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Tholins: A Gas Phase Computational Study of Methanimine and Related Species

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Abstract

Titan bas been referred to as the “gem of the Solar System.” This significance comes from its dense atmosphere, which is the only atmosphere in our Solar System other than Earth’s that is dense enough to produce a hydrological cycle (or methanological cycle, in the case of Titan). Scientists in the fields of astrobiology and astrochemistry believe that Titan’s current atmospheric conditions could resemble that of the primordial Earth, and as such is being studied to further our understanding of how life forms. While Titan’s atmosphere contains an abundance of organic molecules, methanimine (MA) and related species the methyl amino radical (MAR) and methyleneamine cation (MEC) are of particular interest. Scientists believe that MA, MAR, and MEC are precursors to organic aerosols called tholins, which are defined as nitrogen-containing molecules that are thought to be precursors to amnio acids. The purpose of this research is to gather three crucial pieces of information to understand the role of these molecules in Titan’s atmospheric chemistry: 1) determine the major formation and destruction reactions for MA and related species, 2) obtain the most up-to-date rate coefficients for those reactions, and 3) obtain abundance versus time data for MA and related species. Tholin production is observed at most altitudes, but this research focuses on the upper atmosphere (500+ km), which has largely been unstudied until recent years. While MA, MAR, and MEC have all been studied, a comprehensive list of reactions and rate coefficients has not been completed since 2010. The data from this study suggest that MA, MAR, and MEC are present at concentrations deemed important for tholin production and agrees with data presented by other chemical models.

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Chapter 1: Introduction

Humans have long asked the questions "How did life form?" and "Has life formed elsewhere in the Solar System or the Universe?" Many theories have been proposed to answer these questions, but scientists have much research to do before definitively answering them. This research seeks to add a piece to that puzzle.

1.1 The Origin of Life

The first major theory of life was the spontaneous generation hypothesis, the ideas of which were first synthesized by Aristotle.[33] This hypothesis stated that life emerges quickly and spontaneously from non-living matter, such as flies emerging from decaying meat, or mice appearing inside cloth after wrapping cheese in it. This belief held strong until the Renaissance, when interest in anatomy started growing and scientists began to dismantle the idea. William Harvey, a physiologist in the 17th century, discovered that all animals are produced via eggs.[16] Others, such as Francesco Redi, made discoveries that showed how flies emerged from decaying meat and that eggs require fertilization, but still the idea of spontaneous generation persisted—many still hoped that lower forms of life emerged spontaneously. Finally, in the in the 1850s and 60s, Louis Pasture disproved the theory altogether with his experiments showing that even the most minute creatures developed from "germs" that fell from the air.[20] This theory of "biogenesis" took root—that is, life can only form from other living organisms. This theory was prevalent until the 1920s, when two scientists simultaneously and independently published articles that contradicted the long-held belief of biogenesis and laid the foundation for the modern theory of how life formed.

In the 1920s, Alexander Oparin and J. B. S. Haldane each independently published works titled *The Origin of Life*. Oparin's work[33] was published in 1924, while Haldane's[22] was published in 1929. Both stated that, in order for life to form, significant organic synthesis needed to take place, and postulated what conditions would have needed to be present on the primordial Earth for this synthesis to occur. Advances in astronomy and geochemistry led Oparin to the conclusion that the early Earth would have been devoid of oxygen, and the composition of the atmosphere would have been primarily methane, ammonia, free hydrogen, and water vapor.[33] Haldane suggested that a reducing atmosphere could have easily formed simple organic molecules via energy sources such as heat, lightening, and ultra violet (UV) radiation.[22] They concluded that the organic compounds made in this process would have dissolved in the ocean and, combined with abundant energy sources, would have undergone chemical evolution to form more complex organic structures and eventually primitive life forms.[17] These ideas contradicted the autotrophic view of life at the time, which stated that living organisms first produced organic matter via photosynthesis. Instead, Oparin and Haldane concluded that organic synthesis occurred *before* the emergence of life.

The Oparin-Haldane hypothesis emerged, and suggested that inorganic molecules underwent chemical evolution in a reducing atmosphere to form the building blocks of life.[17, 33] They suggested that simple inorganic molecules—such as NH_4, H_2, CO_2, H_2O—could have gradually formed a primordial soup of amino acids and nucleotides which could have further reacted to from complex polymers like proteins and nucleic acids. Oparin believed these could have been self-replicating and formed colonies of proteins that carried out metabolism.[33] Haldane believed the complex polymers became encased in membranes to from cell-like structures.[22] It would be another 30 years before scientists like Stanley Miller and Harold Urey began to prove parts of the Oparin-Haldane hypothesis.

