Photochemical Generation of Hydrocarbon Haze

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Overview

The Problem:

explain presence of liquid
H$_2$O on >3.8 Ga Earth

The Explanations:

Accepted (and other) hypotheses

The Chemistry:

An experiment to quantitatively test a reasonable explanation
Solar Evolution and Temperatures on Earth

The Faint Young Sun

\[ F = \sigma T^4 \]

\[ T_{\text{eff}} = \left[ \frac{F (1-\alpha)}{\sigma} \right]^{1/4} \]


I-H\(_2\)O present on Earth

Modern Greenhouse Effect

\(2.75 \text{ Ga}\)

\(T_s\)

\(T_{\text{eff}}\)

\(273\text{ K}\)
Evidence for liquid water: sedimentary rocks >3.8 Ga

Direct Evidence:
- Banded Iron Formation (BIF) indicates sedimentary rock
- U-Pb isotope ratio dating of zircon via SHRIMP

Ample indirect evidence:
- metamorphic rocks

Island of Akilia, southern West Greenland
(aerial photo)
The Greenhouse effect basics

- 6000K Blackbody
- Sun
- Atmosphere: Haze, O₂/O₃, CO₂, CH₄
- Surface: 255K Blackbody

Wavelength [μm]
## Analysis of Proposed Solutions

<table>
<thead>
<tr>
<th>Hypothesis</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decrease Albedo</td>
<td>Very Simple</td>
<td>Not sufficient flux increase with $\alpha=0$</td>
<td>not sufficient</td>
</tr>
<tr>
<td>Alter Earth’s Inclination</td>
<td>Well modeled, no climate change</td>
<td>Can’t explain current inclination</td>
<td>more data necessary</td>
</tr>
<tr>
<td>Increase CO$_2$</td>
<td>Simple effect</td>
<td>Contradicts geological record</td>
<td>contributing effect</td>
</tr>
<tr>
<td>Increase CH$_4$</td>
<td>Simple effect</td>
<td>Large flux necessary is unphysical</td>
<td>contributing effect</td>
</tr>
<tr>
<td>Form Haze Layer</td>
<td>Corresponds with existing data</td>
<td>Difficult to quantify net effect</td>
<td>lab data required</td>
</tr>
</tbody>
</table>
**Chemical mechanisms: $\text{CH}_4 \rightarrow C_2H_m$**

**Methane Branching Ratios**

For $h\nu = \text{Lyman } \alpha$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>Branching Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_4 + h\nu$</td>
<td>$^1\text{CH}_2 + \text{H}_2$</td>
<td>$q_1 = 0.41$</td>
</tr>
<tr>
<td>$\text{CH}_2 + 2\text{H}$</td>
<td></td>
<td>$q_2 = 0.51$</td>
</tr>
<tr>
<td>$\text{CH} + \text{H} + \text{H}_2$</td>
<td></td>
<td>$q_3 = 0.08$</td>
</tr>
<tr>
<td>$\text{CH}_3 + \text{H}$</td>
<td></td>
<td>$q_4 = 0.00$</td>
</tr>
</tbody>
</table>

**Photofragment Reactions (a)**

$$2 \left( \text{CH}_4 + h\nu \rightarrow ^1\text{CH}_2 + \text{H}_2 \right)$$

$$2 \left( ^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H} \right)$$

$$\text{CH}_3 + \text{CH}_3 + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M}$$

**Net Reactions**

$$2 \text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + 2\text{H} \quad (a)$$
**Chemical mechanisms:** $\text{CH}_4 \rightarrow C_2H_m$

**Methane Branching Ratios**

For $h \nu = \text{Lyman} \alpha$

\[
\begin{align*}
\text{CH}_4 + h \nu & \rightarrow ^1\text{CH}_2 + \text{H}_2 & q_1 &= 0.41 \\
\text{CH}_2 + 2\text{H} & \rightarrow & q_2 &= 0.51 \\
\text{CH} + \text{H} + \text{H}_2 & \rightarrow & q_3 &= 0.08 \\
\text{CH}_3 + \text{H} & \rightarrow & q_4 &= 0.00
\end{align*}
\]

**Photofragment Reactions (b)**

\[
\begin{align*}
\text{CH}_4 + h \nu & \rightarrow ^1\text{CH}_2 + \text{H}_2 \\
\text{CH}_4 + h \nu & \rightarrow \text{CH}_2 + 2\text{H} \\
^1\text{CH}_2 + \text{H}_2 & \rightarrow \text{CH}_3 + \text{H} \\
\text{CH}_2 + \text{CH}_3 & \rightarrow C_2H_4 + \text{H}
\end{align*}
\]

**Net Reactions**

\[
\begin{align*}
2 \text{CH}_4 & \rightarrow C_2H_6 + 2\text{H} & \text{(a)} \\
2 \text{CH}_4 & \rightarrow C_2H_4 + 4\text{H} & \text{(b)}
\end{align*}
\]
Chemical mechanisms: $\text{CH}_4 \rightarrow \text{C}_2\text{H}_m$

