Mon. Not. R. Astron. Soc. **384,** 605–610 (2008) doi:10.1111/j.1365-2966.2007.12687.x

Amino acids produced from the ultraviolet/extreme-ultraviolet irradiation of naphthalene in a H_2O+NH_3 ice mixture

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Accepted 2007 November 5. Received 2007 November 1; in original form 2007 June 30

ABSTRACT

In this work, we show that the irradiation of naphthalene ($C_{10}H_8$), the smallest polycyclic aromatic hydrocarbon (PAH), mixed in a H_2O+NH_3 ice mixture with 4–20 eV (62–310 nm, i.e. in the ultraviolet/extreme-ultraviolet ranges) photons at 15 K leads to the formation of an organic residue where many amino acids were identified. However, the distribution of these amino acids is different from what was reported in previous laboratory experiments where ice mixtures containing other sources of carbon (CO, CO_2, CH_4 and CH_3OH) were irradiated with ultraviolet photons, indicating that amino acids can be formed via several mechanisms. This result also implies that naphthalene, and probably other PAHs, constitute a non-negligible source of interstellar carbon likely to form organic molecules after photolysis, supporting a scenario where molecules of biological interest could be formed in many different astrophysical environments before being delivered to the early Earth by meteorites.

Key words: astrochemistry – molecular processes – methods: laboratory – ISM: molecules.

1 INTRODUCTION

Observations of the interstellar medium (ISM) in the infrared (IR) range have revealed the varied and complex chemical composition of the interstellar solid matter, consisting of silicate and carbonaceous cold grains on top of which species such as H_2O, CO, CO_2, CH_3OH and NH_3 are condensed (Dartois et al. 2002; Gibb et al. 2004; and references therein).

On the other hand, laboratory simulations showed that ultraviolet (UV) irradiation of interstellar ice analogues at low temperature containing CO, CO_2, CH_4 and/or CH_3OH as carbon sources mixed with H_2O and NH_3, leads to the formation of complex organic molecules (Agarwal et al. 1985; Briggs et al. 1992; Bernstein et al. 1995; Muñoz Caro & Schutte 2003) including amino acids (Bernstein et al. 2002; Muñoz Caro et al. 2002; Nuevo et al. 2006, 2007).

Amino acids are the building blocks used by terrestrial living organisms to synthesize proteins. However, their origin and to a larger extent the origin of the biomolecules that triggered the apparition of life on the primitive Earth remain unknown. Amino acids were identified in meteorites (Kvenvolden et al. 1970; Cronin & Pizzarello 1997, 1999; Engel & Macko 1997), favouring an extraterrestrial origin for such organic molecules and their subsequent delivery to the Earth via meteorites (Oró 1961; Brack 1999).

At the same time, the discovery of a series of diffuse interstellar bands (DIBs) in the UV, visible and IR ranges (Russell, Soifer & Willner 1977; Sellgren, Werner & Dinerstein 1983) revealed the presence of another group of molecules in the ISM. Indeed, some of these DIBs are commonly assigned to polycyclic aromatic hydrocarbons (PAHs) (Puget & Léger 1989; Sellgren 2001; Mulas, Malloci & Benvenuti 2003), which could account for 17 per cent of the cosmic carbon, and therefore constitute a huge reservoir of carbon-bearing compounds and thus of organic molecules in the Universe (Puget & Léger 1989).

PAHs are stable hydrocarbon compounds only made up of aromatic rings bound together and arranged in most of the cases in a two-dimensional structure, and are believed to be formed in the ejecta of carbon-rich asymptotic giant branch (AGB) stars (Matsuura et al. 2005; Boersma, Hony & Tielens 2006). They are present in a wide variety of interstellar environments, including planetary and reflection nebulae, photodissociation regions, and the diffuse ISM (Allamandola, Tielens & Barker 1989; Roelfsema et al. 1996; Allamandola, Hudgins & Sandford 1999). In dense molecular clouds, PAHs may be strongly depleted due to their condensation on to cold interstellar icy grains, where their IR features were detected in absorption (Smith, Sellgren & Tokunaga 1989; Sellgren et al. 1995; Bregman, Hayward & Sloan 2000; Chiar et al. 2000). They

