Synthesis of amino acids by impact reactions in nitrogen gas using a light-gas-gun (Simulation experiment of reactions by asteroid's impacts)

ガス銃を用いた窒素ガス衝突反応によるアミノ酸合成（小惑星衝突模擬実験）

Grad. School Science & Technol., Shizuoka Univ. Tetsu Mieno (sptmien@ipc.shizuoka.ac.jp),
Dept. Physics, Shizuoka Univ. Kazuki Okochi, Kazuhiko Kondo
PERC, Chiba Inst. Technol. Keisuke Kurosawa
ISAS/JAXA, Sunao Hasegawa

Abstract In order to investigate synthesis of carbonaceous products by asteroid's impact onto Titan and other satellites / planets, simulation experiments have been carried out using a 2-stage light gas gun. A small polycarbonate with about 6.5 km/s is injected into a pressurized target chamber filled with 1 atm of nitrogen gas, to collide with an ice + hexane + iron target (an iron target or an ice + iron target). After the impact, produced black soot is carefully collected and analyzed by a high-performance liquid chromatograph (HPLC). As a result, about 0.04 – 8 pmol of glycine, and a lesser amount of alanine are found in the samples, when the ice + hexane + iron target is used. In case of the ice + iron target and the iron target, less amino acids are detected. Synthesis of the amino acids is also supported by the measurement using FTIR and LD-ToF-MS.

1. Introduction

Huge amount of organic compounds have been produced in space. This is confirmed by the alalysis of organic compound in carbonaceous meteorites such as the Murchison meteorite. [1, 2] It can be considered that a part of organic compounds has been produced by impact reactions in space. They are stored in surface of planets and scattered into space. Recently, it was suggested that organic compounds were produced on early Earth by simulation experiments of oceanic impacts. [3] To investigate the origin of life on Earth, various models of the primitive Earth are proposed, and simulation experiments for chemical evolution based on these models have been performed [4, 5] Titan, the largest moon of Saturn, has attracted much attention in studies of organic reactions in space. Titan is about 5150 km in diameter. The mean density, surface pressure and temperature of Titan are 1.88 g/cc, 147 kPa and 90 K, respectively. An attractive feature of Titan is its dense nitrogen atmosphere [6] So, we expect that amino acids were produced on Titan's surface by the impacts of asteroids.

In the previous simulation experiment concerning impact reactions on Titan's surface, production of many carbon clusters were confirmed, [7] and the possibility of production of amino acids and nitride polymers is expected. Therefore, we carried out laboratory simulation experiment of asteroid impacts using a 2-stage light-gas-gun, and tried to find amino acids from carbon soot synsisized by impact reactions under a nitrogen-gas atmosphere. [8]

2. Experimental

The experiment is carried out using a 2-stage light-gas-gun at ISAS/JAXA, Sagamihara. This gas gun can accelerate a polycarbonate bullet 7.1 mm ϕ (or a stainless steel bullet 3.2 mm ϕ) to about 6.5 km/s under a vacuum of 0.1 Pa, and the bullet collides with an ice + hexane + iron target (an iron target or an ice + iron target) in a pressurized chamber. A schematic of the pressurized chamber is shown in Fig. 1. At the end of the target chamber, the pressurized impact chamber is set, which is 255 mm in diameter and 250 mm long, and made of stainless steel. To collect the produced soot sample, the inside wall of the chamber is covered with clean aluminum sheets. The pressurized chamber is at first evacuated by a rotary pump, and then 1 atm of nitrogen gas is introduced. A bullet penetrates the aperture of the chamber, 65 mm in diameter covered with a 0.1 mm thick aluminum film, and hits the iron target 76 mm in diameter and 25 mm thick. The target can be cooled down to about −50 °C by thermal conduction of a copper rod, which is cooled by liquid nitrogen. On the iron target, thin ice/water (water + hexane) layer about 2 mm thick can be set by covering with a thin aluminum-sheet. After the impact, the soot is carefully collected using propanol and a brush.

In order to detect production of amino acids, the produced soot, which deposits on the inner wall of the pressurized chamber, is analyzed. A part of the soot is refluxed in pure water for 8 h at 100 °C. The water is then filtered using a 0.2 μm membrane filter and condensed. Then, the sample is reacted with dabsyl chloride to make dabsyl-amino acids [9]. 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, λ = 465 nm). 200 μl of the dabsylized sample is injected into the HPLC analyzer.