Methane Branching Ratios

$\text{CH}_4 + h\nu \rightarrow \text{CH}_2 + \text{H}_2 \quad q_1 = 0.41$

$\text{CH}_2 + 2\text{H} \quad q_2 = 0.51$

$\text{CH} + \text{H} + \text{H}_2 \quad q_3 = 0.08$

$\text{CH}_3 + \text{H} \quad q_4 = 0.00$

for $h\nu = \text{Lyman } \alpha$

Photofragment Reactions (c)

$$2 \ (\text{CH}_4 + h\nu \rightarrow \text{CH}_2 + 2\text{H})$$

$$\text{CH}_2 + \text{CH}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$$

net $$\text{2 CH}_4 \rightarrow \text{C}_2\text{H}_2 + 2\text{H}$$

Net Reactions

(a) $$2 \ \text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + 2\text{H}$$

(b) $$2 \ \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + 4\text{H}$$

(c) $$2 \ \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + 2\text{H}$$
Photosensitized Dissociation and Larger Hydrocarbons

Photosensitized Dissociation
\[ \text{C}_2\text{H}_2 + h\nu \rightarrow \text{C}_2\text{H} + \text{H} \]
\[ \text{C}_2\text{H} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3 \]
\[ \text{net} \quad \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \]

C\text{\textsubscript{2}} to C\text{\textsubscript{4}}: An Example
\[ \text{C}_2\text{H}_2 + h\nu \rightarrow \text{C}_2\text{H} + \text{H} \]
\[ \text{C}_2\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_2 + \text{H} \]
\[ \text{net} \quad 2\text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_2 + 2\text{H} \]

In General for Polyynes
\[ \text{C}_2\text{H}_2 + h\nu \rightarrow \text{C}_2\text{H} + \text{H} \]
\[ \text{C}_2\text{H} + \text{C}_{2n}\text{H}_2 \rightarrow \text{C}_{2n+2}\text{H}_2 + \text{H} \]
\[ \text{net} \quad \text{C}_2\text{H}_2 + \text{C}_{2n}\text{H}_2 \rightarrow \text{C}_{2n+2}\text{H}_2 + 2\text{H} \]
A small problem with current quantitative models

\[ x \text{C}_n\text{H}_m \text{ (gas)} \xrightarrow{k} y \text{C}_n'\text{H}_m' \text{ (solid)} \]

“the species C\(_3\)H\(_4\), C\(_4\)H\(_2\) and HC\(_3\)N were allowed to go to soot at an arbitrary rate”


“at CH\(_4\)/CO\(_2\) ratios lower than this critical value [unity], most of the CH\(_4\) undergoes oxidation, rather than polymerization, so organic haze does not form.”

The Experiment

1) Photochemical production of particulates
   reactants: CH$_4$ and CO$_2$
   He carrier gas
   120-230nm photolysis with D$_2$ arc lamp

2) *in situ* Optical Detection/Characterization
   Detect 632.8nm scatter/reflection from particulates
   Monitor reservoir of gas to constrain chemistry
Experiment Schematic

D₂ Lamp

Beam Dump

Polarizer

Fiber Launch (Input)

HeNe Line Filter

Polarizer

Fiber Launch (Output)
Observed Scatter and Reflectance Signal

Rayleigh scatter is greatly reduced

Zero Mie scatter at $\theta=90$ for any size parameter, $\chi = r/\lambda$

Observed flux must be from multiple scattering
Inside the reaction chamber
Output from Multi-Channel Scaler

2.6ms scan with 1kHz optical modulation

30K scans averaged per dataset

Rise/fall times excluded
Hydrocarbon Formation with $CH_4$

Concentration/Pressure Dependence

- Reproducibility of signal
- Similar formation timescale
Time Series RGA-MS Data: $[\text{CH}_4] = 70 \text{ torr}$
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Time Series RGA-MS Data: $[\text{CH}_4] = 70$ torr
CH$_4$ Pressure Dependence

Same number density of CH$_4$ with and without He

- Order of magnitude larger signal at 700 torr
- Can be kinetic or microphysical effect
Particulate formation with both CO₂ and CH₄

- Comparable optical scatter
- Notable difference formation timescale
Modelling the observed signal

Microphysics and Kinetics

Rate of Scatter increase:
- chemical reaction rates
  for $C_nH_m$ species up to $n=4$:
    74 photodissociation reactions
    194 chemical reactions (31 3-body reactions)
- nucleation properties
  (particle size distribution function)

Rate of Scatter decrease:
- depletion of reactants
- decrease in VUV flux
  coating surface of $MgF_2$ window
  shielding from haze formation
- nucleation
Summary

Designed, assembled, and tested photochemistry reaction chamber

Observed formation of particulate haze with $CH_4$ and preliminarily with $CO_2$

Started models and experiments to determine the kinetics pertinent to haze formation
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