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Reaction of Methane and UV-activated Perchlorate: Relevance to Heterogeneous Loss of Methane in the Atmosphere of Mars

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Abstract

The absence of significant detectable signatures of organic molecules in the atmosphere and on the surface of Mars is a major unsolved puzzle. One possible explanation is that perchlorate-rich Martian soils, activated by solar ultraviolet (UV) radiation, create an environment favorable for the rapid oxidation of organics such as alkanes (including methane or CH₄). In this paper, we measured product formation rates from the methane-perchlorate-UV system at room temperature. Our results show that magnesium perchlorate (Mg(ClO₄)₂•6H₂O) surfaces exposed to UV light at wavelengths reaching the Mars' surface accelerate the decomposition of methane (CH₄), resulting in the formation of carbon dioxide (CO₂), carbon monoxide (CO), and volatile chlorine oxides. The production rates for CO₂ and CO on UV-activated perchlorate surfaces are 2.5 and 4.5 times higher, respectively, than in the absence of perchlorate. In addition, with UV radiation exposure, perchlorate (ClO₄⁻) decomposes to chlorate (ClO₃⁻) and chlorine oxides. These results are incorporated into a simple box model to estimate the near-surface atmospheric methane lifetime. The model gives a lifetime on the order of hours to months depending on assumptions, substantially shorter than ~300 yrs calculated from methane loss by gas-phase chemistry alone.

Introduction

In situ detection of methane (CH_4) on Mars by NASA's Mars Science Laboratory (MSL) Curiosity rover has raised important questions about the sources and sinks of Martian methane; a seasonally varying background level of ~ 0.4 ppbv has been observed with spikes reaching ~ 21 ppbv. [Webster *et al.*, 2015, 2018] The ExoMars Trace Gas Orbiter's (TGO's) first analysis of the Martian atmosphere at various points around the globe finds an upper limit of methane at 0.05 ppbv [Korablev *et al.*, 2019], 10–100 times less than all previous reported detections. To explain the lack of significant detection of CH_4 , a better understanding of the methane loss processes close to the surface of the planet is needed.

Martian CH_4 sources can be either biotic or abiotic. Martian CH_4 is a potential biosignature. Constraining the production and degradation processes of the smallest organic molecule is crucial for our understanding of the geochemistry of the planet and the possibility of extant or future life. [Weiss *et al.* 2000; Yung *et al.* 2018]

The primary fate of CH_4 in the atmosphere of Mars is oxidation to CO_2 and H_2O . This is thought to be initiated by the reaction $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$, where the OH radical is derived from the photolysis of H_2O . However, this reaction has a high activation energy, resulting in a long gas-phase lifetime for CH_4 . Based on photochemical models and the current understanding of the composition of the Martian atmosphere, the predicted CH_4 photochemical lifetime is about 300 years [Summers *et al.* 2002; Krasnopolsky *et al.*, 2004]. Recent measurements of the low background abundance and short lifetime of methane by MSL, TGO and Mars Express PFS instrument [Webster *et al.*, 2018; Yung *et al.*, 2018; Korablev *et al.*, 2019; Giuranna *et al.*, 2019] have raised important questions about the sources and sinks of Martian CH_4 . In Earth's atmosphere, more than 90% of the methane comes from biological activity. The recently detected methane plumes in the Martian northern hemisphere sparked great interest because of their possible biological origin [Giuranna *et al.*, 2019]. To explain the rapid changes in CH_4 , as reported by [Webster *et al.* 2018], the methane lifetime has to be shorter than 1 year, which is incompatible with the standard working models of the chemistry of the Martian atmosphere. [Lefevre *et al.*, 2009] These short lifetimes indicate methane detected today has been injected into the atmosphere recently. More importantly, the short lifetime suggests that physical and/or chemical sinks control the Martian methane budget in a way that is quite different from Earth. A potential explanation for the shorter lifetime of CH_4 on Mars is heterogeneous uptake and reaction with the Martian surface.

Detections of perchlorate salts on Mars' surface by the Mars landers, including the Phoenix Mars lander and the Curiosity rover [Hecht *et al.*, 2009], opened new possibilities for the heterogeneous sinks of Martian methane. The Wet Chemistry Laboratory onboard the Phoenix lander detected 0.4 – 0.6 wt% perchlorate in the top 5 cm of the soil. The Sample Analysis at Mars (SAM) instrument onboard the Curiosity rover obtained a similar result [Glavin *et al.*, 2013]. With the observation of chlorinated hydrocarbons with SAM [Freissinet *et al.*, 2015], it has been postulated that the oxidation reactions on perchlorate could be a major sink for small organics on the Martian surface, explaining the absence of organic detection. Gough *et al.* investigated methane oxidation with perchlorate under Martian temperatures and

detected no carbon dioxide production after 72 hours of exposure [Gough *et al.*, 2011]. Although no evidence of surface oxidation of small organics was shown on perchlorate salt alone, it was proposed that with the entrance of cosmic rays and unshielded ultraviolet (UV) light into the lower Martian atmosphere, these surface degradation reactions could become possible. In addition, the possibility of surface oxidation on chlorate salts should also be considered. [Mitra *et al.*, 2019] [Martin *et al.*, 2020]

A study by [Carrier *et al.*, 2015] described one possible explanation: highly reactive oxychlorides and radicals can be produced both from oxidation of mineral chlorides to perchlorate by the action of UV irradiation and from the radiolysis of perchlorates by the action of cosmic gamma and X-rays. The reactive intermediates produced from these pathways are capable of attacking organics such as CH₄ by oxidizing and/or chlorinating them. Recent laboratory studies have shown significant oxidative capacity of perchlorate surfaces when activated by energetic electrons [Turner *et al.*, 2016][Gobi *et al.*, 2016], which are more abundant on the Martian surface compared with Earth. Gobi *et al.* explored the radiolytic decomposition of glycine (H₂NCH₂COOH) under simulated Martian conditions in the presence of perchlorate by energetic electrons. Their experiments show that the rate constants for glycine decomposition in the presence of Mg(ClO₄)₂/H₂O were a factor of two higher than that for pure glycine, suggesting that energetic oxygen atoms (O) released from ClO₄⁻ have a significant effect on the decomposition rates. Within the Mars-relevant temperature range (160 – 260 K), the oxidation rate is nearly temperature independent. In addition, the formation rates of CO₂ and CO are both accelerated in the presence of ClO₄⁻ by a factor of up to 5, suggesting a mechanism of active oxygen-initiated chemistry.

