Chemical reactions impacting the potential of Planetary habitability.

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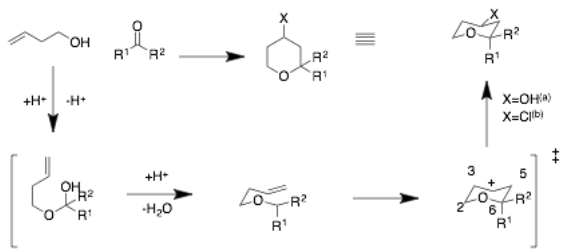
Introduction: Chemical processes on the emerging worlds are important and interesting. Complex molecules are constantly formed from the pre-existing simpler molecules. Complex organic molecules such as Polyhydroxylated compounds (polyols) such as sugars, sugar alcohols and sugar acids are considered to be the precursors of nucleic acids of life- DNA, RNA and cell membranes. Formation of complex molecules on planetary surfaces has been postulated by many path ways. Meteoric amino acids have been extensively studied.
On early planetary surfaces where the Ph is usually acidic, the reactions of smaller aldehydes and allylic alcohols can lead to the formation of complex pyranose molecules. Understanding the acid catalyzed Prins type cyclization and cleavage reaction pathways can give an answer to the key pathways involved in the formation of Precursors of amino acids, Nucleic acids, DNA and RNA.



Scheme 1: Mechanism of the synthesis of THP rings by Prins reaction(a) When H_2SO_4 was used. (b) When HCl was used.

Discussion: The enantiomeric composition of abiotically produced amino acids is racemic, in contrast to the homochirality (almost exclusively L-enantiomers) found in biological systems on Earth. A few meteoritic amino acids, most notably isovaline, have been found to exhibit an L-enantiomeric excess.(see reviews and references therein: Ref [1] Aponte 2016, [2] Elsila et al., 2016).

The formation of Amino acids, the key building blocks of life might have been a two step process. 1) Acid catalyzed cyclization reaction, resulting in the formation of substituted pyran moiety and 2) ring opening / cleavage of pyran ring resulting in selective chiral prebiotic precursor molecule. The Prins type Cyclization acid catalyzed reaction and formation of tetrahydropyran derivatives in the context of evolving planetary surfaces has never been explored . On early planetary surfaces where the pH is usually acidic.

On Mars the phoenix lander detected minerals that indicated ~ neutral pH in the soil (but there are supposed to be some acidic areas). However, on Earth there are acidic environments -even today- that are analogs of likely locally acidic environments billions of years ago. Recently Mars ice deposit[4] and "warm and wet" early Mars climate scenario[5] have been reported.

So there were probably a lot of local environments good for acidic chemistry, where the reactions of smaller aldehydes and allylic alcohols can lead to the formation of complex pyranose molecules.

Understanding the Prins reaction pathway[3] at various temperatures and under conditions similar to that of icy moons can give an answer to the key pathways involved in the formation of Precursors of Nucleic acids, DNA and RNA.

Summary: Exploring the formation of acid catalyzed cyclization reaction products under warm-wet/ wet-cold/cold-dry/ dry-hot cycles on planetary conditions is paramount reaction to improve our understanding of the origin and evolution of life . This concept to understand the formation and cleavage of cyclic ethers like substituted pyran, piperidine, thiopyrans under conditions including UV irradiation can hold a key to guide our search for life elsewhere.

References: [1] Jose ́C. Aponte, Hannah L. McLain , Jason P. Dworkin, Jamie E. Elsila (2016), *Geochimica et Cosmochimica Acta, 189*, 296–311. [2] Elsila J. E., Aponte J. C., Blackmond D. G., Burton A. S., Dworkin J. P. and Glavin D. P. (2016), *ACS Cent. Sci., 2*, 370–379. [3] E. Hanschke (1955) Chem. Ber., *88*, 1053 – 1061. [4] C. M. Stuurman, G. R. Osinski, J. W. Holt, J. S. Levy, T. C. Brothers, M. Kerrigan, B. A. Campbell. (2016) *Geophysical Research Letters, 43* (18), 9484. [5] J.Davis, J.M., Balme, M., Grindrod, P.M., Williams, R.M.E., and Gupta, S., (2016), *Geology*, *44*, 847–850.