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## ТЕРМОДИНАМІЧНІ ХАРАКТЕРИСТИКИ ОКСИМУ ФУРФУРОЛУ

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Ефузійним методом Кнудсена визначена температурна залежність тиску насиченої пари оксиму фурфуролу, за якою розрахована ентальпія сублімації. Енергія згорання речовини визначена в калориметрі з ізотермічною оболонкою та статичною калориметричною бомбою. Одержані дані дозволили розрахувати ентальпії утворення оксиму фурфуролу в твердому і газоподібному станах. Розрахована ентальпія згорання оксиму фурфуролу допомогою програми Gaussian-09. Ентальпія утворення сполуки в газоподібному стані розраховувалась за адитивною схемою Бенсона. Знайдений невідомий інкремент необхідний для розрахунку.

**Ключові слова:** енергія згорання; ентальпія згорання; ентальпія утворення; ентальпія сублімації; оксим фурфуролу.

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## THERMODYNAMIC PROPERTIES OF FURFURAL OXIME

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The sublimation enthalpy was calculated from the temperature dependence of vapor pressure determined by Knudsen effusion method. Energy of combustion was determined in precise calorimeter with an isothermal static shell and bomb. The obtained data allowed to calculate the formation enthalpy of oxide furfural in solid and gaseous states. The combustion enthalpy of furfural oxime was calculated using Gaussian-09 program. The formation enthalpy of the compound in the gaseous state was calculated by Benson additive scheme. The unknown increment required for calculation was determined.

**Key words:** combustion energy; combustion enthalpy; formation enthalpy; sublimation enthalpy, furfural oxime.

**Problem setting and analysis of publications.** Furfural oxime (FO) is a heterocyclic compound that exhibits biological activity, and therefore is used in pharmacy as starting material for the synthesis of biologically active compounds with a wide range of medicinal properties [1]. Defined entalpic properties fill the databases of thermodynamic variables and allow calculating the energy balance of the processes of its synthesis, purification and subsequent use.

**The purpose of the work.** To determine the entalpic properties of furfural oxime in the condensed and gaseous states using experimental and calculation methods.

**Experimental.** The paper presents the results of experimental determination of the standard combustion, formation and sublimation enthalpies of crystalline FO.

To a solution 34,8h (0.4 mol) of freshly-distilled furfural and 34.8 g (0.5 mol) of hydroxylamine hydrochloride in 60 ml of water a solution of 26.5 g (0.25 mol) of potassium carbonate in 100 ml of water was added during 2 hours with constant mixing. The resulting mixture was heated for 5 hours. After cooling, FO was extracted using ether (3 portions of 100 ml). The combined extracts were washed with a little portion of water and dried above anhydrous sodium sulfate. The residue was fractionally distilled in a vacuum, taking a fraction with the boiling temperature of 96-97°C/5 mmHg with its subsequent crystallization. Reaction yield was 41-42 g (93-94 %).

The structure of the substance was confirmed by the results of the gaseous analysis during the calorimetric studies and NMR spectroscopy. <sup>1</sup>H NMR spectra were recorded on a Varian 600 instrument (600 MHz) solvent DMSO – d<sub>6</sub>. Chemical shifts (δ ppm) are stated, relative to the DMSO signal (2.5 ppm): <sup>1</sup>H NMR (600 MHz, DMSO) δ 6.64 (d, *J* = 3.3 Hz, 1H, fur), 7.21 (d, *J* = 3.5 Hz, 1H, fur), 7.54 (t, *J* = 3,8 Hz, 1H, fur), 7.77 (s, 1H, CH), 11.81 (s, 1H, OH).

The samples of FO received after various crystallization quantities, namely, samples number 1 and 2 selected after 3 and 4 recrystallizations respectively were used for thermo chemical studies. Also, the purity degree of the substance was confirmed by the constancy of vapor pressure, sublimation and combustion enthalpies of the samples taken at different stages of purification.

*Effusional research.* Enthalpy of sublimation of the substance was determined by a combined effusional Knudsen method. Features of the integrated effusional setting are similar to those described in [3]. The design of the camera and membranes was taken from [4]. Methodology of experiments was selected according to recommendations [3].

