J Therm Anal Calorim (2017) 130:1145–1152
DOI 10.1007/s10973-017-6396-z

# A calorimetric study of L-, D- and DL-isomers of tryptophan

**Daniela Gheorghe[1] · Ana Neacşu[1] · Iulia Contineanu[1] · Speranţa Tănăsescu[1] · Ştefan Perişanu[2]**

Received: 28 April 2016 / Accepted: 7 April 2017 / Published online: 28 April 2017


**Abstract** The enthalpies of combustion and formation in solid state of tryptophan stereoisomers (L- and D-) and of their racemic mixture are reported (−406.6 ± 3.1, −407.4 ± 2.1, −410.7 ± 2.3 kJ mol$^{-1}$, respectively) and compared to the literature and calculated data. The transformation (melting—decomposition) points and the associated thermal effects were determined from DSC curves in the temperature range between ambient and beyond the melting—decomposition temperatures. Samples without further purification as well as dried samples were used in the experiments. The chiral purity of the enantiomers was checked by means of polarimetry. The values of the enthalpies of formation in crystalline and ideal gas state are compared with those calculated by group additivity methods. They highlight the relative stability of tryptophan and suggest the higher stability of the racemic mixture. The melting—decomposition process revealed by DSC and thermogravimetry is discussed in relationship with the previous treatment of samples.

✉ Ana Neacşu
anna_matache@yahoo.com

✉ Ştefan Perişanu
stefan.perisanu@upb.ro

Daniela Gheorghe
chiscan_danny@yahoo.com

Iulia Contineanu
icontineanu@yahoo.com

Speranţa Tănăsescu
stanasescu2004@yahoo.com

[1] Institute of Physical Chemistry "Ilie Murgulescu" of the Romanian Academy, 202 Splaiul Independentei, 060021 Bucharest, Romania

[2] Department of General Chemistry, Polytechnic University of Bucharest, 1 Polizu St., 011061 Bucharest, Romania

**Keywords** Combustion · Formation enthalpy · DSC · TG · Group additivity

## Introduction

Tryptophan (molar mass 204.225 g mol$^{-1}$) belongs to the heterocyclic amino acids being an indolic derivative and the most widely amino acid distributed in nature [1]. The principal role of L-Tryptophan in the human body is as a constituent of proteins. It is an essential amino acid in the human diet.

L-Tryptophan functions as a biochemical precursor for serotonin (a neurotransmitter), which is synthesized via tryptophan hydroxylase. It can be also metabolized into melatonin (a hormone allowing the entrainment of the circadian rhythms of several biological functions) as well as into vitamin B3 (nicotinic acid) [2].

D-Tryptophan is sometimes found in peptides that have been produced naturally [3].

A single literature value of the enthalpy of formation of L-Tryptophan is available, −413.99 kJ mol$^{-1}$ [4]. It was corrected to −415.27 kJ mol$^{-1}$ by Cox and Pilcher [5]. No data about the enthalpy of formation of D-Tryptophan were found in the literature as well as for the racemic mixture. Several direct experimental investigations of the thermodynamic properties of conformational isomers of amino acids have been carried out previously by us [6–10] Ribeiro da Silva et al. [11] and Yang et al. [12]. Other thermochemical data on amino acids were reported by the present authors, as well [13–15].

The aim of this paper is to measure for the first time the energy of combustion of D- and DL-Tryptophans and to compare the enthalpies of formation of all tryptophan's stereoisomers (value of the L-isomer determined both by us

and by Tsuzuki et al. in 1958) between them and with values calculated by group additivity. We also intended to bring more information about their thermal behavior in function of the isomer type and of previous thermal treatments.

## Experimental

### Materials

The reagents used in this work were obtained from Sigma-Aldrich (D-Tryptophan and DL-Tryptophan) mass fraction purities ≥98 and 99%, respectively, and from Merck (L-Tryptophan for biochemistry, assay ≥99%). The only impurities amounting at least 0.1%, (other than water) certified by the manufacturer consist of other amino acids (≤0.3%), having very close massic enthalpies of combustion to that of the main component so that they do not alter significantly the final results. The three compounds were used without further treatment (type 1 samples), or dried in a vacuum oven for 3 h at 363 K and preserved in a desiccator before use, in order to eliminate adsorbed water (type 2 samples).

