Bull. Chem. Soc. Jpn., ***70***, *1021—1026 (1997)*

Formation of Organic Compounds in Simulated Interstellar Media with High Energy Particles

Takashi Kasamatsu, Takeo Kaneko, Takeshi Saito,† and Kensei Kobayashi*

Department of Physical Chemistry, Faculty of Engineering, Yokohama National University, Hodogaya-ku, Yokohama 240

†Institute for Cosmic Ray Research, The University of Tokyo, Midoricho, Tanashi, Tokyo 188

(Received December 16, 1996)

Abiotic formation of amino acid precursors in interstellar dusts (ISDs) by cosmic radiation was quantitatively examined. In order to study the formation of organic compounds in ISDs, ice mixtures of carbon monoxide (or methane), ammonia, and water made in a cryostat at 10 K were irradiated with high energy protons. Irradiated ice products were warmed up to room temperature, while sublimed gases were analyzed with a quadrupole mass spectrometer. Some hydrocarbons and alcohols were detected. Amino acid precursors, which gave amino acids after acid-hydrolysis, were detected in non-volatile products remaining on the substrate at room temperature. *G*-values of glycine precursors from methanol, ammonia, and water in solid state irradiation were about 6×10^{-4}, which was about two orders less than those in gasous state irradiation. The present results suggest that a considerable amount of organic compounds formed in extraterrestrial environments were supplied to the primitive earth before the origin of life.

In 1996 McKay et al. reported that there were possible relic biogenic activity in a Martian meteorite ALH 84001, which evoked our interest in the existence of extraterrestrial life.[1)] If life could be born not only on our earth but also on Mars, generation of life seems to be quite inevitable in space. Then how was life born on the earth or on the other celestial bodies?

For the generation of life, bioorganic compounds are essential. It has been supposed that most bioorganic compounds essential to the first life were formed in the planets. Various kinds of simulation experiments have been performed to examine how these compounds were abiotically synthesized in primitive planetary environments. Most of these experiments are conducted to examine the formation of bioorganic compounds after giving energy to mixtures of simple molecules containing the essential elements such as carbon, hydrogen, oxygen, and nitrogen. In Miller's pioneering experiment in 1953, a gas mixture of methane, ammonia, hydrogen, and water was subjected to a spark discharge, and many kinds of organic compounds including some amino acids were detected in the product by paper chromatography.[2)] Following this experiment, many experiments simulating reactions in primitive earth atmosphere were conducted. A mixture of methane, ammonia (or nitrogen) and water was used as starting material in most of the simulation experiments in 1950—1970s, since it was thought that the primitive earth atmosphere had been a "strongly-reduced"-type atmosphere. In these experiments, spark discharge, ultraviolet light, heat, shock wave and so on were used as energy sources, and a variety of amino acids were found in the products.[3—5)] In these days, however, the primitive earth atmosphere is thought to be "mildly-reduced," containing carbon monoxide, carbon dioxide, nitrogen, and water.[6)] If the primitive atmosphere was "mildly-reduced"-type, formation of amino acids and other bioorganic compounds essential for origin of life would have been quite difficult by using conventional energy sources like spark discharge and ultraviolet.[7,8)] Kobayashi et al. had paid attention to cosmic rays as an energy source for chemical evolution. They performed a proton irradiation experiment using a gas mixture of carbon monoxide, nitrogen, and water vapor as a starting material since protons are main components in cosmic rays. A wide variety of amino acids were found in high yield in irradiation products after acid-hydrolysis.[9)] When some other types of gas mixtures with a carbon source and a nitrogen source (e.g., a mixture of methane and ammonia) were irradiated with high energy protons, bioorganic compounds such as amino acids were also formed in high yields.[10)]

It is known that various kinds of organic compounds exist in space, e.g., in interstellar molecular clouds, comets, and carbonaceous chondrites. When comets and meteorites fall to planets, it is possible that they can supply organic compounds to the planets. It is supposed that organic compounds in comets were formed in their precursor bodies, interstellar dust particles (ISDs). ISDs in dense clouds were covered with ice mantles containing such volatiles as water, carbon monoxide, ammonia. In order to simulate reactions in ISDs, ice mixtures of carbon monoxide (or methane), ammonia and water made in a cryostat were irradiated with high energy protons or ultraviolet light. Organic compounds such as nitriles were detected in the products by infrared spectroscopy, but bioorganic compounds could not be detected in them.[11,12)] Briggs et al.[13)] suggested that glycine was formed after ultraviolet irradiation of an ice mixture of carbon monoxide, methane, ammonia, and water, but the experiments were not conducted quantitatively.

