Pyrolysis of High-Molecular-Weight Complex Organics Synthesized from a Simulated Interstellar Gas Mixture Irradiated with 3 MeV Proton Beam

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High-molecular-weight organic matter synthesized from mixtures of carbon monoxide, ammonia, and water gases similar to those found in the interstellar medium were irradiated with a 3 MeV proton beam and analyzed by Curie-point pyrolysis with detection by a gas chromatograph and a mass spectrometer (Pyr–GC–MS). A wide variety of organic compounds, not only a number of amide compounds, but also heterocyclic and polycyclic aromatic hydrocarbons (PAHs), were detected among the products of the pyrolysis. Detection of biologically interesting compounds, such as glycolamide ($HOCH_2CONH_2$), is also cosmochemically interesting. The present data show that primary and primitive organic matter serving as "precursors" to bioorganic compounds, such as amino acids, nucleic acid bases, and sugar, might have been formed in a gaseous mixture of similar composition to that of the interstellar dust environment. Consequently, the matrix of extraterrestrial organic compounds delivered by comets and meteorites may have played an important role in the early stages of chemical evolution on the primitive Earth.

The idea that organic matter, including biologically important compounds, such as amino acids and nucleic acid bases, was delivered to early Earth from extraterrestrial sources is strongly supported by the detection of a large variety of organic compounds in comets and carbonaceous chondrites from the interstellar medium.[1–6] Cooper et al. have found a kind of sugar analog in the Murchison meteorite, which fell over the Australian town of Murchison in 1969, and in the Murray meteorite, which fell in Kentucky in 1950.[7] Both of these carbon-rich meteorites are thought to be fragments of asteroids, rubble from the building of our Solar System. The Murchison meteorite has been particularly well studied,[8] and the detection of amino acids, the molecular building blocks of proteins, helped to establish that these basic components of bioorganic molecules can be formed in extraterrestrial environments.

In addition to the presence of fundamental organic materials, enantiomeric excesses of meteoritic amino acids,[9–11] that is, biomolecular chirality, also plays an important role in triggering stereochemical molecular evolution. Asymmetric photolysis of racemic mixtures of amino acids has been performed using a chiral source of circularly polarized light.[12–16] The photostability of amino acids,[17] and the survivability limits for extraterrestrial delivery[18] have been experimentally reviewed.

Greenberg et al. proposed a cyclic evolutional model of interstellar dust (ISD) where organic compounds are formed and transformed in ISD as they travel in molecular clouds and diffuse clouds, and are then formed in comets where they are preserved in the proto-solar system.[19,20] A representative carbon source is carbon monoxide, and the predominant nitrogen source is ammonia.[19,20] Interstellar media are irradiated with galactic cosmic rays and secondary photons of ultraviolet radiation. However, little is known about the primary radiation products, because they are complex organic molecules.

Kobayashi et al. suggested that the primary products of proton irradiation obtained from mixtures simulating the primitive earth atmosphere (carbon monoxide, nitrogen, and water) were amino acid precursors (molecules which are converted to amino acids following hydrolysis) and not free amino acid analogs.[21,22] It has been recognized that amino acid precursors[23–25] and nucleic acid base precursors[26] were formed in the irradiation experiments from interstellar gas mixture components. Recent experiments that involve irradiating mixtures containing methanol by UV[27–30] and quantitative analysis[24] have also contributed significantly to the study of extraterrestrial organics. However, the matrix of the irradiation products has not yet been clarified.

Here, we report on the composition of high molecular organics synthesized from simulated interstellar media with high-energy proton irradiation. The pyrolysis experiment here revealed the primary composition of interstellar dust organics and elucidated their morphological aspects. The present results have significant implications regarding the extraterrestrial origins of amino acid precursors, such as meteoritic organic compounds and interstellar dust particles.

Experimental

Materials. Ultra-pure grade carbon monoxide and ammonia gases were purchased from Nihon Sanso Co. Deionized water was further purified with a Millipore Milli-Q LaboSystem^{TM} and a Millipore Simpli Lab-UV (Japan Millipore Ltd., Tokyo, Japan)

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to remove both inorganic ions and organic contaminants. All glassware was heated in a high-temperature oven (Yamato DR-22) at 500 °C prior to use to eliminate any possible contaminants.