Specific rotations $[\alpha]_{\lambda}^{25}$ of the investigated compounds were determined on solutions in deionized water for checking the amino acid optical purity. A 341 Perkin Elmer polarimeter was used in the D line of sodium, with glass cells (1 cm path length), at 298 K. Table 1 contains our values compared to the literature data [16, 17].

### Methods

#### *Combustion calorimetry*

A Parr Instruments model 6200 microprocessor-controlled isoperibol bomb calorimeter was used in combustion experiments together with type 2 samples. Temperature is measured with a high precision electronic thermometer using a specially designed thermistor sensor. Measurements were taken with 0.0001 K resolution. The jacket temperature is held constant for isoperibol operation. We have used the semimicro kit because the compounds under study were not available in large amounts. This bomb can handle samples that range from 25 to 200 mg. High purity oxygen 99.998% was used for combustion. Calorific-grade benzoic acid supplied by Parr, having heat of combustion 26.454 J $g^{-1}$, was used for the standardization of the combustion calorimeter. The determined calorimeter constant was 2338.3 ± 2.8 J $K^{-1}$.

**Table 1** Specific rotations of L-, D- and DL-Tryptophan

| Amino acid | Concentration/ g $10^{-2}$ $mL^{-1}$ | $\alpha_{\lambda}^{25}$ | $[\alpha]_{\lambda}^{25}$ | $[\alpha]_{\lambda}^{25}$ (literature) |
|---|---|---|---|---|
| L-Tryptophan | 1.004 | −0.033 | −32.87 | −31.50 [16] |
| D-Tryptophan | 0.504 | +0.017 | 33.73 | 32.45 [17] |
| DL-Tryptophan | 0.7532 | 0 | 0 | – |

The samples were pressed into pellets of 3 mm diameter. The pellets were weighed with a Mettler-Toledo microbalance with an accuracy of ±2 × $10^{-6}$ g. The final solution from the bomb was analyzed for the presence of nitric acid (about 20% from the total nitrogen) by titration with solution of $Na_2CO_3$ 0.1 mol $L^{-1}$. The heat due to nitric acid formation was obtained using the value of the enthalpy of formation of nitric acid solution—$\Delta_f H_{HNO3}$, aq = −58.8 kJ $mol^{-1}$ [5].

At least five runs were retained for each isomer. Some runs were rejected because of doubt about combustion completeness. In runs used in data calculation, there was no evidence of soot formation in the bomb. Typical results of the combustion measurements for the three compounds are given in Table 2. The uncertainties represent two standard deviations of the mean. $\Delta U$(fuse) and $\Delta U$(ign) were calculated from the mass of cotton and $\Delta_c u$(cotton) = 16.240 ± 20 J $g^{-1}$ [18] and from the mass of the fire and $\Delta_c u$(Ni–Cr) = 5.86 kJ $g^{-1}$ (certified by the fabricant), respectively. 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 approximate equation, recommended in the case of compounds with carbon, hydrogen and oxygen of $C_aH_bO_c$ general formula [5]:

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

where $p_{\text{init}}$ stands for the initial oxygen pressure and $-\Delta U^{\text{exp}}$ for the experimental energy of combustion, $a$, $b$ and $c$ being the numbers of carbon, hydrogen and oxygen atoms from the molecular formula of the compound, respectively. $\Pi$ is calculated in percents from the experimental value. The above equation applies fairly well in the case of nitrogen-containing compounds as well [5].

#### *Thermoanalytical methods*

*DSC* A Perkin Elmer power-compensated DSC (model 8500) was used for the measurement of the enthalpies of the processes occurring during heating (fusion and decomposition). All measurements were taken in sealed pans and inert atmosphere ($N_2$). The scan rate was 10 K $min^{-1}$.

The calorimeter was calibrated with indium ($\Delta_{fus}H = 28.46$ J $g^{-1}$). The areas of the peaks corresponding to the standard and studied substances were used