In the present study, formation of organic compounds in simulated ISDs was quantitatively examined. Carbon monoxide, ammonia, and water were selected as starting materials since they are strongly suggested to be present in comets and ISDs as major volatile constituents.[14—17] Methane and methanol, which are also suggested to be in ISDs,[12,14] were used in some experiments. Carbon dioxide, which is also suggested to be in comets,[14] was not used in starting mixtures, because abiotic yields of organic compounds from carbon dioxide were much less than those from carbon monoxide or methane.[7,9] We used high energy protons as energy sources, since major energy sources in space are ultraviolet light and cosmic rays, and major components of the latter are high energy protons.[18] Then ice mixtures of carbon monoxide (or methane, methanol), ammonia, and water ("simulated ISD ices") were irradiated with high energy protons.

Experimental

1. Apparatus. The apparatus used to make "simulated ISD ices" was composed of a cryostat, a gas mixer, and a quadrupole mass spectrometer: a copper substrate located in the specially-designed cryostat (Iwatani Type CRT-006-0000) was cooled down to 10 K with a cold head (Iwatani Type D105) and a helium compressor (Iwatani Type CW301). The gas mixer was composed of three mass flow controllers and valves (KOFLOC, Japan) to make a gas mixture of three components in a desired mixing ratio. The quadrupole mass spectrometer (Balzers Model QMG064) was used for analysis of volatile compounds.

A Shimadzu LC-6A high performance liquid chromatograph system with a cation exchange column (Shimadzu Shim-Pack ISC-07lS1504, 4.6 mm i.d.×25 cm) was used to determine non-volatile compounds (amino acids) after post-column reaction with *o*-phthalaldehyde (OPA) and *N*-acetyl-L-cysteine, where a Shimadzu RF-535 fluorometric detector was used.[19]

2. Reagents. Carbon monoxide and ammonia used as starting materials for proton irradiation were made by Sumitomo Seika Co., and methane was made by Nihon Sanso Co. All were of UHP grade. Water was purified with a Milli Q^{TM} system.

3. Proton Irradiation of Ice Mixtures of Carbon Monoxide (or Methane), Ammonia, and Water. Figure 1 shows a schematic representation of an apparatus for proton irradiation of simulated ISDs. A gas mixture of carbon monoxide (or methane), ammonia, and water vapor (1 : 1 : 1 in volume)[20] was made with the gas mixer. This mixture was made to flow (3.0 $\mathrm{cm^3\,h^{-1}}$ each) against the copper block located in the cryostat evaculated to 10^{-6}—10^{-7} Torr (1 Torr = 133.322 Pa) with a turbo molecular pump for ca. 1—2 h, in order to make the simulated ISD ices. The estimated thickness of the ice was 50 μm, which was almost the same as the range of the protons used. The ice mixtures were irradiated with 2.8 MeV protons (beam diameter: ca. 2 cm) from a van de Graaff accelerator at Tokyo Institute of Technology at ca. 0.1 μA for ca. 2 h. The total energy deposited to the simulated ISD ice during irradiation was ca. 1.1×10^{22} eV. Blank runs were also performed in the same manner, without any irradiation.

4. Analysis of Volatile Products. After irradiation, the temperature of the metal block was naturally raised to room temperature at the rate of ca. 60 $\mathrm{K\,h^{-1}}$, while generated gases were analyzed with the quadrupole mass spectrometer (ionization voltage: 100 eV; *m*/*z* 1—64 were scanned for 128 s) located between the cryostat and the turbo molecular pump. After analysis of volatile products, residual matter on the metal block was recovered with water, which was subjected to amino acid analysis.

