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Amino acids formed from the UV/EUV irradiation of inorganic ices of astrophysical interest

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Abstract

An experiment where a H_2O:CO_2:NH_3 = 1:1:1 ice mixture was irradiated using the ultraviolet/extreme ultraviolet (UV/EUV) light provided by a synchrotron beam in the broad 4–20 eV (62–310 nm) range at 16 K is presented here. The main originalities of the present work are the composition of the starting ice mixture, since it did not contain any organic compound, in particular no methanol (CH_3OH) nor methane (CH_4) as for previous similar experiments, and the photon energy range. Several amino acids were produced: nine were identified of which seven could be quantified, and some others tentatively identified using high-performance liquid chromatography (HPLC). This result shows that it is possible to form complex organics such as amino acids from the irradiation of ice mixtures containing C-, H-, O- and N-atom bearing compounds, whatever the organic/inorganic nature of these compounds. Only the distribution of the formed amino acids is different from previous experiments. This discrepancy may be due to the starting mixture composition and/or the different energy range used for the irradiation. These two parameters are discussed in regard of their implications for the formation of amino acids in the laboratory and in astrophysical environments.

Keywords: Molecular processes; Methods: data analysis; ISM: molecules

1. Introduction

Over the last 30 years, many experiments where ices of astrophysical interest were irradiated by a H_2-flow discharge lamp providing mainly Lyman-α (121.6 nm, 10.25 eV) and 160 nm (7.75 eV) photons at low temperature (10–80 K) were performed (Hagen et al., 1979; Agarwal et al., 1985; Briggs et al., 1992; Bernstein et al., 1995; Muñoz Caro and Schutte, 2003). They led to the production of a refractory, organic residue after warming the samples up to room temperature. In the last 5 years, the chemical composition of these residues could be revealed thanks to the significant improvement of the chemical analytical techniques. Many complex organic molecules were found, among which amino acids (Muñoz Caro et al., 2002; Bernstein et al., 2002; Nuevo et al., 2006, 2007), the building blocks of proteins for all living organisms on Earth.

Many amino acids were previously detected in meteorites (Kvenvolden et al., 1971; Engel and Macko, 1997; Cronin and Pizzarello, 1997, 1999). These organic compounds are generally believed to be delivered by meteorites and other small Solar System bodies (comets, interplanetary dust particles – IDPs), and their origin is a key point to

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understand how life emerged on the primitive Earth 3.8 billion years ago (Oró, 1961). However, the link between the organic matter found in meteorites and, on the one hand, observations of organics in the interstellar medium (ISM) and, on the other hand, the results obtained in laboratory simulations of ice irradiations has yet not been clearly established.

In the present work, we clearly identify nine amino acids and tentatively identify some others after irradiation of a fully inorganic starting ice mixture H_2O:CO_2:NH_3 = 1:1:1 with a synchrotron beamline in the broad 4–20 eV (62–310 nm) energy range, from ultraviolet to extreme ultraviolet (UV/EUV). The main discrepancy between the amino acids found in this work and those detected in previous experiments of ice irradiations is their distribution, which is discussed in the general context of the formation of amino acids in laboratory simulations and in astrophysical environments.

2. Experimental

2.1. UV irradiation at low temperature

The experiment was carried out in an ultra-high vacuum chamber (vacuum pressure: $P \sim 10^{-10}$ torr) cooled down to 16 K by a helium closed cycle cryostat. A gas mixture was deposited onto a cold substrate (KBr window) fixed to the cryostat. The temperature of the substrate inside the chamber was controlled within a ±0.5 K accuracy between 16 and 300 K.

The gas handling system is equipped with stainless steel bottles and a Baratron MKS 122 A gauge to control the pressure. Before preparing the gas mixture and cooling the chamber down to 16 K, the system was baked up to 400 K for 12 h, and then cooled back down to room temperature. Three different bottles were used for holding the individual gases: H_2O (triply distilled) vapor, CO_2 (Sigma–Aldrich, 99.999% purity) and NH_3 (Sigma–Aldrich, 99.5% purity). The gases were transferred in a fourth bottle to be mixed, where they remained for 5 min before being injected into the cold vacuum chamber for deposition. The composition of the gas mixture and the relative proportions between its components were controlled by their partial pressures in the mixing bottle.

