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THE ENTHALPIES OF COMBUSTION AND FORMATION OF *L*-α-GLUTAMIC AND 6-AMINOHEXANOIC ACIDS

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The energies of combustion of crystalline *L*-α-glutamic and 6-aminohexanoic acids were measured in a static bomb adiabatic calorimeter, in pure oxygen at 3040 kPa. Corrections were made for the heats due to the ignition of sample and for the nitric acid formation. The derived enthalpies of formation for *L*-α-glutamic and 6-aminohexanoic acids are $\Delta_f H^0_{cr}=-1002.6\pm1.1$ kJ mol^{-1} and $\Delta_f H^0_{cr}=-641.6\pm1.2$ kJ mol^{-1}, respectively. The data of enthalpy of formation are compared with literature values and with estimated values by means of group additivity, using parameters recommended by Domalski and Hearing.

Keywords: *amino acids, enthalpy of formation, heats of combustion, static bomb*

Introduction

Although the oldest measuring technique in thermochemistry, combustion calorimetry is still largely used for theoretical and practical reasons. The theoretical interpretation of heat of combustion data refers mainly to obtaining valuable information about the structure and stability of investigated compounds. Among nowadays practical applications, those involving fuels [1], solutions to some environment problems [2] and drugs study [3] have to be mentioned.

Continuing our preoccupations concerning the thermochemical study of nitrogen containing organic compounds, particularly amino acids [4–7], the enthalpies of combustion and formation of another two compounds, namely *L*-α-glutamic and 6-aminohexanoic acids were measured.

The knowledge of the thermodynamic properties of amino acids can serve as a tool for a better understanding of the properties of proteins which contain them.

The two studied amino acids are very different: *L*-glutamic acid is a dicarboxylic α-amino acid while 6-aminohexanoic acid has a long paraffinic chain between the two functional groups. The glutamic acid plays an important role in transaminase and transdesaminase reactions, turning to α-keto-glutaric acid. A connection is made in this way, between the metabolism of proteins and that of carbohydrates. The 6-aminohexanoic acid acts as an inhibitor of fibrinolysis.

The energies of combustion of the isomeric aminohexanoic acids were already measured by Sabbah *et al.* [8] including that of 6-aminohexanoic. The enthalpies of formation of *L*-glutamic acid were measured many years ago by Sakiyama and Seki [9] and more recently by Yang *et al.* [10]. We have considered that it would be interesting to observe the influence of the aliphatic chain, intercalated between the two functional groups, on the values of the corresponding enthalpies of formation.

Experimental

Apparatus and experimental procedures

The adiabatic calorimeter with static bomb and the basic experimental procedures used in this investigation have been already described [5]. The calorimeter is of the Parr Instruments type, locally built. It is provided with an electronic system, which allows it to work in adiabatic conditions, with a difference of 0.002°C between the temperatures of the calorimeter vessel and that of the shield. The calorimetric bomb is a cylinder, with a volume of about 300 mL, made of stainless steel, as well as its accessories. The temperature rise, following the combustion was measured in two ways:

- for glutamic acid – by means of a differential Beckmann thermometer, the temperature rise due to the combustion reaction being considered as the difference between the final and initial temperature values, when the difference between two consecutive readings is about 0.002°C.
- for aminohexanoic acid – by means of a Pt resistance thermometer, with $R=100$ Ω, previously calibrated, connected to a HP34812A multimeter.The temperature measurement accuracy was of 10^{-2} Ω corresponding to a temperature difference of $2.5\cdot10^{-3}$ K.

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The initial temperature was 25.000±0.002°C and the initial pressure was 3040 kPa.

The samples to be burned were pressed into pellets and weighed with an accuracy of 0.01 mg. The bomb was flushed with purified oxygen for three minutes, then sealed and filled with oxygen at the initial pressure mentioned above. After combustion, the gas mixture from the bomb was evacuated. The walls and fittings of the bomb were washed with bidistilled water and the resulting solution was saved. For glutamic acid the combustion was run in presence of a cotton fuse, as an auxiliary of combustion.

Calibration

The calorimeter constant was determined by means of benzoic acid combustion (standard referece material 39I from NIST). The considered certified value of energy of combustion of benzoic acid was 26454.8 ±3.7 J g^{-1}. The calorimeter constant was calculated from the results of more ten combustion runs.

The two constant values, obtained with the temperature instruments mentioned above were 9118.5±1.7 J K^{-1} and 23.221±0.12 kJ Ω^{-1}, respectively. The first constant was used for the energy of combustion of *L*-glutamic acid and the second for that of 6-aminohexanoic acid.

