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Organic degradation under simulated Martian conditions

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Abstract. We report on laboratory experiments which simulate the breakdown of organic compounds under Martian surface conditions. Chambers containing Mars-analog soil mixed with the amino acid glycine were evacuated and filled to 100 mbar pressure with a Martian atmosphere gas mixture and then irradiated with a broad spectrum Xe lamp. Headspace gases were periodically withdrawn and analyzed via gas chromatography for the presence of organic gases expected to be decomposition products of the glycine. The quantum efficiency for the decomposition of glycine by light at wavelengths from 2000 to 2400 Å was measured to be $1.46 \pm 1.0 \times 10^{-6}$ molecules/photon. Scaled to Mars, this represents an organic destruction rate of $2.24 \pm 1.2 \times 10^{-4}$ g of C m^{-2} yr^{-1}. We compare this degradation rate with the rate that organic compounds are brought to Mars as a result of meteoritic infall to show that organic compounds are destroyed on Mars at rates far exceeding the rate that they are deposited by meteorites. Thus the fact that no organic compounds were found on Mars by the Viking Lander Gas Chromatograph Mass Spectrometer experiment can be explained without invoking the presence of strong oxidants in the surface soils. The organic destruction rate may be considered as an upper bound for the globally averaged biomass production rate of extant organisms at the surface of Mars. This upper bound is comparable to the slow growing cryptoendolithic microbial communities found in dry Antarctica deserts. Finally, comparing these organic destruction rates to recently reported experiments on the stability of carbonate on the surface of Mars, we find that organic compounds may currently be more stable than calcite.

Introduction

Unique among all scientific experiments were those carried out by the Viking Landers on the surface of Mars. For the first time, in situ analyses of the surface of another planetary body were made. The Viking biology experiments, in particular, analyzed the surface material of Mars for evidence of microbial life. Although the results of these experiments mimicked a biological response in some respects, it is widely held [*Klein*, 1978, 1979; *Oyama et al.*, 1977, 1978; *Oyama and Berdahl*, 1977, 1979] that they were not produced biologically, but rather resulted from a highly reactive surface chemistry [*Klein*, 1978; *Oyama et al.*, 1978]. One reason for this interpretation was the striking results of the gas chromatograph mass spectrometer (GCMS), which showed that the Martian surface soils had no organic compounds, at least within the detection thresholds of the instrument. These were parts per billion for organics with three or more carbons, and parts per million for organic molecules with one or two carbon atoms [*Biemann et al.*, 1977; *Biemann and Lavoie*, 1979].

The presence of indigenous organic compounds, recently detected in the Mars meteorites EETA 79001 [*Wright et al.*, 1989] and ALH84001 [*McKay et al.*, 1996] casts a new light on the null results from the Viking Lander experiments. Questions regarding organics near the Martian surface may now be directed at the details of their fate and distribution, rather than their mysterious lack of existence. Meteoritic material is estimated to reach the Martian surface at rates of between 2700 and 202,200 metric tons per year [*Flynn and McKay*, 1990], resulting in Martian soil that is as much as 58% meteoritic debris. Furthermore, because of Mars' low gravity and atmospheric pressure, much of the meteoritic material may arrive unmelted. Since organic carbon should comprise up to 10% of meteoritic material deposited on Mars, lack of organics on Mars implies that an active mechanism for destroying them is present [*Klein*, 1979]. Since this source of organic carbon remained undetected, it must be concluded that it is being destroyed at rates greater than its influx. Organic compounds produced by biological activity, either life or the past remains of life, may be meeting a similar fate.

One possibility which could account for the destruction of organic compounds on Mars is the presence of a highly oxidizing surface. The existence of oxidants in the Martian regolith was inferred from the results of the Viking Lander's biology experiment package, particularly the Labeled Release (LR) and Gas Exchange (GEX) experiments. The evolution of CO_2 from the LR experiment is consistent with the presence of a thermally labile oxidant such as H_2O_2 [*Klein*, 1979], which can act to destroy organics. H_2O_2 is produced in the atmosphere [*Kong and McElroy*, 1977; *Hunten*, 1979] and may possibly be produced by weathering processes in the presence of iron in the soil [*Huguenin et al.*, 1979]. H_2O_2 produced in the atmosphere is almost certainly transported into the soil, where it may have been responsible for the results of the Viking LR experiment [*Bullock*

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et al., 1994]. The existence of alkali and alkaline earth superoxides [*Oyama et al.*, 1976; *Oyama and Berdhal*, 1977; *Ballou et al.*, 1978] have been proposed to explain the evolution of O_2 in the GEX, as well as to provide a destruction mechanism for organic compounds. Photochemical processes have also been used to suggest an explanation for the creation of oxides in the Martian soil [*Hunten*, 1979, 1987]. In addition, there are explanations for the responses of the GEX and LR experiment that do not posit the existence of oxidants in the Martian soil. For example, *Banin and Rishpon* [1979] and *Banin and Margulis* [1983] suggest that intrinsically reactive clays may explain the results of both the LR and GEX. *Fanale et al.* [1982] proposed that O_2 released in the GEX was desorbed from the soil. More recently, *Plumb et al.* [1989] were able to duplicate both the magnitude and kinetics of both the GEX and LR experiments with peroxinitrates, which they propose may be present in Martian soil.