Vacuum system of the installation created dilution of 0.1 Pa during 45±15 s. Mass of the effused substance during the experiment ( $\Delta m_{ef}$ ) was determined by the weight difference between the camera masses before and after the experiment using weight VLR-20 with an accuracy of  $\pm 5 \cdot 10^{-6}$ g. Accuracies of the sample temperature (T) maintaining and effusion duration ( $\tau$ ) were  $\pm 0.1$  K and  $\pm 10$  s, respectively.

Reliability of the installation was determined in a series of experiments determining the temperature dependence of the vapor pressure for reference benzoic acid K-1 in the temperature range of 322.7-354.1 K using three membranes with the following hole diameters: 0.450 mm (the membrane A); 0.475 mm – B; 0.375 mm – C; thickness of these membranes is 0,059mm. Volatile impurities that might distort the results were removed in the initial stage of the experiment (formation of the sample surface). This step was considered completed when the effusion speed reproduced within  $\pm 1$  % at a fixed temperature. The results of experimental temperature dependence of the vapor pressure determination for benzoic acid using three membranes were processed by least squares method and approximated as a linear equation:  $\ln P$  (Pa) =  $(33.13 \pm 0.92) - (10535 \pm 89) \cdot 1/T$ ; with the correlation coefficient  $R=0,998$ . The calculated value of the sublimation enthalpy for benzoic acid was  $87.6 \pm 0.7$  kJ/mol with an average temperature  $T_m = 338.4$  K. This value is consistent with the value obtained by Torez-Gomez using calorimetric method at  $T = 335.0$  K ( $\Delta_{sub}H = 87.5 \pm 0.3$  kJ/mol) [5]. Hereinafter, the standard deviations of the mean values were calculated using Student's criterion for significance level of 5 %.

Measuring the vapor pressure for FO was similar to the experiments with benzoic acid. Results of effusion measurements, including vapor pressure of the substance in the solid state (*P*), linear equations of the temperature dependence of the vapor pressure in the coordinates of Clapeyron-Clausius equation, the value of the enthalpy of sublimation ( $\Delta_{sub}H$ ) temperature range of the research ( $T_m$ ) are presented in Table 1. The melting point was determined by capillary method ( $T_{fus} = 366.3 \pm 1.5$  K).

*Calorimetric studies.* Combustion energy of FO was determined by calorimeter V-08-MA with an isothermal shell ( $\pm 0.003$  K). The energy equivalent of calorimetric system ( $W = 15300 \pm 9$  J/V) was determined with an accuracy of  $\pm 0.06$  % by the combustion of reference benzoic acid K-1, combustion energy of which was  $\Delta U_C = -26434.4$  J/g, taking into account Jessup's factor.

The substance remained in solid aggregate state under normal conditions. Before the experiment, FO was grinded in chalcedony pounder, pressed into a tablet and placed in a platinum cup. Before the experiment tablet was soldered in terylen vial to prevent substance oxidation prior to the experiment.

Ignition of the samples during the experiment was initiated by capacitors discharge via nichrome wire that ignited a cotton thread. The initial pressure of oxygen previously cleared of flammable contaminants, carbon dioxide and water, was 32 kPa. The temperature of the beginning of the main period in all experiments was 298.15 K.

