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A Study of Chemical Modeling for Several Precursors of Tholins in Titan's Atmosphere

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Abstract

Titan, one of the moons of Saturn, has an atmosphere rich in organic molecules. It is similar to the atmosphere of Primordial Earth. In Titan's atmosphere, there are highly abundant conjugated organonitrogen hetero-polymers called Tholins. Experimental studies have revealed that Tholins can react with nitric acid solution to produce amino acids, suggesting that these compounds could help initiate the life on Earth. To better understand the chemistry of Tholins, computer modeling is necessary. This work focuses on investigation of a radical reaction pathway involving hydrogen cyanide and radical form of methanimine that could lead to Tholin formation, along with analysis of other potential species that could have a role in Tholin synthesis. The specific compounds that were examined were hydrogen cyanide, a radical form of methanimine, and cyanamide. A gas phase chemical reaction model was built to simulate Titan's atmosphere. Role of reactions of studied compounds were carefully examined in the gas model. In addition, Gaussian was used to compute energies, dipole moments, and other properties of these compounds. The conclusions reached in this work were that all three studied precursors may play important role in Tholin synthesis.

Keywords: Titan, Tholin, Chemical Modeling

1. Introduction

Titan's atmosphere is the subject of much intense research in recent years. When the Voyager 1 probe passed through the Saturnian system, it confirmed the presence of hydrocarbons and other organic molecules in the atmosphere. It is believed that these molecules are formed in reactions involving ultraviolet radiation (UV) and species of charged particles[2]. Tholins are a class of molecule that exists in this environment. They are organonitrogen hetero-polymers that are highly conjugated. It was proposed that the pathway responsible for their formation involves radical reactions of methane, acetylene and hydrogen[4-8, 12, 13, 18, 20]. Titan's upper atmosphere is bombarded by light from the Sun that is in the 160nm range, which is necessary for radical dissociation of methane into H, CH_2, and other products.

Tholins are possibly related to the history of life on earth. It is very likely that Tholins were formed in our own atmosphere in the past, before life had developed, as we have a nitrogen dominated atmosphere, and hydrocarbons were much more common in the pre-biotic atmosphere[10, 14-16]. These Tholins, when synthesized in a laboratory setting, have been reacted with mixtures of water and nitric acid. These reactions yield a solution of amino acids, which are the building blocks of proteins are necessary for life[1, 9]. It should be noted that while Titan has many similarities to pre-biotic Earth, it also has many differences. One of those differences is that Titan has little to no carbon dioxide present in its atmosphere. Currently, CO_2 makes up about 0.3% of our atmosphere and plays a role as a major greenhouse gas.

In order to better understand the nature of the reactions that both produce and destroy these Tholins, modeling of these reactions must be performed. This is accomplished using codes developed from the Astrochemistry group at Ohio State University that are normally used to model reactions in the interstellar medium. The codes have been used to investigate reactions surrounding Ethanimine and a few other molecules near Sagittarius B2 and the Taurus Molecular Cloud 1[21]. This project focused on using this computer model to examining a reaction pathway and several precursors that could lead to Tholin formation, and testing its viability using computer modeling. This formation pathway was based upon a substructure proposed by Khare *et al.* [1]. The reactions that will be investigated will be examined in conditions that are based on Titan's upper atmosphere, due to its prominent UV exposure. Most of the compounds present here are gaseous organic compounds.

2. **Modeling Methods**

2.1 Chemical Model

In order to simulate the reactions taking place in Titan's upper atmosphere, a computer model was used. This model was developed by the Astrochemistry Group at the Ohio State University to model chemical reactions in the interstellar medium[21]. All of the reactions are in the gas phase. The model operates based on using the Arrhenius Equation to determine reaction rate constants over the course of time.