Perchlorate-rich Martian soils activated by solar ultraviolet (UV) radiation, can also create an environment favorable to the rapid oxidation of organics such as CH₄; Figure 1 illustrates a possible scheme of the oxidation process. However, until now, no experimental studies have been carried out on reactions of CH₄ + perchlorate + UV. We have now conducted experiments that show that methane undergoes oxidation either on or in the presence of UV-activated perchlorate surfaces to generate CO₂ and CO.

Experiment

We have investigated the reaction between CH₄ and Mg(ClO₄)₂/H₂O activated by UV at room temperature. Figure 2 (a) and (b) show the schematics of our experimental setup. We used a mercury lamp as the UV source (The manufacturer (Oriol) specified that the mercury lamp's UV emission was > 90% at 254 nm and < 10% at 185 nm) which was characterized using a photodiode and bandpass filters. Most of the power is transmitted in the 254 nm line, with 0.8 mW/cm² reaching the sample surface after the quartz window. The quartz window transmits about 80% of the 254 nm light. The intensity at 185 nm was too low to measure with the photodiode and was only detected with a photomultiplier tube (PMT). It was found to be reduced by 50% after passing through the quartz window. The emission from the 313 and 365

nm lines is much weaker and is not expected to contribute to photochemistry. Therefore, we consider any changes caused by the UV light to be due to the 254 nm emission. UV radiation reaching the surface of Mars cuts off at wavelengths shorter than 200 nm depending on the dust loading [Gomez-Elvira *et al.*, 2014], making the mercury lamp a reasonable analog for the purposes of this study.

Magnesium perchlorate hexahydrate ($\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$) (Sigma Aldrich, 99%) was used to prepare samples. The samples were made by dissolving 426 mg $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 38 ml distilled H_2O , adding about 0.5 ml of the solutions on the surface of CaF_2 window (1" diameter) substrate and evaporating the solvent H_2O at room temperature, then the samples were put into the vacuum chamber (total volume of the chamber is about 3 liters). The mass deposited on the surface was about 7 mg. The average thickness of the resulting sample was roughly 7000 nm (using the estimated sample density of 1.98 g cm^{-3} [Lewis, 1992] [Turner *et al.*, 2016]). The perchlorate on the window was hydrated.

First, we conducted experiments to study the products of $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ activated by UV. The vacuum chamber was evacuated to roughly 1 mTorr for the $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ + UV experiment. At the beginning, IR absorption spectra of $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ on the CaF_2 window were collected through two CsI windows mounted on the vacuum chamber. Then, the $\text{CaF}_2/\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ window was irradiated with UV light from a mercury lamp through a quartz window. After several hours of UV irradiation, the CaF_2 window was rotated 90 degrees to face the IR probe beam whereupon IR transmission spectra of UV-activated $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ were acquired over the frequency range $400 - 10000 \text{ cm}^{-1}$ with spectral resolutions of 0.5 and 1 cm^{-1} using a liquid N_2 cooled MCT detector type A.

For the CH_4 + UV-activated perchlorate experiment, after the $\text{CaF}_2/\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ window was mounted inside the vacuum chamber, it was then pumped down to about 1 mTorr. The chamber was then closed to the pump and CH_4 was added. We use relatively large CH_4 partial pressures to establish the occurrence of perchlorate reactions and compensate for the short optical path length (about 3") of the reactor. CH_4 was exposed to a thin film of $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ in the reaction chamber in the presence of UV light generated by the mercury lamp. Changes in the perchlorate surface and gas contents were analyzed by a Fourier Transform Infrared (FTIR) spectrometer after several hours of exposure to UV light. A small leak was detected in the chamber which resulted in the observation of background CO_2 signal.

Results and Discussion

The concentrations of $^{13}\text{CO}_2$ and ^{13}CO were determined from the FTIR data using the program MALT [Griffith 1996]. This was necessary due to the relatively low resolution of the spectrometer (0.5 or 1 cm^{-1}) and the narrow absorption features. The ν_3 asymmetric stretch was used to determine the concentration of $^{13}\text{CO}_2$, while the fundamental band was used for ^{13}CO . Example spectra for ^{13}CO and $^{13}\text{CO}_2$ and the contour fit can be seen in Figures 3a and 3b.

I) UV + Perchlorate

Figure 4a and 4b show a typical set of IR spectra of $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ after UV irradiation for increasing time periods. Our results show that after UV irradiation, new products are formed. The products include $\text{Mg}(\text{ClO}_3)_2$ in the solid phase and chlorine oxides Cl_xO_y (including ClO_2 , Cl_2O_4 , Cl_2O_6 , Cl_2O_7 and possibly their complexes). The chlorine oxides are quite volatile, diffusing into the gas phase where they are deposited onto the CsI windows. Our findings indicate that O and Cl atoms are likely generated in UV photolysis of $\text{Mg}(\text{ClO}_4)_2$ and they may react with CH_4 . Under UV radiation (254 nm), O and Cl atoms can be generated as follows.

The chlorine oxides (Cl_xO_y) were observed in the condensed phase, but not in the gas-phase. Possible explanations are that the chlorine oxides have 1) undergone polymerization reactions; and/or 2) condensed on the salt (CsI) windows. Consequently, there was not enough gas-phase Cl_xO_y to be detected.

