Formation of Amino Acids from Possible Interstellar Media by γ-rays and UV Irradiation

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Formation of amino acids from mixtures of methanol, ammonia and water in various phases by γ-rays and UV irradiation were quantitatively verified. A wide variety of amino acids were detected in every hydrosate of the product. Each G-value (the number of formed molecules per deposit energy of 100 eV) was around 10^{-2} order, which was independent from the phase of the starting materials and kind of the energy.

Wide variety of organic compounds have been discovered in extraterrestrial environments, which are discussed from the content of the emergence of life on the primitive Earth. Extraterrestrial organic compounds, have been discussed from the following points of view: (i) Source of organic compounds for the first terrestrial biosphere,[1] and (ii) fossils of chemical evolution in prebiotic environment.[2] Greenberg et al.[3] proposed a cyclic evolutionally model of interstellar dusts: Organic compounds were formed and transformed in interstellar dusts (ISDs) when they travels in molecular clouds and diffuse clouds, then they were preserved in comets when ISDs grown as comets in the proto-solar system. Thus it seems that the first step of the abiotic formation of organic compounds takes place in ISDs in molecular clouds. Representative carbon sources for abiotic formation of organics are carbon monoxide, formaldehyde and methanol, and a major nitrogen source is ammonia.[2,4] Nitrogen (N_2) may exist in ISD environment, but it cannot be detected spectrometrically.[5] Those ices are irradiated with UV from neighboring stars and galactic cosmic rays. There have many studies to simulate possible chemical reactions in ISDs. Kasamatsu et al.[6] showed that amino acid precursors (molecules which provide amino acids after hydrolysis) were formed when an icy mixture of carbon monoxide, ammonia and water were irradiated with high energy protons. Briggs et al.[7] showed that a variety of organic compounds including glycine was found in the product by UV irradiation of simulated ISD environment at 12 K. Recent simulation experiments[8,9] also reported the abiotic formation of other types of amino acids in ice mantles at 12 K. Most of the previous works are, however, not quantitatively examined abiotic formation of organic compounds. Here we compared the G-value rate (the number of formed molecule/100 eV)[10] of amino acids with γ-rays and UV photons from various phases; solid phase at 77 K, liquid phase at 293 K and gaseous phase at 353 K.

Methanol and ammonia used were of ultra pure grade as starting materials for irradiation experiments. Deionized water was further purified with a Millipore Milli-Q LaboSystem™ and a Millipore Simpli Lab-UV (Japan Millipore Ltd., Tokyo, Japan) to remove both inorganic ions and organic contaminants. All the glass wares were heated in high temperature oven (Yamato DR-22) at 500 °C in prior to use in order to eliminate any possible contaminants.

A starting mixture of methanol and ammonia aqueous solution was prepared; the molar ratio of methanol, ammonia and water was 1 : 1 : 2.8. For the UV irradiation, the mixture was sealed in a quartz vessel. The three phases of the mixture was achieved as follows: The solid condition was made in liquid nitrogen bath to keep at 77 K. The liquid condition was performed at ambient temperature. Starting gas mixtures were filled in a Pyrex glass tube: Methanol for 350 Torr, ammonia for 350 Torr over liquid water which provide 20 Torr of water vapor at 353 K with heating coil wrapped. A 150 W deuterium lamp with a MgF_2 window (Hamamatsu Photonics L1835) was used for UV (<15 eV) irradiation. Since irradiation window was attached with quartz window, above 160 nm wavelength was obtained. The energy deposit was 3.1×10^{20} eV each.

The same kind of the gas mixture in three phases sealed in Pyrex tubes were irradiated with γ-rays (1.2–1.3 MeV) from a ^{60}Co source in Research Center for Nuclear Science and Technology, University of Tokyo. The energy deposit was 2.3×10^{19} eV each. After irradiation, an aliquot of the irradiation products was hydrolyzed with 6 M HCl at 110 °C for 24 h. Amino acids in the hydrolyzed and unhydrolyzed fraction were analyzed with an ion-exchanged HPLC system where a post-column derivatization with o-phthalaldehyde and N-acetyl-L-cystein was applied.[11] The HPLC system used was composed of two high performance liquid chromatograph pumps (Shimadzu LC-6A), a cation exchange column (Shimpak ISC-07/S1504, 4 mm i.d. × 150 mm), a post column derivatization system, and a Shimadzu RF-535 fluoromeric detector.

