

Analysis of amino acids synthesized by impact reactions in nitrogen gas using a light-gas-gun (Simulation experiment of reactions on Titan)

窒素ガス中高速飛翔体衝突により合成されるアミノ酸の分析 (タイタン模擬実験)

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Abstract In order to investigate synthesis of amino acids by asteroid's impact onto Titan and other satellites / planets, simulation experiment has been carried out using a 2-stage light gas gun. A small polycarbonate bullet with about 7 km/s is injected into a pressurized target chamber filled with 1 atm of nitrogen gas, to collide with an ice + iron target (an iron target or an ice + hexane + iron target). Produced black soot is carefully collected and analyzed by a high-performance liquid chromatograph (HPLC). As a result, many kinds of amino acids (glycine, alanine *etc.*) are detected in considerable amount. When the ice + hexane + iron target is used, production rate of the soot and content of the amino acids are large. Synthesis of the amino acids is also supported by the analysis by FT-IR.

1. Introduction

Huge amount of carbonaceous molecules and particles have been produced in space. A part of them have been stored on the surface planets and satellites. When evolution of the surface took place, carbons on the surface could have reacted to make complex organic molecules. [1- 3] Here, we are interested in evolution of carbons on Titan surface, where huge methane and carbonaceous molecules have been stored on the surface. [4] And, a lot of asteroids have hit the surface for long years, which would make impact reactions in nitrogen atmosphere, and produced many kinds of organic materials including amino acids. The products were stored on the dark and cold surface, while a part of them was diffused into space. [5, 6] A model explaining this process is shown in Fig. 1. We could expect storage of organic materials on Titan, which will be explored in future using space probes. To make clear the production process of amino acids by asteroid's impacts, simulation experiment using a 2 staged-gas-gun has been carried out. [7, 8] Produced carbonaceous black soot is carefully collected and analyzed using a high-performance liquid chromatograph (HPLC). During the analysis, the hot-water reflux method and the dabsylation method are used. [9, 10]

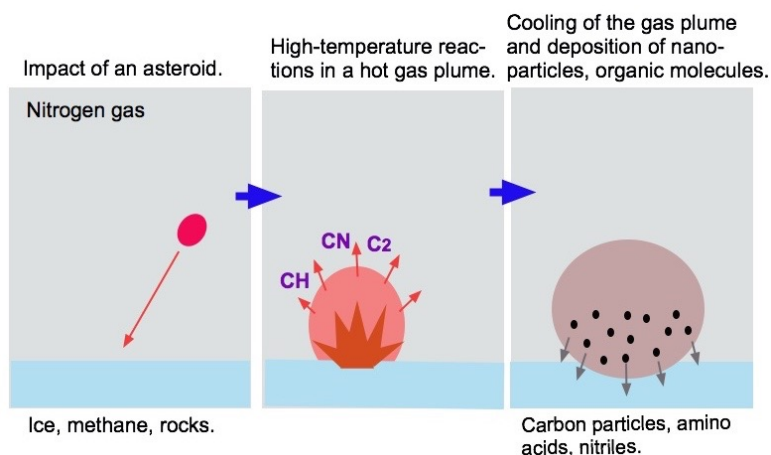


Fig.1 Model figures explaining the impact reactions on Titan.

2. Experimental

The experiment is carried out using a 2-stage light-gas-gun at ISAS/JAXA, Sagami-hara. This gas gun can accelerate a polycarbonate bullet 7.1 mm ϕ (or a stainless steel bullet 3.2 mm ϕ) to about 7 km/s under a vacuum of 0.1 Pa. The bullet collides with an ice + iron target (an iron target or an ice + hexane + iron target) in a pressurized chamber. A schematic of the pressurized chamber is shown in Fig. 2, which is 255 mm in diameter and 250 mm long, and made of stainless steel. At the end of the target chamber, the pressurized impact chamber is set. To collect the produced soot, inside wall of the chamber is covered with clean aluminum sheets. The pressurized chamber is at first evacuated by a rotary pump, and then 100 kPa of nitrogen gas is introduced. A bullet penetrates the aperture of the chamber, 65 mm in diameter covered with a 0.05 mm thick aluminum film, and hits an iron target 76 mm in diameter and 25 mm thick. The target can be cooled down to about $-50\text{ }^{\circ}\text{C}$ by thermal conduction of a copper rod, which is cooled by liquid nitrogen. On the iron target, thin ice (ice + hexane) layer about 2 mm thick can be set by covering with a thin aluminum-film. After the impact, produced black soot is carefully collected using 2-propanol and a brush.

