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On the possibility of gly and ala amino acids on Titan

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Abstract. In view of the possible production of formaldehyde and acetaldehyde in Titan's atmosphere, the production of α-amino nitriles, the precursors of glycine and alanine amino acids, is explored in the upper atmosphere of Titan. The presence of glycine and alanine amino acids or their precursor amino nitriles can be used as a diagnostic respectively for the presence or absence of water locally on the surface of Titan.

Keywords : Titan, formaldehyde, acetaldehyde, α-amino nitrile, glycine and alanine amino acids

1. Introduction

Titan is Saturn's largest moon. It is the only satellite in the solar system with a dense atmosphere about 1.6 times denser than Earth's atmosphere. Titan's atmosphere is mainly composed of N_2 with a little methane and other organic molecules. The sharp CH_4 fluorescent emission lines can be seen through 3μ atmospheric window in between strong telluric CH_4 absorption lines. The CH_4 emission mainly arises at 400-750 km altitudes and has been verified by VIMS/Cassini imaging conducted during the close encounter with Titan (Kim et al. 2005). The minor constituents include the nitriles, CO, CO_2 and other hydrocarbons. Data on atmospheric constituents were first obtained from UVS (Ultraviolet spectrometer) and IRIS (Infrared Interferometer Spectrometer) on board Voyager 1 and Voyager 2 spacecrafts (Yung et al. 1984) and data on CO were obtained from ground based radio observations of CO line at 115 GHz (Muhlehman et al. 1984; Marten et al. 1988). The recent Huygens-Cassini mission is equipped with various facilities to study Titan's atmosphere and the surface. Huygens probe landed on

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Titan's surface from Cassini spacecraft on January 14, 2005. The Gas Chromatograph Mass Spectrometer (GCMS) on board Huygens probe detected CO_2, C_2N_2, C_2H_6 and benzene on the surface and identification of other constituents is in progress. (Niemann et al. 2005). A large number of complex hydrocarbon molecules were found in the upper reaches of the atmosphere (Waite et al. 2005). The surface temperature of Titan is $\sim$95K, somewhat warm due to the green-house effect produced by its atmospheric gases. This temperature is close to the triple point of methane.

Surface temperatures are too cold to support liquid water on Titan. Nevertheless, tectonic events in the water-rich interior or impact melting and slow refreezing may lead to episodic availability of liquid water (Carl Sagan et al. 1984). There is reason to believe that a liquid layer in Titan's interior is maintained to the present probably because ammonia is mixed in it.

Geological features on Titan's surface suggest cryo-volcanoes (Sotin et al. 2005), clustering of its mid latitude clouds is also taken as evidence for possible cryo-volcanoes (Roe et al. 2005). All these suggestions include out-gassing of methane into the atmosphere (Tobie et al. 2006). The apparent evidence for cryo (water/water-ammonia) volcanism seen in the Cassini orbiter radar images (Elachi et al. 2005) and the Visual and Infrared Mass Spectrometer (VIMS) observations (Sotin et al. 2005) suggest that temperatures are probably much higher in the hotbeds, enough for water-ice to melt. Assuming an initially completely liquid dome, the freezing time scales of cryo-volcano Ganesa Macula on Titan's surface are $\sim 10^2$-10^5 years implying that liquid water or water-ammonia environments lasted therein for this period of time (Niesh et al. 2006). The presence of radiogenic isotope argon-40 in Titan's atmosphere indicates that volcanoes spew plumes of water and ammonia.

In additions to the lines of water vapor at 228 cm^{-1} (43.86 μ) and 254 cm^{-1} (39.37 μ) detected by European Space Agency's (ESA) artificial satellite ISO (Infrared Space Observatory) observations of Titan in 1997 (Coustenis et al. 1998), Cassini's CIRS (Composite Infrared Spectrometer) observations detected water at 170 cm^{-1}, 203 cm^{-1} and 208 cm^{-1} in the Titan's atmosphere (Nixon et al. 2006). The water vapor supposedly enters Titan's atmosphere in the form of water-ice particles sputtered from Saturn's rings and satellites which then vaporize. Titan has no magnetic field. For a while it also orbits outside the Saturn's magnetosphere. During this time, therefore, Titan's atmosphere is exposed to intense solar wind.