**Table 2** Typical results of combustion experiments for L-, D- and DL-Tryptophan

| Amino acid | L-Tryptophan | | D-Tryptophan | | DL-Tryptophan | |
|---|---|---|---|---|---|---|
| Sample | 1 | 2 | 1 | 2 | 1 | 2 |
| $m_p$/g | 0.086521 | 0.085006 | 0.081549 | 0.081076 | 0.073958 | 0.07664 |
| $\Delta T$/K | 1.0458 | 1.0277 | 0.9987 | 0.9941 | 0.8978 | 0.9443 |
| $Q$/J | 2445.43 | 2433.51 | 2335.30 | 2324.54 | 2099.36 | 2208.09 |
| $q_{HNO3}$/J | 6.56 | 5.86 | 5.71 | 5.95 | 5.29 | 5.73 |
| $q_i$/J | 11.27 | 18.68 | 11.41 | 11.90 | 24.65 | 13.56 |
| $q_{cotton}$/J | 38.83 | 64.16 | 69.49 | 70.61 | 30.47 | 75.66 |
| $-\Delta_c u$/J g$^{-1}$ | 27,609.2 | 27,583.9 | 27,574.6 | 27,580.0 | 27,569.1 | 27,570.9 |
| $-\Delta_c U$/kJ mol$^{-1}$ | 5638.62 | 5633.47 | 5631.57 | 5632.67 | 5630.44 | 5630.80 |
| $-\Delta_c U°$/kJ mol$^{-1}$ | 5637.76 | 5632.61 | 5630.71 | 5631.81 | 5629.58 | 5629.94 |
| Mean value: $-<\Delta_c U°>$/kJ mol$^{-1}$ | 5634.5 ± 3.0 | | 5633.7 ± 2.3 | | 5630.4 ± 2.3 | |

$m_p$—mass of compound burned in each experiment; $\Delta T$—temperature rise; $Q$—total evolved heat observed; $q_i$—energy used to ignite the sample; $q_{cotton}$—energy of burned cotton; $q_{HNO3}$—energy of nitric acid formation; $\Delta_c u$—massic energy of combustion of the sample, molar energy of combustion; $\Delta_c U°$—non-corrected molar energy of combustion; $\Delta_c U°$—standard molar energy of combustion

to calibrate the instrument and calculate the thermal effects of the investigated tryptophans.

*TG* Thermogravimetric measurements were taken between ambient and 723 K, by means of TGA–DTA/DSC SETSYS Evolution 17 in argon atmosphere. Metallic substances of 99.999% purity were used to perform the calibration in temperature, together with alumina crucibles containing samples weighing 1.5–2 mg. The scan rate was 10 K min$^{-1}$.

*FT–IR* The various functional groups present in the sample were identified and confirmed by recording the FT–IR spectrum, at room temperature, in the range 4000–625 cm$^{-1}$, using Thermo Scientific Nicolet iS10 FT–IR spectrophotometer with an attenuated total reflection (ATR) method.

## Results

### Combustion energy

For calculating the enthalpies of formation, the following values were considered: $\Delta_f H°_{CO_2}(g) = -393.51 \pm 0.13$ kJ mol$^{-1}$, $\Delta_f H°_{H_2O}(g) = -285.83 \pm 0.042$ kJ mol$^{-1}$ [19]. Our data for the solid-state enthalpies of formation are shown in Table 3, together with the literature values [4, 5].

The values of the enthalpies of formation of the enantiomers are identical within experimental error, while that of the racemic form seems to be more negative.

### DSC

The DSC determinations were performed on two types of samples: type 1 (Fig. 1) and type 2 (Fig. 2).

Only one endothermic peak (with a shoulder) is recorded for the enantiomers, in the temperature range 540–577 K in the case of type 1 samples. The temperature range of the peaks is considerably higher than that of other amino acids (under 520 K) (Table 4).

It may be seen that the curves of the two enantiomers are similar. However, differences of 1–4 K between the characteristic temperatures of the peaks are observed, which become smaller at lower scan rates. They are due to different morphologies of the samples. A similar behavior was observed in the case of the isomers of proline [6], threonine [7], aspartic acid [9] and serine [10]. Our maximum temperatures of the peaks of the enantiomers (570 and 566 K) are in reasonable agreement with most literature values, i.e., 570 K [20], 563 K [21], but not with the temperature

**Table 3** Enthalpies of combustion and formation of isomeric tryptophans

| Amino acid | $-\Delta_c U°$/kJ mol$^{-1}$ | $-\Delta_c H°$/kJ mol$^{-1}$ | $-\Delta_f H°$/kJ mol$^{-1}$ (this work) | $-\Delta_f H°$/kJ mol$^{-1}$ (literature) |
|---|---|---|---|---|
| L-Tryptophan | 5634.5 ± 3.0 | 5637.0 ± 3.0 | 406.6 ± 3.1 | 413.99 [4] |
| | | | | 415.27 [5] |
| D-Tryptophan | 5633.7 ± 2.0 | 5636.2 ± 2.0 | 407.4 ± 2.1 | – |
| DL-Tryptophan | 5630.4 ± 2.3 | 5632.9 ± 2.3 | 410.7 ± 2.3 | – |

