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Synthesis of Biologically Important Precursors on Titan

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Abstract—A versatile mix of organic and inorganic species on Titan interacts to generate ingredients appropriate for prebiotic evolution and, possibly, the development of biotic systems. Titan's thick atmosphere is made up mostly of nitrogen gas, a variety of hydrocarbons, ionization products, and radical species resulting from photodissociation processes. Here, we describe organic synthetic schemes based on acetylene, cyanamide, and hydrocyanic acid, and leading to the production of biologically important molecules such as amino acids. In these schemes nitrogen may substitute for the lack of oxygen as an alternative to support the development or sustenance of biotic systems. In addition, we suggest that electron-transfer, ionic, and radical reactions constitute the basis for Titan's complex organic chemistry in an otherwise kinetically slow environment.

Keywords: acetylene—amino acids–cyanamide—methane—nitrogen—Titan

Introduction

With a size nearly 1.5 times that of Earth's Moon, Titan is the second largest moon in our solar system and the largest among Saturn's 56 (currently known) satellites. The presence of a thick-reducing atmosphere and a cold surface harboring hydrocarbon surface reservoirs qualifies Titan as a large-scale planetary-size laboratory ideally suited for in-situ study of prebiotic evolution processes that may parallel those that occurred on our planet 4.5 billion years ago. Titan is the only moon in the solar system with a thick atmosphere that contains large amounts of nitrogen and methane. These ingredients are believed to have existed in the early atmosphere of Earth, and therefore it is reasonable to envision that the presence of the atmosphere, combined with the occurrence of certain chemical reactions, may produce an environment having the conditions that precede the evolution of life (Chela-Flores, 2001). Since Titan's conditions are in some respects different from those that existed on early Earth (Zubay, 2000), the course of prebiotic evolution on Titan may take a similar, but not necessarily identical, pathway to prebiotic evolution on Earth. In this paper, we describe the environmental conditions that prevail in Titan's atmosphere and on its surface based on data obtained from the Cassini-Huygens mission, and we then suggest various plausible organic synthetic schemes that may lead to the production of biologically significant precursors on Titan.

The Environment of Titan

In order to assess the nature and extent of chemical synthetic pathways in an environment, the conditions and properties of that environment as well as the abundance of chemical precursors within the environment must be determined. Most of what is known about the nature of Titan and the properties of its atmosphere and surface comprises a compilation of fairly recent data from the Cassini-Huygens mission and Voyager I observations. The Cassini-Huygens mission arrived in the Saturnian system in the summer of 2004. The Cassini Orbiter released the Huygens probe on December 25, 2004. The probe descended into Titan's atmosphere on January 14, 2005. The probe's 2-hour and 27-minute descent through the atmosphere and nearly 2-hour transmission from the surface gave us a wealth of data (Owen, 2005). The probe carried on board a mobile chemistry lab equipped with a gas chromatograph, a mass spectrometer (both of these instruments allowed the identification of most chemical species encountered as the probe descended through the atmosphere), and a pyrolyzer to analyze aerosols. The gas chromatograph and mass spectrometer helped to identify and quantify chemical ingredients in the atmosphere by collecting gas samples that were filled at high altitude for analysis later in the descent. The aerosol collector and pyrolyzer collected aerosols via a pump that allowed their capture onto filters for chemical composition analysis via vaporization and subsequent passage to the gas chromatograph and mass spectrometer for chemical analysis. Since the Huygens probe detected several chemicals and several others were detected by recent flyby measurements from the Cassini spacecraft, the Cassini-Huygens mission represented powerful proof for the viability of the reactions described here and the plausibility of such chemistry.

Data from the Cassini-Huygens mission as well as earlier data obtained reveal that Titan's atmosphere is dominated by nitrogen gas (N_2). This gas accounts for approximately 90% of the chemical species found in Titan's atmosphere. The remaining 10% appear to be composed mainly of methane and argon, followed by a mixture of hydrocarbons that are the products of methane photochemistry (Fulchignoni et al., 2005).