The model contains two separate libraries. The first is a library of chemical compounds. This library lists each compound with an entry defining the types and numbers of atoms of the compound, as well as the charge on the molecule. It also includes several important species on dust grains and the free electrons. The second library is a list of chemical reactions. Each reaction contains data related to the Arrhenius Equation. Reaction rates are given by

$$k = \alpha \times \left(\frac{T}{300}\right)^{\beta} \times e^{-\frac{\gamma}{T}} \tag{1}$$

α is defined as the constant part of the pre-exponential variable of the rate, β represents the temperature dependent part, and γ is related to the activation energy. T is defined as temperature in degrees of Kelvin. Reaction coefficients of the reactions used in the program were cited from the astrochemistry reaction network from Ohio State University[21], as well as the National Institute of Standards and Technology Chemical Kinetics Database (NIST)[22].

Gaussian computer modeling was also used to examine individual compounds. These values were going to be compared to the values of energy and dipole moment for molecules whose reaction constants were known, so that the reaction constants of the compounds of interest could be estimated.

2.2 Chemistry of Tholins

It was found that readings taken by the Voyager 1 probe of Titan's atmosphere indicated that there was an abundant variety of organic molecules present in the atmosphere[3]. An IR scan of Titan's atmosphere indicated the presence of nitriles, alkanes, amines and aromatic compounds. Once this data was obtained, further experiments could be performed to determine exactly what compounds were being detected, since IR data can only give information about functional groups. In an experiment by Ehrenfreund *et al* [2], a mixture of nitrogen and methane was irradiated using UV radiation to simulate the conditions present in the upper atmosphere of Titan. This process yielded a substance that we today call a Tholin. Tholin was analyzed using a variety of techniques including mass spectroscopy, pyrolysis and IR spectroscopy. Mass Spectrum analysis led to the conclusion that the formed compound was a polymer, and, combined with the IR spectroscopy data, it was determined that the compound was composed mainly of nitrogen and carbon. This information was used to propose a substructure for the Tholin, which is presented in Figure 1.

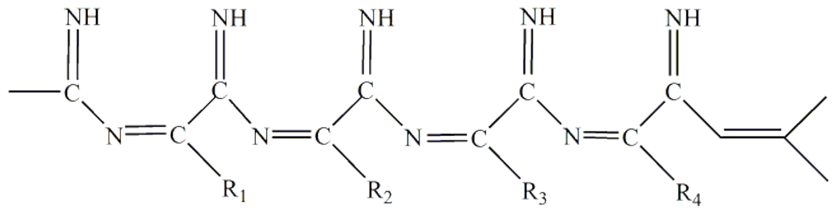

Figure 1 Proposed N_2/CH_4 tholin substructure by Ehrenfreund *et al* [2].

This structure is highly conjugated, which could lead to the optical effects, such as the tan coloration associated with both Titan's atmosphere and the product of Ehrenfreund's experiments. The R groups shown in the above diagram would be substituted with Hydrogen for simplicity, but other groups are possible, such as alkyl, amine, nitriles, and aromatics, among many others. One suggested reaction pathway leading to Tholin Synthesis is initiated by the photodissociation of Hydrogen gas via UV radiation, which is known to happen in the 160 nm range. The products of this reaction are two hydrogen radicals. Hydrogen radicals then react with hydrogen cyanide to form a radical form of methanimine, or methylene amidogen radical (H_2CN). The reactions following are then all radical reactions that involve the polymerization of the radical with other compounds that would possibly be present in Titan's upper atmosphere.

The first two steps in the reaction mechanism to form Tholins have been well studied and the rate coefficients are available from literature such as OSU reaction network [21] and NIST [22]. The constants related to these two reactions are given in the Table 1.

Table 1 Reaction Coefficients Of First Two Steps Of Proposed Reaction Mechanism To Form Tholins.