5. Proton Irradiation of Gas Mixtures of Carbon Monoxide (or Methane), Ammonia, and Water. In Pyrex glass tubes with

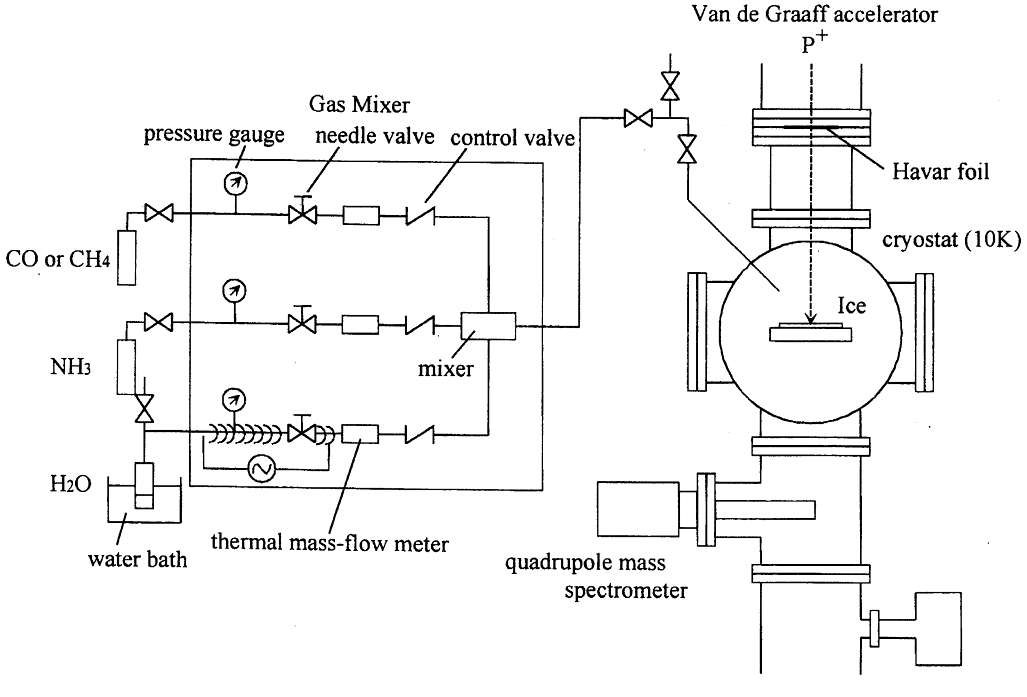

Fig. 1. Apparatus for proton irradiation of simulated ISD ice mixtures.

Haver foil windows, gas mixtures of 350 Torr of carbon monoxide (or methane), 350 Torr of ammonia, and 1 mL of liquid water were introduced with various mixing ratios. The gas mixtures were irradiated with 2.8 MeV protons (beam diameter: ca. 1 cm) from a van de Graaff accelerator (Tokyo Institute of Technology) at ca. 0.3 μA for about 1 h.

6. Irradiation of Gaseous, Liquid and Solid Mixtures of Methanol, Ammonia, and Water. Mixtures of methanol and 25% ammonia aqueous solution (50 : 71 v/v) were sealed in glass tubes (Fig. 2). In order to keep samples in gas, liquid or solid state, each glass tube was thermostated with liquid nitrogen (77 K) or water bath (298 K or 353 K). Volume of the starting materials at 298 K in liquid state was 9 mL (for solid or liquid phase irradiation) or 10 μL (for gaseous phase irradiation). These samples were irradiated with 35 MeV protons (beam diameter: ca. 1 cm) from a Sector Focusing (SF) cyclotron (Institute for Nuclear Study (INS), the University of Tokyo) at ca. 0.1 μA, or 15 MeV electrons (beam diameter: ca. 1 cm) from linear accelerator (INS, the University of Tokyo) at ca. 1 μA. After irradiation, a part of the products was acid-hydrolyzed and analyzed by high performance liquid chromatography.

7. Amino Acid Analysis. A part of the irradiation products in aqueous solution was acid-hydrolyzed with 6 mol dm^{-3} hydrochloric acid (383 K, 24 h). After removing acid, the hydrolyzed products were analyzed by high performance liquid chromatography. Unhydrolyzed products were analyzed in the same matter.

