SURVIVABILITY OF SMALL BIOMOLECULES DURING EXTRATERRESTRIAL DELIVERY: SIMULATION EXPERIMENTS ON AMINO ACID PYROLYSIS.
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Introduction: The hypothesis on exogenous origin of organic matter on the early Earth [1-9] is strongly supported by the detection of a large variety of organic compounds, including amino acids and nucleobases, in carbonaceous chondrites [10-17]. Whether such complex species can be successively delivered by other space bodies (comets, asteroids and interplanetary dust particles) is unclear and depends primarily on capability of the biomolecules to survive high temperatures during atmospheric deceleration and impacts to the terrestrial surface.

In continuation of our studies on the pyrolysis of small biomolecules and its implications for extraterrestrial delivery [18-20], here we report the results of pyrolysis experiments to estimate survivability (as % recovery) of 9 simple amino acids in the temperature range of 400-1000 °C with 100 °C increments, in oxygen-free (N_2) atmosphere. α-Amino acids are known to form cyclic dipeptides piperazine-2,5-diones (PDs) under pyrolysis; this class of compounds is also of primary interest in the present context, since PDs preserve amino acid residues intact (PD hydrolysis results either in regeneration of the starting amino acids or in formation of linear dipeptides, both being building blocks for the chemical evolution). For this reason we quantified PD yields along with amino acid recovery.

Experimental: Commercially available amino acids glycine (Gly), L-α- and β-alanine (Ala and β-Ala, respectively), α-aminoisobutyric acid (Aib), L-valine (Val), L-leucine (Leu), L-proline (Pro), L-phenylalanine (Phe), L-glutamic (Glu) and L-pyroglutamic acid from Sigma were used as received. Authentic samples of PDs cyclo-Gly$_2$, cyclo-Aib$_2$, cyclo-(L-Ala)$_2$, cyclo-(DL-Ala)$_2$, cyclo-(L-Val)$_2$, cyclo-(DL-Val)$_2$, cyclo-(L-Leu)$_2$, cyclo-(DL-Leu)$_2$ and cyclo-(L-Pro)$_2$ were synthesized according to [21]. The experimental setup was described earlier [19,20].

Analysis of amino acid recovery and PD yields was performed by HPLC technique. A Hewlett-Packard 1090 Series II Liquid Chromatograph was used, with columns of 125×4 mm I.D. (LiChrospher 100 RP-18 stationary phase, 5 μm particle size), 100×2.1 mm I.D. (5 μm Hypersil ODS RP-18) or 250×4 mm I.D. (5 mμ Spherisorb ODS 2 RP-18). UV detection was performed at 200 nm wavelength. Doubly distilled deionized water was used as a mobile phase for isocratic elution in the case of Gly, Ala, β-Ala and Aib; 0.1% aqueous solution of TFA for isocratic elution in the case of Glu; H_2O--MeOH 80:20

(v/v) for isocratic elution in the case of Pro; 0.1% TFA--MeOH 80:20 (v/v) for isocratic elution in the case of Phe; H_2O--MeOH uniform gradient from 0 to 100% MeOH at 20 min in the case of Val, and from 0 to 100% MeOH at 10 min in the case of Leu. Flow rate was 1 (for the 100 and 125 mm columns) or 2 ml min^{-1} (for the 250 mm column); column temperature, 45 °C.

Results and Discussion: Amino acid recovery plotted against pyrolysis temperature is presented in Fig. 1. Of the nine amino acids tested, Glu and β-Ala decompose completely already at 400 °C. Other amino acids are more stable. At 400 °C, the highest values of recovery were obtained for Ala and Val, about 10 and 13% respectively; for Gly, Aib and Leu they are in the range 3-4%, and lower than 1.5% for Pro and Phe.
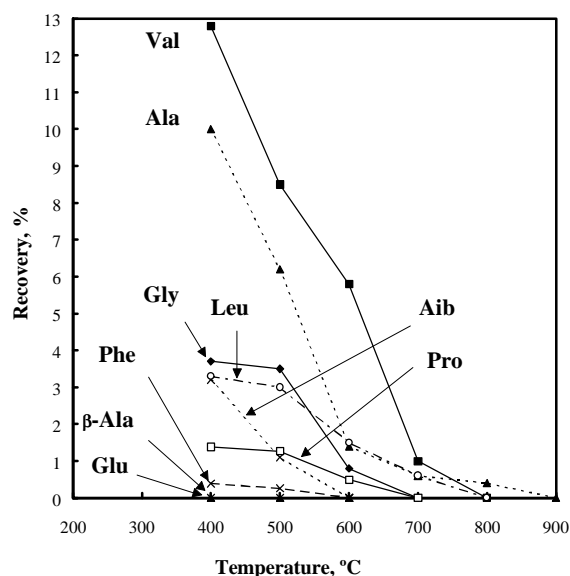

Fig. 1. Amino acid recovery as a function of pyrolysis temperature.