The gas mixture was then deposited at 16 K onto the KBr window from a small capillary tube. The composition of the deposited ices were monitored by a Fourier-transform infrared (FTIR) spectrometer (Perkin-Elmer FTIR-1600) with a 4 cm^{-1} resolution, the signal being averaged over 12 scans. The mixture irradiated in this work had a H_2O:CO_2:NH_3 = 1:1:1 composition. The ice film thickness after deposition was about 2–5 μm. When the system reached equilibrium, i.e. reached a pressure of a few 10^{-10} torr, the ice film was irradiated with UV/EUV photons until a total integrated photon dose of about 2×10^{20} photons, corresponding to an irradiation time of ~5 h.

The UV/EUV light was provided by a synchrotron beamline at the NSRRC (National Synchrotron Radiation Research Center) in Hsinchu, Taiwan, where the incident photon flux was monitored by an in-line gold mesh (~90% optical transmission, mesh current: ~4 μA), calibrated with a standard photodiode (International Radiation Detectors, Inc.). The photon beam was focused on the sample, with a 2×6 mm^2 size at the sample location. The incident photon energy used for our irradiation was in the 4–20 eV range, with an average energy of about 6.07 eV (204 nm) and a photon flux of about 1.2×10^{16} photons cm^{-2} s^{-1}, i.e. about 1.4×10^{15} photons s^{-1} on the KBr window.

After irradiation, the sample was slowly warmed up to room temperature at about 5 K min^{-1}. During the warming up, infrared spectra were recorded every 10 K between 40 and 300 K. The system was then cooled down again to 16 K, to deposit a new ice film to be irradiated for 5 h, and warmed up again to room temperature after irradiation, and so on for a total of 6 times.

Mathis et al. (1983) estimated the photon flux in the diffuse ISM to be:

$$F_{\text{diffuse ISM}}\ (\text{UV}) = 8 \times 10^7 \text{ photons cm}^{-2}\ \text{s}^{-1}, \quad \text{for } E_{\text{photons}} \geqslant 6 \text{ eV}, \tag{1}$$

the flux for the dense medium being estimated to be about 3 orders of magnitude smaller. Therefore, in terms of dose each second of irradiation in our experiment may correspond to about 5 years of irradiation in the diffuse ISM, for $E_{\text{photons}} \geqslant 6$ eV. The total duration of irradiation (about 30 h) may thus correspond to about 5.4×10^5 years in the diffuse medium, i.e. a little bit more than half a million years, and to about 5×10^8 years in the dense medium. These timescales might however be overestimated because of the contribution of EUV photons, which are more efficient than UV photons for the photo-degradation of organics.

2.2. Chemical analysis at room temperature

The KBr window covered with the sample was removed from the system and washed with 1 mL of distilled water. The extracted solution and an equivalent volume of 12 M HCl (Merck) were pipetted and transferred into a glass vial. The vial and the tips of the micropipette were pre-treated with HPLC-grade *n*-hexane (Merck), in order to remove organics which could remain on the vessel walls. The vial was then sealed for hydrolysis, performed at 110 °C for 24 h. After hydrolysis, 25 μL of the solution was buffered at pH 10.2 in equivalent volume of a 0.4 M borate solution in water (Agilent PN 5061-3339), kept refrigerated at 4 °C, before being derivatized with OPA (*o*-phthalaldehyde, Agilent PN 5061-3335) with 1 μL ali-

quots of the OPA reagent in a conical vial, capped immediately and refrigerated at 4 °C.

Then 20 μL of the solution were injected into an Agilent 1100 Series high-performance liquid chromatography (HPLC) device, equipped with an Agilent Zorbax Eclipse-AAA column (length: 150 mm; outer and inner diameters: 4.6 mm and 3.5 μm, respectively). The mobile phase was divided into two fractions: (A) a solution of 40 mM Na_2HPO_4 (5.5 g Na_2HPO_4 monohydrate into 1 L water, adjusted to pH 7.8 with a 10 M NaOH solution) – and (B) an acetonitrile (ACN), methanol (MeOH) and water mixture, with relatives proportions ACN:MeOH:H_2O = 45:45:10 (in volumes).

