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PREBIOTIC CHEMISTRY

Transfer of Asymmetry between Proteinogenic Amino Acids under Harsh Conditions

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Abstract The heating above 400 °C of serine, cysteine, selenocysteine and threonine leads to a complete decomposition of the amino acids and to the formation in low yields of alanine for the three formers and of 2-aminobutyric acid for the latter. At higher temperature, this amino acid is observed only when sublimable α-alkyl-α-amino acids are present, and with an enantiomeric excess dependent on several parameters. Enantiopure or enantioenriched Ser, Cys, Sel or Thr is not able to transmit its enantiomeric excess to the amino acid formed during its decomposition. The presence during the sublimation-decomposition of enantioenriched valine or isoleucine leads to the enantioenrichment of all sublimable amino acids independently of the presence of many decomposition products coming from the unstable derivative. All these studies give information on a potentially prebiotic key-reaction of abiotic transformations between α-amino acids and their evolution to homochirality.

Keywords Amino acid · Sublimation · Enantioenrichment · Transfer of asymmetry

Introduction

The understanding of the sublimation of an enantioenriched compound began with several observations of changes of the enantiomeric excess in partial sublimations (Pracejus 1959;

Dedicated to the memory of Professor James P. Ferris

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Kwart and Hoster 1967). The partial sublimation of chiral compounds has been rationalized by Garin et al. (1977) and then in the well-known book of Jacques et al. (1981) by the sentence: "the initial sublimate always possesses the composition of the vapor eutectic". Few studies were then devoted to the sublimation of enantioenriched compounds before the work of Soloshonok et al. 2007 reporting the sublimation of an enantioenriched carboxylic acid. The same year, Perry et al. (2007) and Fletcher et al. (2007) published the first articles on the sublimation of an enantioenriched amino acid. In the case of α-alkyl substituted derivatives the behavior of the enantioenriched amino acids sublimed at low temperature was first rationalized by Bellec and Guillemin (2010) and then, with more amino acids, by Tarasevych et al. (2013). A behavior of kinetic conglomerate was unambiguously demonstrated starting from mixtures of enantiomers of one amino acid and that in the conditions of very slow sublimations at low temperature (around 100 °C) used by the authors. Starting from the racemate and an enantiomer, the behavior is strongly dependent on the studied amino acid. Probably due to the very low vapor pressure of amino acids at this temperature and because such sublimations with condensation of the gaseous phase correspond to an open system, the experimental conditions are more or less close to the thermodynamic equilibrium. The composition of the gaseous phase is thus different of the one of the vapor eutectic (euatmotic) in many experiments. In non-thermodynamic conditions of sublimation of serine, Perry et al. (2007) have proposed the formation of octameric clusters previously observed by mass spectrometry (Yang et al. 2006) to explain the results.

In the context of prebiotic chemistry, little attention has been paid to the transmission of homochirality between biologically important molecules, and particularly when using sublimation. In 2011, it has been demonstrated that an α-alkyl-α-amino acid (Val, Leu, Ile, Ala) can be sublimed under air in an Erlenmeyer placed on a plate heated at the very high temperature of 500 °C (Viedma et al. 2011). In the case of an enantioenriched sample (40% of enantiomeric excess (*ee*)), some of them, Val and Ile, gave an enantioenriched sublimate of the whole mixture, a property not observed for two other ones, Ala and Leu. A lively interest was thus aroused by the increase of *ee* under harsh conditions (500 °C) with an unusual technique but without clear understanding of the reaction pathway although the nature of the formed crystals (racemate or conglomerate) was associated to the properties of each amino acid (Viedma et al. 2011, 2012).

Starting from this work, we have demonstrated (Tarasevych et al. 2015) that such reiterative high temperature sublimation (RHTS) of an enantioenriched amino acid mixed with a racemic one leads to the deracemization of the latter with a handedness identical to the one of the enantioenriched amino acid. Using one enantiopure and several racemic amino acids, an unambiguous and unprecedented synergistic effect was observed leading to deracemized amino acids with higher *ee*s than those observed with mixtures containing fewer components.