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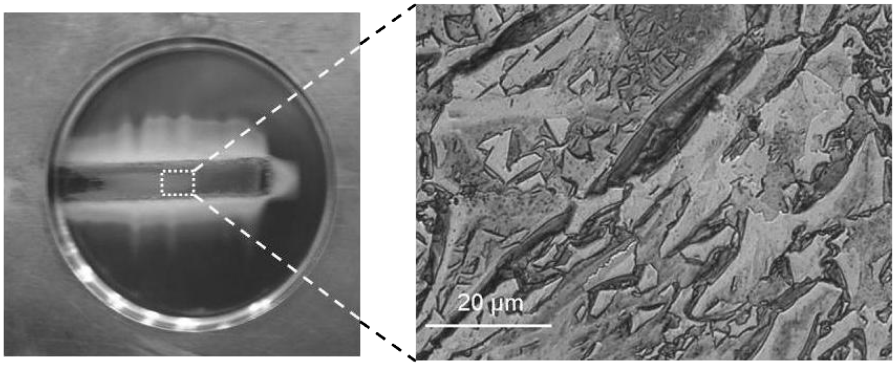


Figure 1. Picture of the KBr substrate covered by the organic residue (left-hand panel) produced after UV/EUV irradiation of the $C_{10}H_8+H_2O+NH_3 = 1{:}1{:}1$ mixture with 4–20 eV photons at 15 K, and enlargement (× 200, right-hand panel) recorded with a microscopy device equipped with a CCD camera. The left-hand image shows clearly that the residue has the rectangular shape of the synchrotron beam. The right-hand image, recorded with the microscope (size: approximately 56 μm × 75 μm), shows the complex structure of the organic residue.

may also condense on cold astronomical objects such as comets and interplanetary dust particles (IDPs) (Allamandola, Sandford & Wopenka 1987; Clemett et al. 1993).

Recent UV irradiation of neutral PAHs in their pure form and frozen in H_2O-rich ices was performed in the laboratory to study the possible connections between the PAHs observed in interstellar environments and those identified in meteorites and IDPs (Bernstein et al. 1999, 2001). The results of these studies agree with the IR detection of PAHs in dense clouds (Sandford, Bernstein & Allamandola 2004; Bernstein, Sandford & Allamandola 2005), indicating that they may be present in dense clouds with relative abundances of 1–5 per cent with respect to H_2O ice, that is, abundances close to that of solid NH_3 in protostellar environments (Dartois et al. 2002), and showing a weak but significant reactivity of such compounds to UV photons.

In this work, we report the results obtained after the irradiation of naphthalene ($C_{10}H_8$), the smallest PAH only consisting of two aromatic cycles, in a $H_2O{:}NH_3 = 1{:}1$ ice mixture with ultraviolet/extreme-ultraviolet (EUV) photons in the 4–20 eV (62–310 nm) range at 15 K. We show that amino acids can also be formed from the UV/EUV irradiation of a starting mixture containing a PAH as the only carbon source, and discuss the astrochemical implications of this result supporting an extraterrestrial origin of molecules of biological interest and their subsequent delivery to the early Earth.

2 EXPERIMENTAL

2.1 Irradiation of the $H_2O+NH_3+C_{10}H_8$ mixture

In a vacuum chamber (pressure maintained under 5×10^{-10} torr), naphthalene ($C_{10}H_8$) vapour and a H_2O+NH_3 gas mixture were deposited on to a cold IR-transparent substrate (KBr crystal). The reagents used to prepare the mixture were $C_{10}H_8$ (powder, Sigma–Aldrich, 99 per cent purity), H_2O (liquid, triply distilled) and NH_3 (gas, Sigma–Aldrich, 99.5 per cent purity). The deposition on to the KBr substrate was performed at 15 K by injecting a $H_2O{:}NH_3 = 1{:}1$ gas mixture and the $C_{10}H_8$ vapour through two separate stainless steel thin tubes (2-mm inner diameter).