High Energy Proton Irradiation. A Pyrex glass tube shown in the schematic drawing in Fig. 1 was filled with inorganic gases (350 Torr of carbon monoxide and 350 Torr of ammonia over liq-

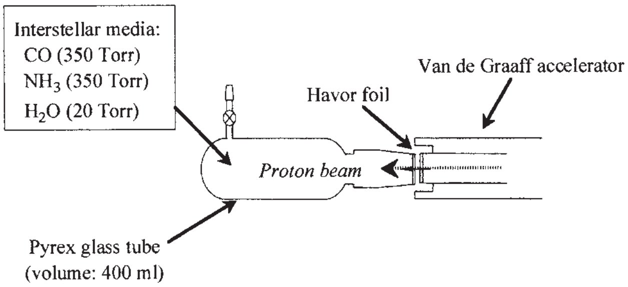

Fig. 1. Schematic diagram of the experimental setup for irradiating (3 MeV proton) the gas mixtures simulating interstellar media.

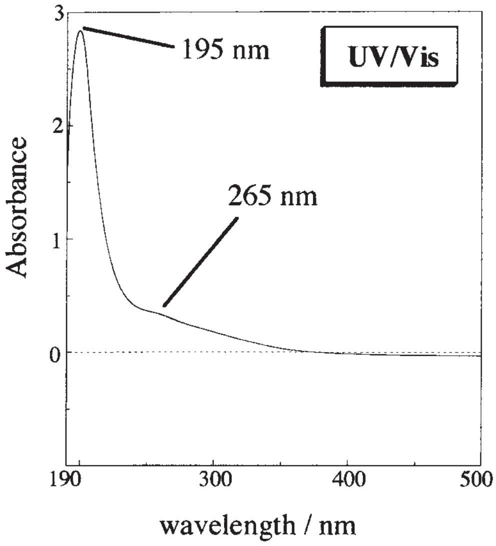

Fig. 2. Ultraviolet absorbance of proton irradiation products. Peaks at 195 nm and 265 nm were observed.

