

FORMATION OF AMINO ACID PRECURSORS IN PRIMITIVE PLANETARY ATMOSPHERE BY GALACTIC AND SOLAR/STELLAR COSMIC RAYS K. Kobayashi¹, R. Aoki¹, H. Abe¹, Y. Kebukawa¹, H. Shibata², S. Yoshida³, H. Fukuda⁴, K. Kondo⁴, Y. Oguri⁴ and V. S. Airapetian⁵, ¹Department of Chemistry, Yokohama National University (79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan, kkensei@ynu.ac.jp), ²Osaka University, Japan, ³National Institute for Radiological Sciences, Japan, ⁴Tokyo Institute of Technology, Japan, ⁵NASA Goddard Space Flight Center, MD, USA.

Introduction: Following Miller's historical spark discharge experiment in 1953 [1], a large number of experiments were conducted presuming that the early Earth had a strongly reducing atmosphere containing methane and ammonia. In these experiments, amino acids were directly formed by spark discharges, ultraviolet light, and other sources. Current models of the early Earth atmosphere were modified to less reducing environments, such as a mixture of CO₂, N₂ and trace amount of reducing carbon species like CH₄ [2]. Simulation experiments suggest, however, that amino acid formation is strongly inhibited under these conditions [3]. The chemistry of the early Earth prebiotic atmosphere was resembling the Titan's atmosphere (N₂-rich atmospheres with small amount of CH₄). We examine the formation of amino acids from such slightly reducing gas mixtures by applying ionizing radiation to simulate the action of galactic and solar energetic particles, though they have been ignored as prebiotic energy sources for their lower energy fluxes [4]. We also discuss the formation of amino acids in simulated Titan atmosphere under ionizing radiation.

Experimental: A gas mixture of N₂ (350 Torr) and CO₂ + CH₄ (total 350 Torr) were introduced to a Pyrex tube together with 5 mL of pure water. The gas mixture was irradiated with 2.5 MeV protons from a Tandem accelerator (Tokyo Tech, Japan). The same composition of gas mixtures were subjected to spark discharges by using a Tesla coil. In order to simulate reactions in Titan stratosphere, A gas mixture of N₂ (665 Torr) and CH₄ (35 Torr) was also irradiated with 2.5 MeV protons from the Tandem accelerator or 290 MeV/u carbon ions from HIMAC (NIRS, Japan). Each product was acid-hydrolyzed and was subjected to amino acid analysis by cation exchange HPLC with post-column derivatization with o-phthalaldehyde and N-acetyl-L-cysteine.

Results and Discussion: *Early Earth Simulations.* Amino acids were detected when gas mixture with CH₄ molar ratio (r_{CH_4}) was as low as 0.5 % was irradiated by energetic protons. The maximum of G-value in production of glycine is reached at r_{CH_4} =5%. However, when the same mixture is subject to the irradiation by the spark discharge (accelerated electrons) or UV irradiation, amino acids were not detected for r_{CH_4} lower than 15 %. Considering fluxes of various energies on the primitive Earth [5], energetic protons appear to be an efficient factor to

produce N-containing organics than any other conventional energy sources like thundering or solar UV emission irradiated the early Earth atmosphere.

Titan Simulations. Aerosol was formed when the gas mixture of 95 % N₂ and 5 % CH₄ was irradiated with the 2.5 MeV protons, and amino acids were detected after hydrolysis of the aerosol. When the gas mixture was irradiated by 290 MeV/u carbon ions, amino acids were also formed, though only a small fraction of the particle energy was deposited in the gas mixtures. We can conclude that aerosol (*tholins*) can be formed in stratosphere of Titan by the action of energetic protons in the form of galactic and solar cosmic rays. Comparing the production in the upper atmosphere of Titan by plasma discharges and that in the lower atmosphere by cosmic rays [6], the latter outputs much larger concentration of amino acid precursors-containing *tholins* in Titan's simulated atmosphere. Characterization of simulated stratospheric *tholins* made by plasma discharges and simulated tropospheric *tholins* produced by irradiated protons suggest that these two categories of *tholins* could be distinguished from each other. Thus, we can expect that the origin of *tholins* on the surface of Titan deduced in future Titan missions.

Role of Solar Energetic Particle Events (SEP) in Prebiotic Chemistry. Besides galactic cosmic rays, frequent SEPs associated with solar explosive events could have served as energy sources for prebiotic chemistry in the atmosphere of early Earth. Frequent superflares have been observed in young sun-like stars [7], which suggests that high energy SEPs produced during solar magnetic storms could have been efficient in supplying energy for efficient production of HCN and N₂O [8]. Further experimental studies of effects of solar/stellar energetic particle events on prebiotic chemistry on planets/exoplanets are in progress.

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