The relative proportions between the components of the $H_2O{:}NH_3$ gas mixture (1:1) were controlled from the partial pressures inside the bottle where they were mixed before deposition. The relative proportion between naphthalene and the H_2O+NH_3 ice mixture in order to obtain a final $C_{10}H_8{:}H_2O{:}NH_3 = 1{:}1{:}1$ mixture was determined by mass spectrometry using a quadrupole mass spectrometer (QMS) (Pfeiffer Prisma-200). The typical thickness of the ice film was approximately 1–3 μm, measured by monitoring the variation in interference fringes of a He-Ne laser light reflected by the KBr substrate.

Although different from the composition expected for ices in astrophysical environments (Dartois et al. 2002; Gibb et al. 2004), this mixture was used as a model to understand how a molecule, as complex as naphthalene from an astrophysical point of view, behaves when irradiated with UV/EUV photons in an ice matrix containing water, the most-abundant ice component in the ISM, and ammonia, a nitrogen-bearing source required to produce organic molecules such as amino acids, present in the ISM with debated abundances. A relative abundance of solid NH_3 of $\leqslant 7$ per cent with respect to water ice in protostellar environments as reported by Dartois et al. (2002) supports a starting mixture composition where naphthalene and ammonia are mixed in equivalent proportions, as it is the case in the present experiment.

The resulting $C_{10}H_8{:}H_2O{:}NH_3 = 1{:}1{:}1$ condensed mixture was irradiated with 4–20 eV (62–310 nm) photons (UV/EUV range) provided by the high-flux synchrotron beamline (zeroth order of the white light, using a $450\,\mathrm{mm}^{-1}$ grating) of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The beam had a $\sim 0.48\,\mathrm{cm}^{-2}$ rectangular shape (see Fig. 1, left-hand panel), so that only a fraction of the total deposited molecules were irradiated. The irradiation was performed until a typical total integrated incident photon dose of about 1.6×10^{20} photons was reached, so that the average number of photons per deposited molecule was about 0.5, integrated during the whole experiment (240 min).

In the diffuse ISM, the photon flux was estimated to be (Mathis, Mezger & Panagia 1983):

$$F_{\mathrm{diffuse\ ISM}}(\mathrm{UV}) = 8 \times 10^{7}\,\mathrm{photons\,cm^{-2}\,s^{-1}}, \tag{1}$$

for $E_{\mathrm{photons}} \geqslant 6$ eV. In the dense ISM, this flux is assumed to be at least three orders of magnitude smaller, due to the high opacity of molecular clouds in the UV range (Shen et al. 2004). In terms of photon dose, and regarding the effective surface of the sample irradiated by the synchrotron beam, the experiment reported in this work may thus correspond to an irradiation time of about 4×10^5 yr in the diffuse ISM, and therefore higher than 4×10^8 yr in the dense medium.

Such time-scales may, however, be overestimated because of the presence of energetic photons in the EUV range ($E_{\mathrm{photons}} \geqslant 12$ eV). The EUV range usually defines the spectral range from soft

X-rays to 106 nm (11.7 eV), corresponding to the LiF cut-off (Wu et al. 2002, and references therein). Such photons are essentially emitted by stars, including the Sun, due to atomic line transitions (Judge & Pietarila 2004; Peter, Gudiksen & Nordlund 2006), so that circumstellar environments are affected by such radiation. However, the intensity of stellar EUV light may be two to three orders of magnitude lower than in the VUV (vacuum ultraviolet) range (Rees 1989; Meier 1991).

After warming up to room temperature, the organic residue remaining on the KBr substrate had the same rectangular shape as the synchrotron beam (Fig. 1, left-hand panel), indicating that it was produced only from the UV/EUV irradiation of the starting mixture. A few minutes after removing the substrate from the vacuum chamber, an image of the residue was recorded at room temperature with a Motic B1 Series microscopy device, equipped with a Moticam 2000 2.0 M CCD camera (Fig. 1, right-hand panel). Two lenses of enlargements ×10 and ×20 were used. In parallel, a blank experiment where a KBr substrate without any deposition was irradiated by 4–20 eV photons at NSRRC under the same conditions as the $C_{10}H_8+H_2O+NH_3$ mixture was performed.

