Prebiotic Atmospheric Chemistry on Titan

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Space missions and ground-based observations have revealed that Titan's atmosphere is the site of extraordinarily complex chemistry, far surpassing that in other solar system environments. This natural laboratory offers us the opportunity to study the complex organic chemistry that likely leads to the production of the basic building blocks of biological molecules. Cassini measurements have revealed the presence of organic molecules with molecular masses over 100 amu. Although these newly discovered molecules cannot be identified with current data, the availability of carbon, nitrogen, oxygen, and hydrogen atoms from N_2, CH_4, and CO, the presence of photochemically-produced aromatic molecules (benzene and toluene) and reactive nitrogen molecules (ammonia, methylamine, amidogen) suggests that the molecules in Titan's atmosphere may be similar in structure and contain the same functional groups as pre-biological molecules on Earth. Thus, further study of the gas phase and aerosols composition on Titan should provide insight into the chemical processes that produce biological building blocks; heterocyclic aromatics, amino acids, nucleic acid bases, etc. Investigating this chemistry is a necessary step in the quest to understand the origin of life as a consequence of naturally occurring processes in planetary environments. Titan is alone in our solar system in hosting photochemistry of this complexity and therefore offers us a unique opportunity to investigate the beginning of biological synthesis.

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1. Introduction

The presence of organic molecules and an associated chemistry in Titan's atmosphere followed directly from Kuiper's detection of CH_4. Subsequent ground-based observations discovered that the atmosphere was thick with aerosols (Danielson *et al.*, 1973). Voyager observations of Titan discovered many photochemical species, revealing a rich atmospheric chemistry (Kunde *et al.*, 1981; Hanel *et al.*, 1982). It has been assumed since that time that the aerosols are the end product of this organic chemistry. This implies that some complex chemistry occurs in the atmosphere of Titan and that there is a continuum of photochemically-produced species, from relatively simple molecules (HCN, C_2H_6, etc.) to very large molecules. Present day models for photochemistry have yet to make much progress into this chemistry. Typically the chemistry is followed up to the production of molecules with 6-8 atoms (Yung *et al.*, 1984; Toublanc *et al.*, 1995; Lara *et al.*, 1996; Wilson and Atreya, 2004; Lavvas *et al.*, 2008a,b). For more complex molecules, reaction rate data is scarce and observational constraints on the densities of more complex molecules rare. Aerosol models on the other hand generally begin by postulating the production of seed nuclei with molecular weights of tens of thousands of amu (Toon *et al.*, 1980; Cabane *et al.*, 1992; Lebonnois *et al.*, 2002; Lavvas *et al.*, 2008a) . About the chemistry of the intermediate region, the region of complex organic molecules, we know very little, but this is essential territory if we want to understand how biological molecules are synthesized in planetary environments.

Biological molecules, including proteins, sugars and nuclei acids are built from smaller structures such as amino acids and the nucleic acid bases (Uracil, Adenine, Cytosine, Guanin, and Thymine). These biological building blocks are moderately complex molecules with molecular masses of 100-200 amu. They are composed primarily of carbon, nitrogen, oxygen and hydrogen, though several building blocks contain other elements. While it is generally thought that true biological molecules are synthesized through aqueous chemistry, perhaps aided by catalysis on surfaces, the building blocks can by synthesized by gas phase chemistry, or, to be more precise, molecules with a comparable complexity and some similarities in structure to amino acids and nucleic acid bases can be synthesized by photochemistry in planetary atmospheres. This is clear from measurements by Cassini, to be described below.

That organic molecules are produced by photochemistry in many planetary atmospheres is well known, but previous investigations of the synthesis of photochemical molecules have largely been limited to relatively small, stable species. Although interesting questions remain, production of these simple organics is fairly well understood, in the sense that we have identified the dominant chemical pathways for production and loss. To understand the chemistry of life, we need to go further and investigate the chemistry of the biological building blocks. The next step is to study the production of amino acids, heterocyclic aromatics, nucleic acid bases, etc., i.e. the basic building blocks of biological molecules. Titan is unique in

