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Thermodynamic properties of the methyl esters of *p*-hydroxy and *p*-methoxy benzoic acids

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ABSTRACT

The vapor pressures of crystalline and liquid phases of methyl *p*-hydroxybenzoate and of methyl *p*-methoxybenzoate were measured over the temperature ranges (338.9 to 423.7) K and (292.0 to 355.7) K respectively, using a static method based on diaphragm capacitance gauges. The vapor pressures of the crystalline phase of the former compound were also measured in the temperature range (323.1 to 345.2) K using a Knudsen mass-loss effusion technique. The results enabled the determination of the standard molar enthalpies, entropies and Gibbs free energies of sublimation and of vaporization, at $T = 298.15$ K, as well as phase diagram representations of the (p,T) experimental data, including the triple point. The temperatures and molar enthalpies of fusion of both compounds were determined using differential scanning calorimetry and were compared with the results indirectly derived from the vapor pressure measurements. The standard ($p^\circ = 10^5$ Pa) molar enthalpies of formation, in the crystalline phase, at $T = 298.15$ K, of the compounds studied were derived from their standard massic energies of combustion measured by static-bomb combustion calorimetry. From the experimental results, the standard molar enthalpies of formation, in the gaseous phase at $T = 298.15$ K, were calculated and compared with the values estimated by employing quantum chemical computational calculations. A good agreement between experimental and theoretical results is observed. To analyze the thermodynamic stability of the two compounds studied, the standard Gibbs free energies of formation in crystalline and gaseous phases were undertaken. The standard molar enthalpies of formation of the title compounds were also estimated from two different computational approaches using density functional theory-based B3LYP and the multilevel G3 methodologies.

1. Introduction

In previous works the vapor pressures of several methyl benzoates were measured at different temperatures allowing the determination of thermodynamic properties of sublimation and vaporization. The comparison of the derived results with the ones related to the parent benzoic acids enabled estimations of the enthalpy of intermolecular hydrogen bonds O–H···O [1–3]. In order to determine the enthalpy of similar intermolecular bonds existing in methyl *p*-hydroxybenzoate, it was decided to measure the vapor pressures of this compound and of methyl *p*-methoxybenzoate in the crystalline and liquid phases. To get a more complete thermodynamic characterization of these two compounds, it was planned to determine their enthalpies of combustion, similarly to what has been done recently for other substituted benzenes [4–7].

p-Hydroxybenzoates (parabens) are esters of *p*-hydroxybenzoic acid that find extensive application as antimicrobial preservatives in a wide array of consumer products (cosmetics, foods, toiletries,...) as well as in pharmaceuticals preparations, being the methyl, ethyl, propyl and butyl *p*-hydroxybenzoates the most used ones [8]. Methyl *p*-methoxybenzoate is present in some mushroom species [9] and unifloral honeys [10] and participates in the synthesis of new pharmaceuticals [11] being commonly used as synthetic flavoring compound in the perfume and flavor industry [12,13].

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2. Experimental

2.1. Materials and purity control

Methyl *p*-hydroxybenzoate ($C_8H_8O_3$, CASNR 99-76-3) and methyl *p*-methoxybenzoate ($C_9H_{10}O_3$, CASNR 121-98-2), were obtained commercially and were further purified by repeated sublimation under reduced pressure previously to the experimental study. Their final mass fraction purity was found to be better than 0.999 by (gas-liquid) chromatography performed using an apparatus Agilent 4890D 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 carrier gas. Table 1 presents the initial purity (from certificate of analysis of the supplier) and the final purity achieved after purification of the samples. The amount of carbon dioxide recovered in combustion calorimetric experiments also confirmed the high purity of the samples. The average ratio of the mass of carbon dioxide recovered after combustion to that calculated from the mass of samples used in each experiment and the respective expanded ($k = 2$) uncertainties of the mean were (1.0002 ± 0.0003) for methyl *p*-hydroxybenzoate and (1.0002 ± 0.0005) for methyl *p*-methoxybenzoate. The specific densities used to calculate the true mass, from the apparent mass in air, were $\rho = 1.217\ \text{g} \cdot \text{cm}^{-3}$ and $\rho = 1.149\ \text{g} \cdot \text{cm}^{-3}$, for methyl *p*-hydroxybenzoate and methyl *p*-methoxybenzoate, respectively [14].

2.2. Differential scanning calorimetry

A Setaram (model DSC 141) differential scanning calorimeter was used to detect possible phase transitions that might occur in the crystalline phases and to determine the temperature and enthalpy of fusion of the purified samples of each compound studied. The calibration of the power scale of the calorimeter was performed using high-purity indium (mass fraction > 0.99999) and its temperature scale was calibrated by measuring the fusion temperature of high purity reference materials (naphthalene, benzoic acid, tin and indium [15]). The recorded thermograms of the experiments were performed with samples sealed in aluminium crucibles under a nitrogen atmosphere. Six fresh samples of each compound, were scanned from $T = 298$ K to about 20 K above the melting temperature, at a heating rate of $3.3 \cdot 10^{-2}\ \text{K} \cdot \text{s}^{-1}$. No (solid-solid) transitions were detected between $T = 298$ K and the melting temperatures of the two compounds studied. The determined onset temperatures of fusion, T_{fus}, and the enthalpies of fusion, $\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^{\text{o}}\ (T_{\text{fus}})$ are presented in table 7.

