

Amino acid formation from simulated mildly-reducing primitive atmospheres by spark discharges, UV irradiation and proton irradiation

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Supply of bioorganic compounds such as amino acids were crucial for the generation of life on the Earth. If the primitive Earth atmosphere was strongly reducing, endogenous formation of bioorganic compounds was easy by conventional energies such as thundering [1]. In these days, however, it is commonly thought that the primitive Earth atmosphere was not so strongly reducing but only mildly reducing: Its major constituents could have been carbon dioxide and nitrogen, together with some reducing gases as minor components [2]. In the present study, we examined possible formation of amino acids from mildly reducing gas mixtures by spark discharges (thundering), UV (solar radiation) and proton irradiation (cosmic rays).

A gas mixture of 350 Torr of carbon dioxide + methane with various mixing ratio and 350 Torr of N₂ were introduced to a glass tube with 5 mL of pure water. The gas mixtures were subjected to spark discharge by using a Tesla coil, were irradiated with UV light from a deuterium lamp (Hamamatsu Photonics L1835), or were irradiated with 2.5 MeV protons from a Tandem accelerator (Tokyo Tech, Japan). Estimated total energy deposit to the system was 860 kJ (spark discharges), 140 J (UV irradiation) and 3.2 kJ (proton irradiation), respectively. The resulting products were recovered as aqueous solutions, and were subjected to amino acid analysis by HPLC before and after acid hydrolysis. Hereafter the starting gas mixtures are referred to as their methane molar ratio ($r = P_{\text{CH}_4} / (P_{\text{CO}_2} + P_{\text{CH}_4} + P_{\text{N}_2})$).

In the unhydrolyzed samples, only traces of amino acids were detected. In the case of spark discharges, hydrolyzed samples gave various amino acids if molar ratio of methane was 15% or more, but we could not detect amino acids in the products when molar ratio of methane was 10% or less. In the case of UV irradiation, small amounts of amino acids were detected in the hydrolyzed sample whose methane ratio was 40 % or more. Thus we can say that there is a threshold of methane molar ratio in the production of amino acid precursors by spark discharges or UV irradiation.

On the other hand, we detected amino acids in the proton irradiation products after hydrolysis, even when methane molar ratio was as low as 0.5 %. Glycine yields by proton irradiation was strongly correlated to the molar ratio of methane, and no threshold of methane ratio for the production of amino acid precursors was observed.

In the case of UV irradiation, none of CH₄, CO₂ or N₂ can be dissociated or ionized efficiently by near UV. Amino acid precursors might be formed by triggered by dissociation of water molecule. Further confirmation of the production of such trace amount of amino acids by UV irradiation is necessary.

On the primitive Earth, the energy flux of thundering is estimated to have been much more than that of cosmic rays, but energy yield (G-value) of amino acids by proton irradiation (cosmic rays) was more than that by spark discharges (thundering). By considering them, it is concluded that thundering was a more important energy source than cosmic rays if the methane molar ratio was quite high. On the other hand, if the methane molar ratio was lower than 10%, we cannot expect the formation of amino acids by thundering, while cosmic rays would have been still effective energy sources in quite mildly reducing atmospheres. Sole solar UV light could not be an effective energy source for the production of amino acids in mildly reducing atmosphere, but its flux was so huge. We should examine possible synergy effect of the solar UV and other energies such as cosmic rays

and thundering.

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[2] J. F. Kasting, *Science*, 259, 920-926 (1993).

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