

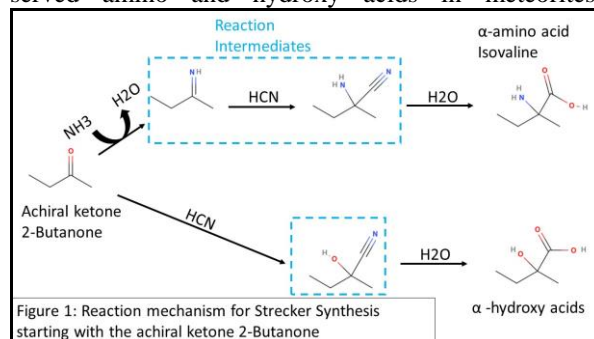
Re-Evaluating the Plausibility of the Strecker Cyanohydrin Formation Pathway for Hydroxy Acids in Meteorites. Ernest K. Lewis¹ and Aaron S. Burton^{*2}, ¹NASA Postdoctoral Program Sr. Research Fellow, Administered by USRA, NASA Johnson Space Center, Houston TX 77058 (ernest.k.lewis@nasa.gov), ²Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, Houston, TX 77058 (*aaron.burton@nasa.gov)

Introduction: Miller's demonstration that amino acids, and subsequently hydroxy acids, could be produced from simply CNO and H-bearing precursors during exposure to spark discharges profoundly changed our understanding of the origins of life.[1] The products of these well-known experiments were predominantly α -amino, α -hydrogen, and α -hydroxy, α -hydrogen acids.

The Strecker cyanohydrin pathway has been well characterized as a consequence of its extensive utility for the synthesis of α -amino and α -hydroxy compounds. A key feature of this pathway is the reversibility of the cyanide additions to oxo- and imine-bearing molecules. In the case of aldehydes and imines, hydroxy and amino nitriles are generally stable.

The amino acid isovaline is of particular interest for prebiotic chemists because it is fairly abundant in certain meteorites, and it has been found in L-enantiomeric excesses, of extraterrestrial origin, of up to 20% in many of the meteorites in which it has been found.[3] Meteoritic amino acids are the only known example of enantiomeric excesses occurring without biological intervention; understanding the origins of the isovaline enantiomeric excesses may be key for understanding how life ended up with predominantly L-amino acids in its proteins. Because isovaline is an α -amino acid, it has been presumed to have formed in meteorites by Strecker cyanohydrin chemistry; this is supported by the observation that its hydroxy acid analog, 2-hydroxy-2-methylbutanoic acid has also been found in meteorites that contain isovaline. However, this conclusion has not been tested experimentally, and no Strecker synthesis intermediates (i.e., amino/hydroxy-nitriles or amides) have been detected directly in meteorite extracts. Here we investigate the plausibility of Strecker cyanohydrin experimentally by searching for these key reaction intermediates directly, by gas chromatography-mass spectrometry (GC-MS) and this is shown in Figure 1. Starting with the achiral ketone 2-butanone, the overall reaction mechanism has two pathways where if the first step is ammonia addition, followed by cyanide, then the α -amino nitrile precursor to isovaline is formed. If the first step is addition of HCN, then the hydroxynitrile precursor to hydroxy acids is formed. Our studies focused on developing the methods and technique to examine the reaction intermediates shown in Figure 1 (blue dotted boxes). The stability of these intermediates and the relative rates of their hydrolysis to amino and hydroxy ac-

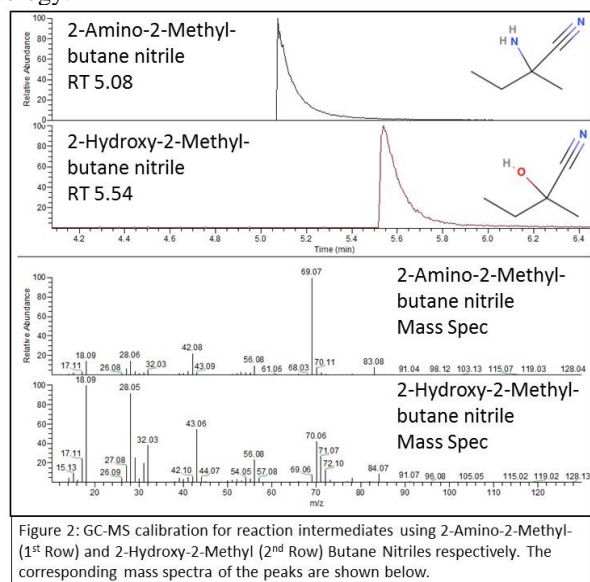
ids, versus their decomposition back to NH_3 , CN, and 2-butanone, should be a determining factor for the observed amino and hydroxy acids in meteorites.



Samples and Analytical Approach: Individual Strecker-type reactions were performed with the ketones acetone and butanone; and the aldehydes formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde. Preliminary Strecker reactions were initiated with the addition of NaCN and NH_4Cl in equimolar amounts, and allowed to react in order to examine the effects of steric hinderance, and carbonyl reactivity of the reagent precursors. The GC-MS method was developed and optimized using pure standards of 2-hydroxy-2-methyl-butanenitrile and 2-amino-2-methyl-butanenitrile to obtain baseline peak separations on a standard Restek Rxi-5ms column (30m length, 0.25mm ID, 0.25um film thickness). The GC temperature profile was set for ramp of 5 °C / min starting from 40 °C up to 75 °C, then increased to 300 °C at 125 °C / minute to desorb everything from the column. The ISQ Mass spectrometer was operated in electron impact (EI) mode at 70 eV, and scanned between 10-225 m/z with total run times averaging around 10 minutes. Aliquots of reaction samples were taken and analyzed for both hydroxy- and aminonitriles as a function as a function of time, temperature and reagent concentration. Solvents dichloromethane (DCM), acetonitrile (ACN), methanol (MeOH) and water were explored in order to determine the effects of solvent composition on reagent rates and compound stability. Limit of detection studies were performed on authentic standards. In parallel, new methods for comparing aqueous extracts from milligram and smaller meteorite samples, which are characterized mineralogically post-extraction, are being developed with the application of ion-mobility mass spectrometry systems. Ion mobility can provide a means for rapid cross comparisons, along with a novel

2D analysis of complex reaction mixtures in the future that are directly pertinent to organics analyses in meteorites and other astromaterials.[4]

Results and Discussion: Analytical detection limits for the 2-hydroxy-2-methylbutanenitrile and 2-amino-2-methylbutanenitrile were measured along with other reaction by-products using various aldehydes. Shown in Figure 2 are the GC separations and Mass Spectra of the calibrants used to develop this methodology.



On-going research is examining the lifetimes of these Strecker reaction intermediates within aqueous environments. While the 2-amino-2-methylbutanenitrile seems to be stable in aqueous systems, the 2-hydroxy-2-aminobutanenitrile degrades rapidly. This hints that there could be some stability and reactivity issues when extrapolating this reaction mechanism to that of a meteorite parent body during aqueous alteration. This limited stability of 2-hydroxy-2-aminobutanenitrile would seem to make it unlikely that 2-hydroxy-2-methylbutanoic acid observed in meteorites is formed by the Strecker cyanohydrin pathway, raising the possibility that different chemical mechanisms are responsible for this compound, and perhaps isovaline as well.

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