The preservation or amplification in complex mixtures of properties observed for a pure compound is probably a prerequisite to possess some potential significance in prebiotic chemistry. However, why such an enantioenrichment occurs in these sublimations remain misunderstood and we have developed several studies to know the scope and limitations of this reaction. One of the first questions was to determine if this property was limited or not to α-alkyl-α-amino acids (Ala, AABA, Leu, Ile, Val, n-Val, n-Leu) (Tarasevych et al. 2015). We report here studies on the RHTS of four proteinogenic amino acids, Ser, Cys, Sel and Thr which are known to give on heating a chiral amino acid among other products.

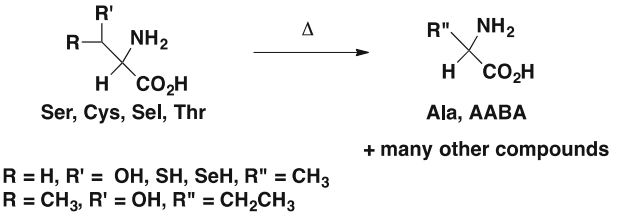
Results and Discussion

In function of the temperature, the heating of serine, cysteine, selenocysteine and threonine leads to a partial or complete decomposition of the amino acid and to the formation of alanine for the three formers and 2-aminobutyric acid for the latter in quite low yields (Fischer and Leuchs 1902; Daft and Coghill 1931; Wieland and Wirth 1949; Basile et al. 2011; Dery et al. 2015) (Scheme 1). A pioneering work on the sublimation around 200 °C of serine has been reported 10 years ago in quite particular conditions (Perry et al. 2007): starting from a sample of serine with a small *ee* (3%), a huge increase of the ee up to 90% was observed in the sublimate and attributed to the selective sublimation of a homochiral octameric cluster. Alanine, ethanolamine and other compounds were also formed. Following this work, we performed the sublimation of pure serine at 500 °C applying our standard conditions of sublimation (Tarasevych et al. 2015). In this case, neither Ser nor Ala was detected in the sublimation products. Our previous work being based on the sublimation of mixtures of amino acids (Tarasevych et al. 2015), we then studied the sublimation-decomposition of Ser in the presence of one or more other amino acids in the aim to determine the role played by these amino acids and their *ee*s. We will successively describe in this paper the results obtained at various temperatures with serine, in different ratios with enantiopure valine, then with non-racemic valine, with other amino acids and then starting from cysteine, selenocysteine or threonine.

The Influence of Temperature on the Process Heating of either form of serine (L, D or DL) by itself at 300 °C gave a mixture of serine and racemic alanine in 11 and 5.9% yields respectively determined by ^{1}H NMR with an internal reference of glycine. The homochirality of serine is lost during the formation of alanine showing a reaction pathway involving an achiral intermediate (Fischer and Leuchs 1902; Bada and Shou 1978; Yaylayan et al. 2000; Takahashi et al. 2011).

Starting from a Ser-Val mixture, we then studied the influence of the temperature on the *ee* of the alanine formed. At 300 °C, L-serine with L-valine in a 1:1 M ratio gave alanine in 11.6% yield with a 14.6% *ee* (L). Serine was still present in the decomposed mixture but in slightly lower amount (8.5%) comparing to the experiment with pure L-serine (11%).