Results and Discussion

1. Profile of Total Pressure in Cryostat. Figure 3 shows changes in total pressure in the cryostat after irradiation of an ice mixture of carbon monoxide, ammonia, and water when the temperature was raised to room temperature. There are some peaks at 50, 130, and 190 K. The major compound found at 50 K was carbon monoxide in the starting material, judged from the peaks at $m/z = 12$, 16, and 28 in mass spectrum. Similarly, it was judged that ammonia was mainly evaporated at 130 K and that water was evaporated at 190 K. These results are in good agreement with the observation that the major compounds found in the tail of a comet were mostly water when the temperature of the active area of a comet is about 200 K.[14)]

2. Volatile Products. In this experiment, it is difficult to analyze volatile products by gas chromatography, because the quantity of products is very small and sampling is difficult under the conditions below 10^{-3} Torr. So we analyzed the products with a mass spectrometer.

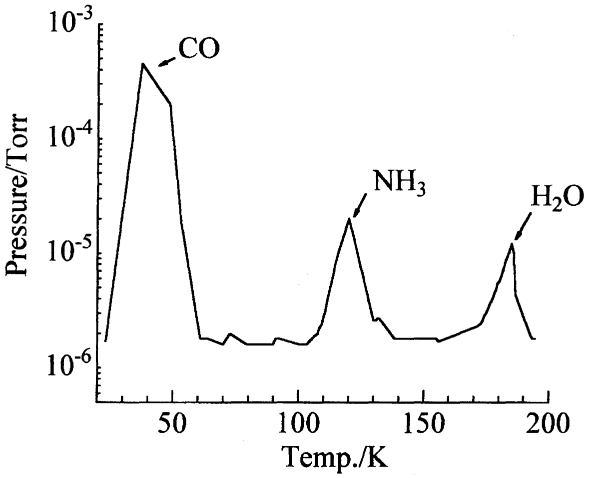

Fig. 3. Total pressure profile of the volatile compounds after irradiation of an ice mixture of carbon monoxide, ammonia, and water (mole ratio=1 : 1 :1).

The compounds which mostly have an influence on the total pressure in the cryostat seemed to be starting materials. By mass spectrometry, however, we observed some products other than the starting materials, which gave several peaks around $m/z = 30$ and 44.

When ice mixtures of carbon monoxide, ammonia, and water were irradiated, methane ($m/z = 12$—16) and carbon dioxide ($m/z = 44$) were detected in volatile products at 80—90 K. It was shown that carbon monoxide was disproportionally converted to methane and carbon dioxide by proton irradiation.

When ice mixtures of methane, ammonia, and water were irradiated, C_2-hydrocarbons such as ethane and ethylene ($m/z = 25$—30) and C_3-hydrocarbons ($m/z = 39$—44) were detected in volatile compounds in the products sublimed at 80—90 K. Considering the melting points, the boiling points, and the vapor pressures at 80 K of ethane and ethylene, ethane and ethylene seemed to be sublimed at the same time.[12)]

When carbon monoxide is converted to hydrocarbons or

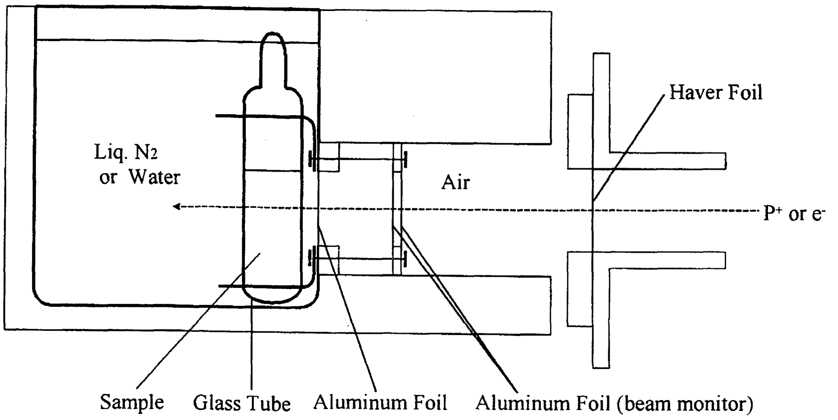

Fig. 2. Apparatus for proton or electron irradiation of the mixture or methanol, ammonia, and water. Gaseous phase: 353 K, Liquid phase: 293 K, Solid phase: 77 K.

other organic compounds, hydrogen must be supplied from other compounds. When we irradiated gas mixtures with protons, the yields of amino acids were the same both in the case that protons went through the sample or stopped in the sample,[19] which suggested that hydrogen is mainly supplied from water or ammonia, not from proton beams.

