Formation and Solubility of Organic Aerosols in the Atmospheres of Titan and Early Earth

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Abstract

☑ Aerosol producing experiments simulating atmospheric chemistry on Titan & Early Earth.

☑ Examined effects of O-bearing gas species, CO & CO_2, in aerosol producing mechanisms.

☑ Examined aerosol's solubility to various solvents & performed UV-Vis spectroscopy for the solvents.

☑ Aerosols would have provided N-, O-bearing conjugated heterocyclic molecules on early Earth.

Introduction

In the upper atmosphere of Titan, complex photochemistry driven by solar UV irradiation and Saturn's magnetospheric particles bombardments is producing various hydrocarbons and N-bearing organic aerosols [1]. Similar organic chemistry might have occurred in a CH_4-containing atmosphere of early Earth [2].

Previous studies have performed irradiations of cold plasma or UV light to the gas mixtures of N_2 and CH_4 [3] or N_2, CH_4, and CO [4], simulating the chemistry in Titan's atmosphere. However, the formation mechanisms of early Earth tholin are still poorly examined. Moreover, organic aerosols produced in the atmospheres of both Titan and early Earth would have undergone further chemical reactions with liquids on the surfaces. Yet, solubility of early Earth tholin to the solvent has not been studied.

Objectives: (1) To examine the effects of O-bearing, CO & CO_2, in aerosol producing mechanisms. (2) To examine the early Earth aerosol's solubility to various solvents. (3) To discuss the role of atmospheric chemistry in abiotic syntheses of high-molecular weight organic materials.

Methods

- 1 Titan condition and 4 early Earth conditions.
- Tholins were produced by irradiating 10W, 13.56 MHz Radio Frequency discharge (cold plasma) at room temperature.

Table 1. Experimental Conditions (units: Pa)

Name	N_2	CH_4	CO	CO_2	Total P
Titan	90	10	0	0	100
CO 30%	63	7	30	0	100
CO 1%	89	9.9	1	0	100
CO_2 20%	72	8	0	20	100
CO_2 3.5%	87	9.7	0	3.5	100

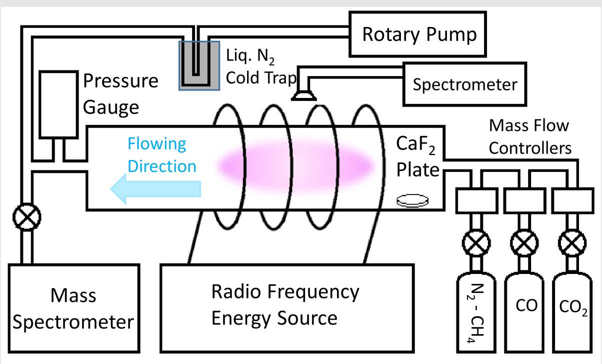
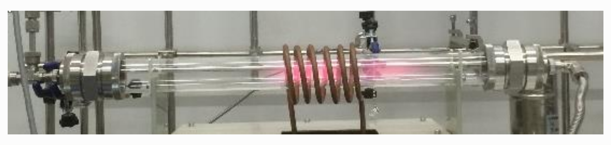


Fig. 1. Schematic of Experimental Setup

Analyses

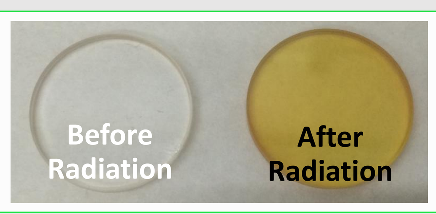
Gas Phase Tholin

- Emission Spectroscopy
- Mass Spectrometry



Thin Tholin on CaF_2 Plate

- FT-IR
- Ellipsometry



Gathered Tholin

- Solvent Extraction
- UV-Vis Spectroscopy

Fig. 2. Analysis Chart. Figures represent the image of the samples used in the analysis.