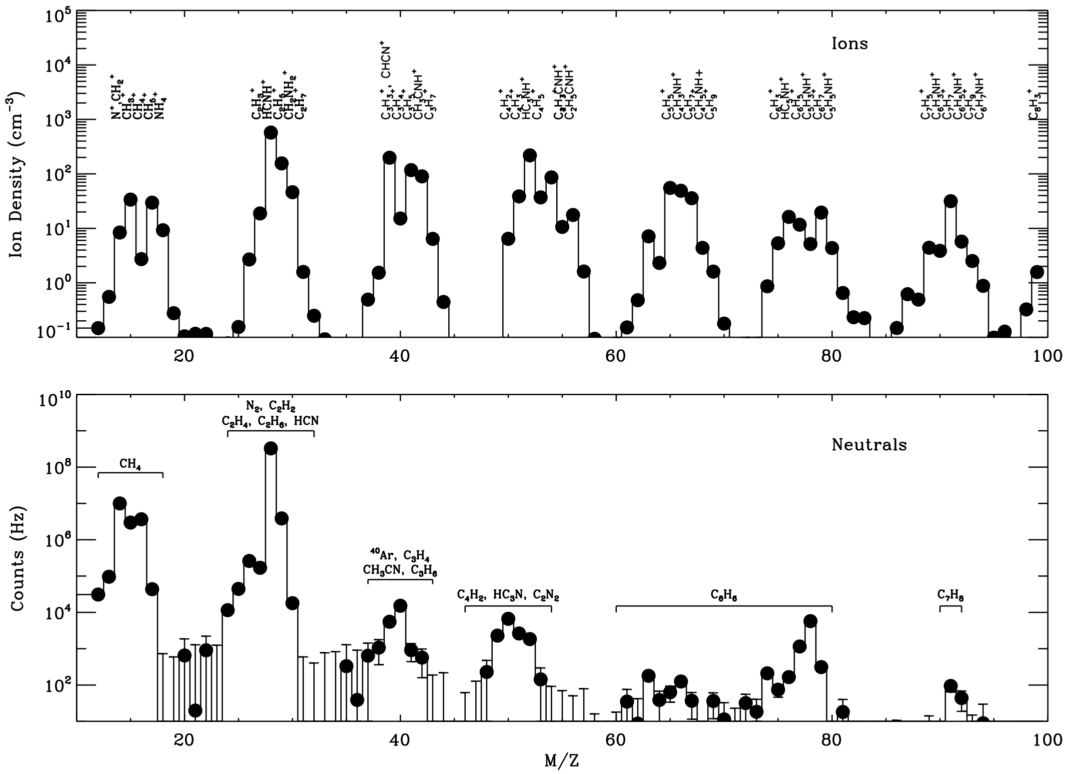

Figure 1: The top and bottom figures show examples of the INM ion and neutral spectra

that the photochemistry of its atmosphere goes beyond production of simple organics to synthesis of molecules with a complexity comparable to these biological building blocks. Titan's upper atmosphere is the best laboratory available to us for the study of the synthesis of complex organic molecules through naturally occurring chemical processes.

2. Cassini Contributions

Cassini has advanced our understanding of the chemistry of Titan's atmosphere by providing better precision and coverage of the abundant, stable hydrocarbons in the stratosphere through remote sensing observations (Vinatier *et al.*, 2007; de Kok *et al.*, 2007; Teanby *et al.*, 2007). This comes primarily through the availability of high resolution limb profiles and mapping sequences possible in a orbital mission. These observations are now interpreted with photochemical models containing thousands of reactions (Wilson and Atreya, 2004; Lavvas *et al.*, 2008b; Hörst *et al.*, 2008; Vuitton *et al.*, 2008) and sophisticated 3D general circulation models that are quite successful in explaining observed latitudinal trends (Lebonnois *et al.*, 2001; Hourdin *et al.*, 2004; Rannou *et al.*, 2006). Continued analyses and interpretation of these observations will put the chemistry of these simple molecules on a firm basis. Remote sensing however is limited to relatively small and abundant molecules. The biggest surprises in Cassini observations came from the *in situ* measurements. These direct observations of the atmosphere revealed the existence of heavier molecules and a far more complex chemistry than had been imagined previously.

