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THERMAL BEHAVIOR OF GLUTAMIC ACID AND ITS SODIUM, LITHIUM AND AMMONIUM SALTS

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Glutamic acid (H_2glu) and its lithium, sodium and ammonium monosalts were submitted to thermal analysis using thermogravimetry (TG) and differential thermal analysis (DTA). The main goal of these studies was to compare the relative thermal stability and to evaluate the effect of the counter ion in the thermal decomposition pathways. Salts were obtained by direct neutralization of the purified acid with LiOH, NaOH or NH_4OH and were characterized by elemental analysis (C, H and N) and IR spectroscopy. Decomposition occurred after conversion to the pyroglutamic acid or the respective pyroglutamates and ammonium salt loosing NH_3 being converted to H_2glu before decomposition.

Keywords: *food additives, glutamate alkaline salts, thermal stability*

Introduction

Amino acids are of great biological importance as many of them are essential for human life [1] being the basic units of proteins. Their thermodynamical properties play an important role in biology and have been extensively reported in the last century [2].

Glutamic acid (H_2glu), a non-essential amino acid, was first isolated from wheat gluten in 1866 by Ritthausen. In 1908 Ikeda found that monosodium glutamate (NaHglu) is a beneficial active component of the algae *Laminaria japonica*, used for a long time in Japan as a flavor improver of soups and similarly prepared food. Currently NaHglu is used in numerous food products as a flavor enhancer. H_2glu is abundant in most proteins, but is particularly high in milk proteins (21.7%), wheat (31.4%), corn (18.4%) and soy (18.5%). Molasses also contains relatively high amounts of glutamic acid [3].

L-glutamate is an amino acid widely present in brain as an exciting neurotransmitter in the vertebrate's central nervous system. Most of the *L*-glutamic acid found in brain is due to the local conversion of *L*-glutamine and intermediates of the Krebs cycle [4].

Glutamic acid also plays an important role in transaminase and transdesaminase enzyme reactions, turning to α-keto-glutaric acid. A connection is made in this way, between the metabolism of proteins and carbohydrates [5].

Vlase *et al*. previously investigated the thermal decomposition of H_2glu [6] and its sodium and potassium salts [7]. They proposed that during the decomposition of H_2glu and its salts dimerization to diketopiperazine occurs.

In this work the thermal decomposition of H_2glu and its lithium, sodium and ammonium salts are investigated in order to understand the thermal degradation pathways of such compounds using thermogravimetry (TG) and differential thermal analysis (DTA). From these results we found that the decomposition intermediate is pyroglutamate instead of the diketopiperazine.

Experimental

Materials

Synthesis and characterization of glutamate salts

Glutamic acid (technical grade) was recrystallized by dissolving the product in warm water and cooling the resulting solution. Salts were obtained by direct neutralization of the purified acid with LiOH, NaOH or NH_4OH. The resulting precipitates were washed with cold acetone and dried in an oven at 40°C under reduced pressure for 12 h and characterized by elemental analysis and FTIR.

Methods

Characterization of thermal degradation intermediates

Thermal degradation intermediates of the H_2glu, LiHglu, NaHglu, NH_4Hglu, were obtained at temperatures indicated by the TG curves. A certain amount

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of sample was inserted into a 200×20 mm glass tube, to which a thermometer was attached. This set was then inserted into a glycerin bath and heated up to the desired temperature. Finally the thermal decomposition product was characterized by FTIR and ^{1}H NMR.

Equipment

The compounds were characterized by FTIR spectroscopy (KBr pellets) in a Nicolet 5SXC FTIR spectrophotometer. C, H and N contents were determined by elemental analysis using a Fisons EA 1108 CNHS-O instrument. The TG/DTG and DTA curves were recorded using a SDT-Q600 simultaneous TG-DTA thermal analyzer controlled by Thermal Advantage (4.2.1) software, both from TA Instruments, under a 100 mL min^{-1} nitrogen or air flow, in Al_2O_3 pans, at 10°C min^{-1} heating rate with sample masses of ca. 5 mg for each compound at atmospheric pressure.

Results and discussion

Elemental analysis

The prepared salts are listed in Table 1. The given formulas are in a good agreement with the elemental analyses.

Table 1 Elemental analysis of H_2glu and their salts

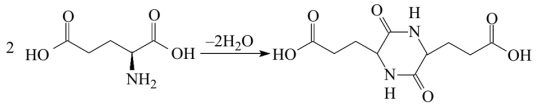
Compound	Found (calc.)/%		
	C	N	H
H_2glu	41.17 (40.81)	10.14 (9.52)	6.57 (6.16)
LiHglu	38.62 (39.20)	9.49 (9.15)	5.67 (5.27)
NaHglu·H_2O	32.71 (32.09)	8.28 (7.48)	5.72 (5.39)
NH_4Hglu·H_2O	33.29 (32.96)	14.92 (15.38)	9.19 (7.75)

Thermoanalytical results

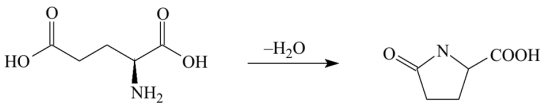
H_2glu

The thermal events, residues, mass losses and temperature ranges observed in each step of the recorded TG/DTG and DTA curves of the analyzed compounds are in Table 2. TG/DTG curves are presented in Fig. 1a while the DTA curves are in Fig. 1b.

