7. Formation of Amino Acids and Polypeptides from Formaldehyde and Hydroxylamine in Modified Sea Mediums

By Martha Ventilla and Fujio Egami
Mitsubishi-Kasei Institute of Life Sciences,
11 Minami-ooya, Machida-shi, Tokyo 194

In 1949 J. D. Bernal first suggested that life might have originated on the surface of clays at the land-sea interface. Clay deposits might have served to adsorb and concentrate the dilute organic substances of primeval oceans, thus simultaneously protecting them from photochemical degradation and providing catalytically active surfaces mediating the formation of prebiotic monomers and their subsequent polymerization.1)

The first experimental work involving clays was reported by Akabori et al. who condensed formaldehyde or acetaldehyde with polyglycine dispersed on kaolin2) and they further provided experimental support for the Akabori's hypothesis of "abiotic fore-protein formation".3)

The formation of prebiotic polypeptides has been achieved from activated amino acids such as amino acid adenylates or amino acid ATP system in the presence of different clays.4,5)

Taking into consideration that metal ions had to contribute to chemical evolution in primeval sea water and expecting the concerted catalytic action of clay and metal ions, we have been investigating the formation of biomolecules in modified sea mediums, in which the concentration of sodium chloride is lower and that of transition metal ions is higher than in sea water. The present paper is a preliminary note on the formation of amino acids and polypeptides from formaldehyde and hydroxylamine in these mediums.

Experimental. All the reagents used were of analytical grade and double distilled water was employed throughout the experiments. Special care was taken in the selection of clays (Kukita Yakuhin Kogyo Co. Japan) and Chelex (BioRad, U. S. A.). All were of high purity with no measurable organic contamination.

The experiments were carried out in 5 ml ampules sealed under nitrogen. Each sample was kept in a shaking air bath for 120 hrs at 80°C. The composition of the reaction mixture was as follows: 0.25 M formaldehyde; 0.05 M hydroxylamine; 10⁻⁴ M Cu²⁺, Co²⁺, Mn²⁺, Mo⁶⁺,
Fe$^{3+}$, Zn$^{2+}$ ions; 50 mg potassium phosphate (dibasic). To this reaction mixture the following solid catalysts were added; acid clay (A), kaolin (K), montmorillonite (M), and Chelex-100 (Ch).

The extraction of the reaction products was carried out in 5 steps, combining centrifugation and treatment with distilled water, weak and strong alkali and acidic solutions. The extracted material was lyophilized and separated in subsequent chromatographic steps, using Biogel P-2, (to separate the low and high molecular fractions) Dowex 50 (H$^+$) (to separate neutral and acidic components) and Dowex 1(OH$^-$) (to eliminate unreacted hydroxylamine) columns. The extract was lyophilized again and dissolved in a small volume of water (low-molecular fraction: 0.6 ml, high-molecular fraction: 0.5 ml). The amino acid content of the monomeric and polymeric fractions (following acid hydrolysis) was carried out employing ninhydrin and fluorescamine. The analysis of amino acids was accomplished with JEOL 6AH Amino acid Analyser. Identification of oligo- and polysaccharides was done using Shimadzu Gas Chromatograph GC 4 BM. The quantity of sugars was estimated with the method of Goldstein.

Results and discussion. Although the nature of reaction products must be further confirmed by other methods in larger scale experiments, it is certain that not only various amino acids but also polypeptides were formed from formaldehyde and hydroxylamine in the experimental mixture. It may be regarded as a result of the concerted catalytic action of clay and metal ions. It remains to be elucidated, which metal ions really contributed to the reaction.

The results are summarized in Tables I and II. The estimated values reflect a lower yield of amino acids than produced in the presence of clay catalysts due to difficulties in complete extraction. As expected from the starting materials, Gly was the main component both in the low and high-molecular fraction. It is consistent with the finding of Oro et al. The low-molecular fraction contained only a very small amount of Ser and Ala besides Gly (Table I). On the contrary the high-molecular fraction formed in the presence of clays contained a series of amino acids tentatively identified as Gly, Ser, Asp, Glu, Leu, and Ileu in substantial amounts (Table II).

One possible explanation for the finding could be, that in the catalytic systems used, in the presence of solid phase and metal ions the rate of polymerization of these amino acids was much greater than the rate of formation. The other possibility could be, that as Akabori hypothesized, there is formation of a polyglycine backbone with the stepwise addition of one or more formaldehyde residues.
As shown in Table II, kaolin gave the highest yield of different amino acids among various clays. It may be due to its physicochemical characters different from other clays. Besides clays, Chelex, an artificial cation carrier, was used as a model with the hope to explain the catalytic mechanism of clays. As expected, Chelex revealed a similar catalytic activity. The finding will contribute to the elucidation of the reaction mechanism.

In course of the present research, the formation of monosaccharides and their polymers was also observed. It will be reported after their chemical characterization.

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References