



# A thermochemical study of serine stereoisomers



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## ABSTRACT

The combustion and formation enthalpies in the solid state of serine stereoisomers (L- and D-) and of their racemic mixture,  $-736.6 \pm 2.1$ ,  $-739.4 \pm 2.3$ ,  $-744.0 \pm 1.2$  kJ mol<sup>-1</sup> are reported and compared to literature and calculated data. The transformation points (melting and decomposition) and the associated thermal effects were determined from the DSC thermograms in the temperature range between 300 K and beyond the melting–decomposition temperatures. The high negative values of the enthalpies of formation (over  $-700$  kJ mol<sup>-1</sup> for a molecular formula C<sub>3</sub>H<sub>7</sub>NO<sub>3</sub>) highlight the stability of serine. Important differences between enantiomers and racemic are noticed. The decomposition mechanism is discussed in relation to the data obtained by means of DSC.

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## 1. Introduction

The present work continues our thermochemical characterization of amino acids and of their derivatives. In previous papers the thermochemical properties of the following compounds were reported: alanine [1], aspartic acid (stereoisomers L-, D- and DL-) [2], L- $\alpha$ -glutamic acid [3], the isomers of amino benzoic acid [4], asparagine (anhydrous and monohydrate), glutamine [5], proline (stereoisomers L-, D- and DL-) [6] and of threonine (stereoisomers L-, D- and DL-) [7].

L-Serine (L-ser) is one of the proteinogenic amino acids. It is not essential to the human diet, since it is synthesized in the body from other metabolites, including glycine.

Serine is hydrophilic due to the hydrogen bonding capacity of the hydroxyl group between its molecules and with polar substrates.

L-Serine is required for the metabolism of fat, tissue growth and the immune system as it assists in the production of immunoglobulins and antibodies. It is a constituent of brain proteins and nerve coverings and is also important in the formation of cell membranes. It is also involved in the metabolism of purines and pyrimidines and consequently in the function of RNA and DNA.

D-Serine, synthesized in the brain from L-serine, serves as both a neurotransmitter and a gliotransmitter. D-Serine, present as a signaling molecule in the brain, was the second D-amino acid discovered to naturally exist in humans, soon after the discovery of D-aspartic acid [8–10].

The literature values for the enthalpy of formation of L-serine range between  $-730.2$  and  $-740.3$  kJ mol<sup>-1</sup> [11–14]. No data about the enthalpy of formation of D-serine was found in literature and only one for the racemic ( $-739.0$  kJ mol<sup>-1</sup>) [15]. Direct experimental investigations of the thermodynamic properties of conformational isomers with chiral centers have been carried out occasionally [1,2,6,7,16].

The aim of this paper is to establish the most probable values for the enthalpies of formation of serine's stereoisomers and to bring more information about the thermal behavior of serines.

## 2. Experimental

Reagents, L-, DL-, and D-serine used in this work were obtained commercially from Sigma–Aldrich (DL- and D-isomers) mass fraction purities  $\geq 98\%$  and from Merck (L-serine for biochemistry). The three compounds were used without further purification, but they were dried at 90 °C and preserved in a desiccator before use. Impurities contained by amino acid reagents, as reported by producers, consist of compounds with similar structures, mainly other amino acids, having specific heats of combustion very close to that of the main component.

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High purity oxygen 99.998% was used for combustion. Calorific grade benzoic acid supplied by Parr, having heat of combustion  $26.454 \text{ J g}^{-1}$ , was used for the standardization of the combustion calorimeter.

A Parr Instruments model 6200 microprocessor controlled isoperibol oxygen bomb calorimeter was used in combustion experiments. 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 semi micro kit because the compounds under study were not available in large amounts. This bomb can handle samples that range from 25 to 200 mg. The samples were pressed into pellets of 3 mm diameter. The pellets were weighed with a Mettler-Toledo microbalance with an accuracy of  $\pm 2 \times 10^{-6} \text{ g}$ . The determined calorimeter constant was  $2338.3 \pm 2.8 \text{ J K}^{-1}$ .

The final solution from the bomb was analyzed for the presence of nitric acid (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 solution  $-\Delta_f H(\text{HNO}_3, \text{aq}) = -58.8 \text{ kJ mol}^{-1}$  [17].

A PerkinElmer power compensated DSC (model 8500) was used for the measurement of the enthalpies of the processes occurring during heating (fusion and decomposition). The calorimeter was calibrated with indium ( $\Delta_{\text{fus}}H = 28.46 \text{ J g}^{-1}$ ). The areas of the peaks corresponding to the standard and studied substance were used to calibrate the instrument and calculate the thermal effects of serines.