In the DTA curve the sharp endothermic peak at 205°C indicates that melting occurs. The TG/DTG curves reveal that just after melting, a mass loss takes place which can be attributed to the release of one molecule of water. Based on stoichiometric calculations [6, 7] a dimerization reaction was suggested with the formation of diketopiperazine, represented by the following reaction:



However, according to the Merk index [8], the reaction is actually the loss of water with the formation of pyroglutamic acid (Hpyr):



In both cases the loss of one mole of water/mol H_2glu takes place. In the absence of adequate characterization by auxiliary techniques it is very difficult to affirm which one is the most correct proposal. IR spectra of the H_2glu presented in Fig. 2a, showed typical amino acid bands such as the axial deformation of R – NH_3^+ at 3100 and 2600 cm^{-1} and the characteristic absorption of the carboxyl group at 1600–1590 and 1400 cm^{-1} [9].

The product of the first thermal event collected at 200°C (Fig. 2b) was characterized by FTIR. Compared its IR spectrum to the reference one, taken from the Aldrich IR library [10] the product was pyroglutamic acid (Hpyr), according to the. In addition, ^{1}H NMR spectra of the residue at 200°C presented three sets of peaks that agreed with the spectra for the Hpyr simulated with the ACD Labs ^{1}H NMR software. Based in these spectral evidences is possible to say that the Hpyr is produced during the H_2glu decomposition.

After the formation of the Hpyr, the decomposition takes place in two consecutive steps, without any residue in the crucible at 700°C.

NH_4Hglu·H_2O

TG/DTG curves suggested that the decomposition of NH_4Hglu·H_2O occurred in such way that in first step the hydration water is lost. Then, the anhydrous compound looses one mole of ammonia.

These observations were easily confirmed by heating in the glass tube from room temperature to 200°C, since after condensation of water a characteristic smell of ammonia could be detected. In addition, a small piece of cotton impregnated with phenolphthalein solution became to red after contacting with liberated vapors upon heating. These events appear as endothermic processes in the DTA curve and may lead to the formation of H_2glu.

The IR spectrum of the NH_4Hglu·H_2O is presented in Fig. 2c and is remarkably different of the IR spectrum of the decomposition product at 200°C (Fig. 2d). The spectra in Figs 2b and d are very similar, suggesting that NH_4Hglu·H_2O after loss of hydration water and ammonia the H_2glu is produced

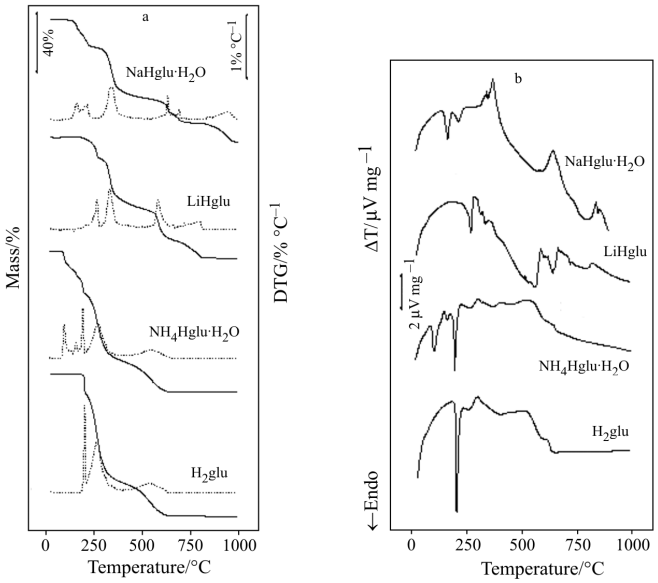


Fig. 1 a – TG/DTG and b – DTA curves of the studied salts

at 200°C. Above 200°C the shape of the TG/DTG and DTA curves are the same than the H_2glu itself (Fig. 1) has confirming this hypothesis.

LiHglu

TG/DTG curves for this compound agreed with the elemental analysis data confirming that the salt is anhydrous. The TG profile presented four thermal events. The first one was attributed to the conversion to lithium pyroglutamate (Lipyr) resulting 13.65% of mass loss between 187–269°C. According to the DTA analysis, melting occurs before the LiHglu→Lipyr conversion.

After this stage, thermal decomposition of Lipyr occurred in the 269–462°C temperature range producing a carbonaceous residue. The third thermal event is related to the burning of this material generating probably Li_2CO_3 at 700°C (TG: 26.91; Δm calc.=24.14%). Finally the carbonate decomposes during the last stage leading to 15.43% residue in the TG curve. This can be due to the presence of Li_4OCO_3 type of lithium oxycarbonate (calc.=16.95%) or Li_2O (calc.=9.76%) or their mixture. The characterization of this residue is difficult, since it is not crystalline and synthesizes in the crucible.