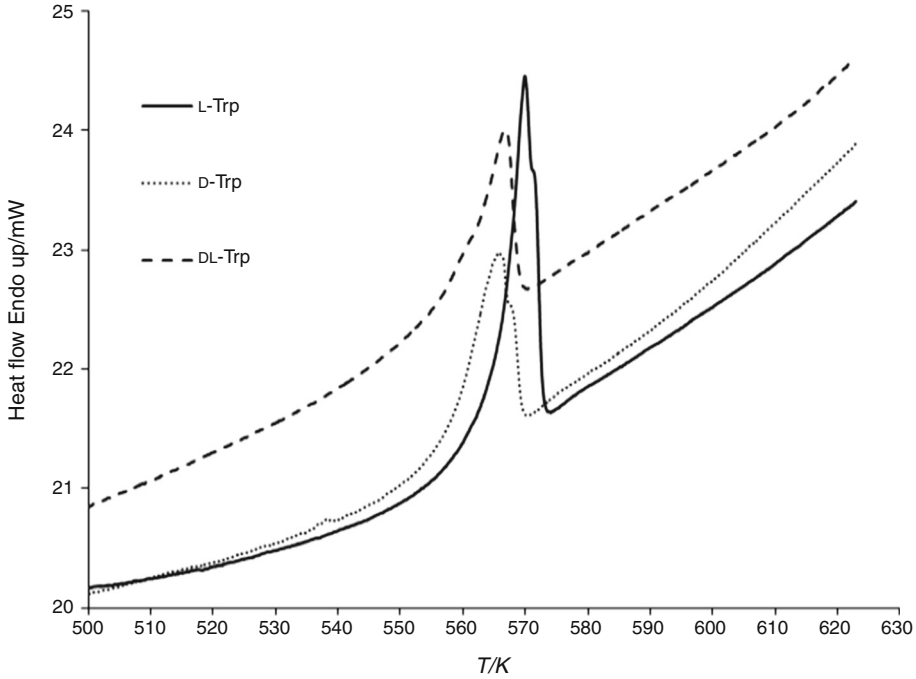


**Fig. 1** DSC curves of L-, D- and DL-Tryptophan (type 1 samples)

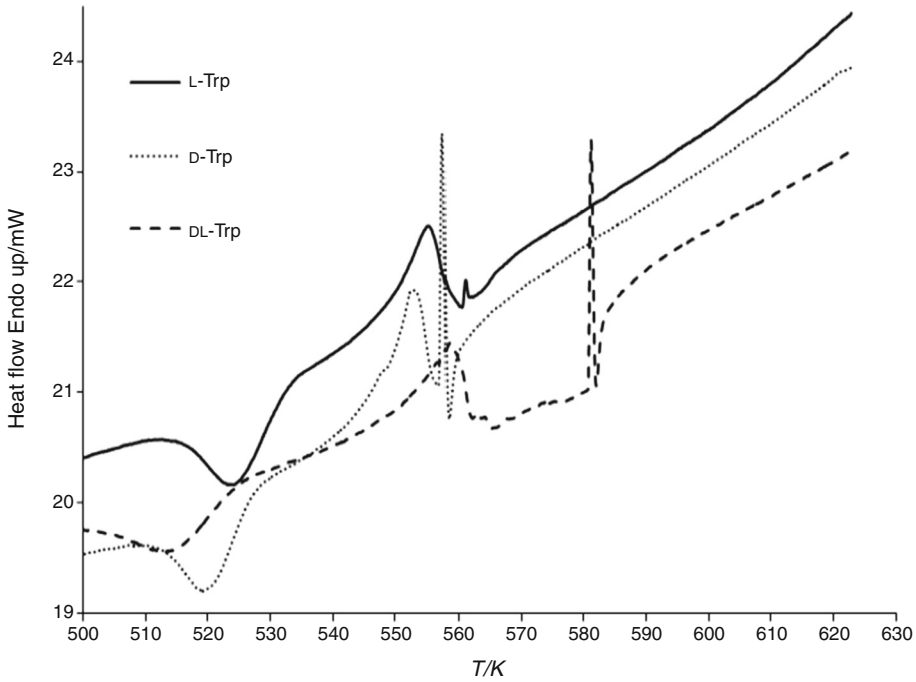


**Fig. 2** DSC curves of L-, D- and DL-Tryptophan (type 2 samples)

range reported by authors [22] (517–541 K). The thermal effect (62.5 kJ $mol^{-1}$) is in relative agreement with that obtained by Rodante et al. [20].