Results and Discussion

Emission Spectroscopy

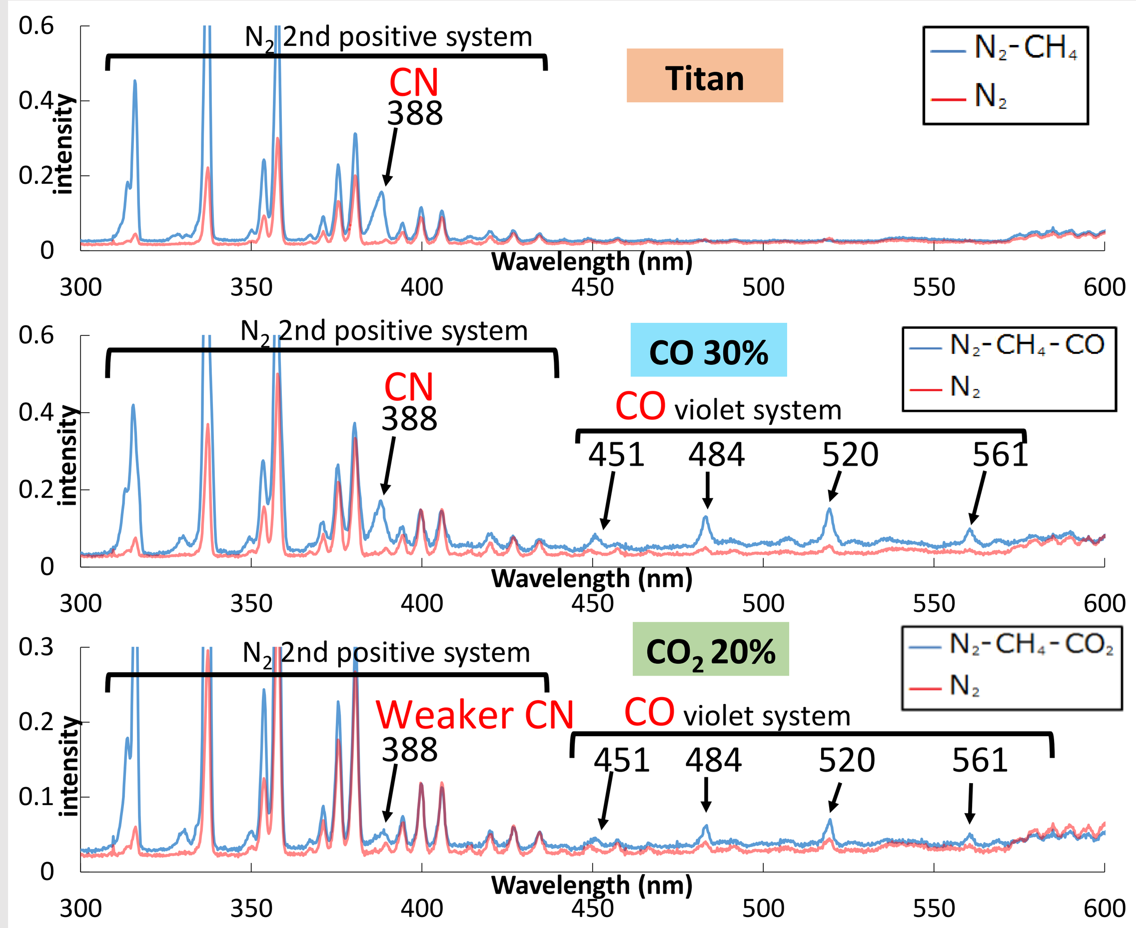


Fig. 3. Emission spectra of gas phase tholin.

