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Stability of Aspartic Acid at 77°K under Gamma Radiation in a Comet Cores Simulation: Implications for Chemical Evolution Studies

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Abstract The synthesis of organic matter in a simulated primitive environment (terrestrial or extraterrestrial) has been widely studied. The stability of organic matter of biological significance, exposed to energy fields in primitive conditions, is equally important in the context of chemical evolution. We present a detailed analysis of the stability of prebiotic organic molecules under the effect of ionizing radiation at a low temperature, simulating a comet core. The laboratory simulation consists of icy phases of prototype organic matter and a mineral in a physical mixture. This chemical system was irradiated with gamma radiation at 77°K. The icy phases are methanol, formic acid, and aspartic acid in aqueous solution, in the presence of sodium montmorillonite as silicates surface.Our results show the stability of aspartic acid in this comet core simulation. We have been identified some radiolytic products of this mixture: ethylene glycol, glycolaldehyde, formamide, alanine, glycine and succinic acid. The products were identified by Gas Chromatography (GC) and High Performance Liquid Chromatography-Electrospray Ionization-Mass Spectrometry (HPLC-ESI-MS). The protection role of the clay in the radiolysis of aspartic acid was observed in this mixture. This result may be due to an energy transfer from the clay. At pH=4, aspartic acid is adsorbed onto the clay at the interlayer channel as is shown in the X-ray diffractograms (XRD).

Keywords: comets, chemical evolution, aspartic acid, clay minerals, gamma radiation

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1. INTRODUCTION

Chemical evolution of organic matter is a part of an integral evolution of the planet and the universe. Thus, the chemistry involved on the prebiotic Earth must have been constrained by global physical chemistry of the planet [12]. Studies of chemical evolution intend to explain the abiotic formation of organic compounds of biological relevance and the possible mechanisms that increased the biological compounds complexity. For those studies, we have to consider primitive environments, energy sources, abiotic synthesis of organic matter from simpler compounds, and stability and preservation of organic matter.

There are many places that have been proposed for the processes of prebiotic importance, terrestrial environments (hydrothermal vents, geysers, etc.) [3], and extraterrestrial environments (comets, meteorites, and asteroids) [14].

Comets are formed mainly by ices (H_2O, CO, CH_3OH, CO_2, CH_2O_2, etc.), silicates, and organic matter [5]. It is proposed that these bodies could have brought water and organic material to the primitive Earth. This contribution might have been fundamental in chemical evolution [7]. These bodies are always exposed to radiation from hundreds of KeV and TeV. Ionizing radiation can be very efficient in promoting changes, even in the cores of these bodies. The chemical action of ionizing radiation consists essentially of producing chemically reactive species (free radicals, radical-ions) [2]. An example of ionizing radiation is gamma rays. This energy may have been of great importance to induce chemical reactions, due to its high penetrating power, high efficiency for the synthesis of organic compounds, and its abundance. Some properties like the energy deposition are very close to some protons in cosmic rays, which facilitate the study of molecules exposed to a high radiation field [4].

In 2009, was announced by [6] that scientists had identified one of the fundamental chemical building blocks of life in a comet for the first time: glycine. Amino acids are essential molecular components of living organisms on Earth, but the proposed mechanisms for their spontaneous generation have been unable to account for their presence in Earth's early history [1]. The delivery of extraterrestrial organic compounds has been proposed as an alternative to generation on Earth [11].

The aim of this work is to study the stability of prebiotic organic molecules under ionizing radiation (gamma rays of ^{60}Co) at 77°K, simulating a comet core (icy phase consisting of methanol, formic acid and aspartic acid) and sodium montmorillonite as silicates. Some of the radiolysis products of the mixture used in this study have been detected in comets and other icy bodies, except aspartic acid. Our results may suggest the interconversion of these molecules induced by radiation, forming important compounds of biological importance in a comet core or other extraterrestrial environments, even if they are at low concentrations.

2. MATERIALS AND METHODS

2.1 Glassware and chemicals

The presence of impurities in samples that are irradiated can give rise to errors. Therefore, the glassware was treated with a warm mixture of HNO_3 and H_2SO_4 for 60 minutes, followed by a rinsing with bi-distilled water and heating in an oven at 350 °C overnight. Triple distilled water was used for all aqueous solutions samples. Methanol and formic acid used were of HPLC quality. High-purity L-aspartic acid and KOH (Sigma, Co., USA) were employed in all the experiments. Na-Montmorillonite (101 meq Na^+/100 g) from the Source of Clay Minerals Repository of the Clay Mineral Society was used to anchor the amino acid.

