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The standard enthalpies of formation of L-asparagine and L-α-glutamine

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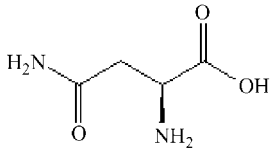
ABSTRACT

The energies of combustion of L-asparagine and L-α-glutamine were measured in a static bomb adiabatic calorimeter. Corrections were made for the heats due to the ignition of sample and for the nitric acid formation. The derived enthalpies of formation in solid state of asparagine monohydrate, nonhydrated asparagine and glutamine are respectively -1084.1 ± 3.0, -788.1 ± 4.7 and -834.3 ± 4.6 kJ mol^{-1}. The data of enthalpy of formation are compared with the literature values and with estimated values by means of group additivity, using parameters recommended by Domalski and Hearing. The discrepancies between experimental and calculated values are explained by considering the number and strength of intermolecular hydrogen bonds. The dehydration of asparagine monohydrate and the possible melting of the three amino acids were investigated by means of DSC. Glutamine melts without considerable decomposition at about 182 °C, while asparagines decompose during the fusion process (208 °C).

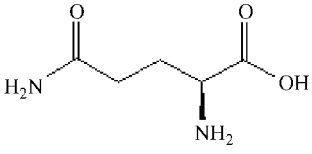
1. Introduction

The present work continues our thermochemical characterization of amino acids and of their derivatives. In previous papers the thermochemical properties of aspartic acid (isomers L-, D- and DL-) [1], of L-α-glutamic acid [2] and of the isomers of amino benzoic acid [3] were reported. Both compounds, which are the objects of the present study are important from the biological point of view.

Asparagine is one of the 20 most common natural amino acids in living organisms. It has carboxamide as the side chain's functional group. Like glutamine, it is considered a non-essential amino acid. The amide group does not carry a formal charge under any biologically relevant pH conditions. The amide is rather easily hydrolyzed, converting asparagine to aspartic acid. This process is thought to be one of the factors related to the molecular basis of aging [4].



asparagine



glutamine

Asparagine has a high propensity to hydrogen bond, since the amide group can accept two and donate two hydrogen bonds. Since the side chain can make efficient hydrogen bond interactions with the peptide backbone, asparagines are often found near the beginning and end of alpha helices, and in turn motifs in beta sheets of proteins. Its role can be thought as "absorbing" the hydrogen bond interactions, which would otherwise need to be satisfied by the polypeptide backbone. However asparagine is found on the surface as well as buried within proteins. It also provides key sites for N-linked glycosylation, modification of the protein chain with the addition of carbohydrate chains [5].

Glutamine, the amide of the glutamic acid is also one of the 20 amino acids encoded by the standard genetic code. It has an extra methylene group if compared with asparagine and consequently has more conformational entropy and thus is less useful in N-linking. Glutamine is also crucial in nitrogen metabolism. Ammonia (formed by nitrogen fixation) is assimilated into organic compounds by converting glutamic acid to glutamine. The enzyme that accomplishes this is called *glutamine synthetase*. Glutamine can, hence, be used as a nitrogen donor in the biosynthesis of many compounds, including other amino acids, purines, and pyrimidines [5].

The biochemical role of glutamine is as a donor of amino groups in many biosynthetic reactions. Asparagine is involved converting one amino acid to another as well. Glutamine donates an amino group, which reacts with β-aspartyl-AMP to form asparagine and free AMP [6]. Glutamine likewise asparagine, is important in the metabolism of the toxic ammonia in the human organism. Nervous system needs asparagine to maintain the equilibrium. The main use of glutamine as a supplement within the diet is as a means of replenishing the body's supply of amino acids that have been used during exercise, everyday activities or illness [7].

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Table 1
Combustion data of asparagine monohydrate.

m/g	ΔT/K	Q/J	q_i/J	q_b/J	q_n/J	$-\Delta_c u^{exp}$/J g^{-1}	$-\Delta_c U^{exp}$/kJ mol^{-1}	$-\Delta_c U^0$/kJ mol^{-1}
0.97309	1.388	13,074	51	565	31	12,770	1917.3	1916.9
1.56754	2.202	20,742	50	627	39	12,775	1918.0	1917.7
1.19172	1.695	15,965	51	621	20	12,815	1924.0	1923.7
1.51043	2.132	20,083	52	708	33	12,771	1917.5	1917.1
1.26701	1.791	16,869	52	603	18	12,783	1919.3	1918.9

Mean value $\Delta_c U^0$: −1918.9 kJ mol^{-1}; standard deviation: ±2.8.

