

Research Article

Reduction in Haze Formation Rate on Prebiotic Earth in the Presence of Hydrogen

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Abstract

Recent attempts to resolve the faint young Sun paradox have focused on an early Earth atmosphere with elevated levels of the greenhouse gases methane (CH₄) and carbon dioxide (CO₂) that could have provided adequate warming to Earth's surface. On Titan, the photolysis of CH₄ has been shown to create a thick haze layer that cools its surface. Unlike Titan, however, early Earth's atmosphere likely contained high amounts of CO₂ and hydrogen (H₂). In this work, we examine haze formation in an early Earth atmosphere composed of CO₂, H₂, N₂, and CH₄, with a CO₂/CH₄ ratio of 10 and a H₂/CO₂ ratio of up to 15. To initiate aerosol formation, a broad-spectrum ultraviolet (UV) energy source with emission at Lyman- α was used to simulate the solar spectrum. Aerosol composition and total aerosol mass produced as a function of reagent gas were measured with an aerosol mass spectrometer (AMS). Results show an order of magnitude decrease in haze production with the addition of H₂, with no significant change in the chemical composition of the haze. We calculate that the presence of H₂ on early Earth could thus have favored warmer surface temperatures and yet allowed photochemical haze formation to deliver complex organic species to early Earth's surface. Key Words: Atmosphere—Atmospheric compositions—Carbon dioxide—Early Earth. *Astrobiology* 9, 447–453.

I. Introduction

THE PRESENCE OF LIQUID WATER at 3.8 Ga, despite a faint young Sun, requires that powerful greenhouse gases were present on early Earth. Recent attention has focused on an early Earth warmed by modest amounts of CH₄ in combination with CO₂ (Pavlov *et al.*, 2001a). Before the appearance of methanogens, which allowed for a steady flux of CH₄ to reach the atmosphere, the ratio of CO₂ to CH₄ may have been quite high (Kasting and Howard, 2006). Volcanic activity and interstellar dust particles could have delivered small amounts of CH₄ and larger amounts of CO₂ during the period on Earth before the arrival of life but after the presence of liquid water (Pavlov *et al.*, 2001a).

It is also well known from studies of Titan that CH₄ photochemistry can produce organic haze particles. If present on early Earth, this haze may have protected developing

life from harmful UV radiation and protected the CH₄ and other greenhouse gases below this layer from rapid photolysis (Sagan and Chyba, 1997). Additionally, prebiotic organic chemistry could have provided a source for some of the more complex organic molecules later found in living organisms (Miller, 1998). However, a thick layer of this hydrocarbon haze could have produced an antigreenhouse effect, similar to that seen on Titan, which would have counteracted the greenhouse warming effect from CO₂/CH₄ and cooled Earth to below-freezing temperatures (McKay *et al.*, 1999; Pavlov *et al.*, 2001b). On Titan, stratospheric haze absorbs 40% of the incoming solar radiation, which results in an antigreenhouse effect (McKay *et al.*, 1999). Trainer *et al.* (2006) found that a CO₂/CH₄ ratio of unity produces a higher organic flux than that which occurs in the atmosphere of Titan. Trainer *et al.* (2006) also found that O atoms released from the photolysis of CO₂ was incorporated into these particles. If the optical

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properties of the oxygenated early Earth haze, which are of course unknown, were similar to those of present-day Titan's, then significant cooling may have occurred.

While there are similarities between Titan and early Earth, haze chemistry on early Earth would differ from Titan's due to a lower expected mixing ratio of CH₄ as well as the presence of CO₂. In addition to CO₂ and CH₄, H₂ could also influence the haze-production chemistry. Recent research suggests that, at 4 Ga, H₂ may have been present in the atmosphere in mixing ratios 2–3 orders of magnitude higher than previously believed (Tian *et al.*, 2005). Calculating the H₂ balance with a lower escape rate, Tian *et al.* (2005) suggested that H₂ could have constituted up to 30% of the early atmosphere, which is assumed to have had a total pressure of about 1 bar. If H₂ was indeed present in high amounts on early Earth, then study of the effect of the H₂ level on haze synthesis would be important for a more accurate picture of the organic aerosols that could have been a part of the ancient atmosphere. If high amounts of H₂ lingered into the Archean, the level of haze production presented in Trainer *et al.* (2006) could also have been affected.