The compounds were detected by fluorescence of their OPA derivatives at 450 nm (excitation wavelength: $\lambda_{ex} = 250$ nm) and identified by comparison with a standard sample of 18 proteinaceous amino acids (Agilent PN 5061-3330), which is a solution of amino acids dissolved (1 nmol μL^{-1}) into 0.1 M HCl stored in 1 mL vials. Each injection of 20 μL into the HPLC system contains about 2.86 nmol of each amino acid. A list of the amino acids and the chromatogram of the standard sample are given in Table 1 and Fig. 1 (trace b), respectively.

3. Results and discussion

3.1. Identification of amino acids

The UV/EUV irradiation of the H_2O:CO_2:NH_3 = 1:1:1 ice mixture with 4–20 eV photons led, after warming the sample up to room temperature under dynamic vacuum and chemical analysis (see Section 2.2), to the production of an organic residue containing several amino acids. Fig. 1 shows the chromatograms of the residue (trace a) and the standard (trace b), allowing a direct identification of the proteinaceous amino acids present in the residue.

We searched for amino acids among the proteinaceous standard compounds (see Section 2.2), except cystine (Cys) and methionine (Met) since they contain sulphur and our ice mixture did not contain any sulphur-bearing component (see Table 1). Two steps are important in this chemical protocol:

- *Acid hydrolysis.* This step has mainly two effects on the chemistry of the compounds. The first one is to break chemical bonds, in particular peptidic (amide) bonds from peptides (small amino acid polymers) and proteins. The second one is to oxidize some specific reduced chemical functions into carboxylic acid and amino groups.
- *Derivatization.* When derivatized, free amino acids (released after hydrolysis) are chemically modified for a better separation in the chromatography column and an identification by fluorescence of their OPA derivatives (see Section 2.2).

It is thus important to notice that in laboratory irradiation experiments the amino acids detected in organic residues are obtained after chemical treatment, and not directly after photolysis of the starting ice mixtures. However, in order to search for amino acids in meteorites such as the Murchison and Murray carbonaceous chondrites (Engel and Macko, 1997; Cronin and Pizzarello, 1997, 1999), a specific extraction of the organic phase and a chemical treatment similar to the one presented here have also to be performed, so that the results obtained in laboratory simulations and after analyses of extraterrestrial material are comparable.

Nine amino acids could be clearly identified in our residue and six others tentatively detected. They are listed in the upper and lower parts of Table 2, respectively. The 9 amino acids were identified by direct comparison with the standard sample (see Table 1 and Fig. 1, trace b). We could estimate the concentrations, and thus the quantities and masses for at least seven of them (Cols. 3 and 4 of Table 2, respectively). The reported quantities and masses are extrapolated for the whole sample, taking all the dilutions of the chemical protocol into account (Section 2.2). For both the standard and the residue samples, the peaks for every amino acid were integrated, most of the time after a deconvolution using gaussian functions when peaks were overlapping. Many peaks could not be identified in the chromatogram of the residue, due to the lack of standard for non-proteinaceous amino acids and other compounds.

The 9 identified amino acids are mainly small compounds, with aliphatic lateral carbon chains. Glycine (Gly) is the simplest amino acid (only 2 carbon atoms), then comes alanine and serine (3 carbon atoms). Their quantities were found to be small, from 1.2 (isoleucine, Ile) to

Table 1
List of the 18 amino acids contained in the standard sample, whose chromatogram is shown in Fig. 1 (trace b), with their chemical formula and molecular weight

