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THERMAL ANALYSIS OF SOME α-AMINO ACIDS USING SIMULTANEOUS TG–DSC APPARATUS. THE USE OF DYNAMIC THERMOGRAVIMETRY TO STUDY THE CHEMICAL KINETICS OF SOLID STATE DECOMPOSITION

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ABSTRACT

A study of the thermal stability of some α-amino acids by simultaneous TG–DSC measurements and kinetic calculations with the dynamic TG technique was carried out. Three different scales of thermal stability were found from the thermodynamic and kinetic data.

INTRODUCTION

The thermodynamic properties, in water, of 19 'standard' α-amino acids have been studied extensively in our laboratory [1–7]. These α-amino acids have one carboxyl group and one amino group, both linked to the α-carbon atom.

'Standard' α-amino acids differ in the structure of the side-chains (here called R groups), the polarization of which is the criterion used to classify these compounds into four groups: (1) a class with apolar or hydrophobic chains; (2) a class with uncharged polar chains; (3) a class with polar chains having positive charge, and (4) a class with polar chains having negative charge.

Because the carboxyl and amino groups linked to the α-carbon atom and the functional groups of the side-chains are used to identify each α-amino acid, it is important to know their thermodynamic properties. For this, the first, second and third ionization processes of these compounds were measured in water by calorimetric techniques. The dominant effect influencing the ionization processes was found to be solvation of ions and molecules which, in turn, depends on the different side chains and on the different groups within each side-chain. A detailed thermodynamic analysis of the following effects, which influence the ionization processes, has been presented in ref. 7:

(i) the solvation effects of a molecule having a particular atom at different positions in its skeleton;

(ii) the solvation effects on different classes of α-amino acids;

(iii) the thermodynamic effects on different classes of α-amino acids;

(iv) the thermodynamic effects on α-amino acids having similar structures.

The aim of this work is to correlate the side-chain structures of some solid α-amino acids with their thermal behaviour by simultaneous TG–DSC.

It is well known that solid α-amino acids have high melting points because of hydrogen bonding between the COO^- and NH_3^+ groups linked to the same α-carbon atom. This dipolar ion structure should be the main determinant of general thermal behaviour. However, the effect of the side-chain is enough to allow the thermal behaviour of α-amino acids to be differentiated both between and within classes.

Many studies on the thermal analysis (DTA, DSC, TG) and the kinetics of the decomposition processes of α-amino acids have been reported [8–17]. Most of the aliphatic α-amino acids adopt a double layer structure, as shown by neutron diffraction [16]. The alkyl side-chains are nearly perpendicular to the double layer and neighbouring layers are held together by dispersion forces. These compounds undergo phase transitions, which were related (by means of DSC and X-ray measurements) to a conformational change in the alkyl chain, to a rearrangement of the layers along the stacking direction and to the appearance of a completely different hydrogen bond network.

The α-amino acids studied in this work were L-phenylalanine, L-leucine, L-threonine, L-cysteine · H_2O,HCl, L-lysine,HCl and L-arginine,HCl. Leucine and phenylalanine belong to the same class but have aliphatic and aromatic side-chains, respectively. Threonine and cysteine have polar groups (hydroxyl and mercapto), respectively, while arginine and lysine belong to the fourth α-amino acid class and are differentiated by the number of NH_2 groups.

EXPERIMENTAL PROCEDURE

The experimental measurements were carried out by means of a simultaneous TG–DSC Stanton Redcroft 625 connected to a computer (Olivetti 250). Instrument calibration was performed with standard indium and tin samples of known temperatures and enthalpies of fusion.

For decomposition studies under dynamic conditions the TG-DSC apparatus was set up as follows. Samples (15–18 mg) were weighed into aluminium pans placed in a nitrogen-filled dry-box. In order to avoid oxidative decomposition of the samples, the TG–DSC system was flushed with nitrogen gas both below the open pan (at a flow-rate of 50 ml min^{-1})

and above it (at a flow-rate of 30 ml min^{-1}). In this way, the gases evolved during the thermal decomposition experiment are continuously removed. The heating rate was always 10 °C min^{-1}, and at least two runs for each compound were made.

All the thermodynamic quantities were calculated using the Stanton Redcroft Data Aquisition System Trace 2, Version 4. A dynamic (non-isothermal) TG technique was used in the kinetic study of decomposition reaction experiments.

The compounds (Carlo Erba RP) were used without further purification.