Finally, a Fourier transform IR spectrometer (Perkin–Elmer FTIR-1600) was used to record IR spectra between 4000 and $500\,cm^{-1}$ with a $4\,cm^{-1}$ resolution, the angle between the IR and synchrotron beams allowing us to record IR spectra before, during, and after irradiation.

2.2 Chemical analysis of the organic residue

The sample on the KBr window was extracted gently with a scraper (previously washed with distilled water and *n*-hexane), in order to avoid potassium ions (K^+) from the substrate to be dissolved in the extracted solution. The sample was then dissolved in 0.5 mL of a CH_3OH:H_2O = 20:80 solution (CH_3OH from Merck, 99.5 per cent purity). In parallel, 0.2 mL of extracted solution and the equivalent volume of 12 M HCl (Merck, >99.99 per cent purity) were pipetted and transferred into a glass vial. The vial and the tips of micropipette were pre-treated with *n*-hexane (Merck) to remove the organic matter that may remain on the vial and tip walls.

The vial was then sealed for hydrolysis, performed at 110°C for 24 h. After hydrolysis, 0.1 mL of the solution was buffered with 0.5 mL of a solution of 0.4 M borate (pH 10.2) (Agilent PN 5061-3339) in a conical tube, and then derivatized with 0.1 mL of OPA (*o*-phthalaldehyde, Agilent PN 5061-3335) reagent, mixed with 3-mercaptopropionic acid dissolved in the borate buffer.

After derivatization, 20 μL of the derivatized sample were injected into an Agilent 1100 Series high-performance liquid chromatography (HPLC) device, equipped with a vacuum degasser, a quaternary pump, a 20-μL sampling loop (Rheodyne 7725, USA), a column oven, a fluorescence detector, and an Agilent Zorbax Eclipse AAA column (length: 150 mm, inner diameter: 4.6 mm, packed with 3.5-μm-size particles). The mobile phases were prepared with 40 mmol L^{-1} Na_2HPO_4 buffer at pH 7.8 (solution A) and a CH_3CN:CH_3OH:H_2O = 45:45:10 (in volumes) mixture (solution B). The separation was performed with the gradient elution. The flow rate of the mobile phase and the column temperature were set at 2.0 mL min^{-1} and 40°C, respectively. The fluorescence detector was set at excitation and emission wavelengths of 340 and 450 nm, respectively. The total quantity of amino acids in the whole sample was thus 350 times bigger than what was detected in the volume injected into the HPLC device.

The amino acids were identified by comparison with an amino acid standard solution (Agilent PN 5061-3330), containing 1 nmol μL^{-1} of 16 proteinaceous primary amino acids, namely aspartic acid (Asp), glutamic acid (Glu), serine (Ser), histidine (His), glycine (Gly), threonine (Thr), arginine (Arg), alanine (Ala), tyrosine (Tyr), cystine (Cys), valine (Val), methionine (Met), phenylalanine (Phe), isoleucine (Ile), leucine (Leu) and lysine (Lys), and one secondary amino acid, namely proline (Pro). Obviously, since the irradiated starting mixture did not contain any sulphur-bearing molecule, cystine (Cys) and methionine (Met) were not detected in the organic residue. 0.1 mL of this standard solution was buffered at pH 10.2 with 0.5 mL of borate, and derivatized by 0.1 mL of OPA reagent. 20 μL of the derivatized solution were pipetted and diluted into 0.8 mL of the borate buffer. Finally, 20 μL of the standard solution were injected into the HPLC device. The quantity of each amino acid in the injected volume was thus about 70 pmol (1 pmol $=1 \times 10^{-12}$ mol).

The same chemical protocol (extraction and acid hydrolysis) was performed on the blank sample (see Section 2.1) and showed no peak in the 0–15 min retention time range, indicating that the amino acids detected after the photolysis of the $C_{10}H_8+H_2O+NH_3$ mixture were not due to contamination.