The parameters of the curve of the racemic mixture are similar to those of enantiomers.

For type 2 samples (Fig. 2), an exothermic peak is recorded first in the range 513–531 K, which is followed by two endothermic effects. The maxima of the first endothermic peaks of the three isomers are situated at somewhat lower temperatures than those found for type 1 samples. As regards the second endothermic peak, it is different for the three isomers. This peak is situated around 560 K for the enantiomers and is much smaller for the L-Enantiomer than for D-. In the case of the racemic mixture, this peak is situated at 580 K. (Table 5).

## Thermogravimetry

Thermogravimetric records for type 2 samples show a first step fast mass loss of 20–24% starting at 526–538 K,

**Table 4** DSC data of isomeric tryptophans (type 1 samples, 10 K $min^{-1}$)

| Amino acid | $T_{onset}$/K | $T_{max}$/K | $T_{end}$/K | $\Delta H$/kJ $mol^{-1}$ |
|---|---|---|---|---|
| L-Tryptophan | 543 ± 0.8 | 569 ± 1.2 | 576 ± 0.47 | 62.5 ± 0.9 (melting- decomp.) |
| D-Tryptophan | 542 ± 1.6 | 566 ± 2 | 571 ± 1.2 | 58.3 ± 0.8 (melting- decomp.) |
| DL-Tryptophan | 548 ± 1.2 | 566 ± 2.8 | 570 ± 1.6 | 65.3 ± 1.2 (melting- decomp.) |

**Table 5** DSC data of isomeric tryptophans (type 2 samples, 10 K $min^{-1}$)

| Amino acids | Peak | $T_{onset}$/K | $T_{max}$/K | $T_{end}$/K | $\Delta H$/kJ $mol^{-1}$ |
|---|---|---|---|---|---|
| L-Tryptophan | 1 | 514 ± 1 | 523 ± 1 | 529 ± 1 | −51.0 ± 1.7 (crystallization) |
| | 2 | 552 ± 1 | 556 ± 1 | 558 ± 1 | 38.8 ± 1.4 (melting- decomp.) |
| | 3 | 560 ± 1 | 562 ± 1 | 563 ± 1 | 1.1 ± 0.3 (decomposition) |
| D-Tryptophan | 1 | 514 ± 1 | 520 ± 1 | 526 ± 1 | −33.3 ± 1.9 (crystallization) |
| | 2 | 549 ± 1 | 553 ± 1 | 557 ± 1 | 28.4 ± 1.1 (melting- decomp.) |
| | 3 | 556 ± 1 | 557 ± 1 | 558 ± 1 | 6.4 ± 0.8 (decomposition) |
| DL-Tryptophan | 1 | 508 ± 1 | 513 ± 1 | 523 ± 1 | −50.3 ± 0.9 (crystallization) |
| | 2 | 554 ± 1 | 558 ± 1 | 562 ± 1 | 54.6 ± 2.1 (melting- decomp.) |
| | 3 | 580 ± 1 | 581 ± 1 | 582 ± 1 | 7.1 ± 1.5 (decomposition) |

**Table 6** Thermogravimetric data of isomeric tryptophans (type 2 samples, 10 K $min^{-1}$)

| Amino acid | $\Delta m$/%/T/K | $\Delta m$/%/T/K | $\Delta m$/%/723.15 K |
|---|---|---|---|
| L-Tryptophan | −21.76/538.15–587.15 | −60.86/587.15–723.15 | −83.24 |
| D-Tryptophan | −20.04/533.15–583.15 | −58.70/583.15–723.15 | −82.03 |
| DL-Tryptophan | −24.57/526.15–581.15 | −52.85/581.15–723.15 | −81.40 |

followed by a continuous mass decrease in the sample. At 723 K, a mass reduction of over 80% is observed for both L- and D-Enantiomers and the racemic mixture. (Table 6; Fig. 3) Our curves are similar to that reported by Mello et al. [23] for the L-Enantiomer. The same authors state that only small molecules ($NH_3$, $CO_2$, $H_2O$) evolved during the first step. Table 7 shows comparative data of thermal analysis data on tryptophan of different authors.

