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Thermodynamics and kinetics of decomposition processes for standard α-amino acids and some of their dipeptides in the solid state

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Abstract

Thermodynamic and kinetic data of the thermal decomposition process of the "standard" α-amino acids in the solid phase are presented in this work and correlated with the features of the four classes into which these compounds are classified in the liquid phase.

The thermal stability of the components of the various classes is mainly linked to the decarboxylation process which, in turn, is influenced by the side-chains. The heat effects of the chemical processes and physical transitions, and the kinetic quantities of the decomposition processes of these compounds are presented.

Three series of dipeptides have also been studied in the solid phase. In the first series, the mutual influence of two α-amino acids makes the dipeptides less stable than the independent free components. In the second, the methyl group plays a fundamental role in the thermal stability just as it does in the liquid phase where it is the key factor in the mutual influence of the different dipeptide structures. Finally, in the third class, a symmetrical system averages the thermodynamic quantities of the components.

INTRODUCTION

The thermodynamic properties in water of 19 "standard" α-amino acids have been studied extensively in our laboratory [1–7]. 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,

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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: the solvation effects of a molecule with a particular atom at different positions in its skeleton; the solvation effects on different classes of α-amino acids; the thermodynamic effects on different classes of α-amino acids; and the thermodynamic effects on α-amino acids having similar structures.

Dipeptides (which are compounds made up of two α-amino acids) are the smallest parts of proteic chains.

The calorimetric study of the mutual structural influences of α-amino acids has been the subject of three papers [8–10] from our laboratory. In the first [8], the influence of the structure of valine, which was one component of each dipeptide, upon a number of other α-amino acids as the second component, and the reciprocal influence of these other α-amino acids upon the structure of valine, were investigated using valil–valine as a reference structure. In the second paper [9], the influence of a methyl substituent group upon some structures of "standard" α-amino acids was studied. The third [10] reported the reciprocal influence of structures in a series of dipeptides where the reference structure was glycine.

It is also 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 the 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 and TG) and the kinetics of the decomposition processes of α-amino acids have been reported [11–20].

Most of the aliphatic α-amino acids adopt a double layer structure, as shown by neutron diffraction [19]. 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 have been related (by means of DSC and X-ray measurements) to a conformational change in the alkyl chains, to rearrangement of the layers along the stacking direction and to the appearance of a completely different hydrogen-bond network.

The "standard" α-amino acids and some dipeptides were also studied in the solid state in our laboratory [21–23] by simultaneous TG–DSC measurements. Using these techniques, α-amino acids with similar structures [22] but belonging to different classes can be grouped by their thermograms which have the same shape, although this does not give enough information on their thermal structural variation. That is, in the solid phase, the thermal behaviour of "standard" α-amino acids is influenced by their structures, while in the liquid phase the polarization of the side chains is

the criterion used to divide these compounds into four classes: 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.

In addition, the thermal behaviour of the dipeptides in the solid phase was compared with that of the independent free α-amino acids contained in them [23].

The aim of this work was to ascertain if it is possible to correlate our experimental kinetic and thermodynamic data of the thermal decomposition of "standard" α-amino acids with the features of the four classes into which the above cited compounds are classified in the liquid phase. The thermodynamic data of the thermal behaviour of some dipeptides were also considered and compared with those of the independent free α-amino acids contained in the dipeptides.

The α-amino acids studied were L(−)α-alanine (Ala), D(+)valine (Val), L(−)leucine (Leu), L(−)isoleucine (Ile), L(−)proline (Pro), L(−)phenylalanine (Phe), L(−)tryptophan (Trp), L(−)methionine (Met), L(−)glycine (Gly), L(−)serine (Ser), L(−)threonine (Thr), L(−)cysteine (Cys), L(−)tyrosine (Tyr), L(−)aspargine (asp), L(−)glutamine (glu), L(−)lysine (Lys), L(−)arginine (Arg), L(+)aspartic acid (Asp) and L(+)glutamic acid (Glu).

The dipeptides considered were valil–valine (Val–Val), valil–leucine (Val–Leu), valil–proline (Val–Pro), valil–tryptophan (Val–Trp), valil–serine (Val–Ser), valil–tyrosine (Val–Tyr), seril–alanine (Ser–Ala), seril–glycine (Ser–Gly), alanil–threonine (Ala–Thr), glycil–threonine (Gly–Thr) and tyrosil–valine (Tyr–Val).