Analysis of the final solutions

Three samples of solution of 50 mL were titrated separately, with 0.1 N NaOH solution, using methyl orange as indicator. The mean value of three titrations was used for the calculation of the amount of nitric acid resulting from combustion (about 20% from the total nitrogen). The heat due to nitric acid formation was obtained, using a value $\Delta_f H_{HNO_{3aq}} = -57.8$ kJ mol^{-1} for the enthalpy of formation of the nitric acid [9].

Results

Combustion energy of the samples

The determination of combustion energies for the samples was done in the same way as for the calibration of the calorimeter. The results are given in Table 1 for the glutamic acid and in Table 2 for the 6-aminohexanoic acid.

In order to bring the experimental values of energy of combustion to the standard state (T=298.15 K and P=1001.325 kPa) corrections were made with the Washburn equation [12] recommended in the case of compounds with carbon, hydrogen and oxygen of $C_mH_nO_q$. The general formula:

$$\Pi\% = \frac{-0.3\, mP_{\text{initial}}}{-\Delta U^{\text{exp}}}\left[1 - \frac{1.1(n-2q)}{4m} + \frac{2}{P_{\text{initial}}}\right] \qquad (1)$$

Table 1 The combustion of *L*-α-glutamic acid[a]

m/g	$\Delta\theta$/K	Q/J	q_c/J	q_i/J	q_n/J	$-\Delta_c u^{\text{exp}}$/J g^{-1}	$-\Delta_c U^{\text{exp}}$/kJ mol^{-1}	$-\Delta_c U^0$/kJ mol^{-1}
0.83095	1.436	13102.118	354.551	50.828	11.549	15265.890	2246.235	2245.681
0.82475	1.429	13033.912	319.293	53.504	11.323	15337.732	2256.639	2256.085
0.68095	1.188	10839.981	378.591	54.841	12.001	15264.778	2245.905	2245.531
0.52240	0.914	8340.985	324.832	31.433	8.602	15268.223	2246.411	2245.857
0.84984	1.459	13304.981	256.129	51.832	16.532	15274.041	2247.268	2246.714

Mean value – 2247.9736 kJ mol^{-1}; standard deviation from the mean ±1.09; [a] m – mass of the burned substance, $\Delta\theta$ – temperature rise; Q – total evolved heat observed; q_i – energy used to ignite the sample (calculated from mass of the fire and $\Delta_f H_{Fe_2O_3}$=6.688 kJ g^{-1}); q_c – energy of burned cotton (calculated from the mass of cotton and $\Delta_c H_{cotton}$=16.241 kJ g^{-1}); q_n – energy of nitric acid formation; Δu^{exp} – energy of combustion of the sample, molar energy of combustion; $\Delta_c U^0$ – standard molar energy of combustion

Table 2 The combustion of 6-aminohexanoic acid[b]

m/g	$\Delta R/\Omega$	Q/J	Q_i/J	q_n/J	$-\Delta_c u^{\text{exp}}$/J g^{-1}	$-\Delta_c U^{\text{exp}}$/kJ mol^{-1}	$-\Delta_c U^0$/kJ mol^{-1}
0.87995	1.046	24047.54	50.828	14.943	27253.554	3575.120	3574.815
1.04195	1.234	28369.66	52.166	16.983	27161.100	3562.990	3562.810
1.00200	1.179	27105.21	51.163	19.023	26981.059	3539.373	3539.194
0.80020	0.949	21817.51	51.497	17.890	27178.355	3565.255	3565.076
1.03010	1.222	28093.78	53.504	23.324	27198.281	3567.868	3567.688
0.93375	1.109	25495.91	51.163	16.076	27232.846	3572.403	3572.223

Mean value – 3568.52 kJ mol^{-1}; standard deviation from the mean ±1.18; [b] $\Delta\Omega$ – change in the resistance of the platinum thermometer; for the rest of the key see footnote in Table 1 was used, where P stands for the initial oxygen pressure and $-\Delta U^{\text{exp}}$ for the experimental energy of combustion, m, n, and q being the numbers of carbon, hydrogen and oxygen atoms from the chemical formula of the compound, respectively. Π is calculated in percents from the experimental value. The above equation applies fairly well in the case of nitrogen compounds as well [13].

Standard enthalpies of combustion and formation

The standard combustion enthalpies of the samples were calculated using the following equation:

$$\Delta H=\Delta U+\Delta nRT$$

$$\Delta n = \Sigma n_{\text{prod}} + \Sigma n_{\text{react}}$$

Δn is the change of the gas mole number in the combustion reaction. R=8.314 J mol^{-1} K^{-1}; T=298.15 K.