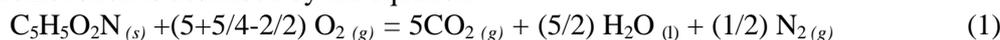
Table 1

**Furfural oxime effusional studies results**

Sample	$T$ , K	$\Delta m_{ef}$ , g	$\tau$ , s	$P$ , Pa	Sample	$T$ , K	$\Delta m_{ef}$ , g	$\tau$ , s	$P$ , Pa					
(A)														
1	316.1	0.0031	1844	7.630						2	318.8	0.0064	1831	16.94
	324.8	0.0132	1841	32.99							322.4	0.0098	1835	25.83
	329.3	0.0213	1852	53.28							331	0.0264	1839	70.34
	333.8	0.0364	1833	92.50	336	0.0438	1831	118.1						
(B)					(C)									
2	318.8	0.0067	1831	16.56	1	316.1	0.0072	1844	10.14					
	322.4	0.0106	1835	26.35		324.8	0.0268	1841	38.40					
	331.0	0.0265	1839	66.80		329.3	0.0393	1852	56.26					
	336.0	0.0455	1831	116.2		333.8	0.0649	1833	94.51					
1	316.1	0.0030	1844	7.920	2	318.8	0.0140	1831	19.88					
	324.8	0.0124	1841	32.83		322.4	0.0232	1835	33.10					
	329.3	0.0210	1852	55.42		331.0	0.0468	1839	67.65					
	333.8	0.0347	1833	93.15		336.0	0.0767	1831	112.2					
$\ln P(\text{Pa}) = (40.71 \pm 0.75) - (12080 \pm 246) \cdot 1/T$ ; $\Delta_{sub}H = 100.4 \pm 2.0$ kJ/mol (at $T_m = 327.4$ K)														

A quantitative analysis for combustion products like mono- and carbon dioxide, soot and nitric acid was performed after every experiment. Quantity of formed carbon dioxide was determined by Rossini's method [6] with an accuracy of  $\pm 1 \cdot 10^{-4}$  g. Reliability of gas analysis was confirmed in a series of experiments with burning of the reference benzoic acid. The content of carbon monoxide was controlled using indicator tubes with accuracy  $\pm 5 \cdot 10^{-6}$  g. Quantity of the soot formed on the platinum cup was determined by weighing with an accuracy of  $\pm 5 \cdot 10^{-6}$  g.  $\text{HNO}_3$  content was determined by titration with 0.1N KOH solution.

Reaction of FO combustion is described by the equation:



Combustion energy ( $U_{C(298.15)}$ ) in the experiment conditions was calculated as:

$$-U_{C(298.15)} = \frac{W \cdot \Delta T - q_{fuse} - q_{\text{HNO}_3} - q_{ter} + q_{carbon}}{m_{exp}}, \quad (2)$$

where  $m_{exp}$  – substance sample mass, burned during the experiment;  $W$  – energy equivalent of calorimetric system,  $\Delta T$  – true temperature rise;  $q_{fuse}$  – heat of cotton thread burning energy correction;  $q_{\text{HNO}_3}$  – heat of nitric acid solution formation energy correction;  $q_{carbon}$  – soot formation energy correction;  $q_{ter}$  – heat of terylen ampule burning energy correction.

Energies were calculated using heats of combustion (J/g) in bomb conditions: of cotton thread – 16704.2; soot – 32800, terylen – 22944.2; heat of  $\text{HNO}_3$  solution formation – 59000 J/mol [7]. Carbon dioxide quantity formed during burning of 1 g of cotton thread and terylen was equal 1.6284 g and 2.2862 g respectively.

Calorimetric determination of combustion energy for FO results and combustion completeness are listed in Table 2.

Standard combustion enthalpy  $\Delta_c H^0_{298.15}$  (kJ/mol) for FO was calculated using Uoshbern correction  $\pi$  [8, 9], and expansion work correction  $\Delta nRT$ .

Formation enthalpies (kJ/mol):  $\text{CO}_{2(g)} = 398.512 \pm 0.046$ ;  $\text{H}_2\text{O}_{(l)} = 285.829 \pm 0.040 \pm 1 \cdot 10^{-4}$ ;  $\text{N}_{2(g)} = 0$ ;  $\text{O}_{2(g)} = 0$  [10] were used for calculation of the standard formation enthalpy  $\Delta_f H^0_{298.15}$  of FO from the combustion reaction equation.

Table 2

**Results of calorimetric determination of combustion energy for FO**

Sample	$m_{exp}$ , g	$\Delta T$ , V	$q_{fuse}$ , J	$q_{HNO_3}$ , J	$q_{ter}$ , J	$q_{carbon}$ , J	$-U_{C(298,15)}$ , J/g	$m_{exp}/m_{calc}$ *
1	0.35916	0.28273	116.4	7.1	-	25.4	23314	1.0001
	0.18068	0.28099	110.0	8.9	-	22.5	23260	1.0000
	0.23347	0.41989	102.2	12.4	905.8	27.2	23263	0.9998
2	0.25708	0.46096	117.2	14.2	966.4	27.6	23271	1.0001
	0.31255	0.54645	97.4	23.6	994.7	32.6	23284	0.9999

\* $m_{exp}/m_{calc}$  – completeness of FO combustion during experiment.