Tian *et al.* (2005) proposed that, in a system with small amounts of CH₄ and larger amounts of CO₂, the presence of H₂ would actually assist in photolytic haze production. Theoretically, H₂ could titrate out the O derived from CO₂ photolysis by forming H₂O, which would thus allow a more Titan-like aerosol particle to form from the remaining CH₄ chemistry. According to Tian *et al.* (2005), significant amounts of hydrocarbon haze could be produced in this scenario, on the order of 10⁹ to 10¹⁰ kg year⁻¹. However, H₂ is also known to have a saturating effect on hydrocarbon aerosols formed in the absence of oxygen-containing compounds (Stribling and Miller, 1987). The effect of H₂ on production of CO₂/CH₄ hazes, however, has not been directly studied in the laboratory. Estimates from Tian *et al.* (2005) were based on previous model work done by Pavlov *et al.* (2001b).

Here, we perform laboratory experiments to determine whether an organic haze can form in a simulated prebiotic Earth atmosphere with high amounts of CO₂. We also examine the effect of adding H₂ to such mixtures. The chemical nature of the aerosols formed over a range of CO₂/H₂/CH₄ mixtures is analyzed and the implications for a prebiotic Earth discussed.

II. Experimental

A. Aerosol generation

The system used to perform these experiments has been discussed previously (Trainer *et al.*, 2004, 2006). The gases were first combined in a mixing chamber where they were allowed to equilibrate for 12 hours to assure homogeneity. The gas mixture was then flowed into a reaction chamber via a Mykrolis mass flow controller at a flow rate of 60 sccm. As the reagent gases passed through the reaction chamber, they were exposed to UV radiation by way of a Hamamatsu broad-spectrum UV lamp with a wavelength range from 115–400 nm. Photochemical reactions within the cell produced organic haze particles. The residence time for the gas inside the reaction chamber was 5 minutes. Note that particles in the real atmosphere would have far longer reaction times than those in the present work.

B. Particle characterization

Aerosol composition as a function of reagent gas was measured with a quadrupole-based aerosol mass spectrometer (AMS) (Jayne *et al.*, 2000; Canagaratna *et al.*, 2007). The reacted particle/gas mixture flowed from the reaction chamber into the AMS, where excess gas was pumped away and the particles were focused into a tight beam with an aerodynamic lens. The AMS can be used in either the particle time-of-flight mode or in mass spectrum mode. The particle time-of-flight mode uses the terminal velocity of the particles in vacuum to determine their aerodynamic diameter, d_{va} , (DeCarlo *et al.*, 2004), while in mass spectrum mode all particles are analyzed without size selection. The chemical composition of the particles was determined by flash vaporizing the particles on a heated surface under high vacuum, followed by electron impact ionization and mass analysis via a quadrupole-based mass spectrometer. With this technique, we were able to measure the mass spectra of the aerosol compounds in real time without the need for collection.

The AMS was ideally suited to these experiments because its inlet and differential pumping system concentrate the particles by a factor of 10⁷ relative to gaseous compounds, thus minimizing gas phase interferences. In addition to composition and size information, the AMS also supplies information on the mass concentration ($\mu\text{g m}^{-3}$) of the particles sampled based on a calibration of the electron impact ionization signals (Jimenez *et al.*, 2003). We thus used the AMS to determine the changing production rates of the haze particles quantitatively as the reagent gas mixture was varied. The signals from gas-phase species such as CO₂ were removed by subtracting the signal while sampling the gas mixture without the light source turned on.

A scanning mobility particle sizer (SMPS) was also used to study the size distribution and overall production rate of the particles as the reagent gas mixture was changed. The particles were flowed into the SMPS after the reaction, and size and particle count data were taken. The SMPS consists of a differential mobility analyzer (DMA model 3081, TSI) and a condensation particle counter (CPC model 3022, TSI). The differential mobility analyzer sizes particles based on their electrical mobility, while the condensation particle counter grows the particles to optically detectable sizes by exposing them to supersaturated butanol vapor and counts these enlarged particles using a laser beam and a photodetector. The SMPS has a lower detection limit for particle size detection than the AMS, which allows smaller particles (down to a mobility diameter of 14 nm) to be detected. In contrast, the efficiency of particle detection by the AMS drops off sharply at aerodynamic diameters less than 50 nm d_{va} (Jayne *et al.*, 2000).