1.2 Space Exploration, Titan, and the Prebiotic Earth

One of the main goals of exobiology is to relate chemical processes occurring elsewhere in the Universe to the origin and evolution of life on Earth.[34] There are three main candidates for this study in our Solar System: Mars, comets, and Titan.[8] Of particular interest among them is Titan, which is the most similar to the primordial Earth in physical features such as liquid on the surface, atmospheric density, energy sources, complex chemical reactions, and geological processes (summarized in Table 1.1).[19] Three ways to study Titan have been proposed, the second of which is important to this work:

1. To study prebiotic processes on Titan as if they are the same as what occurred on Earth;
2. To study Titan as practice modeling complex organic chemistry networks, even if the conditions may not be like the primordial Earth; or
3. To study surface-aerosol-atmosphere interactions that have nothing to do with the origin of life.[8]

The ability to explore space has drastically increased our understanding of the formation of life. The United States' National Aeronautics and Space Administration (NASA) first launched three missions, Pioneer 11, Voyager 1, and Voyager 2, which provided the data that eventually inspired a full-fledged mission to Titan: the Cassini-Huygens mission. On October 15, 1977, NASA launched its Cassini-Huygens probe and orbiter to explore Titan and has led to many discoveries that have aided in our understanding of the types of processes that could of have formed life on Earth.

That mission has offered the bulk of raw scientific data pertaining to Titan. The orbiter and probe reached Titan in December 2004. The probe landed on the surface in January 2005, and the orbiter continued to collect data from Titan and Saturn until September 2017. This mission has provided an enormous amount of data that scientists are still processing today. Some of the types of data provided by this mission included: infrared, visible, and ultraviolet spectroscopies/mapping; ion and neutral mass spectrometry; radar mapping; magnetospheric imaging; and plasma spectroscopy.

Studying Titan—which is referred to by Morgan Cable *et al*. as "the gem of the Saturnian system, an icy world laden with organics"[5]—could fill out many gaps in our understanding of life. Titan was chosen by NASA because of its hydrological (or methanological) cycle, which is unique to only Earth and Titan in our Solar System. Scientists in the fields of astrobiology and astrochemistry believe that Titan's current atmospheric conditions resemble that of the primordial Earth, and as such is being studied to further our understanding of how life forms. The composition of Titan's atmosphere likely directly influences that of its dunes and lakes, as the atmosphere is the main source of particle distribution to the surface.[5] While Titan's surface features are intriguing, with lakes and mountains—which are believed to have been created by methane-ethane rivers and lakes[10]—the atmosphere is of interest in this research because it is rich in organic chemistry[38, 41] and features an anti-greenhouse effect.[31] These features are important in the study of life on Earth because both have been proposed to have been present on the early Earth.[8, 23]

The composition of Titan's atmosphere is primarily nitrogenic, composing of 95-98% v/v.[5, 15] Other gases present are methane (1.5-5%), hydrogen (0.1-0.2%), and carbon monoxide (0.005%), with trace amounts of ethane, acetylene, hydrogen cyanide, cyanoacetylene, carbon dioxide, and water vapor.[5, 8, 15]

Table 1.1 Comparison of Prebiotic Earth and Titan Conditions*

	Prebiotic Earth	**Titan**
Energy Sources	Solar UV	Solar UV
	Lightening	Magnetospheric e^-
	Cosmic ray ionization	Cosmic ray ionization
Atmosphere		
Pressure	1 bar	1.5 bar
Major Components	N_2, CO_2	N_2
Minor Components	H_2O, organics	CH_4, H_2, CO
	(CH_4, NH_3 if reducing)	
Ocean	H_2O with dissolved N_2	CH_4, $C2H_6$ with dissolved N_2
Temperature	273-373 K	70-180 K
Oxidation State	Unknown	Reducing
Prebiotics Present	HCN, HC_3N, H_2CO	HCN, HC_3N, $HCNH^+$

*Adapted from Clarke 1997[8]

Production of gaseous hydrocarbons and nitriles on Titan happen through many polymerization processes and creates aerosol particles that fall to the surface.[5] There are both exogenous and endogenous processes that are driving the organic chemistry on Titan. At higher altitudes, short-wave UV radiation, extreme UV (EUV), and energy from Saturn's magnetosphere drive reactions. Methane absorbs short-wave UV rays to form radicals that then form short hydrocarbons.[5, 24] EUV radiation causes radicals and ions to form, as well as atoms in ground and excited states.[24] At medium altitudes, long-wave UV radiation is the main source of energy, which causes photolysis of short hydrocarbons to create longer hydrocarbons and more complex organic molecules. Spherical particles combine to form aerosols which then react with gas-phase radicals at lower altitudes; the aerosols act as a condensation point for other species in the troposphere such as HCN and CH_4 as they fall to the surface.[26]