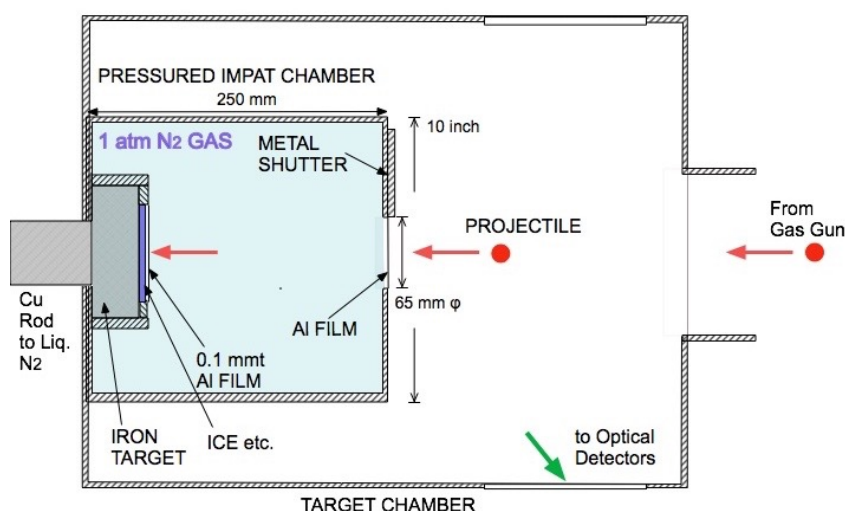


Fig. 2 Schematic of the pressurized chamber in the target chamber.

In order to detect produced amino acids, the produced soot is analyzed. A part of the soot is refluxed in pure water for 8 h at $100\text{ }^{\circ}\text{C}$. Then, the water is filtered using a $0.2\text{ }\mu\text{m}$ membrane filter and condensed. The sample is reacted with dabsyl chloride to make dabsyl-amino acids at $70\text{ }^{\circ}\text{C}$ [11]. A standard amino acid solution including 17 amino acids and a blank (pure water) are also reacted same way. The prepared samples are analyzed by a HPLC with a UV/VIS detector (Jasco Gulliver System, $\lambda = 465\text{ nm}$). 200 μl of the dabsylized sample is injected into the HPLC analyzer.

To measure the molecular structure, Shimadzu 8700 Fourier transform infrared spectrometer (FT-IR) is used. First, a drop of sample is put on a CaF_2 plate (20 mm in diameter, 1 mm thick) by using a pipette, and dried. And then, the sample and the background are measured. Each spectrum is obtained after 100 scans and averaging.

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3. Experimental Results

The deposited carbon soot on the aluminum sheet is shown in Fig. 3. The black soot consists of carbon nano-particles, metal nano-particles and carbonaceous molecules. The HPLC charts obtained by analyzing the collected carbon soot results are shown in Fig. 4 and 5. The chart from pure water (blank) is also described for comparison. These data are compared with that of standard amino acids including 17 amino acids. From the data, we can confirm synthesis of glycine and alanine in the samples, when the ice + iron target and the ice + hexane + iron target are used. Peaks of serine and leucine are sometimes detected in these targets. It is shown that about 400 pmol of glycine is included in 1 mg of the soot in case of the ice + iron target. Similar amount of alanine is included in this soot. About 1.5 nmol of glycine is included in 1 mg of the soot in case of the ice + hexane + iron target. On the other hand, in case of the iron target, amino acids are less detected.



Fig. 3 A photograph of carbon soot deposited on the aluminum sheet set on the inner wall.

As the carbon soot includes amino acids, clear peaks of chemical bonds could be measured by FT-IR.

Therefore, FT-IR spectrum is measured for the collected soot sample. Figure 6 shows a typical FT-IR chart in case of the ice + hexane + iron target. There are clear absorptions at around 3000 cm^{-1} (NH_3^+ stretching band) and around 1500 cm^{-1} (CO_2^- stretching band), which correspond to the typical bands of glycine, and are similar with signals from standard glycine. Effects from another among acids are also included.

4. Discussions

It was confirmed that amino acids were detected in this experiment. But it is necessary to consider the possibility of inclusion of contamination. The contamination from a target chamber to a pressurized impact chamber is considered. After the injection of a bullet, it is possibility of inflow of impurities from the aperture. However, a metal shutter closes the aperture to prevent the inflow of impurities from the outside. During the collection of soot, careful operation was done. The iron targets, the aluminum sheet, sampling bottles were heat-treated at $500\text{ }^\circ\text{C}$ to remove organic impurities.

To confirm the influence of the impurities from the aluminum sheet, we collected the impurities from an aluminum sheet, which was not used for the impact experiment, and analyzed by the HPLC. Peaks corresponding to the amino acids were not detected. Thus, it is can be confirmed that the amino acids detected in this study are synthesized by the impact reactions.

