



Thermodynamic properties of isomeric iso-butoxybenzoic acids: Experimental and theoretical study



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ABSTRACT

Standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation at the temperature $T = 298.15$ K of the 2-, 3-, and 4-iso-butoxybenzoic acids were measured using the combustion calorimetry. Standard molar enthalpies of vaporization and sublimation were derived from the vapor pressure temperature dependencies measured by the transpiration method. Molar enthalpies of the solid state phase transitions were measured by the DSC. Thermodynamic data on alkoxy substituted benzoic acids available in the literature were collected and combined with own experimental results. This data set on alkoxybenzoic acids was evaluated by using quantum-chemical and group-additivity methods.

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1. Introduction

Alkoxybenzoic acids have become an object of recent increasing interest due to their new applications. They are used as flavoring substances and preservatives of fragrance in cosmetic formulations [1]. As some of them are natural products, they are good candidates for pharmaceutical co-crystals [1]. Several alkoxybenzoic acids and their derivatives reveal biological activity as inhibitors of phosphodiesterase [2]. The majority of the papers on alkoxybenzoic acids deals with *n*-alkoxy derivatives. It is due to their liquid crystal properties. Esters of these compounds with triethanolamine were found to be discotic mesogens [3]. It is noteworthy that these compounds easily form mixed supramolecular liquid crystals induced by hydrogen bonding which have a much wider mesophase range than their individual components [4,5]. For all the isomers of methoxybenzoic acid molecular and crystal structures have been determined by X-ray diffraction method [2,6]. The investigated compounds form

dimeric molecules with a moderately strong intermolecular hydrogen bonds. Several polymorphs have been observed due to the flexibility of the molecule [1]. Thermochemistry of the methoxy substituted benzoic acids has been evaluated recently [7]. The molar enthalpy of formation and sublimation on benzoic acids with the *n*-alkoxy-substituents were also reported [8,9]. The lack of the data for branched alkoxy-substituted benzoic acids was the reason to investigate the iso-butoxy benzoic acids (see Fig. 1) in the present paper.

The new results together with the thermochemical data on alkoxybenzoic acid available in the literature (see Table 1) have been checked for internal consistency using the quantum chemical and the group-additivity methods.

2. Materials and methods

2.1. Materials

Samples of iso-butoxybenzoic acids were synthesized from the commercially available bromo-iso-butoxybenzenes according to a general procedure given on Fig. 2. Necessary details are given below for each isomer as follows.

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Table 1
Thermochemical data at $T = 298.15\text{ K}$ ($p^\circ = 0.1\text{ MPa}$) for alkoxybenzoic acids (in kJ mol^{-1})^a.

| Compounds | St. | $\Delta_c H_m^\circ$ | $\Delta_f H_m^\circ$ (cr) | $\Delta_{\text{cr}}^\circ H_m^\circ$ | $\Delta_1^\circ H_m^\circ$ | $\Delta_f H_m^\circ$ (liq) | $\Delta_f H_m^\circ$ (g) |
|--------------|-----|----------------------|---------------------------|--------------------------------------|----------------------------|----------------------------|--------------------------|
| 2-Isobutoxy- | liq | -5715.1 ± 1.6 | – | – | 95.6 ± 0.6 | -614.3 ± 2.2 | -518.7 ± 2.3 |
| 3-Isobutoxy- | cr | -5678.4 ± 2.6 | -651.0 ± 3.0 | 120.7 ± 1.4^b | 99.2 ± 0.9 | -629.5 ± 3.2^c | -530.3 ± 3.3 |
| 4-Isobutoxy- | cr | -5672.8 ± 1.7 | -656.6 ± 2.2 | 119.0 ± 0.6 | 104.1 ± 2.1^b | -641.7 ± 3.0^c | -537.6 ± 2.3 |
| 4-Etoxy- | cr | – | -605.5 ± 1.8 [9] | 121.8 ± 1.1^b | 95.5 ± 2.8^b | -579.2 ± 3.2^c | -483.7 ± 2.1 |
| 4-Butoxy- | cr | – | -647.1 ± 2.5 [9] | 123.2 ± 1.0 | 108.8 ± 2.6^b | -632.7 ± 3.5^c | -523.9 ± 2.7 |
| 4-Octyloxy- | cr | – | -767.9 ± 3.9 [9] | 159.6 ± 2.6^b | 126.7 ± 3.8^b | -745.0 ± 4.8^c | -608.3 ± 4.7 |

^a Uncertainties correspond to expanded uncertainties of the mean (0.95 confidence level).

^b From Table 3.

^c Calculated from the experimental $\Delta_f H_m^\circ$ (cr)-values (this table) and the sum of the solid state phase transitions with enthalpies $\sum \Delta_{\alpha}^\circ H_m^\circ$ values from Table 3.

4-Isobutoxybenzoic acid. A solution of 4-bromophenyl-iso-butyl ether (40.0 g, 0.175 mol) in diethyl ether was added dropwise to a solution of *n*-butyllithium (0.183 mol) in dry diethyl ether (200 ml) and dry tetrahydrofuran (THF) (20 ml) at -70°C . The temperature did not exceed -65°C . After completion of the addition the mixture was stirred for one hour at -70°C . The mixture was carefully poured on 140 g of dry ice in diethyl ether (100 ml). After completion of this step, 200 ml of water was added. The mixture was acidified to $\text{pH} = 6$ with 3 M aq. HCl. The aqueous phase was extracted with ether (100 ml). The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. Recrystallization from hexane yielded with 4-iso-butoxybenzoic acid (15.03 g, 44.2%) as a white powder with the melting point of $139\text{--}141^\circ\text{C}$ (lit. 142°C [10]). $^1\text{H NMR}$ (400 MHz, acetone- d_6): 7.00 (d, 2H), 7.96 (d, 2H), 2.04 (m, CH), 3.84 (d, CH_2), 1.20 (d, CH_3). 2- And 3-iso-butoxybenzoic acid were synthesized in similar manner.