To understand Titan and glean information about how life formed, scientists have posited three main criteria: observations (Cassini-Huygens), laboratory experiments (tholins), and theoretical models (the subject of this research, which uses information compiled from the other two). Our understanding of Titan is constantly changing as more scientists take interest in researching the moon. If the Earth did in fact have a reducing atmosphere, scientists believe that Titan's current atmosphere could be an analogue to that of the primordial Earth's.[8, 30] It should be noted, however, that the lack of data concerning the Earth's early atmosphere makes a direct comparison to Titan inaccessible, and it's possible that Earth's atmosphere was solely reducing, solely neutral, or a mixture that evolved over time.[8] There are many scientists that do favor a reducing atmosphere, citing that without it a reservoir of organic compounds likely could not have been formed.[8, 14]

1.3 Tholins

Carl Sagan and Bishun Khare created the first tholins in 1979. They were inspired by another experiment completed many years earlier in 1953: the Miller-Urey[32] experiment. Miller and Urey simulated a simple primordial atmosphere by boiling a water mixture containing methane, ammonia, and nitrogen. In the gaseous portion of the system a cathode and anode were placed at close proximity to simulate an energy source. They discovered that five amino acids were formed: glycine, α-alanine, and β-alanine were identified, and aspartic acid and α-aminobutyric acid were suspected.[32]

With the new information about Titan from NASA's Voyager probe, Sagan and Khare decided to do this experiment in conditions similar to Titan's atmosphere. They discovered a rusty colored product, which the team deemed "tholins," a term derived from the Latin word tholos, meaning "dim" or "unclear," but was translated by the team as "muddy" (see Figure 1.2).[5]

Tholins are aerosols created in lab experiments that mimic the energy sources and atmospheric conditions of Saturn's moon, Titan. Tholins does *not* refer to the molecules or aerosols on Titan, only those simulated in the laboratory. They are nitrogen containing molecules that are thought to be precursors to amino acids, which are the building blocks for life.[5, 9] Tholins have been analyzed via mass spectroscopy, pyrolysis, and IR spectroscopy, and this data suggests that tholins are a polymer composed of mostly nitrogen and carbon, and a proposed structure for the polymer is presented in Figure 1.1.[35]

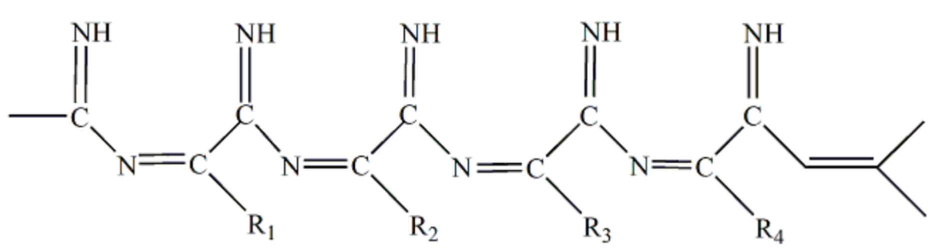

Figure 1.1 Proposed Structure of tholins[12]

Cable *et al.* points out that our understanding of tholins is limited to the biases and limitations of the scientists studying them, and thus is only a useful tool in teaching us about the organic chemistry occurring on the moon. It is important to note that what is found on Titan may be very different from the conclusions scientists make by studying tholins on Earth.

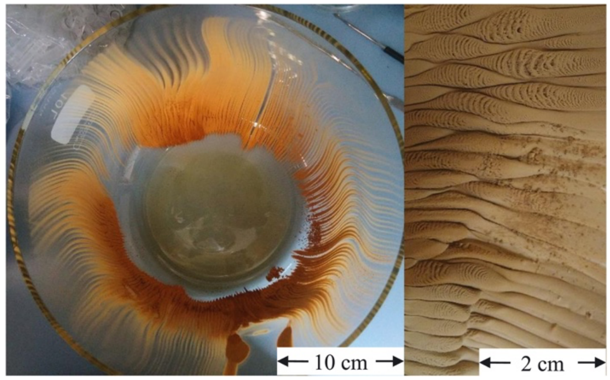

Figure 1.2 Depiction of tholins created by the Lethuillier group[27]

1.4 Previously Studied Compounds

There are various types of compounds and reactions that have been previously studied in relation to Titan and tholin production—some of the major ones will be summarized here. HCNH+ and $C_2H_5^+$ have been found to be important in copolymer growth that is found in tholins.[11] It has been suggested that tholins could be composed HC_3N and HC_3N—HCN polymers, as well as HCN and CH_2.[5] HCN and C_2H_3N have been proposed to be tholin growth units.[25, 36]

1.5 Species of Interest

Scientists use computer models and data from NASA's missions to study the organic chemistry occurring on Titan. Many species and reactions have been extensively studied in the mission to expand those computational models, with the goal of eventually simulating the formation of amino acids in Titan's atmosphere.

In this study, methanimine (MA), its related species the methyl amino radical (MAR) and the methyleneamine cation (MEC), as well as its precursors (CH_3, N^+, CH_4, NH, and NH_3) are of interest. MAR is an important intermediate in the formation of MA[3] and the density of MEC is closely linked with MA through proton exchange reactions.[46] The density and optical properties of MA have been studied, but to our knowledge no abundance over time data has been presented for MA or its related species (see Table 1.2). This data is important to show that not only is MA present currently, but that it has been present at sufficient levels for tholin production.