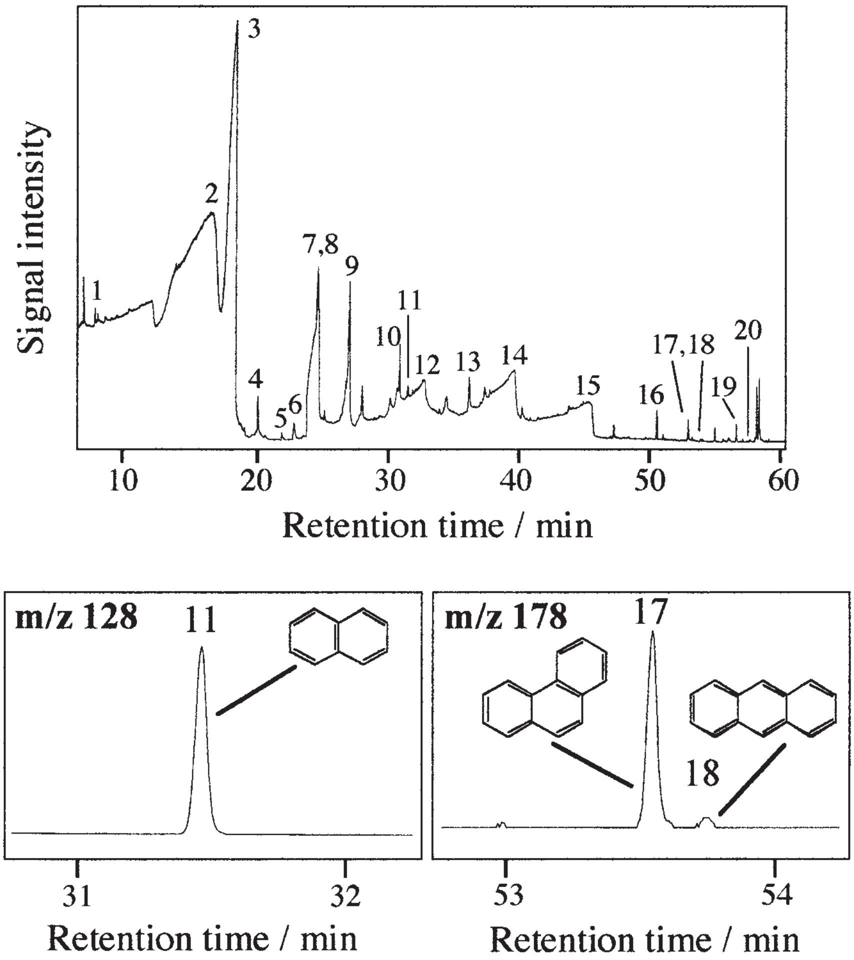

Fig. 3. Total ion chromatogram of Curie point pyrolysis products detected with GC–MS. The peak numbers are as follows: 1, 2-Butanamine; 2, Formamide; 3, Acetamide; 4, 2-Propenamide; 5, Guanidine; 6, 1-Hexanol; 7 and 8, Imidazole + Pyrazole; 9, Aminopyradine; 10, 2,6-Pyradinediamine; 11, Naphthalene; 12, Glycolamide; 13, Pyradinecarboxamide; 14, Urea; 15, Oxamide; 16, Alkanenitrile ($C_nH_{2n+1}N$); 17, Phenanthrene; 18, Anthracene; 19, Alkanenitrile ($C_nH_{2n+1}N$); 20, Methylanthracene.

uid water providing 20 Torr of water vapor at room temperature) simulating the interstellar gas mixtures, and subjected to high-energy proton irradiation, simulating that comprising cosmic rays. Irradiation conditions found in interstellar dust containing amino acid precursors were simulated using 3 MeV proton irradiation generated by a van de Graaff accelerator at the Tokyo Institute of Technology. The total energy applied to the gas mixture was 4000 J, equivalent to the product of the number of particles delivered and the ionization energy loss of a single particle in the gas mixture. The irradiation was performed at ambient room temperature for 2 h.

Curie Point Pyrolysis with GC–MS Method. After irradiation, an aliquot of the radiation products was freeze-dried. Aliquots of yellow-brown colored residue were wrapped in pyrofoil (Japan Analytical Industry). A Curie-Point Pyrolyser JHP-5 (Japan Analytical Industry) was directly connected to a gas chromatograph and a mass spectrometer (Shimadzu GCMS-QP2010). Prepared pyrofoil samples were inserted in the furnace and pyrolyzed at the Curie point of 764 °C for 10 s. The pyrolyzed compounds were carried through the GC–MS system with helium (>99.9999%). A DB-5 capillary column (30 m × 0.25 mm i.d., J&W Scientific) was used for GC separation with the following oven temperature program: increase from 30 to 40 °C at a rate of 1 °C/min, from 40 to 60 °C at 2 °C/min, from 60 to 100 °C at 3 °C/min, from 100 to 200 °C at 4 °C/min, and from 200 to 350 °C at 5 °C/min. The MS was scanned every 0.30 s over m/z of 40–500 with the electron-impact mode set at 70 eV. The data were recorded on a computer and a search of the NIST mass spectra library (the National Institute of Standards and Technology, USA, 1998) for matching mass fragmentograms was used to identify the organic compounds released by pyrolysis.

Ultraviolet (UV) Absorbance. After irradiation, an aliquot of the radiation products was analyzed for UV absorbance by a JASCO V-550 UV/Vis Spectrophotometer (JASCO Co.) to observe the maximum absorbance spectra.

Results and Discussion

UV Absorbance of Irradiation Products. The maximum UV absorbance was observed at 195 nm with a slight shoulder peak on 265 nm (Fig. 2). The peak at 195 nm is typical of organic compounds. The peak around 265 nm might suggests the presence of cyclic compounds, such as aromatic or heterocyclic compounds.