C. Gas mixtures

The composition of the early Earth atmosphere before the emergence of life is very uncertain. Recent work has suggested that H₂ might have been a significant part of that atmosphere and compromised up to 30% of early Earth's air (Tian *et al.*, 2005). In the present work, we examine two scenarios in which the atmosphere might have had varying amounts of H₂. Primarily, we will focus on the prebiotic atmosphere proposed by Tian *et al.* (2005), which is suggested to have high H₂ and CO₂ with a small abundance of CH₄

(0.01 bar CO₂ and 0.001 bar CH₄). Thus, our gas mixtures will have mixing ratios of 1% CO₂ and 0.1% CH₄. Additionally, we examine the effect of H₂ concentration in an atmosphere with a higher CH₄ abundance, which is likely to represent early Earth after methanogens evolved (0.01 bar CO₂ and 0.01 bar CH₄). In each of these cases, the CH₄/CO₂ mixtures in a N₂ background had varying H₂ up to 15 times that of CO₂ with a total experimental pressure of 0.79 bar (chosen to be approximately the ambient pressure in Boulder, Colorado).

III. Results

Previous work by Pavlov *et al.* (2001a) suggested that organic haze formation chemistry would stop above a CO₂/CH₄ ratio of unity. Trainer *et al.* (2006) performed experiments on these mixtures and instead found a peak in aerosol production at a CO₂/CH₄ ratio of unity. For higher amounts of CO₂, haze production did decrease, with the highest ratio studied being 5/1 CO₂/CH₄. Thus, it was initially believed that particles might not form at all in a 10/1 CO₂/CH₄ (C/O ratio of 0.55) ratio. However, here we find measurable particle mass produced, using both the AMS and SMPS under all conditions studied.

Figure 1 shows aerosol mass spectra for particles produced by UV irradiation of 10/1 CO₂/CH₄ mixtures with varying amounts of H₂. It can be seen (Fig. 1, bottom panel with 0% H₂) that a significant amount of aerosol mass is formed, even with this large excess of CO₂. The mass spectrum reveals that the particles produced are highly oxidized, with dominant peaks at mass-to-charge ratio (m/z) 44 (likely CO₂⁺) and m/z 73 (likely C₄H₉O⁺), with much lower mass signals at the m/z values greater than 60. Low particle mass at high m/z regions suggests particles formed of molecules that contain many functional groups, rather than longer-chained hydrocarbons (Zhang *et al.*, 2005).

The chemical composition of the haze formed from a 10/1 CO₂/CH₄ mixture is very similar to one formed from a 5/1 mixture (Trainer *et al.*, 2006). This can be seen in Fig. 2, where the intensity of each AMS peak is shown for both experiments, along with the one-to-one line. The scatter is larger for $m/z > 100$, due to the signal falling into the noise. In general, there is good agreement in the mass intensities for both experiments, with m/z 's of 28 and 44 being the largest peaks in both experiments. Additionally, the total organic mass produced in both cases is the same within experimental error. This suggests that aerosol production pathways stay consistent in