II) UV + Perchlorate + CH_4

We performed a set of experiments in which methane was exposed to a thin film of $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ in the reaction chamber in the presence of UV light from the mercury lamp. Changes in the perchlorate surface and gas composition were analyzed by the FTIR after many hours of exposure to UV light. Figures 5a and 5b illustrate the IR spectra indicating changes in the gas composition when exposing CH_4 to $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ with and without UV exposure. We use relatively large CH_4 partial pressures to establish the occurrence of perchlorate reactions and compensate for the short optical path length of the reactor. Our findings show that (1) Increased amounts of CO_2 and CO are observed in the presence of UV-activated $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$, and (2) CH_4 is oxidized on or in the presence of UV-activated $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ and produced CO and CO_2 . The observation of a background CO_2 signal without UV comes from a small leak in the chamber, not from the $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O} + \text{CH}_4$ reaction without UV. This will be demonstrated in the following $^{13}\text{CH}_4$ experiment.

In addition, for the CH_4 + perchlorate + UV reaction, when different CH_4 pressure were used, the production rates of CO_2 appear to be the same (see figure 5a and 5b). Also the data appear to indicate that the rate of product formation is constant over time (during our detection period of a few days). This can be explained as follows. The sample surface is completely covered with CH_4 via adsorption at low CH_4 pressure. As a result, increasing the CH_4 pressure does not increase the CH_4 concentration on the surface. Therefore the experiments do not show an increase in products when methane pressure is increased. In addition, the sample surface is not a monolayer, but a multilayer porous surface. Perchlorate can be considered in excess (or at a constant concentration). Therefore, the rate of product formation is constant over time. Our results indicate that the reaction is most likely photon-limited.

III) UV + Perchlorate + $^{13}\text{CH}_4$

We performed isotopically labeled experiments to investigate the oxidation of methane with UV-activated $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$. Methane- ^{13}C ($^{13}\text{CH}_4$) of about 30 torr was added to the system, as shown in Figures 6a and 6b. The production of $^{13}\text{CO}_2$ and ^{13}CO proves that they are generated from the oxidation of the added $^{13}\text{CH}_4$. The background $^{13}\text{CO}_2$ signal without UV (at time 0) comes from the impurities of the methane- ^{13}C ($^{13}\text{CH}_4$) lecture bottle. Our results show $^{13}\text{CH}_4$ is oxidized on or in the presence of UV-activated $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ and produced $^{13}\text{CO}_2$ and ^{13}CO . The $^{13}\text{CO}_2$ and ^{13}CO bands were analyzed for each trace in Figures 6a and 6b using the program MALT. The production rates of $^{13}\text{CO}_2$ and ^{13}CO were obtained; they are estimated to be 0.42 and 0.53 mTorr/hour (listed in Table 1) for $^{13}\text{CO}_2$ and ^{13}CO , respectively. A number of control experiments were conducted for reactions of UV + $^{13}\text{CH}_4$ and Perchlorate + $^{13}\text{CH}_4$ only. These control experiments will be discussed in the following sections.

We have also found that the surface conditions (i.e. roughness or surface area) of perchlorate may play a role in the reaction. We have noticed that when the perchlorate surfaces have a smooth and glossy appearance, the enhanced production of $^{13}\text{CO}_2$ and ^{13}CO was not observed. More studies on characterization of the perchlorate surfaces are needed to better understand this reaction. However, it is not possible that the reaction was occurring on the CaF_2 substrate. The reason is that the control experiment of CH_4 + UV was conducted with CaF_2 window in the chamber where oxidation occurred much more slowly. If the reaction were occurring on the CaF_2 window, the control experiment of CH_4 + UV should have the same result as CH_4 + UV + $\text{Mg}(\text{ClO}_4)_2$ or much faster product generation. A possible explanation for the enhanced reaction on “rough” surfaces is that the surface areas are larger, therefore the reaction on the “rough” surface is faster.

IV) UV + $^{13}\text{CH}_4$ and other control experiments

We have carried out a number of control experiment, in order to confirm that the generation of CO_2 and CO are the result of UV-activated perchlorate reacting with CH_4 .

UV + $^{13}\text{CH}_4$ (no perchlorate)

An experiment with conditions similar to the ***UV + Perchlorate + $^{13}\text{CH}_4$*** case was conducted for ***UV + $^{13}\text{CH}_4$*** without $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ on the CaF_2 window. Figure 7a compares the $^{13}\text{CO}_2$ production from ***UV + $^{13}\text{CH}_4$*** without $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ and from ***UV + $^{13}\text{CH}_4 + \text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$*** . It depicts that more $^{13}\text{CO}_2$ was generated with $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ in the system. Our MALT analysis shows that the $^{13}\text{CO}_2$ production rate from ***UV + $^{13}\text{CH}_4$*** without $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ is about 0.16 mTorr/hour, compared to 0.42 mTorr/hour with $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$. Figure 7b compares the ^{13}CO production from ***UV + $^{13}\text{CH}_4$*** without $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ and from ***UV + $^{13}\text{CH}_4 + \text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$*** . It illustrates that more ^{13}CO was generated with $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ in the system. Our MALT analysis shows that the ^{13}CO production rate from ***UV + $^{13}\text{CH}_4$*** without $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ is about 0.12 mTorr/hour, compared to 0.53 mTorr/hour with $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$. Table 1 lists the production rates of $^{13}\text{CO}_2$ and ^{13}CO at different conditions. These results show that the presence of perchlorate enhanced the $^{13}\text{CO}_2$ and ^{13}CO production by up to a factor of 2.5 and 4.5, respectively. Without perchlorate, the ***UV + $^{13}\text{CH}_4$*** reaction generates a small amount of $^{13}\text{CO}_2$ and ^{13}CO , where the O likely comes from the photolysis of leaked ***O₂ + Perchlorate + $^{13}\text{CH}_4$ (no UV)***

As shown in Fig. 8a and 8b, we conducted perchlorate + $^{13}\text{CH}_4$ reaction without UV. The production rates for $^{13}\text{CO}_2$ (0.02 mTorr/hour) and ^{13}CO (0 mTorr/hour) were very small or negligible. Fig. 9 compares the formation rates of $^{13}\text{CO}_2$ (panel a) and ^{13}CO (panel b) as determined by the FTIR data under different experimental conditions.