2.2 Preparation of samples

Water solutions of L-aspartic acid ($1x10^{-4}$ $molL^{-1}$, the pH of the solutions was naturally acidic, pH=4), methanol (0.4 $molL^{-1}$), and formic acid (0.01 $molL^{-1}$)were prepared. To prepare the clays-aspartic acid system, 0.1 g of clay was mixed with 5 mL of the aspartic acid solution ($1x10^{-4}$ $molL^{-1}$) in continuous agitation on a plate at 150 rpm for 30 min. The clay was dried at 80 ^{o}C overnight and ground in an agate mortar for diffraction X-ray analysis. Water solution of hydroxide potassium (0. 1 $molL^{-1}$) was prepared to desorption process after irradiation procedure.

2.3 Irradiationprocedure

The samples were exposed to gamma irradiation with a cobalt-60 Gammabeam 651PT facility at Instituto de CienciasNucleares, UNAM, at liquid nitrogen temperature (77°K) inside a Dewar flask. Irradiation doses were from 0 to 600 kGy. The dose rate was determined to be 280 Gy/min using the ferrous ammonium sulfate-cupric sulfate dosimeter [16] at 77°K. The samples were bubbled with argon (20 minutes) to eliminate dissolved oxygen.

2.4 Radiolysis experiments

Four systems (A, B, C, and D) were performed, varying the number of components, from the simplest to the more complex mixture. After irradiation procedure, the samples were defrosted at room temperature and immediately analyzed by chromatographic and spectrometry techniques.

(A) Methanol and formic acid

Aliquots of 5 mL of methanol (0.4 $molL^{-1}$) and 5 mL formic acid (0.01 $molL^{-1}$) were placed in a glass tube inside a Dewar to were irradiated.

(B) Aspartic acid

Aliquots of 10 mL of aspartic acid $1x10^{-4}$ ($molL^{-1}$) were placed in a glass tube inside a Dewar to were irradiated.

(C) Methanol, formic acid, and aspartic acid

Aliquots of 5 mL of methanol (0.4 $molL^{-1}$), 5 mL formic acid (0.01 $molL^{-1}$), and 5 mL of aspartic acid ($1x10^{-4}$ $molL^{-1}$) were placed in a glass tube inside a Dewar to were irradiated.

(D) Methanol, formic acid, and aspartic acid-montmorillonite system

Aliquots of 5 mL of methanol (0.4 $molL^{-1}$), 5 mL formic acid (0.01 $molL^{-1}$), and 0.1 g of aspartic acid-montmorillonite system were placed in a glass tube inside a Dewar to were irradiated.The samples were defrosted at room temperature and to analyzed the stability of aspartic acid;process of desorption were carried out by adding 5 mL of KOH (0.1 $molL^{-1}$) to the solid previously separated by centrifugation (30 min at 25 000 rpm at 20 ^{o}C). The remaining of the aspartic acid was done after three cycles of treatment with KOH. After this procedure, clay was removed from liquid fraction by centrifugation and dried at 80^{o}C overnight and ground in an agate mortar for diffraction X-ray analysis.

2.5 Analysis

The analysis of volatile products was performed in a, SRI 8610C Gas Chromatograph equipped with a capillary column. The column was MXT (length 30 m). The identification of the products was based on their retention times and co-injections with standards. The temperature program was: isothermal (70^{o}C) for 1. 5 min, heating rate of 10 °C min^{-1} up to 120 ^{o}C, isothermal (120^{o}C) for 5 min, heating rate of 10 °C min^{-1} up to 210 ^{o}C, and isothermal (210 ^{o}C) for 6 min. High Performance Liquid Chromatography was performed on HPLC system (515-pump from Waters Corp.), coupled to a Single Quadrupole Mass Detection (SQ-2 manufactured by Waters Corp.), with an Electrospray Ionization Negative mode (ESI-) source. Analysis was done within 5.0 min in Symmetry C-18 column (4.6 x 75 mm, 3.5 μm spherical particle size, by Waters Corp.) under an isocratic elution of mobile phase

(50 % acetonitrile - 50 % water) at a constant flow of 0.4 mL min^{-1}.Definite sample volume (20 μL) was injected using a loop. The clay was analyzed by X-ray diffraction with a Siemens D5000 diffractometer.