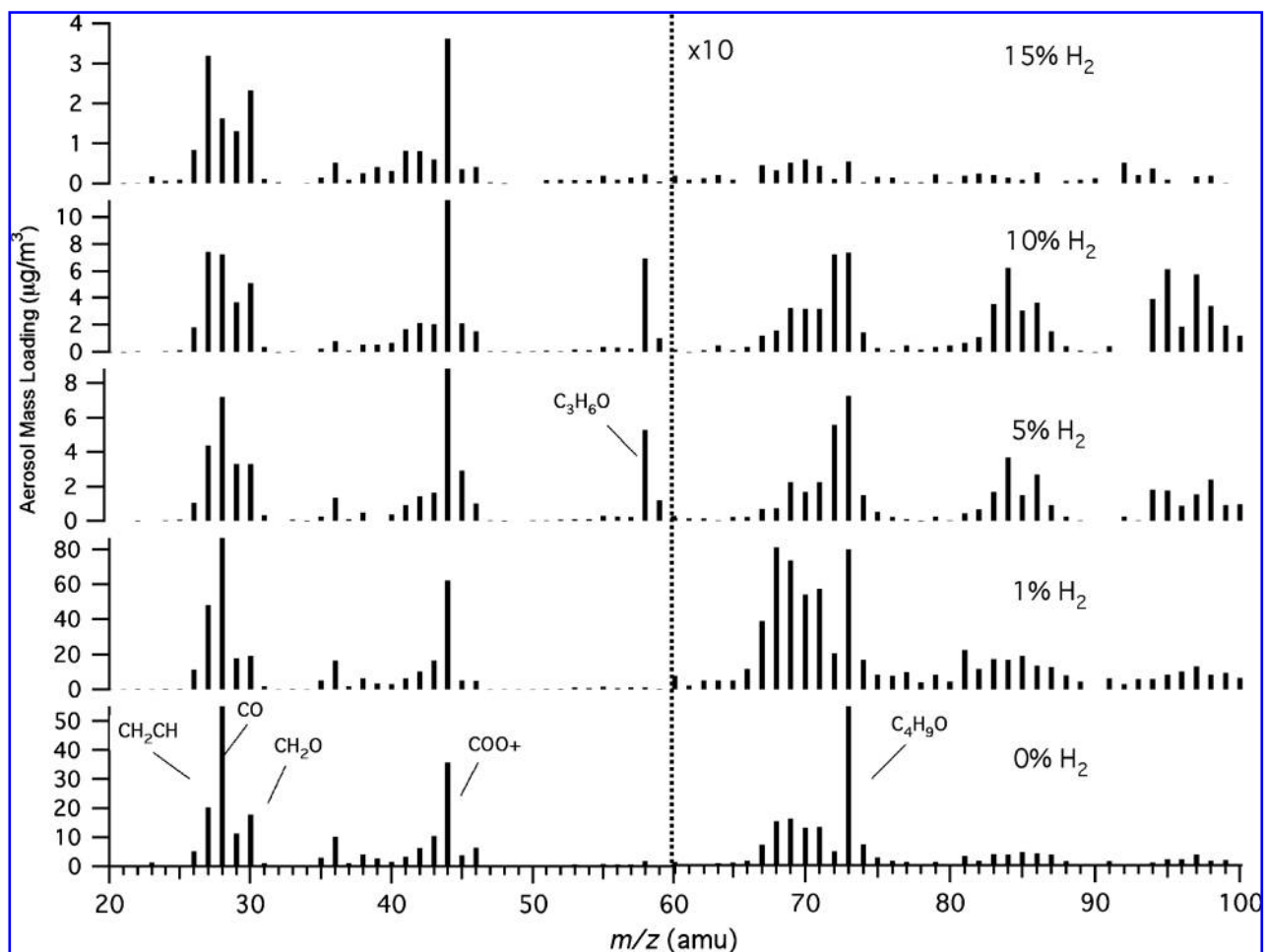


FIG. 1. Aerosol mass spectrometer spectra of particles found from the photolysis of 1/10 CH₄/CO₂ in N₂ with varying amounts of H₂. Each spectrum represents an average of multiple spectra from experiments with the same relative gas phase concentration. Data to the right of the dashed line at m/z 60 are multiplied by 10 for ease of viewing.

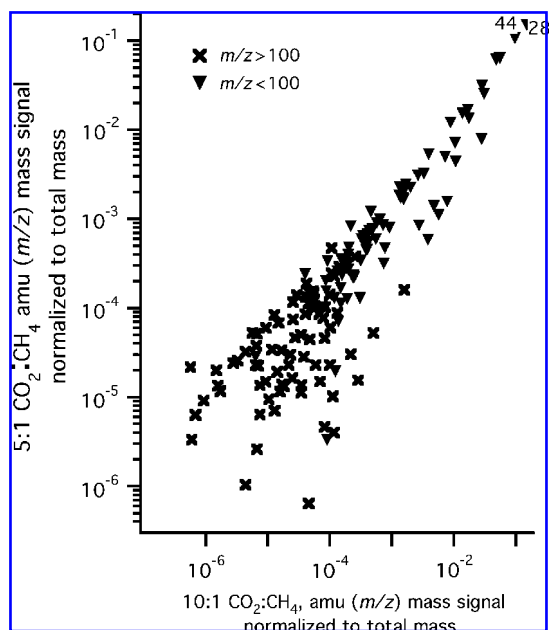


FIG. 2. Peak-by-peak comparison of the AMS spectral intensities for particles formed from 10/1 CO_2/CH_4 compared to earlier work by Trainer *et al.* (2006) with 5/1 CO_2/CH_4 . In each case, the peak intensities are normalized to total aerosol mass. Triangles indicate $m/z < 100$, x's indicate $m/z > 100$. The two major peaks are labeled.

mixtures where CO_2 concentrations exceed CH_4 concentrations.