RESULTS AND DISCUSSION

Trends of thermal behaviour in the compounds examined are given in Figs. 1–9. The values of the thermodynamic and kinetic quantities related to TG and DSC measurements are reported in Tables 1–6.

The simultaneous TG–DSC system is a very useful tool for investigating organic compounds since it combines, in a single run, transformations which occur without mass change (melting, crystallization, polymorphic changes) and transformations with mass change (chemical reactions, decomposition, vaporization, oxidation). Consistent TG and DSC values are obtained even with small samples.

In the present study the thermal stability, the overall enthalpy and the kinetic activation energy of the various processes are considered.

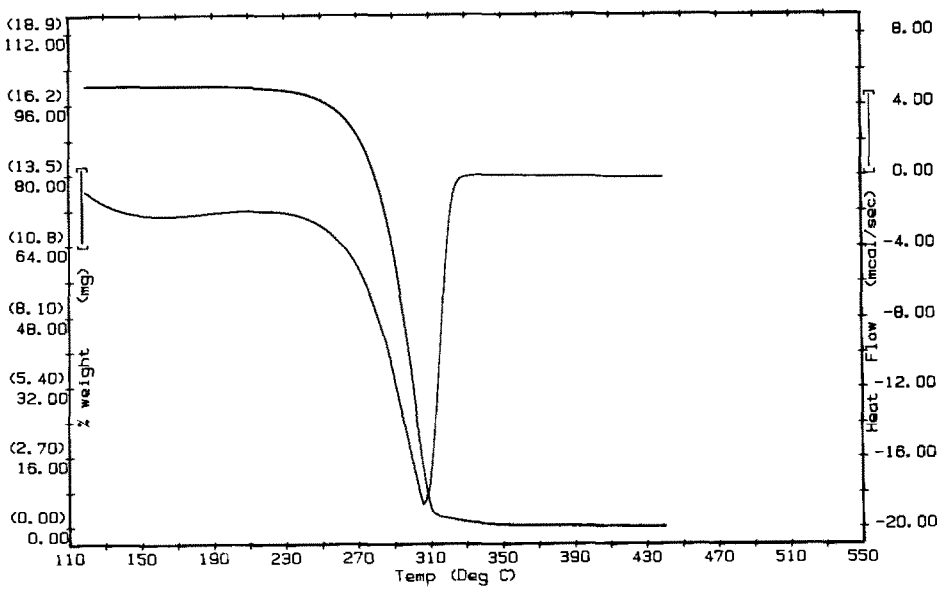

Fig. 1. DSC and TG curves of L-leucine.

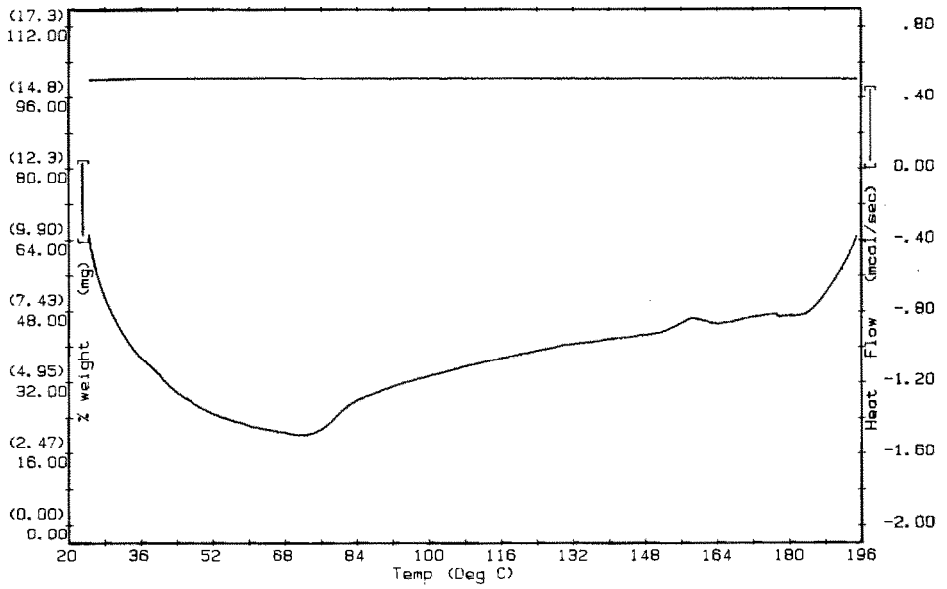

Fig. 2. DSC curve of L-leucine in the phase transition region.