5. Conclusions

To investigate production of amino acids by impact reactions on Titan, the experiment is carried out using a 2-stage light gas gun. We collect the soot produced after the impact, refluxing by pure water and dabsylizing. The HPLC analysis shows peaks corresponding to glycine and alanine in the samples, for which the ice + iron target, the ice + hexane + iron target, and the iron target are used. There are peaks from another amino acids. From the FT-IR spectrum, the stretching vibration bands

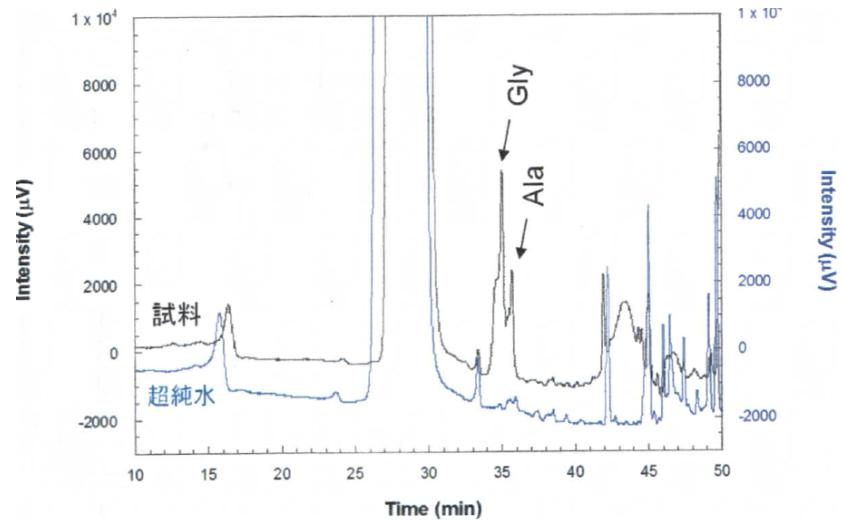


Fig. 4 Peaks of glycine and alanine in the HPLC chart, where a polycarbonate bullet hits an ice + iron target under $p(\text{N}_2)=100\text{ kPa}$.

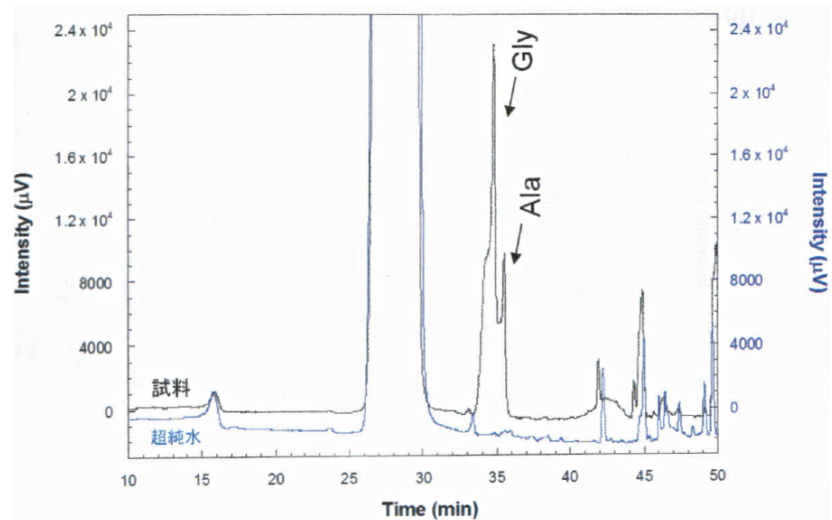


Fig. 5 Peaks of glycine and alanine in the HPLC chart, where a polycarbonate bullet hits an ice + hexane + iron target under $p(\text{N}_2)=100\text{ kPa}$.

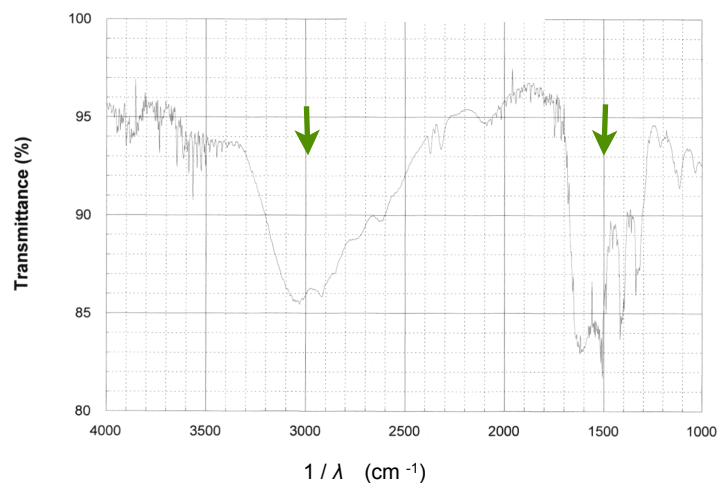


Fig. 6 A FT-IR chart of the sample, where a polycarbonate bullet hits an ice + hexane + iron target under $p(\text{N}_2)=100\text{ kPa}$.

from amino acids are detected. These results suggest that amino acids have been produced by the impact reaction.

Acknowledgments

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