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Evolution of interstellar ethanolamine towards amino acids and peptides

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Abstract

Complex organic molecules formed in interstellar molecular clouds are inherited into protoplanetary systems, where subsequent processing may preserve, transform, or enhance their prebiotic potential. Although amino acids have been produced in laboratory simulations of astrophysical ices, the extent to which chemically rich interstellar intermediates evolve into more complex biomolecular structures under astrophysical conditions remains unclear. Here we show that energetic processing of ethanolamine, a molecule detected in the interstellar medium and meteorites and considered a key intermediate in prebiotic chemistry, leads to the formation of amino acids, dipeptides and cyclodipeptides (diketopiperazines). The concurrent formation of amino acids and peptides suggests

that ethanolamine provides an efficient non-aqueous pathway to molecular complexity in irradiated astrophysical ices. These findings demonstrate that a simple interstellar molecule can evolve into biomolecular building blocks through energetic processing prior to planetary accretion, extending the range of environments that can support prebiotic chemical evolution and strengthening the case for an extraterrestrial contribution to the molecular inventory available on early Earth.

1 Introduction

The abiotic processing of volatile species in cold interstellar molecular clouds drives the formation of increasingly complex organic molecules through irradiation and grain-surface chemistry [1]. As this material is incorporated into protostellar systems and subsequently evolves within protoplanetary disks, it undergoes further thermal and radiative processing that can both diversify and restructure its chemical inventory. Although the degree to which this inherited molecular complexity is preserved or reprocessed remains uncertain, analyses of cometary and meteoritic material indicate that a substantial fraction of interstellar organics survives incorporation into planetesimals [2]. These include molecules of prebiotic relevance such as precursors of amino acids, sugars, and nucleobases, suggesting that early planetary environments may have been seeded with a chemically rich exogenous reservoir.

Within this framework, ethanolamine ($\text{HOCH}_2\text{CH}_2\text{NH}_2$) represents a particularly compelling example of an intermediate molecule that bridges interstellar chemistry and prebiotic evolution. It forms spontaneously on the surface of dust grains in the interstellar medium (ISM) at low temperatures, due to the condensation of the most abundant species (H, C, CO, and NH_3) available in the ISM, without the need for energetic inputs [3]. Furthermore, laboratory simulations of interstellar ice analogues composed of abundant molecules such as water, methanol, ammonia, and hydrogen cyanide have shown that ethanolamine can be formed alongside other amino acids through UV-driven processing under astrophysical conditions [4]. Its detection in the gas phase of interstellar molecular cloud G+0.693–0.027 in the Sagittarius B2 complex [5] confirms both its efficient formation and stability in the ISM. Its presence in meteoritic material such as the Almahata Sitta meteorite [6], supports the idea that such chemically versatile species can form in space and be delivered to planetary surfaces. Its survival across interstellar, circumstellar, and solar system environments has also been investigated in recent years [7, 8].

As the simplest species containing both alcohol and amino functional groups, it is a key intermediate in the synthesis of phospholipids and contributes to the formation of essential biomolecular classes, including aminosugars, sphingolipids, and glycoproteins [9]. The polymerisation of its dehydrogenated form, the aminoketene molecule, was shown to yield peptides [10–12]. Energetic processing fragments the ethanolamine molecule into smaller, identifiable species, while also providing tentative evidence for the formation of larger, more complex products based on relatively simple detection techniques such as infrared spectroscopy and quadrupole mass spectrometry [13, 14].

However, the extent of ethanolamine reprocessing in high-energy environments, particularly in circumstellar and solar system settings, and the formation of more complex prebiotic species, remains poorly constrained, highlighting the need for more sensitive, high-resolution analytical methods to reliably identify complex products.

