



A DSC STUDY OF ALPHA AMINOBUTYRIC ACID GAMMA IRRADIATED

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abstract: The behaviour on heating of irradiated with gamma rays and non-irradiated DL- α aminobutyric acid (DL- α AMB) was investigated comparatively, by means of differential scanning calorimetry. (DL- α AMB) decomposes before melting, the two processes being overlapped.

key words: DSC; alpha aminobutyric acid; gamma irradiation

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Introduction

Most often, studies on irradiated compounds are performed with the aim to investigate how radiation modifies the properties of the compound. For example, irradiation may introduce lattice defects and trapped charges, which alter the subsequent behaviour, such as the thermal stability [1].

A suitable method of thermal analysis for investigation of the effect of ionising radiation on molecules of biological importance, such as amino acids is differential scanning calorimetry (DSC). The thermal analysis of organic compounds is usually combined with chemical analyses, in order to identify the products of thermal decomposition. Neutron diffraction study established that aliphatic amino acids are found in solid state as zwitterions. COO⁻ and NH₃⁺ groups of each amino acid molecule are bound by hydrogen bonds achieving a double layer structure [2]. The side-chains are nearly perpendicular to the double layer and dispersion forces hold neighbouring layers together. These compounds may undergo phase transitions, which were related (by means of DSC, X-ray measurements) to a conformational change in the side chain, to a rearrangement of the layers along the stacking direction and to the appearance of a completely different hydrogen bond network [3].

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Alpha amino-butyric acid is known to present polymorphic transitions, with values of the transition temperature between 207 and 247°C and a heat of transition (ΔH , kJ·mol⁻¹) with an average value of 4.91±0.29 [4].

During thermal reactions, alpha amino acids (including DL- α amino-butyric acid) form a range of products (CO, NH₃, linear and cyclic compounds) thus, quantitative measurements are difficult because of the wide temperature span over which the thermal processes take place.

Experimental

Reagents

DL- α amino-butyric acid was Fluka reagent of purity $\geq 99\%$.

Irradiation

Amino acids samples were irradiated with gamma rays from a ¹³⁷Cs source (Gammator type) with an initial activity of 800 Ci and a dose rate of 1.02·10²Gy/h. The irradiation dose was determined by means of the Fricke dosimeter. Exposure periods ranged between 7-120 hours.

The DSC thermograms of irradiated and non-irradiated samples of DL- α amino-butyric acid were recorded by means of a Perkin Elmer 1B calorimeter, in static air, using sealed standard aluminium crucibles, not tightly closed. The samples weight was between 3 to 7 mg. The calorimeter was calibrated with indium ($\Delta_{\text{fus}}H=28,46 \text{ J}\cdot\text{g}^{-1}$, calibration constant $K=1,6219 \text{ J/u.a.}$). The runs were performed between 330÷573 K with 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 34812 A, serving as an interface with the computer, provided with the Benchlink data acquisition software. The acquired data were transferred to the Origin 5.0 software for graphical processing and calculation of thermal effects.

Results and discussions

The DSC curves recorded for non-irradiated and irradiated DL- α amino-butyric acid (DL- α AMB) are shown in Fig. 1.

It can be seen from DSC thermograms that the shape of endothermic curves of irradiated samples of amino acid (DL- α AMB) is similar to that of non-irradiated one. The maximum of the peaks is placed at about 277°C (for non-irradiated DL- α AMB) and at 274°C (for irradiated DL- α AMB). DL- α AMB starts to decompose at about 266°C.

The temperature values obtained from DSC curves for non-irradiated and irradiated DL- α AMB with different doses are shown in Table 1.

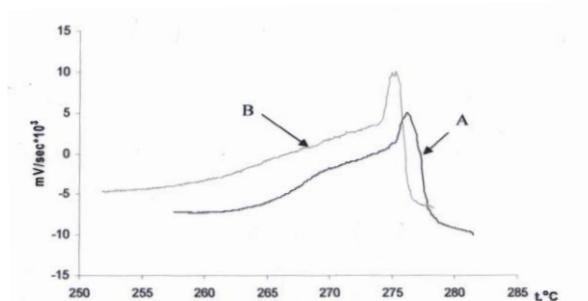


Fig. 1 DSC thermogram of DL- α AMB: A-non-irradiated, B-irradiated 120h.

Table 1 DSC parameters for DL- α AMB non-irradiated and irradiated with different doses.

