



Thermochemistry of uracil and thymine revisited



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ARTICLE INFO

Article history:

Received 15 December 2014

Received in revised form 13 March 2015

Accepted 17 March 2015

Available online 24 March 2015

Keywords:

Uracil

Thymine

Thermochemistry

Enthalpy of formation

Enthalpy of sublimation

Vapour pressure

Quantum chemical calculation

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 $-(337.6 \pm 0.9)$ $\text{kJ} \cdot \text{mol}^{-1}$ 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.

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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 $9 \text{ kJ} \cdot \text{mol}^{-1}$ and the more recent value reported by Ribeiro da Silva et al. [3] deviates by $17 \text{ kJ} \cdot \text{mol}^{-1}$ 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 and 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 $12.1 \text{ cm}^3 \cdot \text{s}^{-1}$ and a capillary column HP-1 (methyl silicone gum), column length, inside diameter, and film thickness $10 \text{ m} \cdot 0.53 \text{ mm} \cdot 2.65 \mu\text{m}$. The temperature program of the GC started at $T = 373$ K, followed by a heating rate of $0.42 \text{ K} \cdot \text{s}^{-1}$ 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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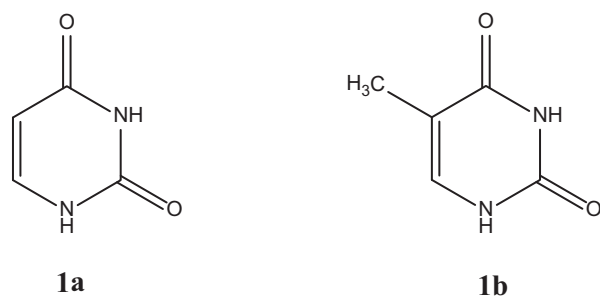


FIGURE 1. Molecules studied in this work: uracil (1a) and thymine (1b).

procedure has been described previously [5]. The solid sample was pressed into pellet and weighed with a microbalance with 10^{-6} g resolution. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The energy equivalent of the calorimeter v_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39j, N.I.S.T. with $\Delta_c u^\circ = 26434 \pm 1.5 \text{ J} \cdot \text{g}^{-1}$ according to the certificate). Correction for nitric acid formation was based on the titration with $0.1 \text{ mol} \cdot \text{dm}^{-3}$ NaOH (aq.). The relative atomic masses used for the elements C = 12.010600, H = 1.007975, O = 15.999400 and N = 14.006855 were calculated as the mean of the bounds of the interval of the standard atomic weights recommended by the IUPAC commission in 2011 [6] for each of these elements. The sample masses were reduced to vacuum, taking into consideration their density values (Table 2). For converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states, the conventional procedure was applied [7]. We used small polythene pieces as an auxiliary material (see table 2) in order to reach completeness of combustion. Results from combustion experiments are given in tables 3 and 4.

2.3. Vapour pressure measurements

Vapour pressures and enthalpies of sublimation, $\Delta_{\text{cr}}^{\text{g}} H_m$, of nucleobases were determined using the transpiration method [11,12]. Enthalpies of sublimation were derived from vapour pressure temperature dependences. A sample of approximately 0.5 g was mixed with glass beads and placed in a U-shaped tube of length 10 cm and diameter 0.5 cm. Preheated nitrogen stream was passed through the U-tube at constant temperature (± 0.1 K) maintained by an air bath. The flow rate of the nitrogen stream was measured using a soap film bubble flow metre (± 0.2 – 0.3 %) and optimised in order to reach the saturation equilibrium of the transporting gas at each temperature under study. In our setup the upper limit of the flow rate was about $11 \text{ dm}^3 \cdot \text{h}^{-1}$. Thus, we carried out the experiments in the using flow rates ranging from (4 to 9) $\text{dm}^3 \cdot \text{h}^{-1}$ which ensured that the transporting gas was in saturated equilibrium with the coexisting solid phase in the saturator. The transported material was condensed in a cold trap at room temperature. The amount of condensed product was determined by weighing (± 0.0001 g) of the trap.

The saturated vapour pressure p_i at each temperature T_i was calculated from the amount of product collected within a definite period of time. Assuming that Dalton's law of partial pressures

TABLE 2

Formula, density ρ ($T = 293$ K), massic heat capacity c_p ($T = 298.15$ K), and expansion coefficients $(\delta V/\delta T)_p$ of the materials used in the present study.