Thermal stability

Although leucine and phenylalanine are in the same amino acid class, they show quite different thermal behaviour.

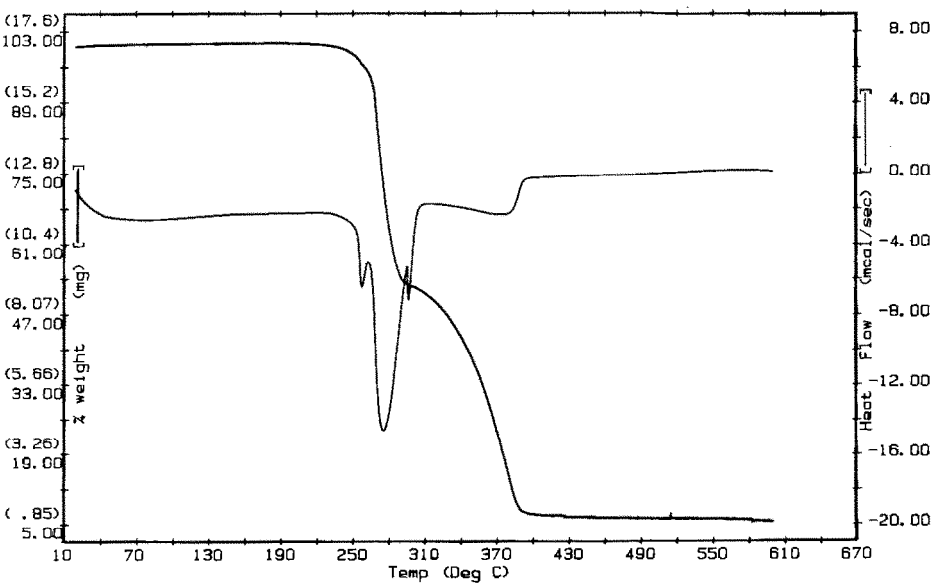

Fig. 3. DSC and TG curves of L-phenylalanine.

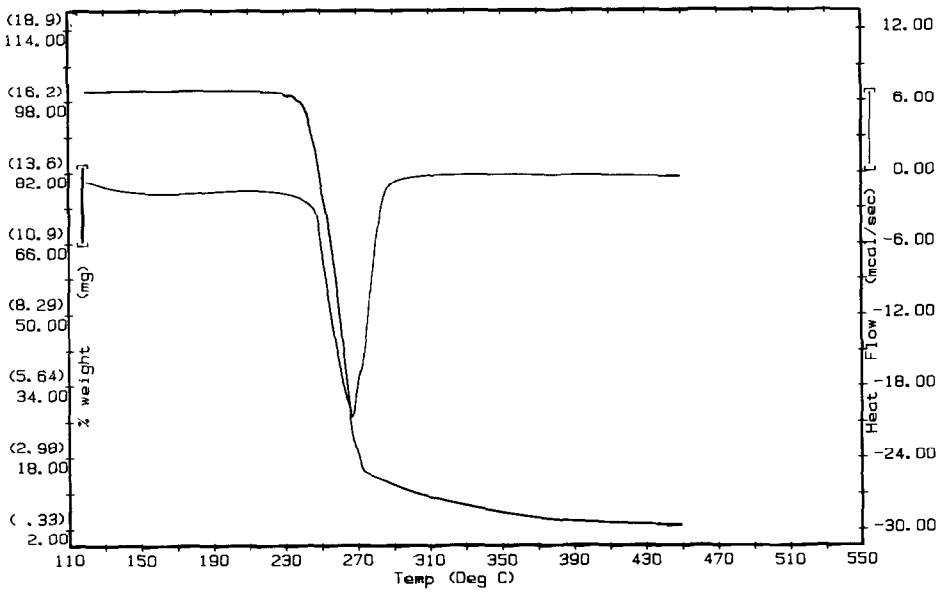

Fig. 4. DSC and TG curves of L-threonine.