Table 1.2 Species of Interest

Species	Chemical Formula
Methanimine (MA)	CH_2NH
Methyl amino radical (MAR)	$CH_3NH•$
Methyleneamine cation (MEC)	$CH_2NH_2^+$

Moreover, a comprehensive list of reactions and rate coefficients for MA related reactions has not been completed since 2010 by the Yelle group.[46] It is important to update reaction lists as new studies are completed that discover new reactions pertinent to Titan and as new and better models shed light on theoretical rate coefficients and reaction networks.

1.6 Conclusion

To answer the question of how life formed life, humans have had through various hypothesis: from the spontaneous generation hypothesis of Aristotle's time to the discovery of fertilization and eggs in the 17th century, to the theory of biogenesis that emerged from Louis Pasture's work. Oparin and Haldane suggested in the 1920s a new theory of the origins of life, which became the modern theory of how life formed: the Oparin-Haldane hypothesis.

Inspired by the work of Oparin and Haldane, Miller and Urey decided to test the Oparin-Haldane early Earth hypothesis by completing an experiment in which they place an electrode in a reducing atmosphere. They found amino acids in the resulting product, suggesting that Oparin and Haldane's hypothesis that a reducing atmosphere could formed the building block for life abiotically.

Miller and Urey, in the late 1970s, were inspired by both the Oparin-Haldane hypothesis and the results of Miller-Urey experiment and decided to test the hypothesis again in the newly discovered conditions of Titan, which many had agreed could be similar to the primordial Earth. Their experiment yielded a muddy brown product consisting of nitrogen containing molecules and amino acids. The team deemed this product tholins, which are nitrogen containing aerosols that are produced in simulated Titan conditions on Earth. These aerosols are what give rise to the orange haze on Titan.

Many scientists have been inspired by the work of Carl Sagan and Bishun Khare, as well as by the vast amount of data obtained from the NASA and European Space Agency's Cassini-Huygens mission to Titan. Scientists have developd and used computer models to simulate tholins and tholin precursors in order to understand the organic chemistry on the moon, as well as to begin to understand the origins of life.

This research utilizes such a model in order to study the abundance of one of tholins' precursors: MA, as well as related species MAR and MEC. However, before that can be accomplished, two other goals must be completed: first, obtaining a comprehensive list of formation and destruction reactions for all three species and second, obtaining up-do-date the rate coefficients for all reactions (as well as updating older ones).

Chapter 2: Chemical Model

To study the complex chemistry happening in our solar system and the interstellar medium (ISM), scientists employ kinetics-based chemical models. In this chapter, The Ohio State University's (OSU) extensive chemical model[37] will be introduced and the underlying equations will be briefly discussed. Then, the parameters of the model will be presented, such as reactions, physical conditions, and rate coefficients.

2.1 Modeling Methods

While thermodynamics plays an important role in astrochemistry, it has been clearly observed that kinetics plays a bigger role in the abundances of molecules in space, as evidenced by the large abundance of free radicals and unsaturated hydrocarbons.[42] The Van't Hoff equation relates the rate constant of a reaction to temperature:

$$\ln\frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H^0}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \textbf{Equation 2.1}$$

Van't Hoff argued that the individual rate coefficients are affected by temperature and the Gibbs activation energies of the forward and reverse reactions.[42] He concluded that the rate coefficients vary by temperature according to the Arrhenius equation:

$$k = Ae^{\frac{-Ea}{RT}} \qquad \textbf{Equation 2.2}$$

where A is the pre-exponential factor, E_a is activation energy, T is temperature, and R is the universal gas constant. Van't Hoff's ideas can be expanded upon to relate Gibbs energy to the rate coefficients, taking into account both entropic and enthalpic factors.[42] One of Van't Hoff's students, D. M. Kooij, proposed a modified equation that added temperature dependance of the energies of the forward and reverse reactions, called the modified Arrhenius equation:

$$k(T) = AT^{m}{}^{\frac{-Ea}{RT}}$$ **Equation 2.3**

The OSU model uses a version of the modified Arrhenius equation to compute the rate constants for each reaction in the network:

$$k(T) = \alpha(T/\tau)^{\beta}\, e^{\frac{-\gamma}{T}}$$ **Equation 2.4**

where α, β, and γ are coefficients, and τ depends on the temperature at which the coefficients were calculated.[45] α is related to the pre-exponential factor and γ is related to the reaction barrier. A reaction barrier is defined as the amount of energy required to start a reaction. The β term was added to account for the temperature dependance of the pre-exponential factor. τ is usually either set to 300 K or 1 K. The model utilized in this study sets τ to 300 K, as 1 K is used for low temperature rate coefficients.

