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Standard Enthalpy of β-Alanine Formation

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Abstract—In an isoperibolic calorimeter with a stationary bomb, the value of the combustion energy of crystalline β-alanine ($\Delta_c U^0$) was determined at 298.15 K, from which standard enthalpies of combustion ($\Delta_c H^0$) and formation ($\Delta_f H^0$) have been calculated. The obtained results are compared with literature data.

Keywords: enthalpy of combustion, enthalpy of formation, β-alanine
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INTRODUCTION

The present work is the continuation of the systematic study of the thermochemical properties of amino acids. In [1], we defined the enthalpy of formation of α-amino acids: L-serine, L-arginine, and L-tyrosine, in order to refine the available literature values of $\Delta_f H^0$ for these compounds. In this work, the enthalpy of combustion and formation of β-alanine was determined, as the presented values in the literature [2–5] have a discrepancy up to ~250 kJ/mol. It is known that β-alanine plays an important role in various biological processes, and reliable data on the enthalpies of combustion and formation are necessary in thermodynamic calculations.

EXPERIMENTAL CONDITIONS

The sample used for the study was obtained from Sigma-Aldrich. The content of carbon, hydrogen, and nitrogen in β-alanine were 40.53, 8.05, and 15.77 wt %, respectively according to the certificate; these values were 40.44, 7.92, and 15.72 wt % according to theoretical calculation. The content of impurities was less than 0.02% in total for metals, less than 0.005% for sulfur, and 0.002% for chlorine. Weight loss upon drying is less than 0.05%, and the ash content (sulfonated) is less than 0.05%.

Prior to the study, the sample was additionally purified by recrystallization from the mixture of water with ethanol. The obtained crystals were filtered, washed with ethanol, and dried at a reduced pressure of 1.3 kPa and then at 1.3×10^{-3} kPa. According to the IR spectrum (on a Bruker Tensor 27 device with the ATR method), no traces of water or alcohol were in the sample prepared for combustion. After purification β-alanine was stored in a box in an atmosphere of dry argon.

The molecular mass of β-alanine, which was calculated from the 2007 atomic masses [6], is equal to 89.09318. The value of the density of the substance (1.421 g/cm^3) is taken from a paper [2].

To measure the energy of combustion of β-alanine, a precision calorimeter of the Dickinson type was used with a stationary self-sealing bomb [1]. The temperature rise was measured by a copper thermometer of resistance ($R_{298} \approx 50$ Ohm) incorporated into a bridge circuit with sensitivity of $\sim 5 \times 10^{-5}$ K. Ignition of the sample was carried out by the passing of current through a platinum wire (diameter is 0.1 mm) in contact with it.

The energy equivalent of the calorimeter with an empty bomb (W), which was determined in a series of calibration experiments by the combustion of reference benzoic acid (purity is 99.997 mol. %), was 58265.1 ± 6.3 J/Ohm. The heat of the combustion of acid under certified conditions is 26432.5 ± 1.9 J/g; an amendment, which was calculated by the Jessup formula [7], was introduced for a slight deviation from these conditions [7]. The ignition energy in calibration experiments and in the experiments with β-alanine was constant and was not taken into account in the calculations.

The picking of substance for combustion was carried out in the chamber in the atmosphere of dried argon. The optimal conditions for combustion of the substance were preselected. As a result, the weighed amount of β-alanine was ~0.50 g, and it was compressed into a tablet. To exclude the interaction of the sample with water vapors, the tablet was hermetically sealed in an ampoule made of polyester film. Benzoic acid was used to achieve complete combustion of β-alanine. The ampoule with the substance was placed in a platinum crucible over a tablet of benzoic acid. In a bomb, 2 cm^3 of distilled water was poured, and it was

Table 1. Combustion energy of β-alanine, $C_3H_7O_2N$ at 298.15 K

m, g	Q, J	$q_{\text{b.a.}}$, J	q_f, J	$q\text{HNO}_3$, J	q_s, J	q_{st}, J	A, %	$-\Delta_c u^0$, J/g
0.527878	13813.5	3647.8	505.2	31.4	0.7	9.6	99.97	18224.3
0.499020	13777.9	4171.5	480.1	29.9	0.7	9.6	100.00	18210.7
0.501315	13778.1	4066.3	544.8	30.5	0.8	9.6	99.99	18207.6
0.496265	13902.6	4321.3	500.5	32.0	2.0	9.8	99.97	18218.2
0.489506	13764.4	4306.8	504.5	31.9	0.3	9.6	99.99	18206.0
0.499056	13733.9	4086.7	518.4	29.6	0.5	9.6	99.97	18214.6
						Average	99.98 ± 0.02	18213.6 ± 7.2

Table 2. Formation enthalpy of β-alanine (kJ/mol) at 298.15 K

Literature source				Present work
[2]	[3]	[4]	[5]	
−558.04 ± 0.31	−310 ± 1.5	−547.1 ± 1.1	−559.1 ± 0.9	−557.6 ± 0.7

then washed with oxygen and filled to pressure of 3.04 MPa. Under these conditions, a sample was burned without the formation of a significant amount of soot.