Titan's atmosphere is denser than that of any terrestrial planet except Venus (Gehrels & Mathews, 1989). The data obtained by the Cassini-Huygens mission clearly indicate the presence of a highly reducing atmosphere where very active photochemistry occurs (Fulchignoni et al., 2005). A dense brown-orange aerosol haze shields the lower atmosphere and surface. This haze appears to be composed of hydrocarbon and nitrogen photochemical products in the form of radical reaction end products (Gibbard et al., 1999; Israel et al., 2005). Solar radiation drives the photodissociation of methane into methyl radicals ($\bullet CH_3$) or carbene ($:CH_2$) and other related species and hydrogen gas. Due to Titan's low gravity, most of the hydrogen escapes into space (Gehrels & Mathews, 1989). The hydrogen mixing-ratio stabilizes at 0.2% and reaches steady state with escape (Lebonnois et al., 2003). The generated hydrocarbon radicals become the starting point for numerous radical chain reactions whereby initiation, propagation, and recombination of radicals occurs and results in the production of heavier hydrocarbons. Methane seems to be the main greenhouse gas on Titan. The abundance of methane in the lower atmosphere of Titan is suggestive of a greenhouse effect stronger than that observed on Earth. This conjecture is supported by the difference in surface reflectivity between Titan and Earth. However, much of the incoming solar radiation is reflected off Titan's atmosphere, resulting in an "anti"-greenhouse effect. The dissociation of methane, due to atmospheric photoprocesses, ultimately leads to the production of numerous organic species via highly reactive radicals. The two main dissociation products of methane are ethane (C_2H_6) and acetylene (C_2H_2). Acetylene is a precursor for the synthesis of more complex species such as biologically important molecules. Recent data reported about the conditions on Titan have immensely enhanced our understanding of the Titan environment (see, for example, Artemieva & Lunine, 2003; Flasar et al., 2006; Lorenz et al., 2006). A model of Titan's lower atmosphere, surface, and subsurface that summarizes our interpretation about the current conditions and the most significant processes occurring is shown in Figure 1.

The Surface and Subsurface Environment

An estimate of the amount of methane in thermodynamic contact with the atmosphere, either on the surface or accessible in a near-surface water-ice crust, is very crude and no upper boundary value has been reported as of yet (Lunine et al., 1999). Various remote sensing data indicated that while it is unlikely that methane-bearing liquids cover the entire surface (Smith et al., 1996), substantial amounts of methane are likely to be hidden in high-latitude crater-lakes or subsurface reservoirs (Lorenz & Lunine, 1997). Such reservoirs were inferred based on measurements by the Huygens probe and verified via a July 22, 2006, flyby of the Cassini Orbiter (Kerr et al., 2006; Stofan et al., 2007). In a flyby on April 30, 2006, aimed at Xanadu, one of the major features on Titan, radar images taken by Cassini showed two prominent circular features likely to be calderas or impact craters. Sand dunes, discovered in previous flybys, crisscross Titan's surface. It is likely that these dunes are made up of organic sand grains overlaying a water-ice bedrock (Lorenz et al., 2006). Numerous curvy features appear indicating possible fluid flows. In a flyby on October 25, 2006, high-resolution infrared views of Titan were captured by Cassini. The images reveal a large mountain range (about 150 km long and nearly 1.5 km high), dunes, and a deposit of white material that may be hydrocarbon snow or a layer of organic substances that resembles a volcanic flow. This information, along with previously collected data, provides new insights on the height and composition of geologic features on Titan (Lorenz et al., 2006).

The exobiological importance of the Titan environment becomes obvious when it is realized that it harbors most of the raw materials for life, including

