ATMOSPHERIC ACETYLENE AND THE GLYOXYLATE SCENARIO

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Introduction

.Acetylene is an abundant component in Titan's atmosphere and there is about 1% of acetylene in Titan lakes [1] Also, it is one of the products or irradiation of methane-containing atmospheres [2] and it can be an component of an early Earth atmosphere. In spite of its occurrence, acetylene has been traditionaly overlooked as a prebiotic precursor until recently. UV irradiation of an acetylene-rich atmosphere over an urea solution subjected to freeze-melt cycles (which generates an interstitial eutectic) lead to the formation of pyrimidines, purines and hydantoins [3]. We postulated that the mechanism of prebiotic formation of hydanoins involves the formation of glyoxal and glyoxylic acid by photochemistry of acetylente in presence of water. An efficient prebiotic formation of glyoxylic acid is necessary for the hypothetical glyoxylate scenario proposed by Eschenmoser [4] for the prebiotic origin of carbohydrates and 'biochemical' carboxylic acids. It is also been suggested as ancient backbone component in the early evolution of RNA [5]., In order to substantitate the prebiotic plausibility of the glyoxylate, we investigated whether acetylene could be an efficient precursor of glyoxylic acid and other molecules related to the glyoxylate scenario.

•[1] Cordier D. et al. (2009) Astrophys. J. Lett. 707, L128. [2] Kasting, J.F. et al. (1983) Precambrian Res. 20, 141-148. [3] Menor-Salvan C. and Roig Marín-Yaseli M. (2013) Chem. Eur. J. 19, 6488-6498. [4] Eschenmoser A. (2007) Tetrahedron 67, 12821-12844. [5] Bean H.D. et al. (2006) Orig. Life Evol. Biosph. 36, 39-63. [6] Menor-Salvan C. et al. (2008) Chem. Biodiv. 5, 2729-2739

• Experimental model consist in the irradiation at 254 nm of a controlled atmosphere formed by acetylene and water vapor over a small pool of pure water, ammonia or urea solutions in the range -25ºC to RT.

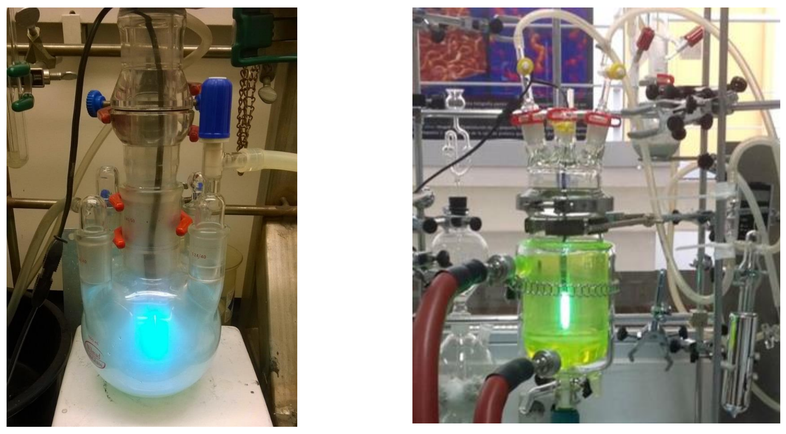
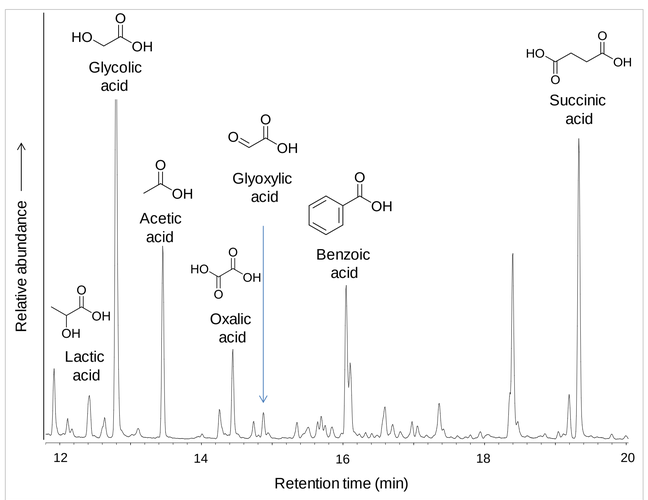
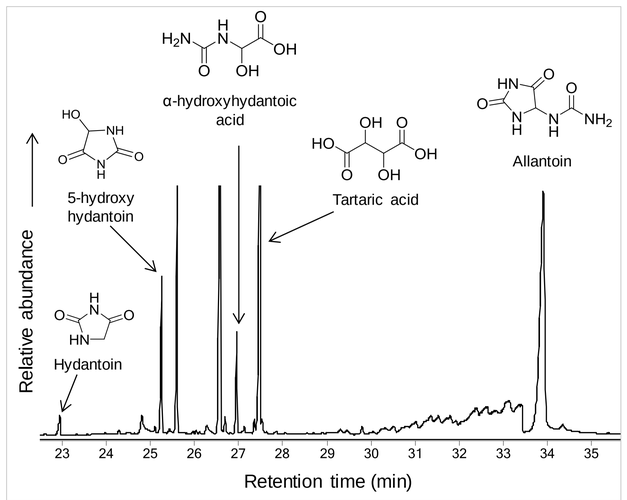


