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Adamantanes: Benchmarking of thermochemical properties

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ABSTRACT

Standard molar enthalpies of formation of 2-adamantanone and 1-adamantanol were measured by using high-precision combustion calorimetry. Vapour pressures of 2-adamantanone, 1-acetyl-adamantane, 1- and 2-carboxy-adamantanes were measured by using the transpiration method. Standard molar enthalpies of sublimation of this substituted adamantanes at 298.15 K were derived from vapour pressure temperature dependences. The standard molar enthalpy of solution of 1-acetyl-adamantane in cyclohexane was measured with the high-precision solution calorimetry. An empirical procedure based on the solution calorimetry was developed to derive sublimation enthalpies of substituted adamantanes independently. Molar enthalpies of fusion of 1-acetyl-adamantane, 1- and 2-carboxy-adamantanes were measured with help of DSC. Thermochemical data on oxygen containing adamantane derivatives were collected and evaluated. Gas-phase enthalpies of formation calculated with the high-level quantum-chemical method G3MP2 and compared with the experimental results. The consistent data set of the benchmark quality is suggested for practical thermochemical calculations.

1. Introduction

Enthalpies of formation of molecules are most frequently used for a quick assessment of energetic balance of practically relevant chemical reactions. This century quantum chemical (QC) methods for calculation of the gas-phase enthalpies of formation have reached a precision and accuracy that (for small- to mid-sized molecules) matches that of experimental techniques [1,2]. However, for large-sized molecules the accuracy of the experimental data (derived with help of combustion calorimetry) becomes less accurate solely due to the fact that the final uncertainty includes not only uncertainty of the very precisely measured combustion energy (as a rule they are better than 0.01% of combustion energy), but they also take into account uncertainties of the large number of CO_2 and H_2O molecules involved in the combustion reaction as the final products. According to the most comprehensive compendium by Pedley [3] the experimental data for the large organic molecules (containing about 10–15 carbon atoms) the reliable and accurate enthalpies of formation in the condensed state exhibit uncertainties at the level 3–6 $kJ \cdot mol^{-1}$. From our experience with the high-level quantum-chemical methods (e.g. G*-family), calculations of large molecules of that size are very time-consuming task even for a powerful cluster of computers. Moreover, the computed at the high level of theory gas-phase enthalpies of formation require validation with the reliable experimental data of a benchmark quality. Only comparison with the high-quality experimental data helps to reveal deficiencies and improve QC methods. The adamantane and its derivatives are remarkable class of organic cage compounds. They are large but it was possible to complete the QC calculations of a large number of compounds within a reasonable time. These molecules are strained [4] and could be challenging for the high-level computational methods.

In the frame of the current study, we collected from the literature available information for thermochemical studies on the oxygen containing adamantane derivatives: 2-adamantanone, 1-adamantanol, 2-adamantanol, 1-acetyl-adamantane, 1-carboxy-adamantane, 2-carboxy-adamantane, and 1-carbomethoxy adamantane (see Fig. 1). In order to check and support available numerical values we have performed additional thermochemical measurements by using combustion, solution, and differential scanning calorimetry, as well as with the transpiration method. We evaluated the experimental results collected, and the consistent reliable set of gas-phase enthalpies of formation was used for mutual validation of the experimental and theoretical (calculated with the G3MP2 method) results.

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