Formation of Complex Amino Acid Precursors by Cosmic Rays in Interstellar Environments

*Kensei Kobayashi[1], Soushi Kuramoto[1], Tomohito Sato[1], Miki Nakayama[2], MITA Hajime[2], Satoshi Yoshida[3], Hitoshi Fukuda[4], Yoshiyuki Oguri[4], Hiromi Shibata[5], Yoko Kebukawa[1]

1. Department of Chemistry, Yokohama National University, 2. Fukuoka Institute of Technology, 3. National Institutes for Quantum and Radiological Science and Technology, 4. Tokyo Institute of Technology, 5. Osaka University

Wide variety of amino acids have been detected in water-extract of carbonaceous chondrites (CCs) [1], and it is suggested that such extraterrestrial amino acids are important for chemical evolution toward the generation of the first life on the Earth. It was shown that meteoritic amino acids increased after acid-hydrolysis, which means that at least a part of amino acids found in CCs are *precursors* of amino acids. Experiments simulating interstellar and asteroid environments showed that amino acid *precursors*, rather than free amino acids, were formed in prebiotic reactions [2, 3]. Amino acid precursors, however, have not been characterized. It has often been said that a-amino acids found in CCs were formed by the Strecker-type reactions. If so, aminonitriles (NH_2-CHR-CN) are precursors of a-amino acids, but the evidence has not been shown, nor aminonitriles have not been detected in CCs. Hydantoin has been identied in extracts of CCs [4], and it is a candidate of precursors of glycine. Extraterrestrial amino acid precursors found in CCs were probably synthesized in molecular cloud environments [2] or small celestial bodies [3]. We irradiated possible interstellar media, such as mixture of carbon monoxide, ammonia and water to simulate possible reactions among interstellar media in dense clouds. The irradiation products were analyzed by HPLC and mass spectrometry to characterize amino acid precursors in the products.

Experiment: A gaseous mixture of CO and NH_3 was sealed in a Pyrex glass tube with liquid water. The gaseous mixture was irradiated with 2.5 MeV protons from a Tandem accelerator at Tokyo Institute of Technology. Total quantity of electricity was 2 mC. The irradiation products is hereafter referred to as CAW. A mixture of CH_3OH, $NH_3$and H_2O (molar ratio 1:1:2.8) was sealed in a pyrex glass tube, frozen in liquid nitrogen, and irradiated with 290 MeV/u carbon ions from HIMAC accelerator (NINS, QST, Japan). The irradiation products is hereafter referred to as MeAW.

Aminoacetonitrile, a precursor of glycine, in CAW and MeAW was determined by cation-exchange HPLC after derivatized with orthophthalaldehyde and N-actyl-L-cysrtein. Hydantoin in the both product was determined by reversed-phase HPLC. Both products were fractionated by gel filtration chromatograpy (column: Shodex OHpak SB-802.5 HQ) and/or ultrafiltration (Pall Ultrafiltration device 3K). Each fraction was acid-hydrolyzed and amino acids in the fractions were determince by the cation-exchange HPLC (shown above). Both products were also characterized by LC/Orbitrap-MS.

Results and Discussion: Both CAW and MeAW had little amino acids before hydrolysis, but various amino acids were detected after hydrolysis. Glycine was predominant in all the case. Thus, not free amino acids but amino acid precursors were formed in the simulation experiments. It was shown that neither aminoacetonitrile nor hydantoin were major glycine precursors, but complex amino acid precursors were major amino acid precursors. In the case of CAW, amino acid precursors whose molecular weights were over 3000 were predominant. Peaks of m/z = 1000 or over were detected by mass spectrometry. These results strongly suggested that complex amino acid precursors with large molecular weitghts could be directly generated from small molecules such as CO or CH_3OH in interstellar environments. It was suggested that the Strecker-type reaction was not a major pathway of amino acid formation in molecular

clouds: Flash-and-quench-type reactions might be important for the formation of complex molecules in space.

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