Irradiation time, h	$t_{initials}$, °C	t_{max} , °C	t_{final} , °C	Δt ($t_{initial}-t_{final}$), °C
0	260.02	276.04	280.1	20.08
7	262.15	278.79	283.66	21.51
15,5	262.46	274.86	280.9	18.44
24	260.09	278.06	300.76	40.67
48	257.13	273.6	280.2	23.07
72	259.56	277.36	280.73	21.17
120	257.82	273.7	279.48	21.66

From Table 1 results that the initial temperature t_i ($259.9 \pm 2.2^{\circ}\text{C}$) and final temperature (end temperature) t_f ($281 \pm 1.41^{\circ}\text{C}$) of irradiated samples have similar values with those of non-irradiated sample of DL- α AMB ($t_i=260^{\circ}\text{C}$, $t_f=280^{\circ}\text{C}$). The decomposition process proceeds in two steps, the first process is observed as a “shoulder”, followed by a peak. The onset temperature of the peaks is lower than that reported in literature (307°C) as decomposition point [5]. The decomposition temperature is influenced by the pressure inside the crucible, because all DSC runs were performed in closed, but not perfectly sealed crucibles. A comparison of the DSC curves obtained for the irradiated and non-irradiated samples revealed a shift of the peaks corresponding to the decomposition process towards lower temperatures.

In order to establish the influence of radiations upon the thermal behaviour of DL- α AMB, the weight loss of the irradiated and non-irradiated samples was measured. The weight loss of DL- α AMB is shown in Fig. 2 as a function of the irradiation time.

The weight loss of irradiated samples is lower than that of non-irradiated ones, by about 10%. The non-isothermal process proceeding in a wide temperature range ($>20^{\circ}\text{C}$) is accompanied by a significant weight loss of 75-89%, which proves that DL- α AMB strongly decomposes by heating. The weight loss and the enthalpy of decomposition present a continuous decrease with the irradiation dose. The effect of decreasing values of enthalpy characterizing decomposition as a result of irradiation has already been mentioned in literature [6]. The values of decomposition enthalpy are presented in Table 2.

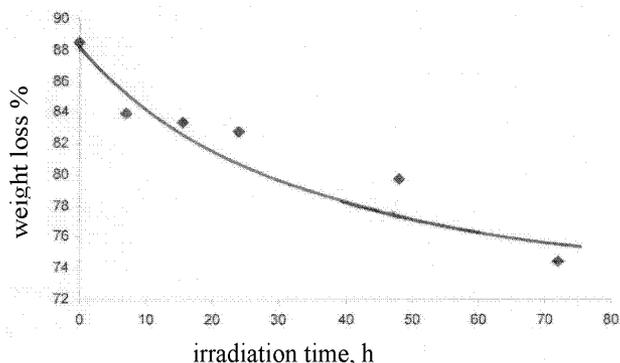


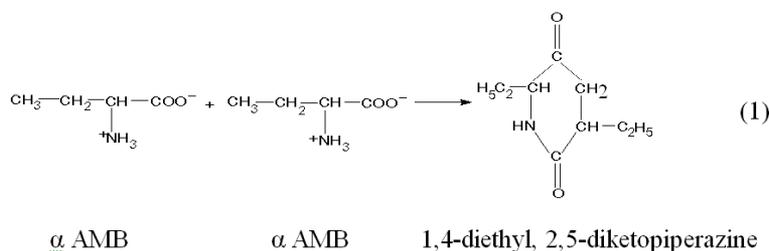
Fig. 2 Weight loss variation of DL- α AMB with irradiation times.

Table 2 The enthalpy of decomposition values for DL- α AMB irradiated and non-irradiated.

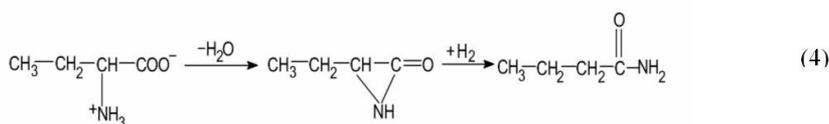
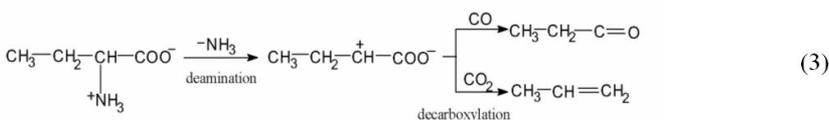
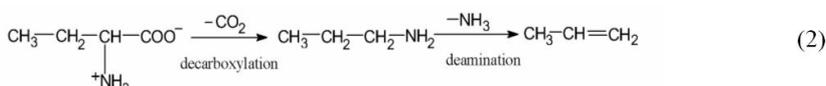
Irradiation time, <i>h</i>	ΔH decomposition, <i>kJ/mol</i>
0	112.79
7	108.65
15.5	97.76
24	88.26
48	82.74
72	78.48
120	71.57

The significant changes of the values of the decomposition enthalpy as a result of irradiation suggest a decrease in the content of amino acid relative to the initial value, changes in the crystal structure and the implication of decomposition products. The decomposition as a result of radiolysis affects the physico-chemical properties of the compound [7]. All the effects observed including decreases of the decomposition enthalpies and weight loss after irradiation are related with the formation of defects of the crystal lattice, as the energy of the ionizing radiation is high enough to cause even the break of covalent bonds, moreover to disturb weaker interactions stabilizing the crystal lattice.

