Long-term Stability of Glycine, Alanine, and Phenylalanine on Titan's Surface Subject to Cosmic Ray Flux

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Abstract

The potential commonality of prebiotic chemical processes on Titan and the primitive Earth makes Titan a prime body of astrobiological interest. Amino acid synthesis can occur if the abundant simple organics on Titan's surface can mix with liquid water. Because events that melt surface ice, such as impacts, are rare, it is essential to recognize how long the synthesized molecules remain intact on Titan's surface. The degradation of biomolecules in extraterrestrial environments can be estimated by combining theoretical work about energy deposition on the surface with experimental results from irradiation of organic molecules. We modelled the destruction of amino acids on the surface of Titan, something absent in current literature. We chose Glycine, Alanine, and Phenylalanine as our molecules of interest due to relevant experimental results for their radiation stability at Titan temperatures. Titan's thick atmosphere prevents solar radiation and energetic particles trapped in Saturn's magnetosphere from reaching the surface. The dominant source of energetic radiation at the surface of Titan is the diminished flux of Galactic Cosmic Rays (GCR's) that penetrate the atmosphere. Sittler Jr et al. (Icarus, 2019) modeled surface GCR flux to be ~10^-9 ergs/cm^3/s. Using the GCR flux, in conjunction with the half-life doses at T=100 K from Gerakines et al. (Icarus, 2012), we estimate the half-lives to be 7.69 x 10^12;, 5.07 x 10^12, and 5.82 x 10^12 years for Glycine, Alanine and Phenylalanine, respectively. These extraordinarily long half-lives on Titan's surface, as compared to similar calculations for amino acids on Mars, Europa, or Pluto, are directly the result of reduced energy deposition due to the atmosphere. We thus conclude that the degradation of these three amino acids by GCR flux is insignificant over geological time, and will not be an essential factor in interpreting the chemistry from Titan's surface samples from future missions, such as Dragonfly.

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Introduction

Saturn's largest moon, Titan, is the only other place in our solar system known to have a dense, nitrogen dominant atmosphere along with stable, liquid hydrocarbon lakes on its surface. Titan has an inventory of complex organic compounds, as measured by the Huygens probe and predicted by experiments and simulations, suggesting the potential formation of prebiotic molecules that serve as precursors for life as we know it. The plausible commonality of prebiotic chemical processes on Titan and the primitive Earth makes Titan a prime body of astrobiological interest.

One of the prebiotic molecules serving as an essential building block of life on Earth is amino acids. Amino acid formation requires the presence of liquid water in its chemical pathway. Liquid water may be available on the surface at sites of impact craters resulting from meteorites striking the crust, releasing sufficient heat to melt the water-ice temporarily. However, events like impacts are rare and infrequent, making it crucial to study how long these precursor molecules, such as amino acids, can remain intact in the water-ice on Titan's surface. To explore this, I combined the theoretical work about the energy deposition on Titan with models of amino acid destruction due to radiation. The rarity of liquid water on Titan's surface and its infrequent mixing with hydrocarbons compels us to study the preservation of potential biosignatures, helping us understand the prebiotic chemical pathways of Titan and the primitive Earth.

Background

Given the likely destruction of amino acids, it is essential to identify the energy sources present on Titan's surface and how much energy they provide. Due to the vast distance from the Sun, Titan only receives about ~1% of the solar flux that reaches the Earth. Titan's thick atmosphere, acting as a layer of protection, allows for only 10% of the incident solar flux to reach the surface, suggesting that solar radiation is not a significant source of energy on Titan. UV photons and energetic particles from Saturn's magnetosphere dissociate and ionize the nitrogen and methane molecules in Titan's atmosphere, preventing these particles from reaching the surface (Hörst, 2017). Radiocarbon is another potential energy source; however, a previous theoretical study indicates that it would only be in small reservoirs that are not on the surface (Lorenz et al., 2002). That aligns well with Huygens measurements, which only detected C-12 and C-13 in Titan surface samples (Niemann et al., 2010). Another potential energy source is Galactic Cosmic Rays (GCRs), consisting of high-energy particles present everywhere in space. As these cosmic rays penetrate an atmosphere, they begin to cascade down as smaller, energetic particles, serving as the dominant source of radiation on the surface of Titan (Hörst, 2017; Sittler Jr et al., 2019).

I pioneered the biomolecule degradation analog for Titan, contributing to existing studies of extraterrestrial environments. I focused on the amino acids: Glycine, Alanine, and Phenylalanine, due to the availability of experimental literature detailing the irradiation of these molecules at Titan-relevant temperatures with a proton beam, simulating the effects of GCRs (Gerakines et al., 2012). They identified the dissociation of specific bonds in the IR spectra indicating amino acid destruction and developed models of rates of amino acid destruction. Based on the results, they devised half-life doses (measured in eV/16 amu) for each sample; the half-life dose is the required amount of energy to destroy 50% of a sample.