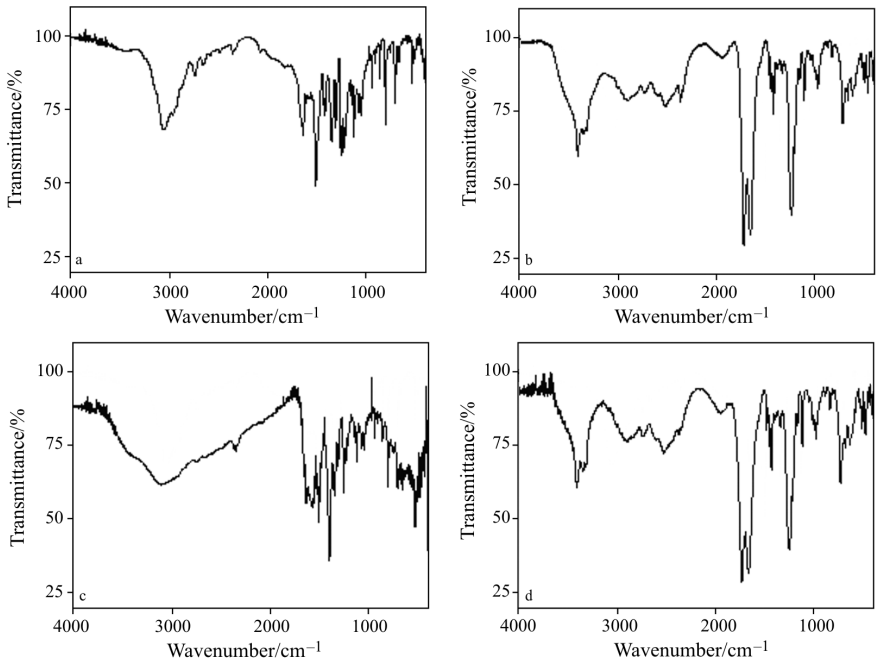


Fig. 2 IR spectra of a – H_2glu, b – residue of H_2glu collected at 200°C, c – NH_4Hglu and d – residue collected of NH_4Hglu at 200°C

Table 2 Decomposition path and representative thermoanalytical data of H_2glu and its salts

Process	Mass loss/%		Temperature range/°C
	found	calc.	
$H_2glu \rightarrow Hpyr + H_2O$	12.50	12.24	190–210
$Hpyr \rightarrow$carbonaceous residue	54.60	–	210–377
Carbonaceuous residue burning	32.73	–	377–650
$NH_4Hglu \cdot H_2O \rightarrow NH_4Hglu + H_2O$	9.67	9.89	79–113
$NH_4Hglu \rightarrow H_2glu + NH_3$	10.06	10.37	113–177
$H_2glu \rightarrow Hpyr + H_2O$	12.00	12.24	177–218
$Hpyr \rightarrow$carbonaceous residue	44.07	–	218–378
Carbonaceous residue burning	22.64	–	378–650
$LiHglu \rightarrow Lipyr + H_2O$	13.65	11.77	187–269
$Lipyr \rightarrow$carbonaceous residue	34.21	–	269–462
Carbonaceous residue burning	25.23	–	462–701
Residue Li_2CO_3	26.91	24.14	701
Residue: Li_2O, Li_4OCO_3 or mixture	15.43	–	>820
$NaHglu \cdot H_2O \rightarrow NaHglu + H_2O$	9.49	9.63	107–181
$NaHglu \rightarrow Napyr + H_2O$	10.51	10.65	181–270
$Napyr \rightarrow$carbonaceous residue	33.40	–	270–500
Carbonaceous residue burning	17.71	–	500–767
Residue Na_2CO_3	27.89	28.32	767
Residue Na_2O (?)	12.03	16.56	1150

$NaHglu \cdot H_2O$

In agreement with the elemental analysis, TG/DTG curves showed that this salt contains one molecule of crystalline water, which is lost during the first mass loss step. After dehydration the anhydrous salt looses one constitution water molecule producing sodium pyroglutamate according to the IR spectra of the residue at 200°C (not shown).

Then the third, fourth and fifth thermal decomposition events can be observed showing similar behavior to the lithium salt, i.e. thermal degradation of Napyr in carbonaceous residue, followed by production of Na_2CO_3, and, finally, its conversion to Na_2O.

Conclusions

The main conclusion of this work is that pyroglutamic acid is formed during the first degradation step of glutamic acid, as well as in its sodium and lithium salts. After the loss of the hydration water and ammonia, the ammonium salt undergoes decomposition via glutamic acid. It can be also stated that the substitution of the α-amino carboxylic group is preferred which is in agreement with its higher acidity. If substitution occurs in another carboxyl group the pyroglutamate will not be formed.

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