Sublimation–decomposition of a mixture of racemic DL-serine in the presence of enantiopure L-valine with a 2:1 Val:Ser molar ratio was then performed at 500, 430 and 350 °C. At 500 °C, the *ee* of Ala reached 40.5% (L). Decreasing temperature down to 430 °C gave a mixture containing L-alanine with a 23.4% *ee*. Further lowering of the temperature of the process (350 °C) caused further fall of the disbalance in the alanine enantiomer ratio (16.0% *ee* L) (Table 1). A sample solubilized and dried before sublimation (Table 1, entry 5) gaves *ee*s slightly smaller. To demonstrate that such behaviors are not intrinsically correlated to the presence of oxygen in the gas phase (a non-realistic prebiotic scenario) we performed an experiment in an atmosphere of nitrogen. Similar results were observed but with a lowering of



Scheme 1 Formation of Ala or AABA in the thermal decomposition of Ser, Cys, Sel, Thr

the *ee* of Ala (Table 1, entry 6). The dependence of the nature of the gas phase in the *ee*s but not in the general behavior of amino acids has already been observed in other experiments (Tarasevych et al. 2015).

It should be noted that when L-serine and DL-valine are used in a molar ratio of 1:0.5, no enantiomeric excess was observed in the formed product, confirming the chiral inductor being L-valine and the inability of serine to play this role.

Changing the L-Val:DL-Ser Molar Ratio To study how the molar ratio between enantiopure L-valine and serine affects the resulted *ee* of alanine, we prepared a series of mixtures that were sublimed under air at the same temperature (500 °C) in standard conditions. We found that decreasing the ratio between L-Val and DL-Ser (1:0.25 to 1:7) the *ee* of alanine is increasing and then decreasing (Table 2), the highest *ee*s of alanine being obtained with mixtures containing comparable amounts of valine and serine (1:0.5, 1:1, 1:2) with maximal value at 1:1 M ratio. It should be noted that in the same type of experiments with mixtures of L-Val and Ser (1:0.5), independently on the nature of starting chiral form of Ser (either L, D, or DL), Ala was obtained with similar *ee*s (35–40%) at 500 °C. The molar ratio between valine and alanine in the sublimate was about 12:1 starting from a molar ratio of 1:1 between valine and serine.

Results with Enantioenriched Valine and DL-Serine We studied the process of alanine deracemization induced by non-racemic mixtures of valine with a 1:0.5 Val:DL-Ser molar ratio. In the experiments with L-enriched mixtures of valine (9.4, 26.9 and 46.2% *ee*), we observed *ee*s of L-valine (12.8, 34.7 and 63.7% resp.) corresponding to enantioenrichments (Table 3) (Fig. 1, disks and dashed line). The *ee*s of the formed alanine in function of the *ee*s of the starting valine has features of a linear growth shape (Fig. 1, triangles and line).

Sublimation of Serine with Isoleucine, Complex (Ternary) Mixtures and other Chiral Compounds Besides valine, we tried another chiral α-amino acids in the role of asymmetric inductor (Table 4). Sublimation at 500 °C of racemic serine with enantiopure D-isoleucine in a 0.5:1 M ratio led to the formation of D-alanine with a 21.9% *ee*, a data lower than the one obtained with L-valine. With more complex mixtures containing one enantiopure

Table 1 Influence of temperature, presolubilization and gas phase composition

Entry	Temperature (°C)	Ala *ee* (L) (%)
1[a]	300	14.6
2[b]	350	16.0
3[b]	430	23.4
4[b]	500	37.8
5[b,c]	500	29.8
6[b,d]	500	17.8

[a] L-Val:Ser in a 1:1 M ratio

[b] L-Val:Ser in a 2:1 M ratio; time of heating: 15 min

[c] The mixture of L-Val and DL-Ser was presolubilized in water followed by evaporation, drying in vacuo and sublimation/decomposition

[d] Sublimation/decomposition of the mixture in an atmosphere of nitrogen

Table 2 Influence of the ratio between enantiopure valine and racemic serine on the resulted enantiomeric excess of alanine (500 °C, 15 min)

Entry	L-Val:DL-Ser molar ratio	Ala *ee* (L), %
1	1:0.25	27.9
2	1:0.5	40.5
3	1:1	51.5
4	1:2	42.7
5	1:3	36.6
6	1:4	31.4
7	1:7	24.8

inductor (valine) and two racemic components (leucine and serine), we observed that a synergystic effect takes place when increasing the number of components (Table 4, entry 2), a result consistent with our previous studies (Tarasevych et al. 2015): sublimation of a mixture of D-valine, DL-leucine and DL-serine in 1:0.25:0.5 M ratio gave sublimate containing almost enantiopure D-valine (95% *ee*), D-leucine and D-alanine with 37.2 and 42.6% *ee*, respectively.

