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Chemical evolution of organic molecules under Mars-like UV radiation conditions simulated in the laboratory with the “Mars organic molecule irradiation and evolution” (MOMIE) setup

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A B S T R A C T

Understanding the evolution of organic matter on Mars is a major goal to drive and discuss past, present and future *in situ* analyses. Here we demonstrate the ability of the MOMIE (for Mars organic molecules irradiation and evolution) laboratory device in giving both *in situ* qualitative and quantitative data on the evolution of organic molecules under simulated Martian surface ultraviolet light (190–400 nm), mean temperature (218 ± 2 K) and pressure (6 ± 1 mbar). We describe the chemical evolution of glycine, an amino acid, which is very rapidly processed when exposed to direct ultraviolet radiations, with a molecular half-life of 231 ± 110 h on Mars consistent with existing results. Moreover we report the first tentative detection of peptide bond formation activated by UV radiation reaching the Mars surface. We show that organics as simple as glycine could experience multiple chemical pathways at Mars, both in the solid and gaseous phase. Finally, we derive the quantum efficiency for the photodestruction of glycine of $2.18 \pm 1.45 \times 10^{-3}$ molecule photon^{-1} in the 200–250 nm wavelength range. This value is significantly higher than previous estimates done by methane evolved measurements. Current and future studies performed with this simulation setup could produce kinetic and chemical insights into the evolution of organics on Mars.

1. Introduction

As for the Earth, organic matter has been brought to the surface of Mars since its formation, mainly through meteoritic, micrometeoritic and cometary input (Botta and Bada, 2002; Flynn, 1996). Moreover, abiotic synthesis, potential prebiotic chemistry or even past biological activity on Mars could have increased the quantity and the diversity of Martian organic molecules. Organic matter is therefore expected to be present at the surface/subsurface of the planet at concentration levels detectable by space instrumentation. However the Viking and Phoenix landers, partly devoted to detect organics in soil samples, failed to provide absolute evidence of the presence of any organic molecule at their landing sites (Biemann, 1979; Biemann and Lavoie, 1979; Biemann et al., 1976; Boynton et al., 2009). This non detection may be explained by (1) the absence of organics in the soil samples (Biemann, 2007; Biemann and Bada, 2011), or (2) the low sensitivity of the analytical instruments to detect the organic content of the samples (Navarro-Gonzalez et al., 2006), or (3) the functioning of the instruments inducing the decomposition of the organics due to the reactivity of the soil during heating (Navarro-González et al., 2010; Navarro-Gonzalez et al., 2011) or preventing the detection of peculiar molecular structures (Benner et al., 2000). These results motivated a characterization of the Martian environmental conditions likely to have an impact on the quantity and the nature of organic matter. Three main environmental conditions have been proposed to initiate processes impacting organic matter at the surface of Mars: (1) ultraviolet light from the Sun (Oro and Holzer, 1979), (2) oxidation processes at the surface and subsurface (Quinn and Zent, 1999; Zent and McKay, 1994), and (3) energetic particles radiation from galactic cosmic rays (nuclei) and solar flares (mostly protons and electrons) (Dartnell et al., 2007; Kminek and Bada, 2006; Molina-Cuberos et al., 2001).

UV radiation would interact with the first millimeter of the regolith (Cockell and Raven, 2004; Córdoba-Jabonero et al., 2005;

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France et al., 2010) and energetic particles would interact with organics buried in the first meters of depth (Dartnell et al., 2007; Kminek and Bada, 2006), whereas oxidation processes could be efficient until 200 m of depth (Bullock et al., 1994; Zent, 1998).

Studying the influence of these surface environmental conditions on organic molecules is of prime interest to understand the chemical evolution of organic matter at Mars, to finally guide and discuss past, present and future *in situ* analyses. In this paper we present an experimental device enabling to simulate and follow *in situ*, at mean Mars temperature and pressure, the evolution of organic molecules submitted to ultraviolet photons in the range of energy representative of those reaching the surface of Mars.

2. Mars-like UV laboratory simulation setups: State of the art and new developments

Table 1 highlights some key parameters of former laboratory simulations submitting pure or mixed organic molecules to simulated Martian ultraviolet light (Hintze et al., 2010; Johnson and Pratt, 2010; Oro and Holzer, 1979; Schuerger et al., 2008; Stalport et al., 2008, 2009, 2010; Stoker and Bullock, 1997; Ten Kate et al., 2005, 2006) (for a comprehensive review including meteoritic material irradiation, read Table 2 in ten Kate (2010)). Among these parameters, the use of a Xenon arc lamp as the irradiation source has proven to better reproduce the energy and relative abundance of the ultraviolet photons (190 to 400 nm) supposed to reach the surface of Mars (Schuerger et al., 2003) compared to mercury, hydrogen or deuterium lamps that poorly match the solar irradiance at these wavelengths. Moreover, temperature and pressure also have to be representative of the Martian ones for several reasons. First because temperature can influence the kinetic of the reactions taking place in the simulation reactor (Ten Kate et al., 2006), as pressure may also do (Keppler et al., 2012). Second because the chemical stability and physical state (solid or gas) of the products is largely dependent of these parameters. Temperature and pressure control is also essential during the analyses of the samples. Indeed, if analyses are required to be done outside the reactor, residues obtained after the simulation can be altered by the laboratory conditions (heating upon return to room temperature and pressure, humidity, atmospheric gases etc.). Thus, when it is possible, analysis should be made during the simulation at constant environmental conditions in order to retrieve information on both the kinetic of transformation and the nature of the products (quantitative and qualitative results, as indicated in Table 1).

