

CHEMICAL EVOLUTION OF ORGANIC MOLECULES UNDER MARS-LIKE UV RADIATION CONDITIONS SIMULATED IN THE LABORATORY WITH THE MOMIE SETUP. O. Poch^{1,2}, P. Coll², C. Szopa³, F. Stalport², T. Georgelin⁴, M. Jaber⁴, J.-F. Lambert⁴, ¹Center for Space and Habitability, University of Bern, Switzerland (olivier.poch@cs.h.unibe.ch), ²LISA, Université Paris-Est Créteil, Université Paris Diderot, CNRS, France, ³LATMOS, UPMC Univ. Paris 6, Université Versailles St-Quentin, CNRS, France, ⁴LRS, UPMC Univ. Paris 6, CNRS, France

Introduction : The search for organic carbon at the surface of Mars, as clues of past habitability or remnants of life, is a major science goal of Mars' exploration. Understanding the chemical evolution of organic molecules under current Martian environmental conditions is essential to support the past, present and future analyses performed *in situ*. What molecule can be preserved? What is the timescale of organic evolution at the surface?

The Mars Organic Molecules Irradiation and Evolution (MOMIE) setup : We address these questions by performing laboratory investigations dedicated to monitor qualitative and quantitative evolutions of several organic molecules under simulated Martian surface ultraviolet light (190-400 nm), mean temperature (218 ± 2 K) and pressure (6 ± 1 mbar), using the Mars Organic Molecules Irradiation and Evolution setup [1].

Samples consisted of thin deposits (from 10 nm to 10 μ m) of a molecular compound or of synthetic smectite clay nontronite in which the molecular compound has been embedded (Figure 1).

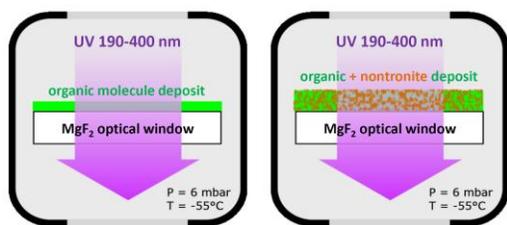


Figure 1 : Scheme of two possible configurations of the sample inside the MOMIE reactor.

We studied organic molecules representative of endogenous and exogenous sources at Mars, and spanning a wide range of chemical functions: an amino acid (glycine), an aromatic hydrocarbon (chrysene), a nucleobase (adenine), a carboxylic acid (mellitic acid) and urea. To match closely their mineral environment at Mars, some of these molecules were put in interaction with nontronite, one of the most abundant clay mineral detected on Mars [2], especially in Gale crater [3]. Both pure organic deposits and deposits of organics mixed with nontronite (Figure 1) were submitted to the simulated Mars surface conditions in the MOMIE

setup. This experimental protocol enables to assess the effect of the clay mineral on the chemical evolution of the organic molecules.

Results of the laboratory simulations : During the evolution of the samples at Martian simulated conditions, qualitative and quantitative changes were monitored, mainly using transmission infrared spectroscopy (Figure 2).

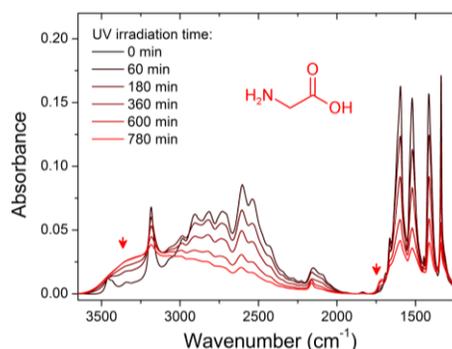


Figure 2 : *In-situ* infrared transmission spectra of a sample of pure glycine at -55°C and 6 mbar and under UV irradiation similar to the Martian one. We observe the decreasing absorbance of the main infrared bands of glycine and the rise of new absorptions (red arrows) [1].

