FORMATION OF AMINO ACID PRECURSORS IN SLIGHTLY-REDUCING PRIMITIVE ATMOSPHERES BY SOLAR ENERGETIC PARTICLES

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Abstract

Introduction: A large number of laboratory experiments have been performed to examine possible formation of bioorganic compounds such as amino acids in primitive Earth atmosphere. When strongly reducing gas mixtures containing methane as a major carbon species were used as starting materials, various energies including spark discharges could form amino acids. Since energy flux of thundering on the primitive Earth was estimated to as large as 1024eV m-2yr-1[1], thundering is a most effective energies to produce bioorganic compounds there. Galactic cosmic rays (GCRs) were also a possible energy source, but the flux of GCR was estimated to 2.9 × 1021eV/(m2 yr) [2] that is much lower than that of thundering, and were ignored as a major energy source for prebiotic chemistry. However, recent observation of superflares from young Sun-like stars [3], large flux of solar energetic particles (SEPs) associated with solar coronal mass ejections and superflares from the young Sun can be expected as additional energies for prebiotic evolution [4,5].
Current models of the early Earth atmosphere were modified to less reducing environments, such as a mixture of CO2, N2and small amount of reducing carbon species like CO or CH4[6]. It is suggested that amino acid production in such gas mixtures are difficult than that in strongly reducing ones by spark discharges [7]. Here we examine the formation of amino acids and carboxylic acids from slightly reducing gas mixtures such as CO2-CH4(trace)-N2-H2O type gas mixtures by particles irradiation, and spark discharges. We also made a study on possible roles of solar UV light in prebiotic formation of bioorganics.

Experimental: Seven hundred Torr of gas Mixtures of N2(350 Torr), CH4(0-350 Torr) and CO2(balance) and 5 mL of pure water were put in a Pyrex tube. We hereafter refer the gas composition to as rCH4 = pCH4/ (pCO2+ pCH4+ pN2). The gas mixtures were subjected to (i) proton irradiation with 2.5 MeV proton beam produced in a Tandem accelerator at Tokyo Institute of Technology, Japan via a Havar foil window; (ii) spark discharges

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between two tungsten electrodes by using a Tesla coil; and (iii) UV irradiation from a xenon lamp via a fused silica window. Amino acids in the resulting aqueous phase were determined by cation exchange HPLC before and after acid-hydrolyzed. Carboxylic acids in the products were determined by GC/MS before and after alkaline hydrolysis.

Results and Discussion: Both spark discharges and proton irradiation gave little amino acids before acid-hydrolysis. Spark discharges could yield amino acids after hydrolysis only when gas mixtures with high rCH4 ($> 15\%$) were used. On the other hands, proton irradiation experiments could yield amino acids after acid-hydrolysis even when rCH4$= 0.5\%$. It was suggested that amino acid precursors, not free amino acids, could be formed by GCRs and/or SEPs in slightly reducing primitive atmospheres.

A wide variety of mono- and dicarboxylic acids were detected before and after hydrolysis of discharge and proton irradiation products even when a rCH4$= 0$. We can say that carboxylic acids could be formed in primitive Earth even when it had non-reducing atmospheres.

Only UV irradiation did not yield amino acids at all, since N2could hardly be dissociated with solar UV. It was suggested that SEPs as well as GCRs could produce HCN and N2O in the early Earth's atmosphere [4], which could be take part in photochemical reactions. We are to study synergetic effects of SEPs and high flux of solar UV in prebiotic formation of N-containing organics.

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