Complex organic aerosol formed in the lower Titan atmosphere

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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. In 2005, Huygens probe sent the analytical data about organic aerosol in Titan atmosphere to the Earth in the Cassini-Huygens Mission. It implied the presence of water ice and liquid methane on the surface, too. Since it is supposed that Titan has somewhat similar environments to the primitive Earth, simulation experiments have been done, but UV light and electric discharges are mainly used as energy sources. Khare and Sagan reported that the organic aerosols were produced by electric discharges in simulated Titan atmosphere. They named them tholins which 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 have been few laboratory studies on tholins-formation by cosmic rays. In this study, we irradiated proton beams to the mixture of nitrogen and methane, and analyzed the structure, the chemical composition, and molecular weight of the resulting aerosols (named PI-tholins), in order to simulate possible reactions in the lower Titan atmosphere. We also considered the mechanisms that yielded amino acids after hydrolysis of the PI-tholins. On the other hand, magnetosphere electrons could be effective for the formation of organic molecules in the upper atmosphere of Titan. Thus we compared PI-tholin with the tholin formed by plasma discharge (named PD-tholins)

A mixture of methane (5%) and nitrogen (95%) was irradiated with 3 MeV protons from a van de Graaff accelerator. The resulting PI-tholins was analyzed by Pyrolysis (Py)-GC/MS and FT-IR to estimate the structure. 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 heterocyclic compounds were detected by Py-GC/MS, showing that quite complex organics were formed from the simulated Titan atmosphere by proton irradiation. The molecular weights of the PI-tholins estimated were mainly less than 1000. MALDI-TOF-MS spectra implied that the PI-tholins had -CH2- structure, since a group of peaks with mass intervals of 14 were observed: It was changed to 15 when 13CH4 was used as starting material. The results of FT-IR shows the presence of C-N, nitrile group and N-H in the structure. These results were consistence with the Huygens mass spectrum data. Microscopic observation showed that the complex organic aerosols had the structure bigger than 0.01 mm. In cold and dry environment such as Titan, these complex organics might be condensed and aggregated. It was shown that amino acids incorporated oxygen atom during hydrolysis of tholins, since 18O atoms were included when hydrolysis was performed in H218O.

Glycine was predominant, whose G-value was 0.03 when 5% methane was used. Indigenousness of amino acids was checked with their D/L ratio and/or by mass spectrum of amino acids after labeled with stable isotope (13CH4). 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.

PD-tholins were produced by plasma discharge in 1 Torr of a mixture of 10 % methane and 90 % N2 by using plasma discharge facility RFX-600 (NASA Ames Research Center). Discharges were continued at 100 W for 72 hours. PD-tholins had similar chemical structures to PI-tholins. But the energy yields (G-value) of amino acids in PD-tholins was 0.000091, which was much less thatn that in PI-tholins. It was implied that cosmic rays in the lower Titan atmosphere was much more effective to form complex organics yielding amino acids than other energies in the upper Titan atmosphere.