Photochemical Pathways: Monomers to Polymers

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Don’t follow… (Keck Study) July 6-10, 2015
Titan - Atmosphere

Haze

Clouds

Altitude

INMS

UVIS

CIRS

GCMS

Thermosphere/Ionosphere

Mesosphere

Detached Haze

Main Haze

Stratosphere Troposphere

Temperature (Kelvin)

Pressure (Pa)

Altitude (km)
Titan’s Interior Water Oceans


Diagram showing the interior layers of Titan, including the upper icy crust, atmosphere (N₂, CH₄), water ice I, water ocean, high pressure water ices, and core. The graph on the right illustrates the pressure and temperature conditions for different layers, including Ih, liquid, V, VI, R₆, Rᵥ, Rᵥ/₁, Rᵥ/₂, Rᵥ/₃, and Rᵥ/₄.
Earth-Like Photochemistry on Titan?

Maximum Wavelength on Titan shifted to 700 nm

Karkoschka et al., PSS 60 (2012)342
Habitability is the Potential for an Environment to Harbor Life IF it were to exist there.

Let’s first understand the Physical, Chemical, and Geological conditions of a Body before talking about its Habitability!
Is Titan’s atmosphere photochemically more active than thought before?

Condensation of small and medium molecules

Condensed Ices

Gas-phase

Condensed on Aerosols

Photochemistry in Lakes on the Surface

Gudipati et al., Nature Communications 4(2013)1648
Dipole Moment
### The Molecules of Titan


<table>
<thead>
<tr>
<th>Molecule</th>
<th>$S_0 - S_1$ (first excited singlet state) threshold</th>
<th>$S_0 - T_1$ (first excited triplet state) threshold</th>
<th>$S_0$ (ground state) dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acetylene (C$_2$H$_2$)</strong></td>
<td>237$^a$, 231$^*$</td>
<td>346$^a$, 295$^*$</td>
<td>0</td>
</tr>
<tr>
<td>Diacetylene (C$_4$H$_2$)</td>
<td>286$^b$, 301$^c$, 298$^*$</td>
<td>387$^e$, 385$^*$</td>
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<td>Triacetylene (C$_6$H$_2$)</td>
<td>355$^c$, 348$^*$</td>
<td>450$^*$</td>
<td>0</td>
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<tr>
<td>Hydrogen Cyanide (HCN)</td>
<td>$\sim$155$^f$</td>
<td>$\sim$225$^f$</td>
<td>3.02$^d$, 2.7$^*$</td>
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<tr>
<td>Cyanoacetylene (HC$_3$N)</td>
<td>260$^a$, 267$^b$, 269$^*$</td>
<td>341$^*$</td>
<td>3.73$^d$, 3.33$^*$</td>
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<td><strong>Cyanodiacylene (HC$_5$N)</strong></td>
<td>353$^b$, 329$^*$</td>
<td>421$^*$</td>
<td>4.33$^g$, 3.9$^*$</td>
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<td>Cyanotriacetylene (HC$_7$N)</td>
<td>371$^*$</td>
<td>477$^*$</td>
<td>4.3$^*$</td>
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<tr>
<td>Cyanogen (C$_2$N$_2$)</td>
<td>300$^b$, 355$^c$, 272$^*$</td>
<td>350$^*$</td>
<td>0</td>
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<td><strong>Dicyanoacetylene (C$_4$N$_2$)</strong></td>
<td>280$^b$, 350$^*$</td>
<td>390$^*$</td>
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<tr>
<td>Dicyanodiacylene (C$_6$N$_2$)</td>
<td>407$^*$</td>
<td>551$^*$</td>
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</table>

Accessible with solar UV-VIS
Polar Molecules Ice and Clouds first in Titan’s Atmosphere


Similar molecular weight

Surface coverage

Temperature (K)

HC5N

HCCCCCN
175 K (~4D)

NCCCCCN
165 K (0D)
Titan – Altitude vs. Photochemistry


The diagram illustrates the distribution of VUV, VIS, and VIS-IR regions across different altitudes (km) and temperatures (K) for Titan's atmosphere.

