ORGANIC CHEMISTRY AND EXOBIOLOGY ON TITAN

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Abstract. Exobiology is not only the study of the origin, distribution and evolution of life in the universe, but also of structures - including at the molecular level, and processes – including organic chemical transformations - related to life. In that respect, with its dense nitrogen atmosphere, which includes a noticeable fraction of methane, and the many organic compounds which are present in the gas and aerosols phases, Titan appears to be a planetary object of prime interest for exobiology in the Solar system, allowing the study of chemical organic evolution in a planetary environment over a long time scale. We describe here some aspects of this extraterrestrial organic chemistry which involves many physical and chemical couplings in the different parts of what can be called 'Titan's geofluid' (gas phase, aerosol phases and surface solid and maybe liquid phases). The three complementary approaches which can be followed to study such chemistry of exobiological interest are considered. Those are experimental simulations in the laboratory, chemical and photochemical modeling and of course observation, using both remote sensing and in situ measurements, which is an essential approach. The Cassini-Huygens mission, that offers a unique opportunity to study in detail the many aspects of Titan's organic chemistry, is discussed and the many expected exobiological returns from the different instruments of the Cassini orbiter and the Huygens probe are considered.

1. General View

With a dense N_2-CH_4 atmosphere rich in organics, and the possible presence of hydrocarbon lakes on its surface, Titan appears to be a natural laboratory in which to investigate chemical evolution toward complex organic systems in a planetary environment over a long time scale. The Cassini-Huygens mission offers a unique opportunity to study in detail extra-terrestrial organic processes in this environment, and consequently this mission has important implications for the fields of exobiology and the origin of life on Earth.

1.1. Exobiology, extra-terrestrial organic chemistry and the origin of life

Organic Chemistry is – generally speaking – the chemistry of carbon; it includes the chemistry occurring in living systems. With the development of space exploration, our knowledge of extra-terrestrial organic chemistry has been drastically

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improved. It is now clear that organic chemistry is widely distributed in the universe. In particular, it is present on many planetary bodies of the outer solar system. Exobiology can be considered as the study of the origin, evolution and distribution of life in the universe. The synthesis and evolution of organics in planetary environments is an important aspect of Exobiology. It is one of the initial steps of the chemical evolution that must have preceded the formation of living systems on Earth. It is also an important source of organics in extra-terrestrial environments, such as Jupiter, Saturn and especially Titan.

Since the pioneering work of Stanley Miller (1953) demonstrating the possible abiotic formation of biomolecules as a part of the chemical evolution of a planetary environment, our knowledge of the processes that may have led to the emergence of life on our planet has been drastically improved. It now looks very likely that life appeared on the Earth after a long period of chemical evolution that preceded the development of terrestrial biology, involving the transformation of simple but reactive organic molecules, or their oligomers, into biomacromolecules through physical-chemical processes of increasing complexity. These organics, precursors of the prebiotic syntheses, are mainly small organic compounds with multiple bonds in their structures, such as nitriles and aldehydes, especially HCN, HC_3N, C_2N_2 and HCHO. The evolution of HCN in aqueous solution, through the formation of a tetramer, can produce adenine, one of the purine bases, which, like the pyrimidine bases, are the constituents of the nucleotides, building blocks of the nucleic acids in current living systems. HCN polymerization processes can also produce complex oligomers which, after hydrolysis, release purine and pyrimidine bases and amino-acids, the building blocks of proteins. Similarly, the chemistry of HC_3N in aqueous solution can produce pyrimidine bases while the aqueous chemistry of formaldehyde can produce the biological sugars (for a review, see Raulin, 1990). In addition C_2N_2 can act as a chemical agent, allowing the condensation of the monomers to form the biopolymers.

Thus from only a small number of different organic compounds as starting materials, the 'prebiotic chemist' can produce most of the building blocks of the biomacromolecules. However, extrapolation of those laboratory data to planetary environments is not obvious and many questions still remain to be solved. First, the possible origin of these organics on the primitive Earth is still controversial. They could have formed directly in the atmosphere, if it was reducing, or have been brought by meteoritic or cometary impacts (Chyba *et al.*, 1990; Oro *et al.*, 1997), or even have been formed together with biomonomers in primitive submarine hot springs (Shock *et al.*, 1995, and refs. included).

