Laboratory simulations of Titan tholins formed by cosmic rays

*Hitomi Abe[1], Kazushi Fukuda[2], Kotaro Kondo[2], Yoshiyuki Oguri[2], Hajime Mita[3], Keita Nanbu[4], Takahito Ouchi[4], Yasuji Muramatsu[4], Yoko Kebukawa[1], Kensei Kobayashi[1]

1.Yokohama National University, 2.Tokyo Institute of Technology , 3.Fukuoka Institute of Technology, 4.University of Hyogo

Titan is the largest moon of Saturn, which has a dense atmosphere mostly consisted of nitrogen and methane. It has been suggested that Titan's atmosphere is an analogue of that of primitive Earth, which is no more remained. Thus the study of the chemical evolution in Titan's atmosphere could give us many important suggestions, and it draws our special attention from the point of view of astrobiology.
Organic materials were detected in Titan's atmosphere. It indicates that an active organic chemistry occurs due to irradiation by solar UV light, Saturnian magnetospheric electrons and cosmic rays as energy sources. Many simulated experiments have been performed by using these energies. Complex organic materials produced in laboratory simulations have often been called tholins, which contain hydrocarbon, nitrile and heterocyclic aromatic moieties. Tholins could give amino acids after interaction with water.
Most laboratory works have simulated reactions in the higher atmosphere of Titan, where solar UV and Saturnian magnetospheric electrons are considered major energies. In the lower atmosphere, however, cosmic rays could have larger contribution than UV [1]. However, there is not many laboratory simulations using cosmic rays. Taniuchi et al. (2013) studied tholins formed by proton irradiation and the produced tholins were analyzed by SEM, AFM, pyrolysis GC/MS and MALDI-TOF-MS [2]. The tholins yielded a wide variety of amino acid precursors after acid hydrolysis, but the structures of amino acid precursors were little known. In this study, we irradiated gas mixtures simulating Titan atmosphere with high energy protons to investigate possible structures and formation mechanisms of tholins.
We prepared a 700 Torr (93 kPa) of gas mixture of nitrogen (95%) and methane (5%) as a simulated Titan tropospheric atmosphere: The pressure corresponds to that of Titan at an altitude of 10 km. The gas mixture was introduced to a Pyrex tube with a Havar foil window. KBr substrates were also placed in the Pyrex tube to sample the products including insoluble fractions. The gas mixtures were irradiated with protons from a Tandem accelerator at Tokyo Institute of Technology. After proton irradiation, KBr substrates were taken out of the tube and were subjected to FT-IR and XANES analysis. XANES analyses were carried at NewSUBARU synchrotron facility at University of Hyogo. The products on the inside Pyrex tube were collected with several kinds of solvents which has different polar character, and were analyzed by ESI-MS. An Aliquot recovered with each solvent was hydrolyzed and subjected to amino acid analysis by ion exchange HPLC.
ESI-MS indicated that tholins made by proton irradiation contained amino acid precursors such as hexamethylenetetramine. XANES and FT-IR analyses showed that the tholins contained amine groups and aliphatic moieties. No clear evidences of aromatic groups were observed. Characteristics of water soluble fraction of the tholins were difference from those of the whole tholins. Spectroscopic results showed that some O-containing groups in the whole tholins, which suggested that trace amount of water could have contaminated to the gas mixture at room temperature. We are now designing the experiments at low temperature to avoid water vapor contamination.
References:
[1] C. Sagan, W. R. Thompson, *Icarus*, 59, 133-161 (1984).
[2] T. Taniuchi, Y. Takano, K. Kobayashi, *Analytical Sciences*, 29, 777-785 (2013).

Keywords: Astrobiology, Titan, cosmic ray, chemical evolution, ESI-MS, FT-IR spectroscopy

