



Research paper

Determination of molar enthalpy of sublimation in case of orotic acid as obtained from experimental and computational data

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ABSTRACT

Saturated vapor pressure, $\ln(p/Pa) = (-21316 \pm 511)/(T/K) + (41.64 \pm 0.11)$, and enthalpy of sublimation of orotic acid, $\Delta_{\text{sub}}H_m^0(T_m) = 177 \pm 4$ kJ/mol, were determined by means of Knudsen effusion mass spectrometry in the temperature range of 423–493 K. The computational approaches supported the experimental results reported. The theoretical estimation of the gas-phase enthalpy of formation for orotic acid was done with different working reactions used.

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1. Introduction

Orotic acid is 6-carboxyuracil, which is also called vitamin B13. It can be characterized by a wide range of biological and pharmacological activities, but mostly as a precursor in biosynthesis of pyrimidine nucleotides [1,2]. The orotic acid samples can be used in clinical chemistry to diagnose some inherited diseases associated with urea cycle disorder [3]. It is widely applicable as medicine serving for the prevention and the treatment of heart and vascular diseases [4]. Orotic acid is a dietary constituent; its salts can be employed for nutritional purposes in food supplements as source of both orotic acid and various minerals [5].

For a theoretical analysis of the stability of substances in the solid state, the important parameter is the energy of the crystal lattice, which is related to the enthalpy of sublimation [6]. The thermochemical characteristics of vapor formation of orotic acid in combination with structural characteristics make it possible to identify and characterize various types of intra- and intermolecular interactions. For uracil derivatives, related compounds of orotic acid, the different sublimation behavior has been studied. As shown, it occurs due to the presence of hydrogen bonds in their solid state. The unsubstituted uracil can easily form a intermolecular hydrogen bonds towards three dimensions with increasing complexity associated with the availability of the N–H groups [7], meanwhile the 1,3-dimethyluracil is not able to form conventional hydrogen bonds [8].

The thermochemical characteristic of orotic acid, such as experimental values of enthalpies of sublimation and formation, are still unknown. In this letter, we report the thermochemical study of orotic acid using the Knudsen effusion technique. The aim of the paper is to obtain enthalpy of sublimation for orotic acid applying experimental and theoretical approaches.

2. Experimental details

Present study deals with high temperature mass spectrometry, namely Knudsen effusion method with mass-spectrometric analysis of evaporated species (KEMS) [9]. Orotic acid sample was obtained commercially from Aldrich Chemical Co. [CAS Registry No. 65-86-1] and used without further purification. It was loaded into effusion cell in an argon atmosphere. Then, the effusion cell was installed and heated up in an evaporator of mass-spectrometer. Temperature was controlled by a controller TERMODAT-128K5 and measured by a Pt–Pt/Rh (10%) thermocouple. Deviations of actual temperature from the adjusted did not exceed ± 1 K. Molecules of orotic acid were entering in ionization region, where they were ionized by an electron bombardment ($E_{\text{ion}} = 70$ eV, $E_{\text{acc}} = 3$ keV). Formed positive ions were analyzed in magnetic mass-analyzer MI-1201 (90°, $r = 200$ mm, resolution 500) according to the mass to charge ratio m/z . Currents of ions with the specified m/z values were detected by a Faraday cup, and their intensities were measured by an electrometer ($R = 1 \times 10^{12} \Omega$).

The part of the signal of ion current originated by ionization of a molecular beam leaving the effusion cell was separated from the background by a shutter situated between the effusion cell and

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the ionization chamber. The ion currents measured are correlated with orotic acid pressure by an equation:

$$p = (k/\sigma)(I \cdot T)$$

where k is the constant of the instrument sensitivity, the ionization cross section σ is calculated by summing the ionization cross section from each atom in the molecule, I is the measured ion currents for each species, T is temperature of the Knudsen cell.

The stainless steel effusion cell (orifice diameter 0.35 mm, channel length 0.15 mm) with the sample of orotic acid (typical mass of the loaded sample was 20 mg) was placed in the evaporator of ion source. The cell was heated in a vacuum ($p = 10^{-4}$ Pa) in temperature range of 373–423. At this stage, the degassing of sample occurred in ion source region, that was believed to be complete at decreasing the $I(\text{H}_2\text{O}^+)$ signal value up to background level of device. After the preliminary stage, the temperature was increased and at $T \geq 423$ K the ion currents with mass numbers $m/z = 68$ and 156 (the most intense ions according to electron ionization mass spectrum of orotic acid [10]) were fixed by a moveable shutter. Just two most intense signals were considered as ions formed by ionization of orotic acid. The ion of $m/z = 156$ corresponds to the molecular ion of orotic acid formed at first step of ionization process. We assume that a reasonable mechanism for formation of the ion of $m/z 113$ involves the loss of NHCO group from molecular ion of $m/z 156$. The most intense ion of $m/z 68$ is formed by decarboxylation of the ion of $m/z 113$. Key fragmentation pathway for orotic acid was made and presented in Fig. 1.