EXPERIMENTAL PROCEDURE

The experimental measurements were carried out on a Stanton–Redcroft 625 simultaneous TG–DSC connected to an Olivetti 250 computer. Instrument calibration was performed with standard indium and tin samples of known fusion temperatures and enthalpies of fusion. For decomposition studies under dynamic conditions, the TG–DSC apparatus was set up as follows. Samples (5–6 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 were continuously removed. The heating rate was always 10°C min^{-1}, and at least two runs were made for each compound. All the thermodynamic quantities were calculated using the Stanton–Redcroft acquisition system trace, version 4.

A dynamic (non-isothermal) TG technique was used in the kinetic study of the decomposition reaction.

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

The simultaneous TG–DSC system is a very useful tool for investigating organic compounds because it combines, in a single run, weight loss and heat change processes so that transformations that occur even with small weight changes (chemical reactions, decomposition, vaporization, oxidation processes) can be distinguished from those occurring without weight change (melting, crystallization, polymorphic changes).

Thermodynamic data include the initial temperature of decomposition, the weight percent loss and the enthalpy values of the various processes (melting, crystallization, polymorphic changes, decomposition, chemical reactions) occurring as the temperature increases.

Kinetic data include the kinetic energy of activation E_a related to the overall decomposition processes.

RESULTS AND DISCUSSION

α-Amino acids

The features of the four classes correlated with our experimental data.

First class

Five of these α-amino acids have aliphatic chains: α-alanine, leucine, isoleucine, valine and proline. Two have aromatic side-chains: phenylalanine and tryptophan. Methionine contains a sulphur atom within the aliphatic chain.

α-Alanine lies near to the line which separates polar (without charge) from hydrophobic α-amino acids. Proline differs from all the other standard α-amino acids: it is in fact an imino acid.

Second class

The compounds of the second class (serine, threonine, tyrosine, aspargine, glutamine, cysteine and glycine) have polar (without charge) side-chains. The polar character of serine, threonine and tyrosine is due to their hydroxyl group, that of asparagine and glutamine to their amidic groups and that of cysteine to its sulphidic group. Glycine is sometimes classified as an apolar α-amino acid. Cysteine and tyrosine have the most polar groups of this class, i.e. thiolic and hydrophenolic groups.

Third class

The compounds of this class have six carbons atoms. Lysine has a positively charged aminic group at the ε-position of its side chain and arginine has a guanidinic group with positive charge.

TABLE 1

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

Compound	Overall stage of decomposition	
	T (°C)	W (%)
First class		
L(−)α-Alanine	217–358	100
D(+)Valine	161–323	98.2
L(−)Leucine	207–342	99.3
L(−)Isoleucine	201–331	98.7
L(−)Proline	218–330	95.5
L(−)Phenylalanine	237–401	93.2
L(−)Tryptophan	270–503	76.2
L(−)Methionine	236–367	96.0
Second class		
L(−)Glycine	226–573	65.0
L(−)Serine	213–500	79.5
L(−)Threonine	228–327	93.3
L(−)Cysteine, H_2O, HCl	120–600	93.7
L(−)Tyrosine	293–577	74.4
L(−)Asparagine	77–521	64.4
L(−)Glutamine	173–481	64.5
Third class		
L(−)Lysine, HCl	260–590	87.5
L(−)Arginine	244–589.5	75.6
Fourth class		
L(+)Aspartic acid	212–521	64.4
L(+)Glutamic acid	186–481	68.1

Fourth class

The compounds of the fourth class, aspartic and glutamic acids, have a second carboxyl group which is completely ionized at pH 6.00–7.00 and so have a negative charge.

Thermal stability

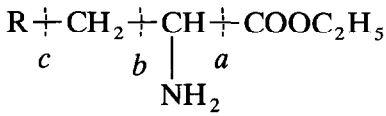
The values of the thermodynamic quantities are given in Table 1. In the first class, the scale of thermal stability referring to the initial temperature of decomposition can be written

Val < Ile < Leu < α-Al < Pro < Met < Phe < Trp

An attempt to explain the thermal stability order can be made by referring to the spectra of the compounds obtained using the GC–MS technique [24]. Although these spectra relate to the fragmentation ions of the reactants, some predictions concerning the thermal processes can be

made from them. For example, the peaks obtained from GC–MS of the ethyl esters of the α-amino acids are due to the fragmentation of the molecules by preferred cleavage of those bonds which lead to energetically more favoured, i.e. the best stabilized, positive ions.