Reactants	Products	α (s^{-1})	β (unitless)	γ (K)	Ref.
H_2	H + H	1.3×10^{-18}	0	0	OSU
H + HCN	H_2CN	7.75×10^{-31}	-2.73	32.09	NIST

Physical conditions and initial abundances are crucial to the chemical kinetics model. The initial conditions were obtained from the European Space Agency's archive of data from their unmanned spacecraft (ESA Planetary Science Archives)[3]. The data was taken from the Huygens probe, which separated from the Cassini spacecraft and fell through Titan's atmosphere and eventually landed on the surface. It was equipped with an array of instruments, such as a Gas Chromatography - Mass Spectrometer, a few cameras, and other instruments that were used to measure Titan's atmosphere. The array of instruments used to observe the characteristics of the atmosphere were referred to as Huygens Atmospheric Structure Instrument, or HASI. The observed data is compared with modeling results, which will be discussed later in this thesis. Parameters included were Temperature, Pressure and density. The parameters are listed in the table below.

Table 2 Physical Conditions Of Titan’s Upper Atmosphere.

Pressure (pa)	322
Temperature (K)	161.3
Density (kg/m^3)	0.0068
Number Density of N_2 (cm^{-3})	1.43842×10^{20}

The initial concentrations of species present in the atmosphere were listed in Table 3. These values were suggested by the Huygens probe's detection [3]. If a compound is not listed, then the molecular abundance was zero.

Table 3 Initial Abundances In Percentage Of Total Density.

Compound	Initial concentration
H_2	1.0×10^{-1}
N_2	9.8×10^{1}
CH_4	1.4×10^{1}

After these parameters were entered a simulation was performed using the gas model software. Three particular compounds were examined. Hydrogen Cyanide (HCN), Cyanamide (NH_2CN) and the methylene amidogen radical (H_2CN). HCN and H_2CN were chosen to be studied because of their role in the postulated reaction pathway of Tholin synthesis. NH_2CN was also chosen because it can react with HCN to start the polymerization to form Tholins. All these three species with many related reactions were already included in the OSU network as known species and they have a few reactions present in the NIST reaction library. For example, HCN can be produced by the following reaction:

$$\mathrm{CH} + \mathrm{N_2} \rightarrow \mathrm{HCN} + \mathrm{N} \tag{2}$$

After all data was entered into the software, a simulation was performed. Time range in the simulation was from 0 years to 10^8 years. Output from this simulation will be discussed in the results section. A second simulation was performed due to the fact that at about 1300 years, most of the compounds of interest had already equilibrated. It was possible that some of the peaks in concentration were not resolving due to the fact that the time step was made almost 10^6 years apart. On the second simulation, the time observed was set to 1364 years with observations taken evenly spaced at every 11 years. Output from the second set of simulations is included in the results section.

3. Results And Discussion

Modeling results are shown in Figures 2-3. Two sets of simulations were run. In the first set of simulations, time ranged from 0 till 10^8 years, which is a typical temporal range used for interstellar medium. The calculation resulted in a much extended view of the concentrations of the compounds of interest. The results are shown in Figure 2, for H_2CN, HCN, and NH_2CN, respectively. Most of calculated abundances reached equilibrium quickly, after only a few thousand years. Because of the amount of activity that was detected in the concentrations of these compounds in the first 1300 years, a second simulation was performed.

