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Research Article

Investigating the Photostability of Carboxylic Acids Exposed to Mars Surface Ultraviolet Radiation Conditions

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Abstract

The detection and identification of organic molecules on Mars are of primary importance to establish the existence of a possible ancient prebiotic chemistry or even biological activity. The harsh environmental conditions at the surface of Mars could explain why the Viking probes—the only efforts, to date, to search for organics on Mars—detected no organic matter. To investigate the nature, abundance, and stability of organic molecules that could survive such environmental conditions, we developed a series of experiments that simulate martian surface environmental conditions. Here, we present results with regard to the impact of solar UV radiation on various carboxylic acids, such as mellitic acid, which are of astrobiological interest to the study of Mars. Our results show that at least one carboxylic acid, mellitic acid, could produce a resistant compound—benzenehexacarboxylic acid-trianhydride ($C_{12}O_9$)—when exposed to martian surface radiation conditions. The formation of such products could contribute to the presence of organic matter in the martian regolith, which should be considered a primary target for *in situ* molecular analyses during future surface missions. Key Words: Mars—Laboratory experiments—UV irradiation—Carboxylic acids. Astrobiology 9, 543–549.

Introduction

Mars is known as a primary astrobiological target in that its past environmental conditions are thought to have been favorable for the emergence of a prebiotic chemistry or even biological activity. Since 2004, several missions to Mars, including the Mars Exploration Rovers Spirit and Opportunity, the Mars Express probe, the Mars Reconnaissance Orbiter, and the Phoenix lander, have provided data that indicate a past sustained presence of liquid water on Mars, probably during the first 500 million years of the planet's history (Squyres *et al.*, 2004; Bibring *et al.*, 2006). Current *in situ* exploration at the martian surface includes specific studies to detect organic molecules that could be fingerprints of biological activity, past or present. While simple volatile organic compounds in the martian atmosphere can be detected from orbit, as may be the case for methane, according to Formisano *et al.* (2004) and Krasnopolsky *et al.* (2004), more complex nonvolatile organics present in the regolith, such as carboxylic acids, cannot be detected without *in situ* measurements at the surface.

In 1976, the Viking gas chromatograph–mass spectrometer (GC-MS) instruments carried out highly sensitive measurements of organic compounds at two locations on the surface of Mars. Surface regolith samples collected down to approximately 10 cm deep were heated to temperatures up to 500°C, and the gases that were released by pyrolysis were analyzed by the GC-MS (Biemann *et al.*, 1976, 1977). No organic molecules of martian origin were found above the detection limits of the instruments at the two different landing sites (Biemann *et al.*, 1976, 1977). The Viking results are puzzling since there are a variety of plausible mechanisms that could contribute to the contemporary accumulation of organic compounds on Mars, as follows: (i) Past environmental conditions at the surface may have been favorable to the emergence of life or prebiotic chemistry, and organic remnants of past or present biological activity may be present (Simoneit *et al.*, 1998); (ii) laboratory investigations (Hubbard *et al.*, 1971, 1973) and photochemical models (Wong *et al.*, 2004) predict the formation of organic gaseous compounds in the martian atmosphere, mainly formaldehyde, ethane, and methyl alcohol; (iii) the exogenous delivery of organic compounds by carbonaceous meteorites and micrometeorites (Clemett *et al.*, 1998; Botta and Bada, 2002; Glavin *et al.*, 2004; Pizzarello *et al.*, 2006) over billions of years would have contributed to the accumulation of organic molecules in the regolith of Mars; the predicted present accretion rate of unaltered meteoritic carbon onto Mars is estimated to be approximately 240 tons per year (Flynn and McKay, 1990; Flynn, 1996; Bland and Smith, 2000).

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There are several explanations why the GC-MS experiments did not detect any organics in the samples analyzed. The most straightforward explanation is the absence of organic species in the collected samples. To verify this, several experimental and numerical modeling studies were conducted to evaluate the possibility for the destruction of the organics at the martian surface. Several destruction processes were proposed, as follows:

(i) Hydrogen peroxide was suggested as a possible oxidizer of the martian surface (Oyama and Berdahl, 1977; Oyama *et al.*, 1977). Photochemical processes indicate the formation of gaseous H_2O_2 in the martian atmosphere (Krasnopolsky, 1993; Nair *et al.*, 1994), which has only recently been detected (Clancy *et al.*, 2004; Encrenaz *et al.*, 2004).