The presence of a slow leak (0.026 sccm) and the small flux of 185 nm light (about 0.06 mW/cm²) from the UV lamp led us investigate possible background photo-oxidation. The manufacturer (Oriel) specified that the mercury lamp's UV emission was > 90% at 254 nm and < 10% at 185 nm. The quartz window of the chamber transmits 80% of the light at 254 nm and 50% of the light at 185 nm. We performed gas-phase chemical modeling including reactions that could be initiated by photolysis of O_2 at 185 nm. What we found is that gas-phase chemistry alone cannot explain the observed abundance of CO_2 during the experiment. Therefore, we find it unlikely that the 185 nm light and the leak of O_2 could explain the observed abundances. Details of this investigation can be found in Appendix II.

Here is a summary of the results described above:

- Reaction ***UV + Perchlorate*** shows that under UV radiation, perchlorate decomposes to chlorate and chlorine oxides, which indicate likely production of O and Cl atoms.
- Reaction ***UV + Perchlorate + CH_4*** shows that CH_4 is oxidized on or in the presence of UV-activated $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ and produced CO and CO_2 .
- Reaction ***UV + Perchlorate + $^{13}\text{CH}_4$*** shows that $^{13}\text{CH}_4$ is oxidized on or in the presence of UV-activated $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ and produced $^{13}\text{CO}_2$ and ^{13}CO .
- Control experiment (reactions ***UV + $^{13}\text{CH}_4$*** and ***Perchlorate + $^{13}\text{CH}_4$***) shows that the productions of $^{13}\text{CO}_2$ and ^{13}CO are enhanced (by factors 2.5 – 4.5) when both ***UV and Perchlorate*** are present along with $^{13}\text{CH}_4$.

Implications for CH_4 Lifetime and HCl production

Assuming the destruction rate of methane (R) in our experiments is limited by the UV flux (ϕ), the former will be proportional to the latter, i.e.,

$$R = \alpha A \phi$$

where A is the surface area of the perchlorate surface, and α is the average number of methane molecules destroyed by each UV photon. Based on the results of our experiments, α is 3.5×10^{-3} molecules photon⁻¹.

Applying the lab-derived α value to Mars, and assuming methane destruction on the perchlorate surface on Mars is also photon-limited, we can compute the methane destruction rate on the Martian surface as 4.8×10^{12} molecules m⁻² s⁻¹. In computing the value, the solar UV flux below 250 nm at the Mars orbit is taken from Yung and DeMore (1999), and a fraction by weight of perchlorate in the surface materials of 5×10^{-3} is assumed.

Based on the reaction rate, the lifetime of methane can then be estimated by dividing the column abundance of methane in the Martian atmosphere by the reaction rate. MSL and TGO report different methane column abundances, so the methane lifetime ranges from shorter than 8 hours to 2.2 days, both of which are significantly shorter than the 330-year lifetime from known photochemical reactions in the gasous phase (Lefèvre and Forget, 2009).

However, the oxidation of methane is accompanied by the reduction of perchlorates, so the methane oxidation rate is capped by the rate of replenishment of perchlorates, such that perchlorates will not be depleted. The replenishment of perchlorates is limited by available oxidants. Based on the estimates of total oxidant fluxes on Mars (Nair et al., 1994), the methane lifetime is revised to be between shorter than 16 days to 100 days, still orders of magnitude shorter than the well-known gas-chemistry's 330-year lifetime. This may account for the apparent contradictions between the observations of TLS vs TGO.

Our results suggest that UV activated perchlorate is an extremely powerful oxidant, consistent with recent findings by [Razaeli Hollis et al., 2021] on the degradation of adenosine monophosphate in a similar environment. Details of the estimation of the methane lifetime on Mars can be found in Appendix 1.

In our experiment we traced the fate of the C in CH₄ to CO and CO₂. No attempt was made to trace the fate of H in CH₄. Most of the H is expected to be oxidized to H₂O. However, it is entirely possible that H can react with Cl in perchlorate to form HCl. Gas-phase HCl was not observed in our experiment. HCl is very sticky and could condense on the salts (CSI) windows. In addition, there was interference from CH₄ bands in the region where HCl peaks were supposed to be.

HCl and its chlorine isotopologues have recently been observed in the atmosphere of Mars by TGO [Korablev et al. 2021; Liuzzi et al. 2021]. Having another reservoir of Cl in the form of HCl may provide a fundamental explanation of the outstanding puzzle of the isotopic fractionations of chlorine in perchlorate within the rocks at Gale Crater [Farley et al. 2016]. Further experiments are urgently needed to prove or disprove the above speculation.

Conclusion

We have conducted studies on reactions of methane + perchlorate + UV light including control experiments in the absence of light and reactants. We have observed the oxidation of methane in the presence of perchlorate surfaces exposed to UV at a wavelength within the spectral range of Martian surface irradiance. UV-activated perchlorate catalyzes the decomposition of methane, resulting in the formation of carbon dioxide (CO₂), carbon monoxide (CO) and volatile chlorine oxides. The production rates on UV-activated perchlorate surfaces are factors of 2.5 and 4.5 faster than those without perchlorate for CO₂ and CO, respectively. The surface conditions (i.e. roughness or surface area) of perchlorate may also play a role in the reaction. In addition, under UV radiation, perchlorate (ClO₄⁻) decomposes to chlorate (ClO₃⁻) and chlorine oxides.

We propose possible reaction mechanisms for the production of CO and CO₂. Under UV radiation (254 nm), ClO₄⁻ can be decomposed to form O and Cl atoms as shown in Rxns 1a - 1c. The O atoms, O(¹D) (which is excited by about 2 eV or 45 Kcal/mol from O(³P)), can react with CH₄ to produce CO and CO₂ as follows.

Other reactions such as CH₃ + ClO₄⁻ may also occur on the sample surface. More studies including isotopic substitution (e.g., Mg(Cl¹⁸O₄)₂) and surface analysis are needed in order to determine the chemical mechanism of methane oxidation.