Leucine shows a single curve (Fig. 1) both for TG and DSC variations, while for phenylalanine this is not so. Leucine decomposes at 207–342°C, with weight percent loss (wt.%) of 99.30% (Table 1). The corresponding enthalpy value 220.92 cal g^{-1} (Table 2) occurs between 232°C and 328°C,

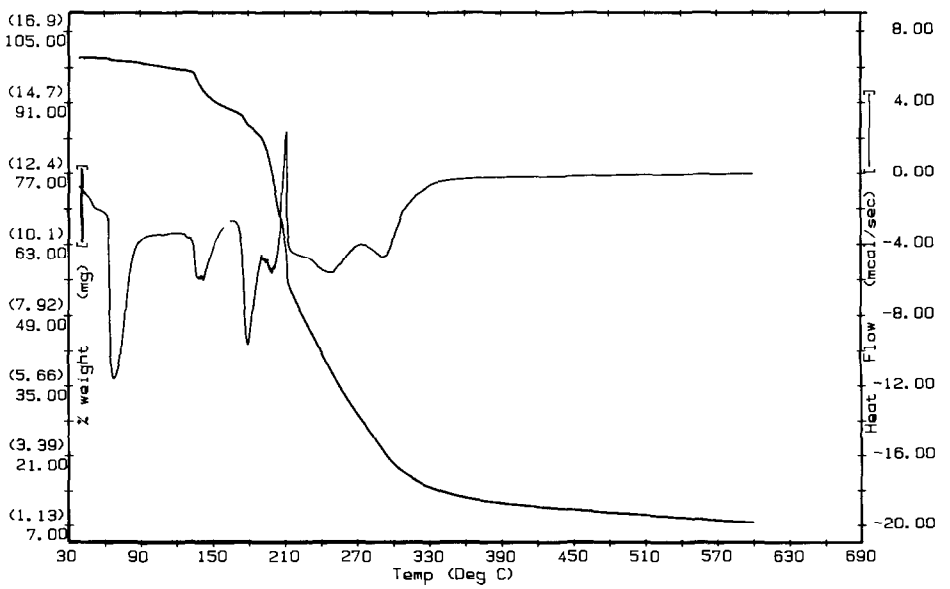

Fig. 5. DSC and TG curves of L-cysteine·H_2O,HCl.

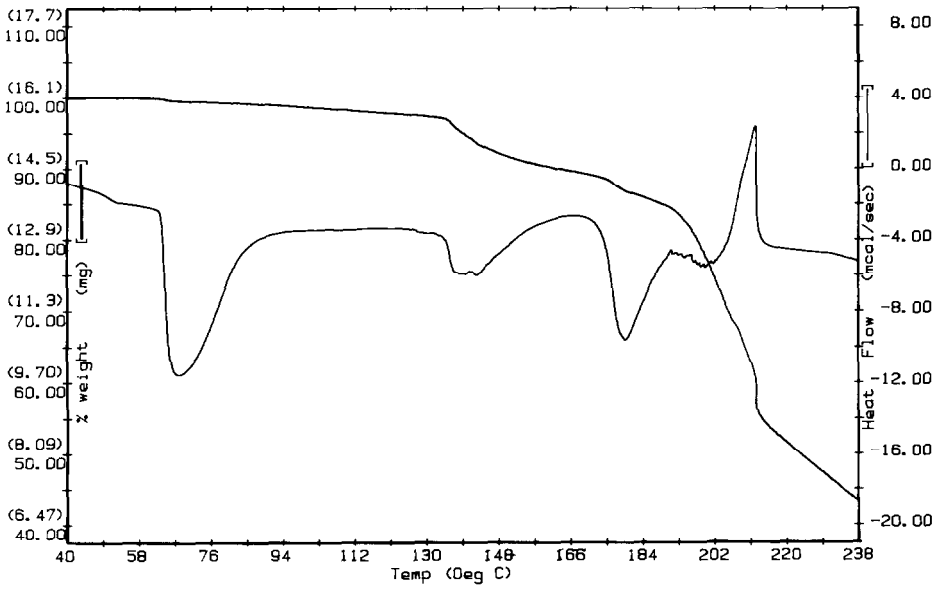

Fig. 6. DSC curve of L-cysteine·H_2O,HCl in the phase transition region.

with a temperature peak at 305.8°C. Furthermore, leucine shows (Fig. 2) a phase transition at 71°C, with $\Delta H = 12.96$ cal g^{-1} (Table 3).