- **VUV** region is shown at the top, covering the thermosphere.
- **VIS** region is located in the mesosphere and stratosphere.
- **VIS-IR** region is present in the troposphere.

The diagram also shows the haze production processes and the condensation of nitriles, leading to the sedimentation of gases such as $\text{N}_2$ and $\text{CH}_4$.
Production of Organic Solid Through Photochemistry
Theoretical Background

In the Condensed Phase

- Weak transitions become stronger
- Exciton interactions lead to new electronic states with lower excitation energy (longer wavelength)

Condensed-phase photochemistry can occur at longer wavelengths than in the gas-phase
The Titan Organic Aerosol Synthesis/Spectroscopy and Chemistry (TOAST) Lab @JPL
Spectroscopy and Photochemistry Setup

laser
Longer Wavelength Photopolymerization

Gudipati et al., Nature Communications 4(2013)1648

Dicynoacetylene (C₄N₂) – detected in Titan’s Atmosphere by Anderson & Samuelson

C₄N₂ Ice

355 nm

266 nm
Photochemistry: A one-photon process (Titan’s Conditions)

One Photon Yields = $k_1 \times \text{(laser flux)}$
Two Photon Yields = $k_2 \times \text{(laser flux)}^2$

$\frac{160}{50} = 3.2$ (1-photon)
$(160/50)^2 = 10.24$ (2-photons)
$1.45E-4/4.6E-5 = 3.15$ (observed)
Comparison with Cassini CIRS/VIMS Data

VIMS: Ratio of NH/CH at 2.8 to 3.5 microns (3500 – 2800 cm\(^{-1}\)) is very small indicating depleted NH in the condensates of Titan’s stratosphere. Could this be due to dominant hydrocarbon ices compared to aerosols or upper atmosphere photochemistry?
Expected UV-VIS Absorption of Ice, Haze, and Surface on Titan

\( C_4N_2 \) Monomer

UV-VIS spectra of \( C_4N_2 \) and Tholin resin

UV spectra and assignments of solid \( C_4N_2 \) film at various stages of deposition at 100 K

Similar extinction

TOAST lab condensed-phase longer wavelength photochemical polymer (tholin?)
Earth-Like Photochemistry on Titan?

Maximum Wavelength on Titan shifted to 700 nm

Karkoschka et al., PSS 60 (2012)342
Organic Polymer (Nitrogen containing) 
When meets with H2O 
Gives Biomolecules (Essential for Life?)
Titan’s atmosphere is depleted of oxygen (and water) 
Surface may have water-ice in contact with organic liquid and solid 
Subsurface is expected to have large reservoirs of water

Formation of Amino Acids and Nucleobases

O. Poch et al. / Planetary and Space Science 61 (2012) 114–123
FIG. 1. Orbitrap positive ion mass spectra of P2CO (top, red), P2COi (top, blue), P5CO (bottom, red), and P5COi (bottom, blue) from 50 to 300 u/q. Asterisks indicate known contaminants. Plotted spectra are an average of 200 spectra with a mass resolution of $10^5$. The observed mass shift in the isotopic samples results from the incorporation of $^{18}$O, which has been confirmed through assignment of the peaks. Hörst et al., ASTROBIOLOGY 12(2012)809
Production of Prebiotic Molecules from Analogs of Titan’s Complex Organics

Formation of Amino Acids and Nucleobases

<table>
<thead>
<tr>
<th>Name</th>
<th>Mass</th>
<th>Formula</th>
<th>Fig.</th>
<th>P2CO</th>
<th>P2COi</th>
<th>P5CO</th>
<th>P5COi</th>
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<td></td>
<td></td>
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<td>111</td>
<td>C₄H₅N₃O</td>
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<td>OT/GC-MS</td>
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<td>adenine&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>isoleucine/leucine&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>OT</td>
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<td>OT</td>
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</table>

