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Pyruvate and glyoxylate formation in HCN polymers using aqueos aerosols

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Abstract

The complex organic substances named as "HNC polymers" are well known as important prebiotic precursors of purines, pyrimidines, amino acids, aldehydes, ketones, pteridines, urea, urea-related compounds and some carboxylic acids. Moreover, aqueous aerosols have been shown to be effective as prebiotic microreactors to the production of hydroxy compounds and di- and tricarboxylic acids. The aim of this work is to check the influence of the air-water interfaces in the synthesis of "HCN polymers" as prebiotic precursors of di- and tricarboxylic acids related to the reductive tricarboxylic acid cycle (rTCA).

1. Introduction

It is largely suggested that hydrogen cyanide is an important reactant in prebiotic synthesis. HCN has been detected in interstellar clouds, in star forming regions, in interplanetary dust, comets and meteorites, in the atmosphere of Titan and Jupiter, and, in a terrestrial context, in volcanic gases and in hydrothermal vents.

The polimerization of HCN in aqueous environment, catalized by bases or by free radicals leads to water soluble products and to insoluble solids, ranging in colour from yellow to black, depending on the degree of polymerization and/or cross-linking processes.

The monomer analysis for these complex materials yields a great number of biological molecules and related compounds [1]. Indeed, the HCN polymers present the ability to release carboxylic acids after acid hydrolysis. Aqueous aerosols are known to improve the production of polar molecules under plausible prebiotic conditions [2]. The aim of this work is to test the possible role of aqueous aerosols in the improvement of the synthesis of carboxylic acids precursors from cyanide polymerization reactions. The carboxylic acids are keystones in the current metabolism. Moreover, Eschenmoser suggested that a relationship exists between HCN and the constituents of the reductive tricarboxylic acid cycle (rTCA) and the "glyoxylate scenario" [3].

2. Material and methods

The bubble-aerosol-droplet cycle, for the solution of NH_4CN (1M) or NaCN (1M), was established using an ultrasonic aerosol generator (BONECO model 7035). The system was maintained at a constant temperature (38º C) with active aerosol generation for 72 hours or 4 weeks, under anoxic conditions. Then, the final suspension was centrifuged. The supernatant and the black insoluble solid were collected and both fractions were freeze dried. Finally, a brown solid and a black solid were obtained. These dried residues were heated at 110ºC in HCl 6 N during 24 h. The acid solutions were freeze dried and then chromatographically analyzed.

Analogous control experiments were carried out in sealed vials using a pool of liquid water.

3. Results

"HCN polymers" were synthesized using aqueous aerosols. In all samples, we have identified amino acids, purines and pyrimidines, carboxylic acids and pteridines in these complex substances by GC-MS. Additionally, carboxylic acids were analyzed by HPLC. Similar qualitative profiles of organics were found in the control experiments. However, the presence of aqueous aerosols increased the amount and diversity of carboxylic acids.

The acids implicated in a plausible inverse Kreb's cycle and the di- and tricarboxylic acids identified in our analysis are shown in Figure 1.

4. Figures

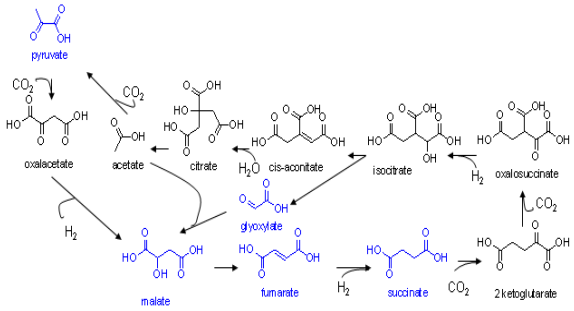

Figure 1: The carboxylic acids detected in our experiments that are related to a plausible reductive tricarboxylic acid cycle (rTCA) are marked in blue.

5. Summary and Conclusions

The identification of di- and tricarboxylic acids from cyanide polymerisation is very interesting from the perspective of a primordial metabolic cycle. Thus, the HCN polymers could be in the central core of a plausible protometabolic system. Indeed, the bubble-aerosol-droplet cycle could have improved notably the emergence of this kind of system.

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