

Photoionization and fragmentation of cyclic dipeptides, experimental and computational efforts on the search of the 'seeds of life'

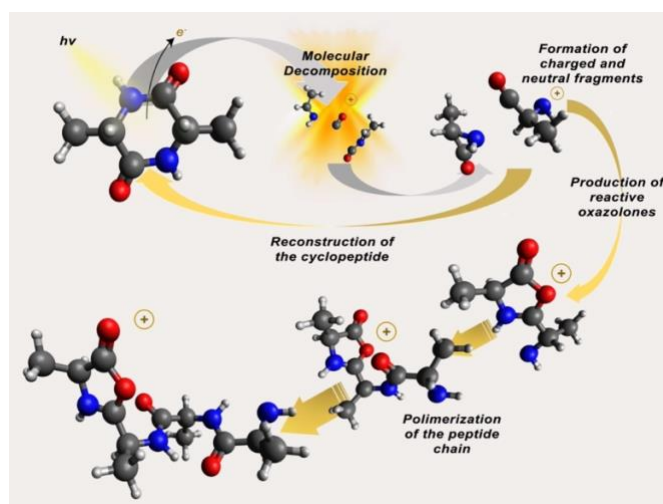
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Since the well-known Miller's experiment [1] in the 50s, the origin of biologically relevant compounds in abiotic conditions has attracted a lot of interest. Several investigations on the synthesis of early Earth organic compounds have been reported and the concept of a 'prebiotic soup', where some kind of activation triggers the spontaneous formation of such species, has been proposed as a likely milieu for the first appearance of complex molecules necessary for life.

In this work, we propose a new and alternative synthetic route for the formation of peptide chains that does not require a catalyst or an aqueous environment. In a collaboration among the groups at CNR-ISM, University Autonoma Madrid, Stockholm University and Elettra Sincrotrone Trieste state-of-the-art experiments and extensive simulations have been combined to show that VUV ionizing radiolysis of cyclo(alanine-alanine) [2,3], one of the simplest 2,5-Diketopiperazines (DKP) produces reactive cationic and neutral fragments such as oxazolidinones intermediates. Reactions of these fragments may lead to the reconstruction of the original cyclic dipeptide, demonstrating that it can survive rather hostile ionizing environments, or to the formation of longer linear peptide chains, thus playing a key role in the early stages of the chemical evolution of the life.

The study of other cyclic dipeptides like cyclo(glycine-alanine) and cyclo(glycine-glycine) provides the opportunity to probe the generality of the proposed mechanisms. The results show complex fragmentations far from trivial or generalisable from one species to another.



The 'smart decomposition' of cyclo(alanine—alanine) dipeptide under VUV irradiation

- [1] Miller, S. L. A "Production of Amino Acids under Possible Primitive Earth Conditions" *Science* 1953, 117 (3046), 528–529.
- [2] D. Barreiro-Lage et al. "Smart Decomposition" of Cyclic Alanine-Alanine Dipeptide by VUV Radiation: A Seed for the Synthesis of Biologically Relevant Species, *J. Phys. Chem. Lett.* 2021, 12, 7379–7386
- [3] J. Chiarinelli et al. "Electron and ion spectroscopy of the cyclo-alanine—alanine dipeptide" *Phys. Chem. Chem. Phys.*, 2022, 24, 5855
- [4] D. Barreiro-Lage et al. "Photofragmentation specificity of diketopiperazines - photoionized cyclic amino acids as precursors of peptide building blocks", to be submitted (2022)