## FTIR

No significant differences were observed between samples dried in a vacuum oven and those which were not subjected to any treatment.

## 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 [24]. As in the case of other amino acids, a zwitterion contribution is taken into account, in the case of the crystalline state. The value of the group parameter [N–$HC_BC_d$] was not found, but it was observed that the parameters for the groups [N–$H(C_B)_2$] and [N–$H(C_d)_2$] are identical. It was concluded that in this case the group parameter value does not depend on the type of $sp^2$ carbon atom so that the same value was used for [N–$HC_BC_d$]. A comparison between experimental and calculated values is given in Table 8.

The experimental and estimated enthalpies of formation in solid state are in fair agreement. Tryptophan differs from this point of view from other amino acids, such as asparagine, glutamine or serine, by the lack of additional stabilization of its molecule, coming from a large number of hydrogen bonds. In the tryptophan crystal, only three hydrogen bonds per molecule are present less than in the case of other amino acids. The hydrogen bond lengths and aromatic interactions show that the racemic structure is more efficiently packed than that of enantiomers, as resulting from X-ray diffraction studies [25, 26]. Consequently, the enthalpy of formation of the DL-isomer is expected to be more negative than those of enantiomers, which seems consistent with our data (Table 8).

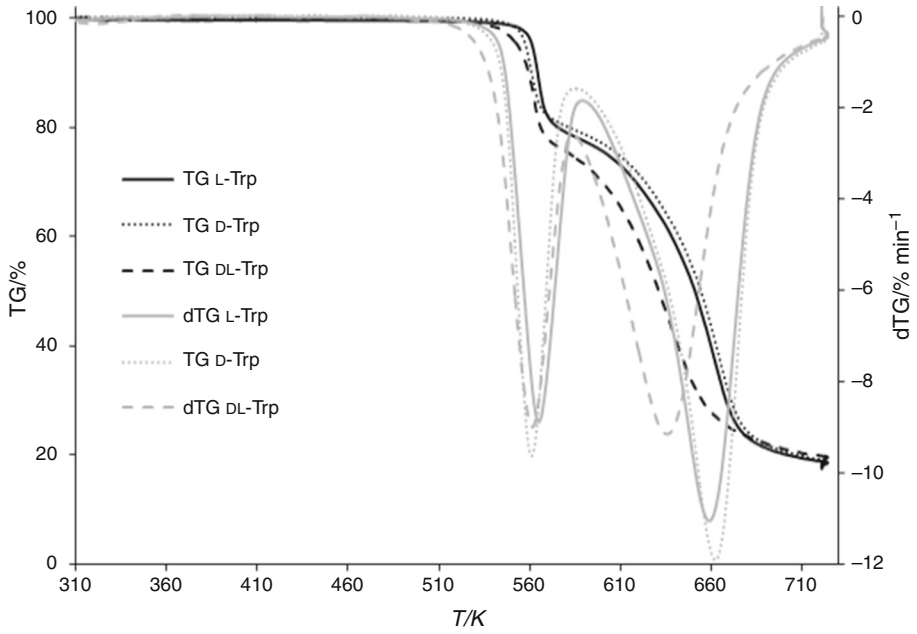


**Fig. 3** TG–DTG curves of L-, D- and DL-Tryptophan (type 2 samples)

**Table 7** Comparative values of melting—decomposition parameters of L-Tryptophan, reported by different researchers

| $T_{onset}$/K | $T_{peak}$/K | $T_{end}$/K | Mass loss % | $\Delta H$/kJ mol$^{-1}$ | Method | Reference |
|---|---|---|---|---|---|---|
| 543 | 570 | 573 | | 63.43 | DSC | This work (type1) |
| 551 | 555 | 558 | | 38.0 | DSC | This work (type 2) Peaks 2, 3 |
| 538 | | 587 | 21.76 | | TG | This work (type 2) |
| 538 | 565 | 586 | | | DTG | This work (type 2) |
| 542 | | | | | DETA | (type 2) [10] |
| 543 | | 590 | 17.45 | | TG | [20] |
| 550 | 570 | 590 | | 76.98 | DSC | [20] |
| 513 | | | | | TG | [22] |
| 517 | 528 | 541 | | | DTA | [22] |
| | 537 | | | | DTG | [22] |
| 551 | 563 | | | | | [21] |
| 566 | | | | | DSC | [31] |
| | 577 | | | | DSC | [23] |