In addition, the spectra share some important similarities with the AMS spectra of C_4/C_5 dicarboxylic acids reported in Takegawa *et al.* (2007). Specifically, the dominance of the 44 and 73 amu peaks, as well as the low mass present in the spectra above m/z of 75, appear in both types of spectra. To compare our spectra to others of known compounds, we normalize all peaks to be the fraction of the total measured signal. Figure 3 shows a comparison of our average 10/1 CO_2/CH_4 (0% H_2) spectra with a normalized standard spectrum analyzed on the AMS of succinic acid ($\text{C}_4\text{H}_6\text{O}_4$) from Takegawa *et al.* (2007). The prominence of m/z 44 and 73, as well as the lack of the hydrocarbon “picket fence” pattern, appear very similar in both spectra. We thus conclude that, in the absence of H_2 , photolysis of CO_2/CH_4 mixtures with a great excess of CO_2 yields highly oxidized organic particles.

Figure 1 also shows how the AMS spectra of particles formed from 10/1 CO_2/CH_4 changes as H_2 is added. It can be seen that there is little change in the spectral signatures as H_2 is increased. While some variations in signal intensity occur at $m/z > 60$, the low signal and randomness in variation suggest some of this may be attributed to noise. Figure 4 shows the normalized intensity of m/z 44 (COO^+) and the integrated intensity of all peaks with $m/z > 60$ as a function of H_2 content in the total gas mixture. It can be seen that neither the relative intensity of m/z 44 nor the relative integrated mass beyond m/z 60 shows a significant change with the addition of large amounts of H_2 . The m/z mass after 60 as a function of total mass does appear to rise for intermediate

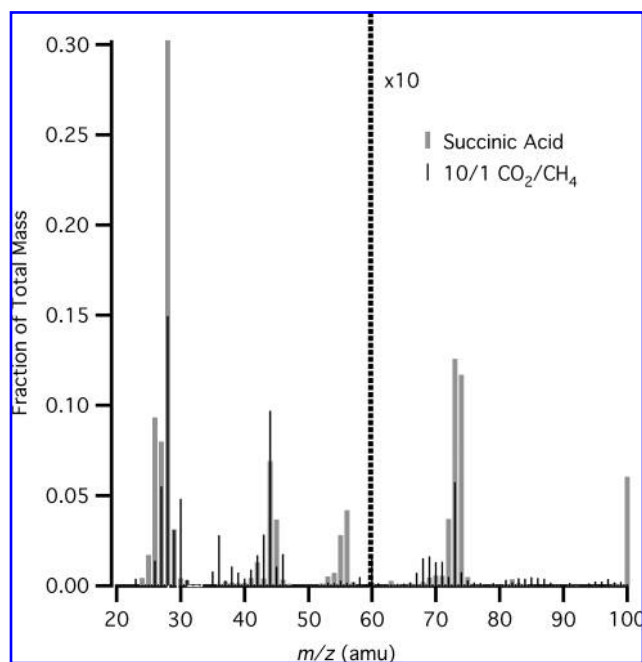


FIG. 3. Comparison of AMS spectrum of 10/1 CO_2/CH_4 ratio (normalized to total mass) with a normalized spectrum of succinic acid, also taken with the AMS (Takegawa *et al.*, 2007).

amounts of H_2 ; however, much of this aerosol signal is near the limit of detection of $0.1 \mu\text{g m}^{-3}$.

While the chemical nature of the particles does not depend strongly on H_2 content in the gas mixture, the haze amount produced varies strongly with H_2 . Figure 5 shows the aerosol mass as a function of H_2 as measured by the AMS and calculated from the SMPS apparent volume (DeCarlo *et al.*,