2.3. Combustion calorimetry

The standard molar energies of combustion were measured using a static bomb calorimeter, equipped with a Parr 1108 model twin valve bomb, made of stainless steel and with an internal volume of $0.342\ \text{dm}^3$. The experimental set-up and technique have been previously described [16,17]. The bomb was calibrated with benzoic acid (NIST Standard Reference Material 39j) whose massic energy of combustion, under bomb conditions, is $-(26434 \pm 3)\ \text{J} \cdot \text{g}^{-1}$ [18]. The calibration results were corrected to give the energy equivalent, ε(calor), corresponding to the average mass of water added to the calorimeter (3119.6 g). The energy equivalent of the calorimeter was determined, from six calibration experiments made in oxygen, at $p = 3.04$ MPa, with $1.00\ \text{cm}^3$ of water added to the bomb, according to the procedure suggest by Coops *et al.* [19], as $\varepsilon(\text{calor}) = (15995.3 \pm 1.1)\ \text{J} \cdot \text{K}^{-1}$. The assigned uncertainty is the standard deviation of the mean. For all the

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

Chemical name	Source	Initial mass fraction purity[a]	Purification method[b]	Final mass fraction purity	Analysis method[c]
Methyl *p*-hydroxybenzoate	Sigma–Aldrich	0.998	Sublimation	0.9998	GC
Methyl *p*-methoxybenzoate	Sigma–Aldrich	0.997	Sublimation	0.9999	GC

[a] As stated in the certificates of analysis of the manufacturer.
[b] Under reduced pressure ($p = 1$ Pa).
[c] (Gas-liquid) chromatography (FID).

TABLE 2
Typical combustion experimental results, at $T = 298.15$ K.[a]

	Methyl *p*-hydroxybenzoate	Methyl *p*-methoxybenzoate
$m(\text{CO}_2, \text{total})/\text{g}$	2.03127	2.04768
$m(\text{cpd})/\text{g}$	0.87554	0.85728
$m(\text{fuse})/\text{g}$	0.00324	0.00267
$\Delta T_{\text{ad}}/\text{K}$	1.34327	1.43590
$\varepsilon_{\text{f}}/(\text{J} \cdot \text{K}^{-1})$	16.56	16.73
$\Delta m(\text{H}_2\text{O})/\text{g}$	0	0
$-\Delta U(\text{IBP})/\text{J}$	21508.25	22991.67
$\Delta U(\text{fuse})/\text{J}$	52.62	43.36
$\Delta U(\text{HNO}_3)/\text{J}$	1.08	0.33
$\Delta U(\text{ign.})/\text{J}$	0.49	0.50
$\Delta U_{\Sigma}/\text{J}$	15.90	15.21
$-\Delta_{\text{c}} u^{\text{o}}/(\text{J} \cdot \text{g}^{-1})$	24485.64	26750.03

[a] $m(\text{CO}_2$, total) is the total mass of CO_2 formed in the experiment; m(cpd) is the mass of compound burnt in the experiment; m(fuse) is the mass of fuse (cotton); ΔT_{ad} is the corrected temperature rise; ε_{f} is the energy equivalent of contents in the final state; $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 3119.6 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(IBP) includes the ignition energy, ΔU(ign.); ΔU(fuse) is the energy of combustion of the fuse (cotton); $\Delta U(\text{HNO}_3)$ is the energy correction for the nitric acid formation; ΔU_{Σ} is the energy correction to the standard state; $\Delta_{\text{c}} u^{\circ}$ is the standard massic energy of combustion.

TABLE 3
Individual values for the standard ($p^{\text{o}} = 10^5$ Pa) massic energy of combustion, at $T = 298.15$ K, of the two compounds studied.[a]

Methyl *p*-hydroxybenzoate	Methyl *p*-methoxybenzoate
$-\Delta_{\text{c}} u^{\text{o}}/(\text{J} \cdot \text{g}^{-1})$	
24479.81	26756.60
24485.64	26750.03
24488.78	26735.13
24470.17	26742.98
24503.17	26734.01
24485.25	26753.87
$-\langle \Delta_{\text{c}} u^{\text{o}} \rangle/(\text{J} \cdot \text{g}^{-1})$	
24485.5 ± 4.4	26745.4 ± 3.9

[a] The uncertainties are the standard deviation of the mean of the individual values.

TABLE 4
Derived standard ($p^{\text{o}} = 10^5$ Pa) molar values, at $T = 298.15$ K, for the two compounds.[a]

Compound	$-\Delta_{\text{c}} U_{\text{m}}^{\text{o}}$	$-\Delta_{\text{c}} H_{\text{m}}^{\text{o}}$	$-\Delta_{\text{f}} H_{\text{m}}^{\text{o}}$ (cr)
	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$
Methyl *p*-hydroxybenzoate	3725.4 ± 1.9	3726.6 ± 1.9	564.8 ± 2.2
Methyl *p*-methoxybenzoate	4444.4 ± 2.0	4446.9 ± 2.0	523.8 ± 2.3

[a] The uncertainties are twice the overall standard deviation of the mean, and include the contributions from the calibration with benzoic acid and from the energy of combustion of auxiliary materials.