Abiotic Synthesis of High-Molecular-Weight Organics from Inorganic Gas Mixture of Carbon Monoxide, Ammonia and Water by 3-MeV Proton Irradiation

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The abiotic formation of high-molecular-weight organics from an inorganic gas mixture of carbon monoxide, ammonia, and water as a result of 3-MeV proton irradiation from a Van de Graaff accelerator was experimentally verified. The inorganic gas mixture was simulated for representative of interstellar medium. The irradiation products included amino acid precursors and the molecular weight distribution ranged from several hundred to a maximum of 3,000. Both proteinous and non-proteinous amino acids were detected after acid-hydrolysis. Thus, the primary irradiation products were not free amino acid analogs but were amino acid precursors having high molecular weight. The present results have significant implications regarding the extraterrestrial origins of amino acid precursors, such as meteoritic organic compounds, and the organic composition of interstellar dust particles.
The generation of life would have required the fundamental building blocks of bio-organic compounds and is believed to have occurred via a process generally described as “Chemical Evolution”. Organic compounds are thought to have been formed and transformed in interstellar dust particles (ISDs) as they traveled in molecular and diffuse clouds, after which they were preserved in comets in the proto-solar system. It therefore seems that the first steps of abiotic organic compound formation occur in molecular clouds of ISDs. The likely carbon sources for abiotic formation of organics in the ISD environment are carbon monoxide, formaldehyde and methanol, while the major nitrogen source is ammonia. Nitrogen (N$_2$) may be present in the ISD environment, but it cannot be detected spectrometrically.

These interstellar media are constantly irradiated with cosmic and ultraviolet (UV) rays from neighboring stars.

Recent experiments using UV irradiation of mixtures containing methanol and quantitative discussion have yielded significant results in the field of interstellar organics. However, little is known about the primary irradiation products. Kobayashi et al. suggested that the primary products from proton irradiation of the primitive earth atmosphere (carbon monoxide, nitrogen, and water) could be only amino acid precursors (molecules which provide amino acids after hydrolysis) not the free amino acid themselves. Miyakawa et al. developed the magneto plasma dynamic arc-jet (MPD arc-jet) to synthesize amino acids from an amorphous substance composed of carbon, nitrogen, and oxygen. It has been confirmed that amino acid precursors and nucleic acid precursors were formed by irradiation of primitive earth atmosphere components, although the matrix composition of the irradiation
products has not been elucidated. Here, we report the abiotic formation of high molecular
weight organics from an inorganic gas mixture of carbon monoxide, ammonia, and water after
high-energy proton irradiation derived from a Van de Graaff accelerator. The present study
investigated the primary irradiation products of interstellar dust organics and elucidated their
morphological aspects.

A schematic view of the apparatus used for the high-energy proton irradiation experiment
is shown in Fig. 1. Irradiation conditions resembled those found in interstellar dust clouds
and proton irradiation simulated the main component of cosmic rays. A Pyrex glass tube was
filled with the following inorganic gas components to simulate the interstellar gas mixture:

- 350 Torr of carbon monoxide
- 350 Torr of ammonia over liquid water, which provided 20 Torr of water vapor at room temperature

Gas mixtures were irradiated with 3 MeV protons generated by a Van de Graaff accelerator at the Tokyo Institute of Technology. Total energy delivered to the gas mixture was 4,000 J, as given by the product of the number of particles delivered and ionization energy loss of a single particle in the gas mixture. Deionized water
was further purified with a Millipore Milli-Q LaboSystem™ and a Millipore Simpli Lab-UV
(Japan Millipore Ltd., Tokyo, Japan) in order to remove both inorganic ions and organic
contaminants. Prior to use, all glassware was heated in a high temperature oven (Yamato
DR-22) at 500°C in order to eliminate any possible contaminants.

50 µl of the irradiated sample was injected into a Gel Filtration High Performance Liquid
Chromatography (HPLC) system composed of an HPLC pump (TOSOH DP-8020) and a UV
detector (TOSOH UV-8020). The columns used were a TSKgel G2000 SWxL (7.8 mm i.d.
x 300 mm) for gel filtration, and an Inertsil ODS-3 (4.6 mm i.d. x 250 mm) for reversed-phase chromatography. The mobile phase was a mixture of 25 mM acetonitrile (75%) and 0.1% trifluoroacetic acid (25%). Molecular weights were calibrated with polyethylene glycol (PEG) and human serum albumin molecular weight standards.