Amino acid	Chemical formula	Molecular weight (g mol^{-1})
Aspartic acid (Asp)	$C_4H_7NO_4$	133.10
Glutamic acid (Glu)	$C_5H_9NO_4$	147.13
Asparagine (Asn)	$C_4H_8N_2O_3$	132.12
Serine (Ser)	$C_3H_7NO_3$	105.09
Glutamine (Gln)	$C_5H_{10}N_2O_3$	146.15
Histidine (His)	$C_6H_9N_3O_2$	155.16
Glycine (Gly)	$C_2H_5NO_2$	75.07
Threonine (Thr)	$C_4H_9NO_3$	119.12
Arginine (Arg)	$C_6H_{14}N_4O_2$	174.20
Alanine (Ala)	$C_3H_7NO_2$	89.09
Tyrosine (Tyr)	$C_9H_{11}NO_3$	181.19
Cystine[a] (Cys)	$C_3H_7NO_2S$	121.16
Valine (Val)	$C_5H_{11}NO_2$	117.15
Methionine[a] (Met)	$C_5H_{11}NO_2S$	149.21
Phenylalanine (Phe)	$C_9H_{11}NO_2$	165.19
Isoleucine (Ile)	$C_6H_{13}NO_2$	131.17
Leucine (Leu)	$C_6H_{13}NO_2$	131.17
Lysine (Lys)	$C_6H_{14}N_2O_2$	146.19

[a] Cystine and methionine were not detected in our sample since they are sulphur-bearing amino acids.

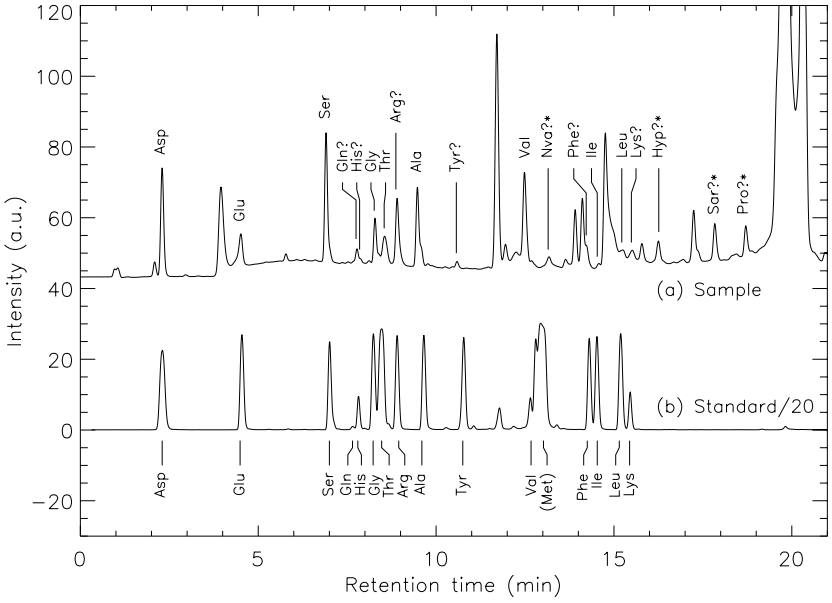

Fig. 1. Chromatograms of (a) the residue (offset for clarity) and (b) the standard (divided by a factor 20 for clarity) samples. Nine proteinaceous amino acids could be identified (see upper part of Table 2). Other amino acids, tentatively detected, are followed by a question mark (?). The four extra tentatively detected amino acids followed by a star (*) were identified from an extrapolation of the standard chromatogram provided in the HPLC device manual.

Table 2
List of the identified and tentatively detected amino acids (see Section 3.1 for details on the identifications of some of these amino acids)

	R_t (min)	Quantity (nmol)	Mass (μg)
Identified amino acids			
Aspartic acid (Asp)	2.30	34.1	4.5
Glutamic acid (Glu)	4.51	11.7	1.7
Serine (Ser)	6.90	56.7	6.0
Glycine (Gly)	8.28	15.5	1.2
Threonine (Thr)	8.55	3.8	0.5
Alanine (Ala)	9.48	28.6	2.5
Valine (Val)	12.49	15.0	1.8
Isoleucine[a] (Ile)	14.57	1.2	0.2?
Leucine[a] (Leu)	15.22	9.7	1.3?
Tentatively detected amino acids			
Glutamine[b] (Gln)	7.69	25.5	3.7?
Histidine[b] (His)	7.86	7.9	1.2?
Arginine[b] (Arg)	8.90	24.0	4.2?
Tyrosine[b] (Tyr)	10.59	2.9	0.5?
Phenylalanine[b] (Phe)	14.23	11.5	1.9?
Lysine[b] (Lys)	15.52	12.9	1.9?

