Synthesis of Meteoritic Reaction Intermediates

Andro. C. Rios[1] and George Cooper[2]

[1]Blue Marble Space Institute of Science, Exobiology Branch, NASA-Ames Research Center, MS 239-4, Moffett Field, CA 94035, andro.c.rios@nasa.gov.

[2]Exobiology Branch, NASA-Ames Research Center, MS 239-4, Moffett Field, CA 94035, george.cooper@nasa.gov.

Introduction: The organic compounds of carbonaceous chondrites are structurally diverse products of the prolonged abiotic chemistry that occurred before and during the early stages of the solar system [1]. They also represent the types of prebiotic compounds that may have participated in chemical evolutionary processes that gave rise to life [2]. Pyruvic acid is a key component of primary metabolism that has recently been found in carbonaceous chondrites [3]. Its prominence in biology has inspired us to explore its chemistry and possible role in the origin of metabolism. Our laboratory investigations have found that pyruvate (the ionized form of pyruvic acid) can serve as a single-source reactant to generate what we term a pyruvate reaction network (PRN). The core of the PRN is driven by pyruvate aldol polymerization and decay reactions. These decay reactions lead to the production of stable and unstable compounds which include mono, di, and tricarboxylic acids and a variety of keto acids.

Finding evidence of this reaction network in meteorites would establish that the chemistry of pyruvate did occur in a prebiotic environment. Many of the known compounds found in pyruvate reaction mixtures were originally detected in meteorite samples by Cooper et al in 2011. However, multiple synthetic origins not tied to pyruvate chemistry might also explain their meteoritic presence. Thus, a search to find compounds unique to the PRN, such as reaction intermediates, would provide stronger evidence to demonstrate its prebiotic relevance. The identity of these intermediates can only be confirmed by acquiring chemical standards, however, as most are not available commercially, they need to be accessed through chemical synthesis.

Experimental: Synthetic experiments were conducted using methyl or ethyl ester precursors for ease of handling, purification and subsequent experimentation. Product purity and structural verification was obtained by LC-MS, ^{1}H and ^{13}C NMR spectroscopy. Laboratory investigations of sodium pyruvate used to model prebiotic chemistry were carried out under aqueous alkaline conditions (pH 10, carbonate buffer) at varying temperatures and concentrations. Time course progress of pyruvate reactions were monitored via liquid chromatography-mass spectrometry (LC-MS and LC-MS/MS) in order to develop a reaction map of pyruvate products. Comparison of synthesized products and isolated pyruvate reaction mixtures with meteorite data and fresh meteoritic samples were made using sample derivatization (TBDMS) procedures prior to GC-MS analyses as previously described. [3]

Results and Discussion: Synthetic investigations have helped identify unsaturated keto acids as precursors to dicarboxylic acid compounds. Four dicarboxylic acids result from thermal or oxidative decarboxylation reactions and have long been known to occur in meteorites [4], [5]. One of these unsaturated keto acids have been matched with two meteorite samples, the other isomers have not been found. However, based on our synthetic experimentation, the one identified in meteorites was found to dominate under most reaction conditions and the others might simply be converting to it through a facile enolization reaction as they progress to equilibrium.

Synthetic work is still underway for matching isomeric mixture of mature PRN compounds i.e., those that are suspected to result from subsequent chemistry of pyruvate aldol trimers in meteorite samples. Based on our reaction monitoring studies the production of these intermediates appear to be part of the pathway for downstream product keto acids.

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