(ii) A chemically reactive component in the regolith could result in the decomposition of organic molecules. This reactivity could be attributed to the presence of one or more inorganic superoxides or peroxides in the martian regolith (Yen *et al.*, 2000) or H_2O_2 diffusion into the regolith (Bullock *et al.*, 1994).

(iii) Though a dense atmosphere of CO_2 could have protected the surface from energetic UV radiation (Molina-Cuberos *et al.*, 2001) in the past, the absence of a protective atmosphere in more recent times may have resulted in the photodestruction of organic molecules (Oro and Holzer, 1979; Stoker and Bullock, 1997; Ten Kate *et al.*, 2005, 2006; Schuerger *et al.*, 2008).

(iv) Because the martian surface is unprotected by a global dipole magnetic field or sufficient atmospheric shielding, the ionizing radiation represented by solar energetic protons and galactic cosmic ray particles could penetrate several meters of depth into martian regolith and damage any present organic matter (Dartnell *et al.*, 2007).

Hydrogen peroxide is obviously a good candidate for the oxidation of organics present at the surface of Mars, and it should be noted that dust devils and dust storms could contribute to a more significant production rate (Atreya *et al.*, 2006). However, results of a theoretical study by Benner *et al.* (2000) on the action of OH radicals on organic molecules of meteoritic origin suggest that the totality of organic material would not be entirely oxidized into volatile organic molecules (*i.e.*, CO_2 and H_2O). The chemical pathways described indicate that organics would be converted into carboxylic acids that could have a significant lifetime and, therefore, be detected. Moreover, it was shown that one of the following possibilities is likely true: (i) the GC-MS experiment was not suited to detect such organics at the surface (Glavin *et al.*, 2001; Navarro-Gonzalez *et al.*, 2006) due to their refractory nature or possible thermal decomposition during pyrolysis heating (Benner *et al.*, 2000), (ii) the investigated sites did not have a high preservation potential for organic material, and there were no organics present. Though the presence of superoxides in the regolith has been attributed to the destruction of organics at the martian surface, prior experimental work used mineral substrates (labradorite, a plagioclase feldspar), a partial pressure of oxygen, and a UV source that do not appear to be relevant to conditions at the surface of Mars.

Carboxylic acids could be among the best organic targets for future missions to the martian surface. Given the high concentration of carboxylic acids known to be present in carbonaceous meteorites, Benner *et al.* (2000) concluded that several hundred grams of meteorite-derived mellitic acid may have been generated per m^2 of martian surface over 3 billion years. These species, however, even if they survived oxidation processes, would still be exposed to the harsh surface irradiation conditions described earlier. As the mineral matrices of martian rocks or meteorite and micrometeorite material where these organic acids would be found are exposed to wind erosion processes (Armstrong and Leovy, 2005), they would disaggregate, which would result in the exposure of the organics to solar light. The amount of mineral disaggregation and organic exposure to UV would be enhanced in dust storms and dust devils.

As a consequence and assuming that the theory of Benner *et al.* (2000) is a good postulate for the oxidation of organic matter on Mars, it is of primary importance to determine whether the oxidation products are resistant to the irradiation conditions at the surface of Mars and, if they are, how long they might remain resistant. It would also be important to determine whether these oxidation products can evolve into other organic molecules that would be resistant to the environmental stresses. Indeed, the organic species that are resistant to these different environmental stresses should be considered the best molecular targets in the search for the existence of "complex" organics on that planet and may offer clues as to the history of this material at the regolith surface. In the event that these oxidation products are not resistant, it would be important to determine the kinetics of their photodissociation to evaluate whether they could accumulate at the surface of Mars.

We initiated the study of the resistance of carboxylic acids under martian surface environmental conditions and developed the Martian Organic Material Irradiation and Evolution (MOMIE) laboratory experiments. These experiments focus on the study of the influence of martian surface solar UV radiation on carboxylic acids potentially present on Mars.