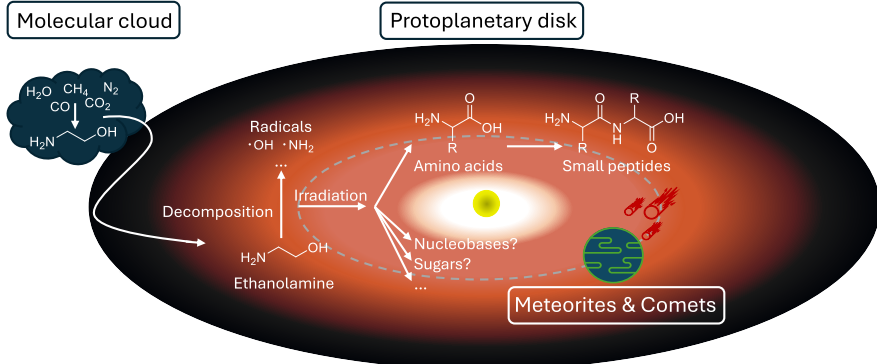


Fig. 1 Astrochemical evolution of ethanolamine. Schematic illustration of the evolution of ethanolamine, a CHON analogue, from molecular clouds [5] through the protoplanetary disk to meteorites and comets [6]. Ionizing radiation drives its chemical transformation, producing prebiotic compounds, including amino acids and peptides, that are relevant to the emergence of life.

With this aim, we perform laboratory simulation of ice irradiation experiments to learn how ethanolamine ice can evolve under the impact of energetic electrons. These studies showed that a series of amino acids, dipeptides, and cyclodipeptides form in ethanolamine ice at 10 K upon processing with energetic electrons as proxies for galactic cosmic rays, and subsequent warming to room temperature. The products were identified from solid organic residues that were dissolved for analysis, without further treatment (e.g. acid hydrolysis, derivatization, or purification). The resulting solution was separated by chromatography and analysed by high-resolution mass spectrometry. These results suggest that ethanolamine formed under dense cloud conditions can evolve into more complex biomolecular structures that persist in high-energy environments prior to planetary accretion. A conceptual overview of the physical picture developed in this work is shown in Fig. 1. The experiments further demonstrate that the formation of dipeptides and cyclodipeptides occurs concurrently with amino acid synthesis under non-aqueous conditions. We will also discuss the possible mechanism of formation of the final products. Such findings broaden the range of environments conducive to abiogenesis, from the circumstellar environment to planetary systems, and support the view that key molecular precursors of life may have an extraterrestrial origin.

Formation of dipeptides under astrophysically relevant conditions has been demonstrated in laboratory experiments involving the energetic processing of interstellar ice analogues [15] as well as the irradiation of amino acids in the solid state [16, 17]. Dipeptide formation has also been observed in the gas phase following energetic processing of van der Waals clusters of amino acids [18]. However, reaction pathways that

bypass the formation of free amino acids may offer significant advantages, primarily because they involve lower activation barriers and are therefore expected to yield peptides more efficiently under interstellar conditions. Recent studies have revealed the spontaneous formation of peptides at low temperatures through reactions involving some of the most abundant constituents of the interstellar medium, namely atomic carbon, carbon monoxide, and ammonia [11, 12]. This mechanism is proposed to proceed via aminoketene intermediates, which can subsequently undergo hydrogenation through H-atom addition to produce ethanolamine. As a result, the energetic processing of ethanolamine may represent an alternative and potentially more efficient route to peptide formation than pathways starting from amino acids.

2 Results

Fourier-transform infrared absorption spectra acquired at successive irradiation intervals (see Extended Data Fig. 4) show that product formation is already substantial after the initial dose of 795 eV/molecule, with no further appreciable increase upon continued irradiation till the final dose of 2450 eV/molecule (check Supplementary Information for the dose calculation). This behaviour is reflected in the concurrent loss of parent ethanolamine features of (NH+OH) twisting mode at 1340 cm^{-1} and combination bands at 1060 and 1020 cm^{-1} and the emergence of new absorption bands assigned to O^{13}CN^- (2107 cm^{-1}), H^{13}CN and $^{13}\text{CN}^-$ (2040 cm^{-1}), and H_2^{13}CO (1680 cm^{-1}) [8, 13] as shown in Extended Data Fig. 4.

We also show the infrared spectrum of the residue at room temperature in Extended Data Fig. 5 that clearly demonstrates the broad amide I (centered around 1625 cm^{-1}), amide II (centered around 1545 cm^{-1}) and amide III (centered around 1295 cm^{-1}) peaks. For comparison we also showed the residues obtained after $\text{Ly}\alpha$ irradiation of ^{12}C and ^{13}C ethanolamine [8]. The monitoring of peptide formation has already been described in the literature using infrared spectroscopy, where up to ten Gaussian fits have been made to show the contribution of different bands. However, in our experiment, one could clearly identify this band without the need of separate Gaussian fittings [11, 16].