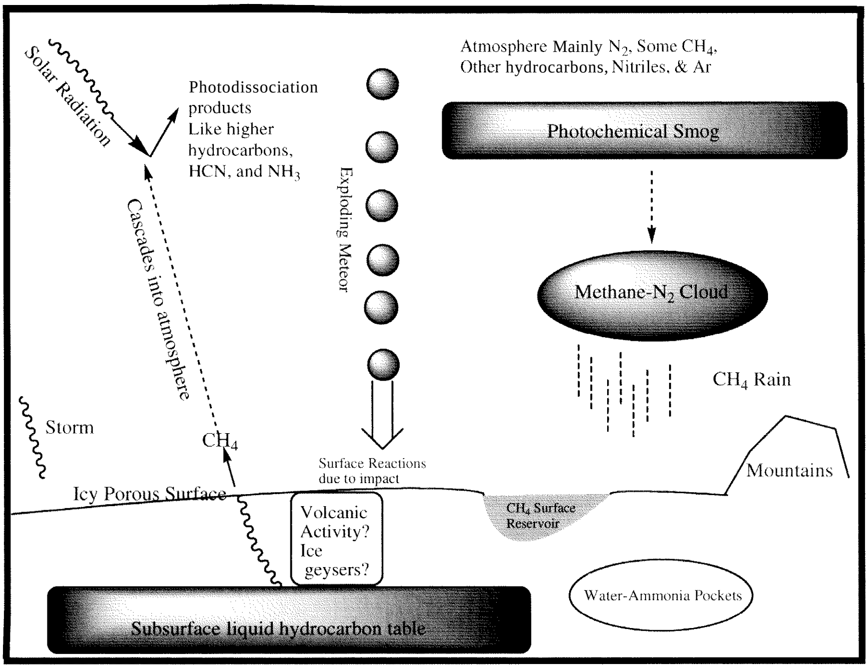

Fig. 1. Model of the general environment of Titan's atmosphere and surface The atmospheric and surface environment is complex, incorporating active exchange and recycling of numerous chemical species in a versatile mix of sources and sinks. Figure not to scale

carbon, nitrogen, and water. Due to its distance from the Sun (approximately $1.4 \times 10'$ km), however, any surface water is likely to exist in the form of ice. Based on models of Titan's thermal history, Fortes (2000) suggested that most of the surface is covered with a crust of water-ice with a deep ammonia-water ocean beneath. Alternatively, the ammonia-water ice layer may be mostly in a solid form with some larger volumes existing in a molten or semi-molten form (Figure 1) due to varying salt content, material heterogeneities, and slight pressure and temperature variations. Both extrapolations would be compatible with Titan accretion models, which indicate that Titan formed in an ammonia-methane–rich circum-planetary nebula that subsequently condensed into Saturn and its satellites, including Titan. Titan probably developed a layered structure with silicates in the core, overlain by a pure silicate covering and a deep ocean of ammonia-water liquid early in its history. As the surface temperatures cooled down, pure water was pushed to the surface, where it froze into ice forming the outer crust, while some of the ammonia-water solution remained liquid underneath.

At the low temperatures that prevail in the lower atmosphere and on the surface today, methane-nitrogen clouds are common and precipitate methane

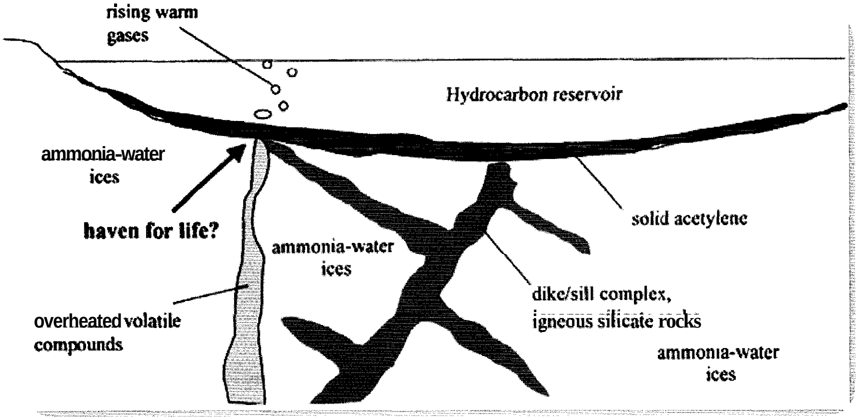

Fig. 2. Promising site for astrobiology at Titan. Overheated volatile compounds heat the interface between the hydrocarbon reservoir and underlying silicates and water-ammonia ice. A chemical energy source is available in the form of solid acetylene, which accumulates on the bottom of the reservoir (modified from Schulze-Makuch and Grinspoon, 2005).

rain. As a result, the surface is a range of dunes of organic sand on frozen ice with lenses of hydrocarbon surface reservoirs. These surface bodies are likely composed mainly of a hydrocarbon-methane mixture and some dissolved N_2 (Lunine, 1993; Lunine et al., 1999). Images from Titan clearly show dark, low-albedo features on the surface, suggesting liquid hydrocarbon reservoirs on some parts of the surface and bright areas consistent with ice or rock-ice regions on other parts of the surface. The Huygens Probe verified these predictions when it detected elevated methane levels near the surface (Owen, 2005).

