Organics on Mars : Laboratory studies of organic material under simulated martian conditions

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Chapter 4

The effects of martian near surface conditions on the photochemistry of amino acids

In order to understand the complex multi-parameter system of destruction of organic material on the surface of Mars, step-by-step laboratory simulations of processes occurring on the surface of Mars are necessary. This paper describes the measured effects of two parameters, a CO_2 atmosphere and low temperature, on the destruction rate of amino acids when irradiated with Mars-like ultraviolet light (UV). The results show that the presence of a 7 mbar CO_2 atmosphere does not affect the destruction rate of glycine and that cooling the sample to 210 K (average Mars temperature) lowers the destruction rate by a factor of 7. The decrease in the destruction rate of glycine by cooling the sample is thought to be predominantly caused by the slower reaction kinetics. When these results are scaled to martian illumination conditions, cold thin films of glycine are assumed to have half-lives of 250 hours under noontime peak illumination. It has been hypothesised that the absence of detectable native material in the martian regolith points to the presence of oxidising agents. Some of these agents might form via the interaction of UV with compounds in the atmosphere. Water, although a trace component of Mars' atmosphere, is suggested to be a significant source of oxidising species. However, gaseous CO_2 or adsorbed H_2O layers do not influence the photodestruction of amino acids significantly in the absence of reactive soil. Other mechanisms such as chemical processes in the martian regolith need to be effective for rapid organic destruction.

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1. INTRODUCTION

Mars is the target for future space missions with the search for traces of extinct or extant life as one of the main goals. Recent space missions have provided a wealth of information about the surface and atmospheric conditions on Mars (e.g. Squyres *et al.*, 2004a,b; Formisano *et al.*, 2004). The martian atmosphere is dominated by CO_2 (95 %). Other major gases in Mars' atmosphere are (percentage by moles) nitrogen (N_2, 2.7 %), argon (Ar, 1.6 %), oxygen (O_2, 0.13 %) and carbon monoxide (CO, 0.08 %). Water (H_2O) is a minor constituent (varying between 10 and 1000 parts per million, Encrenaz*et al.*, 2004a), as well as methane (CH_4, 5 parts per billion, Formisano *et al.*, 2004; Krasnopolsky *et al.*, 2004). The fractional abundance of O_3 in Mars' atmosphere, with a mixing ratio of 10^{-8}, is directly related to the level of O_2, while the abundance of O_2 is regulated by catalytic cycles involving HO_x species. Hydrogen peroxide (H_2O_2) has been suggested as a possible oxidising agent of the martian surface. Photochemical models suggest that the mean column density of H_2O_2 should be in the range 10^{15} - 10^{16} cm^{-2}, and that H_2O_2 and H_2O abundances should be correlated. Encrenaz *et al.* (2004b) report a H_2O_2 atmospheric mixing ratio of 5×10^{-8} around the sub-solar point.

No organic matter was detected in martian regolith samples analysed by the two Viking landers (Biemann *et al.*, 1977). Given the current presumed rate of meteoritic infall, detectable amounts of organic matter should have accumulated at the surface of Mars (Flynn and McKay, 1988). To account for this discrepancy, the effects of UV (ten Kate *et al.*, 2005), gaseous oxidants (Oró and Holzer, 1979) and surface catalysts (Quinn and Zent, 1999) on organic molecules have been examined in laboratory experiments. Of particular interest is the stability of simple amino acids, as they may be important biomarkers searched for by instruments on the payload of future missions to Mars.

When irradiated with Mars-like UV, 300 nm thick polycrystalline films of amino acids degrade with half-lives of around 2×10^{6} s (glycine) and 3×10^{5} s (D-alanine) (ten Kate *et al.*, 2005). However, this destruction was measured exclusively at room temperature and in vacuum (~10^{-6} mbar). In the current paper, we have examined the photostability of glycine samples at low temperature or in the presence of CO_2. These conditions are representative of the equatorial regions of Mars (~210 K, Kieffer*et al.*, 1992) with a low adsorbed water content (Möhlmann, 2002) and no condensed CO_2. Regolith mineralogy and chemistry are not taken into account in these experiments. The experiments and the simulation chamber used for these experiments are described in section 2, where also a description of the used UV source is given. In section 3, we report on the infra-red (IR) spectroscopy of the irradiated glycine samples and we tabulate the half-lives and UV destruction cross-sections measured in the reported experiments. The implications of the obtained results are explained in detail in section 4.

