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ENTHALPY OF FORMATION AND COMBUSTION OF 5-(4-NITROPHENYL)FURAN-2-CARBALDEHYDE AND ITS 2-METHYL AND 2-OXOMETHYL DERIVATIVES IN THE CONDENSED STATE

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Using the precision bomb combustion calorimeter B-08-MA, the combustion energies of 5-(4-nitrophenyl)-furan-2-carbaldehyde, 5-(2-methyl-4-nitrophenyl)-furan-2-carbaldehyde and 5-(2-oxymethyl-4-nitrophenyl)-furan-2-carbaldehyde. Based on the obtained data, the values of enthalpies of combustion and formation of substances in the condensed state are calculated. A comparative analysis of experimentally determined values with theoretically calculated values by additive calculation methods is given.

Key words: 5-(4-nitrophenyl)-furan-2-carbaldehyde; 5-(2-methyl-4-nitrophenyl)-furan-2-carbaldehyde; 5-(2-oxymethyl-4-nitrophenyl)-furan-2-carbaldehyde; combustion energy; enthalpy of combustion; enthalpy of formation.

Introduction

Of particular note are heterocyclic compounds, the structure of which contains a furan fragment belonging to the class of five-membered oxygen-containing heterocycles, which are common in many bioactive compounds and natural products [1–4] and are extremely important intermediates in organic synthesis [5]. Functionalized furans attract the attention of researchers both from the standpoint of studying their valuable properties, and in terms of various modifications to the structure of these substances. In particular, compounds which, in addition to furan, also contain a phenyl moiety, so-called aryl or phenylfurans, are widely used as modifying agents in the synthesis of polymeric materials [6, 7], as catalysts [8, 9] in cellulose processing [10], as well as the synthesis of biologically active compounds, because they show a very wide range of biological activity [11] and less toxic than substances that contain only a functionalized fragment of furan [12]. Compounds with the arylfuran moiety began to be used as components of pharmaceuticals for the treatment of neurodegenerative diseases [13], genetic diseases [14], tobacco dependence to reduce nicotine requirements and eliminate withdrawal symptoms in smokers who chose not to smoke [15], HIV. 1 infection as a component of antiretroviral therapy [16], treatment of tuberculosis [17]. It should also be noted that polymeric materials containing arylfurane fragments also exhibit biological activity [18]. Thus, chitosan polymers modified with chlorine and nitro-containing arylfurans showed greater antimicrobial activity than unmodified chitosan [19, 20].

Despite the rather wide range of applications of this class of substances, their thermodynamic properties in the condensed state have not been studied. Enthalpies of combustion of matter ($\Delta_c H^0_{298}$) are thermodynamic characteristics of individual substances that inform about the energy of internal and intermolecular interactions in compounds. The enthalpy values($\Delta_f H^0_{298}$) calculated on their basis in the condensed state serve as key values in thermodynamic calculations of chemical processes that occur with the participation of these substances.

The presented work is a continuation of thermodynamic studies of arylfuran derivatives, the results of which were published in [21–23].

The goal of this work is determined by bomb calorimetry the combustion energies of 5-(4-nitrophenyl) -furan-2-carbaldehyde, 5-(2-methyl-4-nitrophenyl)-furan-2-carbaldehyde and 5-(2-oxymethyl-4-nitrophenyl)-furan-2-carbaldehyde were and calculate their enthalpies of combustion and formation in the condensed state.

Materials and methods of research

Syntheses of 5-(4-nitrophenyl)-furan-2-carbaldehyde (I), 5-(2-methyl-4-nitrophenyl)-furan-2-carbaldehyde (II) and 5-(2-oxymethyl-4-nitrophenyl)-furan-2-carbaldehyde (III) were carried out according to the scheme shown in Fig. 1, where (I) $R_1 = –H$, $R_2 =–NO_2$; (II) $R_1 = –CH_3$, $R_2 = –NO_2$; (III) $R_1 = –OCH_3$, $R_2 = –NO_2$.