Figure 1: Reactors used in the experiments.

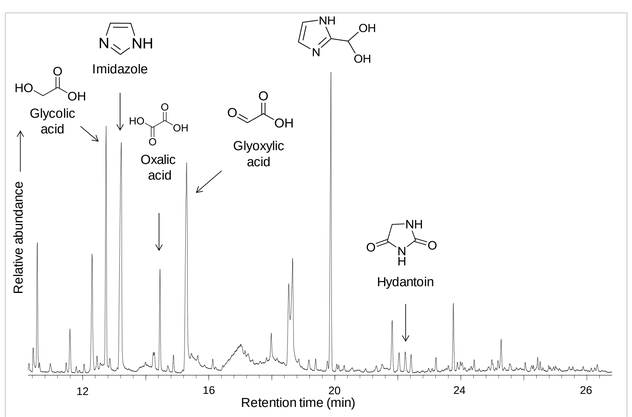
Results



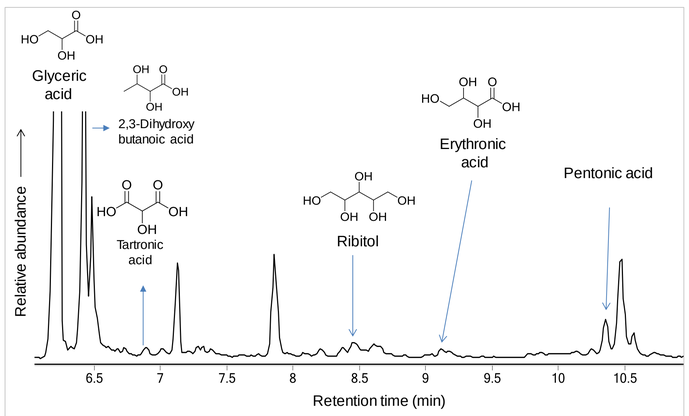
•Fig.1. GC-MS analysis of the product UV irradiation (254 nm, 72 h) of an acetylene atmosphere (100 mmol) over a pure water pool subjected to freeze-melt cycles. Analysis performed after freeze-drying of the water solution followed by silylation with BSTFA. Major product formed is glycolic acid (0.17 mmol)