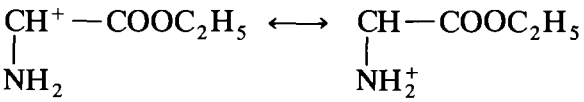
The fragmentation of a generic ethyl ester of α-amino acid



can be considered by cleavage of bonds *a*, *b* and *c*. Cleavage of bond *a* gives rise to the loss of carboxyl group and to the formation of a resonance stabilized ion **I** (amine fragment) obtained by retention of the positive charge on the nitrogen

I

Ion **II** resulting from the cleavage of bond *b* (ester fragment) is also stabilized by the retention of the positive charge on the nitrogen atom



II

The introduction of a heteroatom or aromatic system into the R side chain increases the tendency for cleavage of the other bonds (*c*).

From literature data [24], the following information can be obtained:

(a) the main process of fragmentation for valine, leucine and isoleucine is the loss of the carboxyl group, followed by the loss of the aminic group;

(b) glycine loses the carboxyl group;

(c) threonine fragments give rise to a stabilized ion obtained by water loss and a cyclization process.

(d) the main ion fragment obtained from methionine is represented by the side chain CH_3–S–CH_2^+. Other fragments are CH_2=CH–$\underset{\displaystyle NH_2}{CH^+}$ obtained by the loss of CH_3SH, and the "amine fragment" with the loss of carboxyl group.

From this experimental evidence, the higher initial temperature of decomposition of methionine with respect to that of α-alanine can be related to its greater difficulty in losing the carboxyl group (easier process) due, in turn, to the presence of a heteroatom which favours breakage of the side chain. The longer chains of the other compounds decrease the initial temperature of decomposition, this probably being due to the fact that the

$R-\underset{\underset{NH_2}{|}}{CH}^+$ product obtained by the loss of the carboxyl group undergoes a further decomposition. Therefore, the above thermal stability order is determined by the fact that the bonds break at different positions in the molecules depending on the side chain.

The presence of rings in the side chains gives rise to breakage between the α and β carbon atoms. The decrease in the decarboxylation process that is linked to this fact, could account for the larger values of the thermodynamic quantities of tryptophan and phenylalanine with respect to compounds with aliphatic chains.

In the second class, the order of decomposition is asp < Cys < glu < Ser < Gly < Thr < Tyr. The presence of the second NH_2 group in aspargine (asp) and glutamine (glu) decreases the thermal stability of these compounds by virtue of the loss of this group: the deamination becomes the first process [22]. Desulphydration, deamination and decarboxylation, which occur simultaneously, result in the same effect for cysteine.

The hydroxyl group stabilizes threonine and enhances its thermal stability by virtue of an initial process of water loss. The positions of glycine and tyrosine are due to the shortness of the aliphatic chain (one hydrogen atom) and to the hydrophenolic group which decreases the decarboxylation process.

For the third class, arginine is less stable than lysine and both these compounds show a high initial temperature of decomposition, probably due to the positive charges of the side chains.

Glutamic and aspartic acids, which form the fourth class, differ from one another in only a CH_2 group, while their thermal behaviours show some differences: the presence of an additional CH_2 group in the former leads to a lower temperature of decomposition.

The averages of the initial temperatures of decomposition for the various classes are in the order 4th = 2nd < 1st < 3rd.

The fourth class shows the lowest mean values of thermal stability while the third class shows the highest ones. This can be related to the negatively and positively charged chains. Therefore, it can be hypothesized that a positively charged chain hinders the decarboxylation process from the COO^- group, while for a negatively charged chain, the reverse is true.

It can be concluded that the thermal stability of the various classes is mainly linked to the decarboxylation process, which in turn, is influenced by the side chains.