3 RESULTS AND DISCUSSION

Fig. 2 shows the HPLC chromatogram obtained for the organic residue, where we could identify 13 amino acids, namely, aspartic and glutamic acids, serine, histidine, glycine, threonine, arginine, alanine, tyrosine, valine, phenylalanine, isoleucine and leucine, by increasing retention time in the HPLC column. All peaks could not be identified on this chromatogram, since some of them may be assigned to non-proteinaceous amino acids and/or other aliphatic/aromatic organic compounds. The identified amino acids are listed in Table 1 by increasing retention time in the column.

Alanine was found to be the most-abundant amino acid in our residue, with a measured absolute abundance of 2.2 nmol (1 nmol = 10^{-9} mol), corresponding to a mass of 199 ng, extrapolated to the whole sample. The relative abundances for the other amino acids with respect to that of alanine, derived from their peak intensities after data analyses to separate overlapping peaks, are given in Column 4 of Table 1.

The distribution of the amino acids identified in our organic residue is different from the results reported previously (Bernstein et al. 2002; Muñoz Caro et al. 2002; Nuevo et al. 2006, 2007), in which glycine, the smallest proteinaceous amino acid, was found to be the most-abundant component. Instead, in our residue the most-abundant compound was alanine (with an arbitrary relative abundance of 100.0), and then by decreasing relative abundances: isoleucine (33.9), serine (30.1), phenylalanine (28.4) and valine (27.8). The abundances of aspartic acid (3.6) and leucine (4.6) were certainly underestimated because of peaks overlapping in the sample chromatogram, and by comparison with the abundances of other amino acids containing a short aliphatic lateral carbon chain such as isoleucine, serine and valine. A significant amount of threonine (relative abundance of 13.6) was measured from the chromatogram, unlike what was reported in previous results (Bernstein et al. 2002; Muñoz Caro et al. 2002; Nuevo et al. 2006, 2007). Like serine, this aliphatic amino acid which contains a hydroxy (OH) group is usually only detected with liquid-phase chromatography techniques, but not with gas-phase chromatography.

However, the small absolute quantities of amino acids measured in the residue (with a maximum of 2.2 nmol for alanine) clearly indicate that only a small fraction of naphthalene was converted into amino acids. The chromatogram of the residue (Fig. 2) confirms this hypothesis, since many peaks certainly assigned to other groups of

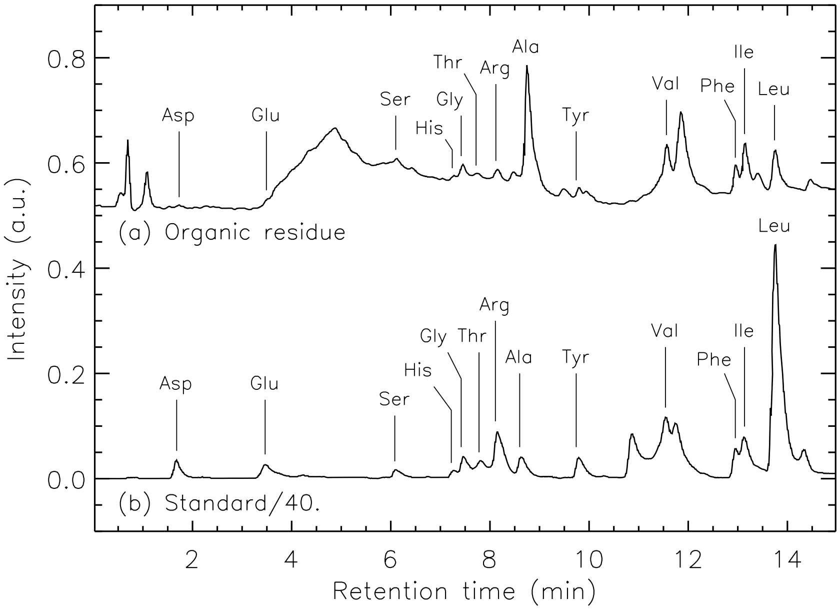


Figure 2. Chromatograms of the organic residue produced after UV/EUV irradiation of the $C_{10}H_8$+H_2O+NH_3 = 1:1:1 mixture with 4–20 eV photons at 15 K (trace a, offset for clarity) and of the standard sample (trace b, divided by a factor of 40 for clarity), measured with HPLC. Thirteen amino acids were identified in the organic residue. The intensity scale is given in arbitrary units.