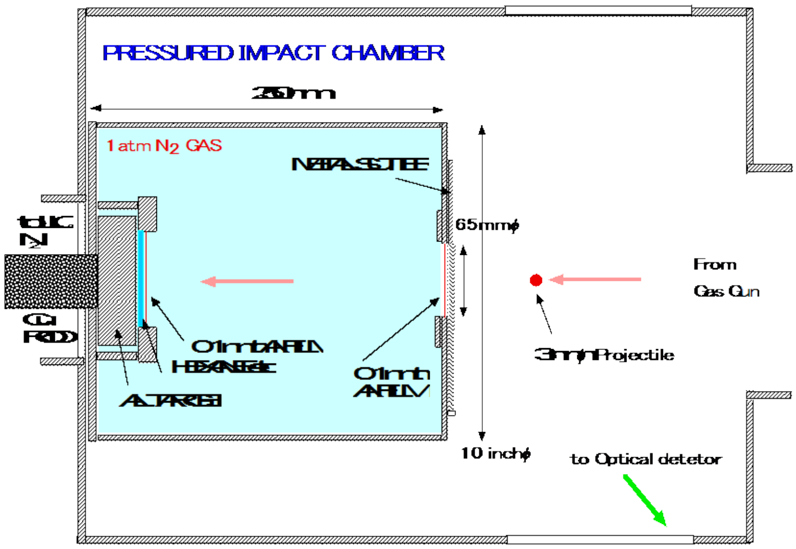

Fig. 1 Schematic of the pressurized chamber in the target chamber.

To measure the molecular structure, a Shimadzu 8700 fourier-transform infrared spectrometer (FTIR) 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 acquired for 100 scans and averaged.

To measure mass spectra of the produced soot, a Bruker AutoFLEX LD-ToF-MS is used. The ToF-MS analysis is performed in the reflector mode, and 50 shots are averaged. The matrix, trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), is dissolved in methanol, and the sample is dissolved in methanol on an ceramic dish, and mixed with DCTB matrix. The samples are put on a target plate.

3. Experimental Results and Discussion

The typical HPLC results are shown in Fig. 2. These data are compared with that of standard amino acids including 17 amino acids and blank. From the data, we can confirm synthesis of glycine and alanine in the samples, when the ice + hexane + iron target and the ice + iron target are used. Peaks of serine and leucine are sometimes detected in the ice + hexane + iron target and the ice + iron target. It is shown that 0.04–8 pmol of glycine and 0.07 – 3.3 pmol of alanine are included in the injected solution in case of the ice + hexane + iron target. In the samples of ice + iron target, 0.02–3.2 pmol of glycine and 0.07– 2.1 pmol of alanine are detected. On the other hand, in case of the iron target, amino acids are slightly detected.

In order to make clear the content of amino acids, more precise HPLC analysis is carried out. First, the aluminum sheets with the soot are cut to small pieces, and their mass is measured. Next, all carbon soot is carefully collected from this small aluminum sheet. From the difference of mass, the collected soot mass is calculated. These samples are treated according to the procedure mentioned above and analyzed by the HPLC. Table 1 represents the quantitative results. It is show that approximately 200–400 pmol/mg of glycine and alanine are included in the carbon soot, when the ice + hexane + iron target is used. In case of the ice + iron target, production of glycine and alanine is estimated to be 161 pmol/mg, and 131 pmol/mg, respectively.

Table 1 The results of quantitative results by the HPLC.

Sample name	Projectile	Target type	Glycine (pmol/mg)	Alanine (pmol/mg)
130628E	polycarbonate	ice + hexane + iron	244	237
121220D	polycarbonate	ice + hexane + iron	429	339
121220C	polycarbonate	ice + iron	161	131

