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Abiotic Synthesis of Amino Acids by Proton Irradiation of a Mixture of Carbon Monoxide, Nitrogen, and Water

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We have shown that proton irradiation simulating the action of cosmic rays and solar flare particles formed proteinous and non-proteinous amino acids such as glycine, alanine, aspartic acid and β-alanine from a mixture of carbon monoxide, carbon dioxide, nitrogen and water. The yield of amino acids per unit energy was the highest obtained among various prebiotic energy sources used. This result suggests the possibility of the formation of amino acids from mildly reduced primitive atmospheres on the earth.

Numerous studies on abiotic syntheses of compounds of biological importance, such as amino acids, under simulated primitive earth atmosphere conditions have been reported since 1950's.[1] In earlier experiments, strongly reduced atmospheres were used as the simulated primitive atmosphere. From a mixture of methane, ammonia and water (sometimes including hydrogen), various amino acids were synthesized with energy sources such as a spark discharge, heat, ultraviolet light, shock wave and radioactivity.[1b,2] From a mixture of methane, nitrogen and water were produced amino acids[3] and all of the five nucleic acid bases.[4] Recent studies[5] on the formation of planets have suggested, however, that high-velocity impacts of planetesimals onto a growing planet resulted in the impact-degassing of volatiles and the formation of an impact-induced atmosphere at high temperature. According to this hypothesis, the resulting impact-induced atmosphere[6] contains carbon monoxide and carbon dioxide as a major carbon source. Therefore, the primitive earth atmosphere may have been "very mildly reduced". When carbon monoxide or carbon dioxide have been used as a carbon source in simulated primitive atmosphere experiments, however, only a trace amount of amino acids has been so far obtained.[7]

We performed proton irradiation of a mixture of carbon monoxide, carbon dioxide, nitrogen and water, simulating the action of cosmic rays and solar flare particles, and obtained various kinds of amino acids in relatively high yield.

In a 420-ml Pyrex glass tube, 40 ml of an aqueous solution of various ions (given in Table 1) and nitrogen gas were mixed with methane or carbon monoxide and introduced into the reaction tube. The gas mixture was irradiated with high energy protons (effective energy: 3.0 MeV, 0.63 μA) generated by a Van de Graaff accelerator at room temperature. After 2.5-5.0 h's irradiation, the resulting aqueous solution was concentrated and hydrolyzed with 6N hydrochloric acid at 105°C for 24 h. An amino acid fraction was obtained by extraction from the hydrolyzate with cation-exchange resin, and was analyzed by ion-exchange chromatography, gas chromatography (GC), mass spectrometry (MS), and gas chromatography combined with mass spectrometry (GC/MS). Resulting gas mixtures were analyzed by gas chromatography.

An ion-exchange chromatogram of the amino acid fraction of the product after 5 h's irradiation of carbon monoxide, nitrogen and water is shown in Fig. 1. Proteinous amino acids such as glycine, alanine, aspartic acid and serine, were detected together with non-proteinous amino acids (β-alanine and α-aminobutyric acid). Major amino acids (glycine, alanine, sarcosine, serine and β-alanine) were identified by both GC and GC/MS with an optically-active column (Chirasil-Val capillary column) after derivatization. The GC/MS analysis by using the optically-active column indicated that alanine and serine are racemic mixtures. When ^{13}C-carbon monoxide was used as a starting material, the resulting amino acids were labelled by ^{13}C. This was proved by MS. Gas phase analysis showed that most of carbon monoxide was consumed within 5 h, and that carbon dioxide was a major product from it. Hydrogen gas was also produced; its concentration at the end of 5 h was 8% of that of carbon dioxide. Thus, the very mildly reduced condition was found at the end of the proton irradiation. Irradiated protons, however, made a "local reduced environment" around them, where amino acids were effectively formed from very mildly reduced atmospheres.

The yield of amino acids in the proton irradiation experiments is summarized in Table 1. When a mixture of methane, nitrogen and water with ammonium ion was used for the starting materials, proton irradiation converted methane into amino acids at the rate of ca. 3 nmol/J (G value was about 0.01). The yield per unit energy was the highest obtained among various prebiotic energy sources used. The yield of amino acids obtained from carbon monoxide was almost the same as that from methane. In a previous investigation, carbon monoxide produced much less amino acids than methane by spark discharges:[7] Only when high concentration of hydrogen and/or ammonia was incorporated in the gas mixtures, a considerable amount of amino acids was obtained.[7,8] The latest hypothesis on the formation of