After each combustion of β-alanine, the carbon dioxide was quantitatively determined in the gaseous combustion products by the Rossini method [8] with an accuracy of $\pm 2 \times 10^{-4}$ g and the absence of CO was qualitatively verified by indicator tubes with a sensitivity of 6×10^{-6} g. The amount of HNO_3 formed during combustion was determined by titration of the bomb solution by 0.1 N of NaOH solution.

When calculating the energy of the combustion of the studied compound, the standard values of the specific energy of combustion of auxiliaries were (–22928 ± 6) J/g [9] for the film and (–26412.2 ± 1.9) J/g for the benzoic acid (the last value were derived from the above mentioned certificate value by introduction of the amendment to the standard state [8]).

The results of experiments on the combustion of β-alanine are given in Table 1, where the following designations are used: m—mass of the sample (determined by weighing on a Mettler balance with a sensitivity of 2×10^{-6} g); Q—total amount of heat liberated in the experiment; $q_{\text{b.a.}}$ and q_f—amendments to the energy of combustion of auxiliary materials (benzoic acid and film); $q\text{HNO}_3$—the amendment to the energy of formation of nitric acid; q_s—the amendment to the presence of soot in the crucible (the specific energy of combustion of soot (–32762 J/g) is calculated from the standard enthalpy of formation of CO_2 [10]); q_{st}–the amendment for the reduction to the standard state [8, 11]; A—ratio of the observed amount of CO_2 to the theoretical in the combustion products; $\Delta_c u^0$—standard specific energy of combustion of β-alanine. The energy of combustion of alanine corresponded to about 67% of the total amount of heat released in the experiment. The CO_2 content in the flue gas is 99.98 ± 0.02&, which indicates the high purity of the sample and the fullness of its combustion. The standard specific energy of combustion was calculated by the formula

$$-\Delta_c u^0 = (Q - q_{\text{b.a}} - q_f - q\text{HNO}_3 + q_s - q_{\text{st}})/m,$$

The mean value of $-\Delta_c u^0$, according to the results of the six performed experiments, was found to be (−18213.6 ± 7.2) J/g, which corresponds to the molar energy of the combustion $\Delta_c U^0$ ($C_3H_7O_2N$ (cr)) = (−1622.7 ± 0.6) kJ/mol and the enthalpy of combustion $\Delta_c H^0$ ($C_3H_7O_2N$ (cr)) = (−1623.3 ± 0.6) kJ/mol for the reaction:

$$\begin{aligned} &C_3H_7O_2N(\text{cr}) + 3.75O_2(\text{g}) \\ &= 3CO_2(\text{g}) + 3.5H_2O(\text{l}) + N_2(\text{g}). \end{aligned} \tag{1}$$

From the value of the enthalpy of combustion $\Delta_c H^0$($C_3H_7O_2N$ (cr)), the standard enthalpy of formation of $\Delta_f H^0$($C_3H_7O_2N$ (cr)) = (−557.6 ± 0.7) kJ/mol was calculated. In the calculation, the values used were

$$\Delta_f H^0(CO_2(\text{g}) = (-393.51 \pm 0.13)\ \text{kJ/mol and}$$

$$\Delta_f H^0(H_2O(\text{l})) = (-285.830 \pm 0.042)\ \text{kJ/mol [10].}$$

The errors of $\Delta_c U^0$, $\Delta_c H^0$ of β-alanine and W are expressed by a 95% confidence interval. The error of $\Delta_f H^0$ as calculated according to the law of accumulation of errors.

RESULTS AND DISCUSSION

The combustion and formation enthalpies for β-alanine have been determined in four papers [2–5] (Table 2). Unfortunately, all of the works have their drawbacks. In [2], there is no analysis of gaseous products of combustion to CO_2. It should be also noted that the error in the energy of combustion $\Delta_c U^0$ of β-alanine is underestimated and expressed as the standard deviation. Converted to a 95% confidence interval, it is equal to ±0.6 kJ/mol. Therefore, the error in $\Delta_f H^0$ of β-alanine in [2] is ±0.7 kJ/mol. In [3], there is no description of the purity of the sample or the analysis of the combustion products to CO_2. In [4] it is not reported what adjustments were taken into account in the calculation of the specific energy of the combustion of β-alanine, and there is no description of the experimental technique. In [5], the sample of β-alanine was of a high degree of purity, which was confirmed by NMR spectroscopy and elemental analysis. However, there are no reports on the measures to protect the sample from the exposure to water vapors in its preparation for combustion. The authors of [5] calculated the mass of burnt material in their calculations from the results of the analysis of gaseous products of combustion on the CO_2 content, rather than the more precise determination of the mass of the substance based on the results of weighting. The given considerable error in the determination of the mass of CO_2 in the combustion products (1.0003 ± 0.0054) is 0.5% and is not taken into account in the errors of the enthalpy of formation of β-alanine.

We recommend considering the data of the present work as the most reliable. The reliability of the value of $\Delta_f H^0$ (cr) of β-alanine measured in the work is based on using a pure sample (confirmed by IR spectroscopy and the results of gaseous analysis of the products of combustion to CO_2) and precision equipment.

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