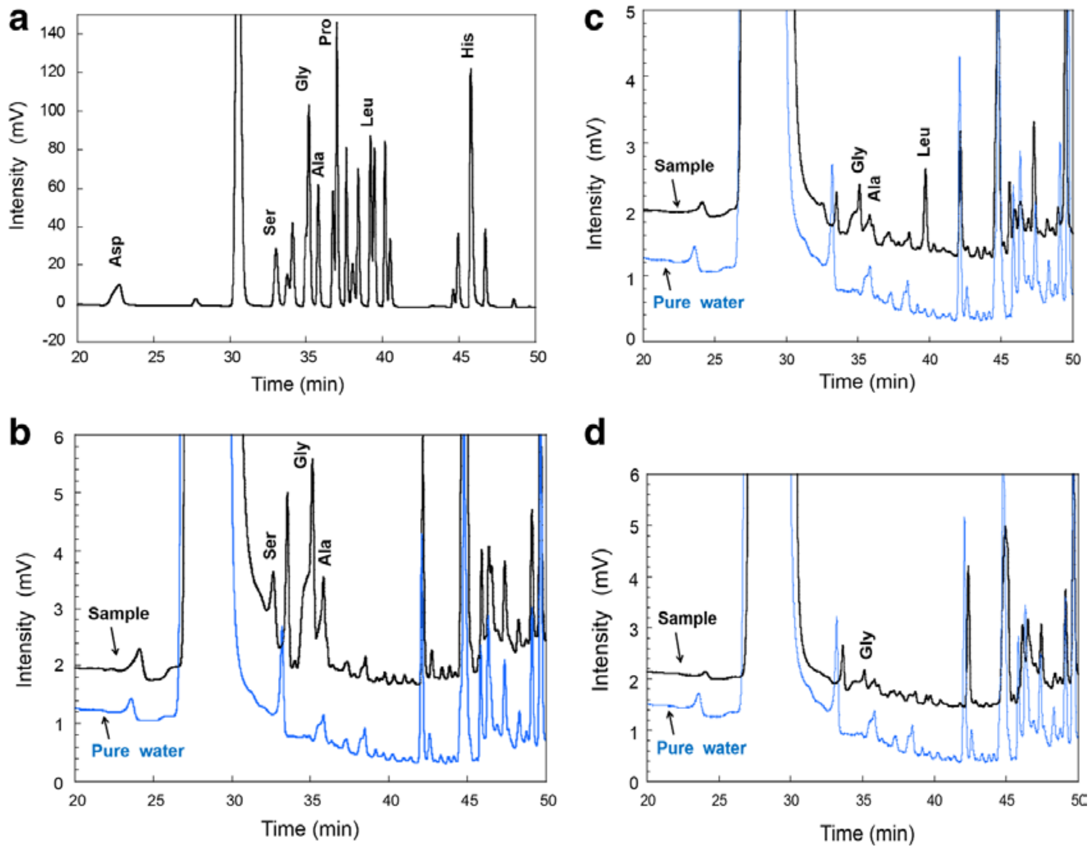

Fig. 2 The typical HPLC results. (a): Standard amino acid solution. (b): The sample when the ice + hexane + iron target is used. Peaks suggesting serine (Ser), glycine (Gly), alanine (Ala) are detected. (c): The sample when the ice + iron target is used. Peaks suggesting glycine, alanine, leucine are detected. (d): The sample when the iron target is used. A small peak of glycine is detected. In (b) ~ (d), blue lines are the signals from pure water (blank).

Mass spectra obtained from the LD-ToF-MS are shown in Fig. 3. These spectra are compared with those from the matrix background signal. In case of the ice + hexane + iron target and the ice + iron target, there are peaks suggesting glycine (M= 75.05) and alanine (M= 89.09). However, these peaks are not clearly detected in the iron target. In the sample of ice + hexane + iron target and the ice + iron target, there are other clear peaks around m/z= 98, 112, 120, and 133.

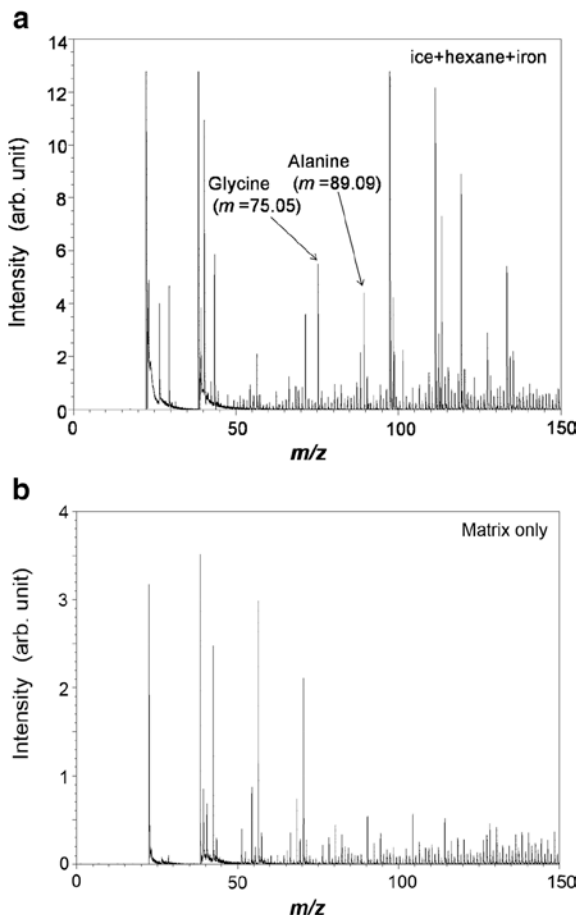

Fig. 3 Typical laser-desorption time-of-flight mass spectra. (a): The ice + hexane + iron target was used. (b): Matrix only. (positive ion mode, 50 shots are averaged)

4. Discussions

It was confirmed that amino acids were detected in this experiment. But it is necessary to consider the possibility of contamination from outside. The contamination from a target chamber to a pressurized impact chamber is considered. Although the aperture of the chamber is covered by an aluminum film before firing, it is torn afterwards and may permit the inflow of impurities. In this study, a metal shutter closes the aperture to prevent the inflow of impurities soon after the impact. Another source of contamination would be on aluminum sheets. Impurities including the amino acid might be sometimes attached onto it. To remove these impurities, the surface of the aluminum sheet is cleaned with pure alcohol before setting it in the inner wall of the pressurized impact chamber. 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 the possibility of production of amino acids by impact reactions on Titan, the experiment is carried out using a 2-stage light gas gun. We collected the soot produced after the impact, and analyzed it by HPLC, FT-IR and LD-ToF-MS. HPLC analysis showed peaks corresponding to glycine and alanine in the samples for which the ice + hexane + iron target and ice + iron target were used. In case of the iron target, only a small amount of amino acids were detected. Mass spectra also showed peaks corresponding to glycine and alanine. From the FTIR spectrum, the stretching vibration of CH at 2950 cm^{-1} and the stretching vibration of CN at 1250 cm^{-1} were identified provisionally. These results suggest that amino acids have been produced by the impact reaction.

Acknowledgments

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