Electron irradiation of uniformly ^{13}C labeled ethanolamine at 10 K produced a residue that was observed both during irradiation at the lowest temperature and after warming the sample to room temperature. To analyze the content of this residue, it was treated as discussed in the Methods section and analyzed with a high-resolution mass spectrometer. In an ultra-high-performance liquid chromatograph mass spectrometer (UHPLC-MS), the identity of molecules is ascertained from their retention time and mass fragmentation patterns in tandem mass spectrometry in comparison to commercial standards (see alanine identification in Fig. 2). We have identified two proteinogenic aliphatic amino acids (alanine, proline), and one proteinogenic amino acid with a polar uncharged side chain (threonine), two linear dipeptides (alanine-glycine, proline-alanine), and one cyclic dipeptide (C^{α} -glycine-alanine). All of these products, summarized in Fig. 3, have aliphatic amino acids in their make up, which were identified in the organic residues isolated following the experiments described in the Methods section. In addition, several products were identified with high confidence, whereas some others remain tentative.

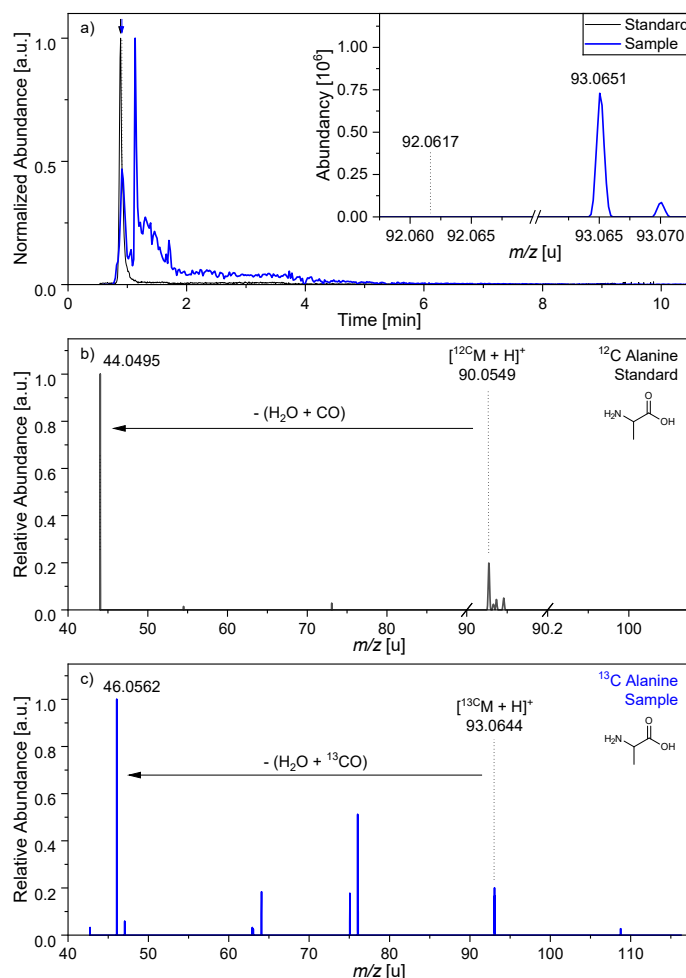


Fig. 2 Identification of ^{13}C -labeled alanine ($^{13}\text{C}_3\text{H}_7\text{NO}_2$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. a) Normalized extracted ion chromatogram of ^{12}C -alanine standard ($RT = 0.89 \text{ min}$) and the ^{13}C -alanine sample ($RT = 0.91 \text{ min}$). The arrows indicate the retention times at which MS^2 spectra were acquired. The inset highlights the presence of the ^{13}C -alanine ion ($[^{13}\text{C}_3\text{H}_7\text{NO}_2 + \text{H}]^+$; $m/z_{\text{calc.}} = 93.0650$) in the analyte and the absence of a significant corresponding partially ^{12}C -alanine ion ($[^{13}\text{C}_2^{12}\text{CH}_7\text{NO}_2 + \text{H}]^+$; $m/z_{\text{calc.}} = 92.0617$) at 0.91 min . b) MS^2 spectrum of ^{12}C -alanine standard with a collision energy (CE) of 40 a.u. at 0.89 min . c) MS^2 spectrum at 0.92 min , confirming the presence of ^{13}C -alanine through its characteristic fragmentation pattern at 40 a.u.