Four stages of phenylalanine decomposition can be recognized from the combination of TG–DSC curves (Fig. 3). The sum of the first and second

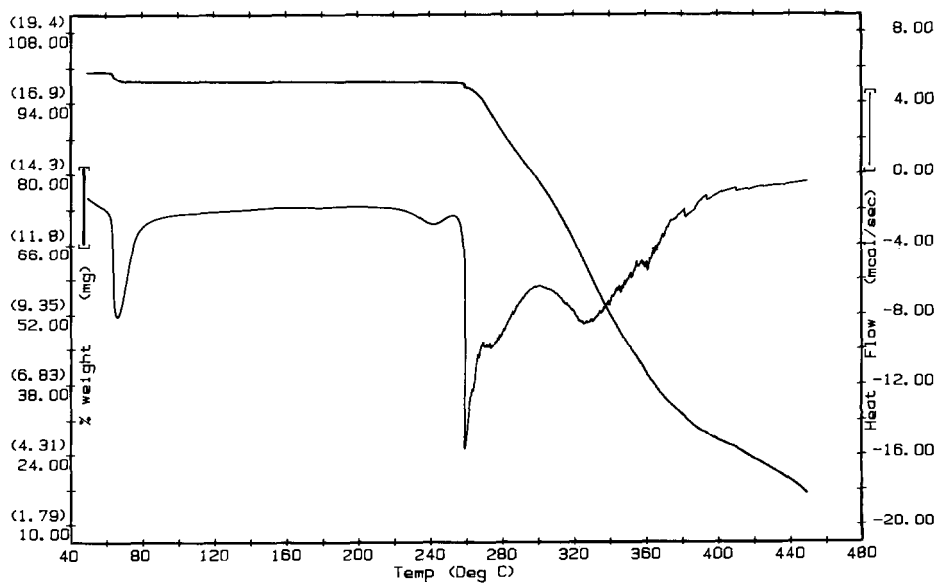

Fig. 7. DSC and TG curves of L-lysine,HCl.

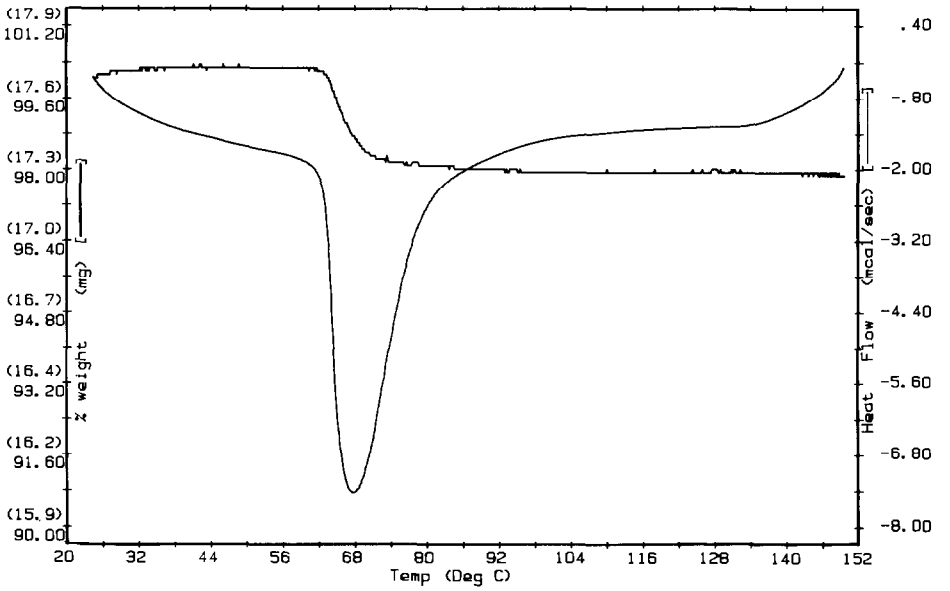

Fig. 8. DSC curve of L-lysine,HCl in the phase transition region.

stages of decomposition, which show respectively a 5.52% and 41.42% weight loss, can be compared to the first of the three stages of the decomposition process described in the literature [14], in which decarboxylation and deamination processes were detected by GC measurements. Melting begins