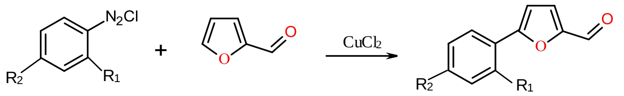

Fig. 1. The reaction scheme of the synthesis of test substances

0.2 mol of predistilled furfural produced by Sigma-Aldrich 99 %, CAS Number: 98-01-1, 2 g of copper (II) chloride and 80 ml of dimethyl ketone were added to the flask. A solution of arenediazonium chloride, obtained by diazotization of 0.21 mol of 4-nitroaniline (≥ 99.5 %, CAS Number: 100-01-6) during the synthesis of compound (I), is gradually added to the obtained solution with intensive stirring; 2-methyl-4-nitroaniline (97 % CAS Number: 99-52-5) – compounds (II); 2-methoxy-4-nitroaniline (98 % CAS Number: 97-52-9) – compounds (III). After the release of nitrogen, the product was filtered and recrystallized from ethanol [24]. Aldehyde samples obtained after different stages of recrystallization rates were used for experimental determination of combustion energies, namely samples No. 1, 2 and 3 were taken after three, four and five recrystallizations, respectively.

Sample identification was performed by NMR spectroscopy. 1H NMR spectra were recorded on a Varian 600 instrument (600 MHz) using DMSO-d6 solvents and acetone. Chemical shifts (δ, ppm) are given relative to the DMSO signal or acetone (2.50 ppm).

(I) ^{1}H NMR (600 MHz. DMSO) δ 7.63 (d. J = 3.7 Hz. 1H. fur). 7.76 (d. J = 3.7 Hz. 1H. fur). 8.17 (d. J = 8.8 Hz. 2H. C_6H_4). 8.39 (d. J = 8.8 Hz. 2H. C_6H_4). 9.73 (s. 1H. CHO).

(II) ^{1}H NMR (600 MHz, Acetone) δ 2.74 (s, 3H, CH_3), 7.27 (d, J = 3.7 Hz, 1H, fur), 7.62 (d, J = 3.7 Hz, 1H, fur), 8.10 (d, J = 8.6 Hz, 1H, C_6H_3), 8.20 (d, J = 8.7 Hz, 1H, C_6H_3), 8.24 (s, 1H, C_6H_3), 9.77 (s, 1H, CHO).

(III) ^{1}H NMR (600 MHz, Acetone) δ 4.20 (s, 3H, CH_3), 7.44 (d, J = 3.6 Hz, 1H, fur), 7.59 (d, J = 3.7 Hz, 1H, fur), 7.97 (s, 1H, C_6H_3), 8.01 (d, J = 8.6, Hz, 1H, C_6H_3), 8.19 (d, J = 8.6 Hz, 1H, C_6H_3), 9.75 (s, 1H, CHO).

The combustion energy of the substances was determined on a precision calorimeter of combustion B-08-MA with an isothermal shell (± 0.003 K) and a static calorimetric bomb. The energy equivalent of the calorimetric system (W = 15277 ± 8 J/V) was determined with an accuracy of ± 0.06 % by burning the reference benzoic acid grade K-1, the content of the main component of which reached 99.995 ± 0.01 mol. %. The heat of combustion of benzoic acid (Δ_cU), taking into account the factor of Jessup was –26432.36 ± 0.08 J/g. This amendment was applied because the conditions of combustion of benzoic acid under the conditions of the experiment (initial pressure of oxygen in the bomb P = 30 atm; weight of benzoic acid m_{ba} = 0.18–0.51 g; volume of the bomb V = 0.325 l; mass of water which introduced into the bomb m_{H2O} = 1 g; temperature T = 298.15 K) differed from the standard ones.

Since under normal conditions the test substances were in a solid state, before the experiment they were ground in a chalcedony mortar and tableted in a mold made of stainless steel using a hand press. Additionally, before incineration, the compressed tablets were sealed in 0.02 mm thick terylene film ampoules, as aldehydes can oxidize under excess oxygen during the preparation period, which will adversely affect the reliability and identity of the results. Terylene also serves as an auxiliary material, as the ignition of the sample occurred simultaneously over the entire surface, which encourages an increase in temperature in the combustion zone and increase the completeness of combustion of the sample. The terylene ampoule was tied with cotton thread and placed in a platinum cup. Ignition of the sample during the experiment was initiated by the discharge of capacitors through a platinum wire, which ignited the cotton thread. The initial pressure of oxygen previously purified from flammable impurities, carbon dioxide and water was 30 atm, and the initial temperature of the main period in all experiments was 298 K.

The mass of the substance burned during the experiment was determined by the amount of CO_2 in gaseous combustion products [25] with an accuracy of $\pm 1\cdot 10^{-4}$g. The content of carbon monoxide was controlled in individual experiments using indicator tubes with an accuracy of $\pm\ 5\cdot 10^{-6}$ g. The reliability of the gas analysis was confirmed by a series of experiments on the combustion of standard benzoic acid in determining the energy equivalent of the calorimetric system. The amount of soot formed on the walls of the platinum cup was determined by weighing the platinum cup with an accuracy of $\pm\ 5\cdot 10^{-6}$ g.