Table 1. List of the 13 amino acids identified in the organic residue produced from the UV/EUV irradiation of the $C_{10}H_8$+H_2O+NH_3 = 1:1:1 ice mixture with 4–20 eV photons at 15 K. Alanine was found to be the most-abundant amino acid, with a measured quantity of 2.2 nmol (1 nmol = 10^{-9} mol), that is, a mass of 199 ng, extrapolated to the whole sample. The abundances reported in Column 4 for the other amino acids are given relatively to alanine. Finally, the quantum yield was calculated for each amino acid (Column 5).

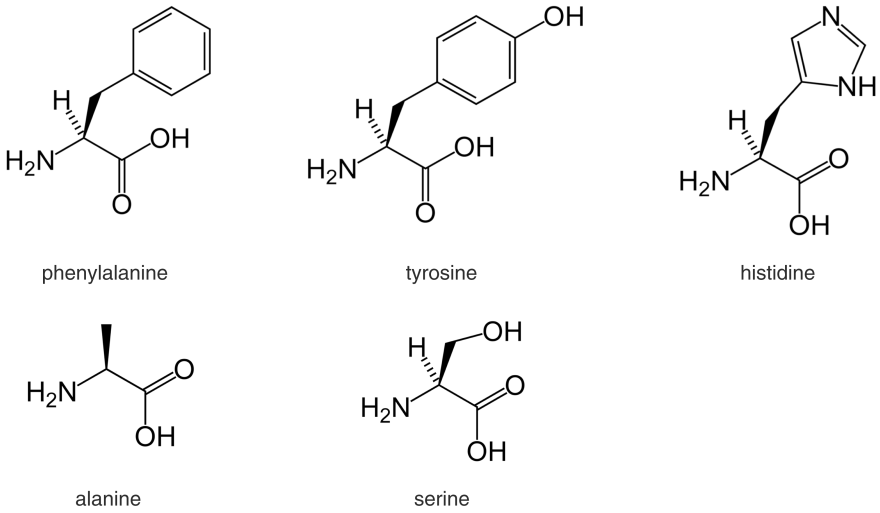
Amino acid	Chemical formula	Retention time (min)	Relative abundance (Ala = 100.0)	Quantum yield ($\times 10^{-6}$)
Aspartic acid (Asp)[a]	$C_4H_7NO_4$	1.73	$\geqslant$3.6	$\geqslant$0.3
Glutamic acid (Glu)	$C_5H_9NO_4$	3.49	8.9	0.7
Serine (Ser)	$C_3H_7NO_3$	6.12	30.1	2.5
Histidine (His)	$C_6H_9N_3O_2$	7.27	19.5	1.6
Glycine (Gly)	$C_2H_5NO_2$	7.46	21.9	1.8
Threonine (Thr)	$C_4H_9NO_3$	7.74	13.6	1.1
Arginine (Arg)	$C_6H_{14}N_4O_2$	8.15	7.0	0.6
Alanine (Ala)	$C_3H_7NO_2$	8.74	100.0	8.4
Tyrosine (Tyr)	$C_9H_{11}NO_3$	9.80	11.9	1.0
Valine (Val)	$C_5H_{11}NO_2$	11.57	27.8	2.3
Phenylalanine (Phe)	$C_9H_{11}NO_2$	12.96	28.4	2.4
Isoleucine (Ile)	$C_6H_{13}NO_2$	13.14	33.9	2.8
Leucine (Leu)[a]	$C_6H_{13}NO_2$	13.75	$\geqslant$4.6	$\geqslant$0.4

[a] The abundances of aspartic acid and leucine may be underestimated because of peak overlapping in the sample chromatogram.

organic compounds were not identified, indicating the presence of other photoproducts of naphthalene eluting with retention times in the same range as amino acids.