This paper investigates whether photochemical processes alone could be responsible for the dearth of organics at the Martian surface, independent of the presence or identity of surface oxidants. In an attempt to simulate organic degradation on Mars, *Oro and Holzer* [1979] irradiated samples of glycine, adenine, naphthalene, and powdered samples of Murcheson meteorite with UV light in an atmosphere containing N_2 or N_2 + O_2. They found that organic degradation occurred under experimental conditions with reaction rates dependent on the quantity of O_2 gas included in the reaction chamber. These results demonstrated qualitatively that organic photooxidation could occur on the surface of Mars, although the experimental conditions did not really represent those occurring on Mars. Our experiments were designed to improve upon the work of Oro and Holzer, who used a medium pressure Hg-arc lamp for the simulated Martian surface solar flux. In particular, we more accurately simulated the UV flux in the crucial range of 2100 - 2400 Å through the use of a Xe-arc lamp. We also took great pains to minimize UV absorption along the optical path through the exclusive use of high density quartz optics. Other similar experiments [*Chun et al.*, 1978, *Pang et al.*, 1982] have shown that organic degradation is photocatalyzed by TiO_2 in the presence of UV light. However, none of these experiments are directly applicable to Mars, and the published results cannot be scaled to allow an estimate of the rate of organic degradation on Mars.

In the present paper, we report the results of experiments to simulate organic destruction under simulated Martian conditions. The results of the experiment are used to estimate the rate at which organic compounds are degraded by ultraviolet light on the Martian surface. By comparing the timescale for organic degradation to the rate at which organic compounds are deposited on Mars by meteoritic infall, we show that organics from this source should not be expected to accumulate on Mars. Our derived organic degradation rate may be interpreted as an upper bound for the globally averaged biomass production rate for extant life on Mars, and compared with organic production rates for typical terrestrial biological communities. Finally, the laboratory-derived destruction rate for organic compounds is compared with reported experiments that measure the UV destruction rate of carbonates under simulated Martian conditions.

Experimental Apparatus

Simulations of the Martian environment took place in specially designed glass vessels, nicknamed Mars Jars, shown in Figure 1.

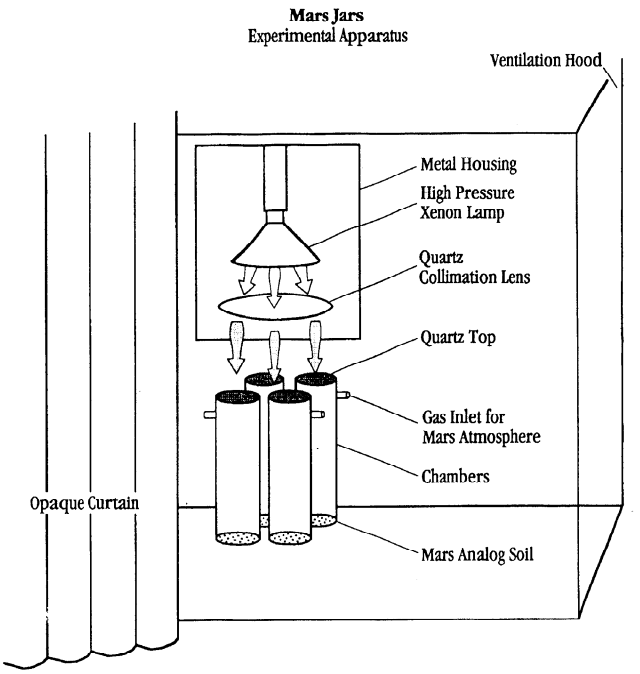

Figure 1. Schematic drawing illustrating the Mars Jars apparatus. The Mars Jars chambers are fitted with vacuum-tight quartz lids and are evacuated via gas inlets fitted with stopcocks. The chambers are irradiated via a 1000 W Xe arc lamp for up to 5 weeks.

Each of these 350 mL containers was fitted with a greaseless stopcock to allow for the introduction and extraction of headspace gases, and a vacuum tight quartz lid. The quartz lids allowed the transmission of UV radiation down to 2100 Å. Clamps and O-ring seals ensured that the Mars Jars remained vacuum-tight over the 5 week duration of the experiments, yet allowed for cleaning and sterilization prior to the introduction of a Mars-analog soil. A soil and/or amino acid mixture was placed into the jars, which were then assembled, filled with gas, and flushed using a gas manifold built for this purpose. Gas in the headspace of the Mars Jars was specially mixed to reproduce the composition of the Martian atmosphere. The gas mixture (hereafter called Mars gas mixture) consisted of 95.59% CO_2, 4.21% Ar, 0.11% O_2, and 0.09% CO and was passed through a filter dehydration stage prior to introduction into the vessels.

