Photochemical formation rates and optical properties of organic aerosols through time-resolved *in situ* laboratory measurements

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Relevance of Aerosols

- Ubiquitous in planetary atmospheres
  - Terrestrial planets: Earth, Venus
  - All gas giants
  - Satellites: Titan

- Important role in radiative transfer
  - Remotely observable albedo/spectra
  - Climate

- Products of photochemistry
  (among other processes)
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Important properties of aerosols

- Chemical composition
- Size distribution
- Morphology
- Optical scattering
- Formation rates
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No *in situ* laboratory measurements for *photochemically* generated aerosols
Experimental Technique

- Irradiate sample gas (VUV) to drive chemistry
- Make continuous, non-invasive measurements
  - Measure concentration of all gas-phase species (mass-spec)
  - Measure optical scattering
- Determine formation rate for gas-phase species
- Use mass balance to determine formation rate of C-C bonds in condensed-phase species
Experiment Schematic

[Diagram of experimental setup with labels: Turbo Pump, PMT, HeNe, Chopper, Gate Valve, Input Fiber, Output Fiber, Cold Cathode Gauge, D$_2$ Lamp, Gas Inlet, Precision Leak Valve, RGA Mass Spectrometer, Manometer, Gauge Valve, Fiber, inletManometer Gas, Spectrometer]
Experiment Optics

Inside Reaction Chamber

- Fiber launch
- Rotation stage
- Beam dump
- Output to detector

632.8nm HeNe laser
A Simple Organic System: Pure CH$_4$

- Predominant hydrocarbon on giant planets and Titan
- Product formation depends on light intensity

\[
\frac{d[\text{products}]}{dt} \propto -\frac{d[\text{CH}_4]}{dt}
\]

\[
-\frac{d[\text{CH}_4]}{dt} = \int_{\lambda_i}^{\lambda_f} \phi_{\text{CH}_4}(\lambda) \sigma_{\text{CH}_4}(\lambda) I(\lambda) d\lambda
\]

- Simplest expectation: $\sim$ linear increase in concentration of gas-phase species
Mass Spec Data $P(\text{CH}_4=70 \text{ Torr})$
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Forming Gas-Phase Species

![Graphs showing the formation of gas-phase species](image-url)
Forming Gas-Phase Species

- **C<sub>3</sub>H<sub>4</sub>**
  - Irradiation Time [hr]
  - Mixing Ratio vs. Concentration [cm<sup>-3</sup>]

- **C<sub>4</sub>H<sub>2</sub>**
  - Irradiation Time [hr]
  - Mixing Ratio vs. Concentration [cm<sup>-3</sup>]

- **C<sub>4</sub>H<sub>10</sub>**
  - Irradiation Time [hr]
  - Mixing Ratio vs. Concentration [cm<sup>-3</sup>]

- **C-C bonds in particles**
  - Irradiation Time [hr]
  - Mixing Ratio vs. Concentration [cm<sup>-3</sup>]

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Film formation on $D_2$ lamp window
Decay of VUV Lamp Intensity

\[ \frac{\text{net } d[H_2]}{dt} \text{ [cm}^{-3}\text{s}^{-1}] \]

\[ k_{\text{atten}} = 0.0158 \text{ hr}^{-1} \]

\[ \tau_{1/2} = 27.4 \text{ hrs} \]

\[ I(t_n) = I(t_{n-1}) \times 0.998 \]

Linear decay model
\[ \chi^2_{\text{min}} = 1.318 \times 10^{22} \]

Exponential decay model
\[ \chi^2_{\text{min}} = 1.503 \times 10^{22} \]
Model Comparisons

(a) $H_2$

(b) $C_2H_2$

(c) $C_2H_4$

(d) $C_2H_6$
Model Comparisons

- \( C_3H_4 \)
- \( C_4H_2 \)
- \( C_4H_{10} \)
- C-C bonds in particles
In situ Optical Scatter from Aerosols

![Graph showing integrated scatter intensity over irradiation time for different methane pressures (P(CH₄)). The graph displays three curves representing P(CH₄) = 70 torr, P(CH₄) = 50 torr, and P(CH₄) = 35 torr.](image-url)
Conclusions

- Photochemically produced aerosols from pure CH$_4$
- Measured net gas-phase hydrocarbon formation rates
- Calculated net condensed-phase C-C bond formation rate
- Measured optical scatter *in situ* from hydrocarbon aerosols
- Further investigations:
  - mixtures including (CH$_4$, CO$_2$, N$_2$, H$_2$)
  - detailed kinetics model to reproduce data
Acknowledgements

- Kristie Boering
- The Boering Group
- The David and Lucile Packard Foundation
- The Lockheed-Martin/SSL Minigrant Program
- The UC Berkeley Center for Integrative Planetary Science