The photochemistry of nitrogen and methane leads to the formation of complex hydrocarbons and nitriles. The organic nature of some of the chemicals found in Titan's atmosphere indicates that this exotic moon of Saturn could harbor some form of life. Amino acid precursors have also been produced in a laboratory experiment simulating Titan's upper atmosphere (Kobayashi et al. 2006). The amino acids are the building blocks of proteins necessary for life. The purpose of the present paper is to explore the possibility of production of two simplest amino acids viz., glycine and alanine in view of the availability of the necessary ingredient molecules in the atmosphere of Titan.

2. Production of formaldehyde and acetaldehyde in Titan's atmosphere

The hydroxyl (OH) radical and atomic oxygen (O) are obtained photolytically from the H_2O molecule (water vapor) in Titan's upper atmosphere:

(i) $H_2O + h\nu$ (λ <242.46 nm) $\rightarrow$ H + OH (Herzberg 1966)

(ii) $H_2O + h\nu$ (λ <130.4 nm) $\rightarrow$ H + H + O (Huebner et al. 1992)

(iii) $H_2O + h\nu$ ($\lambda <$ 98.4 nm) $\rightarrow H_2O^+$ + e (Katayama et al. 1973)

(iv) $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$

(v) OH + hν ($\lambda <$ 282.3 nm) $\rightarrow$ O + H (Huber & Herzberg 1979)

The other sources of energy available to Titan's atmosphere are: (1) the high energy cosmic rays, (2) the intense solar wind when outside Saturn's magnetosphere (3) the trapped energetic charged particles when inside Saturn's magnetosphere and (4) the burning of micrometeoroids in the atmosphere. Dissociation of H_2O molecule from micrometeoroid burning in the atmosphere of Titan provides a source of OH and O (Casavecchia et al. 2006).

The other sources of atomic oxygen are photodissociation of CO and CO_2 that have been observed in Titan's atmosphere:

(vi) $CO_2 + h\nu$ ($\lambda <$ 227.5 nm) $\rightarrow$ CO + O (Okabe 1978)

(vii) CO + hν ($\lambda <$ 111.7 nm) $\rightarrow$ C + O (Krupenie 1966)

The atomic oxygen and hydroxyl radical react with the hydrocarbon radicals to produce formaldehyde and acetaldehyde via reactions as the following:

(viii) CH_3 (X^2A_2) + O (^{3}P) $\rightarrow$ HCHO ($^1A_1$) + H (^{2}S)

(ix) CH_3 (X^2A_2) + OH ($X^2\pi$) $\rightarrow$ HCHO ($^1A_1$) + H_2 ($X^1\Sigma_g^+$)

(x) CH_2 ($^3B_1$) + OH ($X^2\pi$) $\rightarrow$ HCHO ($^1A_1$) + H (^{2}S)

(xi) C_2H_3 ($^2A'$) + OH ($X^2\pi$) $\rightarrow$ $^3CH_3CHO$

(xii) C_2H_5 (X^2A') + OH $(X^2\pi) \rightarrow {}^3CH_3CHO$ + H_2 $(X^1\Sigma_g^+)$

(xiii) $C_2H_5(X^2A')$ + $O(^3P) \rightarrow {}^3CH_3CHO$ + $H(^2S)$

All the above radical-radical reactions are exothermic, spin-allowed, fast and need no activation energy. Because of extremely cold conditions in Titan's atmosphere, only electronic ground states of the species are considered in the above reactions.

Moreover, those chemical reactions are of relevance that require no activation energy. The production of hydrocarbon radicals in Titan's atmosphere have already been discussed in detail (Yung et al. 1984; Toublanc et al. 1995; Lara et al. 1996; Saxena et al. 2003).

3. Possible sources of ammonia in Titan's upper atmosphere

(i) Recent Cassini CAPS (Cassini Plasma Spectrometer) measurements have shown the existence of energetic N^+ ions (E >1 KeV) in the Saturn's inner magnetosphere (Crary et al. 2005). The energetic N^+ ions may get implanted in the Titan's upper atmosphere directly during the latter's passage through the Saturn's magnetosphere and may reappear at plasma energies via sputtering (Sitter Jr. et al. 2005) or indirectly through sputtering from the rings which themselves get similarly implanted with N^+ ions.

