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The standard enthalpies of formation of proline stereoisomers

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ABSTRACT

The combustion calorimetry and differential scanning calorimetry (DSC) techniques have been employed in order to obtain the thermochemical properties of L-, D-enantiomers and racemic mixture of proline.

The large negative values of the enthalpies of formation of the investigated compounds reveal their high stability. The thermal behavior of the compounds was studied by means of DSC in the temperature range between ambient and 250 °C. A combined transformation–melting and decomposition is occurring on heating. The decomposition mechanism is discussed in relationship with the data obtained by means of DSC.

1. Introduction

The present work continues our thermochemical characterization of amino acids and of their derivatives. In previous papers the thermochemical properties of alanine [1], aspartic acid (stereoisomers L-, D- and DL-) [2], of L-α-glutamic acid [3], of the isomers of amino benzoic acid [4], of asparagine (anhydrous and monohydrate), and of glutamine [5] were reported. Despite the biological importance of knowledge of the enthalpies of formation which are necessary, if quantitative studies on the energetics of biochemical reactions are to be performed, many values for amino acids are either lacking or, in other cases, the literature values for the same compound do not agree.

Direct experimental investigations of the thermodynamic properties of separate configurational isomers with one chiral center have been carried out occasionally [1,2]. It is very difficult to find the reasons for differences observed eventually between the values of the enthalpies of formation of D- and L-isomers and regarding their thermal behavior.

Proline is one of the 20 α-amino acids that are commonly met in animal proteins and required for normal functioning of human organism. Proline and its derivative hydroxy proline are unique among these in that the nitrogen atom is part of a ring structure, rather than outside the ring. That is, its amino group, through which it links to the other amino acids, is a secondary amine group in the neutral form of the molecule, not a primary one, as in the other amino acids. Because the proline unit from peptides and proteins lacks a hydrogen atom on the amide group, it cannot act as a hydrogen bond donor, but only as a hydrogen bond acceptor. The distinctive cyclic structure of proline's side chain locks its backbone dihedral angle at approximately −75°, giving proline an exceptional conformational rigidity compared to other amino acids. Hence, proline looses less conformational entropy upon folding. Proline residues are found often at the end of a proteic α-helix as they have a destabilizing effect in the middle of regular secondary structure. They play an important role in determining the shape of protein molecules [6,7]. Proline is commonly found as the first residue of an alpha helix and also in the edge strands of beta sheets.

Proline is not classified as an "essential amino acid" since it can be synthesized by the human body from other compounds through chemical reactions, notably from glutamic acid, which is easily converted into proline.

Some proteins, especially collagen contain up to 20% of prolines. This is a critical condition for maintaining healthy connective tissue and skin of higher organisms, especially at the site of traumatic tissue injury.

L-Proline helps cells survive extreme osmotic stress acting as an osmoprotectant osmolyte. It plays a role in maintaining fluid balance and cell volume and therefore it is used in many pharmaceutical and biotechnological applications.

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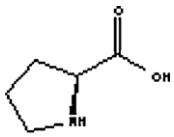

Proline

The literature values for the enthalpy of formation of proline range between −507.6 and −524.2 kJ mol^{-1} [8–10]. The most negative value is for the racemic.

2. Experimental

Materials, L-, DL-, and D-proline studied in this work were obtained commercially from Fluka (the first two) and from Aldrich, respectively. The compounds have the following assessed mass fraction purities: L-proline > 99.5%, D-proline ≥ 99%, DL-proline > 98%. The three compounds were used without further purification, but they were heated to 90 °C and cooled in a desiccator before use, in order to eliminate adsorbed water. High purity oxygen 99.998% was used for combustion. Calorific grade benzoic acid supplied by Parr, having heat of combustion 6318 cal g^{-1}, was used for the standardization of the 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 semimicro kit because the compounds under study were not available in large amounts. This bomb can handle samples that range from 25 mg 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 $\pm 2 \times 10^{-6}$ g. The determined calorimeter constant was 2333.16 ± 2.80 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 – $\Delta_f H_{HNO_3,aq} = -58.8$ kJ mol^{-1}.

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). The calorimeter was calibrated with indium ($\Delta_{fus}H$ = 28.46 J g^{-1}). The aria of the picks corresponding to the processes from the standard and studied substances allowed the calculation of the thermal effects in the later.

The IR spectrum of the enantiomers was recorded by Fourier transform spectroscopy using a Perkin Elmer Spectrum 100 FT-IR spectrophotometer, in the attenuated total reflection mode (ATR). The spectrum obtained with a solid sample, shown in Fig. 1 resulted from an average of 16 scans at 1 cm^{-1} resolution, between 600 and 4000 cm^{-1}.

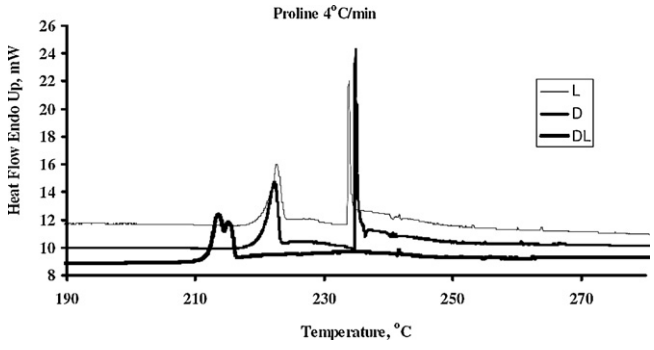

Fig. 1. DSC thermograms of three isomeric prolines.

3. Results

3.1. Combustion energy

At least 6 runs were retained for each compound. 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. The results of the combustion measurements for the three compounds are given in Tables 1–3.

ΔU(fuse) and ΔU(ign) were calculated from the mass of cotton and $\Delta_c h$(cotton) = 16,240 J g^{-1} [11] and from the mass of the fire and $\Delta_c h$(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 [12]:

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

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 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].

The relative error in the determination of the heats of combustion was less than 2‰.

For calculating the enthalpies of formation, 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} [14].

Our data of solid-state enthalpies of formation are shown in Table 4, together with literature values [8–10]. The uncertainties represent two standard deviations of the mean.

3.2. DSC runs

The DSC thermograms of the three isomeric prolines are shown in Fig. 1. It may be seen that the thermograms for the two enantiomers are similar as regards the characteristic temperatures, but the thermal effect corresponding to the second peak is larger in the case of the D-isomer. A similar behavior was observed in the case of the isomers of aspartic acid [15]. Differences were noticed in the DTG and DTA curves of the two enantiomers, obtained by thermogravimetry, as well [16].

The onset, maximum and end temperatures of the peaks measured by us are shown in Table 5. The first peak is ascribed to the fusion process proceeding simultaneously with decomposition. The onset temperatures of this peak at 4 K/min, for the L-, D- and DL-isomers are 217 °C, for the enantiomers and 208 °C for the racemic. Our values are consistent with those from reference [17]. Our values disagree with the smallest values found in literature i.e. 210 °C for L-proline [18] and 189 °C for the racemic [19], and with thermogravimetric data at low heating rate (1 K/min) from reference [16]. However the later reference gives different characteristic temperatures for the enantiomers (e.g. onset decomposition temperature of L-proline ~180 °C and ~190 °C for D-proline).

The lower onset temperature of the racemic indicates that a melting process of the racemic compound is starting at this temperature accompanied by decomposition.

The sensitivity of the onset temperature of the first peak to the heating rate proves that it does not belong only to melting. The