We then tried to find another inductor in mixtures using serine with asparagine, aspartic acid in two or three components mixtures. Similarly we used quartz or calcite (which has only mirror related faces) as possible inorganic inductors. In all cases, only racemic alanine was obtained, (Table 4, entries 3–8) showing that a limited amount of compounds can play the role of inductor.

Results on the Sublimation-Decomposition of Cys, Thr, and Sel Cysteine and threonine have SH and OH groups in the side chain, respectively. Among the numerous products of decomposition of the amino acids obtained on heating, (Moldoveanu 2010), cysteine gives alanine, and threonine leads to 2-aminobutyric acid. We performed a series of sublimation-decomposition of these amino acids in the presence of enantiopure valine (Table 5). High temperature heating of L-cysteine with either L or D valine led to the formation of non-racemic alanine with a *ee* of the same handedness that the initial valine and a yield slightly lower than starting from serine (5–10%). Changing molar ratio between cysteine and valine from 1:0.5 (entry 2) up to 1:8 (entry 7), the *ee* of the formed alanine was gradually increasing from 18.2 to about 52%. Using racemic cysteine instead of enantiopure gave a comparable result (entry 9). Using non-racemic L-Val (20.2% *ee*) induced lower L-Ala *ee* 18.8% (entry 8) comparing to the 34.4% *ee* L-Ala obtained with enantiopure L-Val at the same molar ratio (entry 4); at the same time, the *ee* of valine grew to 30.0% *ee*. In the GC analysis of the products formed on heating DL-threonine with L-valine, we detected peaks corresponding to the enantiomers of 2-aminobutyric acid. However, their concentration with respect to valine was too low and the peaks of L-valine and L-aminobutyric acid overlapped preventing the determination of *ee*s. Starting from a mixture of L-selenocysteine with L-valine under the same conditions led to black decomposition products and no peak of alanine was detected by GC analysis. Decreasing temperature did not give detectable amounts of alanine.

Table 3 Sublimation of enantioenriched L-valine with DL-serine [a]

Entry	Val *ee* (L), % starting	Val *ee* (L), % sublimate	Ala *ee* (L), % sublimate
1	9.4	12.8	3.8
2	26.9	34.7	4.2
3	46.2	63.7	25.1
4	100	100	40.5