Materials and Methods

The MOMIE experiment (Fig. 1) was composed of a glass reactor in which the samples were introduced and irradiated. The samples were powdered with a mortar and then manually placed on the bottom of a 1 cm diameter glass plate. The thickness of each deposit was homogeneous and approximately 0.01 cm, corresponding to a few milligrams in mass. This reactor was put under primary vacuum ($\approx 10^{-2}$ mbar, model TRIVAL E2 vacuum pump). The pump is equipped with an oil separator filter (Pfeiffer Vacuum D-35614) to prevent any contamination by back streaming. The reactor system was actively pumped during the experimental run to evacuate any gases that might be released by the solid sample so as to avoid any modification of the UV radiation flux reaching the solid sample.

The sample had to be cooled to temperatures compatible with those of the martian surface; it has been demonstrated that temperature has a significant influence on the destruction rate of organics (Ten Kate *et al.*, 2006). Therefore, the reactor was cooled to a temperature of approximately 218 K, which is equivalent to the average martian surface temperature (considering seasonal, latitudinal, day/night variations) (Kieffer *et al.*, 1992). This cooling was achieved with a

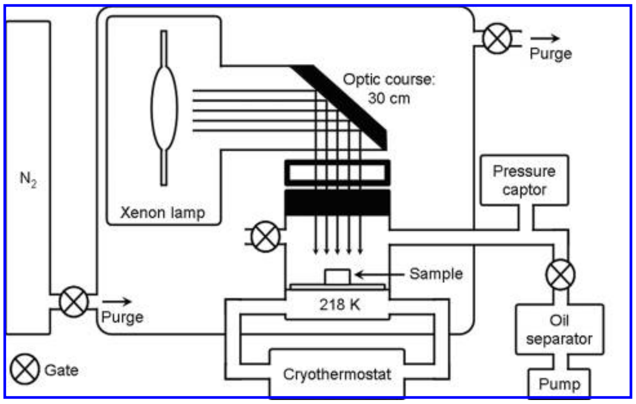

FIG. 1. Schematic of the MOMIE experiment composed of a UV source (xenon lamp), a cryogenic system (average temperature 218 K), an active pumping system ($\approx 10^{-2}$ mbar), and a glass reactor within which the samples are deposited on the bottom of a glass plate. To prevent the absorption of a portion of the lamp UV spectrum by atmospheric gas, the reactor and the lamp were isolated from the laboratory atmosphere in a glove box overpressurized with nitrogen.

cryothermostat (Kryomat LAUDA RUL 80, range 193–373 K) that generated circulation of an appropriate fluid (polydimethylsiloxane) below the sample. The temperature of the organics was controlled with a thermal probe during the irradiation experiment to minimize thermal desorption and thermal decomposition.

The UV source was a 150 W xenon lamp (LOT-ORIEL). The integrated flux in the wavelength range 190–250 nm was $0.23 \pm 0.03\,\mathrm{W/m^2}$ (Fig. 2). This corresponds to the same average integrated flux at Mars for the wavelength range between 0.09 and $0.70\,\mathrm{W/m^2}$ (*i.e.,* calculated from Kuhn and Atreya, 1979; Cockell *et al.,* 2000; Patel *et al.,* 2002). Based on work by others (*i.e.,* Oro and Holzer, 1979; Stoker and Bullock, 1997; Ten Kate *et al.,* 2005), we supposed that this portion of the UV spectrum had the most impact on the organic matter. To prevent the absorption of a portion of the lamp UV spectrum by atmospheric gas, the reactor and the lamp were isolated from the laboratory atmosphere in a glove box overpressurized with pure nitrogen (N_2, purity 99.995%), which does not absorb radiation above 190 nm. A gaseous CO_2 phase was not introduced into the reactor (i) to prevent absorption of the radiation by the gas mixture and (ii) because a martian-like CO_2 atmosphere seems to have no effect on the destruction rate of organic matter (Ten Kate *et al.,* 2006).

It has been postulated that the action of energetic UV photons on the water vapor present in the martian troposphere leads to the formation of OH radicals, which influence the photochemistry of the regolith and the degradation of organic matter (Hunten, 1979). In our experiment, we considered the eventual water vapor presence in the reactor and its influence on the organic degradation rate to be negligible, due to the following:

(i) Before each irradiation, the reactor was heated to a temperature of 343 K for 24 hours. This reactor is in a glove box overpressurized with pure nitrogen. Finally, the active pumping system evacuated the residual laboratory atmosphere.

(ii) Ten Kate *et al.* (2006) indicated that at 10 mbar an atmosphere consisting of 50% CO_2 and 50% water vapor has no influence on the rate of destruction of the organics.