2-Isobutoxybenzoic acid. Colorless liquid. Crude product was distilled under reduced pressure at $160^\circ\text{C}/20\text{ Torr}$ (lit. $135\text{--}136^\circ\text{C}/1\text{ Torr}$ [11]). Yield 55%, $^1\text{H NMR}$ (400 MHz, CDCl_3): 7.01 (dd, 1H), 7.06 (ddd, 1H), 7.50 (ddd, 1H), 8.11 (ddd, 1H), 2.18 (m, CH), 3.98 (d, CH_2), 1.50 (d, CH_3).

3-Isobutoxybenzoic acid. Yield 28.3%, melting point: $79\text{--}80^\circ\text{C}$, $^1\text{H NMR}$ (400 MHz, CDCl_3): 7.11 (ddd, 1H), 7.37 (dd, 1H), 7.62 (dd, 1H), 7.70 (ddd, 1H), 2.11 (m, CH), 3.78 (d, CH_2), 1.04 (d, CH_3).

The products were re-crystallized or distilled under reduced pressure. No impurities (greater than 0.001 mass fractions) could be detected in samples used for the before the thermochemical measurements. The degree of purity was determined using the GC and the DSC methods. Provenance and purity of the compound prepared for thermochemical studies in this work are given in Table S1.

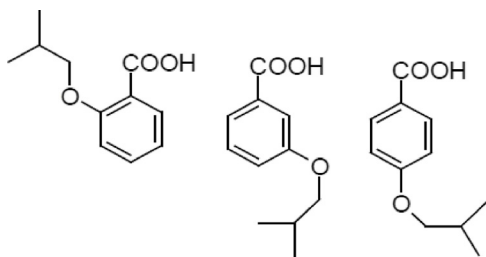


Fig. 1. Compounds studied in this work: 2-iso-butoxybenzoic acid, 3-iso-butoxybenzoic acid and 4-iso-butoxybenzoic acid.

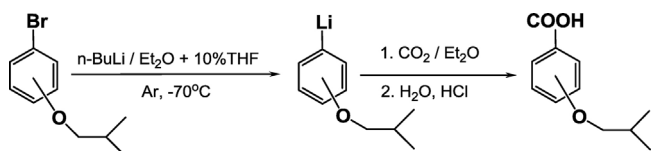


Fig. 2. General procedure for synthesis of iso-butoxybenzoic acids.

2.2. Combustion calorimetry

Standard molar enthalpies of combustion of iso-butoxybenzoic acids were measured with an isoperibolic calorimeter with a static bomb and a stirred water bath. The detailed procedure has been described previously [12]. The liquid sample of the *ortho*-isomer was placed (under an inert atmosphere in a glove-box) in a polythene ampoule (Fa. NeoLab, Heidelberg, Germany). The neck of the ampoule was compressed with a special tweezers and was sealed outside the glove-box by heating of the neck in a close proximity to a glowing wire. Then, the container was placed in the crucible and was burned in oxygen at a pressure 3.04 MPa. The solid samples were pressed into pellets of mass $\approx 700\text{ mg}$, and were burned in oxygen with a mass of 1.00 g of water added to the bomb. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither was detected. The energy equivalent of the calorimeter $\varepsilon_{\text{calor}} = 14816.0 \pm 0.7\text{ J K}^{-1}$ was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). For the reduction of the data to standard conditions, conventional procedures [13] were used. Auxiliary data are collected in Table S2. Correction for nitric acid formation was based on titration with 0.1 mol dm^{-3} NaOH (aq). The residual water content 261.3 ppm in the liquid sample was determined by Karl Fischer titration before starting experiments and appropriate corrections have been made for combustion results. No discernable amount of moisture was detected in the solid samples. Primary results from combustion experiments are summarized in Tables S3–S5.

2.3. Transpiration method. Vapor pressure measurements

Vapor pressures of iso-butoxybenzoic acids were measured using the transpiration method [14,15]. About 0.5 g of a solid sample was dissolved in acetonitrile and mixed with small glass beads in a glass beaker. Under vigorous stirring with spatula and gentle heating the solvent was removed from beaker producing glass beads covered uniformly with the sample. These covered glass beads were placed in a thermostatted U-shaped saturator. A well-defined nitrogen stream was passed through the saturator at a constant temperature ($\pm 0.1\text{ K}$), and the transported material was collected in a cold trap. The amount of condensed sample was determined by weighing with microbalances of 0.0001 g resolution. Material collected in the cold trap was systematically analyzed by the GC, but decomposition products were not detected.

The absolute vapor pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period. Assuming validity of the Dalton's law applied to the nitrogen stream saturated with the substance i , values of p_i were calculated with Eq. (1):

$$p_i = \frac{m_i \times R \times T_a}{V \times M_i}; \quad V = V_{\text{N}_2} + V_i; \quad (V_{\text{N}_2} \gg V_i) \quad (1)$$

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