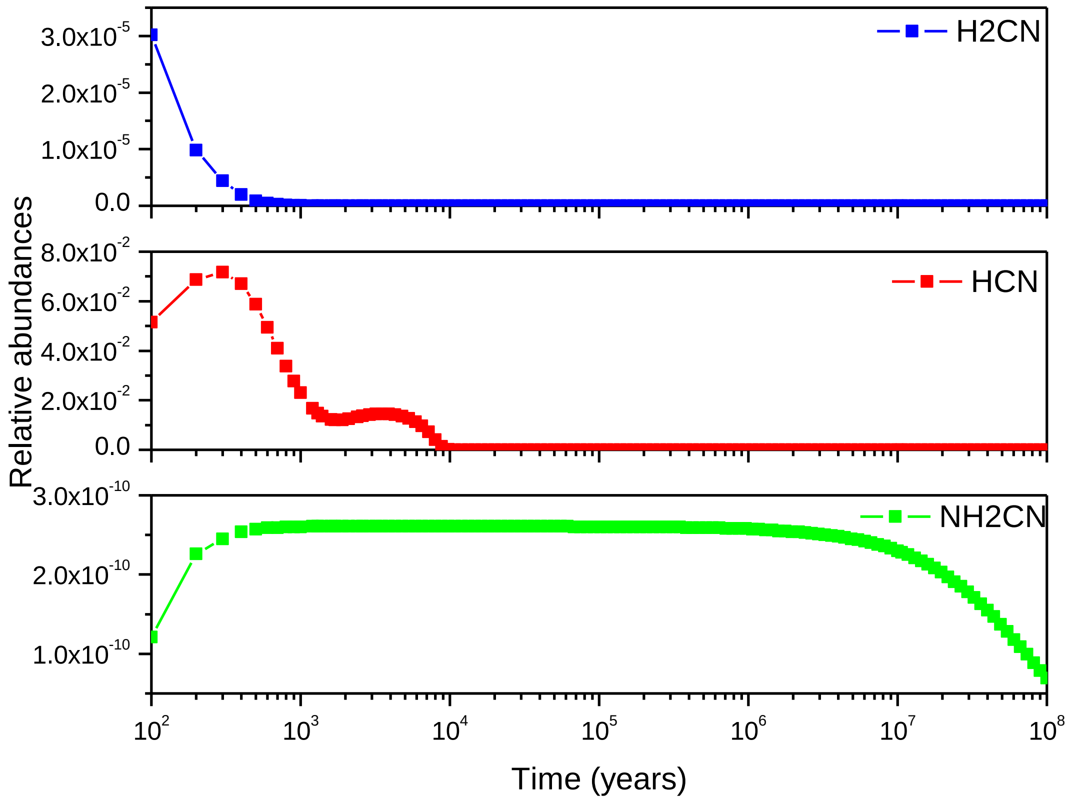

Figure 2. Calculated abundances from the full time range simulation. The simulation was run till 10^8 years. The x-axis is time in units of years, and the y-axis is abundance in units of mole fraction. From top to bottom: H_2CN, HCN, and NH_2CN.

The second set of simulations was performed within the time ranging from 0 till 1364 years. As shown in Figure 3, this resulted in much higher time resolution than the first simulation. In this set, HCN was by far the most abundant compound, comprising about 0.73% of the atmosphere at its peak. This is about double the percentage of CO_2 that is present in our own atmosphere. The H_2CN radical was the next compound examined. It was only present in any significant amount for a few decades, before being destroyed in other reactions and not reformed. NH_2CN was present in a very small concentration, but was present for the entire length of the simulation, unlike the H_2CN radical.

