing. Two of the groups absent in the original database are the acetoxy ( $-\text{OCOCH}_3$ ) and the acetyl ( $-\text{COCH}_3$ ) ones that integrate the four compounds selected for this study – *ortho*, *meta* and *para* acetoxyacetophenones and *para*-methoxyacetophenone. The experimental results of the standard Gibbs energies and enthalpies of sublimation and of the temperatures of fusion determined in this work together with the values of such properties derived recently for fluoro, chloro, bromo and iodo acetophenones [2] and for the three acetoxybenzoic acid isomers [3] were introduced in the database cited above. A new multivariable linear regression analysis having as variables the number of each substituent in each

compound, the temperature of fusion, the number of eventual *ortho* effects between adjacent neighbors and also the eventual influence of substituent groups in the *para* position, enabled an evaluation of the contribution of the acetyl and acetoxy substituents to the volatility and to the enthalpy of sublimation of the compounds studied.

Acetophenone is the simplest aromatic ketone which is used in the synthesis of several pharmaceuticals [4,5], as an ingredient in several fragrances [6], and in the production of important resins [4]. *Ortho*-acetoxyacetophenone was successfully used as substrate in the preparation of a variety of fluorescent 5-aryl-2,3-dicyanofurans [7] and in the synthesis of 1-methyl-3-hydroxyisoquinoline [8]. *Meta*-acetoxy acetophenone is one of the compounds used in the treatment of alpha-1 antitrypsin (AAT) deficiency [9], and is the predominant product in the palladium catalyzed oxy-acetylation of phenyl acetate [10]. *Para*-acetoxyacetophenone takes part of two production processes of *para*-acetoxybenzoic acid [11,12]. *Para*-methoxyacetophenone is a trace constituent of oil of long pepper. It is present in some fruits such as tomato and cranberry, and in anise, sherry, grilled and roasted beef and serves as a flavouring adjuvant and ingredient in nut, vanilla, butter and tobacco flavours [13]. This compound, also known as *p*-acetylanisole, induced negative phototaxis in

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Chlamydomonas, suggesting interference with the activity of flagellar proteins and control of flagellar dominance [14]. The biocatalytic enantioselective reduction of this ketone to (S)-1-(4-methoxyphenyl)ethanol was successfully conducted [15]. This alcohol can be used as a crucial synthon to prepare cycloalkyl [b] indoles for clinical treatment of general allergic response [15]. It also participates in the synthesis and physiological activity of thiophenes and furans [16].

## 2. Experimental

### 2.1. Materials

Table 1 reports information about the source, the purification, and the degree of purity of the compounds studied: *o*-acetoxyacetophenone, *m*-acetoxyacetophenone, *p*-acetoxyacetophenone and *p*-methoxyacetophenone. The degree of purity of the original compounds and of the purified (sublimation) samples were monitored by gas-liquid chromatography performed using an Agilent 4890D apparatus equipped with an HP-5 column (cross-linked, 0.05 diphenyl and 0.95 dimethylpolysiloxane by mass fraction) and a flame ionization detector (FID), using nitrogen as the carrier gas and dimethylformamide as solvent.

### 2.2. Differential scanning calorimetry

A power compensated Perkin Elmer calorimeter (Diamond Pyris 1) was used to determine the temperatures and enthalpies of fusion of the four substituted acetophenones studied and also to identify eventual phase transitions in the crystalline phase of these compounds. The power and temperature scales of the calorimeter were calibrated using several reference materials [17]. The standard uncertainties derived from the calibration results are,  $u(T/K) = 0.2$  and  $u(\Delta_{cr}^{\downarrow}H_m^{\circ}/\text{kJ}\cdot\text{mol}^{-1}) = 0.4$ . Five fresh samples of each compound, sealed in aluminium pans, were scanned under a nitrogen atmosphere from  $T = 173$  K to a temperature ca. 20 K above the melting point, using a heating rate of  $3.3 \times 10^{-2} \text{ K}\cdot\text{s}^{-1}$ . The thermograms of the *meta* and *para* acetoxyacetophenones revealed the existence of a reversible crystalline phase transition ca. 8 K and 14 K, respectively, below the temperature of fusion of these two compounds. For *o*-acetoxyacetophenone and *p*-methoxyacetophenone no phase transitions were observed below their fusion temperatures. The onset temperatures of fusion as well as the molar enthalpy and entropy of fusion of the four compounds studied are presented in Table 4, which also presents the thermodynamic parameters (temperature and molar enthalpy and entropy) associated with the crystalline transitions observed in the *meta* and *para* acetoxyacetophenones. The assigned uncertainties were calculated through the RSS method combining the expanded uncertainties ( $k = 2$ ) of the mean of the experimental runs and the uncertainties calculated from the DSC calibration.