**Table 8** Experimental and calculated enthalpies of formation of Tryptophan

| Amino acid | $-\Delta_f H°$/kJ mol$^{-1}$ (cr,exp) this work | $-\Delta_f H°$/kJ mol$^{-1}$ (cr,calc.) | $-\Delta_f H°$/kJ mol$^{-1}$ (g,exp) | $-\Delta_f H°$/kJ mol$^{-1}$ (g,calc.) |
|---|---|---|---|---|
| L-Tryptophan | 406.6 ± 3.1 | 405.6 [24] | 220.0 | 227.8 [24] |
| D-Tryptophan | 407.4 ± 2.1 | 405.6 [24] | 220.8 | 227.8 [24] |
| DL-Tryptophan | 410.7 ± 2.3 | – | 224.1 | – |

The enthalpy of sublimation of tryptophan could hardly be determined because this compound decomposes during evaporation, even at low pressure [27–29]. Tyunina et al. [27] reported a value of 186.6 ± 4.1 kJ mol$^{-1}$ for the standard enthalpy of sublimation. This value was used in deriving the ideal gas-state enthalpy of formation from Table 8, which is compared with group additivity calculated values [24]. The gas-state experimental and calculated values agree within the cumulated errors.

The endothermic peaks observed on the DSC curves are due to melting accompanied by decomposition. The melting points usually found for amino acids are irrelevant since they decompose, so that the "melting" points vary according to the experimental conditions used by the researcher [30].

The different melting behavior of type 1 and type 2 samples is consistent with the dielectric investigation of premelt of amino acids by Matthews and Riga, who showed a clear difference between the samples taken directly from the bottle (neat), those heated prior to dielectric analysis, and those dried in a desiccator. Tryptophan is an interesting case because its neat and heat-treated samples showed no premelt peak. The absence of a premelt peak is typically associated with a greater amorphous content; in this case, it is possible that desiccation encouraged crystallization of the type 2 samples [31, 32].

As regards the exothermic peak observed in the case of type 2 samples, it is due probably to a crystallization process [33]. As a result of the elimination of water traces during the previous heating, a partially amorphous structure was obtained which transforms into a fully crystalline beyond 500 K.

## Conclusions

The enthalpies of formation of all stereoisomers of tryptophan are reported and discussed in correlation with their structure. A different behavior on heating was observed for samples dried in a vacuum oven compared to those used without any previous treatment.

**Acknowledgements** Support of the EU (ERDF) and Romanian Government, that allowed for acquisition of the research infrastructure under POSCCE O 2.2.1 project INFRANANOCHEM—Nr. 19/01.03.2009, is gratefully acknowledged.