2. Equipment and experimental procedure

2.1 Equipment and experiments

Glycine (99.7 % purity, Merck) was deposited on silicon substrates, to form films with a thickness of 300 ± 50 nm, using a vacuum sublimation system, details of which are given in ten Kate *et al.* (2005). The films produced in this system have been shown to be optically thin (ten Kate *et al.*, 2005). Experiments have been performed in a modified version of the system as used by Peeters *et al.* (2003) (Fig. 1). The system consists of a small vacuum chamber equipped with several gas-inlet ports. A closed-cycle two-stage helium cryostat (Air products, Displex DE-202), which can be rotated while maintaining the vacuum, allows the temperature of the sample to be controlled to within 0.3 K in the range 20-300 K. In this system a Mars-like atmosphere, ~7 mbar CO_2 (Praxair, 99.996 %), was created at room temperature, representing a Mars-like daytime surface temperature in equatorial regions. Alternatively, samples were cooled down to 210 K under vacuum to simulate an average Mars surface temperature. The silicon substrate is mounted on the cryostat, allowing the vapour deposited amino acid sample layer to face either a UV source (see section 2.2) or the beam of a Fourier transform IR spectrometer (Excalibur FTS-4000, BioRad, 4000 to 500 cm^{-1} at 4 cm^{-1} resolution). Simultaneous cooling and using a 7 mbar atmosphere of CO_2 was not possible to achieve in our cryosystem, because CO_2 would selectively freeze on parts of the cryostat that are far colder (~40 K) than the 210 K at which the substrate window was maintained.

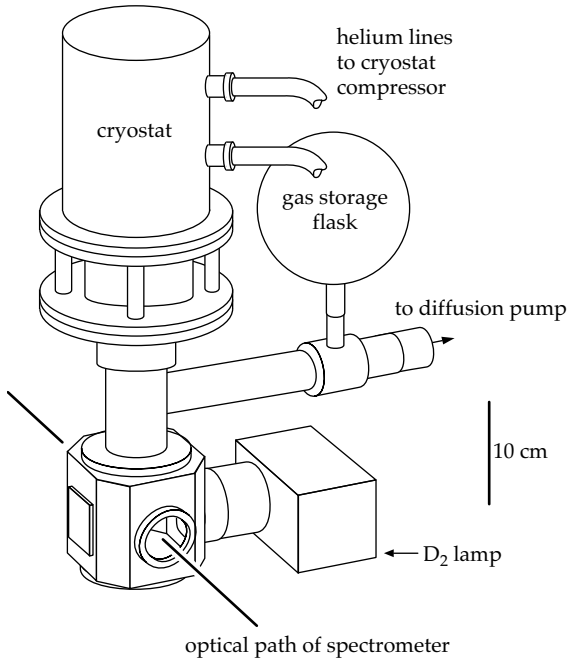

Fig. 1. The cryosystem used for the irradiation of amino acids.

2.2 UV source

The UV source is a deuterium discharge lamp (Heraeus-Noblelight, DX 202), which has been calibrated against a known UV standard (Bentham R48) using a monochromator equipped with a photomultiplier tube. The measured spectrum of the DX202 lamp is shown in Fig. 2 along with a curve

showing a representative noontime UV spectrum for Mars that was calculated for a low atmospheric dust-load by Patel *et al.* (2002). The integrated flux in the wavelength range 190-325 nm (on the amino acid layer) is 1.2×10^{14} photons cm^{-2} s^{-1} in the current system. This is ~12 times lower than the integrated flux on Mars in the same wavelength range (1.4×10^{15} photons cm^{-2} s^{-1}).