Figure 4 shows a mass spectrum of the volatile compounds, which were sublimed at 183 K, after irradiation of an ice mixture of carbon monoxide, ammonia, and water. Peaks at $m/z = 26$—32 and $m/z = 39$—46 were observed. Judging from the vapor pressure[21] and standard mass spectra of methanol and ethanol measured by the same instrument (QMG-064), the peaks at $m/z = 31$ and 46 correspond to the presence of methanol and ethanol in the products, respectively. According to the paper of Hiraoka et al.,[22] methanol can be made by the reaction of solid carbon monoxide and hydrogen atoms. The present results suggest that methanol could be also synthesized from carbon monoxide and water by proton irradiation.

3. Analysis of Non-Volatile Compounds. After the products were recovered with water, we could see nothing remain on the metal block. Among non-volatile compounds, we paid attention to amino acids, since they are expected to be formed much more efficiently than other bioorganic compounds like nucleic acid bases. It has been shown, for example, that nucleic acid bases were yielded only 1% as much as the amount of amino acids, when a gas mixture of carbon monoxide, nitrogen, and water was irradiated with protons.[23]

Amino acids such as glycine and alanine were detected in the proton irradiation products from an ice mixture of carbon monoxide, ammonia, and water after acid-hydrolysis, while only trace amounts of amino acids were detected in the products before acid-hydrolysis (Fig. 5). Such results suggest the possible formation of "amino acid precursors," not free amino acids, from carbon monoxide, ammonia, and water in interstellar dust grains by cosmic radiation. When we made some blank tests using the same ice mixtures without the irradiation, we detected only air in the cryostat by mass spectrometry, and no amino acids were detected in the samples on the substrate.

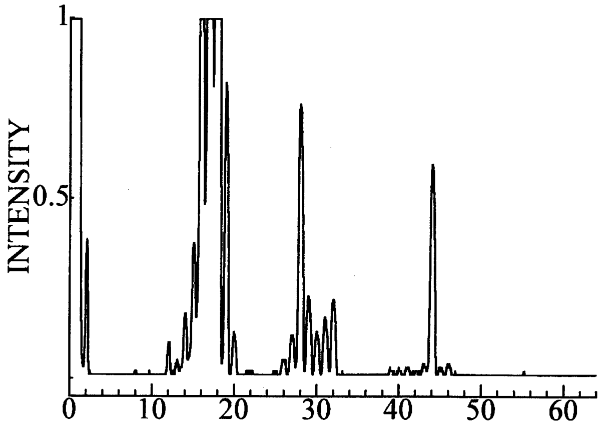

Fig. 4. Mass spectrum of the volatile compounds after irradiation of an ice mixture of carbon monoxide, ammonia, and water (mol ratio=1 : 1 : 1). Sublimation temperature: 183 K.

