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Benzoic acid derivatives: Evaluation of thermochemical properties with complementary experimental and computational methods

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ABSTRACT

Molar sublimation enthalpies of the methyl- and methoxybenzoic acids were derived from the transpiration method, static method, and TGA. Thermochemical data available in the literature were collected, evaluated, and combined with own experimental results. This collection together with the new experimental results reported here has helped to resolve contradictions in the available enthalpy data and to recommend sets of sublimation and formation enthalpies for the benzoic acid derivatives. Gas-phase enthalpies of formation calculated with the G4 quantum-chemical method were in agreement with the experiment. Pairwise interactions of the methyl, methoxy, and carboxyl substituents on the benzene ring were derived and used for the development of simple group-additivity procedures for estimation of the vaporization enthalpies, gas-phase, and liquid-phase enthalpies of formation of substituted benzenes.

1. Introduction

Benzoic acid is well-established reference compound for calibration and testing of thermochemical methods such as combustion calorimetry [1] and equipment for vapor pressure measurements [2–6]. Main requirements for the reference materials are stability, easy way for purification and purity attestation, non-hygroscopicity and possibly low cost. The methyl and methoxy substituted benzoic acids are good candidates to fulfill these requirements and to be used as the reference materials, provided that their thermochemical properties (enthalpy of sublimation, enthalpy of fusion and enthalpy of formation) are of benchmark quality. However, sublimation and vaporization enthalpies of the methyl- and methoxybenzoic acids available in the literature are still in disarray. Evaluation of these data with help of additional measurements using different techniques are desired. In the focus of current study are vapor pressure measurements on benzoic acid derivatives presented in Fig. 1.

From our experience, reliable evaluation of experimental data can be performed, when vapor pressures are independently measured by using at least two different techniques on the same highly pure sample. Mutually consistent sublimation enthalpies obtained from different methods in the same lab but in different temperature ranges can be used as a basis for analysis and evaluation of the available literature data. Joint treatment of the consistent own and literature results for each compound under study helps to avoid a possible systematic error and the evaluated data sets can be recommended for use in further thermochemical calculations.

This contribution complements our previous work on thermochemistry of substituted benzenes [7–8]. The experimental and computational study of the methyl- and methoxy substituted benzoic acids presented in Fig. 1 have been completed, aiming at evaluation of the benchmark quality thermochemical data sets which can be able to afford requirements of reference materials.

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