### 3. Results

#### 3.1. Combustion energy

At least 6 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 1. The uncertainties represent two standard deviations of the mean.  $\Delta U_{(\text{fuse})}$  and  $\Delta U_{(\text{ign})}$  were calculated from the mass of cotton and  $\Delta_c U_{(\text{cotton})} = 16.240 \text{ J g}^{-1}$  [18] and from the mass of the fire and  $\Delta_c U_{(\text{Ni-Cr})} = 5.86 \text{ kJ g}^{-1}$  (certified by the fabricant), respectively. In order to bring the experimental values of energy of combustion to the standard state ( $p = 101.325 \text{ kPa}$ ) at the reference temperature  $T = 298.15 \text{ K}$ , were made with the Washburn approximate equation, recommended in the case of

compounds with carbon, hydrogen and oxygen of  $\text{C}_a\text{H}_b\text{O}_c$  general formula [19]:

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

where  $p$  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 chemical 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 compounds as well [17].

The relative error in the determination of the heats of combustion was less than 1.9%. For calculating the enthalpies of formation, the following values were considered:  $\Delta_f H^0(\text{CO}_2, \text{g}) = -393.51 \pm 0.13 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^0(\text{H}_2\text{O}, \text{l}) = -285.83 \pm 0.042 \text{ kJ mol}^{-1}$  [20]. Our data for the solid-state enthalpies of formation are shown in Table 2, together with literature values [11–15].

The enthalpies of formation of the enantiomers differ by much less than the cumulated errors, while that of the racemic is more negative, probably because of the mixing effect.

#### 3.2. DSC

The DSC thermograms of the three isomeric serines are shown in Fig. 1. Two successive major peaks and a shoulder are recorded for the enantiomers, in the temperature range 223–234 °C. The onset, maximum and end temperatures of the peaks measured at  $10 \text{ K min}^{-1}$  are shown in Table 3.

It may be seen that the thermograms of the two enantiomers are similar. However, differences of 1–3 °C between the characteristic temperatures of the peaks (which become smaller at lower scan rates) are observed, due to different morphologies of the samples. A similar behavior was observed in the case of the isomers of proline [6], serine [7] and aspartic acid [21]. Our maximum temperatures of the first peak of the enantiomers (227.5 and 226.4 °C) are in reasonable agreement with most literature values, i.e., 228 °C [22], 226 °C [23], 232 °C [24], but not with the temperature range reported by Yablokov et al. [25] (198–222 °C). The total thermal effects are close too, but they are divided differently between the two peaks.

Two major endothermic peaks are present at higher temperatures (240–249 °C) for the racemic. This behavior is associated with a higher stability of the later, than the enantiomers, in agreement with its larger negative enthalpy of formation. Serine differs from this point of view from other amino acids that show

**Table 1**  
Typical results of combustion experiments for L-, D- and DL-serine.

Amino acid	L-Serine		D-Serine		DL-Serine	
Sample	1	2	1	2	1	2
$m_p/\text{g}$	0.127617	0.148071	0.133264	0.148922	0.084458	0.139569
$\Delta T/\text{K}$	0.8010	0.9238	0.8372	0.9221	0.5123	0.8350
$-\Delta U(\text{IBP})/\text{J}$	1873.90	2161.19	1958.59	2157.21	1196.50	1956.44
$\Delta u_{\text{HNO}_3}/\text{J}$	5.24	6.81	7.13	5.37	11.73	11.45
$\Delta u_i/\text{J}$	22.19	19.53	12.15	11.44	26.48	33.66
$\Delta u_{\text{cotton}}/\text{J}$	94.84	100.62	111.02	95.81	4.25	5.22
$-\Delta_c u/\text{J g}^{-1}$	13725.7	13738.2	13719.3	13729.2	13664.1	13657.1
$-\Delta_c u^0/\text{J g}^{-1}$	13723.5	13736.0	13717.1	13727.0	13661.9	13654.9
$-\Delta_c U^0/\text{kJ mol}^{-1}$	1442.24	1443.55	1441.57	1442.61	1435.77	1435.04
$-\Delta_c U^0/\text{kJ mol}^{-1}$	$1443.2 \pm 2.1$		$1442.3 \pm 2.3$		$1435.7 \pm 1.2$	

$m_p$  – mass of compound burned in each experiment.

$\Delta U(\text{IBP})$  – energy change for the isothermal combustion reaction under actual bomb conditions.

$\Delta u_{\text{cotton}}$  – energy of combustion of the cotton fuse.

$\Delta u_{\text{HNO}_3}$  – energy correction for the nitric acid formation.

$\Delta u_i$  – energy used to ignite the sample by means of a fire.

$\Delta_c u$  – non corrected massic energy of combustion of compound.

$\Delta_c u^0$  – standard massic energy of combustion.

$\Delta_c U^0$  – standard molar energy of combustion.

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