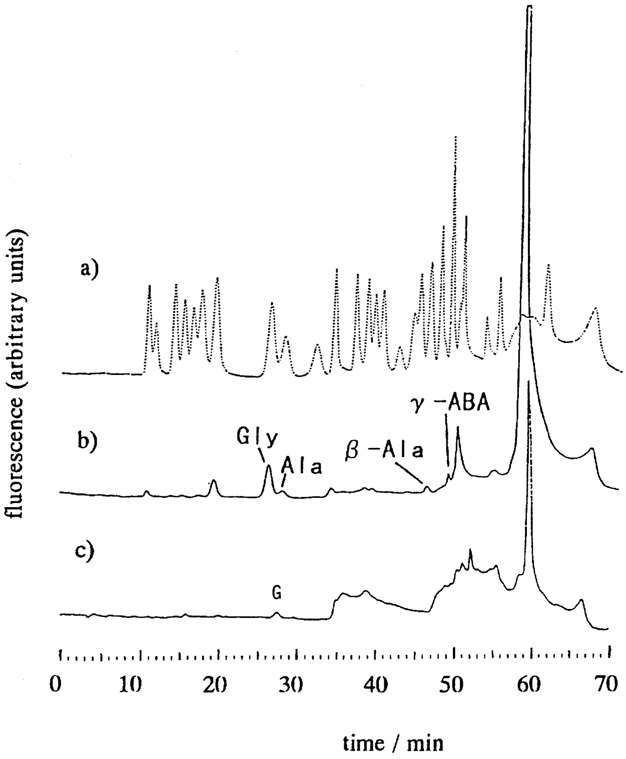

Fig. 5. Ion-exchange chromatograms of amino acids when an ice mixture of carbon monoxide, ammonia, and water (mol ratio=1 : 1 : 1) was irradiated with 2.8 MeV protons. a) Authentic standards, b) acid-hydrolyzed sample, c) unhydrolyzed sample. ABA: aminobutyric acid.

Hereafter we use the G-value (number of formed molecules per 100 eV) of glycine after acid hydrolysis when the formation rate of amino acids is discussed, because (i) glycine is the most abundant amino acid in most of the hydrolyzed irradiation products, and (ii) it was proved that glycine was formed in proportion to total energy deposit if a gas mixture of the same composition was irradiated with high energy particles.[17] *G*-Values of glycine were 10^{-6}—10^{-7} in the irradiation of the ice mixture of carbon monoxide, ammonia, and water. On the other hand, when the gas mixture of the same composition as the ice mixture was irradiated, *G*-value of glycine was ca. 10^{-2}: There is a four-figure difference between the *G*-value of glycine in gas phase and that in solid phase. In the case of similar experiments using methane as a carbon source, *G*-value of glycine in gas phase was ca. 10^{-2}, which was the same as that when carbon monoxide was used as a carbon source; *G*-values of glycine in solid phase were, however, 10^{-3}—10^{-4}, which were only one to two orders less than those in gaseous phase.

4. Analysis of Amino Acids in Proton Irradiation Products from Methanol, Ammonia, and Water. It was shown that there were large differences between the *G*-value of glycine from a mixture of carbon monoxide, ammonia, and water in gaseous phase and that in solid phase. There are some possible reasons why there were difference in *G*-values of glycine in solid and gaseous phase: (i) A part of the carbon source was sublimed during irradiation and that carbon-poor solid phase was irradiated; (ii) it is more difficult to react compounds in solid phase than in gaseous phase by irradiation; (iii) products in gaseous phase can diffuse rapidly to avoid decomposition by further irradiation, while those in solid phase cannot diffuse easily. In order to examine the difference in amino acid yields between solid phase irradiation and gaseous phase irradiation quantitatively, we used methanol as a carbon source for proton irradiation experiments in place of carbon monoxide or methane. The reasons why we chose methanol are: (i) It has been suggested to be in comets and in their precursors, ISDs,[12] and (ii) it is easy to keep the mixture of methanol, ammonia, and water in solid, liquid or gaseous phase during the irradiation.

Figure 6 shows *G*-values of glycine when a mixture of C_1-compound (carbon monoxide, methane or methanol), ammonia, and water in either gaseous, liquid or solid phase was irradiated with high energy protons. Each *G*-value shown was an average of the *G*-values obtained in duplicated runs. The *G*-value of glycine when methanol was used as a carbon source in gaseous phase was ca. 10^{-2}, which was of the same magnitude as that when carbon monoxide or methane was used in gaseous phase. The *G*-value when methanol was used in solid phase or liquid phase was ca. 10^{-4}, which was only two orders less than that when the same mixture in gaseous phase was used. Thus the enormous apparent difference between *G*-values of glycine in gaseous phase and that in solid phase, when carbon monoxide was used as a carbon source, was mainly caused by escape of carbon monoxide from the irradiation area of the solid mixture.

5. Analysis of Amino Acids Formed by Electron Irradiation of a Mixture of Methanol, Ammonia, and Water. When the gas mixtures of methanol, ammonia, and water were irradiated with 35 MeV protons, protons passed through the mixtures in the glass tube, but when the liquid or ice mixtures were irradiated, protons stopped in the mixtures. In the latter case, a saturation effect should be considered: There might have been deficiency of starting materials around the paths of protons caused, since the linear energy transfer (LET) of protons in condensed matter is quite large. In order to compensate the saturation effect, we performed irradiation experiments using electrons as energy sources: LET of electrons are much less than that of protons. The mixtures of methanol, ammonia, and water in solid, liquid, and gaseous phases were irradiated with 15 MeV electrons, which passed through the sample mixtures in all of the three phases.