These data allow the determination of kinetic parameters controlling the evolution of organic molecules directly exposed to the solar UV flux reaching the Mars surface, or in interaction with nontronite clay. The results show that the pure molecules have upper half-lives of 10 to 10^3 hours at the surface of Mars, when exposed directly to Martian UV radiation. Quantum efficiency of photodecomposition from 200 to 250 nm have also been determined for several molecules (Figure 3).

The results indicate that aromatic molecules, especially PAH, are at least ten times more resistant to UV on Mars compared to non-aromatic molecules. Additionally, the quantum efficiency of photodecomposition we derived for glycine ($\sim 10^{-3}$ molecule.photon⁻¹) is three orders of magnitude higher than previous estimates done by methane evolved measurements [1]. This difference is attributed to the multiple chemical pathways (both in the solid and gaseous phases) gly-

cine can undergo under Mars UV conditions, which are better taken into account within the MOMIE setup.

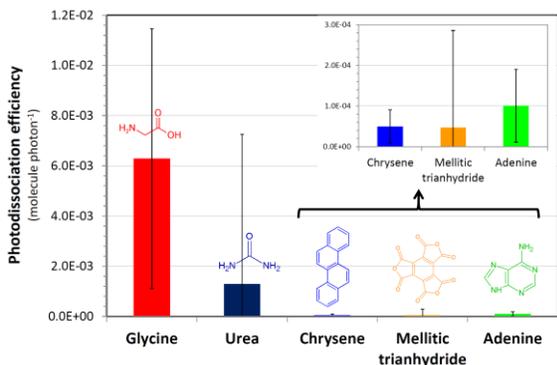


Figure 3 : Quantum efficiency of photodecomposition from 200 to 250 nm for several molecules studied in the MOMIE setup (UV only, no mineral here) [4].

Indeed, *in-situ* infrared spectra and *ex-situ* analyses of the residues obtained after the simulations revealed the formation of solid end-products of chemical evolution. In the case of glycine, we detected the production of a solid residue tentatively produced via polymerization [1]. Red arrows in Figure 2 indicate new absorptions possibly due to H₂O (OH stretching around 3250 cm⁻¹) released by the formation of peptide bonds (C=O stretching of amide at 1680 cm⁻¹). The production of solid residues was also observed after the UV irradiation of adenine and mellitic acid. For these two molecules, the solid photoproducts are probably of higher mass than the parent molecules and they exhibit photo-resistance to further irradiation. FT-IR and UV-Vis spectra showed that these products contain aromatic moieties and extended conjugated systems [4].

Additionally, the study of the evolution of organic molecules in presence of nontronite highlighted a strong protective effect of clay grains of ~10 μm diameter reducing dissociation rates by a factor of 5 for glycine and adenine, whereas a possible catalytic effect was tentatively observed for urea, but need further confirmation [5].

Implications for the search of organic molecules at the surface of Mars : Our laboratory simulations show that when exposed to UV radiation, some specific organic molecules lead to the formation of solid residues, probably of macromolecular nature, which could reach long term stability at the surface of Mars. These kinds of end-products must be targeted by current and future *in-situ* analyses of the Martian soil.

Moreover, our results revealed a pronounced photoprotective effect of nontronite on the evolution of glycine and adenine. Consequently, smectite clay could

be a good target to search for these molecules. Alternatively, the possible catalytic effect observed for urea could indicate a selective protection of organic molecules by nontronite under Mars surface conditions. Further experiments are needed to confirm and enrich this latter result.

Finally, the kinetic parameters we have experimentally determined (Figure 3) provide new input data for numerical modeling of Mars' current reservoir of organic molecules.

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References: [1] Poch O. et al. (2013) *Planetary and Space Science* 85, 188-197. [2] Ehlmann B. et al. (2013) *Space Science Reviews* 174, 329-364. [3] Grotzinger J. et al. (2012) *Space Science Reviews* 170, 5-56. [4] Poch O. et al. *under review*. [5] Poch O. et al. *in preparation*.