Asparagine is isolated frequently in the form of a monohydrate, which dehydrates above 80 °C. The existing thermochemical data for the two forms of asparagine and for glutamine are incomplete and they result from old measurements [8,9]. The enthalpies of combustion and formation of hydrated and nonhydrated asparagine were reported in 1936 [8], while for glutamine only a value for the enthalpy of combustion, from 1957 [9], was found in the literature. Data about the enthalpies of phase transitions are missing.

2. Experimental

2.1. Reagents

Asparagine monohydrate and glutamine (Merck) of purity ≥99% and nonhydrated asparagine (Fluka) of purity >99.5% were used. The impurities certified by suppliers are for the greatest part aspartic and glutamic acids, respectively. Smaller amounts of other amino acids are present too. All these impurities have combustion heats per unit mass, very close to those of the compounds, so they should not affect significantly the accuracy of measurements.

The oxygen used was a high purity gas (>99.98%), from the SIAD Company.

2.2. Apparatus and experimental procedures

2.2.1. Combustion calorimetry

The adiabatic calorimeter with static bomb and the basic experimental procedures used in this investigation have been previously described [1]. 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 by means of a Beckmann thermometer. A difference between stable temperature values within 0.002 K was accepted.

The measurement was performed at 25.0 ± 0.2 °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 pellet was placed in the bombs crucible, in the proximity of the fuse, used for ignition. The combustion was run in the presence of a cotton fuse, as an auxiliary of combustion. The bomb was flushed with purified oxygen for 3 min, then sealed and filled with oxygen at the initial pressure mentioned above.

2.2.2. Calibration

The calorimeter constant was determined by means of benzoic acid combustion (standard reference material 39I from NIST). The certified value of the energy of combustion of benzoic acid is 26,454 ± 3.7 J g^{-1}. The calorimeter constant was calculated from the results of at least ten combustion runs, resulting in a value of 9420 ± 4 J K^{-1}. Some measurements, especially for nonhydrated asparagine were with modified bomb, having a constant of 9097 ± 3 J K^{-1}.

2.2.3. Analysis of the final solution

The walls and fittings of the bomb were washed with bidistilled water and the resulting solution was saved in a 200 mL flask. Three samples of solution of 50 mL were titrated separately, with 0.1N NaOH solution, using methyl orange as indicator. The mean value was used in 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 the value of the enthalpy of formation of nitric acid $\Delta_f H_{HNO_3}$, aq = −58.8 kJ mol^{-1} [10].

2.2.4. Differential scanning calorimetry

A PerkinElmer 1B DSC was used for the measurement of the enthalpy of fusion. The calorimeter was calibrated with indium ($\Delta_{fus}H$ = 28.46 J g^{-1}). Aluminium crucibles were used. In all measurements the calorimeter was operated at 4 mcal K^{-1} sensitivity and 4 K min^{-1} heating rate. The acquisition of experimental data was performed by means of a multimeter HP 34812A, serving as an interface with the computer, provided with the Benchlink data acquisition software. The acquired data were transferred to the Origin software for graphical processing. The area of the peaks corresponding to phase transitions of the standard and studied substances allowed the calculation of the latent heat of fusion of the later. The calibration constant, for the above mentioned operating conditions of the calorimeter amounted to 1.6204 J/unit area.

3. Results

3.1. Combustion energy of the samples

The results of the combustion measurements for asparagine monohydrate, nonhydrated asparagine and glutamine are given in Tables 1–3, respectively. The tables entries include: m, mass (g) of the burned substance, ΔT, temperature rise (K), Q, total measured energy (J), q_i, energy (J) used to ignite the sample (calculated from the mass of the fire and $\Delta_f h(Fe_2O_3)$ = 6.688 kJ g^{-1}), q_b energy of burned cotton (J) (calculated from the mass of cotton and $\Delta_c h_{cotton}$ = 16,137 J g^{-1}), q_{HNO_3}, energy of nitric acid formation (J), Δu^{exp} energy of combustion of sample (J g^{-1}), ΔU^{exp} molar energy of combustion (J mol^{-1}), $\Delta_c U^0$ standard molar energy of combustion (J mol^{-1}).