As has been pointed out by Schuerger *et al.* (2003) a deuterium discharge light source is not an exact fit to the lighting spectrum found at Mars' surface. The deuterium emission

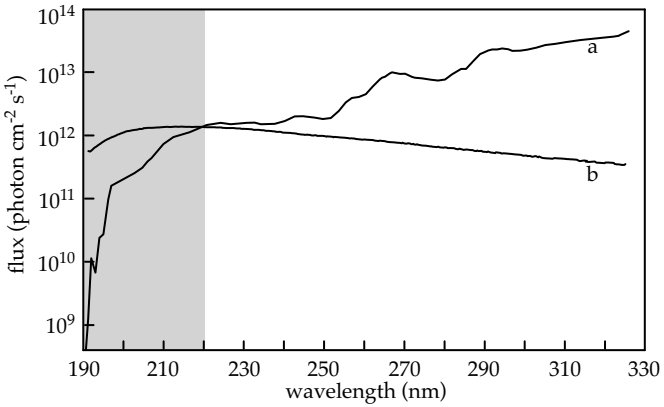

Fig. 2. The lighting spectrum (a) experienced by the equatorial noontime surface of Mars at $L_S = 70°$ and (b) of the deuterium lamp. The grey area marks the 190-220 nm range, which is used in the discussion.

spectrum peaks at around 200 nm, and is deficient in longer wavelengths compared to the UV spectrum at the martian surface. Thus, the work presented here places upper limits on the half-life of a sample under martian conditions.

3. Results

Thin films of glycine deposited on silicon substrates have been irradiated with UV in vacuum (~10^{-7} mbar), in a CO_2 atmosphere (~7 mbar), and at a temperature of 210 K. Multiple experiments have been performed for each modified parameter to achieve high accuracy of the measurements. Fig. 3 shows the natural logarithm of the normalised integrated absorbance ($\ln(S/S_0)$) plotted against irradiation time for all experiments. The slope of the linear fit through $\ln(S/S_0)$ represents the destruction rate. Table 1 lists the temperature of the glycine samples, the average pressure in the system, and the corresponding average destruction rate of the different experiments. Also listed are the half-lives when extrapolated to a martian noontime equatorial UV flux of 1.4×10^{15} photons s^{-1} cm^{-2}. The destruction rates found in the vacuum-only experiments were in agreement with the values found by ten Kate *et al.* (2005), with a small shift within the error bars, due to the use of a different system.

The system can be heated under vacuum prior to the experiments so that water is desorbed from the stainless steel. The maximum amount of water accreted on the disc during 24 hour cooling at 210 K is in the order of 10^{16} molecules cm^{-2}.

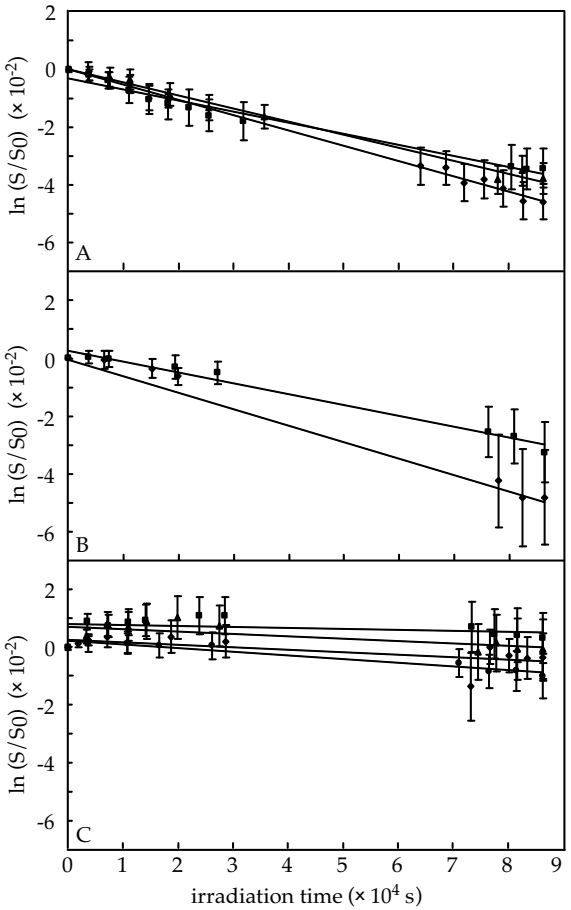

Fig. 3. The natural logarithm of the normalised integrated absorbance ($\ln(S/S_0)$) plotted against irradiation time, for the deuterium irradiation of glycine (A) in vacuum at 294 K, (B) in a 7 mbar CO_2 atmosphere at 294 K, and (C) in vacuum when cooled to 210 K. The different lines represent the destruction rates of the separate experiments that have been performed.

