Stability of Amino Acid Precursors in Simulated Submarine Hydrothermal Vent Environments

*Keisuke Naito[1], Shingo Enomoto[1], Yoko Kebukawa[1], Hitoshi Fukuda[2], Yoshiyuki Oguri[2], Kensei Kobayashi[1]

1. Yokohama National University, 2. Tokyo Institute of Technology

Submarine hydrothermal vents have been found in various regions of deep oceans since their first discovery in 1977. Submarine hydrothermal systems are regarded as promising sites for prebiotic chemistry toward the generation of life [1]. On the other hand, a wide variety of organic compounds have been detected in extraterrestrial bodies such as meteorites and comets. It seems that such extraterrestrial organic compounds including amino acids were supplied to primordial ocean, and were modified in submarine hydrothermal systems.

Imai et al. [2] showed that peptides were formed from aqueous solution of glycine in a flow reactor simulating submarine hydrothermal systems. Miller and Bada [3] pointed out that amino acids were not stable in hot medium. In their works, free amino acids were used as starting materials. Larger part of the amino acids delivered by extraterrestrial bodies seem to be, however, not free amino acids but amino acid precursors: Laboratory experiments suggested that amino acid precursors were formed from possible interstellar media [4]. Thus it is possible that amino acid precursors in extraterrestrial bodies supplied to primordial ocean.

In the present study, stability of amino acid precursors in simulated submarine hydrothermal system was examined. We selected aminoacetonitrile (AAN) and hydantoin (Hyd) as possible glycine precursors. We also used product obtained by proton irradiation of a gas mixture of carbon monoxide, ammonia and water. This product is hereafter abbreviated as CAW, which is a model of complex amino acid precursors, since glycine and other amino acids were detected after hydrolysis of CAW [4]. In order to simulate reactions in submarine hydrothermal systems, we used the flow reactor (previously introduced as supercritical water flow reactor (SCWFR) [5]).

Experimental: 4 mM each of glycine, aminoacetonitrile and hydantoin aqueous solution was prepared. CAW was prepared by irradiation of a mixture of carbon monoxide (350 Torr) and ammonia (350 Torr) and water water with 2.5 MeV protons from a Tandem accelerator (Tokyo Tech).

Carrier used in the flow reactor was either pure water of 1 mM HCl at the rate of 0.5 mL/min; the latter was used to simulate acid submarine hydrothermal fluid. In the flow reactor, each sample was heated for 2 min and then quenched at 0 ℃. As reference run, each sample was injected to the flow reactor with the heater off. The effluents were collected and subjected to amino acid analysis with Shimadzu LC-20A amino acid analyzer after acid hydrolysis and desalting with Bio-Rad AG-50WX8 cation-exchange resin. Recovery ratio was defined as the ratio of glycine amount in each heated sample to glycine amount in the reference sample with acid-hydrolysis.

Results and Discussion: When Gly, AAN and CAW was heated at 300 ℃, recovery ratios of glycine were less than 1% before hydrolysis, but all the recovery ratio increased after hydrolysis. The runs under the acidic condition gave higher recoveries before and after hydrolysis. This suggested that (i) glycine was decomposed mostly, but some glycine changed to combined species, and (ii) these compounds were more stable under acidic environments rather than in neutral environments. On the other hand, hydantoin's recovery was about 5% before hydrolysis, and it increased to 20% after hydrolysis. It was shown that ring compounds like hydantoins were more stable than acyclic compounds in submarine hydrothermal systems. Further studies are in progress to examine possible roles of amino acid precursors in prebiotic chemistry in submarine hydrothermal systems.

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