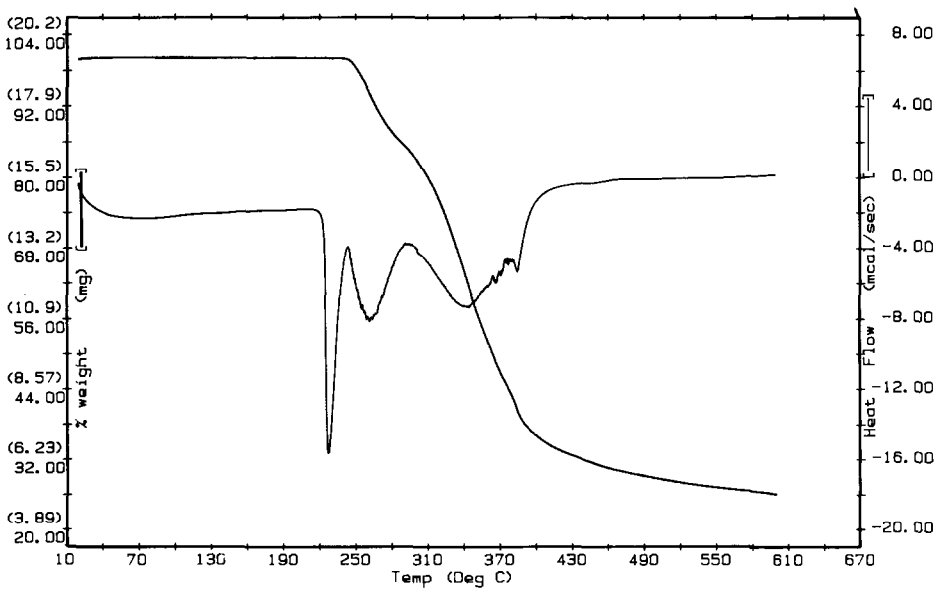

Fig. 9. DSC and TG curves of L-arginine,HCl.

TABLE 1

Thermodynamic parameters for thermal decomposition of α-amino acids from TG measurements

Compound	Stage of decomposition							
	I		II		III		IV	
	T (°C)	W (%)	T (°C)	W (%)	T (°C)	W (%)	T (°C)	W (%)
L(−) Leucine	207.0–342.0	99.30	–	–	–	–	–	–
L(−) Phenylalanine	236.7–263.4	5.52	263.4–295.6	41.42	295.6–300.6	0.60	300.6–401.0	45.65
L(−) Threonine	228.5–326.9	92.32	–	–	–	–	–	–
L(−) Cysteine·H_2O,HCl	120.0–168.0	8.27	168.0–217.0	41.97	217.0–375.0	38.20	375.0–600.0	4.89
L(−) Lysine,HCl	260.0–296.0	18.38	296.0–428.0	57.61	428.0–590.0	11.54	–	–
L(−) Arginine,HCl	244.0–289.0	15.73	289.0–430.0	51.67	430.0–585.0	6.20	–	–

TABLE 2

Thermodynamic parameters of thermal decomposition of α-amino acids from DSC measurements

Compound	Stage of decomposition											
	I			II			III			IV		
	T (°C)	ΔH (cal g^{-1})	Peak (°C)	T (°C)	ΔH (cal g^{-1})	Peak (°C)	T (°C)	ΔH (cal g^{-1})	Peak (°C)	T (°C)	ΔH (cal g^{-1})	Peak (°C)
L-(−) Leucine	232.0–328.0	220.9	305.8	–	–	–	–	–	–	–	–	–
L(−) Phenylalanine	253.4–263.4	389.0	257.6	263.4–295.6	52.3	275.6	295.6–303.8	1.49	297.3	312.4–393.0	27.24	377.0
L(−) Threonine	225.9–309.7	171.7	266.9	–	–	–	–	–	–	–	–	–
L(−) Cysteine·H_2O,HCl	120.0–168.0	14.3	142.5	168.0–201.0	18.1	179.6	217.0–269.7	13.38	247.7	–	–	–
				201.0–217.0	−11.3	212.2	274.1–332.9	11.55	295.4	–	–	–
L(−) Lysine,HCl	260.0–296.0	62.4	259.3	296.0–400.0	55.8	330.0	–	–	–	–	–	–
L(−) Arginine,HCl	244.0–281.0	32.3	268.8	289.0–430.0	117.3	344.8	–	–	–	–	–	–

TABLE 3

Thermodynamic parameters of melting and phase transitions for α-amino acids from DSC measurements

Compound	Phase transition			Fusion		
	T (°C)	ΔH (cal g^{-1})	Peak (°C)	T (°C)	ΔH (cal g^{-1})	Peak (°C)
L(−) Leucine	60.0–90.0	13.0	71.0	–	–	–
L(−) Cysteine·H_2O,HCl	60.0–93.0	33.1	67.5	–	–	–
L(−) Lysine,HCl	60.0–80.0	16.1	67.2	224.0–252.0	2.8	241.5
L(−) Arginine,HCl	–	–	–	220.0–245.0	38.7	227.4

TABLE 4

Degree of decomposition, expressed as a per cent weight loss (W) of α-amino acids at high temperature

