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Thermochemistry of uracil and thymine revisited

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ABSTRACT

Thermochemical properties of uracil and thymine have been evaluated using additional experiments. Standard ($p^0 = 0.1$ MPa) molar enthalpies of formation in the gas phase at $T = 298.15$ K for uracil $-(298.1 \pm 0.6)$ and for thymine $-(337.6 \pm 0.9)$ $\mathrm{kJ \cdot mol^{-1}}$ have been derived from energies of combustion measured by static bomb combustion calorimetry and molar enthalpies of sublimation determined using the transpiration method. The G3 and G4 quantum-chemical methods were used for calculations of theoretical gaseous enthalpies of formation being in very good agreement with the re-measured experimental values.

1. Introduction

Uracil and its derivative thymine (5-methyluracil) are common and naturally occurring pyrimidine derivatives. They are well known for their importance in biochemistry, molecular biology and medicine. They are two of the primary nucleobases. Uracil or pyrimidine-2,4(1*H*,3*H*)-dione (see Fig. 1a) is one of the four nucleobases in the nucleic acid of the RNA. In the DNA, the uracil is replaced by the thymine or 5-methylpyrimidine-2,4(1*H*,3*H*)-dione, (see Fig. 1b). Recently, we published [1] an experimental and computational study on the thermochemistry of three derivatives of the uracil: 5,6-dimethyluracil, 1,3,5-trimethyluracil, and 1,3,5,6-tetramethyluracil. Good agreement between experimental and theoretical (with the composite G3 and G4 methods) gas phase enthalpies of formation was achieved [1]. Surprisingly, for thymine a significant disagreement between the experimental and theoretical values was observed. The experimental enthalpy of formation reported by Sabbah et al. [2] deviates by 9 $\mathrm{kJ \cdot mol^{-1}}$ and the more recent value reported by Ribeiro da Silva et al. [3] deviates by 17 $\mathrm{kJ \cdot mol^{-1}}$ in comparison with the G4 result. This discrepancy has motivated a re-determination of the enthalpies of formation and sublimation for thymine in order to ascertain thermochemical information for this compound. In order to reveal possible experimental shortages, some additional experiments on similarly shaped uracil have been also performed.

2. Materials and methods

2.1. Materials and purity control

All samples used for this work were of commercial origin (see table 1). Prior to experiments the samples were purified twice by re-crystallisation from water and further purified by the repeated vacuum fractional sublimation. No impurities (greater than mass fraction 0.001) could be detected by DSC [4] in the samples used for the thermochemical measurements. DSC curves are given on figures S1 an S2 in the Supporting Information. Samples were additionally analysed with a Hewlett Packard gas chromatograph 5890 Series II equipped with a flame ionisation detector using carrier gas (nitrogen) flow of 12.1 $\mathrm{cm^3 \cdot s^{-1}}$ and a capillary column HP-1 (methyl silicone gum), column length, inside diameter, and film thickness 10 m · 0.53 mm · 2.65 μm. The temperature program of the GC started at $T = 373$ K, followed by a heating rate of 0.42 $\mathrm{K \cdot s^{-1}}$ to $T = 473$ K. No impurities (greater than mass fraction 0.001) could be detected by GC.

2.2. Combustion calorimetry

An isoperibol bomb calorimeter was used for the measurement of energies of combustion of the nucleobases. The detailed

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