3 Discussion

Over the past two decades, the molecular composition of organic residues from ice irradiation experiments has primarily been investigated after careful solvent extraction following chemical treatments such as acid hydrolysis and derivatization, using highly sensitive gas or liquid chromatography coupled to high-resolution mass spectrometry

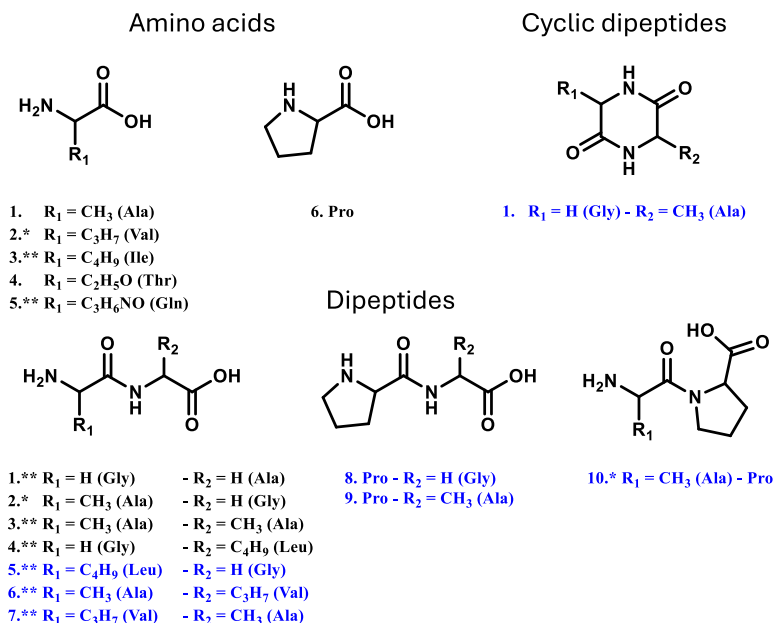


Fig. 3 Summary of the products identified in the experiment. Products identified by mass spectrometry in the refractory residue at room temperature after energetic processing of ethanolamine ice at 10 K and subsequent warm-up. Compounds shown in blue have not been reported in previous ice irradiation experiments. High-confidence identifications are marked with a single asterisk (*), whereas tentative identifications are marked with a double asterisk (**).

[e.g. 4, 19–21]. This approach enables targeted analysis of specific molecular classes, including amino acids and sugars, and provides both qualitative identification and quantitative yields. However, irradiation and thermal processing also produce macromolecular material within the residue. The hydrolysis step subsequently fragments these macromolecules, potentially generating or enhancing the apparent abundance of prebiotic molecules that were not initially present [22]. Indeed, it is believed that the majority of amino acids in such experiments are formed during the hydrolysis [23]. Derivatization itself is a milder processing step which enables reliable quantification and stereochemical information, as can be seen in previous studies [24, 25]. Nevertheless, chemical alterations of the residue cannot be excluded. Consequently, such methods do not preserve the native molecular complexity of the residue. A complementary, global analysis of untreated residues is therefore required to obtain a more comprehensive inventory of the compounds initially formed in the ice.

Recent studies have demonstrated the potential of this strategy, reporting the detection of nucleobases, amino acids, dipeptides and *N*-heterocycles through direct analysis [26], as well as peptides in related residues [11, 12]. However, in most cases, the absence of tandem mass spectrometry (MS/MS) data matched to reference standards limits these assignments to probable identifications [27]. In this context, our results provide unambiguous identification of amino acids and peptides through direct analysis supported by MS/MS comparison with standards. Although the present approach

remains primarily qualitative and does not yet capture the full molecular diversity of the residue, it establishes a robust framework for comprehensive, non-destructive characterization of prebiotic chemistry and paves the way for future studies targeting additional compound classes. Another limitation of this study is the inability to distinguish between enantiomers, despite the recognized prebiotic relevance of homochirality [20].