How complex were the organics synthesized in the atmosphere of the primitive Earth? What were the relative roles of the different energy sources available in this environment, especially UV light and electric discharges? Were gas-solid chemical processes involved in the prebiotic chemistry? Were atmospheric organic syntheses efficient enough to provide the starting materials necessary for chemical evolution toward living systems? Did the dynamics of the atmosphere play a crucial role in chemical evolution? What are the respective roles of the processes in gas phase and in solution and the influence of temperature? How far can prebiotic chemistry proceed in the absence of liquid water? More generally, to what extent can the results of laboratory experiments be extrapolated to the case of real planetary environments? By offering the possibility of studying on-going organic chemistry in a natural planetary environment over a very long period of time, the Cassini-Huygens investigation of Titan could provide answers to some of these questions.

1.2. TITAN

In spite of important differences (first of all from their surface temperatures), as pointed out by Clarke and Ferris (1997), several similarities between Titan today and the early Earth can be emphasized. In particular, both have a dense atmosphere, mainly composed of molecular nitrogen, and an environment very rich in organic compounds. Indeed, several of the conditions necessary for prebiotic chemistry to evolve toward complex organic systems are present on Titan:

1.2.1. *A dense, mildly reducing atmosphere*

Titan's atmosphere is mainly composed (Hunten *et al.*, 1984; Gautier, 1997; Gautier and Raulin, 1997) of nitrogen with a noticeable mole fraction of methane and a very low mole fraction of hydrogen. Simulation experiments in the laboratory (Table 1) suggest that such an atmosphere is one of the most favorable for the synthesis of organics (Raulin *et al.*, 1982; Bossard *et al.*, 1983; Thompson *et al.*, 1991; Coll *et al.*, 1995; de Vanssay *et al.*, 1995).

1.2.2. *The presence of methane*

The existence of methane in Titan's atmosphere is a major puzzle at present. This gas is destroyed so rapidly by photochemistry that the amount we see today will be gone in just 10^7 years. Something must be replenishing this gas – a subsurface reservoir (tapped by volcanism?), or an external source (cometary impacts?). The presence of methane on Pluto and Triton poses a similar enigma (Cruishank *et al.*, 1993; Owen *et al.*, 1993). Given the probable importance of this gas for prebiological chemical evolution on Earth (Miller & Orgel, 1979; Sagan & Chyba, 1997; Kasting, 1997), understanding its origin on Titan has high priority.

1.2.3. *The presence of several sources of energy in the atmosphere*

UV light, energetic electrons from Saturn's magnetosphere and cosmic rays, in particular, allow an efficient transformation of the main atmospheric constituents into more complex compounds (Strobel, 1982; Yung *et al.*, 1984; Yung, 1987; Toublanc, 1992; Lara, 1993, Toublanc *et al.*, 1995; Gautier, 1997).

TABLE I

Organics detected in Titan's atmosphere and in simulation experiments related to Titan

PRODUCTS	TITAN	UV	High energy H, e, γ	Elec. Discharges (Arc & Silent) Room Temp.	Low	Plausible prebiotic source of:
C_2H_6	M	M	M	$<$	$<$	
C_2H_4	$\ll$	$\ll$	$\ll$	$<$	$<$	CH oligomers
C_2H_2	$<$		$<$	M	M	CH oligomers
C_3H_8	$<$	$\ll$	$\ll$	$\ll$	$\ll$	
C_3H_6			$\ll$	$<$	$<$	
CH_3C_2H	$\ll$		$<$	$<$	$<$	CH oligomers
CH_2CCH_2				$\ll$	$\ll$	
C_4H_{10} (a)				$\ll$	$\ll$	
C_4H_2	$\ll$		$<$	$\ll$	$\ll$	CH oligomers
C_6H_6				$\ll$	$\ll$	
C_6H_2, C_8H_2					$\ll$	
other hydrocarbons				many, $\ll$	many, $\ll$	
HCN	$<$		M	M	M	CHN oligomers, a. acids, purines & pyrimidines
C_2N_2	$\ll$			$\ll$	$\ll$	Condensing Agent
CH_3CN	$\ll$		$<$	$<$	$<$	
C_2H_3CN			$\ll$	$<$	$<$	
CH_2CHCN				$<$	$<$	
CHCCN	$\ll$		$<$	$<$	$<$	CHN oligomers, pyrimidines
C_3H_5CN (a)				$\ll$	$\ll$	
CH_3C_2CN				$\ll$	$\ll$	
C_4N_2	solid				$\ll$ (b)	CN (& H) oligomers?
other nitriles				many, $\ll$	many, $\ll$	
CH_3N_3				$\ll$?		
HC_4CN					$\ll$	
other N-organics				$\ll$?		