The experiments were begun by placing the filled Mars Jars under the illumination of a 1000 W Xe short arc lamp. Up to four jars could be accommodated at once, providing varying levels of flux to each one. Since the Xe lamp produced an excess of infrared radiation, a specially designed IR filter, consisting of a 10 cm column of distilled water and a cooling jacket, was attached to the lamp housing. A 2 gallon reservoir, cooled by a fan, and a water pump, were used to cool and circulate water in the IR filter jacket. Due to the copious amounts of UV radiation produced by the lamp, ozone was produced along the optical path of the beam. Therefore the entire arrangement of lamp, IR filter, and Mars Jars was operated within a fume hood (Figure 1). At periodic intervals the Mars Jars were removed from the beam and connected to the manifold for the extraction of headspace gases. The gases were allowed to expand into sample bulbs, which were then used for injection of the sample gases into a Perkin Elmer 900 gas chromatograph. The GC was equipped with a 5 m column, packed with Porasil C (phenylisocyanate-coated glass beads) and flame ionization detector (FID). Hydrocarbon gas

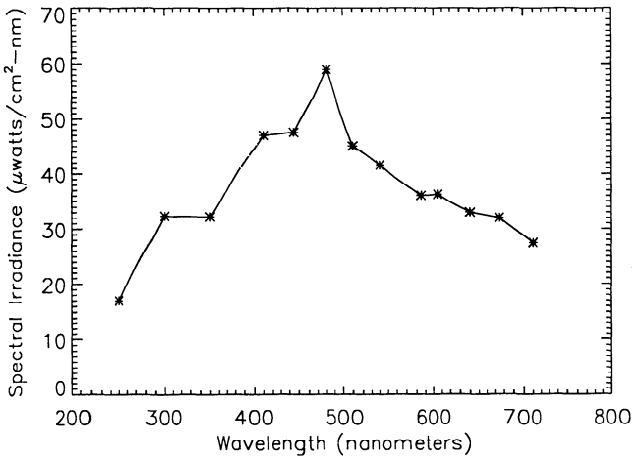

Figure 2. Calibrated spectral irradiance of the Xe lamp used for irradiating the sample chambers.

standards were used to calibrate the GC each time samples were analyzed. The output from the GC was used to drive an HP 3394A integrator for quantifying the sample gases.

Calibrations

In order to calculate the quantum efficiency of the organic degradation in the Mars simulations, an accurate calibration over the spectrum of the Xe lamp was required. UV flux measurements were made using a stable photodiode arrangement calibrated with a National Bureau of Standards (NBS) traceable deuterium UV irradiance standard and a set of characterized UV bandpass filters. Calibrations were performed for 2500, 3000 and 3500 Å bandpass regions. A similar procedure was developed for calibrating the visible flux, using a 1000 W NBS traceable tungsten filament lamp and calibrated visible bandpass filters. The calibrated spectrum from the Xe lamp is shown in Figure 2. For comparison, the UV irradiance at the Martian surface, adapted from *Kuhn and Atreya* [1979], is shown in Figure 3.

The products sought in the photochemical breakdown of glycine were simple hydrocarbon gases, such as methane, ethane, ethylene and propane. For this reason, the phenylisocyanate

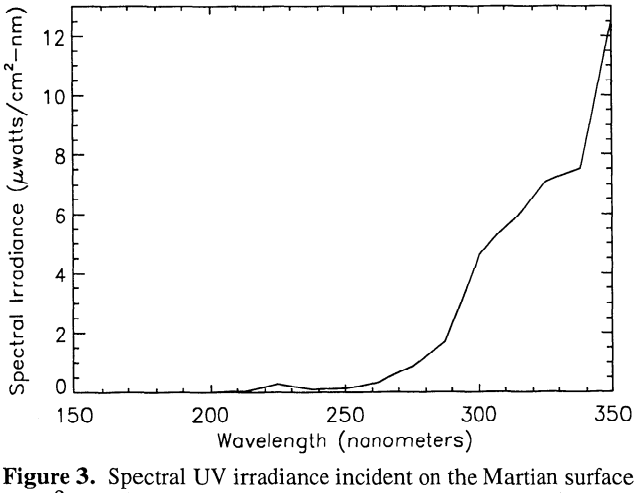

Figure 3. Spectral UV irradiance incident on the Martian surface at 50° N latitude in the spring, adapted from *Kuhn and Atreya* [1979].

packed column and FID detector were used on the GC. The GC/Integrator combination was capable of detecting quantities of hydrocarbon gas down to concentrations of picomoles cm^{-3}. The volumes of the Mars Jars, sample bulbs and GC injector were accurately determined in order to perform the calculations for total amount of each hydrocarbon species produced. In addition, it was necessary to inject two sets of standards before and after each sample run. Standards consist of the injection of known quantities of a mixture of hydrocarbon gases. The sensitivity of the detector was calculated for each species. The sensitivity of the GC for each species is known as the molar response (MR) and is expressed in counts/nanomole. A typical run involved analyzing sets of hydrocarbon gas standards first, then two injections from each sample bulb, one blank injection for background subtraction, and finally, two sets of standards again. By bracketing the analysis with standards and by running background blanks, the statistics for measuring the extremely small amounts of hydrocarbon gas injected in the GC were improved.