Table 1. Average destruction rates of thin films of glycine measured under different conditions in the laboratory when subjected to UV irradiation. Also listed are the extrapolated half-lives of glycine for a noontime equatorial flux on Mars.

temperature (K)	number of repeated experiments	atmosphere (mbar)	destruction rate J (s^{-1})	Mars half-life (s)
294	3	~10^{-7}	$4.5 \pm 2.3 \times 10^{-7}$	$1.3 \pm 0.8 \times 10^{5}$
294	4	~7 CO_2	$4.9 \pm 2.3 \times 10^{-7}$	$1.3 \pm 0.6 \times 10^{5}$
210	2	~10^{-7}	$0.8 \pm 2.9 \times 10^{-7}$	$0.9 \pm 7.5 \times 10^{6}$

The amount of water and other contaminants in the CO_2 gas is in the order of 1 part per million (ppm). The background pressure in the system was in the order of 10^{-7} mbar.

4. Discussion

The effects of low temperature or a CO_2 atmosphere on the photodestruction rate of amino acids have been examined. This has been done by irradiating 300 ± 50 nm thick

polycrystalline films of glycine deposited on silicon discs in the presence of a CO_2 atmosphere or when cooled to 210 K, corresponding to an average temperature on the surface of Mars. The results show no measurable effect of a CO_2 atmosphere on the destruction of glycine. However, when the samples are cooled to 210 K the destruction rate decreases by a factor of 7.

4.1 Effect of a CO_2 atmosphere

Thin films of glycine deposited onto silicon substrates have been irradiated with UV in a CO_2 atmosphere (~7 mbar). Adding a CO_2 atmosphere is assumed to have two effects, extinction of the UV flux reaching the glycine film and formation of O-radicals by photodissociation of CO_2. The extinction of UV can be divided into an absorption and a Rayleigh-scattering component, both with a corresponding cross-section (σ, cm^2), σ_{abs} and σ_{scat}, respectively. The wavelength range displayed in Fig. 2 can be divided into three regions, < 203 nm, 203-220 nm and > 220 nm. In the region > 220 nm the UV extinction is dominated by scattering with a very small cross-section $\sigma_{scat} < 10^{-25}$ cm^2 (upper limit of 10^7 scattered or absorbed photons s^{-1}), and is therefore not further considered in this discussion. In the region 203-220 nm both scattering and absorption contribute equally to the UV extinction, while in the region 190-203 nm absorption is the dominant process (Karaiskou *et al.*, 2004 and Shemansky, 1972). Table 2 gives an overview of the solar noontime UV flux on the surface of Mars and the output of UV flux from the deuterium lamp, as well as the average absorption and scattering cross-sections of CO_2, for the 190-203 and 203-220 nm intervals.

Above 167 nm dissociation of CO_2 occurs only through the reaction:

$$CO_2 \xrightarrow{h\nu} CO + O(^3P) \qquad (1)$$

The upper limit of this reaction is 227 nm. Between 190 and 200 nm the CO-formation quantum yield (Φ_{CO}) is ~1, but above 200 nm this value decreases to 0.16 at 214 nm, and no photodissociation occurs above 227 nm (Okabe, 1978). The formation rate of O-radicals will therefore be dominated by UV in the wavelength range 190-200 nm. As can be seen from Table 2 the UV absorption of CO_2 between 190 and 200 nm is small, leading to an upper limit on the O-radical formation in the order of 10^9 s^{-1}.