Combustion energy and enthalpic characteristics for FO are listed in Table 3.

Table 3

**Energy characteristics of combustion and formation (kJ/mol)  
for FO in condensed and gaseous states**

$-U_{C(298,15)}$	$-\pi$	$-\Delta nRT$	$-\Delta_c H^0_{298,15K}$	$-\Delta_f H^0_{(298,15K), (s)}$	$\Delta_f H^0_{(298,15K), (g)}$
$2588.1 \pm 1,7$	1.9	0.6	$2587.5 \pm 6.5$	$94.6 \pm 1.7$	$6.6 \pm 2.7$

**Discussion.** Thermo chemical characteristics of furfural oxime were measured at different temperatures, due to the conditions of the experiments. The value of the specific heat of crystallization change under standard conditions is needed for converting enthalpy of sublimation at average temperature range to the one at 298K. Heat capacity crystallization change for furfural oxime was calculated using two independent methods.

According to the equation that we proposed in [11], the value of the sublimation enthalpy at 298 K is  $\Delta_{sub}H_{298} = 101.2 \pm 2.1$  kJ/mol. The sublimation enthalpy of FO calculated using group contribution method [12] is  $\Delta_{sub}H_{298} = 101.0 \pm 2.8$  kJ/mol. The calculated results are in good agreement with each other so the average value of the sublimation enthalpy determined by two methods can be used to calculate the formation enthalpy of FO in the gaseous phase,. The value of the formation enthalpy of FO in the gaseous state calculated using sublimation enthalpy at 298 K is shown in Table 3.

Considering the prospects of obtaining thermodynamic values using calculation methods we tried to use two approaches. The first is quantum-chemical – Gaussian-09 program. Calculation of the energies of reactants and products of the combustion of furfural oxime was conducted using the DFT-B3LYP method, with the basic settings 6-311G++ (3pd, 3df). The calculated value of the combustion enthalpy for FO was  $\Delta_c H^0_{298,15K} = -2513.2$  kJ/mol. Taking into account this value the formation enthalpies for FO in the solid phase ( $\Delta_f H^0_{298,15} = -168.94$  kJ/mol) and the gaseous phase ( $\Delta_f H^0_{298,15} = -67.74$  kJ/mol) were calculated. Due to large difference with experimental data, we turned to the more traditional method of determining the enthalpy formation of individual substances in a gaseous state – the group contributions Benson’s method [13]. Group contributions needed to calculate the formation enthalpy for furfural oxime in the gaseous phase are shown in Table 4.

Table 4

**Values (kJ/mol) of the group contributions in furfural oxime**

Fragment	Group contribution $I(\Delta_f H^0_g)$	Fragment	Group contribution $I(\Delta_f H^0_g)$
O-(C <sub>d</sub> ) <sub>2</sub>	-137.24 [13]	C <sub>d</sub> -(C <sub>d</sub> ) <sub>2</sub> (O)	43.40[12]
C <sub>d</sub> -(C <sub>d</sub> )(O)(H)	36.61 [13]	C <sub>d</sub> -(C <sub>d</sub> )(H)(NOH)	33.0
C <sub>d</sub> -(C <sub>d</sub> ) <sub>2</sub> (H)	28.37 [13]	Furan cycle correction	-25.94 [13]

The compound contains unknown group – C<sub>d</sub>-(C<sub>d</sub>)(H)(NOH), value of which (33.0 kJ/mol) was determined from the value of formation enthalpy in the gaseous phase for FO.

**Conclusions.** Enthalpic characteristics of furfural oxime were determined during the current research and the values of sublimation, combustion and formation enthalpies in the solid and gaseous states were calculated. These results extend a database of thermodynamic properties for polycyclic oxygen and nitrogen containing organic compounds and allow optimizing the processes of synthesis, purification and use of FO.

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