Figure 7 shows *G*-values of glycine from the mixtures of methanol, ammonia, and water by proton and electron radiation. In the cases of either proton irradiation or electron irradiation, *G*-values of glycine were almost equal. So the differences in *G*-values of glycine between three phases are not caused by the saturation effect. These results suggest that δ-ray was effective for the formation of amino acid precursors in proton irradiation. In both proton irradiation and electron irradiation, *G*-values of glycine in liquid phase irradiation were the smallest among the three phases.

Conclusion

In proton or electron irradiation experiments, amino acid precursors were formed from mixtures of simple compounds using kinetic energy of particles, but the products might be decomposed by the energy at the same time. When the gas mixtures were irradiated, the condensable products such as amino acid precursors diffused rapidly to the wall of the reaction cell and were trapped there and were protected against destruction by further irradiation. On the other hand, when the liquid or ice mixture was irradiated, products diffused more slowly. Thus irradiation products in the liquid or ice mixtures are apt to be decomposed more easily than those in gas mixtures.

Judging from these results, it seems that the differences in *G*-values of glycine are only two orders of magnitude between the gas mixtures and the ice mixtures when the starting materials with the same composition were used. When carbon monoxide was used as carbon source, however, the *G*-value of glycine in the ice mixture was ca. 1/10000 less than that in the gas mixture. It was mainly due to sublimation of carbon monoxide from the ice mixture during irradiation.

When methanol was used as a carbon source in the solid

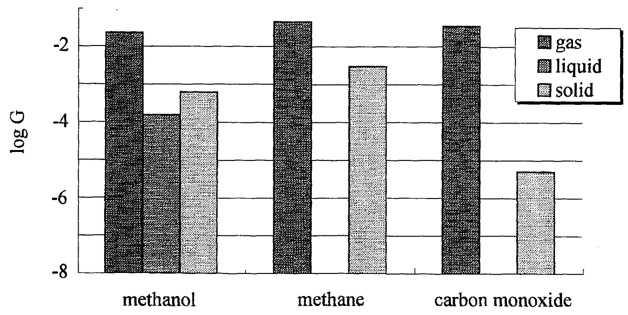

Fig. 6. *G*-values of glycine when mixtures (in gas, liquid, or solid state) of a carbon compound (methanol, irradiated with high energy protons. Mole ratio of methane (or carbon monoxide), ammonia, and water was 1 : 1 : 1, and that of methanol, ammonia, and water was 0.47 : 0.35 : 1.

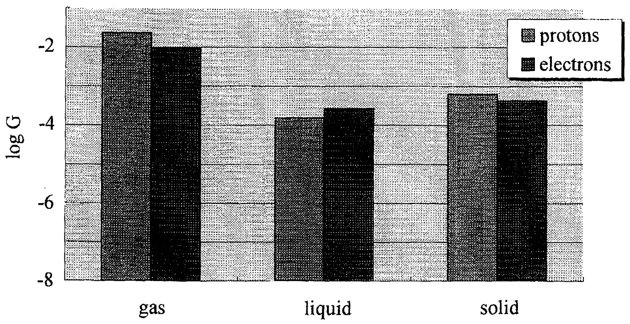

Fig. 7. *G*-values of glycine from a mixture of methanol, ammonia, and water by irradiation with protons or electrons. Mole ratio of methanol, ammonia, and water was 0.47 : 0.35 : 1.

phase irradiation experiments, there was no problem about sublimation from the mixture during irradiation. That was the reason the G-value when methanol was used in solid phase was ca. 10^{-4}, which was two orders less than that in gaseous phase. If the ice mixture of carbon monoxide, ammonia, and water can be made in exact mixing ratio throughout the irradiation, the G-values of glycine in solid phase are expected to be ca. 10^{-4}, which is also two orders less than that in gaseous phase.

Bioorganic compounds such as amino acid precursors are formed by cosmic radiation. The amounts of organic compounds synthesized by radiation are not negligible. It is possible that organic compounds formed in ISD ices were accumulated in comets when the solar system was born, and that they were delivered to primitive earth by comets or their fragments (interplanetary dusts or micrometeorites).[16,17] They are alternative sources of organic compounds for the first biosphere on the earth, other than endogenous organic compounds formed in the primitive earth. It is also possible that these exogenous organic compounds were supplied to other planets such as Mars.