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

TABLE 2

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

Compound	Overall stage of decomposition	
	T (°C)	$\Delta H^{\ominus}$ (cal g^{-1})
First class		
L(−)α-Alanine	210–328	335.4
D(+)Valine	224–321	135.4
L(−)Leucine	232–328	220.9
L(−)Isoleucine	201–322	287.0
L(−)Proline	227–318	214.8
L(−)Phenylalanine	253–393	84.3
L(−)Tryptophan	277–474	119.6
L(−)Methionine	248–324	207.6
Second class		
L(−)Glycine	226–318	251.9
L(−)Serine	213–269	155.6
L(−)Threonine	226–310	171.7
L(−)Cysteine, H_2O, HCl	120–269.7	46.7
L(−)Tyrosine	281–355	148.0
L(−)Asparagine	82–404	294.8
L(−)Glutamine	183–342	222.6
Third class		
L(−)Lysine, HCl	260–400	118.7
L(−)Arginine, HCl	244–430	149.6
Fourth class		
L(+)Aspartic acid	215–451	277.4
L(+)Glutamic acid	195–321	167.5

up to its complete decomposition, can be derived. The enthalpy data are given in Table 2.

The heat scale for the first class is Phe < Val < Trp < Met < Pro < Leu < Val < α-Ala. In this scale, α-alanine requires the largest energy to be completely decomposed. The position of methionine can be explained by the formation of stable decomposition products, i.e. cyclic compounds. The aromatic groups of phenylalanine and tryptophan stabilize the decomposition products.

For the second class, the heat scale is Cys < Tyr < Ser < Thr < glu < Gly < asp. The first position of cysteine is due to an exothermal process involving loss of a diatomic group [21]. The aromatic group stabilizes the decomposition products for tyrosine. For both glutamine and aspargine, the overall enthalpy is large because energy is also required for the loss of the second NH_2 group [22].

For the third class the order is lysine < arginine because the thermal decomposition of lysine gives rise to stable cyclic compounds [24].

TABLE 3

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

Compound	Overall stage of decomposition		
	T (°C)	E_a (kcal mol^{-1})	ln A (s^{-1})
First class			
L(−)α-Alanine	217–358	23.0	19.8
D(+)Valine	161–323	6.7	3.9
L(−)Leucine	207–342	32.2	27.4
L(−)Isoleucine	201–331	28.3	24.1
L(−)Proline	218–330	13.11	10.2
L(−)Phenylalanine	237–401	5.2	2.0
L(−)Tryptophan	270–503	6.2	2.1
L(−)Methionine	236–367	83.1	73.4
Second class			
L(−)Glycine	226–573	5.9	3.2
L(−)Serine	213–500	8	5.7
L(−)Threonine	228–327	38.8	35.5
L(−)Cysteine, H_2O, HCl	120–600	6.4	4.3
L(−)Tyrosine	293–577	11.4	7.8
L(−)Asparagine	77–521	2.6	0.6
L(−)Glutamine	173–481	5.9	2.7
Third class			
L(−)Lysine, HCl	260–590	9.85	6.1
L(−)Arginine, HCl	244–589.5	8.79	4.9
Fourth class			
L(+)Aspartic acid	212–521	2.1	1.4
L(+)Glutamic acid	186–481	6.0	2.8

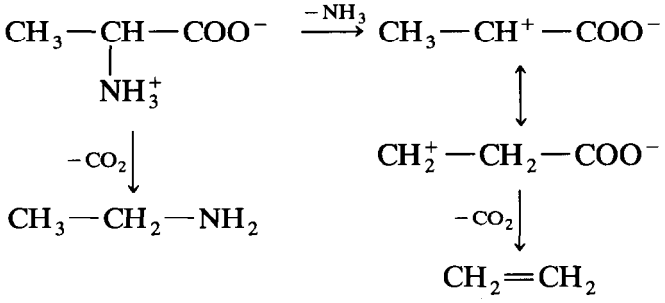
Finally, for the fourth class, the order is glutamic acid < aspartic acid. The presence of an additional CH_2 group in glutamic acid allows the formation of a stable cyclic compound which lowers the overall enthalpy of decomposition [22].

The averages for the overall enthalpies for the various classes are in the order 3rd < 2nd < 1st < 4th, which is symmetrical to that of the thermal stability.

Kinetics

A kinetic-dynamic TG study of the decomposition processes for the present compounds has been carried out using the McCarthy and Green method. The activation energy values, frequency factor ln A and reaction order are reported in Table 3.