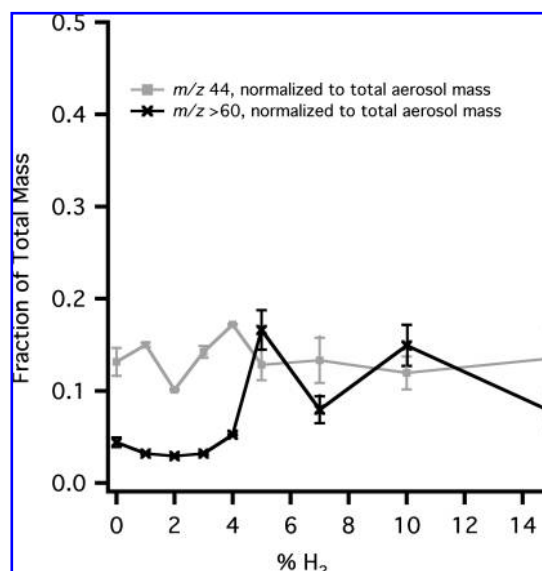


FIG. 4. The average relative mass of m/z 44 and the integrated relative mass for $m/z > 60$ shown as a function of % H_2 . Data was obtained from the photolysis of 10/1 CO_2/CH_4 in N_2 (mass spectra shown in Fig. 1).

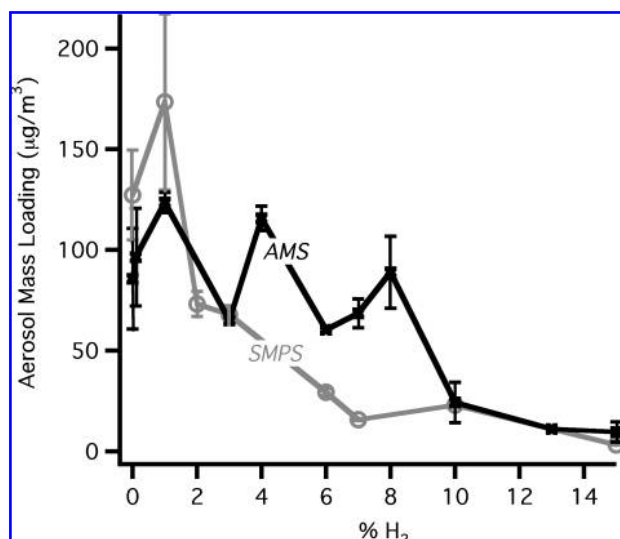


FIG. 5. Total aerosol mass formed from photolysis of 10/1 CO_2/CH_4 in N_2 as a function of H_2 as measured by the AMS and SMPS systems.

2004). A density of 0.8 was chosen for the conversion of the SMPS-measured volume to mass; this value is uncertain. It can be seen that both measurements of the aerosol mass decrease markedly as H_2 is increased, with a small peak in aerosol mass production at 1% H_2 (1/1 CO_2/H_2). Thus, large amounts of H_2 appear to inhibit haze formation without significantly changing the chemical composition of the haze. We repeated these experiments with 1/1 CO_2/CH_4 mixtures and found a similar downward trend in aerosol production with the addition of H_2 and little change in aerosol chemistry.

IV. Discussion

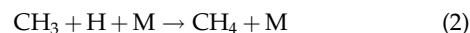
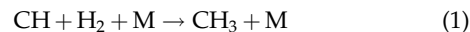
Recent work has suggested that prebiotic Earth might have had high levels of H_2 , up to 0.3 bar of the total atmosphere (Tian *et al.*, 2005). It was predicted that the high H_2 content might favor haze formation on early Earth by tying up CO_2 that would otherwise terminate haze chemistry. In contrast to this prediction, we found that greater mixing ratios of H_2 significantly *reduce* the aerosol mass produced photochemically in all cases studied.

For photolysis, the main source of C available for haze formation comes from methane; CO_2 can photolyze but is only expected to form CO and O with the wavelengths of UV light used in our study. Instead of shutting down haze chemistry entirely, incorporation of oxygen could promote an alternate path for haze formation by forming more oxygenated species with lower vapor pressures. However, the total mass produced is eventually reduced with increasing oxidation, as found by Trainer *et al.* (2006). Some amount of carbon chain linkage is needed to form species with low enough vapor pressure to condense into aerosols.

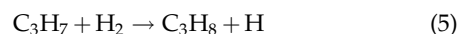
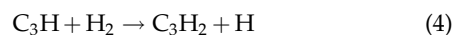
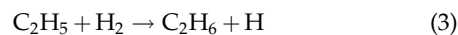
There are at least two possible reasons why H_2 may reduce the haze formation. One idea is that the hydrogen may have reacted with the oxygen, which could lead to less oxygen incorporation present in particles. However, this is not borne out in the experimental results shown in Figs. 1 and 4, where a similar aerosol composition is observed as H_2 is

added. A second possibility is that H_2 may have saturated the gaseous species and, thus, prevented them from continuing the polymerization process.

