

BENCHMARK THERMOCHEMICAL PROPERTIES OF PHTHALIC ACIDS AND PHTHALIC ANHYDRIDE

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This work continues the systematic studies of benzoic acid derivatives. The investigation of phthalic acids and anhydrides has been a popular endeavor for a long time. However, the data for thermochemical properties have been in disagreement until now. Thermal degradation of the acids and hydration of the anhydride make the correct measurement of the enthalpies of formation and the phase transition challenging. We have determined and validated the enthalpies of formation in the crystalline and gaseous state as well as the phase transition behavior of the phthalic acid isomers and phthalic anhydride.

The standard molar enthalpies of formation in the crystalline state were obtained by combustion calorimetry. DSC measurements were performed for the determination of the enthalpies of fusion. The vapor pressures in dependence of the temperatures were obtained from the transpiration and the Knudsen method. From these, the standard molar enthalpies of sublimation were derived. With the experimentally ascertained enthalpies of formation and sublimation, the standard molar enthalpies of formation in the gaseous state were determined. Thermochemical data of the studied compounds from the literature were collected and combined with the results from this work. We have evaluated a set of fusion, vaporization, sublimation and formation enthalpies for the phthalic acids and phthalic anhydride at 298.15 K.

For validation of the experimental data, high-level G3MP2 and G4 quantum-chemical calculations were performed. The enthalpies of formation in the gaseous state were obtained from the atomization procedure and from the construction of well-balanced reactions. The results were in good agreement with the experimental data. Therefore, the evaluated data from this work are recommended as benchmark thermochemical properties of the isomeric phthalic acids and phthalic anhydride.