Decomposition mechanism. Regarding the thermal behaviour of DL- α AMB, researchers [8] reported that a dimerisation reaction with formation of diketopiperazine proceeds on heating.

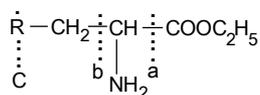


The decomposition products of α amino acids are mainly simple inorganic compounds (CO_2 , H_2O , NH_3 , and CO) along with a variety of volatile organic compounds (amines, nitriles, amides, hydrocarbons etc.) and some less volatile ones (piperazine-2,5-diones and other complex cyclic compounds). The thermal fragmentations of various amino acid molecules is considered as a very complicated process, which involves many reaction pathways, which include decarboxylation, deamination, dehydration and condensation reactions [9,10]. The following reactions could be included in the thermal decomposition of α -amino-butyrac acid similar to those of L-leucine, studied thermogravimetrically by Jie Li et al [11].

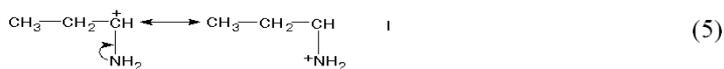


The weight loss, together with the thermograms (Fig. 1) suggests that several reactions are involved in the global endothermic process of decomposition. The start temperature of the thermal effect from the DSC curves has to be attributed, most probably, to the condensation reaction, with formation of diketopiperazine and water.

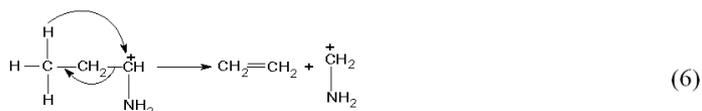
Amino-acids have a very low vapor pressure because of their zwitterion structure and most of them decompose if heated to the temperatures required for vaporization. Esterification was chosen to create a vapour state with a behavior similar to that of the vapor of amino acids. Biemann et al. [12] investigated the thermal stability of 24 amino acids ethyl esters, including α AMB, by means of mass spectrometry. Mass spectra record positive ions which result from the fragmentation of the molecules. For example, the peaks obtained from GC-MS for the ethyl esters of α amino acids are due to the fragmentation of the molecule by preferred breaking of those bonds that result in energetically more favoured ions, the best stabilized positive ions. The fragmentation of a generic ethyl ester of α amino acid can proceed by breaking of one of the bonds a, b and c.



The breaking of bond "a" gives rise to the loss of carboxyl group and formation of a resonance stabilized ion I (amine fragment) obtained by retention of the positive charge on nitrogen.



The decomposition of the aminic fragment consist in elimination of a neutral molecule of olefin, the positive charge is localized on the ionic fragment, which contains the nitrogen atom.



Breaking of “b” bond, between C_α and C_β ends up in the formation of ion II (ester fragment) also stabilized by retention of the positive charge on the nitrogen atom.



Biemann et al. [12] concluded from their mass spectrometry study on the α - amino-butyrac acid ester that the greatest ion fraction belongs to the aminic fragment I, obtained by decarboxylation, which means that this amino acid has the weakest bond between the carboxyl group and C_α atom. This is also proved by a recent study by Lie Jie et al. [11], which concluded that the most favored process in thermal decomposition of α amino acids is decarboxylation.

Conclusions

The DSC curves of irradiated samples of DL- α AMB comparatively with the non-irradiated ones emphasized transformations related to the values of decomposition enthalpies and weight loss.

DL- α AMB decomposes on heating. Decomposition enthalpies (ΔH) and the weight loss (Δm) of irradiated samples have lower values than non-irradiated ones. ΔH and Δm decrease with the increasing of irradiation dose. The weight loss represents 89% for the non irradiated sample and an average value of about 81% for irradiated ones.

The effect of gamma radiations upon the decrease of weight loss and decomposition enthalpy is more significant at short irradiation times.

The presence in the irradiated samples of radiolytic products of amino acid, even in a small concentration, has the same influence as the presence of impurities: damages the crystalline structure of the amino acid, and produces the decrease of the experimental parameters presented in Fig. 2 and Table 2.

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