The authors wish to express their thanks to Mr. K. Kawasaki, Tokyo Institute of Technology, and the staff of the SF cyclotron and the Electron synchrotron, INS, the University of Tokyo, for their kind assistance in the operation of the accelerators. The present work was supported in part by Grant-In-Aid No. 07640653 from the Ministry of Education, Science, Sports and Culture.

References

1) D. S. McKay, E. K. Gibson, Jr., K. L. Thomas-Keprta, H. Vali, C. S. Romanek, S. J. Clemett, X. D. F. Chillier, C. R. Maechling, and R. N. Zare, *Science*, **273**, 924 (1996).

2) S. L. Miller, *Science*, **117**, 528 (1953).

3) C. Sagan and B. N. Khare, *Science*, **173**, 417 (1971).

4) K. Harada and S. W. Fox, *Nature*, **201**, 355 (1964).

5) A. Bar-Nun, N. Bar-Nun, S. H. Bauer, and C. Sagan, *Science*, **168**, 470 (1970).

6) Y. Abe, *Planetary People*, **1**, 111 (1992).

7) G. Schlesinger and S. L. Miller, *J. Mol. Evol.*, **19**, 376 (1983).

8) A. Bar-Nun and S. Chang, *J. Geophys. Res.*, **88**, 6662 (1983).

9) K. Kobayashi, M. Tsuchiya, T. Oshima, and H. Yanagawa, *Origins Life Evol. Biosphere*, **20**, 99 (1990).

10) K. Kobayashi, T. Kaneko, M. Tsuchiya, T. Saito, T. Yamamoto, J. Koike, and T. Oshima, *Adv. Space Res.*, **15**, 127 (1995).

11) M. H. Moore, B. Donn, R. Khanna, and M. F. A'Hearn, *Icarus*, **54**, 388 (1983).

12) L. J. Allamandola, S. A. Sandford, and G. J. Valero, *Icarus*, **76**, 225 (1988).

13) R. Briggs, G. Ertem, J. P. Ferris, J. M. Greenberg, P. J. McCain, C. X. Mendoza-Gómez, and W. Schutte, *Origins Life Evol. Biosphere*, **22**, 287 (1992).

14) T. Yamamoto, "Suisei -Sono Honsho to Kigen-," ed by K. Sakurai and M. Shimizu, Asakura Shoten, Tokyo (1989), pp. 52—77.

15) G. Strazzulla and R. E. Johnson, "Comets in the Post-Halley Era," ed by R. L. Newburn, Jr., et al., Kluwer Academic, Dordrecht (1991), Vol. 1, pp. 243—275.

16) J. M. Greenberg, et al., "The Chemistry of Life's Origins,"ed by G. M. Greenberg, et al., Kluwer Academic Publishers, Netherlands (1993), pp. 1—32.

17) A. Kouchi, *Planetary People* (*J. Jpn. Soc. Planetary Sci.*), **3**, 94 (1994).

18) M. Oda, J. Nishimura, and K. Sakurai, "Uchusen Butsurigaku," Asakura Shoten, Tokyo (1983), p. 24.

19) K. Kobayashi, T. Kaneko, T. Kobayashi, H. Li, M. Tsuchiya, T. Saito, and T. Oshima, *Anal. Sci.*, **7** (Suppl.), 921 (1991).

20) K. Kobayashi, T. Kasamatsu, T. Kaneko, J. Koike, T. Oshima, T. Saito, T. Yamamoto, and H. Yanagawa, *Adv. Space Res.*, **16**, 21 (1995).

21) Chemical Society of Japan, "Kagaku Binran Kisohen," 3 rd ed, Maruzen, Tokyo (1993), Vol. 2, p. 117.

22) K. Hiraoka, N. Ohashi, Y. Kihara, K. Yamamoto, T. Sato, and A. Yamashita, *Chem. Phys. Lett.*, **229**, 408 (1994).

23) T. Tsuji and K. Kobayashi, *Origins Life Evol. Biosphere*, **26**, 347 (1996).