Mass Spectrometry

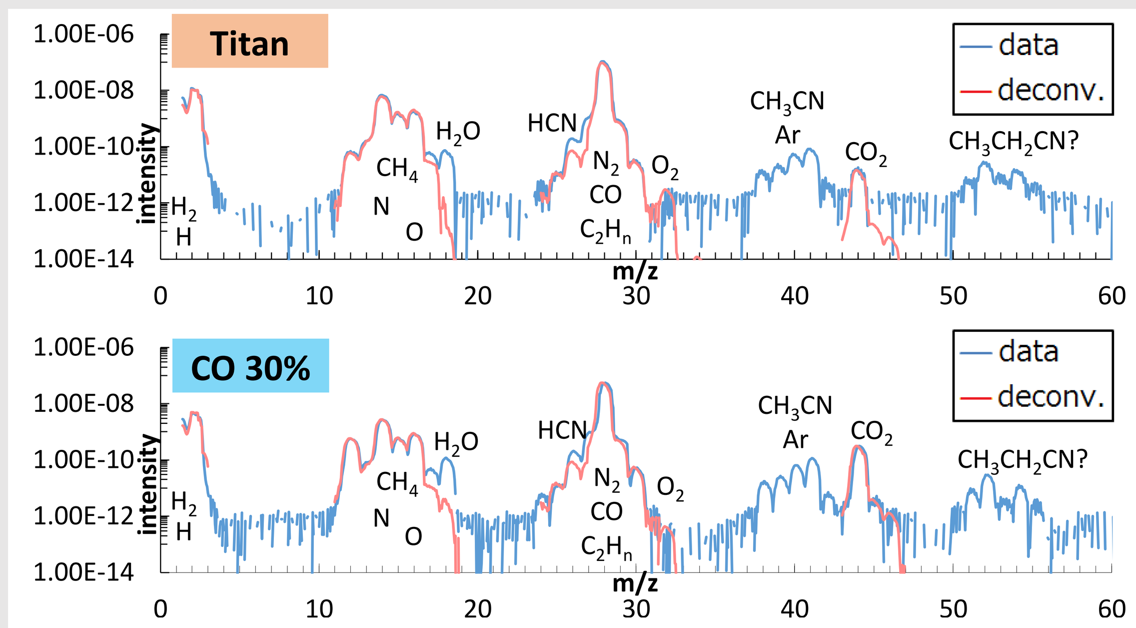


Fig. 4. Mass spectra of gas phase tholin. Mass spectra of pure gas of H_2, CH_4, N_2, O_2, CO, CO_2, C_2H_2, C_2H_4, and C_2H_6 were used for the deconvolution.