Experimental Procedure

The first steps in beginning the experiments involved making sure that everything in the simulation environment was chemically cleaned, sterilized, and kept contaminant free. All glassware, including the Mars Jars and sample bulbs, were rinsed with doubly distilled water, 0.1 M HCl, and then with doubly distilled water again. The vessels were completely wrapped in aluminum foil and baked for 14 hours in an oven kept at 485 °C. The glassware was only unwrapped immediately prior to the introduction of soil and gas. All nonglass items, such as stopcocks and O-rings were also rinsed with doubly distilled water, 0.1 M HCl, and doubly distilled water again. They were then sterilized in an autoclave prior to assembly. For a Mars-analog soil, we used palagonite collected from the Mauna Kea Volcano in Hawaii. This soil was chosen because it represents the best spectral analog to Martian soil [*Singer*, 1982; *Roush et al.*, 1993; *Stoker et al.*, 1993] and there is an extensive literature suggesting the presence of palagonites on Mars [*Toulmin et al.*, 1977; *Soderblom and Wenner*, 1978; *Gooding and Keil*, 1978; *Evans and Adams*, 1979, 1980; *Allen et al.*, 1981; *Singer*, 1982].

Before the start of the experiment, the palagonite to be used was placed in a cleaned and sterilized container and allowed to dry under a stream of helium for 14 hours at 105 °C. For the experiment, 2 mg of the amino acid glycine, in powdered, sterilized form, was mixed with 200 mg of the dried palagonite. 50 mg of the mixture was introduced into each Mars simulation

Table 1. Mars Jars Experimental Protocol

Experiment	Mars Jar	Designation	Description
Mars Sim.	1	High Flux	soil+glycine+Mars gas
Mars Sim.	2	Low Flux	soil+glycine+Mars gas
Mars Sim.	3	High Flux	soil+glycine+Mars gas
Control	4	He Atmosphere	soil+glycine+He
Control	5	Soil Only	soil+Mars gas
Mars Sim.	6	High Flux	soil+glycine+Mars gas
Mars Sim.	7	Low Flux	soil+glycine+Mars gas
Control	8	Glycine Only	glycine+Mars gas
Control	9	Darkness	soil+glycine+Mars gas

Mars Jars 1, 2, 3, 6 and 7 were full experimental runs, containing a Mars-analog gas mixture and Mars-analog soil mixed with the amino acid glycine. Mars Jars 4, 5, 8 and 9 were experiment controls.

jar, and the jars were then assembled and evacuated. In order to remove adsorbed gases, the jars were flushed 3 times with high purity (99.999%) He, to 100 mbar, and then 5 times with the Mars gas. After each flushing, the jars were evacuated to 0.05 torr. Finally, the jars were filled to 100 mbar with the Mars gas mixture and placed under the calibrated Xe lamp. This quantity of initial headspace gas was chosen to allow for multiple extraction and GC analysis of gas products, without introducing significant changes in headspace pressure over the course of the experiments. The jars were irradiated at various flux levels for periods of up to 5 weeks. Flux levels were varied by the location that the jars were placed under the nonuniform beam of the Xe lamp. Every 3 or 4 days, 5 mL amounts of headspace gas were removed for GC analysis. Each time an extraction was made, so was a light flux measurement under the lamp. Also, the soil/glycine mixtures were agitated at the same intervals. The experiments were performed at room temperature. After 7 to 10 such extractions, the pressure of the headspace had diminished to below 50 mbar, and the experiment was terminated.

Table 1 lists all of the experimental chambers that were analyzed. Two experimental chambers, containing the soil + glycine mixture along with Mars gas mixture in the headspace, were run simultaneously under the Xe lamp at a high and low light flux. This basic experiment was performed twice. Numerous control jars were also assembled and irradiated during the course of the experiment. These were designed to provide checks on contamination and to elucidate the nature of the photodegradation process. One type of control used the soil and glycine mixture but substituted ultrapurity He for the headspace gas. The purpose of this control was to determine what, if any, role was played by the composition of the Martian atmosphere. A second control jar was run in which glycine was not added to the soil but other experimental parameters were unchanged. The purpose of this control was to determine whether there was any contribution to the organic gases due to the degradation of any organics already present in the soil before the glycine was added. A third control irradiated glycine without the soil present to see whether the soil played a role in the degradation process. Finally, a jar containing the soil, glycine and Mars-analog gas mixture was kept in darkness for the 5-week duration of an irradiation experiment and periodically sampled to check that the ultraviolet irradiation was truly the source of the organic degradation. This