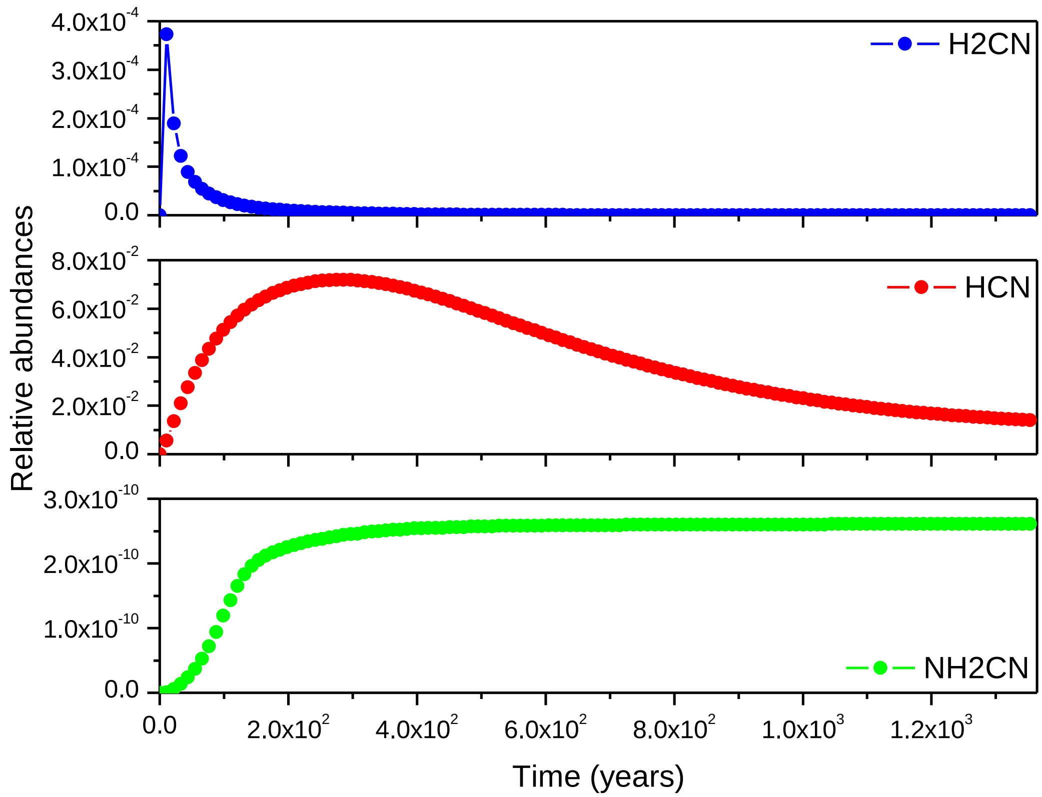

Figure 3. Calculated abundances from the focused time range simulation. The simulation was run till 1364 years. The x-axis is time in units of years, and the y-axis is abundance in units of mole fraction. From top to bottom: H_2CN, HCN, and NH_2CN.

Overall, even with the increased resolution that a shorter run allowed, there were no additional peaks that were able to resolve that were not present in the longer run. There is a good level of agreement between both sets of results, meaning that the likelihood of any kind of abnormalities in the data or errors in the computers calculations is very low.

Given the above results, it can be concluded that all three studied precursors may play important roles in Tholin formation. The role of HCN in the atmosphere of Titan is crucial, given its relatively high concentration when compared to other compounds. The molecular abundance of HCN in Titan's atmosphere rivals that of CO_2 here on Earth. Given how much of an effect that CO_2 has on our atmosphere and the fact that hydrogen cyanide is known for its reactivity, it is likely that hydrogen cyanide has a dominant role in many chemical processes occurring in Titan's atmosphere, including Tholin synthesis. NH_2CN has some structural similarities to the proposed substructure of the Tholin, and the results indicate that it is produced in a large enough amount to have a role in chemical processes in Titan's atmosphere. The results of this work indicate that the H_2CN radical may also has important role in the formation of Tholins, specifically as initiator of chemistry of forming Tholins in Titan's atmosphere. This is because, while its concentration spikes to about 0.00037%, it is quickly consumed due to the next reaction steps leading to Tholin synthesis.

4. Future Directions

This study has been focused on three compounds of that are known to be in Titan's atmosphere. It is possible that other compounds those are abundant and may play an important role in Tholin synthesis.

Tholins have also been detected in other locations in the solar system, such as on Neptune's moon Triton, and on a few asteroids as well. These locations lack a complex atmosphere like Titan, so the process of Tholin synthesis may be different from those in Titan. The atmosphere of pre-biotic Earth is also thought to be similar to Titan's current atmosphere, given a few differences. Processes involving Tholin synthesis in these conditions should also be examined, due to the possibility that Tholins may have had a role in developing life on our own planet.

5. Acknowledgement

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