## References

1. Sidransky H. Tryptophan: biochemical and health implications. Florida: CRC Series in Modern Nutrition; 2002.
2. Ahmad F, Moat AG. Nicotinic acid biosynthesis in prototrophs and tryptophan auxotrophs of saccharomyces cerevisiae. J Biol Chem. 1966;241:775–80.
3. Pallaghy PK, Melnikova AP, Jimenez EC, Olivera BM, Norton RS. Solution structure of contryphan-R, a naturally occurring disulfide-bridged octapeptide containing D tryptophan: comparison with protein loops. Biochem. 1999;38(35):11553–9.
4. Tsuzuki T, Harper DO, Hunt H. Heats of combustion. VII. The heats of combustion of some amino acids. J Phys Chem. 1958;62:1594–5.
5. Cox JD, Pilcher G. Thermochemistry of organic and organometallic compounds. London: Acad. Press; 1970.
6. Contineanu I, Neacsu A, Zgirian R, Tanasescu S, Perisanu S. The standard enthalpies of formation of proline stereoisomers. Thermochim Acta. 2012;537:31–5.
7. Contineanu I, Neacsu A, Gheorghe D, Tanasescu S, Perisanu S. The thermochemistry of threonine stereoisomers. Thermochim Acta. 2013;563:1–5.
8. Contineanu I, Marchidan DI. The enthalpies of combustion and formation of D-Alanine, L-Alanine, DL-Alanine and β-alanine. Rev Roum Chim. 1984;29:43–8.
9. Contineanu I, Marchidan DI. The enthalpies of combustion and formation of L-, D-, and DL-Aspartic acids. Rev Roum Chim. 1997;42:605–8.
10. Neacşu A, Gheorghe D, Contineanu I, Tănăsescu S, Perişanu S. A thermochemical study of serine stereoisomers. Thermochim Acta. 2014;595:1–5.
11. Ribeiro da Silva MAV, Ribeiro da Silva MDMC, Santos LMNBF. Standard molar enthalpies of formation of crystalline L-, D- and DL-Valine. J Chem Thermodyn. 2000;32:1037–43.
12. Yang XW, Liu JR, Gao SL, Hou YD, Shi QZ. Determination of combustion energies of thirteen amino acids. Thermochim Acta. 1999;329:109–15.
13. Contineanu I, Chivu L, Perisanu S. The enthalpies of combustion and formation of L-α-glutamic and 6-amino-hexanoic acids. J Therm Anal Calorim. 2005;82:3–6.
14. Contineanu I, Perisanu S, Neacsu A. Enthalpies of combustion and formation of isomers of the amino-benzoic acid. Rev Roum Chim. 2006;51:323–7.
15. Contineanu I, Neacsu A, Perisanu S. The standard enthalpies of formation of L-Asparagine and L-α-Glutamine. Thermochim Acta. 2010;497:96–100.
16. Dunn MS, Frieden EH, Stodard MP, Brown HV. Quantitative investigations of amino acids and peptides: IX. some physical properties of l(-)-histidine. J Biol Chem. 1942;144:487–500.
17. Berg CP. The resolution of DL-Tryptophane. J Biol Chem. 1933;100(79–83):18.
18. Coops J, Jessup RS, van Nes K. Calibration of calorimeters for reactions in a bomb at constant volume. In: Rossini FD, editor. Experimental thermochemistry (Chapter 3), vol. 1. New York: Interscience; 1956.
19. CODATA Bulletin nr. 28 (April 1978). Recommended key values for thermodynamics; 1977.
20. Rodante F, Marrosu G, Catalani G. Thermal analysis of some a-amino acids with similar structures. Thermochim Acta. 1992;194:197–213.
21. Weast RC. 58-th Handbook of chemistry and physics. Cleveland, OH: CRC Press; 1977–1978. p. C534.
22. Rodriguez-Mendez L, Rey FJ, Martin-Gil J, Martin-Gil FJ. DTG and DTA studies on amino acids. Thermochim Acta. 1988;134:73–8.
23. Mello GS, Cardoso AP, Oliveira EWRS, Siqueira AB. Tryptophan. A proposal of the mechanism of thermal decomposition. J Therm Anal Calorim. 2015;122:1395–401.
24. Domalski ES, Hearing ED. Estimation of the thermodynamic properties of C–H–N–O–S–Halogen compounds at 298.15 K. J Phys Chem Ref Data. 1993;22:805–1160.
25. Hübschle CB, Messerschmidt M, Luger P. Crystal structure of DL-Tryptophan at 173 K. Cryst Res Technol. 2004;39(3):274–8.
26. Görbitz CH, Törnroos KW, Day G. A single crystal investigation of L-Tryptophan with $Z' = 16$. Acta Crystallogr B. 2012;68:549–57.
27. Tyunina VV, Krasnov AV, Tyunina EY, Badelin VG, Girichev GV. Enthalpy of sublimation of natural aromatic amino acids determined by Knudsen's effusion mass spectrometric method. J Chem Thermodyn. 2014;74:221–6.

28. Clyde DD, Svec H. Vapor pressures of some amino acids, U.S. Atomic Energy Commission Research and Development Report. Chemistry (UC-4) TID 1964;4500.
29. Gaffney JF, Pierce RC, Friedman L. Mass spectrometer study of α-amino acids. J Am Chem Soc. 1977;99:4293–8.
30. Wesolowski M, Erecinska J. Relation between chemical structure of amino acids and their thermal decomposition. J Therm Anal Calorim. 2005;82:307–13.
31. Mathews ME, Riga ATJ. Effects of thermal history on solid state and melting behavior of amino acids. Therm Anal Calorim. 2009;96:673–6.
32. Matthews ME, Atkinson I, Presswala L, Najjar O, Gerhardstein N, Wei R, Rye E, Riga AT. Dielectric classification of d- and l-amino acids by thermal and analytical methods. Therm Anal Calorim. 2008;93:281–7.
33. Rawlinson C. Differential scanning calorimetry. Cooking with chemicals. www.mmsconferencing.com/pdf/eyp/c.rawlinson.pdf.