In order to bring the experimental values of energy of combustion to the standard state (T = 298.15 K and p = 101.325 kPa) corrections were made with the Washburn equation [11], recommended in the case of compounds with carbon, hydrogen and oxygen of the general formula $C_aH_bO_c$:

$$\Pi\% = \frac{-0.3ap_{initial}}{-\Delta_c U^{exp}}\left[1 - \frac{1.1(b-2c)}{4a} + \frac{2}{p_{initial}}\right] \quad (1)$$

where p stands for the initial oxygen pressure and $-\Delta U^{exp}$ for the experimental energy of combustion, a, b, and c being the numbers of carbon, hydrogen and oxygen from the chemical formula of the

Table 2
Combustion data of nonhydrated asparagines.

m/g	ΔT/K	Q/J	q_i/J	q_b/J	q_n/J	$-\Delta_c u^{exp}$/J g^{-1}	$-\Delta_c U^{exp}$/kJ mol^{-1}	$-\Delta_c U^0$/kJ mol^{-1}
0.61500	1.030	9,701	35	650	35	14,603	1929.4	1929.0
1.43638	2.405	21,877	37	830	66	14,580	1926.7	1926.3
1.24948	2.106	19,157	43	738	58	14,660	1936.9	1936.5
1.18003	2.009	18,277	47	984	55	14,568	1924.7	1924.3
1.09679	1.847	16,799	48	706	64	14,571	1925.1	1924.7
0.69400	1.149	10,823	44	610	52	14,578	1926.4	1926.0

Mean value $\Delta_c U^0$: −1927.8 kJ mol^{-1}; standard deviation: ±4.5.

Table 3
Combustion data of glutamine.

m/g	ΔT/K	Q/J	q_i/J	q_b/J	q_n/J	$-\Delta_c u^{exp}$/J g^{-1}	$-\Delta_c U^{exp}$/kJ mol^{-1}	$-\Delta_c U^0$/kJ mol^{-1}
1.15240	2.323	21,132	35	812	55	17,555	2565.7	2565.3
1.08980	2.174	19,777	38	632	50	17,487	2555.7	2555.3
1.15035	2.319	21,093	44	849	55	17,512	2559.4	2559.0
1.02028	1.968	18,543	61	603	30	17,494	2556.8	2556.4
0.81890	1.609	15,159	58	700	39	17,538	2563.2	2562.8
0.61533	1.232	11,602	55	700	42	17,554	2565.4	2565.0

Mean value $\Delta_c U^0$: −2560.6 kJ mol^{-1}; standard deviation: ±4.3.

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 [11].

The relative error in the determination of the heats of combustion was of 2–3‰.

3.2. Standard enthalpies of formation

The standard combustion enthalpies of the investigated compounds, in solid state were calculated using the equation:

$$\Delta_c H^0_{(s)} = \Delta_c U^0_{(s)} + \Delta nRT \quad (2)$$

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

For calculating the formation enthalpies, the following values were considered: $\Delta_f H^0_{CO_2}(g) = -393.151 \pm 0.013$ kJ mol^{-1}, $\Delta_f H^0_{H_2O}(l) = -285.83 \pm 0.042$ kJ mol^{-1} [12]. Our results for the heats of formation in solid state are shown in Table 4. They agree within the limits of experimental errors with those from the literature.

3.3. DSC runs

DSC runs in an open crucible for monohydrated asparagine showed two peaks, situated at about 85 and 208 °C (Fig. 1). They should correspond to dehydration and melting processes, respectively, according to the literature [13–15]. A process occurring in the range 80–84 °C, was observed by Bento et al. [16], by means of Raman spectroscopy, which was considered by them to be a phase transition. The dehydration process was confirmed by Rodante et al. [14], by thermogravimetry.