Lunine (1993) predicted that at least 100–200 m of solid acetylene lies beneath liquid hydrocarbon surface bodies. Due to its higher specific gravity, solid acetylene accumulates on the bottom of surface reservoirs. Potentially, the solid acetylene can serve as starting material for various chemical reactions involving a multitude of organic compounds. However, Fortes (2000) indicated that some of the simplest prebiotic reactions on Titan would have half-lives on the order of 10^7 years unless they are somehow accelerated. There are two principal ways to accelerate reactions, by heat or by catalysis. Regions of geothermal activity had been projected to exist on Titan (e.g. Lorenz, 2002; Lorenz et al., 2006; Mirsky, 1997). Such regions could provide the necessary energy to increase the rates of most reactions. The most likely energy sources providing heat to the surface would be volcanism or meteorite impacts. Either or both mechanisms may have created episodes of aqueous chemistry in surface reservoirs on Titan, perhaps lasting thousands of years before freezing over (Lorenz et al., 2000). An especially promising environment for life would thus be a junction or an interface: a hot spring or a geothermal area at the bottom of a hydrocarbon reservoir (Figure 2). This environment would not only engulf a versatile mix of raw materials for organic synthesis but would also provide high enough temperatures for reactions to occur rapidly and some amount of molten water and ammonia as a medium for organic reactions. If this site would include microenvironments with fluid/solid interfaces, zones of fluid accumulation or entrapment, and areas enriched with material that could act as a catalyst (e.g. zeolites, clay), prebiotic evolution would be able to proceed to an advanced stage whereby complex organic synthesis leading to the rise of organized biotic systems may occur.

Organic Synthesis on Titan

In order to decipher Titan's organic chemistry, one needs to evaluate the various classes of organic reactions so that the plausible ones, under Titan's conditions, can be determined. Organic reactions are grouped into several basic types. The most common way of classifying organic reactions is based on the kind of reaction that takes place, and this method divides organic reactions into four classes (McMurry, 2006):

1. Addition reactions involve the adding of one reactant to another to make a bigger molecule. These reactions include many subclasses; most notable among these are halogenation, hydrohalogenation, and hydration reactions. Additions occur under the influence of an electrophile, a nucleophile, or a radical.
2. Elimination reactions are, essentially, the opposite of addition reactions. A single reactant breaks into two products. For instance, under the action of a base, an alkyl halide gives an alkene and hydrogen halide.
3. Substitution reactions are double replacement reactions whereby two reactants exchange parts to give two products. Most radical reactions follow this type.
4. Rearrangement reactions take place when one molecule undergoes a rearrangement of bonds producing an isomeric product. Rearrangement reactions are either 1,2-rearrangements, pericyclic reactions, or metathesis reactions.

While reactions belonging to any of the four classes may occur on Titan, the occurrence of elimination reactions is limited by the presence of strong bases and the occurrence of rearrangement reactions is limited by thermodynamics, as heat is the driving force behind such reactions. In the Titan environment, the presence of hydrocarbons, nitrogen-containing precursors, hydrogen, electromagnetic radiations of various wavelengths, and cold temperatures allows for addition- and substitution-type reactions to become dominant. Among the most prevalent subclasses of organic reactions under the environmental conditions on Titan are radical reactions.

Radicals on Titan and their Chemistry

Titan's atmospheric chemistry is dominated by radical reactions. Some important compounds involved in these reactions include H_2O, CO, and CO_2 (Coustenis & Taylor, 1999). Photolysis of water in the atmosphere yields OH radicals that react with methyl and methylene radicals to produce CO. Alternatively, OH radicals produced may combine to produce some minor amount of hydrogen peroxide. Further reaction of CO with OH radicals yields CO_2. CO and CO_2 may undergo limited exchange between the atmosphere and areas in the surface environment. One of the most significant roles that water plays involves the production of hydroxyl radicals, because OH radicals are very reactive precursors and water ice can be inferred to be the most common compound on Titan's icy surface.