Ethanolamine has been identified as a precursor to glycine under high-temperature (80–160 °C) simulated Archean hydrothermal conditions [28]; however, glycine yields remain significantly low in our electron-irradiation experiments at 10 K. Among aliphatic amino acids, we did not detect measurable amounts of serine after irradiation. One possible explanation, supported by the tentative detection of serine during the warm-up phase after UV irradiation of ethanolamine, is that serine may be sublimated from the ice [8]. Alternatively, the non-detection of glycine and serine may reflect their incorporation into more complex products, as has been observed for glycine in the formation of dipeptides and cyclic peptides. Serine could be incorporated in the residue in a similar way as cycloserine. Consistent with this possibility, *N*-formylglycine and cycloserine were detected in the organic residue of UV-irradiated simulated interstellar ices composed of H₂O, CH₃OH, NH₃, and HCN, while glycine, alanine, serine, and ethanolamine were identified by GC-MS only after hydrolysis[4]. In our experiment, we were able to identify the mass signal for both *N*-formylglycine and cycloserine.

In the present experiments, the precursor ice was subjected to electron irradiation doses comparable to those predicted for dust-trap regions in protoplanetary disks and for Kuiper belt objects [29, 30]. Remarkably, despite this intense processing, amino acids, dipeptides, and cyclic peptides were detected from a single parent molecule, to the best of our knowledge for the first time. Equally noteworthy is the composition of the products. Extensive irradiation is generally expected to promote aromatization, leading to residues enriched in aromatic species. Instead, aliphatic amino acids and dipeptides were the major products in our residues. Recent ALMA observations [31, 32] have revealed amino acid precursors in a planet-forming disk, suggesting that such environments can preserve and further enrich complex organic inventories beyond the main epoch of planet formation. In this context, our results demonstrate that these products can also withstand prolonged exposure to harsh irradiation environments, lending further support to the interpretation of these observations.

Several of the products identified here are consistent with species previously reported in laboratory simulation studies and analyses of returned meteorite samples [33]. In addition, we identify previously unreported compounds, especially di- and cyclo-peptides providing potential targets for future astronomical and meteoritic detections.

Given that our parent molecule is an amino alcohol, a chemically plausible route to amino-acid formation is sequential oxidation proceeding through amino aldehyde intermediates as shown in Extended Data Fig. 6. In this framework, amino acids may arise from a two-step oxidation sequence in which the amino alcohol is first converted into an amino aldehyde and subsequently into the corresponding amino acid. Experimental support for this hypothesis was provided in our previous infrared spectroscopic study, where we identified evidence for the formation of glycinal, the simplest amino

aldehyde intermediate [8]. In the present work, mass spectrometric measurements reveal mass matches consistent with several amino aldehydes. However, assigning these species with high confidence remains challenging because amino aldehydes are intrinsically unstable and only a limited number of reference standards are available. Consequently, while the current data cannot unambiguously confirm their presence, they are nevertheless consistent with the proposed oxidation-driven pathway.

This mechanistic picture is important because energetic processing in astrochemical environments is often treated primarily as a destructive and stochastic phenomenon, with product formation commonly attributed to radical-radical recombination chemistry or at least where one partner is a radical [24, 34, 35]. Our results instead suggest that energetic processing may also promote chemically directed transformation pathways, in which the stepwise oxidation of pre-existing functionalized molecules provides a viable route to amino acid formation. A similar oxidative mechanism seems consistent with the observed predominance of sugar alcohols and sugar acids following the energetic processing of simple molecular mixtures [20]. The formation of dipeptides and cyclic peptides can likewise be rationalized through a combination of oxidation and radical-radical recombination, without requiring a conventional condensation step (see Extended Data Fig. 6). In this scenario, amino alcohols, amino aldehydes, amino acids, or combinations thereof generate reactive radical intermediates that subsequently recombine to form the observed peptide products.

4 Methods

4.1 Electron irradiation experiment

The experiments were carried out in a new setup at the Origins of Life Laboratory at the Max Planck Institute for Astronomy in Heidelberg. The setup consists of two stainless steel chambers that are separated by a gate valve. The first is an ultra-high vacuum (UHV) reaction chamber (pressures below 1×10^{-9} mbar), where the ice-irradiation experiments are conducted, and the samples are annealed to room temperature. The second is an ultra-high vacuum load-lock chamber (pressures below 10^{-8} mbar), which allows samples to be stored under vacuum before removal for wet chemical analysis. This chamber also serves as the sample transfer interface to the reaction chamber. Flag-style gold-plated copper samples ($15 \times 19 \times 1$ mm) are mounted on a X-Y-Z- θ rotary motion manipulator in the UHV chamber so that it can be translated precisely into position for each specific reaction/analytical technique with stepper motor control. The sample holder is in contact with the cold finger of a closed-cycle helium cryostat (Advanced Research Systems) so that a base temperature of 10 K can be reached. The sample temperature was measured using a calibrated silicon diode and controlled by a Lakeshore 336 temperature controller between 10 and 300 K. The reaction chamber is equipped with an electron gun (ES 40C1, Prevac) which can emit electrons between 1-5 keV that induces the chemistry and a Fourier-transform infrared (IR) spectrometer (Bruker Vertex 70v) with a mercury-cadmium-telluride (MCT) detector to collect IR spectra of the sample at 1 cm^{-1} spectral resolution in-situ in reflection-absorption infrared mode during deposition and electron irradiation.