An ion-exchanged chromatogram of the product of UV irradiation of the gas mixture of methanol, ammonia and water was shown in Figure 1. A wide variety of proteinous amino acids such as glycine, alanine, aspartic acid and non-proteinous amino acids such as β-alanine, α- and γ-aminobutyric acid were detected. With the presence of non-proteinous amino acids, indicated that the amino acids found were not contaminated but indigenous to the product. In the unhydrolyzed fraction, only small amount of glycine was detected. It showed that not free amino acids, but amino acid precursors were formed during irradiation. When the same gas mixture was irradiated with γ-rays, hydrolysate of the products gave similar kinds of amino acids. In the both products, the semi logarithmic linear relations between carbon number of amino acid and amount of product are observed.[12]

Hereafter we will use the G-value (the number of formed molecules per 100 eV) of glycine in the hydrolyzed products when the yields of amino acids are discussed, because (i) glycine is the most abundant amino acid in the hydrolyzed products, and (ii) it was proved that glycine was formed in proportion to total energy deposite.[13,14] The G-values of glycine in the irradiation experiments were shown in Figure 2. In both experiments of γ-rays and UV irradiations, G-values were around 10^{-2} in all of the

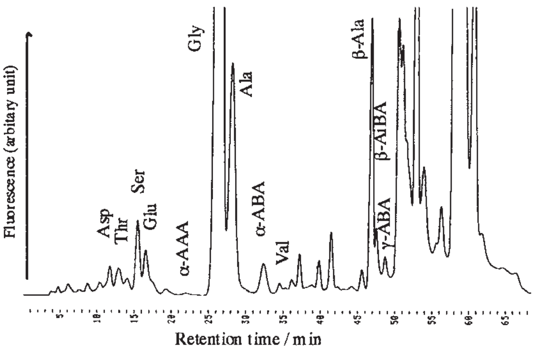

Figure 1. Ion-exchanged chromatogram of UV irradiated sample from the mixtures of CH_3OH–NH_3–H_2O (1 : 1 : 2.8) at 353 K. The fraction was after acid hydrolysis by 6 M HCl. Abbreviations. Asp: aspartic acid, Ser: serine, Thr: Threonine, Glu: glumatic acid, α-AAA: α-aminoadipic acid, Gly: glycine, Ala: alanine, α-ABA: α-aminobutyric acid, Val: valine, β-Ala: β-alanine, β-AiBA: β-aminoisbutyric acid, γ-ABA: γ-aminobutyric acid.

three phases. Particles irradiation experiment such as protons or electrons in same starting material[6] showed that gas phase was most predominant than liquid and solid phase. Since particle beam was focused and fixed, irradiated products might be partly broken. Although in the case of γ-rays and UV irradiation, their photons are sustainable for the target materials. As conclusion, amino acid precursors can be formed equally by cosmic radiation and UV, and the energy yield (G-value) is independent from the phases of starting materials. Thus we concluded that the amounts of organic compounds synthesized by radiation in interstellar space are not negligible. Consequently, exogenous bioorganic compounds are significant sources for the first crucial building blocks of life on Earth. It is also plausible that these exogenous organics were supplied to other planets and satellites such as Mars or Titan.

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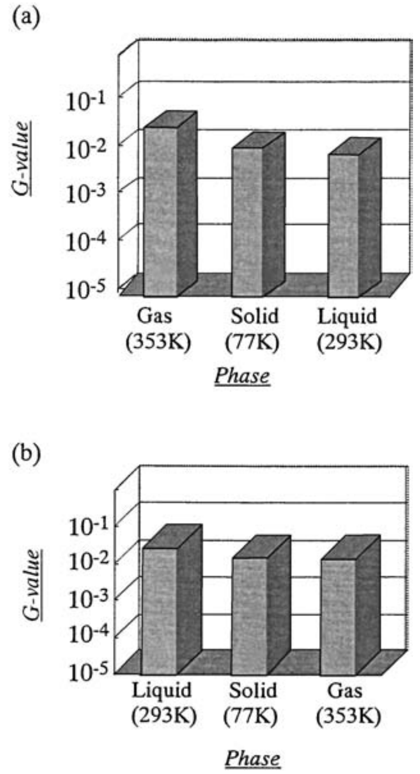

Figure 2. G-values of Glycine obtained from the mixture of CH_3OH–NH_3–H_2O (1 : 1 : 2.8) by (a) UV irradiation and (b) γ-rays irradiation.

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