The activation energies, calculated from the TG curves of the overall weight loss, can be considered as the average activation energies of the various decomposition steps.

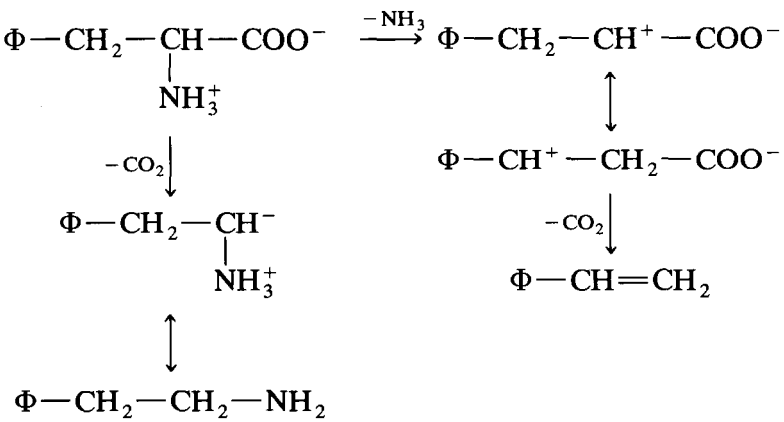


Scheme 1. Mechanism of α-alanine dissociation.

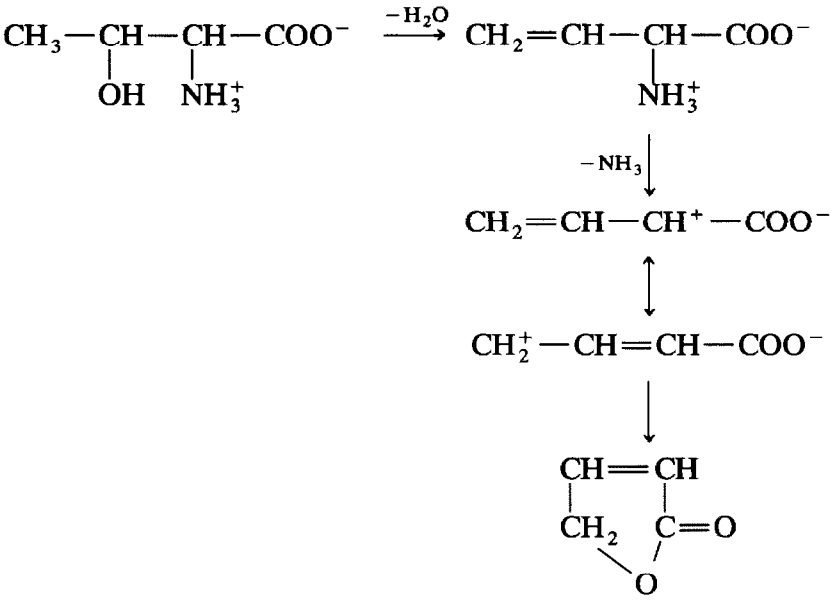
For the first class, the activation energy E_a order is Phe < Trp < Val < Pro < Ala < Ile < Leu < Met. This order can be related to the dissociation mechanism hypothesized in the literature. For example, the mechanism of the α-alanine dissociation is shown in Scheme 1 [13], whereas for phenylalanine the mechanism could be the one shown in Scheme 2 [13].

Comparing the activation energies of these two compounds, it can be observed that the phenyl group has a greater stabilizing effect on the ionization products with respect to that of the aliphatic chain of α-alanine. For this reason, α-alanine, leucine, isoleucine and methionine have greater activation energies than phenylalanine, while tryptophan has an activation energy close to that of phenylalanine. The highest value of methionine can be related to the presence of the heteroatom which allows the breakage of the side chain, thus making it more difficult to lose the carboxyl group.

The activation energies of the second class are in the order asp < glu < Gly < Cys < Ser < Tyr < Thr. Aspargine and glutamine have activation energies very close to those of aspartic and glutamic acids respectively. Therefore, the decomposition mechanisms may be practically the same.



Scheme 2. Mechanism of phenylalanine dissociation.