The reaction chamber, equipped with two laser systems, is also coupled to an Orbitrap mass spectrometer (Thermo Fisher Q Exactive plus) via a custom-designed ion guiding system, which was not used in our experiments.

We have previously performed UV irradiation experiments with ethanolamine, where the details on how to handle it and related information are provided [8]. In the current experiment, ethanolamine (Merck, 99 % purity), in which all carbon atoms were isotopically labeled with ^{13}C , was introduced into the reaction chamber via background deposition such that a several hundred nm ice layer was grown on the gold surface. The ice was grown at 160 K to prevent and minimize the condensation of CO, CO₂, and H₂O on the substrate. The ice thicknesses were measured by the IR spectrometer. The ices were irradiated at 10 K with 3 keV electrons (average flux = 3.1×10^{13} electrons cm⁻² s⁻¹) for about 2 hours to a total fluence of about 2.2×10^{17} electrons cm⁻², with projectile electrons impacting the target ices at an angle of 30° to the normal.

CASINO simulations [36] were checked for the trajectory of the electrons to ensure that the electrons do not penetrate the ice completely and hit the underlying gold surface. After this, the sample was heated with a ramp rate of 0.5 K min⁻¹, and IR spectra were taken during warming up at regular intervals. Once room temperature was reached, the sample was transferred to the load-lock chamber and then removed from there to another high vacuum sample storage device until further ex situ analysis was performed.

4.2 Ex situ mass spectrometric analysis

4.2.1 UHPLC-Orbitrap mass spectrometer

The organic residues were dissolved in about 70 μl of a water/methanol (1:1 by volume) mixture. The sample solution was analyzed using an Orbitrap mass spectrometer (Exploris 480, Thermo Fisher Scientific) in Jena with a mass resolution of $m/\Delta m = 90,000$ at a mass-to-charge ratio (m/z) of 200. The injection is done via an ultra-high-performance liquid chromatograph (UHPLC) system (Vanquish VF-P10-A binary pump, VF-A10-A autosampler, Thermo Fisher Scientific) equipped with a polar modified C18 separation column (Phenomenex Synergi Hydro-RP C-18 RP) at 25° C. Sample solutions were stored within the autosampler at 10° C. The eluent program for this UHPLC setup is as follows: solvent A (H₂O + 20 mM formic acid set to a pH of 4.3 with ammonia), solvent B (acetonitrile) = 100:0 for the first initial 1.0 min, followed by a linear gradient of A:B=0:100 at 7.7 min, and it was kept at this ratio for 3.3 min. The flow rate was 0.4 ml min⁻¹. Column flow was switched at 0.5 min from waste to the MS and at 11.5 min again back to the waste, to prevent source contamination.

For accurate mass and retention time, full scan modes with positive and negative polarity were conducted with a scan range of $m/z = 70 - 300$ and $m/z = 150 - 1000$ at a resolution of 90000. The AGC target was set to "standard" and the maximum IT to "Auto". Other general settings were set as follows: sheath gas flow rate: 50; auxiliary gas flow rate 10; sweep gas flow rate: 1; spray voltage: 3.5 kV; capillary temperature: 325° C; S-lens RF level: 50; auxiliary gas heater temperature: 350° C; acquisition

time frame: 0.5–11.5 min. For negative mode, all values were kept instead of the spray voltage, which was set to 2.5 kV.

For tandem mass spectrometry (MS²), first a full scan mode with positive and negative polarity was conducted with a scan range of $m/z = 100 - 1000$ at a resolution of 90000. Secondly, MS² was measured using an isolation window of 0.4 with a resolution of 15,000 and a fixed first mass of 40. All other values were kept as mentioned above. Collision energies were determined by sufficient fragmentation of standards.

