

# Ab initio simulations and the Miller prebiotic synthesis experiment

Saitta and Saija (1) claim that ab initio simulations of the 1953 Miller experiment (2) provide new insights into the mechanism of prebiotic synthesis of glycine (Gly) and, by implication, other molecules in this classic experiment. However, decades of research into prebiotic amino acid formation in such experiments conflict with their conclusions. Many aspects of their simulations and conclusions are not applicable to Miller-type experiments and add little insight into prebiotic amino acid synthesis.

Saitta and Saija state that “treatment of aqueous solutions under electric fields” indicates that Gly “spontaneously forms” from formamide ( $\text{HCONH}_2$ ). However, in Miller’s experiment, a spark was discharged on a gas phase mixture of  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , etc. Reactive species, such as HCN and aldehydes/ ketones, are formed from the gases by the spark. These subsequently dissolved in the aqueous phase, where reactions such as the Strecker amino acid synthesis yield Gly and other compounds (2). This is supported by measurements of HCN, aldehydes, and amino acids during the course of the experiments. Thus, in the experiments, the spark does not discharge directly on the aqueous phase but rather is several centimeters above it, in contrast to Saitta and Saija’s scenario. Although Saitta and Saija suggest electric fields near mineral surfaces in water might initiate prebiotic synthesis, these fields would be much weaker than those associated with lightning. Amino acid synthesis from Miller-type

reactions likely also proceeds via other complex processes. For example, in simulations of Titan tholin chemistry hydration of dry  $\text{CH}_4/\text{N}_2$  mixtures produces a very similar suite of amino acids as in “wet” Miller-type experiments (3).

As Saitta and Saija note (1), the synthesis of Gly from  $\text{HCONH}_2$  using a “silent” discharge has been known for over a century.  $\text{HCONH}_2$  is made in Miller-type experiments from the hydrolysis of HCN, a gas phase reaction product (2), via aqueous phase hydrolysis. Under the conditions used in Miller’s first published experiment ( $\text{pH} \sim 9$ ,  $100^\circ\text{C}$ ), HCN has a half-life of  $<1$  d, whereas that of  $\text{HCONH}_2$  is  $<1$  h (4). At best,  $\text{HCONH}_2$  is a relatively inert, transient, aqueous-phase by-product of the experiment. Both HCN and  $\text{HCONH}_2$  are more stable at lower temperatures, but the half-life of  $\text{HCONH}_2$  is always shorter than that of HCN. Although some Gly might be formed from  $\text{HCONH}_2$  in for example evaporative basins, the amount would likely be small compared with that derived from aqueous Strecker reactions that yield Gly from even very dilute reactants. It is thus unclear how  $\text{HCONH}_2$  and  $\text{HCOOH}$  could be “key intermediate products” or the “crucible of formation of complex biological molecules.”

There is a large amount of literature showing that, on heating neat (pure)  $\text{HCONH}_2$  above  $100^\circ\text{C}$ , amino acids and nucleobases are produced. However, neat  $\text{HCONH}_2$  is not likely to be geochemically

plausible. There are no known feasible processes for the generation of neat  $\text{HCONH}_2$  in a realistic primitive Earth environment. The hygroscopic nature of neat  $\text{HCONH}_2$  promotes  $\text{HCONH}_2$  hydrolysis (5), indicating that unless there was a robust process of continuously generating neat  $\text{HCONH}_2$ , it would not have been abundant on the early Earth.

**Jeffrey L. Bada<sup>a,1</sup> and Henderson James Cleaves II<sup>b,c</sup>**

<sup>a</sup>*Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093;* <sup>b</sup>*Earth-Life Science Institute, Tokyo Institute of Technology, Minato-ku, Tokyo, 152-8550, Japan; and* <sup>c</sup>*Institute for Advanced Study, Princeton, NJ 08540*

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<sup>1</sup>To whom correspondence should be addressed. Email: jbad@ucsd.edu.