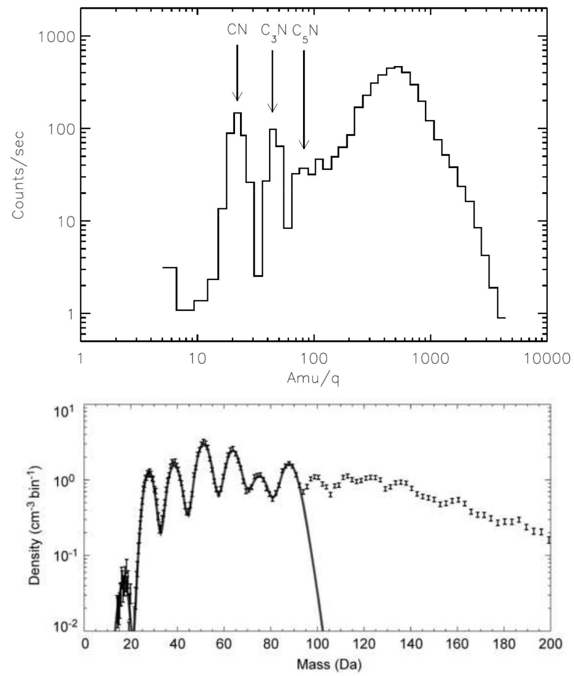

Figure 2: The top figures shows the spectrum of negative ions and aerosols from CAPS/ELS (Vuitton *et al.*, 2009) and the bottom figure the positive ion spectrum from CAPS/IBS (Crary *et al.*, 2009). The solid line represents the INMS ion measurements scaled to CAPS resolution.

Figure 1a shows data from the Ion Neutral Mass Spectrometer (INMS) experiment on the Cassini orbiter in ion mode, where the molecular composition of the ionosphere is measured. The density of roughly 50 molecular ions are measured in the spectrum, about an order of magnitude more than would be detected in any other solar system atmosphere. The spectrum was measure on 16 April 2005, the T5 pass through Titan's atmosphere, in the 1000-1050 km altitude region, which is fairly close to the ionospheric peak. Similarly complex spectra are seen in all measurements in this altitude region (Cui *et al.*, 2009). The large number of ionospheric species is due to the rich neutral composition. Many of the ion species are simply ambient neutral species with a proton attached (for example, CH_4 and CH_5^+, C_6H_6 and $C_6H_7^+$, etc.) and this fact has been used to estimate the density of the associated neutrals (Vuitton *et al.*, 2007). The ions appear in groups defined by the number of heavy atoms (C or N) contained in the molecular ions. The slow decrease of ion density with increasing mass makes it clear that there are many heavy ions beyond the 100 amu limit of the INMS. The mass spectrum of neutral molecules, shown in Fig. 1b also reveals heavy atoms, in particular benzene, but in general is not as sensitive to the minor neutral constituents as the ion spectrum.

Figures 2a shows data from the ion beam spectrometer (IBS) in the Cassini Plasma Spectrometer (CAPS) instrument suite (Waite *et al.*, 2007; Crary *et al.*, 2009). This instrument was designed primarily to measure energetic heavy molecules in Saturn's magnetosphere but measures heavy ions in the ionosphere as well, on each pass of the Cassini orbiter through Titan's upper atmosphere. The ion data show the presence of significant positive ions with masses up to ~ 340 amu. The energy resolution of the the IBS is not sufficient to identify the ions, but the ~ 12 amu periodicity seen so strongly in the INMS spectra is clearly present and implies the existence of molecules with up to 28 heavy (C or N) atoms. Although the poor mass resolution prevents identification of the species and the inference of neutral composition as was done with the INMS results, it is likely that the identity of these ions also reflects the composition of the neutral atmosphere, that is many of the ions should be formed by proton transfer from abundant ions to molecules with large proton affinities. Given the basic composition of the atmosphere these heavy molecules are undoubtedly organic. The identification of these molecules and the study of the associated chemistry could tell us a lot about how naturally occurring chemical process in the atmosphere synthesize large organic molecules.