The quantum (or photon) yield, given by the number of molecules produced divided by the total number of photons, was calculated for each amino acid and reported in Table 1 (Column 5). For alanine, the most-abundant amino acid identified in our residue, the quantum yield was found to be 8.4×10^{-6}, that is, 4.3 times smaller than what Muñoz Caro et al. (2002) obtained for glycine after irradiation of a H_2O:CH_3OH:NH_3:CO:CO_2 = 2:1:1:1:1 mixture with a H_2-flow discharge UV lamp. For phenylalanine, the most-abundant aromatic amino acid, this yield was found to be 6.9×10^{-6}. Finally, the total amino acid quantum yield was found to be 2.6×10^{-5}, that is, 3.8 times smaller than the yield determined by Muñoz Caro et al. (2002) in their experiment.

In terms of molecular yield, which gives the number of carbon atoms in naphthalene converted into structural carbon atoms in the amino acids, we derived a yield for each amino acid formed and a global amino acid yield according to the distribution deduced from Table 1 (Column 4). Since one molecule of naphthalene contains 10 carbon atoms and all the amino acids identified in our organic residue contain up to nine carbon atoms (see Table 1, Column 2), the production yield for a given amino acid was calculated proportionately to its number of carbon atoms. For alanine (three



phenylalanine tyrosine histidine

alanine serine

Figure 3. Chemical structures of the amino acids: phenylalanine, tyrosine, histidine, alanine and serine. These compounds exist in two enantiomeric forms, but only the L-enantiomers are represented here.

carbon atoms) and phenylalanine (nine carbon atoms), these production yields were found to be 8.1×10^{-6} and 6.9×10^{-6}, respectively, that is, of the same order of magnitude. Finally, the average number of carbon atoms per amino acid was calculated to be 4.6 according to their distribution, so that the global molecular yield for the amino acids identified in our residue was found to be 3.9×10^{-5}.

In other words, one molecule of alanine and one molecule of phenylalanine were produced for 1.2×10^5 and 1.4×10^5 molecules of naphthalene deposited on the irradiated surface of the substrate, respectively. More generally, one amino acid was formed for 2.6×10^4 molecules of naphthalene deposited. This clearly indicates again that all molecules of naphthalene were not photodestroyed during these experiments and/or that among the photolysed molecules, only a small fraction were converted into amino acids or their precursors present in the organic residue. Therefore, many other kinds of organic compounds may also have been formed from the photodecomposition of naphthalene. In particular, Chen et al. (2007) have recently shown that hydrocarbons such as methane (CH_4), ethane (C_2H_6) and propane (C_3H_8), or the benzyl radical ($C_6H_5CH_2$) are formed when a $C_{10}H_8$:H_2O:NH_3 = 1:1:1 mixture is irradiated with 4–20 eV photons at 15 K.

We would then like to draw the attention on the formation of the amino acids phenylalanine (Phe), tyrosine (Tyr) and histidine (His) identified in this organic residue. The lateral carbon chains of these three compounds have complex chemical structures containing an aromatic ring (Fig. 3). In the case of histidine, the aromatic ring even contains two nitrogen atoms. In previous reported results where amino acids were identified in organic residues formed from the UV irradiation of interstellar ice analogues (Bernstein et al. 2002; Muñoz Caro et al. 2002; Nuevo et al. 2006, 2007), the detection of such compounds appeared questionable since the photoproduction of aromatic rings from aliphatic (non-aromatic) compounds is not an efficient process. Indeed, the UV photolysis of PAHs was shown to lead only to the addition of chemical groups on the aromatic rings (Bernstein et al. 1999, 2001), but not to their photodecomposition. Their presence in our residue is, however, relevant because the only starting source of carbon is naphthalene, which consists of two aromatic cycles bound together, and because of the presence of photons with energies in the EUV range.

The abundances for these three compounds, with phenylalanine being the most-abundant aromatic amino acid, and the fourth most-abundant amino acid in the whole residue (with a relative abundance of 28.4), are comparable with those of amino acids containing aliphatic lateral carbon chains. This result confirms their high production rate efficiency in our experiment and indicates that the mechanism(s) leading to the formation of amino acids under our experimental conditions is (are) different from when CO, CO_2, CH_4 and/or CH_3OH are used as starting carbon sources.