Compounds	Formula	ρ $\text{g} \cdot \text{cm}^{-3}$	c_p $\text{J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$	$10^{-6} \cdot (\delta V/\delta T)_i$ $\text{dm}^3 \cdot \text{K}^{-1}$
Uracil	$\text{C}_4\text{H}_4\text{N}_2\text{O}_2$	1.62 ^a	1.18 ^c	0.1
Thymine	$\text{C}_5\text{H}_6\text{O}_2\text{N}_2$	1.45 ^b	1.29 ^c	0.1
Polyethylene ^d	$\text{CH}_{1.93}$	0.92	2.53	0.1
Cotton ^e	$\text{CH}_{1.774}\text{O}_{0.887}$	1.50	1.67	0.1

^a Taken from Ref. [8].

^b Taken from Ref. [9].

^c Taken from Ref. [10].

^d Energy of combustion $\Delta_c u^\circ$ (polyethylene) = $-46357.3 \text{ J} \cdot \text{g}^{-1}$; $u(\Delta_c u^\circ) = 3.6 \text{ J} \cdot \text{g}^{-1}$.

^e Energy of combustion $\Delta_c u^\circ$ (cotton) = $-16945.2 \text{ J} \cdot \text{g}^{-1}$; $u(\Delta_c u^\circ) = 4.2 \text{ J} \cdot \text{g}^{-1}$.

when applied to the nitrogen stream saturated with the substance i of interest is valid, values of absolute vapour pressures p_i were calculated as follows:

$$P_i = m_i \cdot R \cdot T_a / V \cdot M_i; \quad V = V_{\text{N}_2} + V_i; \quad (V_{\text{N}_2} \gg V_i), \quad (1)$$

where $R = 8.31446 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase; V_{N_2} is the volume of transporting gas and T_a is the temperature of the soap film bubble flow metre. The volume of transporting gas V_{N_2} was determined from the flow rate and time measurements. The standard uncertainties (u) of the measured vapour pressures have been calculated to be $u(p/\text{Pa}) = (0.005 + 0.025)$ for $p < 5$ Pa and $u(p/\text{Pa}) = (0.025 + 0.025)$ for $p > 5$ (to 3000) Pa. For validation of our uncertainty estimations, we measured vapour pressures for series of aliphatic alcohols [11] and esters [12] where reliable data from different methods were available. It has turned out that vapour pressures of esters derived from the transpiration method were comparable with available high-precision data generally within (1 to 3)% in agreement with our estimations. Experimental results on vapour pressures from the transpiration method are listed in table 5.

Vapour pressures p_i measured at different temperatures were fitted using the equation [11,12]:

$$R \cdot \ln p_i = a + \frac{b}{T} + \Delta_{\text{cr}}^{\text{g}} C_p \cdot \ln \left(\frac{T}{T_0} \right), \quad (2)$$

where a and b are adjustable parameters and $\Delta_{\text{cr}}^{\text{g}} C_{p,m}$ is the difference of the molar heat capacities of the gaseous and the crystalline phases, respectively. The T_0 appearing in Eq. (2) is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from Eq. (2) the expression for the sublimation enthalpy at temperature $T = 298.15$ K was derived:

$$\Delta_{\text{cr}}^{\text{g}} H_m(T) = -b + \Delta_{\text{cr}}^{\text{g}} C_p \cdot T. \quad (3)$$

Values of $\Delta_{\text{cr}}^{\text{g}} C_{p,m} = 20.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for uracil and $\Delta_{\text{cr}}^{\text{g}} C_{p,m} = 25.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for thymine have been calculated according to the empirical procedure suggested by Chickos et al. [13] based on the experimental constant pressure heat capacities $C_{p,m}(\text{cr})$ at 298.15 K. We used $C_{p,m}(\text{cr}) = 131.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [10] for uracil and $C_{p,m}(\text{cr}) = 163.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [10] for thymine. Experimental enthalpies of sublimation of uracil and thymine are given in tables 5 and 6.

2.4. Computational details

Energies of compounds under study were calculated using the G3 [14] and the G4 [15] methods from Gaussian-n series. Details on these methods have been given in our previous paper [16]. G3- and G4-calculated enthalpies of formation for uracil and thymine have been taken from our previous publication on uracil derivatives [1].

TABLE 1
Provenance and purity of the materials.

Material	CAS	Origin	Final purity (mass fraction)
Uracil	66-22-8	Aldrich, >99%	0.999
Thymine	65-71-4	Aldrich, >99%	0.999

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