[a] 1:0.5 M ratio of Val:DL-Ser, 500 °C, 15 min

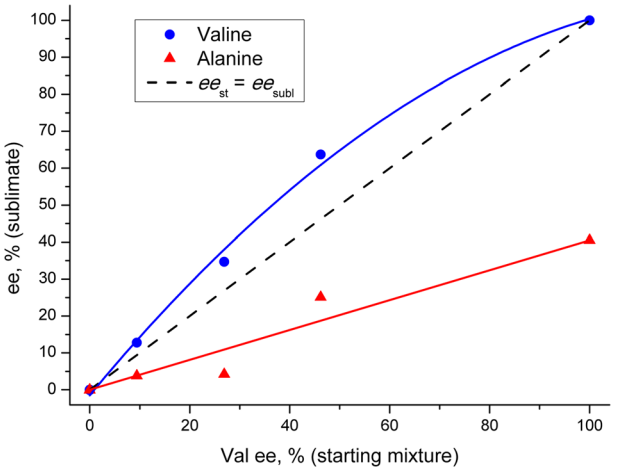


Fig. 1 Sublimation of enantioenriched L-valine with DL-serine

Conclusion

High temperature sublimation-decomposition of racemic or enantioenriched serine gives racemic alanine among other products. Such a thermally unstable amino acid giving another amino acid cannot transmit, even partially, the enantiomeric excess of the starting material. On heating at 500 °C, the presence of one or several α-alkyl-α-amino acids allows the formation of alanine at a temperature where alanine was not observed starting from pure serine. When serine was heated in the presence of enantioenriched valine or isoleucine, alanine was obtained with significant enantiomeric excess and with the same handedness than the one of the starting Val or Ile, evidencing their role as an asymmetric inductor. Sublimation-decomposition of the thermally unstable cysteine revealed the same behavior: formation of racemic alanine in the absence of another chiral amino acid and formation of enantioenriched Ala in the presence of enantioenriched valine or isoleucine. The main behavior of the sublimation reactions at high temperature of mixtures of amino acids containing unstable derivatives and enantioenriched sublimable components is a common preservation of the sublimable α-alkyl-α-amino acids and an enantioenrichment of each. Among all the reactions considered as potentially prebiotic, the reiterative high temperature sublimation of amino acids has a particular place by its simplicity but mainly by a synergistic effect observed in complex mixtures leading to higher

Table 4 Sublimation-decomposition of serine with other chiral compounds

	Starting mixture (molar ratio)	Sublimate, *ee* %
1	L-Ile + DL-Ser (1:0.5)	Ile: 97.7 L, Ala: 21.9 L
2	D-Val + DL-Leu + DL-Ser (1:0.25:0.5)	Val: 94.7 D, Leu: 37.2 D, Ala: 42.6 D
3	L-Asn + DL-Ser (1:0.5)	Traces of rac-Ala
4	L-Asp + DL-Ser (1:0.5)	Traces of rac-Ala
5	L-Asp + DL-Ser + DL-Val (1:0.5:0.5)	rac-Val, rac-Ala
6	L-Asn + DL-Ser + DL-Val (1:0.5:0.5)	rac-Val, rac-Ala
7	DL-Ser + quartz [a]	Traces of rac-Ala
8	DL-Ser + calcite [a]	Traces of rac-Ala

[a] Particles of quartz and calcite with a size of about 0.1 mm

Table 5 Sublimation-decomposition of mixtures of cysteine, selenocysteine and threonine with valine

Entry	Mixture (molar ratio)	Products, *ee* %
1	L-Cys + D-Val (1:0.5)	Ala: 43.8 D [a]
2	L-Cys + L-Val (1.5:0.25)	Ala: 18.2 L, Val: 95.8 L
3	L-Cys + L-Val (1:0.25)	Ala: 29.7 L [b]
4	L-Cys + L-Val (1:0.5)	Ala: 34.2 L [b]
5	L-Cys + L-Val (1:1)	Ala: 38.5 L [b]
6	L-Cys + L-Val (0.25:1)	Ala: 38.2 L [b]
7	L-Cys + L-Val (0.25:2)	Ala: ~52 L[b,c]
8	L-Cys + 20.2% *ee* L-Val (0.5:1)	Ala: 18.8 L, Val: 30.0 L
9	DL-Cys + L-Val (0.5:1)	Ala: 48.1 L [b]
10	DL-Thr + L-Val 0.5:1	AABA,[d] Val: 97.1 L
11	L-Sel + L-Val (1:0.5)[e]	No peaks detected by GC analysis

[a] *ee* of Val > 99.5% (D)

[b] *ee* of Val > 99.5% (L)

[c] Peaks of low intensity

[d] Yield <3%

[e] A series of experiments at 430 and 500 °C were done

enantiomeric excesses for each amino acid, this property being kept even in the presence of the many decomposition products of an unstable component.