Table 2. Noontime solar UV flux at the surface of Mars, UV flux of the deuterium lamp and average absorption (σ_{abs}) and scattering (σ_{scat}) cross-sections of CO_2 for two wavelength ranges.

wavelength range (nm)	Mars flux ‡ (photon cm^{-2} s^{-1})	lamp flux § (photon cm^{-2} s^{-1})	σ_{abs} (cm^2)	σ_{scat} (cm^2)
190 – 203 *	4×10^{12}	1×10^{13}	3×10^{-23}	1×10^{-24}
203 – 220 †	1×10^{13}	2×10^{13}	7×10^{-25}	7×10^{-25}

* Shemansky (1972)

† Karaiskou *et al.* (2004)

‡ Patel *et al.* (2002)

§ measured from 200 nm and up, 190-200 nm adapted from the spectrum provided by Heraeus.

In summary, the total UV extinction in our experiments, through scattering and absorption by CO_2 over the full range of our lamp (190-325 nm), is in the order of 10^9 photons s^{-1}. The formation rate of O-radicals by the photodissociation of CO_2 is ~10^9 per second. These values are both a factor 10^5 lower than the UV flux produced by the deuterium lamp, thus the destruction rate of glycine thin films is *expected* to be dominated by photodestruction by UV. This concurs with the experimental results, presented in Table 1, where we found no effect on the destruction rate of glycine, when a CO_2 atmosphere was added and noontime equatorial illumination on Mars was simulated.

4.2 Effect of cooling

Thin films of glycine deposited on silicon substrates have been irradiated with UV, when cooled to 210 K. This cooling resulted in a lower destruction rate of glycine, which is expected from reaction kinetics. At 210 K water is accreted onto the glycine film as has been shown by background water accretion measurements, see section 3. Water accretion may influence the destruction rate; the reaction rate could either decrease due to UV absorption by the ice layer, or increase due to formation of for example OH-radicals.

Table 3. Absorption coefficients of water and absorbance of a 1.5 nm thick water layer.

wavelength (nm)	absorption coefficient (cm^{-1})	absorbance
190	2×10^{-1}	3×10^{-8}
200	3×10^{-3}	5×10^{-10}
250	1×10^{-4}	2×10^{-11}

The amount of water accreted on the sample during 24-hour cooling is in the order of 10^{16} molecules cm^{-2}, corresponding to a layer-thickness of ~5 H_2O molecules (~1.5 nm). Table 3 shows absorption coefficients of water (Thompson *et al.*, 1963) and the corresponding absorbance of the water layer on our samples at several wavelengths. These absorbances imply that in the wavelength range emitted by the deuterium lamp (190-325 nm) the absorption of UV photons by H_2O molecules hardly plays a role. The decrease in the destruction rate of the glycine film by cooling the sample, as measured in our experiments, is therefore thought to be predominantly caused by the slower reaction kinetics. A model of the upper martian surface from Möhlmann (2004) suggests an average of two monolayers at 200 K, adsorbed on the porous surface of martian soil. If only photodissociation of water adsorbed on amino acid layers is taken into account, the effect of these H_2O monolayers on the surface of Mars is negligible.

4.3 Water vapour

It has been postulated that the action of energetic UV photons on the water vapour present in the martian troposphere leads to the formation of OH-radicals, which influence the photochemistry of the soil (Hunten, 1979). Above 200 nm UV absorption by gaseous water is negligible, between 190 and

200 nm the absorption cross-section is smaller than 10^{-21} cm^2 (Chung *et al.*, 2001; Parkinson and Yoshino, 2003). The amount of residual water present as contamination in the CO_2 atmosphere in the chamber is in the order of 10^{-3} mbar, comparable to the average amount of gas phase H_2O in the martian atmosphere. The water vapour content in the atmosphere of Mars varies between 10 and 1000 ppm (Encrenaz *et al.*, 2004a). The amount of water in our system leads to a total absorption of 10^9 UV photons in the duration of the experiment. This is less than the total UV absorption and scattering by the CO_2 gas present in the system (see section 4.1). A control experiment has been performed in a different system (described in ten Kate *et al.*, 2005), in which a thin film of glycine was irradiated in a 10 mbar atmosphere, consisting of 50 % CO_2 and 50 % H_2O (data not shown here). The destruction rate found in this experiment was the same as the destruction rates of glycine thin films irradiated in vacuum. Photodestruction of H_2O into OH-radicals does not occur at wavelengths longer than 190 nm (Okabe, 1978), so is not expected to play a role in our experiments. On Mars, H_2O will be dissociated efficiently only in upper atmospheric layers, where UV irradiation is not substantially attenuated. The diffusion of radicals, formed by dissociation of water, to the surface, and their subsequent reactions are not well understood. UV irradiation of H_2O vapour close to the surface will not result in a significant amount of reactive species.