Since Kuiper's detection of methane in Titan's atmosphere in 1944, several later measurements established the abundance and versatility of hydrocarbon species in Titan's atmosphere (Coustenis et al., 1999; Lunine et al., 1999). The presence of methane in the atmosphere leads to photolysis upon exposure to sunlight in the UV range. The photolysis of methane leads to the production of radical fragments including $CH_3\bullet$, $CH_2\bullet$, and $H\bullet$. Once produced, some of these radicals produce higher alkanes: For instance, the encounter between two CH_3 radicals produces ethane:

$$H_3C\bullet + \bullet CH_3 \rightarrow C_2H_6 \quad (1)$$

The encounter of two methylenes ($:CH_2$) may produce ethylene (C_2H_4):

$$H_2C: + :CH_2 \rightarrow C_2H_4 \quad (2)$$

Conditions prevailing in kinetically slow environments, such as the atmospheric and near-surface environments on Titan (due to the extremely low temperatures), result in the lowering of the enormous energy produced from the encounter of the methylenes and relieving of the requirement for a third body absorber. The encounter of an ethyl radical and a methyl radical produces propane (C_3H_8):

$$CH_3\bullet + \bullet CH_2CH_3 \rightarrow C_3H_8 \quad (3)$$

In addition, some of these radicals are likely to combine to produce a variety of polymers which condense to form oily droplets that may persist as photochemical fog aerosols, contributing to the thick orange haze engulfing Titan (Coustenis & Taylor, 1999). The radicals in reactions 1–3 above combine in other combinations, yielding other hydrocarbons. Voyager I and II infrared spectrometer data, as well as measurements conducted by the instruments onboard the Huygens probe, confirmed the presence of ethane (C_2H_6), ethene (C_2H_4), acetylene (C_2H_2), propane (C_3H_8), propyne (C_3H_4), and butadiyne (C_4H_2) in the atmosphere of Titan (Fox & Whitesell, 1997; Israel et al., 2005).

Molina-Cuberos et al. (1999) suggested that cosmic rays penetrate deep into the atmosphere of Titan, creating an ionosphere, and even penetrate further to the lower atmosphere, whereby an appreciable electron flux is generated. Some of the methane present in Titan's lower and middle atmosphere will become ionized upon encountering electrons. The ionization of methane is usually followed by a series of ion-molecule collisions that produce, among other species, the ions CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ (Pavia et al., 1996). Such ions are strong Lewis acids (electron-pair acceptors) and, therefore, react with hydrocarbon molecules or nitrogen-containing species in the atmosphere. For CH_5^+, the reaction yields methane:

$$CH_5^+ + RH \rightarrow CH_4 + RH_2^+ \tag{4}$$

In reaction 4, R is an alkyl group and RH is any hydrocarbon encountered by the ion. Reaction 4 is a chain reaction that yields numerous hydrocarbon cations (carbocations), such as methyl, ethyl, or propyl cations. These carbocations are electron-deficient species that serve as Lewis acids, accepting protons from electron-rich species. The reactions of species generated in reaction 4 would, in conjunction with reactions between the radicals described in reactions 1–3, explain some of the rare hydrocarbons detected by the Huygens probe in the Titan environment.

Organic Synthesis of Amino Acids

Given the rich organic inventory of Titan's atmosphere and surface, various organic synthetic schemes can be envisioned. The most promising of these schemes involve either acetylene or hydrocyanic acid. Acetylene is a promising compound for organic synthesis. Acetylene polymerizes exothermally if physically jarred or otherwise disturbed (Lorenz et al., 2000). The energy stored in the triple bond, as well as acetylene's high potential for reactivity, make it difficult to conduct experiments in a laboratory using acetylene at room temperature. However, for temperature and pressure conditions prevalent on Titan's surface, the instability and available energy become an advantage because they allow for enhancement of reaction rates. Both acetylene and hydrocyanic acid have the advantage that they are relatively common on Titan.

Amino Acids from Acetylene via Benzene

Organic synthesis based on acetylene may be initiated via the catalytic self-assembly of three acetylenes (cyclotrimerization) to produce benzene (Abbet et al., 2000; Becker-Heidmann et al., 1995; Enerson et al., 1998):

$$3C_2H_2 + \text{Catalyst} \rightarrow C_6H_6 \tag{5}$$

The catalyst in reaction 5 is essential because for the non-catalyzed reaction the energy barrier is too high for the reaction to occur (Stang & Diederich, 1995).