Experimental Part

All mixtures of amino acids specified in Tables 1-5 (with the exception of entry 5, Table 1) were prepared by careful mechanical grinding with a mortar and a pestle (the initial amounts of amino acids were calculated to get not less than 50 mg of the resulted mixture). Mixtures containing non-racemic valine (Table 3, entries 1–3 and Table 5, entry 8) were prepared from the enantiopure L form and the racemic compound (DL). A mixture of L-Val and DL-Ser specified in Table 1, entry 5, was dissolved in deionized water (10 mL) with slight heating; the resulted solution was cooled to room temperature and evaporated using a rotary evaporator with a water bath heated to 40 °C; the obtained residue was dried in vacuo (0.1 mbar) with a water bath (~40 °C) over several hours (2–3 h).

All the experiments have been performed 2 or 3 times. Variations of generally ±3% with a maximum of 7% were observed in all experiments

A sample of amino acids (50 mg) was poured at once into a 1 L screw-capped Erlenmeyer flask that had been previously heated on a hot plate for 1.5 min (for the temperature see Tables 1-5 and the discussion in the text). The flask was quickly closed and the heating was maintained for another 15 min. After cooling to room temperature the sublimed material was then dissolved in 5 mL of 0.1 M HCl and derivatized according to the procedure described by Hušek (1991) with some modifications. An aliquot of the solution (90 μL) was transferred to a 5 mL vial and diluted with water (270 μL) and pyridine/ethanol mixture (4:1, 240 μL). Ethyl chloroformate (ECF) (30 μL) was added to the solution and the capped vial was vigorously shaken for ~15 s to form an N-ethoxycarbonyl-amino acid ethyl ester. The derivatives were

extracted with chloroform (~1 mL containing 1% ECF) and the organic phase was separated with a pipette, passed through a pad of silica gel. 2,2-Dimethoxypropane (~1 mL) was added and the resulted solution was evaporated and dried in vacuo. The residue was dissolved in dry diethyl ether (~1.5 mL), transferred into a 2 mL GC vial, and a sample volume (1–3 μL) was then injected in the GC chromatograph equipped with a chiral column.

To determine the precise value of the initial enantiomeric excess of valine (Table 3, entries 1–3 and Table 5, entry 8), trace amounts of the mixtures (< 1 mg) were dissolved in a mixture of water/ethanol/pyridine (7.5:4:1, 500 μL) following by the addition of ethyl chloroformate (ECF) (25 μL). Subsequent working up of the reaction mixture as described above gave N-ethoxycarbonyl-valine ethyl esters.

GC capillary CHIRALDEX™ G-TA column (L x I.D. 30 m × 0.25 mm, df 0.12 μm – film thickness) at Shimadzu GC-2014 was used for the analysis of enantiomeric composition of derivatized sublimates of aliphatic amino acids. Conditions for the chiral analysis of N-ethoxycarbonyl-amino acid ethyl esters (alanine, leucine, iso-leucine, valine): total time of the program 126.33 min; carrier gas He, flow control mode – linear velocity, pressure 145.9 kPa, total flow 22.3 mL/min, column flow 1.76 mL/min, linear velocity 40.0 cm/s, purge flow 3.0 mL/min. Column conditions: 90 °C for 3 min; 0.6 °C/min up to 120 °C, hold time 20 min; 0.6 °C/min up to 140 °C, without hold time; 2 °C/min up to 160 °C, hold time 10 min at this temperature. Retention times (min), measured D/L ratio for commercially available racemates: Ala 37.88 (L), 34.44 (D), D/L 1.0032; Leu 59.06 (L), 55.56 (D), D/L 1.017; Val 47.58 (L), 45.28 (D), D/L 1.0024; isoLeu 59.83 (L), 54.08 (D), 1.0855.

To determine absolute yields several sublimates were dissolved in water, the solutions were evaporated using a rotary evaporator at 60 °C; the obtained residue was dried in vacuo (0.1 mbar) with a hot water bath (~40 °C) over several hours (2–3 h). The obtained residues were weighted and dissolved in a standard volume of D_2O. ^1H NMR spectra were recorded on Bruker Avance 400 MHz NMR spectrometer; an internal standard (glycine) was used to calculate the yields, based on the integral area of the peaks.

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