FT-IR

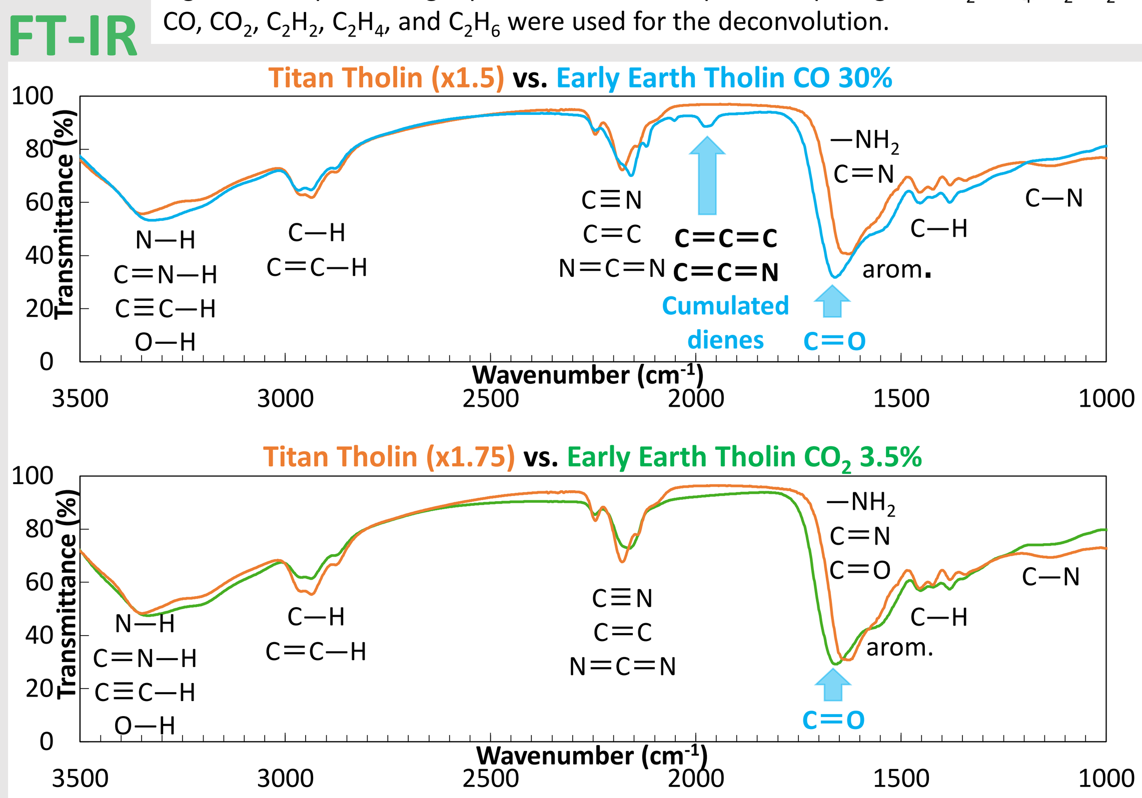


Fig. 5. IR spectra of tholin on CaF_2 plates.

Emission Spectra

- CN radicals in both tholins
- CO radicals in early Earth tholin

Mass Spectra

- CN → HCN → CH_3CN in both tholins
- No O-bearing gas, e.g., aldehyde

IR Spectra

- C=O bonds in early Earth tholin
- Cumulative dienes in early Earth CO tholin

Production Rate

- Low production rate for early Earth tholin
- More CO ≠ lower production rate

Fig. 7. Summary of results from each analyses.

Ellipsometry / Production Rate

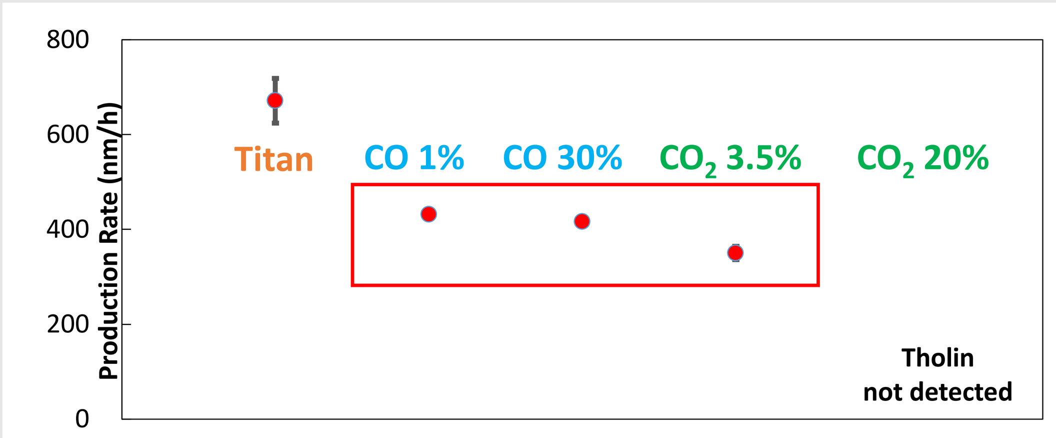


Fig. 6. Production rate of tholin on CaF_2 plate measured by ellisometry.

Suggested Mechanism of Early Earth Tholin Formation

CO: contribution vs. **O: inhibition**

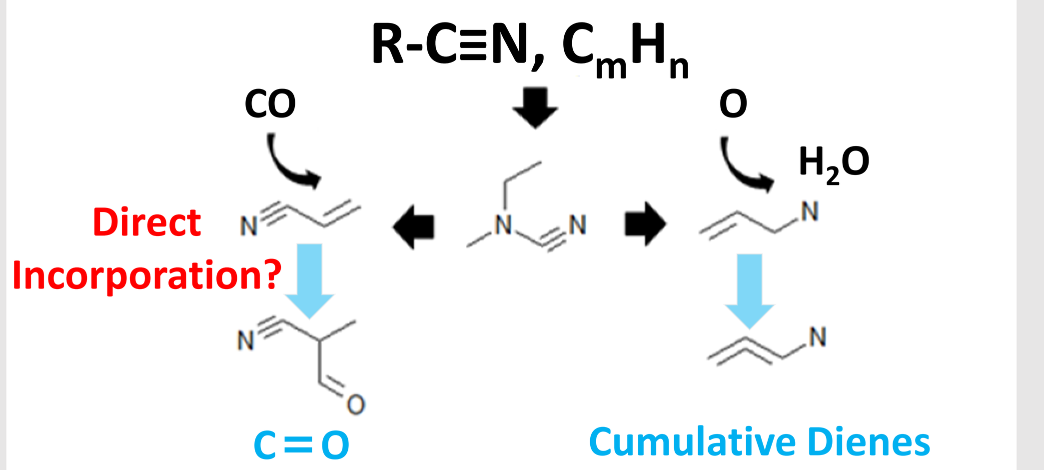
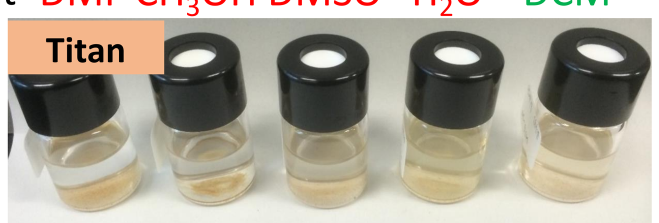