3. RESULTS AND DISCUSSION

3.1 Radiolysis of methanol and formic acid

The stability of methanol is higher than formic acid under gamma irradiation at 77°K (Figure 1). The radiolysis products of this mixture wereglycolaldehyde and ethylene glycol (Figure 2). Both products have been detected in the interstellar medium. Glycolaldehyde is the simplest sugar and an important intermediate in the path toward forming more complex biologically relevant molecules such as ribose. Ethylene glycol, the reduced alcohol of glycolaldehyde, has been identified in the interstellar medium [9]. This suggests that formation of these important pre-biological molecules occurs easily at low temperatures, therefore the irradiation temperature play a role in the chemistry in comets. The possible reaction mechanisms, a product of radiation-matter interaction begins with the water radiolysis in a hydrolysis reaction to get ethylene glycol (Figure 3).

3.2 Radiolysis of aspartic acid

It is important to understand the impact of space conditions (gamma irradiation and temperature) on the organic molecules during space travel and, in particular,

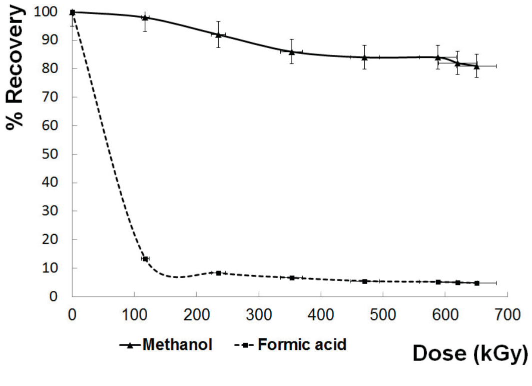

Figure 1: Gas chromatograph analysis was employed to study the mixture in aqueous solution of methanol (0.4 $molL^{-1}$) and formic acid (0.01 $molL^{-1}$) at 77°K.

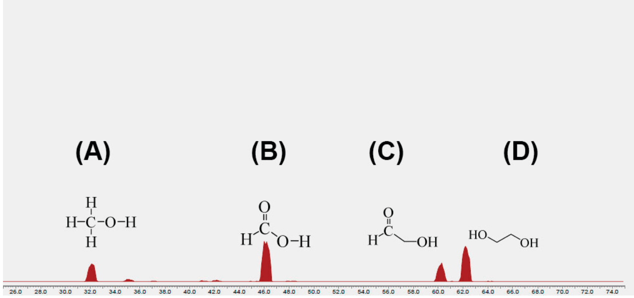

Figure 2: HPLC-ESI-MS was employed to detect radiolysis products of the methanol and formic acid. (A) Methanol (32 g/mol) and (B) Formic acid (46 g/mol) remaining, (C) Glycolaldehyde (60 g/mol), and (D) Ethylene glycol (62 g/mol).

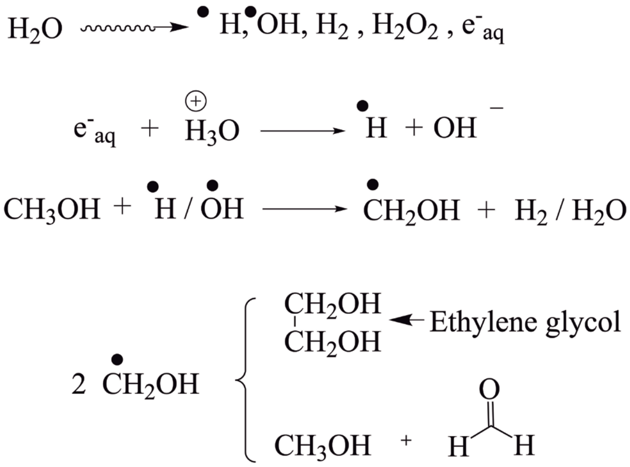

Figure 3: Suggested mechanism for the formation of ethylene glycol from methanol-formic acid radiolysis.

their role in cometary chemistry. The results of irradiation experiments at 70 kGy performed at 77°K show the stability of aspartic acid in aqueous solution (133 g/mol); also show the succinic acid (118 g/mol) as the principal radiolysis product (Figure 4A).The possible route to get it was a deamination reaction via free radicals (Figure 4B) the dominant interaction of radiation in this system is with water molecules. Succinic acid is a dicarboxylic acid, which plays a role in the Krebs cycle; this compound was detected in Tagish Lake meteorite [15].