M: main products; $<$: less abundant by one order of magnitude; $\ll$: by two orders or more.
(a): all isomers.
(b): only in low temperature silent discharge experiment (Coll *et al.*, 1999).

1.2.4. *The presence of a low-temperature tropopause, coupled with the existence of atmospheric hazes*

The submicron particles of the hazes may act as condensation nuclei, allowing the condensation of organics (Sagan and Thompson, 1984) and their transport, through aerosol precipitation, down to the surface of the planet (Figure 1). Such processes can protect the organics from further destruction in the gas phase (Frère, 1989; Frère *et al.*, 1989) and could account for a noticeable loss rate of nitrogen (McKay,1996).

1.2.5. *The possible presence of liquid hydrocarbons at the surface*

The principal product of atmospheric chemistry on Titan is ethane (Strobel, 1982; Yung *et al.*, 1984; Lara *et al.*, 1997). Ethane will condense at the temperature of Titan's surface, as will propane and other photochemical products. One therefore anticipates ponds or lakes of liquid hydrocarbons at the surface, although a global ocean (Lunine *et al.*, 1983; Lunine, 1993; Dermott and Sagan, 1995; Lunine, 1997; and refs. included) can now be ruled out by Earth-based observations (Griffith *et al.*, 1991; Muhleman *et al.*, 1993) including the more recent observations using adaptive optics (Combes *et al.*, 1997), as well as HST observations (Smith *et al.*, 1996). If they exist, such lakes may play an important role in Titan's chemical evolution. By allowing partial or total dissolving of atmospheric organics, the liquid medium provides an additional way to protect the organics formed in the gas phase from destruction by the same sources of energy that produce them. In addition, high energy cosmic rays (Capone *et al.*, 1983) reaching the surface of these hypothetical lakes or seas can induce new organic processes, involving the main constituents but also the dissolved minor species (Raulin, 1987; Dubouloz *et al.*, 1989; and refs. included). In particular CO, and eventually NH_3 which could be synthesized from N_2-H_2 chemistry in the atmosphere or directly in the liquid bodies could lead to further syntheses. From this step, chemical evolution on Titan may have followed a very different path from that on the Earth (Raulin *et al.*, 1992; 1995).

1.3. Chemical couplings in Titan's geofluid

There must be strong couplings between the high atmosphere-low pressure and the lower atmosphere-higher pressure processes. Eddy diffusion should play an important role in these couplings, but the atmospheric aerosols will also contribute.

There must be similar strong couplings between the atmospheric processes occurring in the high atmosphere and the chemical evolution on Titan's surface. The organic compounds formed by UV and magnetospheric electrons in Titan's mesosphere and thermosphere, simple organics or hetero-oligomers, carried by diffusion down to the stratosphere act as condensation nuclei and induce the condensation of organic compounds of smaller molecular weight. The resulting particles precipitate down to the troposphere with dimensions increasing as altitude decreases. Their