The catalyst allows for a reaction pathway that requires a lower energy of activation, thus making it possible for reactants to overcome the energy barrier. A variety of substrates, such as active metal surfaces (Pt, Pd, Ni, etc. . . .), or certain silicates, such as clay minerals or zeolites, may act as surface catalysts that help facilitate reaction 5 (Abbet et al., 2000; Becker-Heidmann et al., 1995). Coustenis et al. (2003) analyzed high-resolution spectra obtained from observations carried out by the Infrared Space Observatory. Their results confirm the presence of benzene in Titan's atmosphere, with a column density of about 2×10^{15} molecules/cm^2. The detected atmospheric benzene may be produced by cyclotrimerization of acetylene on aerosol surfaces in the atmosphere. Some of the produced benzene may wash down and condense with hydrocarbon rain. If in reaction 5 one or more of the acetylenes is an alkyl-substituted acetylene produced by the combination of radicals, then the product will be a substituted benzene (C_6H_5R):

$$\text{H-C} \equiv \text{CR} + 2\text{C}_2\text{H}_2 + \text{Catalyst} \rightarrow \text{C}_6\text{H}_5\text{R} \tag{6}$$

where R can be any alkyl or related group. Once the benzene or alkyl benzene is produced, the synthesis of more complex compounds can occur via simple substitution or addition reactions. For instance, alkyl-nitrobenzene ($RC_6H_4NO_2$) may be produced using $NO_2{}^+$, a highly reactive cation that is formed from ionizing radiation, the decomposition of nitric acid, or the oxidation of ammonia (Solomons, 1996):

$$\text{C}_6\text{H}_5\text{R} + \text{NO}_2^+ \rightarrow \text{RC}_6\text{H}_4\text{NO}_2 \tag{7}$$

Alkyl nitrobenzene ($RC_6H_4NO_2$), the product of reaction 7, may in turn become the precursor for the synthesis of more complex organic molecules such as amino acids, fatty acids, and sugars. A simple illustration of this conversion is the catalytic hydrogenation of the nitro group in alkyl nitrobenzene (the metal surface catalyzed addition of H_2 to the nitro group). It converts the alkyl nitrobenzene to alkyl amino benzene ($RC_6H_4NH_2$) (Solomons, 1996):

$$\text{RC}_6\text{H}_4\text{NO}_2 + \text{H}_2 + \text{catalyst} \rightarrow \text{RC}_6\text{H}_4\text{NH}_2 \tag{8}$$

The oxidation of the R group in $RC_6H_4NH_2$ yields a carboxyl group (COOH), thus producing an amino acid product (Solomons, 1996). If R in reaction 8 is a methyl group, the oxidation of $RC_6H_4NH_2$ using an appropriate oxidizing agent produces para-amino benzoic acid ($HO\text{-}COC_6H_4NH_2$), a promising chemical compound for a biological scheme, as it has the backbone of an amino acid. The advantages of this organic synthetic pathway are that it should theoretically produce high yields of the products and that no liquid water is needed for these reactions to occur (Abbas & Schulze-Makuch, 2002). However, the synthesis is limited by reasonable yields from several intermediary steps and the abundance of a silicate or metal surface to serve as a catalyst in Titan's surface environment.

Amino Acids from Acetylene via Acetic Acid

Upon reaction with abundant ammonia and some methyl iodide in the surface environment, solid acetylene produces 2-butyne ($H_3C\text{-}C \equiv C\text{-}CH_3$):

$$HC \equiv CH \xrightarrow[2.CH_3I]{1.NaNH_2/NH_3} --> \text{Twice} \rightarrow H_3C\text{-}C \equiv C\text{-}CH_3 \quad (9)$$

When exposed to basic H_2O_2, a mole of the product of reaction 9 produces two .moles of acetic acid:

$$H_3C\text{-}C \equiv C\text{-}CH_3 + H_2O_2/OH^- \rightarrow 2H_3C\text{-}COOH(1) \quad (10)$$

The basic environment needed for reaction 10 can be supplied via liquid ammonia-water. Radiation striking the surface-ice may generate hydroxyl radicals (OH•). The subsequent recombination of hydroxyl radicals produces hydrogen peroxide:

$$HO\bullet + \bullet OH \rightarrow H_2O_2 \quad (11)$$

The acetic acid produced in reaction 10 can be used to produce biologically important macromolecules such as amino acids. In the ammonialwater mixture proposed by Fortes (2000), ammonia is very abundant, so that if the carboxylic acid formed in reaction 10 is halogenated and exposed to water in the mixture, and if this encounter is followed by ammonolysis, an amino acid is produced (Solomons, 1996):

$$RCH_2COOH \xrightarrow[2.H_2O.3.NH_3]{1.X_2/P_4 or S_x surface} --> RCH(NH_3)^+COO^- \quad (12)$$

The X_2 in reaction 12 is a halogen, such as chlorine or bromine. Depending on the nature of the alkyl group (R), reaction 12 can generate a variety of amino acids. However, elements and compounds are required that are likely to be rare in the Titan environment, and probably liquid ammonia water is required. Once amino acids are produced, they can self-assemble under slightly acidic conditions in the presence of a catalyst producing peptides by forming amide bonds between the carboxyl group of one and the amino group of another (McMurry, 2006). The formation of the amide bond is accompanied by the loss of water.