Although performed under conditions of considerably higher CH₄ concentrations than those on Mars, these results have potentially important implications for the understanding of CH₄ atmospheric loss processes. As depicted in Fig. 1, perchlorate salt in surface minerals can be photoactivated by UV light from unshielded solar radiation. The UV-activated perchlorate salt will react with methane and/or catalyze the reaction of methane with O from a gas-phase source on Mars. As shown in Appendix 1, a qualitative estimate suggests that photosensitized perchlorate could reduce the lifetime of CH₄ on Mars from 300 years based on gas-phase chemistry to less than 1 year. Further experiments are needed to confirm and extend our preliminary results, and quantitative modeling is needed to relate the laboratory results to

resolve the conflict between MSL and TGO measurements. Implications of a shorter lifetime for the variability of CH₄ on Mars will be carried out in a future study using the model of [Luo *et al.*, 2019].

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Appendix I. Estimating the lifetime of methane in the Martian atmosphere via photosensitized oxidation on perchlorate surfaces [Nair *et al*, 1994][Yung and DeMore, 1999]

1. Efficiency of destruction of CH₄ by photosensitized perchlorate (α)

We will first estimate the efficiency of destruction (α) of CH₄ by photosensitized perchlorate in the photon-limited scenario using the laboratory measurements reported in the main text of this paper.

The total reaction rate R (molecules s⁻¹) is proportional to the surface area of the perchlorate surface A (m²) and the flux of UV photons ϕ (photons m⁻² s⁻¹) hitting the perchlorate surface:

$$R = \alpha A \phi \quad (1)$$

where α is the efficiency of destroying CH₄ by UV photons (molecules photon⁻¹).

In the experiment, $A = 5 \text{ cm}^2$.

The energy of one UV photon with $\lambda = 254 \text{ nm}$ wavelength is $\epsilon = \frac{hc}{\lambda} = 7.8 \times 10^{-19} \text{ J}$, where h is Planck's constant and c is the speed of light.

The energy flux of the UV photons $P = 0.7 \text{ mW cm}^{-2}$. So, the flux of UV photons hitting the perchlorate surface is

$$\phi = \frac{P}{\epsilon} = 9.0 \times 10^{18} \text{ photons m}^{-2} \text{ s}^{-1} \quad (2)$$

The volume of the chamber $V = 2.6 \text{ L}$. The rate of formation for ¹³CO and ¹³CO₂ increased with respect to the control experiment by 0.41 and 0.26 mTorr hr⁻¹ respectively when ¹³CH₄ was in the presence of Mg(ClO₄)₂ and 254 nm. This provides a lower limit to the oxidation rate of methane by perchlorate with UV of 0.67 mTorr hr⁻¹. The volume of the chamber $V = 2.6 \text{ L}$, giving an overall reaction rate of

$$R = 1.6 \times 10^{13} \text{ molecules s}^{-1} \quad (3)$$

Combining equations (1), (2) and (3) we obtain

$$\begin{aligned} 1.6 \times 10^{13} \text{ molecules s}^{-1} &= \alpha \times 5 \text{ cm}^2 \times 9.0 \times 10^{18} \text{ photons m}^{-2} \text{ s}^{-1} \\ \alpha &= 3.5 \times 10^{-3} \text{ molecules photon}^{-1} \end{aligned} \quad (4)$$

2. The UV flux-limited destruction rate of CH₄ at the surface of Mars

The cutoff of UV photons by CO₂ is about 180 nm. Photons with wavelengths longer than 180 nm will be able to penetrate to the surface, except for scattering and absorption of dust. We argue that the dust and the surface are made of the same material, and so in this case activation of perchlorate by UV photons on the surface or on the dust is the same. The solar UV flux below 250 nm at 1 AU for overhead sun is given by

$$F_{250} = 2.49 \times 10^{18} \text{ photons m}^{-2} \text{ s}^{-1} \quad (5)$$

where F_{250} is taken from Table 2.1 of Yung and DeMore (1999).

The fraction by weight of perchlorate in the soil or dust is $f = 5 \times 10^{-3}$ (see main text). It is conjectured to exist as a mixture of Ca(ClO₄)₂ and Mg(ClO₄)₂. We note that the densities of the perchlorates and Martian rock (silicate) are similar, and so we can assume that f is also the mole fraction of perchlorate.

$$\text{Rate of CH}_4 \text{ destruction } \Phi = \frac{1}{9} F_{250} \alpha f = 4.8 \times 10^{14} \text{ molecules m}^{-2} \text{ s}^{-1} \quad (6)$$

where α is from (4). The factor of $\frac{1}{9}$ accounts for the reduction of solar flux because Mars is further from the Sun ($\sim \frac{1}{2.25}$) and converting the solar flux for overhead sun at the equator to a planetary and diurnal mean ($\sim \frac{1}{4}$). We also assume that all photons with wavelengths < 250 nm are as effective as our UV source at 254 nm.

If we assume that photons at wavelengths less than 350 nm are effective as those at 254 nm, we can replace F_{250} by F_{350} in the formula for Φ . In this case, we have from Table 2.1 of Yung and DeMore (1999) $F_{350} \sim 37 F_{250}$, and Φ would be 37 times higher. Therefore, this is significant even if the efficiency α at 350 nm were an order of magnitude less than that at 254 nm. Therefore, the rate of destruction calculated for 254 nm light provides a lower limit of CH₄ destruction in the light-limited case.

3. Lifetime of CH₄ on Mars based on photosensitization limit

From the above discussion, we have estimated the column integrated rate of destruction of CH₄ on Mars. From this we can estimate a mean lifetime of CH₄, if we know its mean column integrated abundance in the atmosphere.