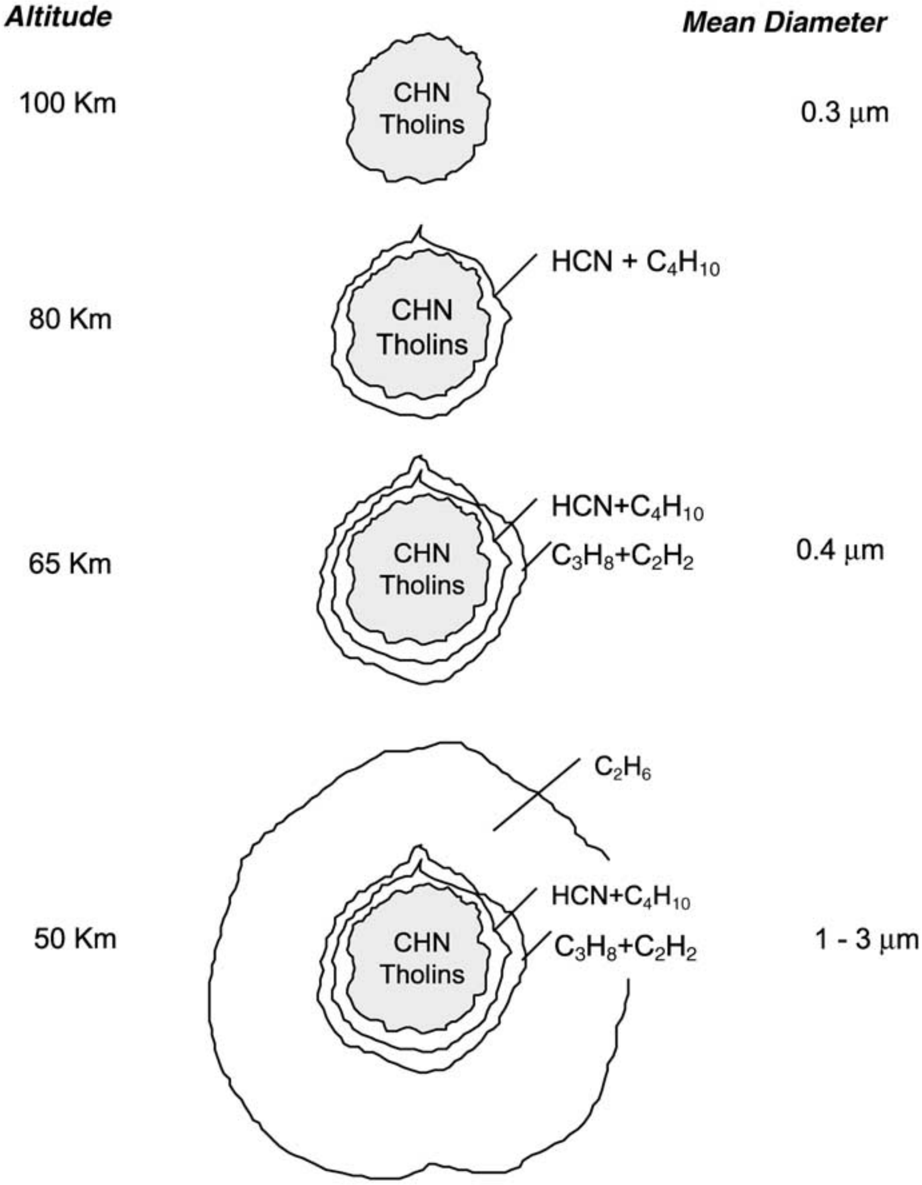

Figure 1. Modelling of the low stratosphere aerosol: evolution of the chemical composition of the particle from 100 km down to the 50 km level (the corresponding particle size increases from about 0.3 μm up to a few μm).

layered structure is formed of compounds that are more and more volatile from their cores to their outermost layers. Haze particles in the stratosphere, they become hail in the high troposphere and rain in the low troposphere (Toon *et al.*, 1988). These particles irreversibly carry most of the organics of very low vapor pressure from the high atmosphere down to the surface.

Because of such couplings, Titan's organic chemistry must be considered as a whole. The Casssini-Huygens mission will have to study globally the chemical evolution going on in the three parts of what composes Titan's prebiotic environment: the atmosphere, the aerosols and the surface. This total system could be called 'Titan's geofluid'.

Depending on the planetary environment, chemical evolution may proceed differently. On the primitive Earth in the presence of liquid water, prebiotic organic chemistry starting from simple reactive molecules allowed the emergence of life. On Titan, with very low temperature conditions, chemical evolution is still going on, but in the absence of liquid water. Studies of the prebiotic organic chemistry on this planetary body may provide information on the atmospheric processes that occurred on the primitive Earth. But such studies could also indirectly furnish important information on the role of liquid water in chemical evolution, since prebiotic chemistry on Titan has evolved in the absence of this universal solvent and source of oxygen atoms, which seems to be a requirement for the emergence of life as we know it. However, Titan's hydrocarbon seas may have evolved in the presence of noticeable traces of dissolved ammonia, playing the role of water. If this were the case, there may be a pseudo-biochemistry still going on in Titan's ocean (Raulin *et al.*, 1992), where ammonia substitutes for water, and N-chemical groups substitute for O-chemical groups, giving 'amono' analogs (Molton, 1974) (Figure 2).

