

Simulating the environment of Europa to investigate the lifetimes and degradation rates of amino acids when irradiated in the presence of salt

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Introduction:

Glycine is an important bio-molecule that has been widely studied in an astrobiological sense. It is the simplest amino acid, and is an essential building block of life. Glycine is prevalent in astrobiology because it has been identified in various environments in space, such as interstellar clouds, meteorites, and comets (Sanford et al., 2020; Lattelais et. al, 2010; Rimola et al., 2022). Glycine formation can be achieved in a variety of different ways (Lee et. al, 2009). Several studies have demonstrated that laboratory experiments irradiating ice-mixtures containing sources of carbon and nitrogen with various types of radiation (e.g: ionizing, UV, and keV electron radiation) have resulted in the formation of wide varieties of amino acids (Sanford et al., 2020; Kobayashi et., 1990).

It has been theorized that glycine can form in a multitude of places in space but specifically on icy bodies in our solar system such as Europa. Europa, discovered by Galileo in 1610, is an icy satellite in orbit around our Solar System's largest gas giant, Jupiter. The moon is bombarded by electromagnetic particles from Jupiter's magnetosphere. Europa is theorized to have the three main requirements for life: water (subsurface ocean), energy sources (e.g. radiolytic chemistry and tidal dissipation), and critical elements for life such as CHNOPS (Hand et al., 2009). Therefore, Europa is a prime focus for astrobiological experiments.

Amino acids can be formed by both biological and abiological processes. Consequently, it is important to understand how easily they can be formed and destroyed at potential targets for future missions, specifically ones that search for evidence which might indicate the existence of extraterrestrial life. These searches typically revolve around the identification of particular biosignatures like commonly found biomolecules: amino acids, sugars, lipids, and nucleobases. To provide context and rule out false-positive detections, it is important to understand the degree to which such compounds could be produced by abiotic processes indigenous to the environment of Europa.

A number of experiments have simulated the radiation environment of Europa to investigate the synthesization of amino acids, as well as nucleobases and other complex molecules, and have found that it is possible for them to form there (Levy et al., 2000; Kimura and Kitadai, 2015). Experimental studies on irradiating amino acids themselves have been conducted to gather information on their lifetimes and degradation rates (Pernet et al., 2013; Orzechowska et al., 2007; Liu and Kounaves, 2020). In regards to Europa, Orzechowska et al., (2007) found that their results indicated the concentration of amino acids; glycine, aspartic acid, glutamic acid, and phenylalanine, within the top meter of ice would be halved within a ~10 year timescale, though there is great variation with depth. However, Europa's surface chemistry is also altered by an additional substance which should be taken into account when conducting experiments such as these – that substance being salt.

Europa's surface is covered with reddish-brown streaks. Numerous studies have been carried out to determine the composition of these streaks (Johnson et al., 1998; Brown and Hill, 1996) and have shown that the colorations could be explained by irradiated salts, such as sodium

chloride (NaCl). Using spectra acquired from the Hubble Space Telescope, Trumbo et al., (2019) presented the detection of a 450-nm absorption indicative of irradiated sodium chloride on the surface of Europa. NaCl's geographic distribution and previous infrared spectra interpreted to reflect endogenous material supplies an explanation for the observed 450-nm feature (Trumbo et al., 2019). Other salts are also thought to be present on Europa, such as magnesium sulfate (Trumbo et al., 2019).

While there are plenty of studies of the salt on Europa, and the radiation synthesizing complex molecules, so far very few studies exist on combining salt with other complex molecules and subjecting them to radiation. The salt environment on Europa is a factor that needs to be investigated further because it could alter the lifetimes of irradiated biomolecules, namely amino acids. Most amino acids are found naturally in their doubly charged zwitterionic state, which could potentially be stabilized by the presence of dissolved salts.

Purpose:

The purpose of this study is to investigate the lifetimes and degradation rates of amino acids when irradiated in the presence of salt to simulate and provide an accurate depiction of what may be happening on the surface of Europa. This will enable more realistic evaluation of the lifetimes of amino acids at the European surface, and may also provide additional signatures from the decay of amino acids.

Methods and Materials

(1) Sample Preparation & Characterization:

Samples of approximately 1000-nm and 100-nm thickness were prepared on flat copper disks (1" diameter) using an Instras Scientific SCK-300P Vacuum chuck spin coater. The disks were finished with 600 grit sandpaper. To achieve the desired thickness, solutions of 1 M Glycine and 1 M NaCl (1000-nm), as well as 0.1 M Glycine and 0.1 M NaCl (100-nm), were prepared and 0.1 μ L of solution was spread over the surface of the disk and spin coated at 500-1000 RPM for approximately 60 seconds and repeated one time. Sample thickness and characterization was performed using a PIKE EasyDIFF reflectance accessory inside of an iS50R FTIR Spectrometer. Conditions and Experiments to be performed: Mixture of glycine 0.1 M + NaCl 0.1 M (1:1) to be irradiated, glycine 0.1 M + NaCl 0.1 M (1:1) not irradiated (blank), glycine 0.1 M irradiated (control). Different concentrations to be prepared: 2:1 and 1:2 (0.2 M glycine and 0.1 M NaCl; 0.1 M glycine and 0.2M NaCl). These concentrations would then give three data points. It was planned to replicate this process using two other amino acids: serine and tyrosine. Other salts such as magnesium sulfate ($MgCl_2$) would be used to replace the sodium chloride in the experiments listed above as well.

