The Robustness of the Urea-Ammonium Formate-Water Mixture as a Prebiotic Solvent

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Introduction:

The dehydration reaction between a phosphate mineral and an organic substance is unfavorable in a water-based environment. On the early Earth it is hypothesized that apatite was the dominant phosphate mineral [1]. Phosphates are poorly soluble and poorly reactive in water under typical (pH \sim 7) conditions. This is problematic because an efficient process for the synthesis of organophosphates relies on the availability of soluble and/or reactive phosphorus compounds.

Purpose of study:

A semi-aqueous solvent consisting of urea (U), ammonium formate (AF), and water (W) was investigated for the range of fluid-forming conditions potentially available. This solvent was chosen due to the prebiotic nature of the compounds and their prebiotic availability [3,4]. In recent work this semi-aqueous solvent, in the 1:2:4 (U:AF:W) molar ratio, has been shown to create formamide under mild conditions. Furthermore, phosphate minerals are increased in solubility and phosphorylate of nucleosides proceed spontaneously in appreciable quantities [5].

Methods:

The solvent, in varying U:AF molar ratios, were analyzed in a mild environment of an open system heated to 70 °C. The solvents were scanned with H-NMR to determine the composition of fluids present in these solvents over a one week period. Following this study the solvents, in varying molar ratios, were then subjected to wet/dry cycling over a 1 month time frame and again analyzed by H-NMR to determine final compositions.

Significance:

This semi-aqueous solvent has demonstrated robustness through various conditions. Independent of initial molar ratios, the composition of this solvent settles onto a specific final composition in which a four compound milieu of urea, ammonium formate, formamide, and water was created. The one-pot, "warm little pond" origin of life hypothesis was suggested by Charles Darwin in 1871. This work gives credence to this postulate demonstrating that the "pond" may actually be a very robust semi-aqueous solvent composed of simple inorganic compounds that arises spontaneously under a number of geochemical conditions, and enhances solubility of phosphates while simultaneously permitting dehydration reactions.

References:

[1] Robert M. Hazen (2013) *American Journal of Science* 313:807-843. [2] Stanley L. Miller (1953) *Science* 117:528-529. [3] R. Lohrmann, L.E. Orgel (1971) Science 171:490-494. [4] Allen M. Schoffstall (1976) Origins of Life 7:399-412. [5] Bradley Burcar, Matthew Pasek, Maheen Gull, Brian J. Cafferty, Francisco Velasco, Nicholas V. Hud, and César Menor-Salván (2016) *Angewandte Chemie* 55:13249–13253.