Several reactions that show the saturating effect of H_2 were presented by Moses *et al.* (2000), and two relevant reactions that demonstrate the reformation of CH_4 from methyl radicals and H/H_2 are



Additionally, H_2 is generally shown to saturate hydrocarbon chains (Moses *et al.*, 2000) in reactions such as



This is a likely explanation for our results because it would not necessarily lead to changes in particle composition. H_2 would saturate methyl radicals and hydrocarbon chains and thus prevent a certain population of product molecules from growing large enough to condense. This would impact the amount of condensed material generated but not the chemistry of the molecules that ultimately lead to aerosol formation. In our experiments, we observed that the organic particles formed remained oxidized, but dropped in production, with the addition of H_2 .

V. Implications for Prebiotic Earth

In the atmosphere of prebiotic Earth, CH_4 and CO_2 could have undergone photolysis and created secondary organic aerosols from the low-volatility photochemical by-products, even with 10 times as much CO_2 as CH_4 . As is the case on Titan, the atmosphere of early Earth may have had rich organic chemistry. Because of their oxygen content, particles made from the relevant prebiotic gas mixtures discussed here are perhaps more biologically interesting than those on Titan. In our simulations, the addition of the reducing gas H_2 did not appear to change the oxygenated nature of these particles, though it did decrease the overall amount of haze. Oxygen incorporation makes these particles capable of hydrogen bonding, an important chemical interaction in biological molecules. Oxygen-containing functional groups are present in most of the building blocks of life, including DNA, RNA, sugars, and amino acids. Miller (1957) showed that the prebiotic synthesis of amino acids could have begun with an aldehyde as a starting material. Thus, prebiotic atmospheric chemistry could have provided organics that subsequently deposited and built up on the surface of Earth, where they would have been important for developing life.

Conversely, a haze layer as thick as that on Titan could also have been a large problem for an early Earth that was already burdened with the faint young Sun paradox. Titan's thick haze layer causes a significant antigreenhouse effect on the moon's surface (McKay *et al.*, 1999). If a similar haze

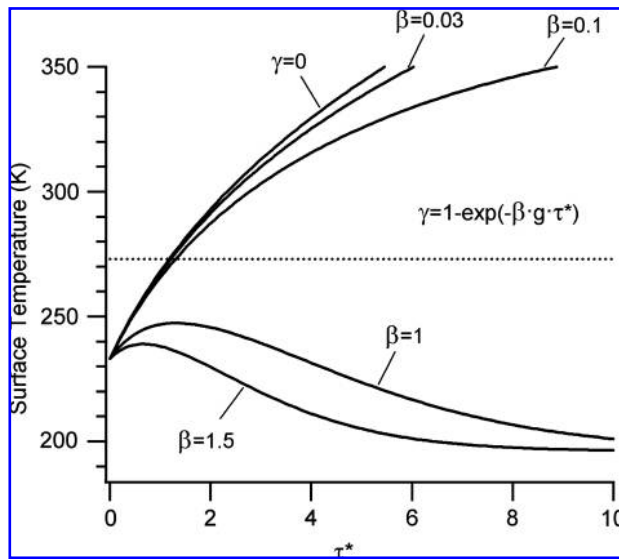


FIG. 6. Surface temperature of early Earth as a function of infrared opacity (τ^*) and antigreenhouse parameter (γ), from calculations in McKay *et al.* (1999). Temperature curves are presented for different β values, which account for the correlation between greenhouse gas concentration and haze production levels. β values are given for different atmospheric conditions in Table 1. These are compared to the base case in McKay *et al.* (1999), represented by $\beta = 1$. The freezing point of water is indicated by the horizontal dotted line at 273 K.

layer existed on early Earth, the greenhouse warming of CO_2 and CH_4 could have been mitigated by this effect and potentially caused Earth's surface temperature to drop below freezing for an optically thick haze layer (McKay *et al.*, 1999; Pavlov *et al.*, 2001b).