### 2.3. Static method (diaphragm capacitance gauges)

The vapour pressures of the condensed phases of *ortho* and *para* acetoxyacetophenones, *para*-methoxyacetophenone, and also the liquid vapour pressures of *meta*-acetoxyacetophenone were measured at different temperatures using a static apparatus based on capacitance diaphragm manometers that was previously fully described and tested [18,19]. 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  $(0.5\text{--}1.3 \times 10^2)$  Pa and gauge II, Baratron 631A11TBFP ( $T_{\text{gauge}} = 473$  K) for pressures in the range  $(3\text{--}1.3 \times 10^3)$  Pa. The expressions  $u(p/\text{Pa}) = 0.01 + 0.0025(p/\text{Pa})$  and  $u(p/\text{Pa}) = 0.1 + 0.0025(p/\text{Pa})$  describe, respectively, the standard uncertainties of the pressure measurements related to gauges I and II. The standard uncertainty of the temperature measurements was estimated as  $u(T/K) = 0.01$ .

### 2.4. Knudsen effusion technique

A mass-loss Knudsen effusion apparatus, enabling the simultaneous operation of nine effusion cells contained in cylindrical holes inside three temperature-controlled aluminium blocks [20], was also used for measurements of vapour pressures of crystalline samples of the three acetoxyacetophenones studied. Each aluminium block is kept at a constant temperature, different from the other two blocks, and contains three cells with different effusion orifices made out of platinum disks of  $(0.0125 \pm 0.001)$  mm thickness. These disks were acquired from Goodfellow Cambridge Ltd. that also measured the diameters of the effusion orifices with an assigned uncertainty of  $\pm 0.005$  mm, yielding the following areas for the orifices:  $A_0(A_1) = A_0(A_2) = A_0(A_3) = (0.636 \pm 0.004) \text{ mm}^2$ ,  $A_0(B_1) = A_0(B_2) = A_0(B_3) = (0.785 \pm 0.004) \text{ mm}^2$ ,  $A_0(C_1) = A_0(C_2) = A_0(C_3) = (0.985 \pm 0.004) \text{ mm}^2$ , where the uncertainties were calculated by the RSS method. The Clausing factors of the effusion orifices were calculated as  $w_0 = \{1 + (l/2r)\}^{-1}$ , where  $l$  is the thickness of the platinum foil and  $r$  is the radius of the orifices, yielding the following results, respectively, for the orifices of series A, B, and C, 0.986, 0.988, and 0.989. For calculating the vapour pressure  $p$  at the temperature  $T$ , Eq. (1) was used. The loss of mass of the sample contained in each cell,  $\Delta m$ , during a convenient effusion time period  $t$ , is determined by weighing the cell to  $\pm 1 \times 10^{-5}$  g before and after the effusion period. In this equation,  $A_0$  is the area of the effusion orifice,  $R$  is the gas constant ( $R = 8.3144598 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  [21]), and  $M$  is the molar mass of the vapour assumed to be monomeric.

$$p = (\Delta m/A_0 w_0 t) \cdot (2\pi RT/M)^{1/2} \quad (1)$$

The standard uncertainties of the vapour pressure and temperature measurements are estimated as  $u(p/\text{Pa}) = 0.01$  and  $u(T/K) = 0.01$ .

**Table 1**  
Source and purification details of the four substituted acetophenones.

Compound	Source	Minimum initial purity	Purification method <sup>a</sup>	Final mass fraction purity (dry basis)	Analysis method <sup>b</sup>
<i>o</i> -Acetoxyacetophenone (CASRN 7250-94-4)	Alfa Aesar	0.98 <sup>c</sup>	Sublimation	0.9968	GC
<i>m</i> -Acetoxyacetophenone (CASRN 2454-35-5)	TCI	0.992 <sup>d</sup>	Sublimation	0.9977	GC
<i>p</i> -Acetoxyacetophenone (CASRN 13031-43-1)	Alfa Aesar	0.99 <sup>c</sup>	Sublimation	0.9979	GC
<i>p</i> -Methoxyacetophenone (CASRN 100-06-1)	Sigma-Aldrich	0.997 <sup>d</sup>	Sublimation	0.9993	GC

<sup>a</sup> Under reduced pressure ( $p \approx 1$  Pa).

<sup>b</sup> Gas-liquid chromatography (Flame Ionization Detector).

<sup>c</sup> Minimum purity degree announced by the supplier.

<sup>d</sup> Analysis certified by the manufacturer.

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