The HNO_3 content formed as a result of the experiment was determined by titration with 0.1 N KOH solution.

Research results and their discussion

The change in internal energy under the conditions of the bomb ΔU_B (J/mol) during the combustion of the studied aldehydes was calculated by equation 1:

$$\Delta U_B = \frac{W\cdot\Delta T - U_{fuser} - U_{ter} - U_{HNO_3} + U_{carb}}{m_{comp}}\cdot M, \quad (1)$$

where W – is the energy equivalent of the calorimetric system; m_{comp} – mass of substance that burned during the experiment; M – molecular weight of the substance; U_{fuser}, U_{ter}, U_{HNO3}, U_{carb} – the amount of internal energy released during the combustion of cotton thread (16704.2 J/g), terylene ampoule (22944.2 J/g), the formation of nitric acid solution (59 J/g) and soot formed (32800 J/g), respectively [26].

ΔT – is the true temperature rise in the calorimetric experiment.

Table 1

The results of experimental determination of combustion energies of derivatives of 5-(4-nitrophenyl)-furan-2-carbaldehyde and its derivatives

Sample	m_{comp}, g	ΔT, V	U_{fuser}, J	U_{HNO_3}, J	U_{carb}, J	U_{ter}, J	–ΔU, J/g	$m^{exp}_{CO_2}/m^{calc}_{CO_2}$
5-(4-Nitrophenyl)-furan-2-carbaldehyde (I)								
1	0.36767	0.56984	88.2	13.6	22.8	–	23462	0.9974
2	0.32411	0.54552	82.5	21.2	25.1	627.3	23535	0.9919
	0.34319	0.58507	74.3	13.0	27.9	818.3	23487	0.9932
	0.37234	0.62328	91.6	14.8	44.8	721.7	23469	0.9982
3	0.34298	0.58507	74.3	13.0	27.9	818.3	23501	1.0000
	0.41217	0.69069	100.5	14.8	31.3	782.4	23498	0.9991
ΔU_{av} = –23492 ± 20 J/g								
5-(2-Methyl-4-nitrophenyl)-furan-2-carbaldehyde (II)								
2	0.31225	0.55657	81.3	12.4	29.5	695.0	24800	0.9965
	0.16935	0.32417	76.1	4.7	27.4	701.7	24785	0.9958
	0.22794	0.41054	78	5.3	50.2	585.4	24802	0.9989
3	0.23310	0.42008	75.9	4.1	35.9	595.3	24788	0.9972
	0.19456	0.36348	67.7	5.3	10.0	663.2	24808	0.9968
	0.26392	0.47616	78.5	12.4	30.5	671.2	24790	0.9973
ΔU_{av} = –24796 ± 14 J/g								
5-(2-Oxymethyl-4-nitrophenyl)-furan-2-carbaldehyde (III)								
1	0.28202	0.47192	79.8	7.7	47.4	714.9	22887	0.9959
	0.21082	0.53318	96.7	4.1	67.2	538.5	22879	0.9949
	0.17640	0.31198	93.0	4.1	65.6	701.6	22863	0.9925
2	0.16029	0.27772	91.1	5.9	63.3	542.4	22875	0.9933
	0.11099	0.20269	94.7	3.0	32.6	497.2	22832	0.9922
3	0.19000	0.32967	87.9	4.7	36.4	646.3	22810	0.9924
	0.17640	0.31198	93.0	4.1	65.6	701.6	22863	0.9944
ΔU_{av} = –22858 ± 24 J/g								

In the table 1 shows the results of calculation of calorimetric determination of internal combustion energy of test substances and their completeness of combustion. Completeness of combustion was calculated as the ratio of the mass of carbon dioxide determined by gas analysis ($m_{CO_2}^{exp}$) to the mass of carbon dioxide calculated from the initial sample of the substance taken for study ($m_{CO_2}^{calc}$).

The change in the energy of combustion of aldehydes under standard conditions ($\Delta_C U^o$) was calculated by equation (2):

$$\mathit{\Delta}_c U^0 = \mathit{\Delta} U_B + \pi, \quad (2)$$

where ΔU_B – the average value of changes in internal energy during combustion of aldehydes in the conditions of calorimetric experiment, kJ/mol; π – Washborn's amendment.