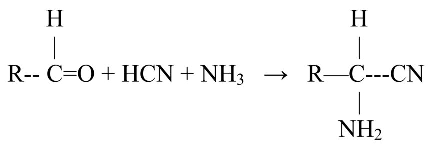
(ii) Cosmic-ray generated reactive He^+ particles, if present, may produce energetic N^+ ions from the dissociative ionization of N_2 in the upper atmosphere of Titan.

The reaction between energetic N^+ ion and H_2 molecule becomes no more endothermic, and eventually leads to the production of NH_3 through dissociative electron recombination of NH_4^+ ion.

(iii) The tiny satellite Enceladus of Saturn produces a plume of liquid water large enough to drench the whole Saturn's system and is also thought to be the source of E-ring (Baker 2005). The possibility of ammonia being mixed in the liquid water as an anti-freezing agent beneath the surface of the satellite cannot be ruled out. Like water-ice particles, the ammonia-ice may also get sputtered into the Titan's upper atmosphere from Saturn's tiny moons or rings. The solid particles of the two ices then vaporize in the upper atmosphere of Titan. As the heat of sublimation of ammonia-ice is about half that of water-ice, the former sublimes faster than the latter.

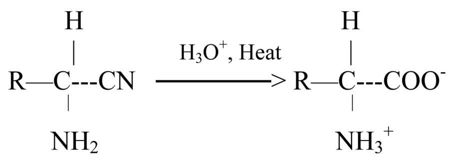
4. Possible production of glycine and alanine amino acids on Titan (Strecker's synthesis)

In the first step of Strecker's synthesis (Solomons 1992), the formaldehyde and acetaldehyde produced as above in Titan's upper atmosphere, react with ammonia (NH_3) and hydrogen cyanide (HCN) to produce α-amino nitriles:

(xiv) 

(α-amino nitrile)

The α-amino nitriles eventually land on the moon's surface during the "hydrocarbon rain". If the landing happens to be in the "impact pond" already having liquid water, the second step of Strecker's synthesis involves the hydrolysis of the nitrile group of the α-amino nitrile that converts the latter to the α-amino acid as follows:

(xv) 

(α-amino acid)

If $R \equiv H$, formaldehyde is converted to glycine and if $R \equiv CH_3$, acetaldehyde is converted into alanine. If the eventual landing of α-amino nitriles produced in the upper atmosphere of Titan happens to be away from liquid water on the surface, these α-amino nitriles will remain frozen on the surface till they come in contact with hot liquid water for the hydrolysis to occur during some surface activity of the type like cryovolcanism in which mixture of hot liquid water and ammonia erupts from beneath the surface or impact of a meteorite creating an impact pond which is then filled with underneath hot liquid water and ammonia.

5. Discussion

During the closest flyby of Titan on April 16, 2005, the Cassini spacecraft came within 1027 kms of the moon's surface. The observations revealed numerous complex hydrocarbons in Titan's outer layer of atmosphere that would be expected to condense and rain down to the surface (Waite et al. 2005). We have chosen Strecker's synthesis for the production of α-amino nitriles in Titan's upper atmosphere as all the ingredient molecules in the synthesis viz., HCHO, CH_3CHO, NH_3, HCN are likely to be present in Titan's upper atmosphere. The α-amino nitriles thus produced from Strecker's synthesis would condense out due to very cold environment and ultimately land on Titan's surface.

Many heavy hydrocarbons and nitriles are expected to be produced photochemically above 500 km altitude (Wilson et al. 2003, Lebnnois et al. 2001) and have indeed been detected at infrared wavelengths (Coustenis et al. 1989; Flasar et al. 2005) and in the Cassini Ion and Neutral Mass Spectrometer (INMS) fly-bys (Waite et al. 2005), but most of them condensed at the low temperatures of the lower stratosphere below 200 km (Wilson et al. 2003). The Gas Chromatogtraph Mass Spectrometer (GCMS) on the Huygens probe could not detect them as it started functioning from an altitude of 146 km downwards. These precipitated molecules can only be detected on the surface (Niemann et al. 2005). The presence of glycine and alanine amino acids or their precursor amino nitriles can, therefore, be used as a diagnostic respectively for the presence or absence of water locally on the surface of Titan.

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