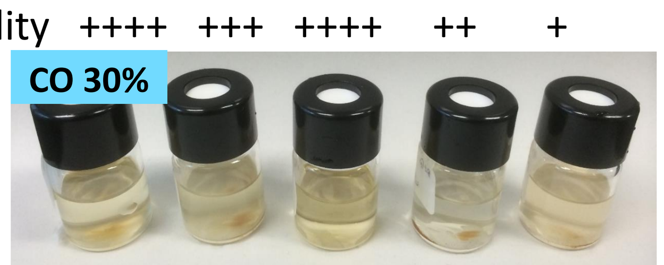
Fig. 8. Suggested formation mechanism of tholin in early Earth condition.

Solvent Extraction

Solvent: Polar: DMF CH_3OH DMSO H_2O; Non-polar: DCM



Solubility ++++ +++ ++++ ++ +



Solubility ++++ +++ ++++ ++ +

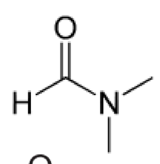
Fig. 9. Results of solvent extraction of Titan tholin and early Earth CO tholin. The number of + represents solubility.

Early Earth & Titan tholins dissolve effectively to polar solvents.

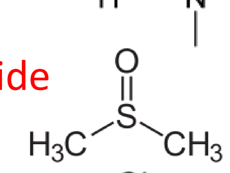
→ hydrophilic structures ex. −C≡N, −C=O

↑matches with previous research [5]

DMF: dimethyl-formamide $(CH_3)_2NCHO$



DMSO: dimethyl-sulfoxide $(CH_3)_2SO$



DCM: dichloro-methane CH_2Cl_2

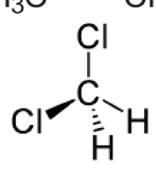
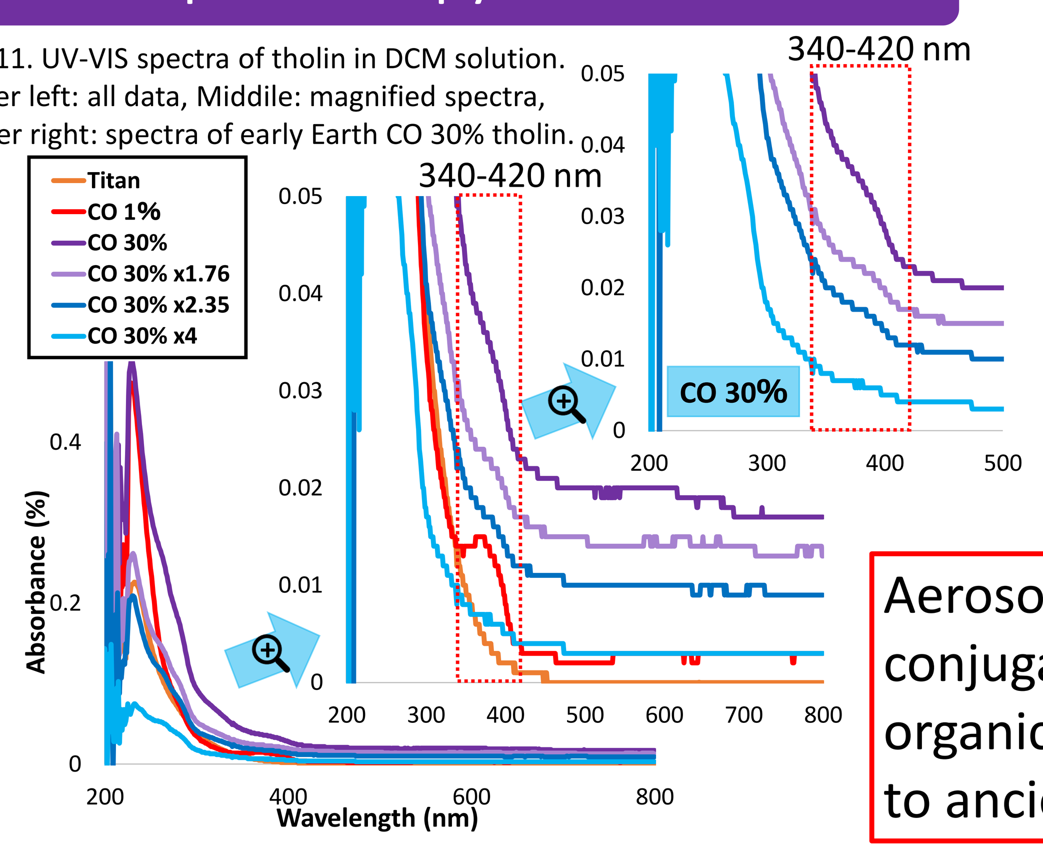