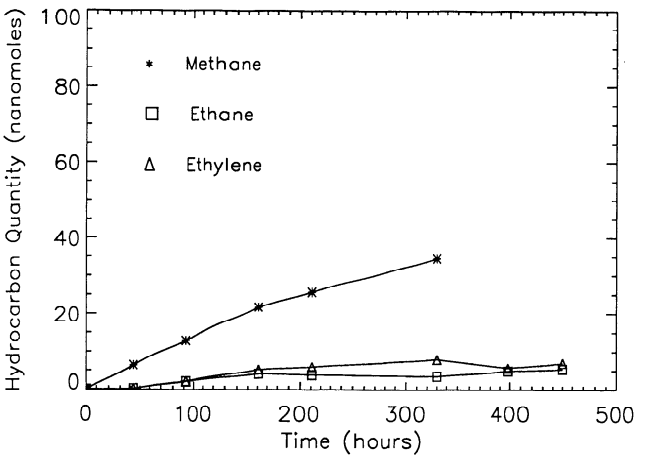

Figure 4b. Measured abundance of hydrocarbons as a function of irradiation time in a Mars simulation chamber which contained soil mixed with glycine and ultrapure He gas in the chamber headspace.

was a biological control performed to ensure that hydrocarbon gas products were indeed produced by the UV degradation of organics, rather than by microbial activity. Although great pains were taken to sterilize all of the apparatus involved, neither the palagonite nor the glycine were heated to high temperatures, for fear of altering them chemically. The hydration state of palagonite grains, for example, would probably have been changed by subjecting the samples to sterilization temperatures. Microbial activity that could produce hydrocarbon gases was tested for by the darkness control jar. Furthermore, if methanogenic bacteria were responsible for the production of hydrocarbons, this would have occurred in darkness as well as in light. In irradiated jars, microbial activity should have been equal to or less than that in the biological control, due to the highly sterilizing UV flux bathing the samples.

Results

Approximately 7 extractions were performed on each of the 10 Mars Jars and controls that were run. At the time of each extraction, flux measurements were also made. Plots of the total

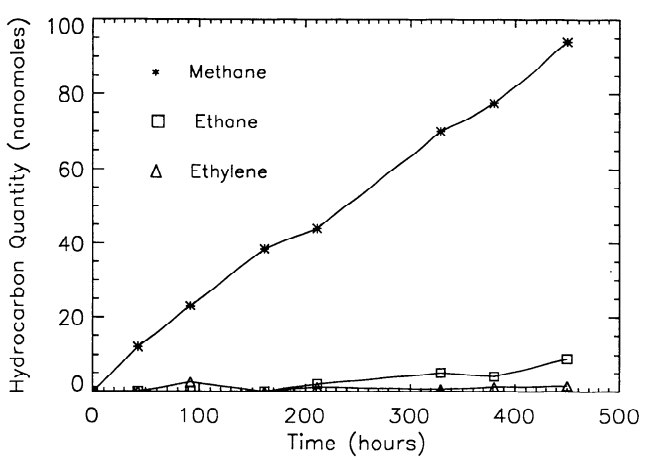

Figure 4a. Measured abundance of hydrocarbons as a function of irradiation time in a Mars simulation chamber which contained soil mixed with glycine and Mars gas in the chamber headspace.

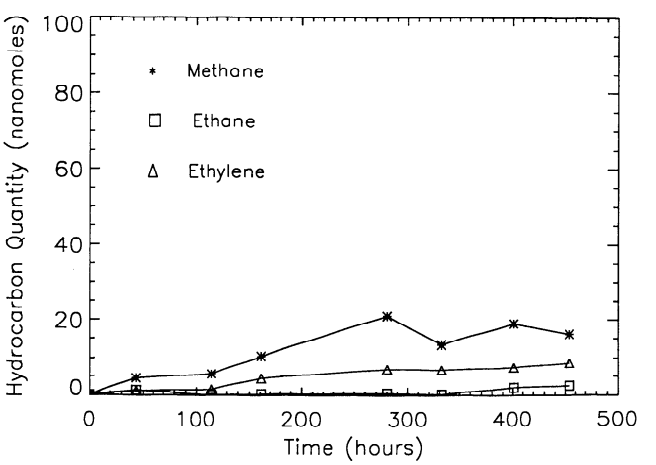

Figure 4c. Measured abundance of hydrocarbons as a function of irradiation time in a Mars simulation chamber which contained soil but no glycine, and Mars gas in the chamber headspace.

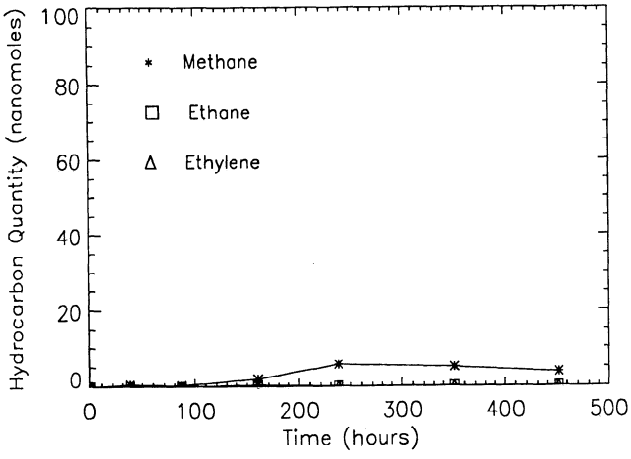

Figure 4d. Measured abundance of hydrocarbons as a function of irradiation time in a Mars simulation chamber which contained glycine only, and Mars gas in the chamber headspace.

hydrocarbon production as a function of time for an example of a soil + glycine Mars simulation and the 3 types of control jars are shown in Figures 4a-4d. Jars which contained soil + glycine + Mars gas produced three simple hydrocarbon gases, CH_4, C_2H_6, and C_2H_4, within detection limits, in their headspaces. As shown in Figure 4a, CH_4 was produced in a typical run at an approximately constant rate of 0.23 nmoles/hr.