The quantities and masses are extrapolated for the whole sample.

[a] Other compounds certainly coelute with the same retention times as isoleucine and leucine, contributing to their peak areas.

[b] These molecules are in fact probably other simpler compounds eluting with the same retention times.

56.7 nmol (serine, Ser) (1 nmol = 10^{-9} mol), showing the high sensitivity of HPLC. Surprisingly, serine was found to be the most abundant identified amino acid in this residue (Table 2). The second most abundant amino acid is aspartic acid (34.1 nmol), followed by alanine (28.6 nmol). Glycine is only the fourth most abundant compound (15.5 nmol).

The abundances of isoleucine (Ile) and leucine (Leu) may be overestimated, because of the presence of other unidentified compounds eluting from the chromatographic column with the same retention times as these amino acids (phenomenon of *coelution*). Their presence in our residue is however probable since they have an intermediate molecular weight.

The results of the present work are thus different from the amino acid distribution observed for previous experiments where glycine was the most abundant amino acid detected, the abundances of the other amino acids decreasing with their molecular weight/carbon chain length (Muñoz Caro et al., 2002; Nuevo et al., 2006, 2007).

Six other amino acids (bottom part of Table 2), namely glutamine (Gln), histidine (His), arginine (Arg), tyrosine (Tyr), phenylalanine (Phe) and lysine (Lys), were only tentatively identified. Our doubts about their identification come mainly from the fact that these amino acids are big compounds, with molecular weights higher than 145 g mol^{-1}, some of them containing a phenyl cycle (Tyr, Phe) or a heterocycle with nitrogen atoms (His), and are therefore not expected to be formed with such high quantities. The molecules identified in our residue for these peaks are thus certainly smaller molecules coeluting with these amino acids, which may however contribute for a small part to the peak areas. One of these coeluants may be ethanolamine, an organic compound whose simple molecular structure contains a primary amino group NH_2 which can also be derivatized by OPA, and which was already identified by Bernstein et al. (2002) in an organic residue analysed with HPLC.

Finally, proline (Pro, $C_5H_9NO_2$, $R_t = 18.71$ min), the only secondary proteinaceous amino acid, and three other non-proteinaceous amino acid, namely norvaline (Nva, $C_5H_{11}NO_2$, $R_t = 13.18$ min), hydroxyproline (Hyp, $C_5H_9NO_3$, $R_t = 16.25$ min) and sarcosine (Sar, $C_3H_7NO_2$,

$R_t = 17.83$ min) may also be present in our residue. Norvaline and sarcosine are isomers of valine and alanine, respectively, and hydroxyproline is a proline molecule where one the hydrogen atoms of the heterocycle was substituted by a hydroxy (OH) group. Proline and sarcosine were already identified in other organic residues (Muñoz Caro et al., 2002; Nuevo et al., 2007), supporting their probable presence in our residue. However, we did not possess the standards for these four compounds, and those tentative identifications were only made by comparison with a standard chromatogram provided by the HPLC device manual and an extrapolation of the retention times to our standard sample.

3.2. Amino acid distribution

The discrepancy observed for the amino acid distribution compared with previous experiments (Muñoz Caro et al., 2002; Nuevo et al., 2006, 2007) may be due to the different composition of the starting ice mixtures irradiated, since previous experiments contained at least one organic compound as a source of carbon, in general methanol or methane. In such a case, the photo-produced organic molecules and their complexity may grow directly from the photolysis of methanol and methane and their carbonaceous skeleton. The observed depletion of glycine, the simplest amino acid, could be a consequence of the use of CO_2 as the unique source of carbon instead of CH_3OH and CH_4.