Chemical models that study astrochemistry typically use a system of differential equations of the type:

$$\frac{dn_i}{dt} = \sum production - \sum destruction$$ **Equation 2.5**

where n_i is the density of species *i* in cm^{-3} and the production and destruction terms include any reactions that produce or destroy species *i*.[44] The model takes a set of defined parameters and initial compositions and then solves the equation as a function of time and computes the evolution of abundance of the species over time. These models are especially important for studying molecules that are not directly observable, such as those without a dipole moment.

2.2 Model Parameters

To set up a chemical model of abundance over time data, a set of physical conditions must first be established, which are shown in Table 2.1. The temperature was chosen based on the altitude of 700 km from data presented in the Fulchignoni et al. 2008 article.[18] The total hydrogen density was chosen based on Titan data presented in the Bertaux et al., 1983 article.[4]

Table 2.1 Physical Parameters of Chemical Model

Parameter	Value
Temperature (K)	170
Total Hydrogen Density (cm^{-3})	3.5×10^{5}

Furthermore, the starting species and their initial concentrations must also be defined. The starting concentrations used for the model of Titan are listed in Table 2.2 and were chosen based on data collected from the Huygens probe.[13] The model considers 13 types of chemical reactions, which are presented in Table 2.3.

Table 2.2 Initial Concentration of Species

Species	Initial Concentration (cm^{-3})
He	1.4×10^{-1}
N	2.14×10^{-5}
O	1.76×10^{-4}
H_2	5.00×10^{-1}
C^+	7.30×10^{-5}
Cl^+	4.00×10^{-9}
F^+	6.68×10^{9}
Fe^+	3.00×10^{-9}
Mg^+	7.00×10^{-9}
Na^+	2.00×10^{-8}
P^+	3.00×10^{-9}
S^+	8.00×10^{-8}
Si^+	8.00×10^{-9}

Table 2.3 Reaction Types Represented in Chemical Model

	Reaction Type	Example
1	Cosmic ray-induced photoionization	$He \rightarrow He^{+} + e^{-}$
2	Cation neutral	$C^{+} + Fe \rightarrow Fe^{+} + C$
3	Anion neutral	$C^{-} + NO \rightarrow CN^{-} + O$
4	Cation addition	$C^{+} + H \rightarrow CH^{+}$
5	Anion deionizing	$C^{-} + C \rightarrow C_2 + e^{-}$
6	Neutral-neutral electron forming	$O + CH \rightarrow HCO^{+} + e^{-}$
7	Neutral-neutral	$C + CH \rightarrow C2 + H$
8	Addition neutral	$C + C \rightarrow C2$
9	Disassociation recombination	${C_2}^{+} + e^{-} \rightarrow C + C$
10	Neutralization	$C^{+} + e^{-} \rightarrow C$
11	Neutralization between ions	$C^{+} + C^{-} \rightarrow C + C$
12	Electron attachment	$C + e^{-} \rightarrow C^{-}$
13	Photochemical	$C + h\nu \rightarrow C^{+} + e^{-}$

The OSU model used in this study was originally developed to study the ISM but was modified for the conditions of Titan. After a review of the literature, it was determined that this research could fill a gap in the information pertaining to methanimine. Several reactions from Yelle's 2010 study were added to the model, as well as reactions that have been discovered since that article's release. A list of the 39 reactions that were added to the model can be found in Table 2.4. Many were chosen from Yelle's article—which summarized many of the reactions pertaining to MA up to 2010—but others were chosen because they were newly discovered in recent studies, as well as from the Kinetics Database for Astrochemistry (KIDA). Reactions 28-30 and 32 did not have rate coefficient data readily available and thus were estimated from similar reactions. The basis for choosing relevant reactions was the speed of the reaction. Those that were too slow (i.e., rates coefficients less than 10^{-16}) were mostly excluded from the list.