Figure 2b shows data from the Electron Spectrometer (ELS) in the CAPS instrument suite (Waite *et al.*, 2007; Coates *et al.*, 2007). This channel of CAPS was designed to measure the distribution of energetic electrons in Saturn's magnetosphere and Titan's ionosphere. The detection of heavy negative ions in Titan's upper atmosphere was not predicted, but they are present on every pass through the ionosphere (Coates *et al.*, 2007). The spectra show clear peaks at low masses which have been identified as CN^-, C_3N^-, and possibly C_5N^- (Vuitton *et al.*, 2009). The spectrum extends to masses of nearly 10,000 amu. It is unlikley that these are individual molecules, rather they are probably aerosols with a negative charge. The number of unmatched electrons on the aerosols is not known and the masses shown in the figure assume a single change. The masses must be multiplied by a factor equal to the number of charges, if the are aerosols are multiply charged, so the true mass could be several tens of thousands of amu. The mass resolution is insufficient to permit identification of molecules in the intermediate region between the simple molecules at low mass and aerosols at large mass. Many of the complex organic ions that make up this intermediate region are probably formed by electron transfer to neutrals with high electron affinities. The smooth nature of the spectrum indicates that the range of masses for these complex organics is continuous. This is consistent with the CAPS/IBS results for positive ions. Molecules grow to sizes of hundreds of amu in Titan's upper atmosphere.

The haze discovered by CAPS/ELS likely extends throughout the upper atmosphere. Additional data on the high altitude haze was provided by the ultraviolet stellar occultation experiment (Liang *et al.*, 2007; Lavvas *et al.*, 2009). The occultation data probes to $\sim$700 km, where the extinction signal becomes too small to measure. Observations by the imaging system show haze at altitudes up to $\sim$600 km before the signal is too small to measure. Neither observation indicates any abrupt termination to the haze so, given the

CAPS detection of haze at 1000 km, it seems likely that the haze distribution is continuous throughout this region. The presence of haze at these altitudes implies that it is synthesized in the upper atmosphere. Estimates of the mass flux indicate that the production rate in the upper atmosphere is a significant fraction of the total haze production on Titan (Lavvas *et al.*, 2009).

It is remarkable that such heavy molecules and aerosols are found in the upper atmosphere at levels where molecular diffusion should rapidly remove them to lower altitudes. This clearly indicates that these heavy molecules and aerosols are formed in the upper atmosphere. It follows that the chemistry is driven by EUV radiation, which is absorbed in the upper atmosphere, rather than FUV radiation, which is absorbed in the stratosphere. In some cases this has been investigated in detail. For example, Vuitton *et al.* (2008) show that C_6H_6 in Titan's upper atmosphere is synthesized primarily by ion chemistry, which then diffuses down to lower altitudes as it is converted to more complex ring molecules. Laboratory experiments by Imanaka and Smith (2007) show that ion chemistry is critical to benzene formation. The realization that EUV-driven chemistry is responsible for production of very complex molecules provides a new direction for research into Titan chemistry. The result was unexpected and, though admirably outfitted for discovery, Cassini was not equipped for an in-depth investigation of this chemistry.

The Cassini mission is ongoing and analysis and interpretation of the results described above will continue, but the main message is clear: We have discovered quite complex organic molecules in the upper atmosphere.

3. Lab Simulations

Identification of the complex molecules discovered by Cassini is not possible with the instrumentation on the spacecraft or from ground-based observations, fortunately laboratory simulations of Titan chemistry can provide some guidance. These experiments were first performed at Cornell University in the 1970s but are now conducted in dozens of laboratories around the world. Laboratory tholins are produced by exposing mixtures of N_2 and CH_4 gas, similar to that in Titan's atmosphere, to energetic electrons or photons. The pressure and the energy input per molecule is usually higher than occurs on Titan, but the basic chemistry is similar. The tholins produced in these laboratory simulations are essentially loose conglomerations of numerous molecules of a range of sizes and elemental composition. These molecules are incorporated into the tholins from the gas phase; thus, tholins can provide us with a sort of archeological record of the gas phase chemistry responsible for creation of aerosols.

Although there must be differences between laboratory tholins and Titan aerosols, the lab tholins provide the great advantage that they can be analyzed with equipment that is far more capable than has been flown on spacecraft. Figure 3 shows a mass spectrum of tholin material created in the PAMPRE simulation chamber (Szopa *et al.*, 2006). This spectrum is obtain by dissolving the PAMPRE tholins in CH_3OH. The weak polarization forces in the solute decompose the