(2) SWEEPS (Space Weathering Environment for Exploring Planetary Surfaces) ultrahigh vacuum chamber:

The experiments were conducted within an ultrahigh vacuum (UHV) chamber designated SWEEPS (Space Weathering Environment for Exploring Planetary Surfaces; Figure Y). The sample and a blank copper reference are mounted simultaneously onto an oxygen-free copper substrate attached to a closed-cycle 2-stage helium cryostat. The cryostat is capable of operating at temperatures from 10 – 1000 K. The vacuum is generated under oil-free conditions using a Pfeiffer turbomolecular pump backed by a second turbomolecular T-85 pumping station. Due to sublimation properties of water under low temperature and vacuum, after an initial vacuum of $\sim 10^{-5}$ torr, the cryostat was cooled to average Europa surface temperature of 100 K (citation) prior to starting the 2nd Turbomolecular pump to achieve pressures of 2×10^{-8} torr for these experiments. The samples are then moved into the analysis chamber by a 16" linear transfer mechanism where they can be analyzed by the FTIR spectrometer, which operates under bidirectional diffuse conditions (incident angle = 30° , emission angle = 0°) comparable to those utilized by the NASA RELAB facility which have been shown to be comparable to observations of remote bodies by spacecraft and telescopes.

(3) Electron Irradiation Experiments:

The samples are mounted such that a stainless steel plate covers the sample and the standard. They are electrically isolated by a macor piece, and attached to a Keithley Picoammeter in order to image the sample location. Once the area has been selected, a mask is generated from an Excel file to identify the 'pixels' within the image of the sample in order to determine the area that will be irradiated. The electron beam is scanned over the sample area approximately every 8 minutes using an electron gun. 1 keV irradiation was performed on thick and thin samples. Unfortunately, there was an incident that prevented the experiments to be performed using 2 KeV electrons as done previously by Mate et al. (2012).

(4) UV Irradiation Experiments:

The experiments were switched to a UV irradiation source using the Hamamatsu source H11978. A 100-nm sample was subjected to four hours of UV irradiation.

Results:

There was no change viewed when irradiating the thick and thin samples with 1 KeV electrons (see figure 1).

Figure 1:

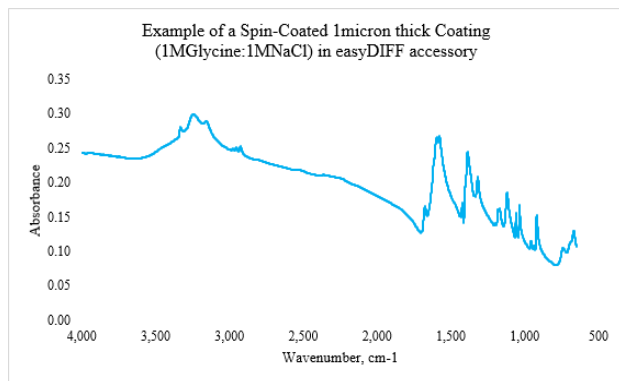
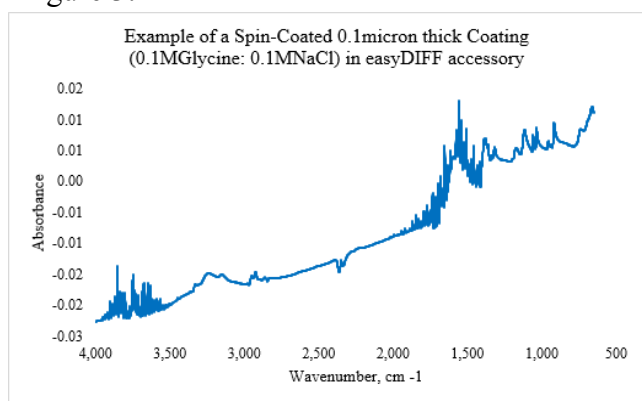


Figure 2:



Figure 3:



Unfortunately when preparing to increase from 1 KeV electrons to 2 KeV electrons, modeling the experiment after Mate et. al (2012), the electron gun was left on while the sample warmed up which caused the filament to burn out. The radiation source was then switched to a UV energy source; however, there was no change after 4 hours of irradiation except for some buildup of water. The experiments were then stopped, the issue being that there was not a strong enough radiation source to continue the study. Had the experiments gone as planned the data would've been analyzed accordingly, the half-life of glycine and the other amino acids (tyrosine, and serine) would have been calculated for all concentrations and compared to previous studies. The half-lives would also have been altered for different astronomical environments and compared to other results similar to the table in Mate et. al (2012).

Discussion/Conclusion

It seems that the UV radiation had no effect on the glycine peaks because the UV source was not strong enough. The results from the experiments using the UV source were anticipated to resemble Oberg et. al. (2015). However, on closer review it looks as though their fluxes were also very small. It seems that their work was publishable because of their spectrometer, which is

under vacuum. Having a spectrometer under vacuum eliminates all traces of elements and compounds from the atmosphere like CO₂ and water which means it is possible to view extremely small changes in the peaks that were not visible in the spectrometer used in this study. Future work should conduct experiments as planned to determine if the salts would have affected the half-lives of the amino acids. If the salts have an effect on the survivability of the amino acids it is something to take into account for future missions that search for biosignatures on Europa.

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