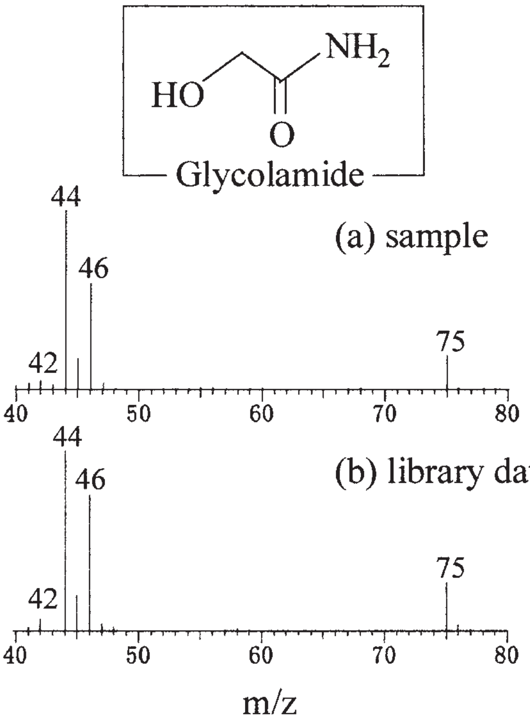

Fig. 4. Mass spectra of (a) the irradiation sample and (b) library data. The similarity of glycolamide ($C_2H_5NO_2$) was 98% in comparison with the NIST mass spectra library data.

Table 1. Relative Abundance of Organic Compounds Released from Pyrolysis Experiment

Compounds	Chemical formula	Relative abundance
Formamide	$HCONH_2$	+++
Urea	$(NH_2)_2CO$	++
Guanidine	$(NH_2)_2C{=}NH$	−
Acetamide	CH_3CONH_2	++++
Oxamide	$NH_2COCONH_2$	+
Glycolamide	$HOCH_2CONH_2$	+
Imidazole and Pyrazole	$C_3H_4N_2$	+++
2-Propenamide	$CH_2{=}CHCONH_2$	+
Aminopyradine	$C_4H_5N_3$	++
2-Butanamine	$C_2H_5CH(NH_2)CH_3$	+
Pyrazinecarboxamide	$C_4H_3N_2CONH_2$	+
(2,6-Pyridinediamine ?)	$C_5H_7N_3$	++
1-Hexanol	$C_6H_{18}O$	−
Naphthalene	$C_{10}H_8$	+
Phenathrene	$C_{14}H_{10}$	−
Anthracene	$C_{14}H_{10}$	−
Methylanthracene	$C_{15}H_{12}$	−
Alkanenitrile analogs	$C_nH_{2n+1}N$	++

Symbols: ++++, +++, ++, +, and − indicate very major, major, moderate, minor, and trace amounts of compounds obtained from high molecular organics by proton irradiation.

Determination of Pyrolysis Products. A wide variety of organic compounds, including not only a number of amide compounds, but also cyclic compounds, were detected. The total ion chromatogram of the Curie-point pyrolysis detected with GC–MS is shown in Fig. 3. Peak number 3, acetoamide (CH_3CONH_2), was the most predominant compound among the other amide analogs. The detection of biologically interesting compounds, such as glycolamide ($HOCH_2CONH_2$), in organic matter are also cosmochemically interesting as a possible precursor of amino acids and/or sugars. The mass fragmentogram of glycolamide ($HOCH_2CONH_2$) had a similarity of over 98% compared with data from the mass spectra library of NIST (Fig. 4). Table 1 gives the relative abundance of organic compounds identified from the pyrolysis analysis. Polycyclic aromatic hydrocarbons (PAHs), naphthalene ($C_{10}H_8$) and phenanthrene ($C_{14}H_{10}$) were detected in minor quantities. The select ion monitoring (SIM) mode showed that the amount of phenanthrene ($C_{14}H_{10}$) was greater than that of anthracene ($C_{14}H_{10}$), as shown in Fig. 3. The chemistry of PAHs is of interest, since PAHs represent one of the most abundant forms of carbon in the interstellar medium, and many variations on these molecules are detected in meteorites and in asteroidal and cometary dust.[31,32] While the formation of basic PAHs in the outflows of carbon-rich stars is understandable, it was not known how PAHs with side groups are formed. When exposed to ultraviolet irradiation, PAHs are altered to secondary products of alcohols, quinones, and ethers.[33]

Kobayashi et al. reported on the abiotic formation of imidazole in the hydrolysate following proton irradiation of a gas mixture of simulated primitive Earth atmosphere.[34] The enzyme imidazole is thought to act as a proto-esterase catalyst in chemical evolution.[35] Although peaks corresponding to imidazole ($C_3H_4N_2$) and pyrazole ($C_3H_4N_2$) were detected in the pyrolysis reactions, these heterocyclic compounds could not be separated, since they have the same molecular formula.