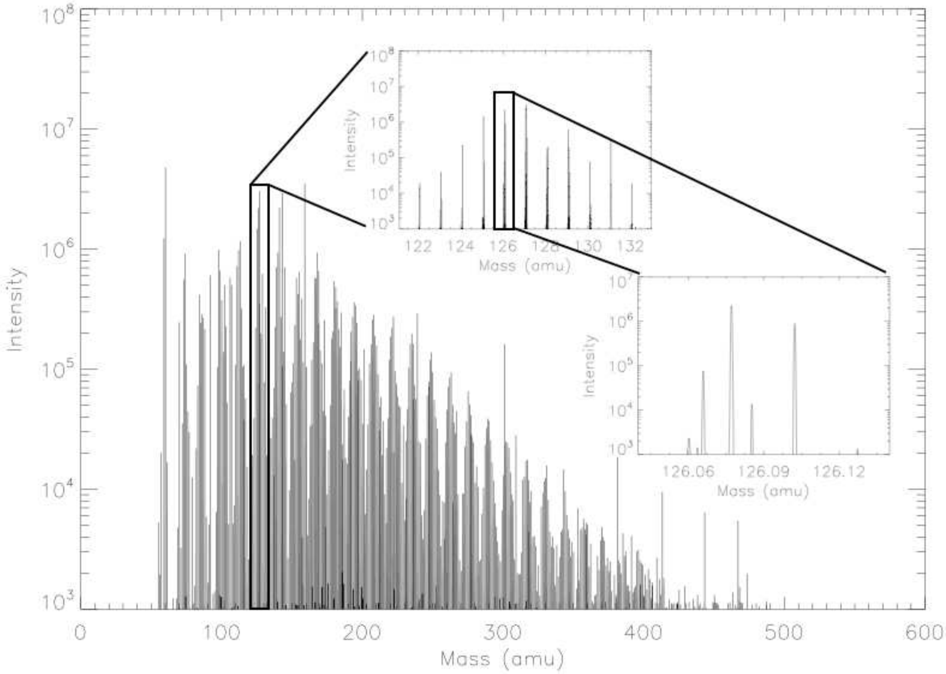

Figure 3: A mass spectrum of tholins from the PAMPRE experiment. The resolution is about 1 ppm.

tholin into its constituent molecules. The solution is injected into the mass spectrometer through an electrospray nozzle, which in positive mode, adds a proton to the neutral molecules, rendering them visible to the mass spectrometer.

The characteristics of tholins are reminiscent of Titan in several ways. The periodicity seen in the INMS and CAPS/IBS spectra is clearly present. This indicates that there are relatively few highly saturated or highly unsaturated molecules present. The tholin mass spectra extends out to hundreds of amu, which is consistent with CAPS/IBS and ELS results. Of course, we cannot say that composition tholins resemble that of Titan aerosols in detail, but the similarity of the gross characteristics that Titan aerosols may have a similarly complex composition. With the proper instrumentation we could obtain spectra of the gas and aerosols in Titan's atmosphere with a complexity similar to what is seen in this PAMPRE/tholin spectrum. Such data would provide us with the information needed to study the synthesis of large organic molecules through naturally occurring photochemistry.

Though laboratory simulations of tholins can provide guidance, especially in the design of experiments, there are undoubtedly differences from the chemistry on Titan. Aerosols are produced in much weaker radiation environment compared to lab simulation. There are no chamber walls, which can affect the chemistry in the lab. Finally, transport over large altitude ranges, which may have very different conditions (pressure, temperature, UV flux) can significantly affect the chemical cycles in a planetary atmosphere and there are no comparable effects in a laboratory. Thus, although tholins are a very useful probe of the some aspects of the chemistry, we will not understand atmospheric chemistry until we have high fidelity compositional measurements of Titan's atmosphere.

4. Summary and Recommendations

In summary, Cassini measurements show the existence of large molecules in Titan's upper atmosphere, at levels that can be sampled directly by spacecraft. We do not know the identity of most of these molecules, but they are undoubtedly organic. The presence of ring molecules, amines, numerous hydrocarbon radicals, and oxygen from CO suggest that molecules similar to biological building blocks on Earth could be formed. This is our best opportunity to study this phase of prebiotic chemistry. We thus recommend that NASA support:

1. A return to Titan with an orbital spacecraft capable of *in situ* sampling of the atmosphere, carrying the instrumentation needed to characterize the energy deposition processes and especially composition of the atmosphere,

2. Development of high ($\Delta M/M < 10^{-5}$) resolution mass spectrometers for spaceflight capable of measuring positive and negative ions and neutral species,

3. The laboratory investigations needed to plan future spacecraft experiments and to support analysis of spacecraft data.

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