The Washborn correction brings the value of ΔU_B to standard conditions, since the value of ΔU_B was obtained as a result of the experiment and belongs to the isothermal combustion reaction of the test substance under the conditions contained in the bomb. This amendment, according to the recommendations given in [21], was calculated according to the so-called simplified Washborn equation, equation (3):

$$\pi = \frac{4.184\cdot P\cdot 0.3}{\Delta U_B}_{a}\cdot\ -1 + 1.1\cdot\ \frac{b-2c}{4a}\ - \frac{2}{P}\ , \quad (3)$$

where P is the initial oxygen pressure in the bomb; $a.\ b.\ c$ – are indices in the formula $C_a H_b O_c$.

The value of the correction calculated according to equation (3) is expressed as a percentage of the calculated value of ΔU_B.

The standard enthalpy of combustion of substances was calculated taking into account the correction for the work of expansion, equation (4):

$$\Delta_c H_{298}^0 = \Delta_c U^0 + \Delta nRT, \quad (4)$$

where $\mathit{\Delta} n$ – is the change in the number of moles of gaseous substances, calculated by the stoichiometric equation of the combustion reaction (5):

$$C_a H_b O_c N_d\ s\ +\ 2a + \frac{b}{4} - \frac{c}{2}\ O_2\ g\ =$$

$$= aCO_2\ g\ + \frac{b}{2} H_2O\ l\ + \frac{d}{2} N_2(g). \quad (5)$$

Formed as a product of combustion of nitrogen-containing compounds, nitrogen gas in the presence of water and oxygen according to equation (6) forms an aqueous solution of nitric acid, the amount of which was determined by titration with potassium hydroxide solution.

$$\frac{1}{2} N_2\ g\ + \frac{5}{4} O_2\ g\ + \frac{1}{2} H_2O\ l\ = HNO_3\ aq\ . \quad (6)$$

The standard enthalpy of formation of the test compounds in the condensed state was calculated by equation (7):

$$\Delta_f H_{298}^0 = a\Delta_f H_{298}^0\ CO_2.g\ + \frac{b}{2}\Delta_f H_{298}^0\ H_2O.l\ +$$

$$+ \frac{d}{2}\Delta_f H_{298}^0\ N_2.g\ - \Delta_c H_{298}^0(C_a H_b O_c N_d.s) \quad (7)$$

using the recommended values of $\Delta_f H_{298}^0\ CO_2.g$ = = –393.512 ± 0.045 kJ/mol [25]. $\Delta_f H_{298}^0\ H_2O.l$ = = –285.830 ± 0.040 kJ/mol [25].

The results of calculations of standard energies $\mathit{\Delta}_C U^o$, enthalpies $\mathit{\Delta}_C H^o$ combustion and formation $\Delta_f H^o_{298}$ of the studied compounds in the condensed state, as well as Washborn's corrections and corrections for the work of expansion are given in Table 2.

Table 2

Combustion energies and enthalpies and formation of investigated compounds in the condensed state, kJ/mol

Substance	$U_{C(298)}$	π	ΔnRT	$\Delta_c H^0_{298}$	$\Delta_f H^0_{298}$
I	–5106.5 ± 4.4	–4.5	1.9	–5104.7 ± 4.4	–224.4 ± 4.4
II	–5737.9 ± 3.2	–5.0	0.6	–5737.3 ± 3.2	–271.1 ± 3.2
III	–5656.0 ± 5.8	–5.2	1.9	–5654.1 ± 5.8	–354.3 ± 5.8

The previously described procedure for the experimental determination and calculation of enthalpies of formation in the condensed state, entails significant costs. Therefore, there is a need to find alternative methods for determining $\Delta_f H^0_{298}$ in the condensed state. Such methods include theoretical methods of calculation, the main task of which is to calculate values as close as possible to experimentally determined. Thus, Cohen [27], Domalsky [28] and Salmen [29] developed theoretical methods of calculation, which belong to the so-called additive methods, the prototype of which is Benson's group additivity method, developed for calculating the enthalpies of formation in the gaseous state. In these methods, the molecule is considered as the sum of additive contributions that characterize the set of groups from which the molecule can be formed. A group in a molecule is referred to as a polyvalent atom together with its ligands, ie the atoms with which it is directly bonded by chemical bonds. Usually, according to the valence nomenclature, the multivalent (central) atom is indicated first, and then its environment (ligands) in parentheses. Table 3 shows the group contributions and their values for the calculation of $\Delta_f H^0_{298}$ in the condensed (solid) state by the methods of Cohen, Domalsky and Salmen.

