

## Possible formation of amino acid precursors near Titan surface by cosmic rays

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Titan, the biggest satellite of Saturn, has dense atmosphere that mainly consists of nitrogen and methane. Voyager observation showed the presence of organic haze in Titan atmosphere. Some scientists suggested the existence liquid hydrocarbon and water ice on surface. Recently, Huygens probe sent the analytical data about organic aerosol in Titan atmosphere to the Earth while in the Cassini-Huygens Mission.

It is supposed that Titan has somewhat similar environments to the primitive Earth, many observations and simulation experiments have been done, where mainly UV light and electric discharges are used as energy sources. Khare and Sagan reported that the organic materials produced by electric discharges in simulated Titan atmosphere (tholin) had structure with hydrocarbons, nitriles, hetero aromatic compounds and so on, and that tholin yielded amino acids after hydrolysis. They simulated the condition of upper atmosphere of Titan. Though cosmic rays are possible effective energy source near the surface on Titan for the formation of organic compounds, there has few laboratory simulations of cosmic ray tholin. In this study, we irradiated proton beam to the mixture of nitrogen and methane to verify the possible formation of cosmic ray tholin in lower Titan atmosphere.

A mixture of methane (1-5%) and nitrogen (balance) was irradiated with 3 MeV proton from a van de Graaff accelerator. The resulting tholin was analyzed by Pyrolysis (Py)-GC/MS and <sup>1</sup>H NMR to estimate the structure. And GPC and MALDI-TOFMS were used to estimate the molecular weight. Identification and quantification of amino acids were done by HPLC and GC/MS after acid hydrolysis.

Many nitriles and nitrogen-containing hetero aromatic compounds were detected by Py-GC/MS, showing that quite complex organics were formed from simulated Titan atmosphere by proton irradiation. <sup>1</sup>H NMR spectrum of tholin in CDCl<sub>3</sub> showed the presence of methyl, methylene and methine protons next to nitrogen, and also heterocyclic aromatic protons. The molecular weight was estimated less than 2000. MALDI-TOF-MS spectra implied that the tholin had -CH<sub>2</sub>- structure, since a group of peaks with mass intervals of 14 were observed: It was changed to 15 when <sup>13</sup>CH<sub>4</sub> was used as starting material.

Amino acid enantiomers in the tholin were identified by GC/MS after acid hydrolysis and derivatization with 2,2,3,3,4,4,4-heptafluoro-1-butanol (HFB) and ethyl chloroformate (ECF), where a Chirasil-val column was used. D/L ratio of alanine was about 1. Proteinous amino acids (Gly, Ala, Val, Asp) were identified, together with non-proteinous amino acids (sarcosine, alpha-aminobutyric acid, beta-alanine). The present results clearly showed the abiotic formation of amino acids from simulated Titan atmosphere. Glycine was predominant, whose G-value was 0.006 when 1% methane was used. Indigenoussness of amino acids was checked with their D/L ratio and/or by mass spectrum of amino acids after labeled with stable isotope (<sup>13</sup>CH<sub>4</sub>). It was suggested that cosmic rays-induced tholin could give amino acids after interaction with surface water ice and/or cometary water ice during meteoritic / cometary impacts.