However, the fact that alanine is the most-abundant amino acid identified in our residue appears surprising since its lateral carbon chain consists of a small methyl (CH_3) group. Another surprising result is the large variety of amino acids detected, showing that photodecomposed aromatic hydrocarbon compounds, where the carbon is totally reduced, can lead to the formation of both reduced and oxidized chemical functions. In particular, our work shows clearly that highly oxidized molecular groups such as carboxylic acids (COOH) can be formed efficiently from the UV/EUV photolysis of naphthalene.

Another interesting point is that alanine was found to be the most-abundant aliphatic amino acid in this residue and phenylalanine the most-abundant aromatic amino acid. The structures of these two compounds are linked since phenylalanine is a molecule of alanine with an aromatic ring substituting one of the hydrogen atoms bound to the carbon atom of the methyl group (Fig. 3). This indicates that the first amino acid formed from the photolysis of naphthalene in our experiment is probably phenylalanine, itself photolysed and photodecomposed into alanine by removing the aromatic ring. The same phenomenon may occur with tyrosine (aromatic) and serine (aliphatic). In this case, the aromatic ring of tyrosine is inserted between the methylene (CH_2) and the hydroxy (OH) groups (Fig. 3). The abundance ratios between, on the one hand, phenylalanine and alanine ($\sim$0.28) and, on the other hand, tyrosine and serine ($\sim$0.39) may support such a mechanism of formation for small aliphatic amino acids from the photolysis of naphthalene. Indeed, assuming that aliphatic amino acids are only formed from the photodecomposition of their aromatic derivatives, the conversion rates of phenylalanine into alanine (0.78) and of tyrosine into serine (0.72), where 1 indicates a total conversion, are of the same order of magnitude. However, the decomposition of histidine into smaller amino acids is not clear.

All these results indicate that 4–20 eV (62–310 nm) photons can photodissociate naphthalene molecules, and maybe also other PAHs, into small fragments, and that these photofragments are reactive enough to interact with OH and NH_2 radicals, readily formed from the photolysis of H_2O and NH_3, respectively, to eventually form organic molecules. Experiments where bigger PAHs are irradiated with photons in the same energy range will be performed in the future. The results obtained will confirm the photodecomposition efficiency of PAHs when they are subjected to UV/EUV photons.

Finally, the presence of a significant variety and quantity of amino acids in the organic residue formed from the irradiation of a mixture of naphthalene in a H_2O:NH_3 = 1:1 ice mixture shows that PAHs may constitute a non-negligible reservoir and source of carbon-bearing compounds for the formation of complex organic molecules under interstellar/circumstellar conditions, in particular molecules of prebiotic or biological interest such as amino acids. Therefore, this result supports an extraterrestrial origin for the biomolecules (or their precursors) that triggered the apparition of life on the early Earth after their delivery via meteorites (Oró 1961; Brack 1999).

4 CONCLUSIONS

In this work, we show that the irradiation of a mixture containing the smallest PAH naphthalene ($C_{10}H_8$) in a H_2O:NH_3 = 1:1 ice mixture with 4–20 eV (62–310 nm) photons at 15 K leads to the formation of an organic residue where a significant variety and quantity of amino acids were identified. This result confirms previous studies of formation of amino acids from interstellar ice analogues in the laboratory, although the amino acid distribution is different due to the different chemical nature of the starting carbon source.

Moreover, our work shows that naphthalene, and probably other PAHs, can be a non-negligible source of interstellar-reduced carbon, from which organic molecules, such as amino acids and other prebiotic compounds may be formed. This result reinforces the hypothesis of an extraterrestrial origin for the biomolecules from which life on the primitive Earth appeared. Irradiation experiments where bigger PAHs are irradiated with similar photon sources should, however, be performed to confirm the reactivity of such compounds and their efficiency to form organic compounds of prebiotic interest.

ACKNOWLEDGMENTS

We are grateful for the support of the NSRRC staff. This work was supported in part by the Ministry of Education under the Aim for the Top University Program (NCU), and by the NSC grants #NSC-95-2111-M-008-006 and #NSC-95-2112-M-008-028, the NSF Planetary Astronomy Program under grant AST-0604455 (C-YRW) and the NASA Planetary Atmospheres Program under grant NAG5-11960 (C-YRW).

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