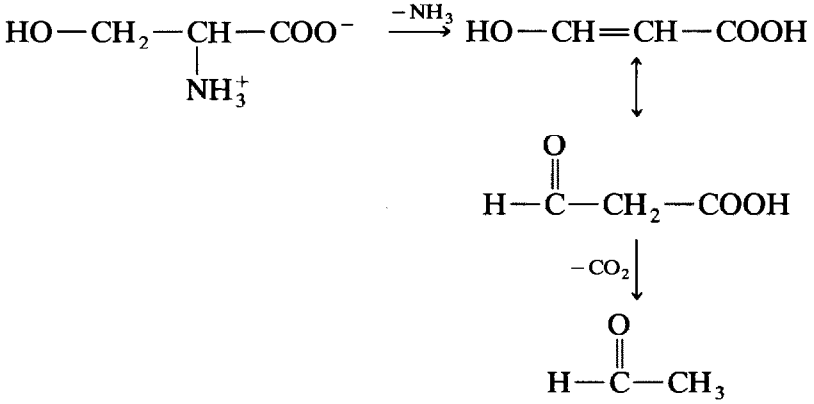


Scheme 3. Mechanism of threonine decomposition.

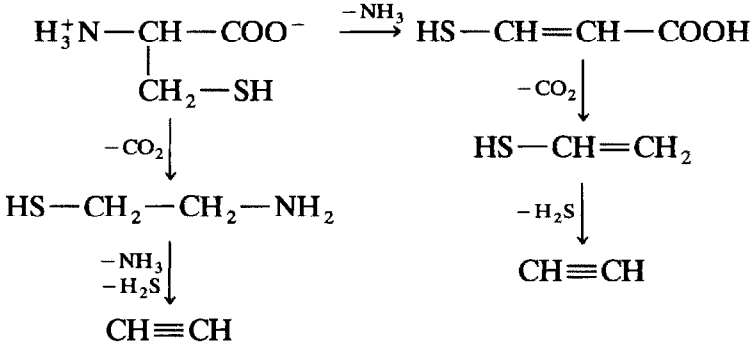
The presence of an additional CH_2 group in glutamine enhances the activation energy with respect to that of aspargine. The position of threonine is due to the absence of the initial loss of carboxyl group, with a consequent increase in the activation energy (Scheme 3) [13].

Despite the similarities in structure, serine has a lower activation energy, following Scheme 4 [13].

Serine and cysteine (Scheme 5) give rise to more stable compounds so that their activation energies are lower than that of threonine.



Scheme 4. Mechanism of serine dissociation.



Scheme 5. Mechanism of cysteine dissociation.

In the third class, lysine shows a greater activation energy than arginine.

In the fourth class aspartic and glutamic acids have values close to those of aspargine and glutamine from which they differ by an amidic group. Again the CH_2 group makes the activation energy of glutamic acid greater than that of aspartic acid.

The mean kinetic values for the various classes are 4th < 3rd < 2nd < 1st.

Summarizing, one may see that the kinetic scale is different from the enthalpic scale which, in turn, is symmetrical to that of thermal stability. It can be noted that the first two scales take into account the various processes which occur in the thermal decomposition, while the third considers only the initial process of decomposition which can be mainly identified with the decarboxylation process.

Dipeptides

The mutual influence of two α-amino acids was studied by comparing the thermal behaviour of these compounds with those of the independent free α-amino acids contained in the dipeptides (Tables 4 and 5). It should be noted that for a series of seven dipeptides, the first component is valine.

Another series can be subdivided into two pairs of dipeptides, with the following characteristics. Each couple has a common component in the dipeptide structure: the former shows threonine as a common second component, and the latter serine as a common first component. The other α-amino acids in the dipeptide structures are α-alanine and glycine. These two compounds, which are the simplest α-amino acids, differ only by one methyl group, to which all differences in the reciprocal influences among the same and different structures can be related. Indeed, in this system of couples, the influences of the same structure (serine or threonine) upon α-alanine and glycine can be considered. Furthermore the influences of glycine and α-alanine upon the structures of serine and threonine can be observed. Finally, a third couple (Tyr–Val and Val–Tyr) is considered. This

TABLE 4

Thermodynamic parameters for overall thermal decomposition of some dipeptides from TG measurements

Compound	Overall stage of decomposition	
	T (°C)	W (%)
Valil–valine	189–321	81.7
Valil–leucine	170–310	96.9
Valil–proline	163–278	86.6
Valil–tryptophan	295–422	81.3
Valil–serine	195–492	96.5
Valil–tyrosine	218–418	90.8
Valil–lysine	248–450	87.8
Seril–alanine	220–425	91.8
Seril–glycine	184–500	62.0
Alanil–threonine	217–400	90.7
Glycil–threonine	70–500	82.0
Tyrosil–valine	192–224	94.8

couple is made up of two α-amino acids which change their positions in the dipeptides.