Most of the current models for GCR energy deposition on Titan are concerned with the ionization of the upper and lower atmosphere. Sittler Jr. et al.'s (2019) simulation extends some of their previous results with the lower atmosphere to the surface, serving as the most recent and relevant model for the GCR energy deposition on Titan. Only about 0.4% of the incident GCR energy makes it to the surface, depositing ~10^{-9} ergs/cm^3/s (Sittler Jr. et al., 2019). I converted this energy deposition into the appropriate units of eV/16 amu/yr, to align with the units from half-life doses.

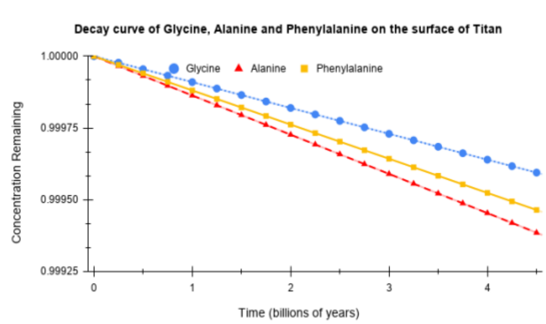
Results

Table 1

Half-life doses and estimated amino-acid half-lives on the surface of Titan

Radiation dose rate[1] (eV/16 amu/yr)	Amino Acid	Half-life dose[2] (eV/16 amu)	Half-life (yr) on Titan	Half-life (yr) on Europa[3]	Half-life (yr) on Mars[3]	Half-life (yr) on Pluto[3]
5.33×10^{-13}	Glycine	4.1	7.69×10^{12}	1.1×10^{7}	3.3×10^{8}	4.7×10^{8}
	Glycine in H2O-ice (1:8.7)	3	5.63×10^{12}	8.0×10^{6}	1.7×10^{8}	4.5×10^{8}
	Alanine	2.7	5.07×10^{12}	7.6×10^{6}	1.7×10^{8}	3.1×10^{8}
	Alanine in H2O-ice (1:11)	2.8	5.25×10^{12}	7.5×10^{6}	2.1×10^{8}	3.7×10^{8}
	Phenylalanine	3.1	5.82×10^{12}	8.7×10^{6}	1.7×10^{8}	4.0×10^{8}
	Phenylalanine in H2O-ice (1:26)	2.4	4.50×10^{12}	6.2×10^{6}	2.0×10^{8}	2.9×10^{8}

[1] Energy deposition on Titan's surface (Sittler Jr. et al., 2019)
[2] Half-life dose at T = 100 K (Gerakines et al., 2012)
[3] Half-lives (Gerakines et al., 2012)



I calculated half-lives using the half-life doses in conjunction with the GCR energy deposition. I performed the calculations for the pure amino acid samples and the amino acids mixed in water-ice. The water-ice samples lay a better foundation, providing a more realistic assumption about the state and presence of the amino acids on the surface of Titan. The formation of amino acids would be in the vicinity of impact craters, where water-ice can melt to make liquid water available.

Table 1 summarizes the results of the half-life calculations, along with a comparison to other extraterrestrial environments. The graph shows the decay curve of the amino acid samples with respect to time. The estimated half-lives of these amino acids are the longest on Titan to its thick atmosphere resulting in a reduced surface energy deposition. That makes Titan the most riveting place in our solar system to seek the preserved results of prebiotic chemical processes. This study of the long-term preservation of simple and complex molecules is essential for the upcoming Dragonfly mission, which will directly sample various Titan materials, including materials from the impact crater melt sheet.

Future Implications

These long lifetimes of biomolecules, like amino acids, allow us to interpret the possible formation of more complex molecules like peptides and proteins. The surface of Titan seems to favor the long-term stability of the amino acids, opening up further avenues of research. We can identify a trend in the half-lives based on molecular structures by testing the stability of other amino acids. The next challenge would be to develop models for the expected abundance of these amino acids on the surface of Titan by analyzing how the presence and stability of amino acids can allow for further chemical reactions. That would consist of theoretical organic synthesis pathways involving simulations and experiments in the context of the freezing impact melt sheet that concentrates the solute over time, potentially driving complex reactions. Further research with nucleic acids, lipids, and sugars can validate our claims for these precursor molecules as well. That would require in-lab experiments with a vacuum-sealed cold chamber, a proton beam, and an IR spectrometer, similar to what I am currently working on in my proposed experiment that I hope to finish over Spring 2020.

We thus conclude that the degradation of these three amino acids by GCR flux is insignificant over geological time and will not be an essential factor in interpreting the chemistry from Titan's surface samples from future missions, such as Dragonfly.

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