If we stopped the DSC before the second process (at about 195 °C) and weighed the crucible we observed a weight loss of about 14%, which stoichiometrically corresponds to the loss of a water molecule. For anhydrous asparagine, only the second peak is found, at approximately the same temperature. Rodante et al. [14] reported that the process considered as melting started at 194 °C, while different "melting" temperatures for the hydrated and anhydrous asparagines (215 and 235 °C, respectively) are found in Ref. [13]. This means that the second peak is not due, at least not exclusively, to the melting process [17]. Davies and Evans [18] reported that they could not prepare thin films of asparagine for IR spectroscopy, from the molten solid, which decomposes during melting.

This was not the case with glutamine, which did not show evidence of decomposition. A well-shaped peak was registered in the case of glutamine, at 182 °C, if tightly closed crucibles were used. This value compares well with the tabulated value [13], 186 °C, and with that of Rodante et al. [14], 183 °C. It seems that glutamine does not decompose in these conditions, so that the thermal effect may be attributed to melting.

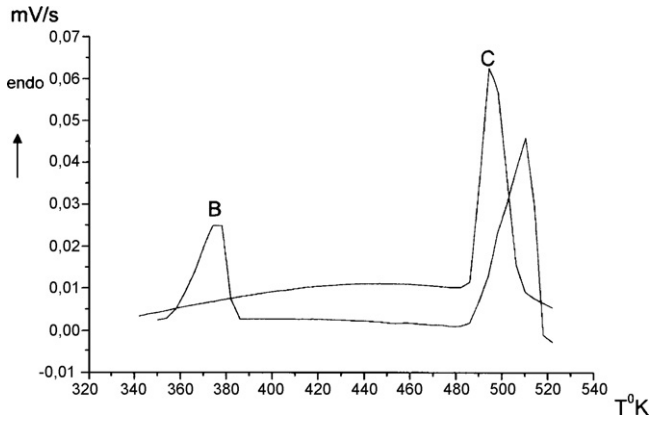

Fig. 1. The DSC runs of monohydrated (B) and nonhydrated (C) asparagines.

Table 4
Enthalpies of formation in solid state of the studied compounds.

Compound	$-\Delta_c H^0$/kJ mol^{-1}	$-\Delta_f H^0$/kJ mol^{-1}		
		Our value	Literature	Group additivity
Asparagine monohydrate	1917.7 ± 2.8	1084.1 ± 3.0	1086.6 ± 0.84 [4]	1076.88
Nonhydrated asparagine	1926.6 ± 4.6	789.4 ± 4.7	789.0 ± 0.9 [4]	791.05
Glutamine	2560.6 ± 4.4	834.3 ± 4.6	824.6 ± 0.9 [5]	820.46

Table 5
Thermal effects measured by DSC for monohydrated asparagines.

m/g	θ_{deh}/°C	ΔH_{deh}/kJ mol^{-1}	θ_{fus}/°C	ΔH (208 °C)/kJ mol^{-1}
0.01453	85.4	54.9	205.0	108.6
0.01481	82.0	50.4	211.3	104.9
0.01415	88.1	46.7	204.9	105.3
0.02832	84.4	47.0	206.4	101.9
0.01195	82.3	45.9	207.9	105.7
0.02445	84.3	53.3	204.6	103.2
Mean value	84.0 ± 2.2	49.7 ± 3.8	206.7 ± 2.6	105.0 ± 2.3

Table 6
Thermal effects measured by DSC for nonhydrated asparagines.

m/g	θ_{fus}/°C	ΔH/kJ mol^{-1}
0.00658	210.2	115.57
0.01244	208.6	112.35
0.01474	211.8	109.52
Mean value	210.2 ± 1.6	112.48 ± 3.02

Table 7
Enthalpies of melting of glutamine.

m/g	θ_{fus}/°C	$\Delta_{fus}H$/kJ mol^{-1}
0.0036	182.3	30.2
0.00446	180.0	28.2
0.0022	183.1	27.9
0.00195	184.0	30.5
0.00198	183.5	26.3
0.00258	180.2	30.8
Mean value	182.2 ± 1.7	29.0 ± 1.8

The thermal effects of the above mentioned processes were calculated from peak areas. Data are shown in Tables 5–7.