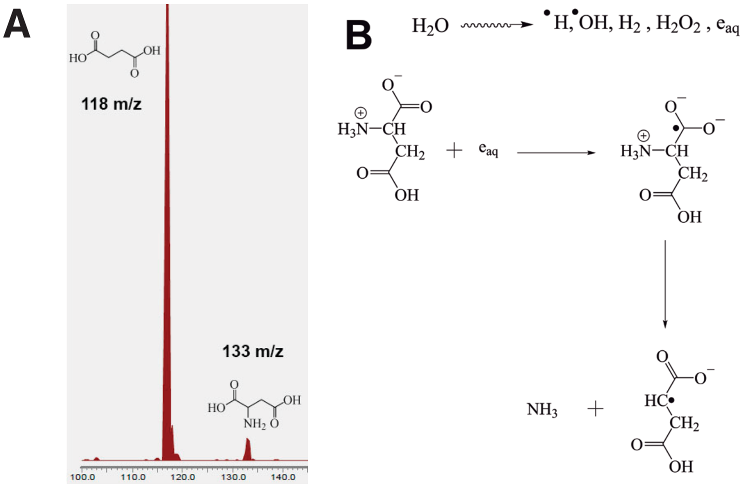

Figure 4: (A) Succinic acid (118 g/mol) and aspartic acid remaining (133 g/mol) were detected of HPLC-ESI-MS analysis, after irradiation procedure at 70 kGy and 77°K. (B) The possible mechanism of a deamination reaction via free radicals.

3.3 Radiolysis of methanol, formic acid and aspartic acid

In this system, the recovery of aspartic acid was higher than in pure aspartic acid solution (Figure 5). This behavior is due to higher reactivity of the methanol and formic acid under gamma radiation.

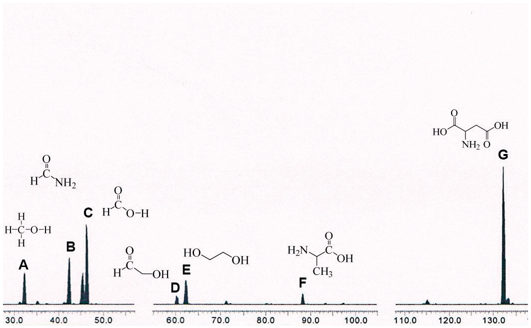

Figure 5: HPLC-MS analysis after gamma irradiation of methanol, formic acid and aspartic acid. We identified (A) Methanol (32 g/mol), (B) Formamide (45 g/mol), (C) Formic acid (46 g/mol), (D) Glycolaldehyde (60 g/mol), (E) Ethylene glycol (62 g/mol), (F) Alanine (89 g/mol), and (G) Aspartic acid (133 g/mol).

Although of aspartic acid stability to gamma radiation, it decomposes in other molecules of biological importance. We identified formamide (45 g/mol); this compound had been identified for astronomers in interstellar medium and has been proposed as a prebiotic source of nucleobases and nucleic acids [8], and alanine (89 g/mol), nevertheless this compound has not been identified in the interstellar medium.

3.4 Radiolysis methanol, formic acid, and aspartic acid-montmorillonite system

After the irradiation procedure, the minerals were removed from the liquid fraction to analyze the liquid fraction of the mixture. Aspartic acid was not identified after gamma irradiation but we identified glycine and alanine in the liquid fraction (Figure 6), this probably could be due to role of clay in the process. Montmorillonite has two different sites of binding. These sites can be either at the edges or in the interlaminar channel[13](Figure 7A).The adsorption of organic molecules on montmorillonite is strongly pH dependent. The irradiation procedure of this mixture was at pH=4to identify the place where aspartic acid bound to the clay, an X-ray diffraction

