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Sublimation of mixtures of α-alkyl amino acids for enantioenrichment.

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Abstract

High temperature sublimations of mixtures of α-alkyl amino acids with, at the minimum, one enantioenriched component allow huge enantioenrichments of the previously racemic or enantioenriched components.

1. Introduction

Recent studies on low or high temperature sublimations of scalemic mixtures of natural amino acids (AAs) highlighted unexpected enhancements of enantiomeric excess (ee) [1-5]. We have investigated systematic studies on the high temperature sublimation of mixtures of mono-alkylated AAs in the aim of rationalizing their properties in this phase transition and to precise the potentialities of the sublimation for enantioenrichment in Astrobiology.

2. Results and Discussion

Subliming at very high temperature (490°C), in a closed cell, mixtures of a racemic AA in the presence of an enantiopure leads the deracemization of the former.
Using one enantiopure and an AA with various ee, an increase for the latter of the ratio between the enantiomer of the same handedness than the one of the enantiopure and the other one was systematically observed (Fig.).
Thus, when one enantiopure (Val) and leucine with ee ranging from 95 % (D) to 95 % (L) were sublimed together, this behavior was observed leading in some cases to a switch of the handedness of leucine. As typical examples, starting from L-Val and 40 % D-Leu in a 4:1 ratio, a 20 % *ee* of D-Leu was obtained after sublimation. In the same conditions, with a 10% ee (D)-Leu, a 20 % (L)-Leu was obtained.

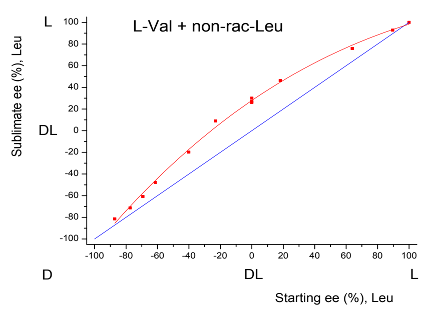

Fig. High temperature sublimation of L-Val (1 equiv.) with Leu (0.25 equiv.).

Using one enantiopure AA and racemic AAs, a strong synergistic effect was evidenced for the most complex mixtures (Table). The efficiency of the sublimation is dependent - on the presence of a gas in the cell and on the nature of the gas – on the temperature of sublimation – on the nature of the amino acids since good results were only observed with 1-alkyl derivatives.

This effect was still observed starting from one enantioenriched AA and racemic AAs. In this case, all the AAs of the starting mixture are enantioenriched after sublimation [7].

Table. High Temperature Sublimation of mixtures of one enantiopure and several racemic amino acids.

Conditions	Starting mixture (equiv.)	Sublimed mixture (ee %)
490°C, air, 3 AAs	L-Leu + DL-Ala + DL-Val 1:0.25:0.25	L-Leu: 99.5; L-Val: 52; L-Ala: 53.1
490°C, air, 6 AAs	L-Val + DL-(Ala, Leu, 2-ABA, norVal, isoLeu, norLeu) 1:6x0.25	L-Val: 100; L-Ala: 50.0; L-Leu: 41.5; L-2-ABA: 55.3; L-norVal: 42.0; L-isoLeu: 20.4; L-norLeu: 39.4
490°C, air	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 100; L-Ala: 49.6; L-Leu: 36.4
420°C, air	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 100; L-Ala: 13.8; L-Leu: 12.5
390°C, air	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 100; L-Ala: 2.5; L-Leu: 1.5
490°C, N_2	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 96.0; L-Ala: 11.6; L-Leu: 17.7
490°C, NO	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 99.8; L-Ala: 55.4; L-Leu: 53.4
490°C, CO_2	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 99.5; L-Ala: 22.2; L-Leu: 24.6
490°C, vacuum	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 100; L-Ala: 3.0; L-Leu: 7.1

6. Summary and Conclusions

The sublimation has been more than under-investigated in Astrobiology. We and some others have already showed that a partial sublimation at low temperature of enantioenriched compounds gives sublimates or residues which can be highly enantioenriched in function of the studied compound and the ee(s) of the starting material. However, segregation of enantiomers gives an ambiguous answer for the origin of homochirality on the Primitive Earth since it has to be explained why only the enriched sample is reacting in the following steps. The selective decomposition of one enantiomer or the racemization of the minor enantiomer into the major one is much more convenient to explain a chemistry based on one kind of enantiomers.

Up to date, only the amino acids contained in meteorites give an answer for the first imbalance between enantiomers. Many other syntheses have produced huge amounts of racemic amino acids on the Primitive Earth. With such small enantiomeric excesses for some amino acids, to determine the way for enantioenrichment is really challenging. The main advantages of our approach are the use of any complex mixture of 1-alkylated amino acids and drastic conditions compatible respectively with the organic syntheses occurring four billions years ago and the warm surface of the Young Earth subjected to frequent meteorite bombardments and to lava flows. Since its effectiveness is enhanced for complex mixtures, multiple high temperature sublimations in a large range of temperatures could be the key of huge enantioenrichments of several monoalkylated α-amino acids on the Primitive Earth at the early stage of the chemical evolution and just after the formation of amino acids.

Acknowledgements

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