Mean column density of the atmosphere (at 6.1 hPa surface pressure) $C_{atm} = 2.28 \times 10^{27} \text{ molecules m}^{-2}$

The mean mixing ratio of CH₄ on Mars, μ , is controversial at present (see discussion in main text). From the MSL background measurements, we have

$$\mu_{MSL} = 4.1 \times 10^{-10}$$

$$C_{MSL} = \mu_{MSL} C_{atm} = 9.4 \times 10^{17} \text{ molecules m}^{-2}$$

However, if we take the upper limit of TGO measurements

$$\mu_{TGO} < 6 \times 10^{-11}$$

$$C_{TGO} = \mu_{TGO} C_{atm} < 1.37 \times 10^{17} \text{ molecules m}^{-2}$$

The estimate of the mean lifetime, Γ , is given by

$$\Gamma_{MSL} = \frac{C_{MSL}}{\Phi} = 1.9 \times 10^5 \text{ s} = 2.2 \text{ days} \quad (7)$$

$$\Gamma_{TGO} = \frac{C_{TGO}}{\Phi} < 2.8 \times 10^4 \text{ s} = 7.9 \text{ hours} \quad (8)$$

The above estimates show for the first time that photosensitized perchlorate could reduce the lifetime of CH_4 on Mars from 300 yrs based on gas phase only chemistry to approximately one day.

4. Lifetime of CH_4 on Mars based on the rate of restoring perchlorate

The above estimate assumes that when the perchlorate is used to oxidize CH_4 , it is instantly restored back to perchlorate by an oxidant on Mars. The potential oxidants in the atmosphere of Mars are: O, $\text{O}(^1\text{D})$, O_2 , OH, HO_2 , and H_2O_2 . O_2 is unlikely to be a powerful oxidant. The combined fluxes of the other oxidants (Nair et al. 1994) are less than

$$\Phi_0 = 10^{11} \text{ molecules m}^{-2} \text{ s}^{-1} \quad (9)$$

for accommodation coefficient of 0.01. Since Φ_0 is significantly less than Φ from (6), we argue that the availability of the oxidants may be the limiting factor. In this case, we have the oxidant-limited lifetime given by

$$\Gamma_{MSL} = \frac{C_{MSL}}{\Phi_0} = 9.4 \times 10^6 \text{ s} = 108 \text{ days} \quad (10)$$

$$\Gamma_{TGO} = \frac{C_{TGO}}{\Phi_0} < 1.37 \times 10^6 \text{ s} = 15.9 \text{ days} \quad (11)$$

Even in this case, the lifetime of CH_4 is much shorter than the that derived from the gas-only chemical destruction. These results are meant to demonstrate the possible importance of heterogenous methane oxidation in the Martian atmosphere. They do not consider a number of important parameters important in heterogeneous chemistry such as pore size distribution, diffusivity effects and total active surface area. In addition, due to the large deviation from Martian conditions in the experimental apparatus (room temperature and 40 mbar), the

results must be taken qualitatively. Further experiments controlling the sample conditions are needed to provide a quantitative picture.

Appendix II. Details regarding the leak and possible ensuring chemistry

The presence of a slow leak (0.026 sccm) and the small flux of 185 nm light from the UV lamp led us investigate possible background photo-oxidation. The manufacturer (Oriel) specified that the mercury lamp's UV emission was > 90% at 254 nm and < 10% at 185 nm. Only the light at 185 nm (6.7 eV) has sufficient energy to photolyze O₂, generating relatively inert O(³P). However, the termolecular reaction between O(³P) and O₂ can lead to ozone, which is rapidly photolyzed by the 254 nm light generating highly reactive O(¹D) as shown in reactions R1-R3.

The rate that O₂ converts to O(¹D) depends on the photolysis cross section of O₂ at 185 nm and O₃ at 254 nm, and the intensity of light at both wavelengths. The 185 nm emission is within the Schumann-Runge bands of O₂, which have sharp rotational fine structure leading to a cross section that varies by orders of magnitude over short ranges. The 185 nm line of Hg does not coincide with the any rotational structure and has the continuum value of $8.8 \times 10^{-21} \text{ cm}^2$. The intensity of the UV lamp was measured to be 1.07 mW/cm² at 254 nm using a photodiode (OPTO DIODE CORP., UVG100) with a bandpass filter. Assuming the lamp's manufacturer specification is correct, the intensity at 185 nm should be 0.12 mW/cm². The quartz window on the chamber transmits 80% of the light at 254 nm and 50% of the light at 185 nm. The photolysis rates were determined with **equations E1 and E2**, where $\sigma_{\text{O}_m, \lambda}$ is the cross section of species O_m at wavelength λ , and ϕ_λ is the photon flux at wavelength λ .

$$\frac{d[\text{O}(\text{}^3\text{P})]}{dt} = \sigma_{\text{O}_2, 185 \text{ nm}} \phi_{185 \text{ nm}} [\text{O}_2] \quad (\text{E1})$$

$$\frac{d[\text{O}(\text{}^1\text{D})]}{dt} = \sigma_{\text{O}_3, 254 \text{ nm}} \phi_{254 \text{ nm}} [\text{O}_3] \quad (\text{E2})$$

Model construction

The main product channel of the reaction between CH₄ and O(¹D) is CH₃ and OH, where OH will react further with methane to generate additional CH₃ and water. CH₃ can react with O₂ to form methyl peroxy radical (CH₃O₂) (**R4**) or self-react to form ethane.

The self recombination of CH₃O₂ can lead to methoxy radical, formaldehyde, and methanol as shown in reaction R5.

From here, CO can form from the photolysis of formaldehyde at 254 nm, and CO_2 from the reaction between CO and OH. In addition to this, reactions were included if there were considered feasible under the experimental conditions. All reactions and rates included in the model are listed in **Tables APP-1 - APP-3**.

Table APP-1. Photochemical processes included in the model, where σ is the cross section at the relevant wavelength. When available, quantum yields available in parentheses. All values are from the JPL data evaluation [Burkholder 2015].