In all cases the recovery decreased with temperature, at a different rate. For Gly, Pro, Leu and Phe the difference between its values for 400 and 500 °C is insignificant; whereas in the case of Ala, Aib and Val, the decrease in recovery at this 100 °C increment is relatively sharp (*e.g.*, more than by half for Aib). Subsequent temperature increase to 600 °C results in total decomposition of Aib and Phe, thus these amino acids are less stable of all studied here. Then Gly and Pro exhibit zero recovery at 700 °C. Val and Leu are not detected anymore at 800 °C pyrolysis, whereas Ala is

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still found at this temperature with 0.4% recovery, and thus turns to be the most stable amino acid under the conditions described.

For Gly, Ala, Aib, Val, Leu and Pro, we analyzed also PD yields. β-Ala as any β-amino acid is unable to form PD; for Phe and Glu, the standards were not available. Glu easily forms pyroglutamic acid (due to intramolecular dehydration) which was quantified instead of its PD derivative. In the case of optically active amino acids (Ala, Val, Leu and Pro used in L-form) PDs form as diastereomeric mixtures due to high-temperature racemization. Plots for the yields of the condensation products are shown in Fig. 2. The most notable feature is a very high yield for Pro PD at 400 ℃, almost 80%. The value for Ala PD is considerably lower, *ca.* 48%, but still much higher than for all remaining PDs and pyroglutamic acid.
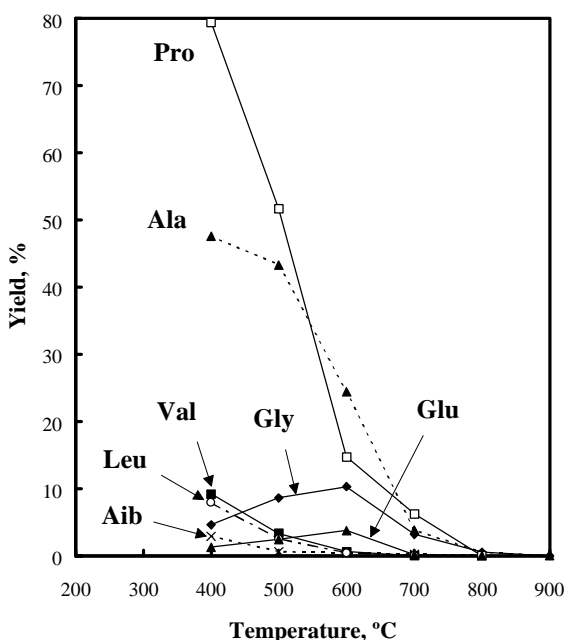

Fig. 2. Yields of PDs and pyroglutamic acid (for Glu) as a function of pyrolysis temperature.

It is interesting to compare the PD yields with the recovery of starting amino acids (Fig. 1). In some cases the former values exceed the latter, that is evident in the case of Gly, Ala and Pro. It is quite understandable for Gly, whose molecules do not have an α-alkyl substituent, so that steric obstructions for its cyclodimerization are very insignificant. Ala with its small methyl substituent exhibits a similar behavior. As the α-alkyl substituent grows, this situation changes: in the case of Val, the recovery is notably lower than the PD yield within the whole temperature interval considered; Aib and Leu present an intermediate case where these values are comparable. In view of this trend, the thermal

behavior of Pro seems unexpected: while its α-substituent is large, and besides it is directly connected to the nitrogen atom (that from common considerations should cause the strongest steric obstructions for cyclodimerization into cyclo-Pro$_2$) yield of the latter turns to be 1-1.5 orders of magnitude higher than Pro recovery.

An interesting feature can be found for Glu and Gly (Fig. 2): while for other amino acids PD yields decrease uniformly, yields of Gly PD and pyroglutamic acid pass through a maximum at about 600 ℃. Complete disappearance of the condensation products is observed for Val and Leu pyrolysis at 700 ℃; for Aib, Pro and Glu at 800 ℃; for Gly and Ala at 900 ℃. Also, interrelation between thermal stability of the starting compounds and related condensation products is not the same for different amino acids. In the case of Gly, while its PD desappears at 900 ℃, the amino acid itself decomposes completely at 700 ℃ (Fig. 1). In the cases of Aib, Pro and Glu a similar situation is observed. For Val and Leu, the amino acids are more stable then the corresponding PDs. Ala represents an intermediate case, where both compounds analyzed are not detected anymore after 800 ℃ pyrolysis.

The results obtained show that amino acids exhibit rather high thermal stability. They have chances to survive to the degree of 1-10% during atmospheric entry heating of space bodies up to 500-600 ℃, even without surface protection typical for meteorites.

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