In the glycine molecule, both the amino group and the carboxylic acid groups are responsible for UV absorption. Photons in the range of 2500 - 2100 Å are absorbed by aliphatic amines, and in the range of 2400 - 2300 Å by carboxylic acids [*McLauren and Shugar*, 1964]. For calculating the quantum efficiency of organic photodegradation, the flux below 2500 Å was considered responsible for the destruction of glycine. It was assumed that the detection of one CH_4 molecule is indicative of the destruction of one glycine molecule. Knowing the area of the soil that was irradiated and the measured UV flux at the position of the Mars Jar, the total flux in the range of 2000 Å to 2500 Å was calculated. The quantum efficiency of the production of a gas species was then calculated by dividing the production rate by the number of photons striking the soil per second.

The average production rates of CH_4, UV light flux, and quantum efficiency of CH_4 production are shown for each Mars Jar in Table 2. Since CH_4 was by far the most commonly observed degradation product, only results for the quantum efficiency of CH_4 are shown in the table. Based on the assumption that each CH_4 molecule results from the breakdown of one glycine molecule, we can estimate the quantum efficiency for organic degradation in these experiments. The average quantum efficiency for the total of 42 extractions was 1.83×10^{-6} CH_4/photon, with the spread in the data characterized by a standard deviation of 0.42×10^{-6}. The production of hydrocarbon gas in the headspace of a control jar that contained He gas + soil and glycine is shown in Figure 4b. Although production rates are lower than those shown in Figure 4a, the UV flux for this jar was also lower. Adjusting for UV flux, the quantum efficiency of CH_4 production in the He control jar (1.84×10^{-6}, Table 2) was essentially the same as for the main experimental jars. Figure 4c shows the production of hydrocarbon gas over time in the headspace of a control jar that contained soil and Mars gas, but no glycine. The CH_4 production rate, 0.027 nmoles/hr was significantly lower than in the main experimental jars. Adjusting for UV flux, the quantum efficiency for CH_4 production in the soil-only jars was 0.37×10^{-6} (Table 2). Finally, hydrocarbon gas production for a control jar with glycine and Mars gas, but no soil, is shown in Figure 4d. Again, the CH_4 production rate was low, at 0.029 nmoles/hr, and the quantum efficiency, 0.47×10^{-6}, was also significantly lower than in the main experimental jars. The hydrocarbon gas production rate in the darkness control jar, which contained glycine, soil, and Mars gas was measured to be extremely low, at 0.002 nmoles/hr (see Table 2). This rate was an order of magnitude below any of the other controls and approximately 2 orders of magnitude lower than the main experimental vessels.

Discussion

A primary source of random experimental error was due to the precision of the GC analysis. For the extractions that were made after only a short period of irradiation, hydrocarbon concentrations in the sample bulbs were close to GC background values. For later extractions, systematic errors in the volume determinations of the manifold, Mars Jars, sample bulbs and GC injection system were compounded. These random and systematic errors conspired to produce a standard deviation of the data of 48%. A more accurate determination of the quantum efficiency of the photodegradation of glycine would require more sensitive hydrocarbon detection in the GC analysis, or substantially higher irradiation fluxes.

Higher order hydrocarbons, such as C_2H_6, C_2H_4, and C_3H_8 were also produced, at rates of about an order of magnitude less. The soil-only control jars also produced hydrocarbon gas upon irradiation, although not as much as in the Mars simulations. It is possible that unknown organic contaminants in the soil were also being destroyed. If this is true, the CH_4 production in the Mars simulations may be interpreted to be due to the breakdown of the glycine plus unknown organics. To consider the breakdown of glycine alone (but in contact with the Mars-analog soil), the CH_4 production rate of the soil-only control jars was subtracted from the CH_4 production rate of the Mars simulations. Subtracting the production rate of the soil-only jar, the calculated quantum efficiency for the destruction of glycine is $1.46 \pm 1.0 \times 10^{-6}$ molecules/photon. In an earlier set of organic degradation experiments in which pure samples of amino acids were irradiated with ultraviolet light, *Oro and Holzer* [1979] found that organic degradation depended on having oxygen present as a component of the headspace gases. However, O_2 was not present in our He control jar, yet the production rates for methane in this jar were high and comparable to those in the Mars gas mixture which contained some O_2. Therefore our results refute the

Table 2. Production Rates and Quantum Efficiencies for Mars Jars Experiments and Controls