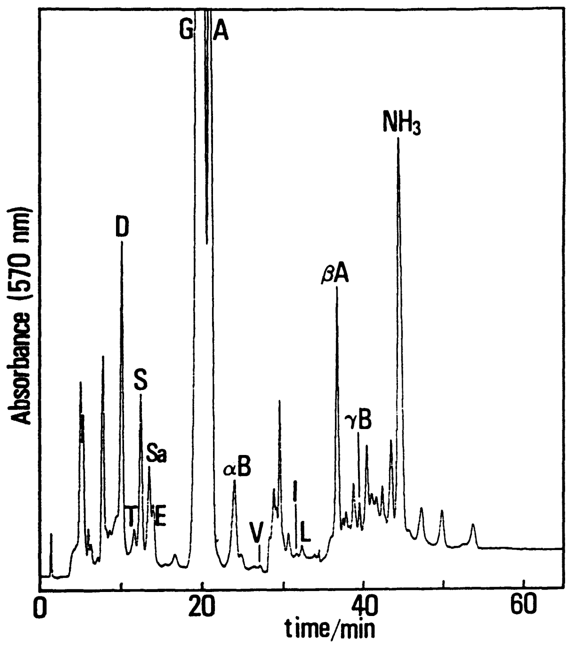

Fig. 1. Ion-exchange chromatogram of amino acids synthesized by proton irradiation (see Table 1, CO-N_2-H_2O, Run 2). Abbreviations: D: aspartic acid; T: threonine; S: serine; Sa: sarcosine; E: glutamic acid; G: glycine; A: alanine; αB: α-aminobutyric acid; V: valine; I: isoleucine; L: leucine; βA: β-alanine; γB: γ-aminobutyric acid.

planets suggested that carbon monoxide was a major carbon source in the primitive earth atmosphere.[6] The present results show that amino acids could be produced from the primitive earth atmosphere by proton irradiation.

Considering the possibility that carbon dioxide was a major carbon source in the primitive atmosphere, we examined the effect of carbon dioxide on the formation of amino acids from carbon monoxide, nitrogen and water. Carbon monoxide could be still present such primitive atmospheres as a minor constituent produced by photo-dissociation of carbon dioxide.[9] In place of carbon monoxide, mixtures of carbon monoxide and carbon dioxide in various ratios ($CO/CO+CO_2$ = 0-100%) were used as a carbon source in the proton irradiation experiments. The formation of amino acids was approximately proportional to the partial pressure of carbon monoxide; carbon dioxide did not inhibit the formation of amino acids from carbon monoxide. This result also indicates that amino acids could be synthesized from carbon monoxide even if carbon dioxide was a major carbon compound and carbon monoxide was a minor one in the primitive earth atmosphere. No amino acid was obtained from carbon dioxide, nitrogen and water.

Among various energy sources for prebiotic synthesis of amino acids on the earth, cosmic rays (galactic cosmic rays) have been regarded as having negligible importance compared to other energy sources, such as spark discharge and ultraviolet light.[10] The role of cosmic rays, however, is shown by this work not to

Table 1. Formation of amino acids by proton irradiation of gas mixtures

	System				
	CH_4-N_2-H_2O			CO-N_2-H_2O	
	Run 1	Run 2	Run 3	Run 1	Run 2
Reaction condition					
Gas mixture[a]					
Methane (Torr)	280	280	280	0	0
Carbon monoxide (Torr)	0	0	0	280	280
Nitrogen (Torr)	280	280	280	280	280
Aqueous solution[b]					
Ammonium chloride (mM)	50	50	0	0	0
Sodium carbonate (mM)	0	0	50	50	50
pH	8.7	8.7	7.0	7.0	7.0
Irradiation energy (kJ)	20	21	19	43	17
Amino acids produced (μmol)					
Aspartic acid	0.16	0.19	0.03	1.63	0.59
Threonine	0.74	0.88	0.18	0.18	0.15
Serine	0.73	0.95	0.11	0.81	0.43
Glycine	19.0	26.0	7.99	19.5	7.40
Alanine	3.84	5.69	1.32	7.86	1.23
α-Aminobutyric acid	0.18	0.62	0.18	0.40	0.29
β-Alanine	0.10	0.36	0.04	2.21	1.61
Total	24.8	34.7	9.85	32.6	11.7
Yield based on total carbon (%)[c]	0.92	1.4	0.38	1.4	0.50
Chemical yield (G-value)	0.012	0.016	0.0049	0.0075	0.0065

a) Gas volume in a reaction vessel is 380 ml.

b) An aqueous solution (40 ml) contains 1 mM (each) $MgCl_2$, $CaCl_2$, $ZnCl_2$, $Fe(NH_4)_2(SO_4)_2$, and Na_2MoO_4, in addition to the two salts indicated.

c) Initial methane or carbon monoxide.

be negligible, not only when methane but also when carbon monoxide is a major carbon source, since amino acids or their precursors were synthesized efficiently by proton irradiation. In addition to galactic cosmic rays, solar flare particles should be considered. At times of maximum solar activity, the flux of solar flare particles (average energy: 10 MeV) is sometimes as high as 10^4 protons/cm^2.[11] On such occasions, the earth atmosphere receives about 1 J $h^{-1}m^{-2}$ of solar energy at high latitudes. Thus solar flare particles can synthesize more than 10^6 moles of amino acids from carbon monoxide and nitrogen per hour on the earth.

The present results suggest that amino acids could have been abiotically synthesized on the primitive earth, not only from a strongly reduced atmosphere, but also from a mildly reduced one, such as a mixture of carbon monoxide, carbon dioxide, nitrogen and water. They give additional support to the "chemical evolution hypothesis" for the origin of life on the earth.

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