

REACTIONS OF NITROGEN HETEROCYCLES IN PLAUSIBLE PREBIOTIC MIXTURES L. E. Rodriguez¹, C. H. House¹ and M. P. Callahan², ¹Department of Geosciences, The Pennsylvania State University, 220 Deike Bldg, State College, PA 16802, E-mail: ler185@psu.edu, ²Solar System Exploration Division and Goddard Center for Astrobiology, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA.

Introduction: The difficulties of synthesizing nucleosides and nucleotides under plausibly prebiotic conditions have led to the opinion that a simpler alternative molecule may have preceded it (*i.e.*, a pre-RNA world) [1]. Several pre-RNA structures have been proposed and synthesized in the lab, but the prebiotic synthesis of their complete monomers and their subsequent polymerization has yet to be demonstrated [2].

A more tenable approach to identifying plausible pre-RNAs may be to explore the reactions of nitrogen heterocycles under conditions that simulate some of the chemical complexity expected for prebiotic Earth. Nitrogen heterocycles may have been readily available on early Earth, and are of particular interest in this bottom-up approach because they are important components of RNA, DNA, and coenzymes [3-5]. In this study, we explore the reactivity of a large set of nitrogen heterocycles in complex prebiotic mixtures produced from a Miller-Urey spark-discharge apparatus. The synthesis of substituted heterocycles may offer potential solutions to the difficulty of glycoside bond formation on free canonical nucleobases and the first step towards a plausible pre-RNA.

Methodology: Spark-discharge experiments were carried out in the presence of water (pH 8) under two different atmospheres: (1) 40% N₂, 10% CO₂, 25% H₂, and 25% CH₄ or (2) 30% N₂, 10% NH₃, 10% CO₂, 25% H₂, and 25% CO. The resulting complex prebiotic mixture was reacted with an individual heterocycle at 30 °C or 80 °C for 1-3 days. A total of 50 heterocycles representing different classes such as pyridines, pyrimidines, triazines, purines, and pteridines were investigated to systematically explore general reaction trends and to increase the likelihood of observing heterocycle adducts. A high resolution linear ion trap-orbitrap hybrid mass spectrometer with a direct analysis in real-time (DART) ion source was used to rapidly analyze the complex chemical profile for each reaction mixture. Heterocycle adducts were tentatively identified using molecular formulae as determined by accurate mass measurements and comparison to controls (*i.e.*, heterocycle reference standards and spark-discharge mixtures).

Preliminary Results: We have produced a large data set due to the very high number of samples that were analyzed. From a preliminary analysis, nitrogen adducts were observed in multiple reaction mixtures. Ongoing work includes extensive data analysis and an

effort to elucidate the exact structure of heterocycle adducts and whether their mechanism of synthesis is robust.

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