

## Energetics of Amino Acid Formation in Slightly Reducing Atmospheres of Primitive Earth and Titan

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It has been shown that strongly-reducing gas mixtures could give amino acids effectively by spark discharges [1]. In these days, however, primitive Earth atmosphere is regarded as only slightly reducing [2]. We examined possible formation of amino acids from a mixture of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub>O with various mixing ratios. Considered energies were spark discharges (thundering), UV and proton irradiation (cosmic rays).

A gas mixture of N<sub>2</sub> (350 Torr) and CO<sub>2</sub> + CH<sub>4</sub> (total 350 Torr) were sealed in a Pyrex tube with 5 mL of pure water. The gas mixture was subjected to spark discharges by using a Tesla coil, was irradiated with UV light from a D<sub>2</sub> lamp (Hamamatsu Photonics L1835) via a quartz window, or was irradiated with protons from a Tandem accelerator (Tokyo Tech, Japan). A gas mixture of N<sub>2</sub> (665 Torr) and CH<sub>4</sub> (35 Torr), simulating Titan atmosphere, was also irradiated with the 2.5 MeV protons. Each product was subjected to amino acid analysis by HPLC after acid hydrolysis.

If the CH<sub>4</sub> molar ratio ( $r_{\text{CH}_4}$ ) was lower than 15 %, amino acids could not be detected by spark discharges nor UV irradiation. Proton irradiation could, however, yielded amino acids even when  $r_{\text{CH}_4}$  was as low as 0.5 %. Considering fluxes of various energies on primitive Earth [3], we can say that most efficient energy source on the bodies with slightly reducing atmospheres was cosmic rays.

Amino acid precursors were also formed from a Titan-type gas mixture. Comparing the production in the upper atmosphere of Titan by plasma discharges and that in the lower atmosphere by cosmic rays [4], the latter would yield much more amino acids in Titan.

[1] Miller (1953) *Science* **117**, 528-529. [2] Kasting (1993) *Science* **259**, 920-926. [3] Kobayashi *et al.* (1998) *Orig. Life Evol. Biosph.* **28**, 155-165. [4] Taniuchi *et al.* (2013) *Anal. Sci.* **29**, 777-785.