In their calculations of antigreenhouse cooling on early Earth, previous researchers have made several assumptions regarding an early Earth haze layer. McKay *et al.* (1999) estimated surface temperatures on early Earth based on a haze layer that had similar absorption features as the Titan haze. They determined an antigreenhouse parameter (γ) that varies with infrared opacity of the atmosphere (τ^*) as given by the equation $\gamma = 1 - \exp(-g\tau^*)$. Here, g is a constant that depends upon the optical constants of the haze that describe how absorbing the particles are in the visible as compared to the infrared. McKay *et al.* (1999) explored two cases for the absorbance of early Earth hazes in which it was assumed that the haze absorption was either similar to that derived for Titan, $g = 0.28$, or slightly darker than Titan hazes, $g = 0.5$. Here, we only show results for the case $g = 0.5$ and thus provide a conservative estimate by assuming that the haze particles may be strongly absorbing. Figure 6 shows a reproduction of the McKay *et al.* (1999) calculation for two

conditions: the atmosphere has no antigreenhouse effect ($\gamma = 0$), and the antigreenhouse effect of a haze layer varies with τ^* as given by the equation (labeled as $\beta = 1$). The temperature curve for the latter case shows that, as the greenhouse gas opacity increases, the antigreenhouse effect of the thickening haze prevents the surface temperature from rising above the freezing point of water.

As can be seen by the equation presented in Fig. 6, we have added an additional term, β , to the original McKay equation for γ . This is to account for an assumption that was inherent in the original calculation, which was that the relationship between the amount of greenhouse gases present and the subsequent haze production levels is comparable to Titan, where only CH_4 is present to form haze. We derived β empirically by comparing the relative amount of organic aerosol produced with different gas mixtures in our experiments to the amount of haze produced with methane alone ($\beta = 1$). Trainer *et al.* (2006) found that a 1/1 mixture of CO_2/CH_4 produced 1.5 times more particle mass than did pure CH_4 . This determined $\beta = 1.5$. The values of β determined in the present work are included in Table 1. Without addressing the optical properties of the haze, we have shown here that the presence of H_2 significantly decreases the haze production level, as does a 10/1 ratio of CO_2/CH_4 . Thus, β is substantially less than unity for the experiments here, including H_2 .

For the original McKay calculation, we set the β value at unity to represent a CH_4 -only atmosphere. Using the values of β reported in Table 1, we revisited the calculations performed in McKay *et al.* (1999), now considering high- H_2 and high- CO_2 environments. We found that, at our reduced aerosol yield, even for the strongly absorbing particles, the antigreenhouse effect would be near 0. Thus, for an equivalent amount of greenhouse warming, we could expect to have only one tenth of the level of haze production and a reduced antigreenhouse effect. These calculations show that, with high concentrations of H_2 , it is reasonable to reach temperatures above the freezing point of water even with a haze layer present. These results also show that the antigreenhouse effect may be dominant for the level of haze production reported in Trainer *et al.* (2006), as shown by the case where $\beta = 1.5$. To understand fully the cooling of such a haze layer, it will be necessary to obtain constraints on the optical properties of these hazes. In addition, while this study probed the effect of H_2 on photochemically produced haze, other variables may be important. For example, our study did not use extreme UV light, which is thought to be important in the photochemistry of Titan's upper atmosphere (Vuitton *et al.*, 2007) and could also have been important on early Earth. Further, the effects of additional gases likely present on early Earth, such as those containing sulfur (Farquhar *et al.*, 2000), were not studied. Further work will examine the effects of energy source and sulfur gases on haze formation chemistry.

TABLE 1. RELATIVE HAZE PRODUCTION FOR SEVERAL SIMULATED ATMOSPHERES

Gas mixture studied	15 H_2 : 1 CH_4 : 10 CO_2	1 CH_4 : 10 CO_2	1 CH_4 : 1 CO_2^a	1 CH_4^a
Haze scaling factor, β	0.03	0.1	1.5	1

^aFrom Trainer *et al.* (2006).

VI. Conclusions

In this study, we found that highly oxidized organic particles are still formed from UV photolysis in an atmosphere with 10/1 CO₂/CH₄. Adding H₂ to these particles does not reduce the oxidation of the organic matter formed, though H₂ does significantly reduce the total amount of aerosol produced. From this observation, we believe that H₂ saturates hydrocarbon chains, which prevented molecules from becoming large enough to condense in our reaction chamber. We estimate that any haze formed in an atmosphere with high H₂ and CO₂ would be optically thin and thus have a minimal antigreenhouse effect, which would allow the combined CO₂/CH₄ atmosphere to provide a net greenhouse warming.

Acknowledgments

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Abbreviations

AMS, aerosol mass spectrometer; m/z , mass-to-charge ratio; SMPS, scanning mobility particle sizer.

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