(iii) The photodestruction of H_2O into OH radicals does not occur at wavelengths above 190 nm (Okabe, 1978).

The samples studied with the MOMIE experiment were organic molecules that included mellitic acid (99% purity, Aldrich), benzoic acid (99.5% purity, Fluka Chemika), and oxalic acid (99% purity, Aldrich). These molecules, particularly mellitic acid, could be the final oxidation products of exogenous or endogenous organic compounds on the surface of Mars, and they could be metastable under martian conditions. No inorganic minerals were introduced in the samples because we focused only on the interaction between the radiation and the studied organics. The influence of minerals on the degradation of organic matter under UV could be very important and (*e.g.,* screening, catalysis) will be investigated in the future.

The first step was to determine whether these molecules absorb UV radiation. We analyzed their UV absorbance spectra with a UV/visible spectrophotometer (Perkin Elmer Lambda 2) in the range of 200 to 400 nm at 0.5 nm resolution.

To follow the evolution and the photostability of the targeted organic molecules, we measured, prior to irradiation, the mass of the organic molecule deposits with a microbalance (Mettler AE163). The samples were deposited onto a glass substrate and introduced into the vacuum chamber. They were irradiated by the Xe lamp for various durations. After irradiation, we measured the mass of the irradiated sample with the microbalance and calculated the ratio between the sample mass loss and the initial mass as a function of irradiation time. We then deduced its lifetime. Uncertainties were evaluated by using the measurement precision of the microbalance. For each molecule, we took into consideration the eventual sublimation effects. For this, the sample was deposited in the reactor, following the same irradiation protocol, except the Xe lamp was off. Thus, we quantified the sample mass loss due to sublimation as a function of time at 218 K and 10^{-2} mbar pressure: the mass loss is 0.5% per hour

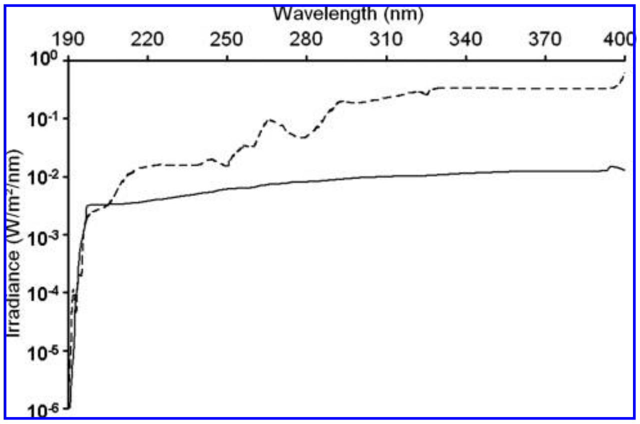

FIG. 2. UV spectrum of the xenon lamp (black line) compared to the solar UV spectrum on the martian surface predicted by Patel *et al.* (2002) at equatorial noontime (dotted line).

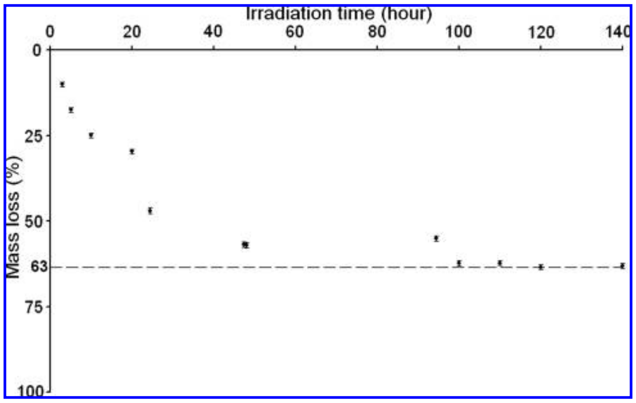

FIG. 3. Mass loss of mellitic acid plotted against irradiation time for the xenon lamp irradiation in vacuum at 218 K. The curve clearly shows the photodissociation of mellitic acid in the first few hours of irradiation, but this horizontal asymptote ($y = -63\%$) could indicate the production of a new compound radiotolerant to UV radiation.

for benzoic acid and 0.8% per hour for oxalic acid. There was no sublimation mass loss for mellitic acid.