If the cycle in reaction 9 occurs once, the resulting product will be propyne ($H_3C\text{-}C \equiv CH$). This will yield formic acid according to reaction 10.

While the carboxylic acids produced by reaction 10 can undergo reaction 12, they may also decompose on naturally occurring powder surfaces to produce ethane, carbon dioxide, and hydrogen gas:

$$2H_3C\text{-}COOH(1) \rightarrow C_2H_6(g) + H_2(g) + CO_2(g) \quad (13)$$

The decomposition of formic acid according to reaction 13 yields methane instead of ethane. Thus, reactions following the general type described in reaction 13 can explain some of the generated hydrocarbons. Reaction 13 is exothermic and may, thus, possibly serve as an energy-yielding metabolic pathway that may be employed by putative biotic systems in a Titan setting.

Amino Acids from Hydrocyanic Acid via Alpha-Amino Nitriles

Photochemical processes occurring in the ionosphere of Titan (e.g. recombinations) release electrons that may impact atmospheric species causing dissociation (Raulin, 1998). Since N_2 is the most abundant species in the atmosphere, it is likely that the dissociation of N_2 due to electron impact in Titan's atmosphere is very common. One of the main products of N_2 dissociation is HCN. It may be produced from ion-irradiated N_2-rich ices containing CH_4 and CO (Moore et al., 2002):

$$CO + CH_4 + N_2 + h\upsilon \rightarrow 2HCN \tag{14}$$

Acetylene; and higher acetylenes, abundant in the surface environment, may undergo hydroboration followed by oxidation with hydrogen peroxide in ammonia to produce an aldehyde (Abbas & Schulze-Makuch, 2002):

$$\text{Terminal Alkyne} + \text{Hindered Borane followed by } H_2O_2 \text{ in Base} \rightarrow \text{Aldehyde} \tag{15}$$

Boron precedes carbon in the periodic table and the high abundance of carbon in Titan's atmosphere and surface environment indicates that the presence of some boron in the surface environment is likely. The presence of numerous gas-phase, liquid, and solid hydrocarbon species containing alkyl groups will make the encounter between such groups and boron possible so that a hindered dialkyl or trialkyl borane is produced. The hydrogen peroxide needed in reaction 15 can be supplied via reaction 11. Once produced, the aldehyde product of reaction 15 reacts with the product of reaction 14 in ammonia to give an alpha-amino nitrile (McMurry, 2006):

$$HCN + \text{Aldehyde} + NH_3 \rightarrow RCH(NH_2)C{\equiv}N \tag{16}$$

If the product of reaction 16 is treated with acid, such as in a hydrothermal vent area, or mixes with the acetic acid produced in reaction 10 and obtains a heat source (bolide impact, volcanism), it produces an alpha-amino acid:

$$RCH(NH_2)CN + H^+ + \text{heat} \rightarrow RCH(NH_3)^+COO^- \tag{17}$$

Reaction 17 is limited by the requirement of a heat source. Reactions 14–16 also illustrate the important role played by nitrogen and ammonia in the Titan environment. Nitrogen is converted to ammonia, which may serve as a solvent that becomes an optimum medium for chemical reactions to occur in the absence of liquid water.

