Peptide Formation from amino acid precursors under simulated submarine hydrothermal environments

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Submarine hydrothermal systems have been recognized as one of most promising sites for chemical evolution toward the generation of the first life on the Earth [1]. In order to examine possible reactions in such environments, laboratory simulations by utilizing autoclaves and/or flow reactors have been conducted. Imai et al. reported that peptides were formed when glycine was subjected to heat-quench cycles in a flow reactor simulation submarine hydrothermal systems [2]. Amino acids have been detected in carbonaceous chondrites, and also in the products of experiments simulating interstellar environments. It should be noted that amino acid precursors rather than free amino acids were formed under extraterrestrial environments. Such exogenous amino acid precursors could have been delivered to the primitive Earth and processed in submarine hydrothermal systems. We studied possible reactions of amino acid precursors in simulated submarine hydrothermal environments.

Experimental: We chose the following compounds or materials for hydrothermal experiments: (i) Free glycine (Gly); (ii) aminoacetonitrile (AAN), a Strecker-type precursor; (iii) hydantoin (Hyd), a glycine precursor found in carbonaceous chondrites; (iv) CAW; complex organic molecules formed by proton irradiation of a mixture of CO, NH_3 and H_2O [3]. CAW gave various amino acids after acid hydrolysis, where glycine was predominant. The CAW stock solution used in this study yielded *ca.*10 mM glycine after acid hydrolysis.

In order to simulate submarine hydrothermal reactions, we used a flow reactor, composed of a HPLC pump, an infrared gold image furnace, a cold bath and a backpressure regulator [4]. Injected aqueous samples could be heated up to 400˚C in the furnace, and then quenched in the ice bath (0 ˚C). Carrier used was purified water (neutral) or 1 mM HCl (acidic). In the present study, 0.25 mL of each sample was processed in the furnace at room temperature (reference) or 200-400˚C for 2 min, and then quenched. Amino acids in the effluent were determined by cation exchange HPLC (Shimadzu LC-20 amino acid analyzer with a fluorescence detector) before or after acid-hydrolysis. Peptides were determined by ion-pair HPLC (Shimadzu LC-20 HPLC system with a UV detector).

Results and Discussion: Stability of each material at 300˚C was examined by using 4 mM of Gly, AAN or Hyd, or 10-times diluted CAW. Hyd, AAN and CAW gave some glycine in unhydrolized products. Recovery was calculated by glycine amount after hydrolysis against the reference. Hyd and CAW were more stable than Gly and AAN.

Peptide formation experiments were performed by using 40 mM each of Gly, AAN or Hyd, or the CAW stock solution. Diketopiperazine (DKP; a cyclic dimer of Gly) and diglycine (Gly_2) were detected in the unhydrolized samples after Gly or Hyd was heat-processed. Hyd gave much more Gly_2 and DKP than Gly. The Best yield of Gly_2 was 1.3 %, which was observed when Hyd was processed at 200 or 250˚C under neutral conditions. CAW gave so many peaks in ion-pair chromatograms, so that we could not identify peptides there.

In order to examine possible catalytic abilities of CAW, 10-times diluted CAW was added to 40 mM Gly or 40 mM Hyd and then heat-processed. Yields of Gly_2 were increased when CAW was added to Gly or Hyd and heated at 200˚C under acidic conditions.

It was shown that amino acid precursors such as Hyd and CAW was more stable than free amino acids, and that amino acid precursors like Hyd could yield more peptides than free amino acids. It was also found that CAW (complex amino acid precursors) could facilitate peptide formation. It is known that CAW has amide bonds in its structure, which could be a reason why CAW could work as a condensing agent.

In summary, amino acid precursors were more plausible starting materials than free amino acids in prebiotic reactions in primordial terrestrial environments. Kurihara et al. [5] showed that organic aggregates could be formed from water-soluble organics in hydrothermal environments. It is of interest to examine whether CAW could give such aggregates after processed in the flow reactor.

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References

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