Mars Jar	Designation	Production, nmol hr^{-1}	Flux, $\mu W\ cm^{-2}$	Q, CH_4/photon
1	High Flux	0.255	201	1.49×10^{-6}
2	Low Flux	0.149	74.8	2.89×10^{-6}
3	High Flux	0.205	155	1.56×10^{-6}
4	He Atmosphere	0.102	65	1.84×10^{-6}
5	Soil Only	0.027	26.4	0.37×10^{-6}
6	High Flux	0.124	117.3	1.27×10^{-6}
7	Low Flux	0.054	33.2	1.92×10^{-6}
8	Glycine only	0.029	77.3	0.47×10^{-6}
9	Darkness	0.002		

suggestion of *Oro and Holzer* [1979] that O_2 is necessary for the significant UV degradation of simple organics such as glycine. We base this conclusion on the fact that we have more accurately simulated the significant UV flux between 2100 and 2400 Å at the Martian surface. It is interesting to note that very little CH_4 was produced in the jar which had glycine but no soil. In addition, the higher order hydrocarbons were not seen. In fact, there was less CH_4 production than in the soil control jar which had no glycine. *Pang et al.* [1982] showed that TiO_2 catalyzed the oxidation of organics in the presence of oxygen. *Sancier and Wise* [1981] have found that photocatalytic oxidation is responsible for organic degradation of organic compounds in ordinary terrestrial sand dunes. Our simulations therefore imply that Martian soil might play a role in the photocatalytic degradation of organic compounds on Mars.

In the biological control (darkness) jar the production rate of hydrocarbon gas was essentially at or near the measurement limits of the experiment. We suspect that this signal is noise, but cannot rule out the possiblity that it represents a very low-rate production of methanogenic bacteria contamination in the experiment. If this was the case, however, since the possible microbial contamination signal is so small, it has no effect on the results obtained from the main experimental vessels in which soil, glycine and Mars gas were irradiated.

We can use the upper and lower bounds on glycine photodegradation, derived from our experiments, to estimate the rate of organic degradation on Mars. In general, more complex organic compounds, also found in carbonaceous meteorites, have UV absorptions at higher wavelengths [*McLauren and Shugar*, 1964]. Since these energies are more abundant in the solar radiation at the Martian surface, higher degradation rates would apply. For example, *Oro and Holtzer* [1979] measured higher UV destruction rates for adenine and napthalene than for glycine. The flux of 2000 - 2500 Å radiation at the surface of Mars is 2.6 mW cm^{-2} [*Kuhn and Atreya*, 1979]. With flux levels of 27 to 201 mW cm^{-2} from the Xe lamp, the Mars simulations provided UV fluxes that were 10 to 80 times those found at the Martian surface. Although the spectral irradiances differ by these amounts, the UV spectrum of the Xe lamp closely simulates that found at the Martian surface, as can be seen by comparing Figures 2 and 3. Scaling our experimental results to Mars, the rate for organic destruction on Mars may be estimated to be $1.87 \pm 1.0 \times 10^{-3}$ g m^{-2} yr^{-1} for molecules with a molecular weight of about 100. The production and loss of organic molecules is often expressed in terms of g per carbon atom. In these terms, then, the measured destruction rate for organics at the surface of Mars is $2.24 \pm 1.2 \times 10^{-4}$ g C m^{-2} yr^{-1}.

This destruction rate may be compared with the estimated flux of organic carbon to the surface via meteoritic infall. An estimate of this rate can be obtained by using the rates of meteoritic flux on Mars from *Flynn and McKay* [1990], and the assumption that 1% of the large fragments and 10% of the small ones is in the form of organic compounds. Upper and lower bounds for the influx of organic carbon are thus 5.2×10^{-5} g m^{-2} yr^{-1} and 6.9×10^{-7} g m^{-2} yr^{-1}. Our laboratory simulations show scaled organic degradation rates that are between 16 and 55 times higher than the upper bound for the meteoritic influx of organic carbon on Mars. If aeolian processes stir the loose layer of soil at the surface, much of the top layer will be exposed to the destructive UV radiation. The conclusion, based upon laboratory simulations, is that UV radiation alone may well be responsible for eliminating organic compounds at the surface of Mars. The lack of organics at the Martian surface is thus not surprising, nor does it require that oxidants play any role in organic destruction.