Indeed, the (photo-) chemical mechanisms leading to the formation of complex organic molecules, in particular amino acids, when irradiating organic vs. inorganic ice mixtures are certainly different. When using methanol and/or methane, glycine may be (one of) the first amino acid(s) formed, other amino acids being formed from glycine or its close derivatives: alanine can be obtained by substituting one α-hydrogen atom by a methyl (CH_3) group, produced from the direct photolysis of CH_3OH or CH_4, and serine by a hydroxymethyl (CH_2OH) group, produced from the (photo-) dehydrogenation of CH_3OH, etc.

In our case, the mixture did not contain methanol or methane, so the carbon chains grew from the photolysis of CO_2 only. In this scenario, glycine could be a secondary product formed from the (photo-) degradation of more complex molecules first formed, in particular the degradation of more complex amino acids. This could for example explain the high abundance of serine over that of alanine in our residue, since the side chain of serine ($-CH_2OH$) is more oxidized than the fully reduced methyl group ($-CH_3$) of alanine. Therefore, serine should be formed in fewer steps than alanine from the reduction of CO_2. Another consequence of the formation of such compounds from the direct photolysis of CO_2 is that the carboxylic (COOH) groups of the amino acids detected in our sample probably come from the addition of a COOH radical, readily formed from the reaction between a photo-excited CO_2 molecule and a H atom (Woon, 2002), rather than from a Strecker-like hydrolysis of a nitrile (C≡N) group.

Another experimental parameter that could have an important effect on the distribution of the amino acids in our work, compared with previous experiments, is the photon energy range used for the irradiation. Indeed, the typical range for the photochemistry of organic molecules is considered to be about 5–10 eV. The presence of higher energy photons ($E > 10$ eV) may have competing effects: they can break more efficiently the starting compounds (in particular CO_2) to accelerate the formation of more complex molecules, but they can at the same time destroy the freshly formed molecules by breaking them into smaller compounds.

EUV photons may also excite and ionize molecules in electronic states that are different (higher) than usual UV photons (Wu et al., 2002), resulting in the production of new molecules via photochemical pathways that are not accessible when using 5–10 eV photons. Energetic ($E > 10$ eV) photons can also provide an energy excess that can be transferred to the photo-dissociated molecules as kinetic energy, dissipated by collision between molecules in the medium. These collisions can favor chemical reaction in the cold (16 K) ice matrix, where the mobility of the molecules is limited, or again destroy the big molecules freshly formed into smaller ones. The equilibrium between formation and destruction processes induced by pure photochemistry and/or photon-induced collisions between molecules in our irradiation experiment is thus probably different from previous studies (Bernstein et al., 2002; Muñoz Caro et al., 2002; Nuevo et al., 2006, 2007) because of the presence of these $E > 10$ eV photons. This could also be an explanation to the different distribution of amino acids observed in our residue.

However, the broad 4–20 eV energy range and its effect on the photochemistry of complex molecules is interesting since several astrophysical environments such as solar-type and extreme helium stars are known to emit a UV/EUV continuum as well as atomic and ionic lines in the UV/EUV range (Judge and Pietarila, 2004; Peter et al., 2006; Pandey et al., 2006). EUV emission lines emitted by comets have also been observed and modelled (Krasnopolsky et al., 2004). These emission lines are due to heavy ions brought to the comets by the solar wind. The nature and distribution of photo-produced complex organic molecules, in particular amino acids, depend therefore certainly strongly on the photon energy range, which can be different from one astrophysical environment to another.

4. Conclusion

We could identified several amino acids in the organic residue formed by the irradiation of a totally inorganic starting ice mixtures with 4–20 eV (62–310 nm) photons. We show that the variety and distribution of such amino acids in organic residues depend on the organic/inorganic nature of the carbon source(s) in the starting material, and/or on the energy range of the photons. In all cases,

these results show that amino acids are always formed after the photolysis and subsequent warming up to room temperature of ice mixtures containing C, H, O and N atoms. From an astrophysical point of view, this means that photo-produced complex organic molecules may be formed in organic-poor astrophysical environments, and that their nature and distribution may change in different environments.

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