Compound	T (°C)	W (%)
L(−) Arginine	585.0	73.7
L(−) Lysine	590.0	87.5
L(−) Cysteine	600.0	93.3
L(−) Phenylalanine	401.0	93.1
L(−) Leucine	342.0	99.3
L(−) Threonine	326.0	92.3

TABLE 5

Enthalpy values for complete decomposition of α-amino acids

Compound	ΔH (cal g^{-1})
L(−) Leucine	233.8
L(−)Arginine	188.25
L(−)Threonine	171.70
L(−)Lysine	137.09
L(−)Phenylalanine	84.89
L(−)Cysteine	78.19

in the third stage and continues in the fourth one. The temperature range of the overall weight-loss process is 236.1–401° C, while the enthalpic processes occur at 253.4–393° C. These figures show that phenylalanine has greater thermal stability than leucine.

Indeed, the initial temperature of decomposition of phenylalanine is higher than that of leucine (Table 1), while at high temperatures the percent of weight loss is smaller for phenylalanine (Table 4). This means that the phenyl group hinders thermal decomposition and makes the processes of deamination, decarboxylation and decomposition more complicated. It can

TABLE 6

Kinetic parameters of thermal degradation of α-amino acids from TG measurements assuming first order reaction

Compound	Stage of degradation											
	I			II			III			IV		
	T (°C)	E_{a_1} (kcal mol^{-1})	ln A_1	T (°C)	E_{a_1} (kcal mol^{-1})	ln A_1	T (°C)	E_{a_1} (kcal mol^{-1})	ln A_1	T (°C)	E_{a_1} (kcal mol^{-1})	ln A_1
L(−) Leucine	207.0–342.0	31.05	26.26	–	–	–	–	–	–	–	–	–
L(−) Phenylalanine	236.1–263.4	57.70	54.53	263.4–295.8	62.78	57.18	–	–	–	300.6–396.0	22.1	15.98
L(−) Threonine	228.5–326.9	38.80	35.48	–	–	–	–	–	–	–	–	–
L(−) Cysteine·H_2O,HCl	120.0–168.0	25.66	30.46	168.0–217.0	33.27	34.69	217.0–375.0	9.58	7.06	375.0–596.6	7.4	2.26
L(−) Lysine,HCl	260.0–296.0	39.98	35.87	296.0–428.0	14.97	10.40	428.0–590.0	–	–	–	–	–
L(−) Arginine,HCl	244.0–289.0	31.83	28.89	289.0–430.0	15.63	10.85	430.0–585.0	14.57	7.44	–	–	–

also be noted that leucine, in aqueous solution, is more stable (from the enthalpic point of view) than phenylalanine as regards the proton loss processes of carboxylic and amino groups [7].

Threonine and cysteine belong to the second class, with aliphatic side-chains bearing, respectively, a hydroxyl and a mercapto group. Threonine shows (Fig. 4) a single decomposition curve, where loss of NH_3 and CO_2, and melting processes occur. From this point of view threonine resembles leucine, with weight change occurring at 228.5–326.9 °C and total weight loss of 92.39%. The enthalpic processes occur at 225–309 °C, with $\Delta H =$ 171.70 cal g^{-1}.

Cysteine shows (Fig. 5) more complex behaviour. At first a transition phase occurs (Fig. 6) with a peak at 67.5 °C having $\Delta H = 33.12$ cal g^{-1} and a weight loss (1%) which can be related to the beginning of water loss. Four stages of decomposition follow, probably loss of remaining water in the first stage (120–168 °C), since the water content of the compound is 10.25 wt%.

In the second stage of decomposition (168–217 °C) the weight loss is 41.97%. It has been reported [14] that in this temperature range deamination (20%) and HCl loss (14%) both occur. Figure 5 shows, for this stage, an endotherm followed immediately by an exotherm. The corresponding weight loss in TG shows that the exotherm is due to the decomposition of the compound. Indeed, an exotherm is often characteristic of a thermal decomposition reaction involving loss of a diatomic gas molecule [19].

The third stage of decomposition (217–375 °C) is a continuation of the deamination, decarboxylation and desulphydration processes. Two endothermic processes occur in this stage. The initial thermal stability of the undissociated molecule of cysteine is lower than that of threonine, but at high temperature its decomposition products are more resistant to the temperature increase. Indeed cysteine and threonine begin their decompositions at 120 °C and 228.5 °C respectively, the former reaches a weight loss of 93.33% at 600 °C, the latter one of 92.32% at 326.9 °C.