Process	σ_{185}/cm^2	σ_{254}/cm^2
$\text{O}_2 \rightarrow 2\text{O}(^3\text{P})$	8.8×10^{-21}	
$\text{O}_3 \rightarrow \text{O}(^1\text{D}) + \text{O}_2$	8.0×10^{-19}	1.2×10^{-17}
$\text{CH}_2\text{O} \rightarrow$ H + HCO (0.38) H ₂ + CO (0.62)		3.19×10^{-21}
$\text{CH}_3\text{O}_2 \rightarrow \text{OH} + \text{CH}_2\text{O}$		3.39×10^{-18}
$\text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{O} + \text{OH}$		3.23×10^{-20}
$\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$	6.72×10^{-19}	6.70×10^{-20}
$\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$	6.78×10^{-20}	
$\text{HO}_2 \rightarrow \text{O}(^1\text{D}) + \text{OH}$	3.68×10^{-18}	7.87×10^{-19}

Table APP-2 Termolecular reactions used in gas phase photochemical model, where K_0 and K_{inf} are the low and high pressure limits. The JPL roll off form was used to determine the effective rate coefficient.

Unless otherwise noted, all values are from the JPL data evaluation [Burkholder 2015].

Reaction	$K_0/\text{cm}^6\text{s}^{-1}$	$K_{inf}/\text{cm}^3\text{s}^{-1}$
$\text{O}(^3\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	6.0×10^{-34}	-
$\text{OH} + \text{CH}_4 + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$	6.9×10^{-31}	2.6×10^{-11}
$\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$	4.0×10^{-34}	1.2×10^{-12}
$\text{CH}_3 + \text{CH}_3 + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M}^a$	-	5.0×10^{-11}
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	4.4×10^{-32}	7.5×10^{-11}

a. [Robertson 2015]

Table APP-3 Bimolecular reactions used in the gas phase photochemical model. Branching ratios are in parentheses. All values are from the JPL data evaluation [Burkholder 2015].

Reaction	$k/\text{cm}^3\text{s}^{-1}$
O(¹D) Reactions	
$\text{O}(^1\text{D}) + \text{CH}_4$ $\rightarrow \text{CH}_3 + \text{OH}$ (0.75) $\rightarrow \text{CH}_3\text{O} + \text{H}$ (0.20) $\rightarrow \text{CH}_2\text{O} + \text{H}_2$ (0.05)	1.1×10^{-10}
$\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$	3.5×10^{-11}
$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$	2.0×10^{-10}
$\text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O}(^3\text{P}) + \text{N}_2$	3.1×10^{-11}
$\text{O}(^1\text{D}) + \text{O}_2 \rightarrow \text{O}(^3\text{P}) + \text{O}_2$	8.95×10^{-11}
$\text{O}(^1\text{D}) + \text{O}_3$ $\rightarrow 2\text{O}(^3\text{P}) + \text{O}_2$ (0.5) $\rightarrow \text{O}_2 + \text{O}_2$ (0.5)	1.2×10^{-10}
HO_x Reactions	
$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	1.8×10^{-12}
$\text{OH} + \text{CH}_2\text{O} \rightarrow \text{HCO} + \text{H}_2\text{O}$	8.5×10^{-12}
$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	1.1×10^{-10}
Organic Reactions	
$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	6.3×10^{-15}
$\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$	1.5×10^{-13}
$\text{CH}_3\text{O}_2 + \text{OH} \rightarrow \text{CH}_3\text{O} + \text{HO}_2$	1.5×10^{-13}
$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2$ $\rightarrow 2\text{CH}_3\text{O} + \text{O}_2$ (0.35) $\rightarrow \text{CH}_2\text{O} + \text{CH}_3\text{OH} + \text{O}_2$ (0.65)	
$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	1.9×10^{-15}
$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	5.2×10^{-12}
$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	5.2×10^{-12}
$\text{HCO} + \text{HCO} \rightarrow \text{CH}_2\text{O} + \text{CO}$	4.48×10^{-11}

Model results and discussion

Figure APP-1. Results from the photochemical model over a period of 22 hours using the software package [Ianni 2019]. Species with abundances smaller than 10^{13} cm^{-3} are not shown for clarity.

The simulation was performed using the software package Kintecus [Ianni 2019] assuming room temperature and 31 Torr of CH_4 . A leak rate of 0.026 sccm was used assuming 20% O_2 and 80% N_2 . The simulation calculated the concentration of all species over a 22 hour period. The results are shown in **Figure APP-1**. Unsurprisingly, the major product was water (154 mTorr), followed by CO (76 mTorr) and CH_3OOH (74 mTorr). After these, H_2 , H_2C_2 , C_2H_2 , CH_2O , and CH_3OH are minor products (< 30 mTorr).

These results do not reflect what was measured experimentally both in magnitude and in product distribution. Experimentally, 1.2 mTorr of CO was observed after 22 hours of UV irradiation without $\text{Mg}(\text{ClO}_4)_2$ present, where the model predicts 76 mTorr. This discrepancy is likely caused by the model considering the entire reaction volume as be irradiated, where in reality only $\sim 20 \text{ cm}^3$ is exposed to the lamp in an entire volume of 2.6 liters. A simple dilution factor would reduce the amount of CO generated to 0.6 mTorr which is similar to the measured value. However, for CO_2 , this would predict only 0.017 Torr where 3 mTorr was observed. Modeling the diffusion from the irradiated region to the rest of the reaction volume and vice versa was out of the scope of this analysis. However, it would result both in an overall dilution and act to slow down much of the relevant chemistry. Therefore, a significant reduction in overall concentration of all products is expected. This makes it unlikely that the photochemistry initiated by 185 nm light could explain the concentrations observed in the experiment.

The model predicts the formation of CO to be faster than CO_2 by a factor of 35, where experimentally they are generated at similar rates. This points to processes outside of gas phase reactions being prevalent in the experiment, as the model did not include any surface chemistry. This disagreement shows that gas phase photochemistry due to the 185 nm irradiation and the leak cannot explain the background contributions to the oxidation of methane.