*Amino Acids from Hydrocyanic Acid **via** UV Photon-Assisted Self-Assembly*

The HCN produced in reaction 14 above may self-combine in aqueous alkaline solutions present on the surface to form amino acids with the assistance of UV photons (Miller, 1998):

$$3HCN + 2H_2O + h\upsilon \rightarrow CHCO_2HNH_2 + CN_2H_2 \qquad (18)$$

In addition to glycine, reaction 18 yields cyanamide (CN_2H_2), which can link amino acids together as the first step in the formation of proteins. Reaction 18 is limited to areas on Titan's surface or interfaces that have liquid water. The HCN that forms due to atmospheric processes may be introduced into the surface environment via hydrocarbon precipitation (Coll et al., 1999). Keller et al. (1998) suggest that HCN can be produced in Titan's ionosphere via the electron dissociative recombination reaction:

$$HCNH^+ + e^- \rightarrow HCN + H \qquad (19)$$

The $HCNH^+$ ion reactant in reaction 19 is produced by the reactions 20–23 sequence:

$$\begin{aligned} &N_2 + h\upsilon \rightarrow N_2^+ + e^- \\ &N_2^+ + CH_4 \rightarrow CH_3^+ + N_2 + H \\ &CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \\ &C_2H_5^+ + HCN \rightarrow HCNH^+ + C_2H_4 \end{aligned} \qquad (20\text{–}23)$$

According to their model, Keller et al. (1998) conclude that ion-neutral chemistry produces $HCNH^+$ as the single major ion species at the ionospheric peak (an altitude of 1055 km).

Discussion

A comparative evaluation of the four synthetic schemes can be made based on the availability of reactants and reagents involved in each of the schemes and the presence, or lack thereof, of the appropriate conditions that make the reaction scheme favorable.

Among the four synthetic schemes leading to the production of amino acids, the first presented reaction sequence, utilizing acetylene via benzene, seems to be the most likely to occur. This is due to the abundance of the required reactants and reagents, and due to the Titan environment, which provides appropriate conditions for this reaction sequence. The recent detection of benzene and phenyls on Titan supports the foregoing discussion (Cassini-Huygens Mission Website, 2006). The other schemes are likely to occur in restricted micro-environments on Titan (e.g. in close association with volcanic activity or at the site of a meteor impact), as they require either a liquid water medium or a heat source, both of which are not common in the general Titan atmospheric and surface environments. Even if minor amounts of H_2O_2 are produced, they are likely to react right away, thus making yields of any reaction requiring H_2O_2 very small. The presence of biologically important molecules coupled with energy-yielding reactions in the Titan environment represents significant steps towards the development and sustenance of biotic systems. Abbas and Schulze-Makuch (2002) described several plausible metabolic pathways that may be employed by biotic systems under Titan's conditions. Most notable was the catalytic hydrogenation of photochemically produced acetylene, which was shown to be an energy-yielding pathway that provides approximately 100 kJ/mol under Titan conditions and should occur rapidly enough to be kinetically feasible (McKay & Smith, 2005). Under Earth conditions, the energy release in radical reactions is an extremely rapid process (Fox & Whitesell, 1997; Solomons, 1996) and would result in internal damage of organisms. On Titan, however, in a kinetically slow environment these reactions may be more controllable and manageable and may thus be used in metabolic pathways (Schulze-Makuch & Irwin, 2004). If so, this would mean a fundamentally different approach of biology to metabolism, since all metabolic reactions on Earth are based on redox-reactions, as far as we know (Irwin & Schulze-Makuch, 2001).

Conclusions

Organic synthesis, based on simple precursors, may lead in the Titan environment to the production of biologically important molecules such as amino acids. Four synthetic schemes leading to the production of amino acids were presented, with the first scheme, based on the catalytic self-assembly of three acetylenes to benzene, being the most likely route, based on theoretical considerations, and now supported by the detection of benzene and other intermediates on Titan. In two alternative schemes, hydrocyanic acid plays a central role. Cassini-Huygens detected HCN in the Titan environment. As new chemical species are detected and identified in Titan's atmospheric or surface environments, more pieces are added to the puzzle of the complex web of chemical reactions occurring in that environment. Controlled laboratory experiments simulating microenvironments on Titan should prove invaluable, and theoretical predictions provided here and elsewhere should be tested. The Cassini-Huygens mission has enhanced our understanding of the chemistry occurring in both the atmospheric and surface environments and of the forces that shape their nature. As more data from the Cassini-Huygens mission are analyzed, we can expect that further insights will be gained with regard to Titan's potential for supporting prebiotic evolution and possibly the subsequent development of life. The diversity and complexity of possible life precursor compounds found will determine whether the course of the pre-biological process has progressed to the stage whereby chemical evolution is leading to the production of significant biomolecules, like proteins and nucleic acids, or whether it was halted at a certain stage.

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