4. Discussion

The experimental enthalpies of formation are compared with values calculated by means of the group additivity method, in the form recommended by Domalski and Hearing [19]. As in the case with other amino acids, a zwitterion contribution was taken into account, because an α-amino acid moiety is present, independent of the functional group at the other end of the molecule. The agreement between the two kinds of values is fair for the anhydrous asparagine, but not for the hydrated one. The difference, for the later, comes from the interaction between amino acid and the water molecules. The energy of this interaction seems to be of the order of 7 kJ mol^{-1}.

The dehydration enthalpy of asparagine monohydrate (49.7 kJ mol^{-1}, Table 5) is compared with the heat of vaporization of water, at the same temperature, 41.4 kJ mol^{-1} [20]. The difference of about 8 kJ mol^{-1} is very close to that between the enthalpies of formation of hydrated and nonhydrated asparagines and accounts for the above mentioned molecular interaction, as well. A smaller value of only 44.9 kJ mol^{-1} is reported in Ref. [14] for the dehydration enthalpy.

The process observed on the thermograms of the two asparagines, starting at about 209 °C is accompanied by a too large thermal effect (over 100 kJ mol^{-1}) to be considered as only melting. Rodante et al. [14] has found a value of 98.5 kJ mol^{-1} for the enthalpy of this process. A decomposition process proceeds simultaneously, probably deamination, as a mass decrease of almost 15% is observed after the run in open crucible between 195 and 240 °C. A fast mass decrease was observed by Rodante et al. [14] too, at temperatures exceeding 215 °C. The enthalpy of the deamination reaction of asparagine to the monoamide of the maleic acid, calculated by means of the group additivity method [19] at 298 K amounts 112 kJ mol^{-1}, a value close to that resulting from the area of the above mentioned peak (Table 5).

The different "melting" temperatures for the hydrated and anhydrous asparagines found in reference [13], are not confirmed by our research. Dehydration which proceeds at a much lower temperature than melting, yields anhydrous asparagine.

A difference of about −14 kJ mol^{-1} is observed between our value of the enthalpy of formation of glutamine and that calculated by means of group additivity. In the structure of L-glutamine the side chain has a nearly planar extended conformation. It is staggered between the carboxylate and α-amino groups. As the crystal structure of most other hydrophilic amino acids, that of L-glutamine is made up of layers (monomolecular), involving head-to-tail sequences of amino acid molecules, connected by N–H–O hydrogen bonds [21]. In the L-glutamine crystal, as well as in that of the racemic, each molecule is involved in 5 hydrogen bonds with neighbour molecules [22] while in simple amino acids crystals only 3 such bonds are observed [23]. The additional hydrogen bonds in glutamine, built by the amide group, accounts at least partially, for the discrepancy of 14 kJ mol^{-1}, mentioned above. At the same time the hydrogen bonds built between the NH_3^+ and COO^- groups are somewhat shorter and consequently stronger, than those from other amino acids [21].

A similar disparity is not observed between the experimental value for the enthalpy of formation of nonhydrated asparagine and that calculated by group additivity. The information in the literature about the structure of its crystal is scarce. It seems that four hydrogen bond are present in the crystalline state. It is reasonable to consider that the system of hydrogen bonds in this crystal is less effective in stabilizing it, than in the case of glutamine, taking into account the tendency of asparagine to hydrate, in which state seven hydrogen bonds are formed [24].

The formation of hydrogen bonds in simple amino acids is not taken into account explicitly in the group additivity scheme. The zwitterion and carboxyl group contributions include probably this effect. This is an explanation of the agreement between experimental and calculated values of enthalpies of formation in the case of aspartic and glutamic acids [2,10,25] despite the four O–H–O hydrogen bonds formed by each molecule [26,27].

The difference of the enthalpies of formation in crystalline state of their amide species with the corresponding amino acids, aspartic acid and glutamic acid is 184 and 169 kJ mol^{-1}, respectively. Liebman et al. [28] obtain for pairs of simple carboxylic acids and amides, differences between solid phase enthalpies of formation between 180 and 190 kJ mol^{-1}, but the difference is lower than 180 kJ mol^{-1} in the case of dicarboxylic acids.

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