

Amino Acids from Icy Amines: A Radiation-Chemical Approach to Extraterrestrial Synthesis. R. L. Hudson^{1,2}, J. P. Dworkin^{1,3}, and M. H. Moore^{1,4}, ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771 ²reggie.hudson@nasa.gov, ³jason.p.dworkin@nasa.gov, ⁴marla.h.moore@nasa.gov.

Detections of amino acids in meteorites go back several decades, with at least 100 such compounds being reported for the Murchison meteorite alone [1]. The presence of these extraterrestrial molecules raises questions as to their formation, abundance, thermal stability, racemization, and possible subsequent reactions. Although all of these topics have been studied in laboratories, such work often involves many variables and unknowns. This has led us to seek out model systems with which to uncover reaction products, test chemical predictions, and shed light on underlying reaction mechanisms. This presentation will describe one such study, focusing on amino-acid formation in ices.

Over the past two years, we have investigated amino-acid synthesis at low temperatures, particularly the production of isovaline and valine. Isovaline is especially interesting, as it is a non-biological meteoritic amino acid that is impossible to make by the oft-invoked Strecker process. Past experiments with the low-temperature energetic processing of ices have uniformly failed to show isovaline formation and, in most cases, also have failed to show any predictive power. Our own approach has been to try and produce amino acids via radiation-chemical pathways using only identified meteoritic compounds. For the cases of valine and isovaline, Figure 1 summarizes reactions observed between CO₂ and two different butylamines. This work showed unequivocally, for the first time, that isovaline and valine can be made by low-temperature energetic processing of a cosmic-ice analog [2].

In each of our CO₂-butylamine experiments, it was a C-H bond adjacent to the amino (-NH₂) group which was altered to form the amino acid of interest, although other reaction sites were possible and, in some cases, important. We now have extended and tested these initial experiments by (a) examining reactions of CO₂ with other butylamine isomers and (b) conducting reactions between CO₂ and smaller amines. In all experiments, ¹³CO₂ + amine ice mixtures were ion-irradiated and warmed under vacuum in Goddard's Cosmic Ice Laboratory, and the residual products were analyzed by LC/ToF-MS in Goddard's Astrobiology Analytical Laboratory. Protocols involved blanks and standards. The use of ¹³CO₂ allowed us to discriminate between authentic reaction products and those from atmospheric CO₂ contamination.

Our recent experiments will be presented at AbSciCon 2010, and so here we describe but one new result, from the irradiation of an icy CO₂ + ethylamine

(CH₃CH₂NH₂) mixture. Two different carbons (methyl and methylene) were available for C-H bond breakage, and so only three amino acids were expected, and chromatographic traces showed that only three were found. See Figure 2 for the reactions. Our combined new and old experiments attest to the predictive power and overall sturdiness of these methods for making amino acids from amines in icy environments.

This work has been supported by a grant from NASA's Exobiology program and by additional funding from the NASA Astrobiology Institute, through the Goddard Center for Astrobiology.

References: [1] Pizzarello, S., Huang, Y., and Alexandre, M. R. (2008) *PNAS*, 105, 3700-3707. [2] Hudson, R. L., Lewis, A. S., Moore, M. H., Dworkin, J. P., and Martin, M. P. (2009) *IAU Symposium: Molecules and Microbes*. San Juan, Puerto Rico (accepted; in press).

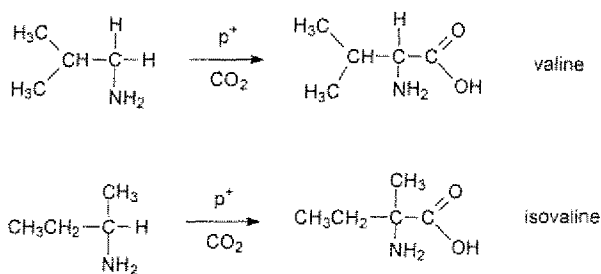


Figure 1

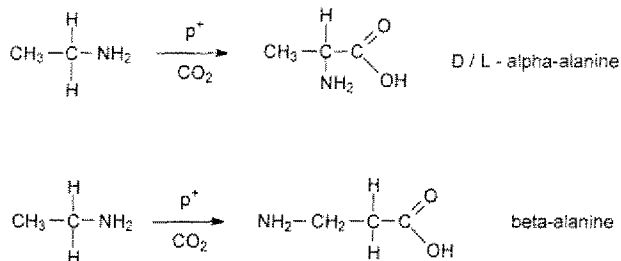


Figure 2