Table 2.4 List of Reactions Added to Model

Reaction	Model	Mechanism			Rate Coefficients			Reference
					α	β	γ	
1	4426	$N_2 + h\nu$	→	$N^+ + N + e$	4.90E-10			46
2	4427	$CH_2NH + h\nu$	→	$HCN + H + H$	1.10E-08			46
3	4428	$N^+ + C_2H_4$	→	$C_2H_3^+$ NH	3.25E-10			46
4	4429	$N^+ + C_2H_4$	→	$C_2H_2^+$ NH_2	1.30E-10			46
5	4430	$HCN^+ + CH_4$	→	$C_2H_3^+ + NH_2$	1.27E-10			46
6	4431	$C_2H_5^+ + CH_2NH$	→	$CH_2NH_2^+ + C_2H_4$	2.70E-09			46
7	4432	$CH_5^+ + CH_2NH$	→	$CH_2NH_2^+ + CH_4$	3.00E-09			46
8	4433	$CH_2NH_2^+ + e$	→	$CH_2NH + H$	1.00E-06	0.70		46
9	4434	$CH_2NH_2^+ + e$	→	$CH_2 + NH_2$	1.00E-07	0.70		46
10	4435	$CH_2NH_2^+ + e$	→	$HCN + H_2 + H$	1.00E-07	0.70		46
11	4436	$H + CH_2NH$	→	$H_2CN + H_2$	4.00E-14			46
12	4437	$N + CH_4$	→	$CH_2NH + H$	3.84E-11		7.50E+02	46
13	4438	$N + C_2H_2$	→	$HC_2N + H$	1.60E-10		2.70E+02	46
14	4439	$N + C_2H_4$	→	$CH_3CN + H$	4.40E-11			46
15	4440	$N + HCN$	→	$N_2 + CH$	1.60E-10		2.70E+02	46
16	4441	$NH + C_2H_2$	→	$HC_2N + H_2$	2.01E-09	-1.07		46
17	4442	$NH + C_2H_4$	→	$CH_3CN + H_2$	2.01E-12	0.11		46
18	4443	$NH + C_4H_2$	→	$C_4HN + H_2$	8.24E-09	-1.23		46
19	4444	$NH + H$	→	$N + H_2$	3.12E-16	1.55	1.03E+02	46
20	4445	$NH + N$	→	$N_2 + H$	2.49E-11			46
21	4446	$NH + NH$	→	$NH_2 + N$	3.12E-22	2.89	1.02E+03	46
22	4447	$NH_2 + N$	→	$N_2 + H + H$	1.2E-10			46
23	4448	$NH_2 + NH_2$	→	N_2H_4	8.97E-20	-3.90		46
24	4449	$NH_2 + H_2CN$	→	$NH_3 + HCN$	5.43E-11	1.06	6.08E+01	46
25	4450	$CH + NH_3$	→	$CH_2NH + H$	1.52E-10	-0.05		29
26	4451	$CH_2NH + {\bullet}O$	→	${\bullet}OH + H_2CN$	5.33E-14			21
27	4452	$CH_2NH + {\bullet}O$	→	${\bullet}OH + HCNH$	2.27E-17			21
28	4453	$CH_2NH + H{\bullet}$	→	CH_3NH	4.00E-14			46*
29	4454	$CH_2NH + H{\bullet}$	→	CH_2NH_2	4.00E-14			46*
30	4455	$CH_2NH + H{\bullet}$	→	$H_2CN + H_2$	4.00E-14			46*
31	4456	$CH_2NH + O$	→	$H_2CN + OH$	7.15E-07			43
32	4457	$CH_2NH + O$	→	$CH_2O + NH$	5.33E-14			46*

Reaction	Model	Mechanism	Rate Coefficients		Reference
33	4458	$CH_2NH + HO_2 \rightarrow NH_2CH_2OO\bullet$	2.85E-13		1
34	4459	$CH_3NH \rightarrow CH_2NH + H$	1.50E+03		3
35	4460	$CH_2NH_2 \rightarrow CH_2NH + H$	1.50E+03		3
36	4461	$CH_3NH + h\nu \rightarrow CH_2NH + H$	1.7E-09	1.63E+00	3
37	4462	$CH_2NH_2 + h\nu \rightarrow CH_2NH + H$	1.7E-09	1.63E+00	3
38	4463	$CH_2^+ + NH_3 \rightarrow H + CH_2NH_2^+$	1.5E-09		2
39	4464	$CH_3^+ + NH_3 \rightarrow CH_2NH_2^+ + H_2$	1.49E-09		2

*Rate coefficients estimated from reference

2.3 Conclusion

While thermodynamics plays an important role in astrochemistry, kinetics has been shown to be more important when studying the abundances of molecules. To study exobiology and astrochemistry, scientists employ kinetics based chemical models. These models often use a modified Arrhenius equation (Equation 2.4) to calculate rates of reactions. This equation involves four parameters that astrochemists have deemed alpha (pre-exponential factor), beta (temperature dependance factor), and gamma (activation energy factor). The fourth is τ which is usually either defined as 300 K (for higher temperature rate coefficients) or 1 K (for lower temperature rate coefficients). Then, the model solves a set of differential equations (Equation 2.5) to compute abundance data as a function of time.

To accomplish this, the model takes into account the initial hydrogen abundance and temperature at a set altitude (700 km, in this study) (Table 2.1), initial concentration of elementary species (Table 2.2). The model can account for 13 types of chemical reaction (see Table 2.3). A total of 39 reactions and their rate coefficients were compiled from literature, KIDA database, and NIST Kinetics Database (Table 2.4). All of this information was utilized by the model to calculate the abundance data for MA, MAR, MEC, and other elementary molecules involved in the MA reaction network that is presented in the next chapter.