<sup>a</sup> Indicates adenine as a nucleotide base.
<sup>b</sup> Indicates isoleucine with leucine as a biological amino acid.
Production of Prebiotic Molecules from Analogs of Titan’s Complex Organics

Formation of Amino Acids and Nucleobases

Hörst et al., ASTROBIOLOGY 12 (2012)809
Formation of Long-Chain Primary Amines


Fig. 3. Nonaqueous separations of 1 mg/mL labeled tholins, with significant primary amine products noted. (A) Tholin samples generated at the University of Colorado at Boulder. (B) Tholins produced at the University of Houston. All samples were labeled at 50 mg/mL with 5 mM Pacific Blue in 25 mM disopropylethylamine in ethanol. Separations were performed in 100 mM tetrabutylammonium acetate and 1.05 M acetic acid in ethanol. Blank is a 1:1 mix of ethanol/DMSO exposed to identical conditions during extraction, labeling and separation. The peak marked ‘u’ is present in all tholins and is at present unidentified. The starred contamination peak (*) is present in all blanks and controls.
Titan is not a sleeping Giant anymore

- Titan’s atmosphere and surface is photochemically active though a couple of orders slower than on Earth.

- In the presence of water-ice, photochemistry could lead to the formation of prebiotic molecules (amino acids and nucleobases) on Titan’s surface and transported to subsurface water oceans that could be Habitable.
Molecules on Titan are capable of harvesting solar photons throughout its atmosphere and on the surface to form complex organics capable of supporting life.
If this Titan's surface boulder were to be water-ice coated with organic solid and exposed to $>350$ nm solar photons, then building blocks of life would be formed here and transported into the interior water oceans – a habitable environment.
Cosmic Rays are NON-Selective with respect to the species interacting. They interact with highest abundant species: $\text{N}_2$, $\text{CH}_4$, $\text{C}_2\text{H}_6$ etc. in Titan’s atmosphere.

Longer-wavelength photons ARE selective. They do not interact with the abundant species if there is no absorption of these photons. They can interact with less abundant aerosols and ices more effectively.

**Fig. 6.** Updated full ionization profile for the nightside, high precipitation conditions, and low solar activity ($\Phi_{\text{Earth}} = 450 \text{ MV}$, Fig. 18 in Paper I). The parts highlighted in gray are the haze layers, including the thermosphere.
Solar photons reaching Titan:
\( \sim 10^{15} \) photons cm\(^{-2}\) s\(^{-1}\) (~200 nm to 650 nm)

If 10% of these photons make it to the main haze layer (temperature <100 K), and cause condensed-phase photochemistry at \( 10^{-4} \) efficiency, then we will have:

\[
10^{15} \times 10^{-1} \times 10^{-4} = 10^{10} \text{ photochemical events cm}^{-2} \text{ s}^{-1}.
\]

Compared to a maximum of \( 10^{1} \) ionization events cm\(^{-3}\) s\(^{-1}\) caused by cosmic rays. Maximum effective aerosol/ice ionization below 500 km: \( 10 \times 10^{-2} \times 500 \times 10^{4} = 5 \times 10^{5} \text{ events cm}^{-2} \text{ s}^{-1}\)

Clearly, photochemical processes in the condensed Titan aerosols and ices dominate the evolution of Titan’s atmospheric molecules.
Can UV-VIS-NIR light that penetrates through into the lower atmosphere and on to the surface; induce chemistry in Titan’s condensed aerosol, ices and solid surface?
Titan's atmosphere as we know now – thanks to Cassini-Huygens

It is expected that most of the larger organic molecules form ices or accrete on aerosols below ~500 km altitude on Titan.
This work has been funded by former NASA NAI “Titan as a Prebiotic Chemical System” at JPL and ongoing NASA SSW funding.