Table 4 shows the results of theoretical calculations of the values of $\Delta_f H^0_{298}$ in the solid state, experimental values and the absolute deviation of the calculated value from the experimental one

Table 3

Group contributions for the calculation of enthalpies of formation in the solid state, kJ/mol

Group	$\Delta_f H^0_{298}$			Group	$\Delta_f H^0_{298}$		
	[27]	[28]	[29		[27]	[28]	[29]
$C - (C_b)(H)_3$	–42.3	–46.7	–108.7	$C_b - (C_b)_2(C)$	12.1	13.9	77.3
$C - (O)(H)_3$	–42.3	–46.7	–41.4	$C_b - (C_b)_2(H)$	6.3	6.53	3.1
$C_d - (C_d)_2(H)$	11.3	17.5	31.7	$C_b - (C_b)_2(O)$	–4.2	1	–67.9
$C_d - (C_d)(H)(O)$	0	25.5	–22.1	$C_b - (C_b)_2(Cd)$	24.3	20.3	60.2
$CO - (C_d)(H)$	–146.9	–120.0	–42.5	$C_b - (C_b)_2(NO_2)$	–26.5	–32.5	–27.6
Furan cycle	–25.1	10.7	–33.4	$O - (C_d)_2$	–138.1	–157.3	–33.4
$C_d - (C_b)(O)(C_d)$	40	27.9	46.6	$O - (C_b)(C)$	–134.7	–122.9	–51
$C_d - (C_d)(O)(CO)$	33.5	7.82	–104.4				

Table 4

The results of the calculation of $\Delta_f H^0_{298}$ using additive schemes in the solid state, kJ/mol

Substance	$\Delta_f H^0_{298}$. (exp)	Cohen [27]		Domalsky [28]		Salman [29]	
		$\Delta_f H^0_{298}$	Δ	$\Delta_f H^0_{298}$	Δ	$\Delta_f H^0_{298}$	Δ
I	–224.4	–191.0	33.4	–181.9	42.5	–56.3	–168.1
II	–271.1	–227.5	43.6	–221.2	49.8	–90.8	–180.3
III	–354.3	–412.0	57.7	–364.8	–10.5	–115.3	–239.0

Judging by the obtained results of the experimental study of $\Delta_f H^0_{298}$ in the solid state, the contribution of the metal and oxymethyl substituent to the second position of the phenolic ring of 5-(4-nitrophenyl)-furan-2-carbaldehyde is –46.7 and –129.9 kJ/mol, respectively. As for the comparison of the experimentally determined values of $\Delta_f H^0_{298}$ in the solid state with the values calculated by the well-known additive methods of Cohen, Domalsky and Salman, a rather significant difference is observed. Thus, the smallest difference between the experimentally determined values and the calculated values is observed using the methods of Domalski and Cohen. According to Salman's method, the calculated values differ from experimental values by 1.5–3 times, which indicates an extremely approximate estimate of additive group contributions in this method. Here it is also worth noting that none of the considered additive methods take into account corrections for intermolecular and interatomic interactions, which are present in complex substances, to which the investigated substances belong.

Conclusion

Based on experimentally determined combustion energies of 5-(4-nitrophenyl)-furan-2-carbaldehyde, 5- (2-methyl-4-nitrophenyl)-furan-2-carbaldehyde and 5-(2-oxymethyl-4-nitrophenyl)-furan-2-carbaldehyde calculated the values of enthalpies of combustion and formation in the solid state, which will add to the database of thermodynamic values and can be used in thermodynamic calculations of chemical processes that will occur with the participation of test substances.

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ЕНТАЛЬПІЇ УТВОРЕННЯ ТА ГОРІННЯ 5-(4-НІТРОФЕНІЛ)ФУРАН-2-КАРБАЛЬДЕГІДУ ТА ЙОГО 2-МЕТИЛ-ТА 2-ОКСОМЕТИЛПОХІДНИХ У КОНДЕНСОВАНОМУ СТАНІ

З використанням прецизійного бомбового калориметра спалювання В-08-МА експериментально визначено енергії згорання 5-(4-нітрофеніл)-фуран-2-карбальдегіду, 5-(2-метил-4-нітрофеніл)-фуран-2-карбальдегіду та 5-(2-оксиметил-4-нітрофеніл)-фуран-2-карбальдегіду. На основі отриманих даних розраховано значення ентальпій згорання та утворення речовин у конденсованому стані. Наведено порівняльний аналіз експериментально визначених величин зі значеннями, теоретично розрахованими за адитивними методами розрахунку.

Ключові слова: 5-(4-нітрофеніл)-фуран-2-карбальдегід; 5-(2-метил-4-нітрофеніл)-фуран-2-карбальдегід; 5-(2-оксиметил-4-нітрофеніл)-фуран-2-карбальдегід; енергія згорання; ентальпія згорання; ентальпія утворення.