The combustion experimental results are given for the following reactions:

- for *L*-α-glutamic acid:

$$\text{HOOC–CH}_2\text{–CH}_2\text{–CH(NH}_2\text{)–COOH}$$

$$C_5H_9NO_4(s)+5.25O_2(g)\rightarrow$$
$$\rightarrow 5CO_2(g)+4.5H_2O(l)+0.5N_2(g)$$

$$\Delta n=0.25$$

- for 6-aminohexanoic acid:

$$\text{H}_2\text{N–CH}_2\text{–CH}_2\text{–CH}_2\text{–CH}_2\text{–CH}_2\text{–COOH}$$

$$C_6H_{13}NO_2(s)+8.25O_2(g)\rightarrow$$
$$6CO_2(g)+6.5H_2O(l)+0.5N_2(g)$$

$$\Delta n=-1.75$$

For the calculation of formation enthalpies of the investigated compounds the following auxiliary values were considered [14]:

$$\Delta_{\text{f}} H^0_{\text{CO}_2\,(\text{g})} = -393.51\pm0.13 \text{ kJ mol}^{-1}$$
$$\Delta_{\text{f}} H^0_{\text{H}_2\text{O}\,(\text{l})} = -285.83\pm0.042 \text{ kJ mol}^{-1}$$

Discussion

The values of the enthalpies of formation of the two amino acids are shown in Table 3. In the last column of this table values of the formation enthalpy from literature are given. Our results are in the satisfactory agreement with those of Pedley [8], for glutamic acid and of Sabbah [9] for 6-aminohexanoic acid, respectively.

The Domalski [15] method of estimation of thermodynamic data was used for the estimation of the enthalpies of formation of the compounds under study and of other amino acids, with similar structure (Table 4). The values obtained by this method are compared with the experimental enthalpies of formation. The discrepancies between experimental and calculated values are smaller for our data than for those from literature. All experimental enthalpies of formation for ω-amino acids are less negative by about 10 kJ mol^{-1}, than those predicted by the group additivity scheme. This is probably because, in this case, a different zwitterion contribution should be considered, than in the case of α-amino acids – probably –44, instead of –55.1 kJ mol^{-1}. A very good agreement between experimental and calculated values of enthalpies of formation is obtained with this value, except for short alkyl chain ω-aliphatic amino acids,

Table 3 The enthalpies of combustion and formation of studied compounds

Compound	$-\Delta_c H^0$/kJ mol^{-1}	$-\Delta_f H^0$/kJ mol^{-1}	$-\Delta_f H^0$/kJ mol^{-1}/literature
L-α-glutamic acid	2247.71±1.09	1002.61±1.09	1009.47±0.8 [10]
6-aminohexanoic acid	3572.81±1.18	641.63±1.18	637.35±0.48 [11]

Table 4 Experimental and estimated enthalpies of formation of some amino acids

Compound	$\Delta_f H^0$ calculated^a/kJ mol^{-1}	$\Delta_f H^0$ calculated^b/kJ mol^{-1}	$\Delta_f H^0$ experimental/kJ mol^{-1}
4-aminobutanoic acid	–588.46	–578.46	–560.12 [3]
5-aminopentanoic acid	–617.87	–607.87	–604.10 [10]
6-aminohexanoic acid	–647.28	–637.28	–637.35
7-aminoheptanoic acid	–676.69	–666.69	–667.40 [11]
8-aminooctanoic acid	–706.10	–696.10	–694.00 [11]
9-aminononanoic acid	–735.51	–725.51	–727.80 [10]
aspartic acid	–972.45	–972.45	
glutamic acid	–1001.86	–1001.86	

[a] Calculated using the value for zwitterion correction recommended by Domalski and Hearing [15], for α-aliphatic amino acids

[b] Calculated with our proposed value for ω-aliphatic amino acids, –44 kJ mol^{-1}

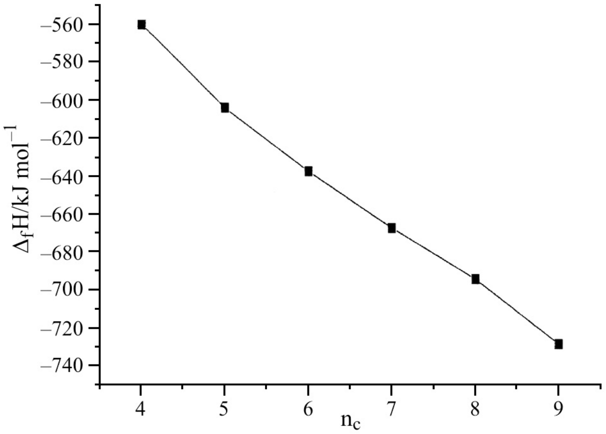

Fig. 1 The dependence of the enthalpies of formation of ω-amino acids on the number of carbon atoms

probably because their structure is differing from that of long chain ones.

The theoretical linear dependence of the heat of formation on the number of carbon atoms, with a slope of –29.41 kJ C atom, for the ω-amino acids is only qualitatively verified by the experimental values (Fig. 1).

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