Standards of amino acids and (cyclic-)dipeptides were purchased from Sigma-Aldrich and analyzed with the same method described above at a concentration of 1 $\mu\text{g ml}^{-1}$. Fragmentation was tested with collision energies of 15, 30, 45, 60 and 90 eV.

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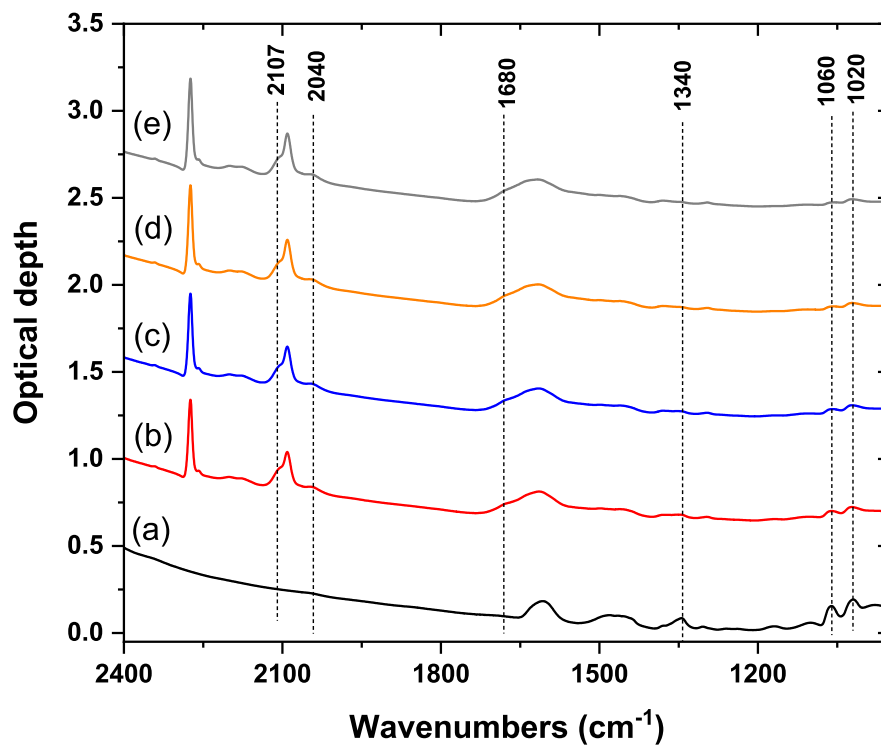
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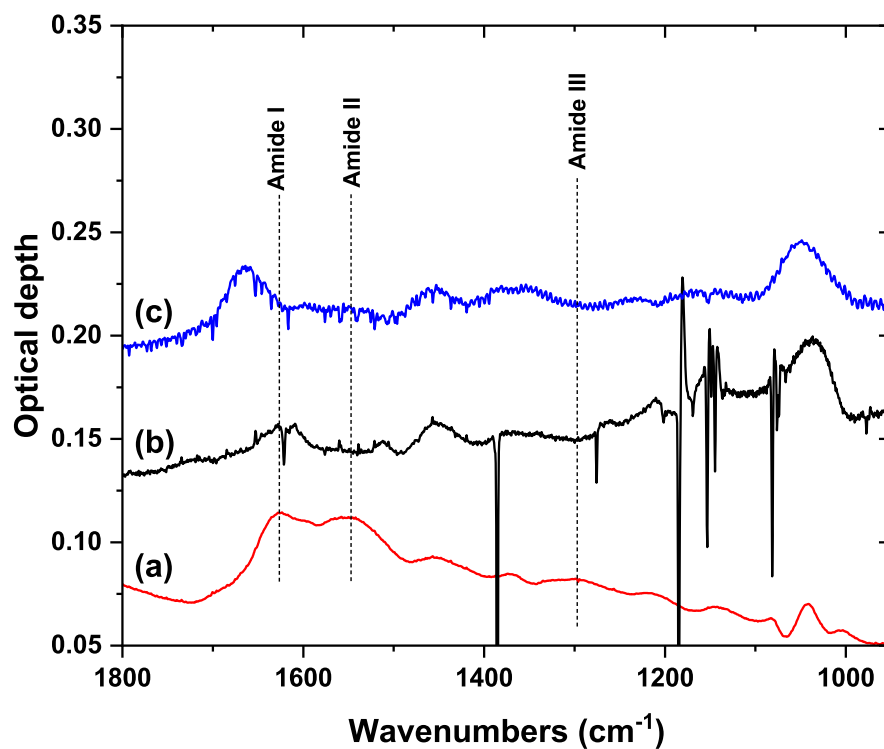
Extended Data.