5. Conclusions

We measured the destruction rate of ~300 nm thick polycrystalline films of glycine deposited on silicon substrates, when irradiated with UV (190-325 nm) in vacuum (~10^{-7} mbar), in a CO_2 atmosphere (~7 mbar), and when cooled to 210 K. Regolith mineralogy and chemistry are not taken into account in these experiments. The results show that the presence of a 7 mbar CO_2 atmosphere does not affect the destruction rate of glycine by UV. The extinction of UV (with an extinction rate of 10^9 photons s^{-1}) and the formation of O-radicals (with a formation rate of 10^9 s^{-1}) are very small compared to the flux of the deuterium lamp. However, cooling the amino acid during irradiation reduces the destruction rate by a factor of 7. A thin layer of water (representative for martian conditions, see Möhlmann, 2002, 2004) accreted on the glycine film did not measurably influence the destruction rate. When the results on thin films of glycine by ten Kate *et al.* (2005) and the results of this work are scaled for martian noontime lighting conditions, glycine exposed to UV at temperatures between 210-295 K has a half-life of approximately 35-250 hours under continuous irradiation. Irradiation of 24 hours in our experiments corresponds to an irradiation time of ~2 hours on the surface of Mars at noontime. Only in the polar regions during their respective summers may sunlight shine on the surface for periods of > 24 hour, however with lower intensity than at the equator. The simple geometric relationship between latitude and surface intensity for a sphere allows one to scale the lifetime of glycine calculated for noon illumination conditions at the equator to other lati-

tudes. Our low temperature experiments performed at 210 K are more representative of mid and high latitude regions on Mars, and indicate that in those environments the destruction rate of amino acids may be reduced further. Furthermore the amount of water adsorbed on the surface has a regional, seasonal and diurnal dependence. Therefore the actual lifetime of exposed glycine on the cold surface of Mars will depend on several parameters. Using the model of amino acids embedded in martian regolith described by ten Kate *et al.* (2005), with a mixing ratio of glycine of 1 part per billion, we find a half-life of glycine of ~ 10^8 years.

Energetic UV photons are suggested to form OH-radicals from the water vapour present in the martian atmosphere (e.g. Nair *et al.*, 1994, Atreya and Gu, 1995). This dissociation takes places most efficiently in upper atmospheric layers, where UV irradiation is less attenuated. The OH-radicals formed in the atmosphere and other photochemical pro-cesses could play a role in the formation of oxidising agents in the regolith (Zent and McKay, 1994). However, OH-radical production on the martian surface can also occur through processes involving adsorbed H_2O, Fe(II)-ions and H_2O_2 (Southworth and Voelker, 2003). It has been suggested that the water abundance plays an important role in controlling reaction kinetics by triggering oxidative reactions involving photochemically produced dry acids that are adsorbed onto the soil (Quinn *et al.*, 2005c). Interaction of UV with Mars-analogue minerals in the presence of an oxygen atmosphere with a partial pressure comparable to that in the martian atmosphere showed the formation of oxygen radicals (O_2^-) on the minerals that likely destroy organic material (Yen *et al.*, 2000). The stability of the intrinsic organic component of martian soil analogues has recently been investigated by Garry *et al.* (2005). Those results support the idea that the key element in the destruction of organic material and micro-organisms is the interaction of accreted water with the soil in the presence of radiation.

In summary, we studied the behaviour of amino acids irradiated by 190 to 325 nm UV in a CO_2 atmosphere and when cooled to 210 K. Our results form a basis for the understanding of more complex processes occurring on the martian surface, in the presence of regolith and other reactive agents. Future research should involve a diurnal UV irradiation and temperature cycle, enabling to simulate the diurnal water frost deposition on the surface. Low temperatures may enhance the stability of amino acids in certain cold habitable environments, which may be important in the context of the origin of life.

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