Complex Organics as Interstellar Dust Matrix. Since the yellow-colored products from proton irradiation were water-soluble, these complex organics also contain hydrophilic groups, such as –OH and –NH– bonds. Unexpectedly high-molecular-weight organic compounds from among the irradiation products were determined by gel filtration chromatography. The molecular-weight distribution ranged from several hundred to about 3000 Da, and peaks corresponding to 2800, 1100, and 800 Da were observed.[36]

A negative correlation between the semi-logarithmic yield of aliphatic amino acids and carbon numbers (C_n) for glycine (2), alanine (3), and α-aminobutyric acid (4) has been reported (Fig. 5).[23] This relationship is also typical of abiotically-formed amino acids, such as those found in carbonaceous chondrites.[8] Based on the linear relationship, it is postulated that larger molecules are synthesized from smaller homologues.

Complex Organics as Precursors of Amino Acids and Nucleic Acid Bases. Among individual amino acids synthesized from gas mixtures representative of the interstellar media, glycine predominates more than any other compound in the proton radiation products at ambient room temperature[23] and 10 K.[25] In order to evaluate the quantitative yields of amino acids, the G-values (number of molecules of glycine formed per 100 eV) after acid-hydrolysis were preliminary reported to be 2.2×10^{-2}.[23] Figure 6 shows the relationship between the total energy deposited to the gas mixtures and the yields of glycine in the hydrolysate. The glycine yield was proportional to the total energy deposit, but was independent of the type of energy. In addition to amino acids, the nucleic acid base of uracil was also detected among the proton radiation products.[26] This strongly suggests that extraterrestrial organic matter is preserved in high-molecular-weight matrices, such as cometary or meteoritic complex organics. Amino acid precursors with complex structures have been shown to be much more stable in interstellar environments than free amino acids.[38] The formation of these organic species from simple starting mixtures under conditions typical of the interstellar medium may have important implications for the organic chemistry of interstellar ice grains, comets, and the origins of life.[39] The present data show that the primary and primitive organic matter that serves as precursors to amino acids and/or nucleic acid bases may be similar in composition to organic matter found in the interstellar dust environment.

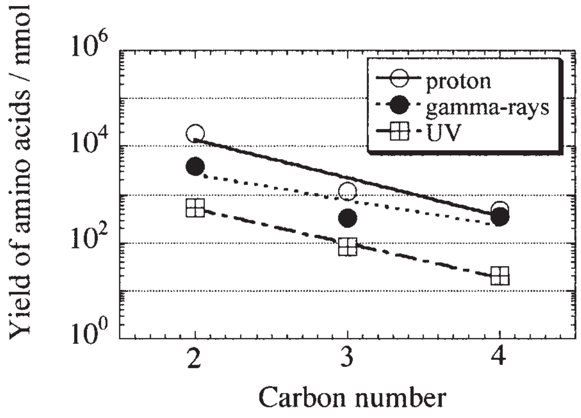

Fig. 5. Yields versus carbon number of amino acids synthesized from the gas mixture of carbon monoxide (350 Torr), ammonia (350 Torr), and water (350 Torr) irradiated with 3 MeV proton beam (○), 1.2 KeV γ-rays (●), and 10 eV ultraviolet (UV) (⊞). Carbon number was 2 for glycine, 3 for alanine, and 4 for α-aminobutyric acid. Modified from the Ref. 23.

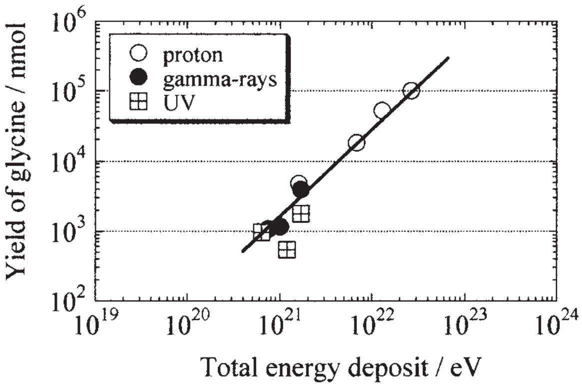

Fig. 6. Energy dependence of glycine formation on the total energy deposited on the gas mixture of carbon monoxide (350 Torr), ammonia (350 Torr), and water (350 Torr) irradiated with 3 MeV proton beam (○), 1.2 KeV γ-rays (●), and 10 eV ultraviolet (UV) (⊞). Modified from the Ref. 23.

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