The ratio $I(m/z = 68)/I(m/z = 156)$ agreed well with mass spectrum of orotic acid. In the range of 423–493 K the temperature increase was carried out stepwise with an interval of 10 K, at each temperature the signal was measured three times. The lower temperature of the experiments was restricted because of measurement limit, plus for upper temperatures (beyond 493 K) a further temperature increase led to the unstable signals of ion currents in the mass spectrum of studied substance. Thus, the signals in the narrow temperature range of 423–493 K were considered as a reliable experimental data.

The absolute saturated vapor pressures p^0 was determined by isothermal evaporation within a prolonged period of time (t) with control of ion current signal stability. The vapor pressure was calculated according to the Knudsen-Hertz equation:

$$p^0 = \frac{m}{sLt} \sqrt{\frac{2\pi RT}{M}}, \quad (1)$$

where m is the mass of the evaporated fraction of substance of molar mass M , s is the area of the effusion orifice (its diameter is 0.4 mm; wall thickness is 0.15 mm), and the Clausing factor L

received as 0.73 in present study. The mass loss of substance in the cell was measured using a GR-200 electronic balance with an accuracy of 0.1 mg.

It might be mentioned that experimental procedure using the apparatus of our group has been tested on cerium tetrafluoride [11], ionic liquids [12] and found to be reliable for determining sublimation and vaporization enthalpies. The sublimation enthalpy for cerium tetrafluoride was confirmed to be well estimated [13] regardless of whether second or third law of thermodynamics was applied.

3. Computational details

Quantum chemical calculations were based on the B3LYP hybrid potential of the density functional theory (DFT) with the 6-31G(d,p) basis set. For the prediction of enthalpy of formation, the G4 theory [14] was used from Gaussian program package [15].

The electrostatic potential surface was generated with Multiwfn program [16] from 0.001 a.u. contour molecular surface of the electron density by marching tetrahedra algorithm.

To obtain enthalpy of formation values, the geometries of the molecules involving in theoretical working reaction were calculated for the predominant conformation of all compounds. The resulting $\Delta_f H_{298}^0(g)$ value was calculated as mean from theoretical reactions.

4. Results and discussion

Thermodynamic study of sublimation of orotic acid was carried out by the Knudsen effusion method with mass-spectrometric control of the vapor composition within the framework of the second law of thermodynamics in the temperature range of 423–493 K. Determination the enthalpy of sublimation of orotic acid was performed on the basis of the Clausius-Clapeyron equation:

$$\frac{\partial \ln P}{\partial T} = -\frac{\Delta H_{sub}(T)}{RT},$$

where a vapor pressure $P = p_i/p^0$ with p_i standing for the partial vapor pressure and $p^0 = 0.1$ MPa, T for a temperature, R for the gas constant (8.3144 J/(K · mol)). The temperature dependences of ion currents were approximated by a linear equation in the integral form:

$$\ln(I_j T) = -\frac{B}{T} + C,$$

where $B = \Delta_{sub} H_m(T)/R$.

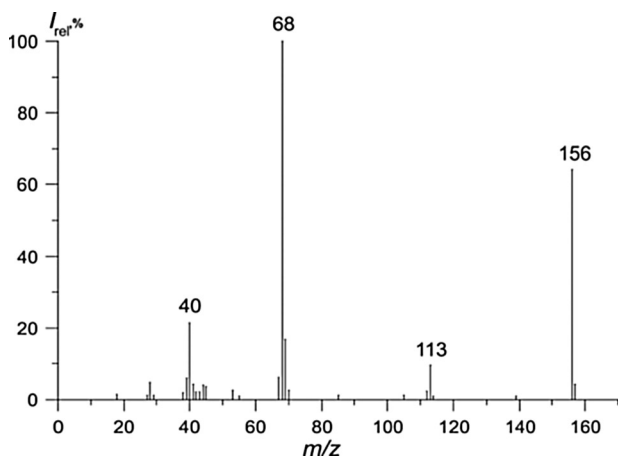
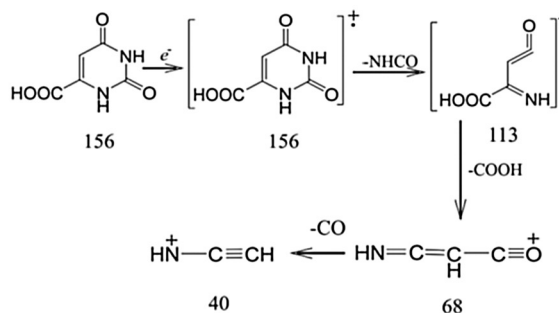


Fig. 1. Mass spectrum of orotic acid (at 75 eV, 463 K) with fragmentation pattern.



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