In aqueous solution proton dissociation from the carboxyl group of threonine is easier than it is for cysteine, while for proton dissociation from the amino group the opposite is true [7]. Finally a comparison between lysine (Fig. 7) and arginine (Fig. 9) shows that both processes of decomposition are rather complex and are preceded by melting. Lysine shows (Fig. 8) a phase transition in the temperature range 60–80 °C with a peak temperature at 67.2 °C and $\Delta H = 16.13$ cal g^{-1}. The weight change (2%) can be attributed to HCl loss. Subsequently an initial melting process occurs in the temperature range $\Delta T =$ 224–252 °C ($\Delta H = 2.75$ cal g^{-1}), followed by three stages of decomposition. Most of the decomposition (87.53%) occurs at $\Delta T =$ 260–590 °C and the first two stages ($\Delta T =$ 260–296 °C and $\Delta T =$ 296–428 °C) are related to decarboxylation and deamination processes. Some noise peaks are seen during the decomposition, probably due to release of gas from within the sample [20].

Arginine also undergoes an initial melting process (220–244 °C; $\Delta H =$ 38.68 cal g^{-1}), followed by three stages of decomposition at 244–585 °C with weight change 73.60%. Arginine is less stable thermally at low temperatures but more stable at high temperatures. Indeed, at 585 °C arginine shows a total degree of decomposition (73.60%) smaller than that of lysine (87.53%). In aqueous solution lysine is less stable than arginine as regards deprotonation of both the carboxyl and amino groups [14].

A complete scale of thermal stability, referring to the initial temperature of decomposition, can thus be written as lysine > arginine > phenylalanine > threonine > leucine > cysteine.

The degrees of decomposition, expressed as per cent weight loss at high temperatures for all compounds are reported in Table 4. The thermal stability with reference to the complete decomposition of the molecules can be written as arginine > lysine > cysteine > phenylalanine > leucine > threonine. The greatest range of thermal stability, considering both scales, is shown by α-amino acids of the third class (arginine and lysine), while the smallest is shown by threonine and leucine.

Enthalpy

The heat effects of the chemical and physical transitions can be calculated from the DSC curves.

If the enthalpy values relating to different ranges of temperatures are added, an overall enthalpy (i.e. the heat that the compound has exchanged with the external system, at constant pressure, up to its complete decomposition) can be derived. These enthalpy data are given in Table 5. The 'heat' scale shows the following order: leucine > arginine > threonine > lysine > phenylalanine > cysteine. Leucine and arginine require a lot of heat for their complete decomposition, while for cysteine and phenylalanine the required amount of heat is small.

Kinetics

Sequences of chemical processes which occur during thermal decomposition have been reported in the literature [10,14].

A kinetics–TG-dynamics study of the decomposition processes for the present compounds has been carried out, using the McCarthy and Green method. The activation energy values, frequency factors ln A, and reaction orders are reported in Table 6.

Since in phenylalanine the activation energy for the first stage of decomposition is smaller than that for the second stage, it can be hypothesized that only decarboxylation (or deamination) occurs in the former, while in the latter both processes take place. The fourth process shows the smallest energy because decomposition of unsaturated and unstable parts of the molecule is occurring.

It can be observed, by comparing the activation energies of the first process, that the phenyl group stabilizes phenylalanine with respect to leucine. This fact agrees with the thermal stability scale referring to initial temperature decomposition but not with the 'heat' scale.

In cysteine, most of the water of crystallization is lost in the first stage of decomposition. The activation energy for the second stage, where both loss of HCl and deamination occur, is greater than that for the first stage, since stronger bonds are being broken. The third stage, which includes continuation of deamination, decarboxylation and dehydrosulphidation processes, shows a lower activation energy. The last stage, with the lowest energy, is related to the formation of a carbonaceous residue.

From the kinetic point of view, cysteine is less thermally stable than threonine, which agrees with the thermal stability scale related to the initial temperature of decomposition. Finally, the comparison of lysine and arginine shows that decarboxylation and deamination processes are involved in the first two stages of decomposition of the former, but the energy of the second stage is lower, by virtue of stabilization of the ions formed.

The three stages for arginine decomposition show decreasing activation energies (arginine is less stable than lysine according to the scale of initial temperature decomposition).

A complete scale for thermal stability from the kinetic point of view can be written as phenylalanine > lysine > threonine > arginine > leucine > cysteine. Comparison with the scale of thermal stability referring to the initial decomposition temperature, shows different positions for phenylalanine and arginine, although the positions of the other compounds are more or less unchanged.

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