As shown in Fig. 2, unexpectedly high molecular weight organic compounds were formed from the inorganic gas mixtures: The molecular weight distribution ranged between several hundred and ca. 3,000 Da, and peaks corresponding to 2,800, 1,100, and 800 Da were estimated. The yellow-colored product was dissolved in water, thus showing the complex organics formed by proton irradiation contain hydrophilic groups, such as -OH, -NH- and similar bonds. An aliquot of the irradiation products was hydrolyzed with 6 M HCl at 110°C for 24 hours. Amino acids in the hydrolyzed and unhydrolyzed fractions were then analyzed in an ion-exchange HPLC system using a post-column derivatization with o-phthalaldehyde and N-acetyl-L-cystein. The HPLC system used was composed of two HPLC pumps (Shimadzu LC-6A), a cation exchange column (Shimpak ISC-07/S1504, 4 mm i.d. x 150 mm), a post column derivatization system, and a Shimadzu RF-535 fluoromeric detector (excitation wavelength: 355 nm; emission wavelength: 435 nm). Column temperature was maintained at 55°C. Gradient elution was performed using eluents A (0.07 M sodium citrate perchloric acid, pH 3.2, containing 7% ethanol) and B (0.2 M sodium citrate boric acid-NaOH, pH 10).

A representative ion-exchange chromatogram of the proton irradiation products is shown in Fig. 3. Relative concentrations of the hydrolyzed amino acids are shown in Table 1. A wide variety of proteinous amino acids, such as glycine, alanine, and aspartic acid, as well as
non-proteinous amino acids, such as β-alanine, α- and γ-aminobutyric acid, were detected in the hydrolyzed fraction. The major components were the C₂, C₃ and C₄ amino acids of glycine, alanine and aspartic acid, respectively. In the unhydrolyzed fraction, only small amounts of glycine were detected. This demonstrates that amino acid precursors rather than free amino acids were formed from the inorganic gas mixture. In order to quantitatively evaluate the yields of amino acids, G-values (number of molecules formed per 100 eV) of glycine after acid-hydrolysis were preliminary given as 2.2 x 10⁻².¹⁵ Glycine was the predominant individual amino acid among the high molecular weight organics. This strongly suggests that extraterrestrial amino acids are contained within high-molecular-weight matrices in cometary or meteoritic complex organics.

Cometary organics are considered to be a possible source of the terrestrial biosphere.³,¹⁶ Complex organic compounds were discovered in the coma of Comet Halley but the presence of free amino acids was not confirmed.¹⁷ The simplest amino acid, glycine, has been the target of telescopic observation of interstellar media in efforts to detect extraterrestrial amino acids.¹⁸ Because of its key role in the formation of proteins, and other bio-molecules, this search is worth resuming, despite the lack of success to date. The possible presence of glycine in molecular clouds has been reported,¹⁸ but the signal has not been confirmed.¹⁹ Recently, successful detection of interstellar glycine was reported by Kuan et al. (2003).²⁰ Hence, the discovery of interstellar glycine²⁰ may strengthen the exogenous study that interstellar molecules could have played pioneering role in the prebiotic chemistry of the early Earth.
Free amino acids are unlikely to abundant in extraterrestrial environments, and taken together with the presence of amino acid precursors in the hydrolyzed fraction of meteorites, the present data is consistent with the notion that high molecular weight organics are formed in ISD clouds. Consequently, high molecular weight extraterrestrial organics containing amino acid precursors delivered by comets and/or meteorites may have played a pioneering role in the early stages of chemical evolution under primitive Earth conditions.

The authors express their sincere thanks to associate editor Prof. L. E. Rehn and an anonymous reviewer for constructive reviewing comments which helped to improve the manuscript. The authors would like to thank Dr. K. Kawasaki from the Tokyo Institute of Technology for his assistance and discussion. This research was supported in part by a Grant-In-Aid (No. 14340170) from MEXT (Ministry of Education, Culture, Sports, Science and Technology, Japan) and the Special Co-ordination Fund for the Archaean Park Project.
References


Gas inlet valve

Gas mixture of carbon monoxide (350 torr), ammonia (350 torr) and water (20 torr)

Havar Foil (2.2 µm)

Van de Graaff accelerator

Proton beam

Pyrex glass tube (volume: 400 ml)

Havar Foil (2.2 µm)

### Table 1

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>% mole</th>
</tr>
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<tbody>
<tr>
<td><strong>Proteinous</strong></td>
<td></td>
</tr>
<tr>
<td>Glycine</td>
<td>88.88</td>
</tr>
<tr>
<td>Alanine</td>
<td>4.73</td>
</tr>
<tr>
<td>Serine</td>
<td>1.14</td>
</tr>
<tr>
<td>Aspartic acid</td>
<td>1.13</td>
</tr>
<tr>
<td>Valine</td>
<td>0.15</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>0.06</td>
</tr>
<tr>
<td>Threonine</td>
<td>0.02</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>tr.</td>
</tr>
<tr>
<td>Leucine</td>
<td>tr.</td>
</tr>
<tr>
<td><strong>Non-proteinous</strong></td>
<td></td>
</tr>
<tr>
<td>α-Aminobutyric acid</td>
<td>3.16</td>
</tr>
<tr>
<td>β-Alanine</td>
<td>0.60</td>
</tr>
<tr>
<td>α-Aminoacidipic acid</td>
<td>0.10</td>
</tr>
<tr>
<td>γ-Aminobutyric acid</td>
<td>0.03</td>
</tr>
<tr>
<td>β-Aminoisobutyric acid</td>
<td>tr.</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100.00</td>
</tr>
</tbody>
</table>