Finally, we analyzed the irradiated samples of mellitic acid with Fourier transform infrared spectroscopy to determine whether new solid organic compounds were produced. We employed an attenuated total reflectance cell composed with a diamond crystal (Golden Gate model, simple reflection, series 10500, Eurolabo Company) adapted with a Fourier transform infrared spectrometer (Perkin Elmer, BX II). The samples were deposited on the crystal surface and compacted by a compression anvil to optimize the sample contact with the diamond. The absorption spectra were obtained in the range of 4000 cm^{-1} to 1000 cm^{-1} at 1 cm^{-1} resolution.

Results

We studied the UV absorption spectra of benzoic, oxalic, and mellitic acids. These molecules absorb UV radiation in the wavelength range 200–250 nm. The thin deposits of mellitic, oxalic, and benzoic acids were irradiated with the UV source in vacuum at a temperature of 218 K. Multiple irradiations were performed for each molecule to achieve high accuracy of the measurement.

For mellitic acid, we first observed a mass loss for irradiation time below 100 hours (Fig. 3). Second, the mass loss of mellitic acid reached a minimum value of approximately −63%. Figure 3 shows the photodissociation of mellitic acid in the first hours of irradiation, though this horizontal asymptote could indicate the production of a new compound that is resistant to UV radiation. After irradiation for times longer than 100 hours, the initially white sample of mellitic acid turned black. This qualitative observation could be another clue with regard to the production of a new compound.

To identify the formation of UV irradiation by-products, we analyzed the irradiated samples with Fourier transform infrared spectroscopy, and the solid samples were analyzed by GC-MS. A derivatization step was required prior to gas chromatography–mass spectrometry analysis to volatilize the refractory compounds. Finally, we used laser desorption–mass spectrometry to determine whether any other nonvolatile organic compounds were produced that could not be detected by derivatization and gas chromatography–mass spectrometry. None of these analyses gave us conclusive results.

The absorption spectra of the samples were compared with bibliographical data (Pouchert, 1975). Analysis of the spectra of the solid irradiated samples of oxalic and benzoic acids indicated that no new infrared bands appeared; thus, no new solid compound was formed.

Conversely, analyses of the mellitic acid irradiated sample spectra (irradiation time more than 100 hours) indicated that a new infrared absorption spectrum appeared by comparison with the non-irradiated mellitic acid spectrum (Fig. 4). The band assignments and wavenumbers of main spectral features of the spectrum of mellitic acid are υ(O-H), υ(C=O), and υ(C-O) in the range 2500–3335 cm^{-1}, 1700–1725 cm^{-1}, and 1210–1320 cm^{-1}, respectively, and δ(O-H) in the range 1395–1440 cm^{-1}. After irradiation, two new infrared peaks appeared: υ(C=O) in the range 1880–1720 cm^{-1}, whereas the peaks υ(O-H) and υ(C=O) disappeared. The lack of the υ(O-H) peak was interpreted as an indication that the new compound is anhydrous. Our interpretation of the infrared spectrum of the irradiated sample based on the available bibliographic data (Pouchert, 1975) led us to identify the new compound as benzenehexacarboxylic acid-trianhydride ($C_{12}O_9$).

For oxalic and benzoic acid, we expected that these molecules would not be radiotolerant. Figure 5 shows the mass loss of benzoic and oxalic acids plotted against irradiation time for all experiments. The slope of the linear correlation represents the destruction rate of these molecules. Their absorption in the 200–250 nm wavelength range drives their photodestruction. We estimated that the half-lives of benzoic and oxalic acids are 0.8 ± 0.2 and 1.8 ± 0.5 hours, respectively. The error bars were based on the microbalance pre-