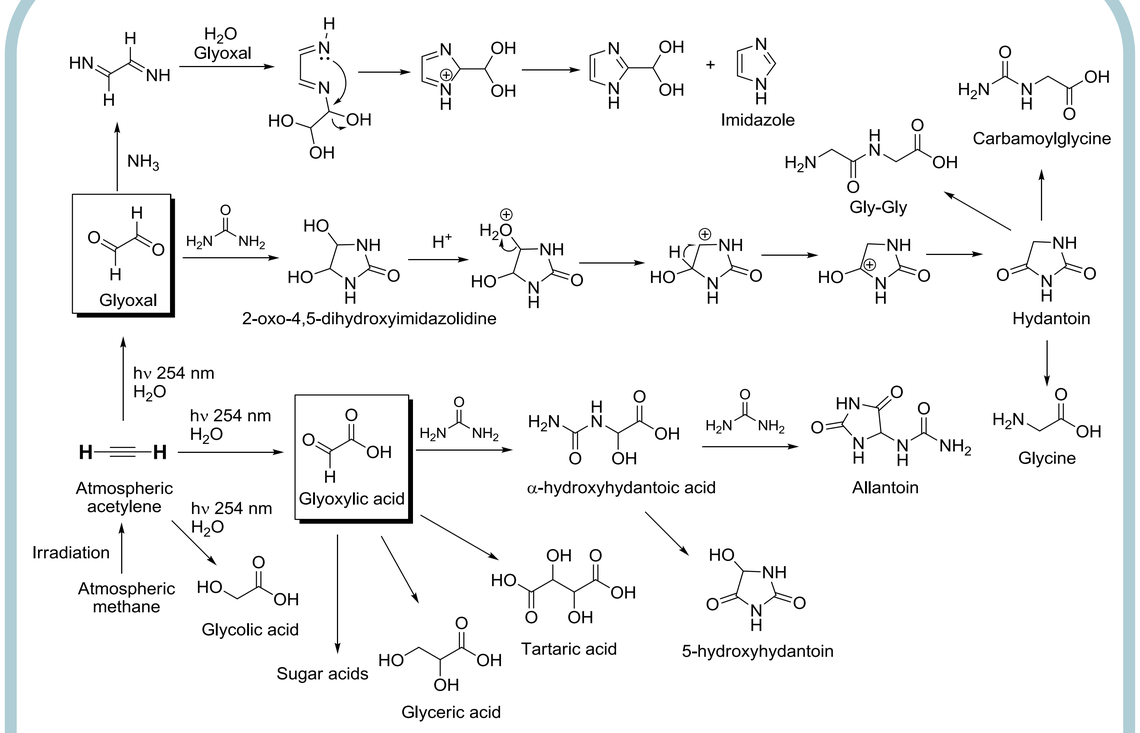
•Fig.2. GC-MS analysis of the reaction between glyoxylic acid (5 mmol) and urea (10 mmol) in water solution under inert atmosphere, subjected to freeze-melt cycles (-25-5ºC) and UV irradiation (254 nm, 72h). Analysis performed after freeze-drying of the water solution followed by silylation with BSTFA. Major product formed is allantoin (3.5 mmol). The two diastereomers of tartaric acid are visible.



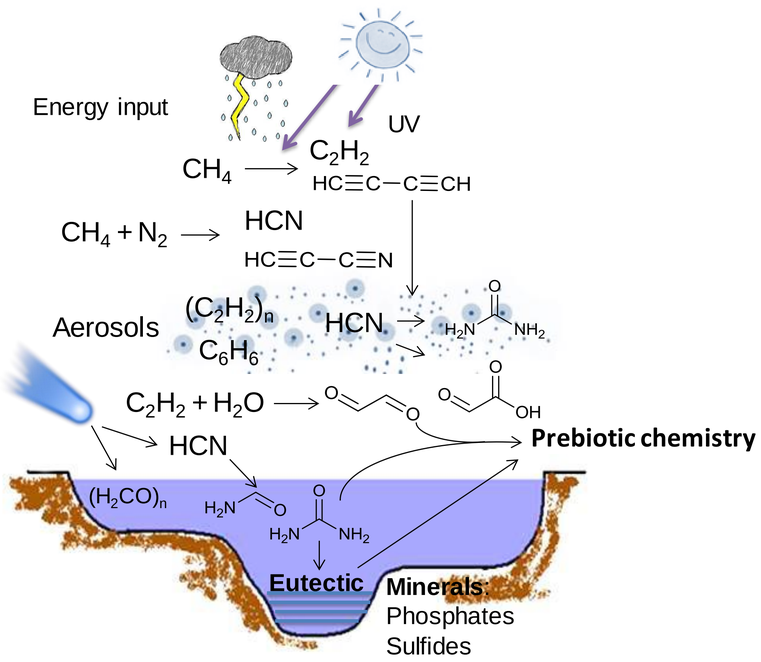
•Fig.3. GC-MS analysis of the product of irradiation of an acetylene atmosphere (100 mmol, 254 nm) over a 1 M ammonia solution (25 mmol) subjected to freeze-melt cycles (-25-5ºC). Analysis performed after freeze-drying of the water solution followed by silylation with BSTFA. These conditions favor the formation of glyoxylate, with calculated 0.7 mmol of free acid in the final product.



•Fig.4. GC-MS analysis of the product of irradiation of an acetylene atmosphere (100 mmol, 254 nm) over a saturated Ca(OH)2 solution. Analysis performed after freeze-drying of the water solution followed by silylation with BSTFA.



•Atmospheric acetylene could be a significant source of prebiotic glyoxylate and five membered nitrogen heterocycles, including imidazole and hydantoin, which is an important prebiotic nitrogen reservoir and potential precursor in the nucleobase chemical space.



Acknowledgements

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