Chapter 3: Results and Discussion

3.1 Abundances of Investigated Species

After the model was complete, abundances for all species in the reaction network were recorded as a function of time in years. The abundances of the species MA, MAR, and MEC are shown in Figure 3.1 on a logarithmic scale for comparison. This data agrees with the data presented in Yelle 2010, which states that the concentration of MA is closely related to MEC through proton exchange reactions and recombination—in the same way that scientists infer the density of ammonia by detection of NH_4^+. Figure 3.1 shows MAR (blue) and MEC (grey) following a similar pattern and leveling off at approximately 1,000,000 years, which appears to agree with the proton exchange and recombination theory.[46] It has also been noted that MAR is important in formation of MA via barrierless dimerization reactions.[40]

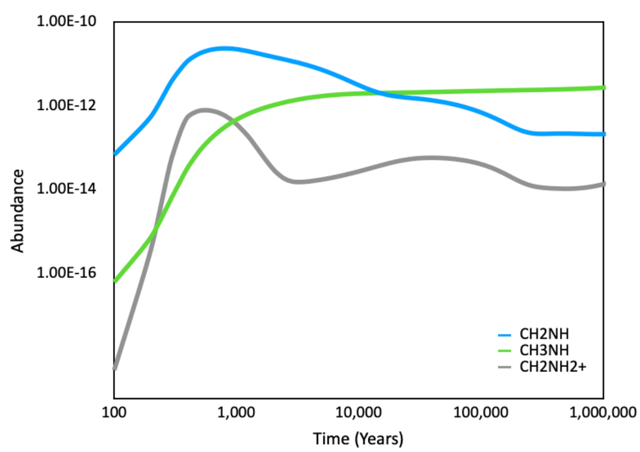

Figure 3.1 Abundances of MA (blue), MAR (green), and MEC (grey) over time, obtained from the model. Shown on a logarithmic scale for comparison.

Data was also collected for the precursors to MA (CH_3, N^+, CH_4, NH, and NH_3), which were chosen based on the reaction network presented in Yelle 2010.[46] The abundance over time data obtained from the model for those precursors is presented in Figure 3.2. The abundances of each of the precursors peak at or before the peak for MA, and slowly decline as they are used up in the formation of MA and other compounds in the model. The exceptions are methane and ammonia which are stable molecules that have been detected at high levels in Titan's atmosphere.[46]

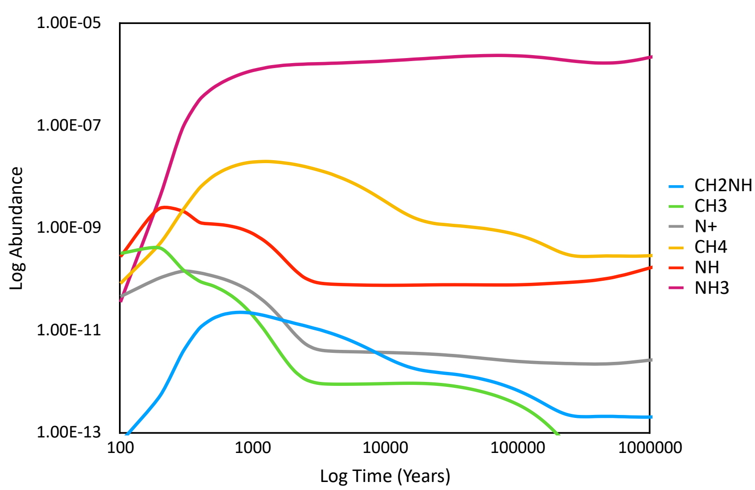

Figure 3.2 Abundance over time data for important precursors to MA (blue line). Presented on a logarithmic scale for comparison.

Table 3.1 shows the peak and final abundances of the three main species of interest, and Figure 3.3 shows this data graphically. The abundances are measured as a ratio to the total density of hydrogen in the atmosphere. These results show that MA and its related species are present at high enough levels (greater than 10^{-15}) to be considered important in tholin production.

Table 3.1 Abundances of Species of Interest

Species	Peak Abundance	Final Abundance
MA (CH_2NH)	2.32×10^{-11}	2.52×10^{-13}
MAR ($CH_3NH\bullet$)	5.88×10^{-11}	5.88×10^{-11}
MEC ($CH_2NH_2^+$)	2.52×10^{-13}	2.57×10^{-14}

The data presented here suggests that MA, MAR, and MEC, are present in Titan's atmosphere, and are present at sufficient levels to be considered in tholin production. As seen in Figure 3.3, the abundance of MAR (which is an intermediate in the formation of MA) does not peak and then level out, like MA and MEC do, which suggests that the model does not contain enough destruction reactions for MAR. This is due to a lack of studies pertaining to MAR, and as such only a few reactions have been proposed.

The data for MA agrees with literature abundances. MA is a neutral compound, and as such cannot be directly measured on Titan. However, as stated earlier, MA abundance can be inferred from MEC abundance, because they are closely related. Losion et al. utilized a new photochemical model to suggest that at an altitude of approximately 700 km the mole fraction (i.e. abundance) of MEC is in the 10^{-13} range,[28] which is close to the data presented in the current study, with a peak at 2.52×10^{-13} and equilibrium at 2.57×10^{-14}. The CASSINI Final Mission Report states that MEC has been detected on Titan and is present at approximately 10 ppm in the upper atmosphere.