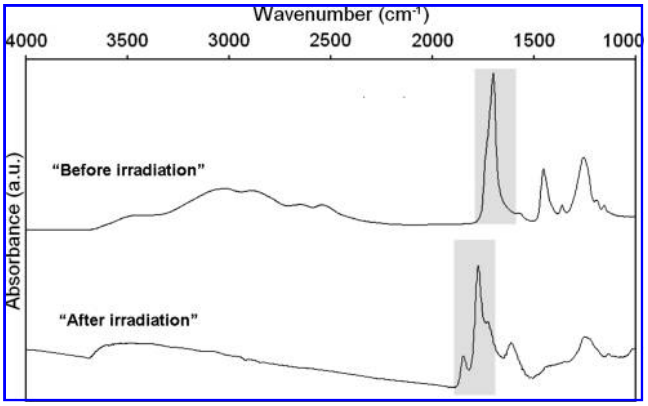

FIG. 4. IR spectra of mellitic acid (top) and irradiated mellitic acid sample (bottom, irradiation time greater than 100 hours) in the range of 4000 cm^{-1} to 1000 cm^{-1} at 1 cm^{-1} resolution. The vertical scale bars show the infrared absorbance in arbitrary units. The bottom spectrum is identical to the benzenehexacarboxylic acid-trianhydride spectrum (Pouchert, 1975). An attenuated total reflectance cell was employed, which consisted of a diamond crystal connected to a Fourier transform infrared spectrometer. The samples were deposited on the crystal surface. They were compacted by a compression anvil to optimize the sample contact with the diamond.

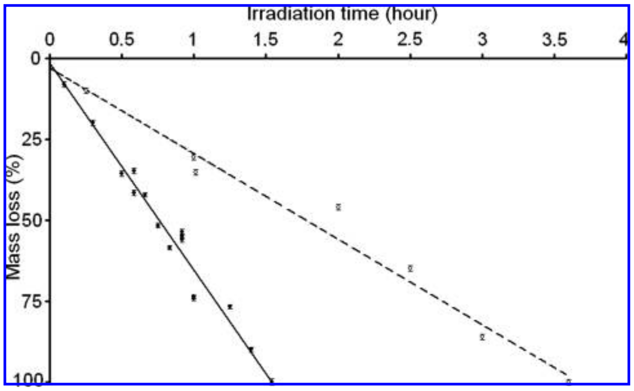

FIG. 5. Mass losses of benzoic (black line) and oxalic (dotted line) acids plotted as a function of irradiation time for xenon irradiation in vacuum at 218 K. The half-life of the benzoic acid under these conditions is 0.8 ± 0.2 hour. For irradiation times greater than 2 hours, the benzoic acid samples were completely photodissociated. The half-life of oxalic acid is 1.8 ± 0.2 hour. For irradiation times greater than 5 hours, the oxalic acid samples were totally photodissociated.

cision, which includes the error in mass measurements taken both before and after irradiation exposure.

As indicated above, the integrated flux of the UV source in the wavelength range 190–250 nm is identical to that of Mars in the same wavelength range; therefore, we conclude that the values of the experimental half-lives of benzoic and oxalic acids should be comparable to the values of their average half-lives on the martian surface, if these compounds are directly exposed to solar UV radiation. To determine whether all benzoic and oxalic acid molecules in the experiments were photodissociated, we carried out irradiations for durations exceeding their expected half-lives ($t = 2.5$, 3, and 16 hours of irradiation for benzoic acid and $t = 5$, 7, 24, and 46 hours of irradiation for oxalic acid). We obtained a complete mass loss for each experiment in accordance with their experimental half-lives.

Discussion

In the Introduction, we mentioned that the organic molecules potentially present on the martian surface are mainly exposed to radiative and oxidative conditions. These environmental stresses could drive the destruction and, thus, result in the absence of organic matter. Carboxylic acids are an attractive target for Mars since they could be metastable intermediates of organic matter delivered by meteorites or produced endogenously under martian oxidizing conditions. Hence, the study of their photostability could provide information about their preservation potential and presence on Mars. We noted that all the carboxylic acids studied interacted with UV radiation as evidenced by their total or partial photodissociation.

Mellitic acid transforms into a UV-resistant compound during irradiation, which we identified to be benzenehexacarboxylic acid-trianhydride ($C_{12}O_9$). There are several possible pathways for the formation of this compound. The first production pathway considers intramolecular chemical reactions (Fig. 6). The energy provided by UV radiation would be sufficient to lead to the rotation of the carboxylic groups. Close OH groups would produce anhydrous groups: one of the nonbonding electron pairs of an oxygen atom of a first OH group forms a connection with the proton of a close second OH group. It forms three nonbonding electron pairs on the oxygen atom that lost its proton. One of these electron pairs would form a connection with a carbon atom that has an electron deficit. This intramolecular reaction would form an oxygen bond between two carbon atoms and a free water molecule. All the carboxylic groups are affected by UV radiation.