The lack of detection of organic compounds in Martian soil has implications for the existence of current life on Mars. Our results for the UV degradation rate of organics may be used to estimate an upper bound for the globally averaged biomass production rate of possible extant organisms at the Martian surface. The original hypothesis (from Viking GCMS) was that lack of organics was supporting evidence for lack of life, i.e. that biological factors were not responsible for the positive response of the Viking LR experiment. However, in order for Mars to be devoid of organics, it is only necessary for the globally averaged biomass production rate to be lower than the UV destruction rate, $2.24 \pm 1.2 \times 10^{-4}$ g C m^{-2} yr^{-1}. This is achievable if biomass is either produced globally, but at a rate lower than $2.2 \pm 1.2 \times 10^{-4}$ g C m^{-2} yr^{-1}, or at reasonably large rates in local oases that cover a small fraction of the surface. As an example of globally produced biomass, ecosystems which have been explored as an analog to organisms on Mars are cryptoendolithic microbial communities [*Friedmann and Ocampo*, 1972; *Friedmann*, 1980]. *Johnston and Vestal* [1991] suggest that cryptoendolithic microbial communities found in the Ross Desert of Antarctica may be the slowest growing communities on Earth. These communities live inside sandstone in Antarctica and metabolize very slowly because conditions allowing biomass production (liquid water) only occur for brief periods each year. *Johnston and Vestal* [1991] report maximum biomass production rates for cyanobacteria in these communities, due to photosynthesis, of 2.6×10^{-5} g C m^{-2} yr^{-1}. *Friedmann et al.* [1993] estimate the long-term net ecosystem productivity of similar communities to be approximately 3×10^{-3} g C m^{-2} yr^{-1}. Thus, our estimated upper bound for global biomass productivity at the Martian surface is comparable to the slow growing cryptoendolithic communities found in the cold dry deserts of Antarctica. On the other hand, most biomass productivity rates in typical terrestrial ecosystems are much higher. For example, tundra and alpine ecosystems typically produce about 140 g C m^{-2} yr^{-1} [*Whittaker*, 1975]. Given the constraint on globally averaged biomass production rates derived here, an ecosystem with similar productivity could cover a small fraction of the surface, producing biomass at a global rate below the average UV destruction rate for organics. Local oases with the biomass productivity of terrestrial tundra and alpine communities could cover as much as 230 km^2 on Mars, generating organics at a rate undetectable by the Viking GCMS.

Mukhin et al. [1996] have recently reported on experiments they performed on the UV photodecomposition of carbonate and sulfate under simulated Martian conditions. Using a Hg vapor lamp, they found a quantum efficiency for the destruction of carbonate of 10^{-5}, which is higher by an order of magnitude than our results for the degradation of glycine. From this extremely high dissociation rate, they suggest that CO_2 release from carbonate dissociation exceeds the loss rate from the atmosphere due to solar wind-induced sputtering, making the process a net source of atmospheric CO_2. Although this could explain the lack of spectroscopically detected carbonate on Mars' surface, their quantum yield was calculated based on the flux of photons at 300 nm. If the results of these experiments are to be taken at face value, it appears that carbonate should be less stable by an order of magnitude than organic compounds with respect to the UV flux at the Martian surface. However, the spectrum of calcite exhibits strong absorption shortward of 200 nm [*Weber*, 1982],

which corresponds to the most likely minimum photon energy required for calcite UV decomposition. Verification of the quantum efficiency of carbonate UV decomposition under simulated Martian conditions is important for understanding the fate of carbon at the Martian surface, either as organics or sequestered in minerals.

Summary and Conclusions

We have performed laboratory experiments to estimate the rate at which organic compounds are destroyed by ultraviolet light and conditions which exist at the Martian surface. The results are that Martian surface conditions, in the absence of surface oxidants, are sufficiently severe to breakdown organic compounds at a rate greater than 8.7×10^{-4} g m^{-2} yr^{-1}. This rate is up to 3 orders of magnitude larger than the rate that organic compounds are supplied to Mars by meteoritic infall. The Martian surface fines that were sampled by the Viking lander were most likely of aeolian origin [e.g. *Arvidson et al.*, 1989] and therefore had been exposed to the high flux of ultraviolet light that would destroy organics. Therefore it should be no surprise that organic compounds were not detected on Mars. The lack of organic compounds on Mars, per se, does not imply the presence of active oxidizing agents present in the soil, since such compounds are not needed to explain this lack.

With organics and possible evidence for past microbial life found in a Martian meteorite [*McKay et al.*, 1996], it is of paramount importance to understand the distribution and fate of organic compounds near the surface of Mars. The standard interpretations of the Viking lander biology experiments bear closer scrutiny at this point. A prototype Viking GCMS instrument, when tested on Antarctica soils containing 0.03% organic carbon, yielded no detectable organics (J.R. Cronin, personal communication, 1995). Coal-like carbon and kerogens, biotic organic matter that has experienced extensive diagenesis, were the organic compounds that remained undetected in the Antarctica soils by the Viking GCMS prototype. This negative result implies that the Viking landers might have failed to detect organic matter present in the Martian soil [*Levin and Straat*, 1981]. Indeed, at the Martian surface, light organics can easily be transported by winds, while inside rocks sturdier organics may exist protected from the harsh UV flux. If the solar UV flux at the Martian surface is the primary mechanism for destroying organics in the loose soils sampled by Viking, it is possible that complex organics and fossilized remnants of life remain ubiquitous and accessible.

The organic destruction rate which we derive may be taken as an upper bound for the globally averaged biomass production rate of any extant Martian organisms. This globally averaged biomass production rate is approximately equal to the productivity of endolithic microbial communities found in dry Antarctica deserts. If niches of small areal extent still exist on Mars where life thrives, productivity rates there could be much higher. Finally, our laboratory results on the destruction rate of organics under simulated Martian conditions, when compared with similar experiments on the stability of carbonates, imply that organics may be more stable than carbonates on the Martian surface.

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