Extended Data Table 1 Detected mass matches of amino/ dipeptide alcohol (R = CH₂OH), amino/ dipeptide aldehydes (R = CHO) and all detected amino acids and dipeptides (R = COOH) detected in this paper. For cyclic dipeptides no analogue aldehyde/ alcohol was searched because they do not contain terminal carboxylic acids. Yet, their formation mechanism would follow the same path as the formation of dipeptides. Schematics of the corresponding alcohol, aldehyde and acid are illustrated in Extended Data Fig. 6.

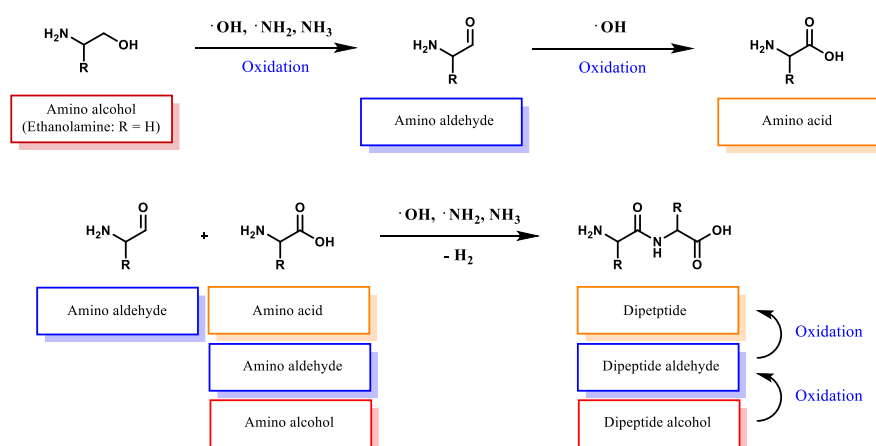
Compound	Formula	[M+H] ⁺ R = CH ₂ OH	[M+H] ⁺ R = CHO	[M+H] ⁺ R = COOH
Ala	¹³ C ₂ H ₆ NR	79.0858	77.0701	93.0650
Pro	¹³ C ₄ H ₈ NR	107.1081	105.0925	121.0874
Val	¹³ C ₄ H ₁₀ NR	109.1238	107.1081	123.1030
Thr	¹³ C ₃ H ₈ NOR	110.0997	108.0840	124.0789
Ala-Gly	¹³ C ₄ H ₉ N ₂ OR	138.1139	136.0983	152.0932
Pro-Gly	¹³ C ₆ H ₁₁ N ₂ OR	166.1363	164.1206	180.1156
Pro-Ala/Ala-Pro	¹³ C ₇ H ₁₃ N ₂ OR	181.1553	179.1396	195.1346



Extended Data Fig. 4 Infrared spectra of ethanolamine before and after irradiation. Infrared spectra of ¹³C-ethanolamine before irradiation (a) and after irradiation with 3 keV at increasing doses of (b) 795, (c) 1180, (d) 1840, and (e) 2450 eV/molecule. The vertical dashed lines indicate the disappearance of bands associated with the parent molecule and the appearance of bands corresponding to irradiation products, respectively.



Extended Data Fig. 5 Infrared spectra of room temperature residues from ethanolamine irradiation experiments. Comparison of the infrared spectra of the room-temperature residues obtained after energetic processing of (a) ^{13}C -ethanolamine with 3 keV electrons, (b) ^{13}C -ethanolamine with $\text{Ly}\alpha$ radiation, and (c) ^{12}C -ethanolamine with $\text{Ly}\alpha$ radiation [8]. The amide I, II and III bands are prominent in the residue produced by electron irradiation.



Extended Data Fig. 6 Proposed reaction pathways in our experiment. Proposed reaction pathways in ethanolamine ice upon electron irradiation leading to the formation of amino acids, dipeptides, and cyclic peptides. In addition to the conventional radical–radical and radical–neutral reaction mechanisms, an oxidative pathway along with most probable radical responsible for the oxidation is suggested.

Supplementary Files

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- [SupplementaryInformation2026.pdf](#)