The second possible pathway is intermolecular chemical reaction: because of the UV radiation energy effects, two close OH groups of two mellitic acid molecules form an oxygen bond between the two molecules. The mellitic acid molecules could then form an anhydrous mellitic polymer. This polymer could explain the UV radiation resistance. It is possible that the new compound is formed by both intra- and intermolecular reactions.

The benzoic and oxalic acids are not radiotolerant when they are directly exposed to UV Mars-like radiation and produce no new solid organic compounds. Based on their photolysis rates, we can determine whether these molecules should have accumulated in the martian regolith over time. The accumulation of carboxylic acids would be due to the difference between their production rates and the different pathways that led to their destruction (UV radiation, for example). We focused on the kinetics of the photodissociation of both molecules to determine whether they are sufficiently stable (or not) and whether they accumulate. We then demonstrated that these molecules would be destroyed and would not accumulate if they were exposed to UV radiation present on the surface of Mars. Based on their stabilities under martian-like surface UV conditions, oxalic and benzoic acids are not the best molecular targets in the search for organic compounds on the surface of Mars.

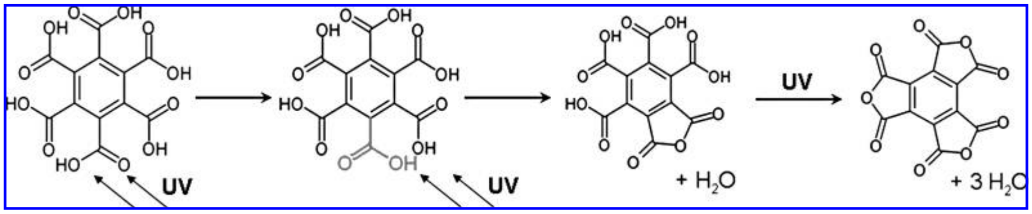

FIG. 6. The proposed intramolecular pathway for the formation of benzenehexacarboxylic acid-trianhydride from mellitic acid.

Conclusion

We developed an experimental setup that reproduced the UV spectrum and energy flux and average temperature on the martian surface to study the behavior and stability of carboxylic acids that could be present on Mars.

We observed that mellitic acid exposed to UV radiation produces a UV radiotolerant compound identified as benzenehexacarboxylic acid-trianhydride ($C_{12}O_9$). In spite of the eventual presence of oxidation processes and UV radiation on the martian surface, compounds produced by photolysis of benzenecarboxylic acids (such as mellitic acid) may have accumulated into the martian regolith. The Sample Analysis at Mars instrument on board the future Mars Science Laboratory mission will employ a chemical derivatization and pyrolysis gas chromatography–mass spectrometry technique that will target a range of carboxylic acids such as mellitic acid in the martian regolith (Meunier *et al.,* 2007).

In contrast to mellitic acid, we noticed that benzoic and oxalic acids were not radiotolerant because they were completely destroyed after only a few hours of exposure to UV radiation (benzoic acid half-life is 0.8 ± 0.2, and oxalic acid half-life is 1.8 ± 0.5 hours). Hence, these molecules do not constitute priority mission targets on the martian surface.

The next step in the study of carboxylic acid photolysis will be the analysis of the gaseous phase molecules produced during irradiation with the intent to understand the evolution and the destruction mechanism of carboxylic acids.

Finally, we will continue irradiation experiments with biomarkers, *i.e.,* organic molecules that can be related either directly or indirectly through a set of diagenetic alterations to biogenic sources and cannot be synthesized by abiotic processes (Simoneit *et al.,* 1998). We will focus on prokaryotic biomarkers (such as hopanoids and hopanes) because if life occurred on Mars it was likely a primitive form of life (such as terrestrial prokaryotic organisms) due to the short period of favorable conditions. Hopanoids and hopanes are able to resist terrestrial alteration by reductive or oxidative environments, diagenesis or catagenesis processes over the course of several billion years (Brocks *et al.,* 1999, 2003). Because of their unambiguous biological nature, these biomarkers represent priority astrobiological targets as well, and we will investigate their photostability with regard to the search for terrestrial prokaryotic-like life on Mars.

Acknowledgment

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Abbreviations

GC-MS, gas chromatograph–mass spectrometer; MOMIE, Martian Organic Material Irradiation and Evolution.

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