There are a vast number of molecules important in tholin production—some of the major compounds studied thus far are: $HCNH^+$ $C_2H_5^+$,[11] purines, pyrimidines, HC_3N

polymers,[5] HCN,[25] C2H3N,[36] and HC_2N_3.[7] MA, in particular, has been of recent interest in tholin precursor studies, which is what spurred curiosity for the current study.

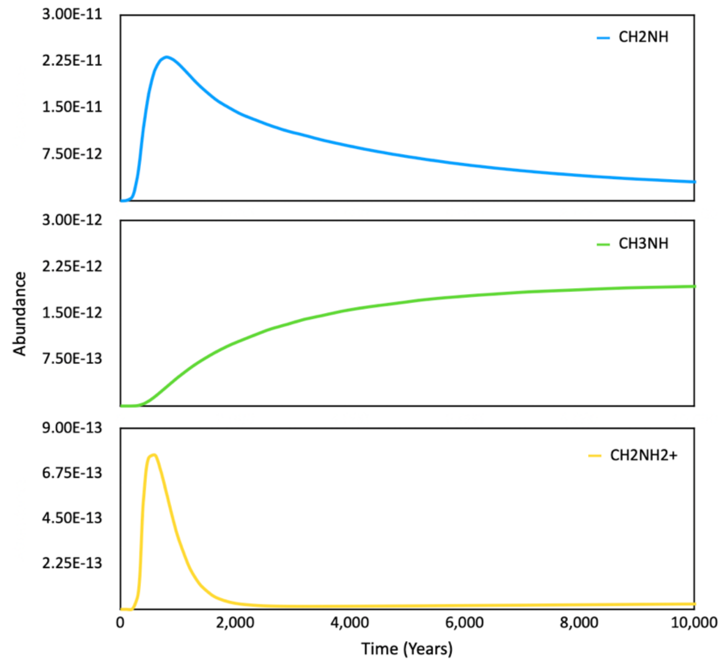

Figure 3.3 Abundances of MA (blue), MAR (green), and MEC (yellow) over 10,000 years.

3.2 Conclusion

Abundance over time data was obtained for MA, MAR, and MEC, as well as the main elementary precursors important in the reaction network (CH_3, N^+, CH_4, NH, NH_3). Yelle et al 2010 stated that the concentration of MA is closely related to that of MEC through proton exchange and recombination reactions, which appears to be true when looking at the data obtained in this study, as the abundance of the MA and MEC seem to follow the same production and loss pattern (Figure 3.1). The abundances of the main MA precursors peak at or before the peak for MA, and slowly decline as they are used up in the formation of MA and other compounds in the model (Figure 3.3). The exceptions are methane and ammonia which are stable molecules that have been detected at high levels in Titan's atmosphere. The peak and equilibrium abundance for MA, MAR, and MEC is shown in Table 3.1. The model was run over a timescale of 100 million years, and the equilibrium abundance is predicted to be the current abundance of MA, MAR, and MEC on Titan. The equilibrium abundance of MEC reported in this study was 2.57 x 10^{-14}, which is similar to the abundance of MEC reported by the Loison et al. group, which was in the 10^{-13} range. NASA reported an observed abundance of MEC as 10 ppm.

Chapter 4: Conclusions and Future Work

4.1 Conclusions

Based on the literature, a list of major formation and destruction reactions for MA and related species was developed, and the most up-to-date rate coefficients for those reactions was determined. A chemical model developed by OSU was then employed to obtain abundance versus time data for MA and related species. Tholin production is observed at most altitudes, but this research focused on the upper atmosphere (500+ km), which has largely been unstudied until recent years. Based on the data obtained from the model, MA is present at sufficient levels to be considered an important precursor to tholins and amino acids. Data about molecules that are related to the MA reaction network was also presented and showed that MAR and MEC are also present at high enough levels to be confirmatory of MA's importance in tholin production. The abundance of MEC (and by association, MA) agrees with data from the photochemical model presented by Loison et al.[28]

4.2 Future Work

The MA reaction network is a complex one, and the work done here is certainly not comprehensive. One recent study found that $CH_3N_2^+$ and $CH_2N_2^+$ may be missing links in the nitrogen cycle of Titan's atmosphere.[6] After looking though the KIDA database it is apparent that $CH_2NH_2^+$ has its own, complex reaction network. While this study did include some reactions with $CH_2NH_2^+$ as they pertained to MA, it could be beneficial to add the entire reaction network for this molecule to the model. Moreover, additional reactions involving MAR will also likely be proposed in the coming years and should be added to the model as they are discovered in order to create a more thorough reaction network.

Another recent discovery is the role of the MA radical cation and its isomer, aminomethylene, in chemical reactions with methane.[39] This would be very applicable to Titan atmospheric chemistry, and would be a good addition to the MA reaction network presented in this work.

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