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Figures

Figure 1

Figure 2

Figure 3a

Figure 3b

Figure 4a

Fig. 4b

Figure 5a

Figure 5b

Figure 6a

Figure 6b

Figure 7a

Figure 7b

Figure 8a

Figure 8b

Figure 9a

Figure 9b

Table 1. Production rates of $^{13}\text{CO}_2$ and ^{13}CO for reaction $^{13}\text{CH}_4 + \text{Mg}(\text{ClO}_4)_2 + \text{UV}$ and control experiments ($^{13}\text{CH}_4 + \text{UV}$ and $^{13}\text{CH}_4 + \text{Mg}(\text{ClO}_4)_2$). Here $^{13}\text{CH}_4$ is at 31 Torr. Uncertainties are given in parentheses in units of least significant digit.

$\text{Mg}(\text{ClO}_4)_2$	UV/254 nm	Production rate (mTorr/hour)		
		$^{13}\text{CO}_2$	^{13}CO	Total ($^{13}\text{CO}_2 + ^{13}\text{CO}$)
Yes	Yes	0.42 (5)	0.53 (7)	0.95 (9)
Yes	No	0.02 (2)	0	0.02 (2)
No	Yes	0.16 (1)	0.12 (2)	0.28 (2)
		Net Total ($^{13}\text{CO}_2 + ^{13}\text{CO}$)		0.6 (9)

Figure Captions

Figure 1. Possible reactions on Mars surfaces. Perchlorate in the soil of Mars can be decomposed by UV irradiation and generate highly reactive species such as O atom, The reactive species are capable of attacking organics such as CH₄ by oxidizing (and/or chlorinating by Cl atom, not shown here) them. .

Figure 2. Experimental setup for UV photolysis of Mg(ClO₄)₂ and its reaction with CH₄, detected with IR absorption spectra. (a) CaF₂ window is connected to a cold finger that is interfaced to a two-stage closed-cycle helium compressor; the CaF₂ window can be cooled from 300 K to 4 K. Here for this work, the temperature is set at room temperature (~300K). (b) UV photolysis is done with a mercury lamp. After UV irradiation, the CaF₂/ Mg(ClO₄)₂ window is rotated 90° to be scanned by the IR beam.

Figure 3. Representative FTIR spectra comparing the experimental data, shown in red, to the least-squares fit result from the program MALT [Griffith, 1996], shown in black, with the residuals shown above each spectrum. (a) Spectrum containing the *P* branch of the ¹³CO₂ ν₃ asymmetric stretch. The partial pressure of ¹³CO₂ was found to be 12 mTorr. (b) Spectrum containing the *P* branch of the ¹³CO fundamental band. The partial pressure of ¹³CO was found to be 22 mTorr.

Figure 4. Mid-infrared spectra of Mg(ClO₄)₂ following UV irradiation for the indicated time periods. Vibrational assignments are annotated on the figure. a) In the 910 -1700 cm⁻¹ region (the spectra were baseline-corrected); b) in the 2600 – 4000 cm⁻¹ region.

Figure 5a. Mid-infrared spectra of Mg(ClO₄)₂/H₂O + CH₄ at 0.5 cm⁻¹ spectral resolution with and without UV irradiation for the indicated time periods at room temperature. The main vibrational bands shown belong to CO₂. The production rate of CO₂ is accelerated in the presence of UV-activated Mg(ClO₄)₂/H₂O. (The spectra were baseline-corrected)

Figure 5b. Mid-infrared spectra of Mg(ClO₄)₂/H₂O + CH₄ with and without UV irradiation for the indicated time periods at room temperature. The main vibrational bands shown belong to CO. The production rate of CO is accelerated in the presence of UV-activated Mg(ClO₄)₂/H₂O. (The spectra were baseline-corrected)

Figure 6a. Mid-IR spectra of Mg(ClO₄)₂ + ¹³CH₄ with UV for the indicated time periods. The main vibrational bands shown belong to CO₂ and ¹³CO₂. (The spectra were baseline-corrected)

Figure 6b. Mid-IR spectra of Mg(ClO₄)₂ + ¹³CH₄ with UV for the indicated time periods. The main vibrational bands shown belong to CO and ¹³CO. (The spectra were baseline-corrected)

Figure 7a. Mid-IR spectra of ¹³CH₄ + UV with and without Mg(ClO₄)₂ for the indicated time periods. The main vibrational bands shown belong to CO₂ and ¹³CO₂. (The spectra were baseline-corrected)

Figure 7b. Mid-IR spectra of $^{13}\text{CH}_4$ + UV with and without $\text{Mg}(\text{ClO}_4)_2$ for the indicated time periods. The main vibrational bands shown belong to CO and ^{13}CO . (The spectra were baseline-corrected)

Figure 8a. Mid-IR spectra of $^{13}\text{CH}_4$ + $\text{Mg}(\text{ClO}_4)_2$ with and without UV for the indicated time periods. The main vibrational bands shown belong to CO_2 and $^{13}\text{CO}_2$. (The spectra were baseline-corrected)

Figure 8b. Mid-IR spectra of $^{13}\text{CH}_4$ + $\text{Mg}(\text{ClO}_4)_2$ with and without UV for the indicated time periods. The main vibrational bands shown belong to CO and ^{13}CO . (The spectra were baseline-corrected)

Figure 9a-b. Comparisons of the formation rates of $^{13}\text{CO}_2$ (panel a) and ^{13}CO (panel b) as determined by the FTIR data under different experimental conditions. The initial concentration of each species was subtracted for ease of comparison. The error bars show the uncertainties (1σ) determined by the nonlinear least squares fitting.

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Highlights

- UV-activated perchlorate surfaces accelerates the decomposition of methane (CH_4)
- Production rates for CO_2 and CO are 2- 5 times higher than without perchlorate
- Methane lifetime on Mars: 300 yrs from CH_4 loss by gas-phase chemistry alone
- Methane lifetime on Mars: < 1 yr from UV-activated perchlorate chemistry
- With UV, perchlorate (ClO_4^-) decomposes to chlorate (ClO_3^-) and chlorine oxides

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