Fig. 10. Chemical structures of the solvents used.

UV-Vis Spectroscopy of DCM Solution

Non-polar!

Fig. 11. UV-VIS spectra of tholin in DCM solution. Lower left: all data, Middle: magnified spectra, Upper right: spectra of early Earth CO 30% tholin.



- Some portions of early Earth & Titan tholin dissolve to the non-polar solvent!
- Early Earth CO tholin has an weak absorption band around 380 nm.
- Absorption in this wavelength suggests the existence of conjugated systems within the tholins.
- Candidate: heterocyclic compounds

Aerosols might have provided conjugated N, O-bearing heterocyclic organic molecules, e.g., (poly?)pyrroles, to ancient oceans on early Earth.

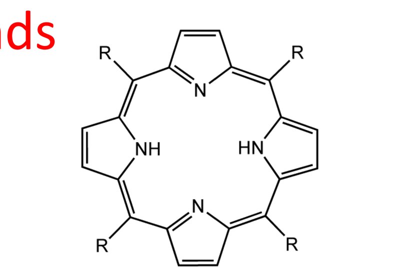


Fig. 12. Porphyrin (tetra pyrrole): An example of conjugated heterocyclic organic molecule used in various organisms.

Conclusions

1. Formation mechanism of Titan tholin: CN radicals → HCN, CH_3CN, aromatics, hydrocarbons → ... → Titan tholin
2. Formation mechanism of early Earth tholin: CN, CO radicals → HCN, CH_3CN, aromatics, hydrocarbons → ... → Early Earth tholin
   Production rate is determined by a balance of (1) contribution of CO (possibly direct incorporation of C=O) and (2) inhibition by oxygen atoms.
3. Early Earth tholin dissolve effectively to polar solvents as Titan tholin does. Though, some portions of both early Earth and Titan tholins dissolve to non-polar solvent such as CH_2Cl_2 and UV-Vis spectra of early Earth tholin in CH_2Cl_2 solution displayed a weak absorption band around 380 nm.
   → N, O-bearing conjugated heterocyclic compounds? (e.g., (poly?)pyrroles) → **Aerosols might have played a key role in chemical evolution.**

References: [1] Strobel D.F. et al. (2009) Titan from Cassini-Huygens (book), Chp. 10. [2] Pavlov A.A. et al. (2001) *J Geophys Res 106*, 23267-23287. [3] Imanaka H. et al. (2004) *Icarus 168*, 344-366. [4] Hörst S.M. et al. (2012) *Astrobiology 12*, 809–817. [5] Carrasco N. et al. (2009) *J Phys Chem A 113*, 11195-11203.