Series having valine as first term

The structure of valine–valine was used as a reference in the study of the series of dipeptides having valine as a common first component; the

TABLE 5

Thermodynamic parameters for overall thermal decomposition of some dipeptides from DSC measurements

Compounds	Overall stage of decomposition	
	T (°C)	$\Delta H^{\ominus}$ (cal g^{-1})
Valil–valine	189–313	148.8
Valil–leucine	170–310	217.7
Valil–proline	163–278	187.9
Valil–tryptophan	295–411	144.6
Valil–serine	195–492	166.4
Valil–tyrosine	281–355	133.8
Valil–lysine	241–378	249.7
Seril–alanine	220–418	294.0
Seril–glycine	184–230	148.0
Alanil–threonine	217–252	134.0
Glycil–threonine	70–250	165.4
Tyrosil–valine	192–395	166.7

analysis of this compound can be carried out by comparing its thermogram with that of valine. The dipeptide shows a higher thermal stability and energy for the complete decomposition than valine, and its first decomposition process is represented by the loss of the carboxyl group.

The thermal stability and the overall enthalpy of valil–serine are lower than the corresponding values of the individual α-amino acids. It can be concluded that valine destabilizes the structure of serine. The first decomposition process is represented by the loss of the CH_2OH group.

The overall enthalpy of valil–leucine is close to those of the two components and the temperature range of decomposition is contained in the sum of the temperature ranges of the decomposition processes of the components. Thus the effect of valine on leucine turns out to be weak.

Taking as a reference the temperature ranges and the enthalpies of decomposition of the components of the dipeptide, it can be observed that valine destabilizes proline, decreasing the temperature range of decomposition and the overall enthalpy. The first process of decomposition can be represented by a carboxyl group.

A comparison between the ranges of temperature and enthalpy values of valine and lysine and the corresponding values of the dipeptide shows that the structure of lysine is weakened by valine. The weight loss of the first decomposition of valyl–lysine indicates a loss of the NH_3 group.

The valine structure makes the tyrosine molecule less stable: the dipeptide is 89% decomposed at 418°C while tyrosine is 78% decomposed at 576°C. In the 218–242°C interval the loss of an NH_3 group can be hypothesized.

In general in this series, the mutual influence of two α-amino acids makes the dipeptides less stable than the single components. A thermal stability scale, referred to the initial temperature of decomposition for this series can be written as Val–Leu < Val–Pro < Val–Val < Val–Ser < Val–Tyr < Val–Lys < Val–Trp. It can be noted that, with the exception of Val–Trp, the thermal stabilities of the dipeptides having α-amino acids belonging to the first class as the second component, are lower than those of the other peptides.

The influence of a methyl group in the second series

The following compounds are now considered: seril–alanine, seril–glycine, alanil–threonine and glycil–threonine. The thermal stability of seril–alanine is greater than that of seril–glycine, both for the initial temperature of decomposition and for the total enthalpy of decomposition. The stability of alanil–threonine is greater than that of glycil–threonine.

Therefore, it can be concluded that, in the solid phase, the methyl group also plays a fundamental role in the thermal stability, just as in the liquid phase where it is the key factor in the mutual influence of the different dipeptide structures [9].

Seril–alanine and seril–glycine lose the CH_2OH group of serine in the first decomposition process, while alanil–threonine and glycil–threonine lose the CH_3–CH–OH group of threonine.

Symmetrical system

In the symmetrical system valil–tyrosine and tyrosil–valine, the thermal stability is equal in the two dipeptides, just as the enthalpy values of the dissociation processes in solution of the three functional groups (carboxyl group, amine group and hydroxyl group of tyrosine) are equal in dipeptides by virtue of the symmetry of the system [9].

In the first process, tyrosil–valine loses one amine group. It can be noted that none of these fragments were caused by breaking of the amidic bond, which proved to be a rather strong bond.

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