Thanks to the expertise gathered by former simulation experiments, the new version of the MOMIE setup combines a representative simulation of Martian environmental conditions (UV range and spectrum, temperature and pressure) along with the capability to conduct qualitative and quantitative chemical analysis *in situ* during the simulation (see Table 1). Additionally, the combination of a nanometer thin organic sample with a high photons flux (see Section 3.2 and Section 3.4) improves the accuracy of the kinetic measurements (photodissociation rates, half-lives) and maximizes the chance of detecting potential solid end-products of the studied compounds. The capabilities of the MOMIE device have been tested with samples of glycine. This amino acid, mainly studied within Martian surface context (Oro and Holzer, 1979; Stalport et al., 2008; Stoker and Bullock, 1997;

Table 2
Spectral assignments and wave numbers of infrared bands of glycine deposits.

Label	Wavenumber (cm^{-1})		Band assignment[e]
	This work (218 K, 6 mbar)	Reference	
a	3457	3437[b]	νOH ?
b	3183	3186[a]	$\nu_{as}NH_3^+$
c	2980	2977[b]	$\nu_{as}CH_2$
d	2905	2899[b]	$\nu_sNH_3^+$
e	2812	2826[a]	$\delta_sNH_3^+ + \omega CH_2$
f	2730	2733[b]	$\delta_{as}NH_3^+ + \rho NH_3$
g	2605	2622[b]	$\delta_{as}NH_3^+ + \nu CN$
h	2538	2532[b]	$\delta_{as}NH_3^+ + \rho CH_2$
i	2150	2135[a]	$\tau NH_3^+ + \delta_{as}NH_3$
j	1690	1745[b]	νCOOH ?
k	1663	1664[a,c,d]	$\delta_{as}NH_3^+$
l	1593	1593[a]	$\nu_{as}COO^-$
m	1520	1524[a]	$\delta_sNH_3^+$
n	1415	1413–1421[a]	ν_sCOO^-
o	1336	1334–1340[a]	ωCH_2

Reference wave numbers are taken from:

[a] Uvdal et al. (1990).

[b] Rosado et al. (1998).

[c] Stievano et al. (2010).

[d] Chernobai et al. (2007).

[e] ν, stretching; δ, bending; ω, wagging; ρ, rocking; τ, torsion; *s*, symmetric; as, asymmetric.

Table 1
Laboratory simulations of the evolution of pure or mixed organic molecules under simulated Mars surface ultraviolet light.

Reference	**Sample phase**	**Temperature (°C)**	**Pressure[a] (mbar)**	**Irradiation source**	**Oxidant(s)**	***In situ* analysis**	**Analysis/results**
Oro and Holzer (1979)	Solid	−10 to 25	0.001 (N_2)	Mercury lamp	Dioxygen gas	No	Qualitative and quantitative
Stoker and Bullock (1997)	Solid	R.T.	100 (CO_2+)	Xenon lamp		Yes	Qualitative and quantitative
Ten Kate et al., 2006	Solid	−63 and R.T.	10^{-7} and 7 (CO_2)	Hydrogen and deuterium lamps		Yes	Quantitative
Schuerger et al. (2008)	Solid	−80, −10 and +20	7.1 (CO_2+)	Xenon lamp		No	Qualitative and quantitative
Stalport et al. (2009)	Solid	−54	0.01 (N_2)	Xenon lamp		No	Qualitative and quantitative
Johnson and Pratt (2010)	Aqueous solution	−135 to +40	7 to 15 (CO_2+)	Xenon lamp	Iron sulfates	No	Quantitative
Hintze et al. (2010)	Solid	−10 and R.T.	6.9 (CO_2+)	Xenon lamp		No	Qualitative and quantitative
Shkrob et al. (2010)	Aqueous solution	−196	1000 (N_2)	Nd:YAG pulsed laser	Goethite, hematite, anatase	Yes	Qualitative
MOMIE setup (this study)	**Solid**	**−55**	**6 (N_2)**	**Xenon lamp**	**Mineral, H_2O/H_2O_2[b]**	**Yes**	**Qualitative and quantitative**

[a] Indications relative to the composition of the gas phase are provided in brackets, "CO_2+" indicate a gas mixture simulating the Martian atmosphere, for more information see Table 2 in ten Kate (2010).

[b] Not presented in this paper, but will be implemented in studies to come. Adapted from ten Kate (2010).