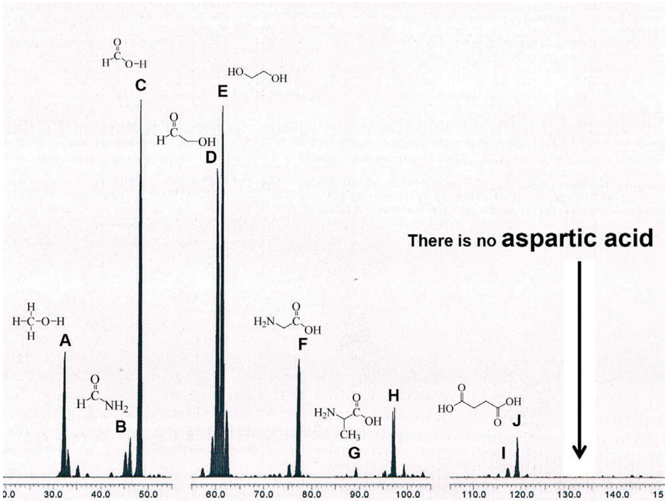

Figure 6: HPLC-MS analysis after gamma irradiation of icy phases, aspartic acid-montmorillonite of sodium system. We identified those compounds: (A) Methanol (32 g/mol), (B) Formamide (45 g/mol), (C) Formic acid (46 g/mol), (D) Glycolaldehyde (60 g/mol), (E) Ethylene glycol (62 g/mol), (F) Glycine, (G) Alanine (89 g/mol), and (H) No identified, (I) Succinic acid, and (J) No identified.

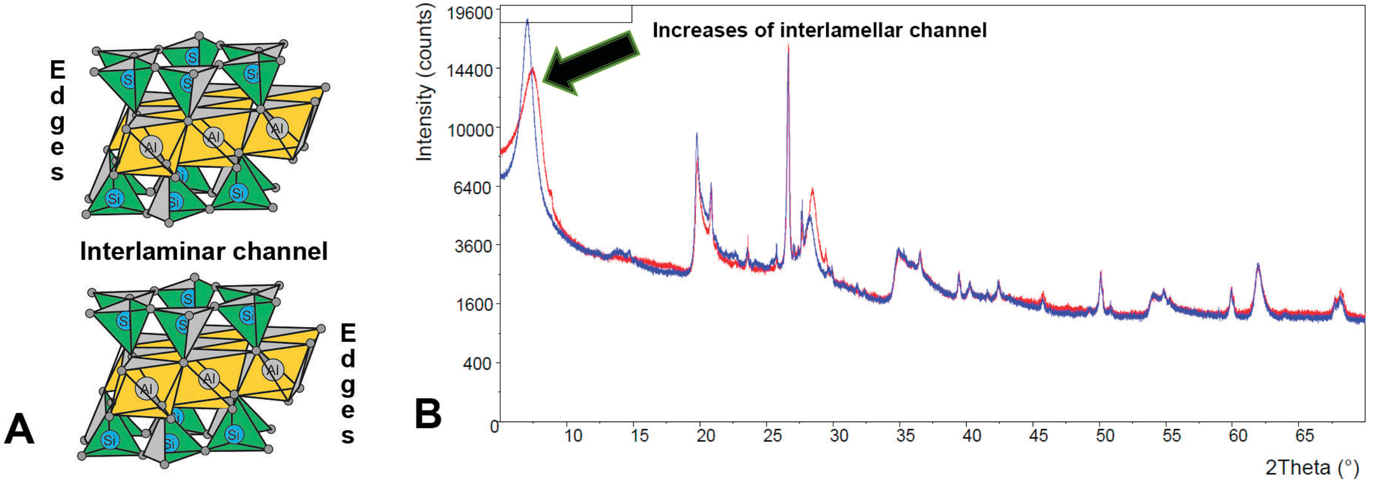

Figure 7: (A) Structure of Montmorillonite of sodium. (B) X-ray diffraction of montmorillonite before and after heterogeneous irradiation.

analysis was performed, and it showed that the adsorption is in the interlaminar channel, due to an increase of the interlaminar channel (Figure 7B). These results suggest the possible role of the solid as(a) protector agents against a source ofenergy radiation; and (b) catalystagentofchemical reactions.Therefore, the mineral surface may have played an important role in chemical evolution [10]. To know how much aspartic acid was protected on the clay we did desorption experiments, the recovery of the aspartic acid was analyzed by HPLC-ESI-MS (Figure 8). The results show when the radiolysis is made in the presence of clay that more than 70% of the aspartic acid survives.

4. REMARKS

The stability observed for the organic compound in this comet core simulation (aspartic acid) is due to higher reactivity of methanol and formic acid under gamma radiation compared to aspartic acid solutions. We identified important compounds related to chemical evolution studies: formamide, glycine, alanine, and succinic acid. Formamide and glycine have been identified for astronomers in the interstellar medium. If aspartic acid existed in extraterrestrial environments at low concentration, it may have formed other small molecules important in the evolution processes; therefore, our results allow us to propose comets as the potential vehicles of matter introduction to the early Earth system during the Heavy Late Bombardment. The role of clays in chemical evolution was a cornerstone that probably helped to shape the complex organization state we call life-not only on Earth.

5. ACKNOWLEDGEMENTS

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