Is Titan's chemistry even more complex than we expect? Are O atoms involved in the surface organic chemistry, because of dissolved CO and precipitated CO_2 (both CO and CO_2 are present in the atmosphere). Are there purine and pyrimidine bases present on Titan? Are there amino acids or their analogues? Are pseudo-polypeptides included in Titan's organic oligomers? To check such hypotheses and try to answer the many associated questions, it is necessary to study in detail Titan's prebiotic geofluid. So far several organic compounds of prebiotic interest (i.e.: the evolution of which can yield bio-organics) have been detected in Titan's atmosphere, but no bio-organics (such as amino-acids or purine or pyrimidine bases). If the Cassini-Huygens mission can demonstrate the presence of such organics on Titan, it will have strong implications for Exobiology.

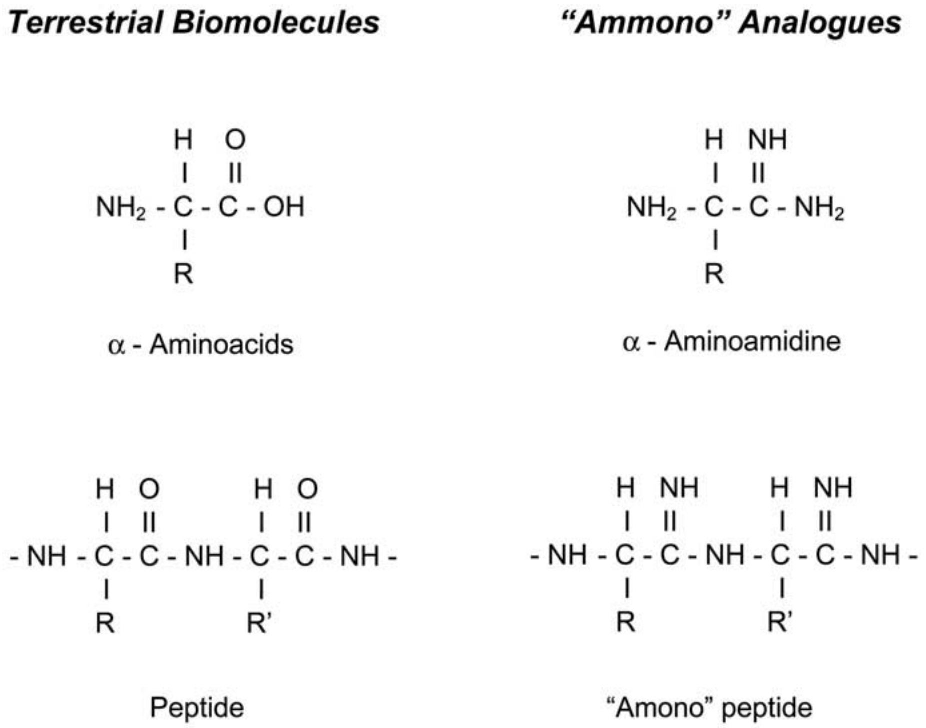

Figure 2. Some biochemical molecules and their analogues in a 'no-O-but-N-atoms' biochemistry.

2. Proposed Approaches and Expected Results

2.1. General approach

To fulfill these objectives, we propose to use simultaneously and in a correlative way the data of most of the instruments on board the probe and several on the orbiter, in particular:

On the probe:

– GC-MS: The Gas Chromatograph-Mass Spectrometer will provide vertical concentration profiles of the main atmospheric constituents and of minor species, especially already detected and new organics, involved in the general evolution of Titan's geofluid. If the probe survives the landing, the GC-MS will also give detailed information about the composition of any liquids or condensed volatiles that may be present on the surface.

– ACP/GC-MS: The Aerosol-Collector Pyrolyser coupled with the GC-MS will provide data on the chemical composition and relative abundances of the organic cores and condensed volatiles constituting the aerosols. If the probe survives the landing, this instrument can also examine the composition of liquid and solid volatile compounds that have accumulated on the surface.

– HASI: The Huygens Atmospheric Structure Instrument will provide temperature and pressure vertical profiles also essential to model the gas and aerosol phases.

– DISR: The Descent Imager Spectral Radiometer will give information on the cloud structure and surface physical state and composition, but also on the photon fluxes versus altitude, crucial data to constrain photochemical modeling of the atmosphere.

– SSP: The Surface Science Package will also provide data on the surface composition and physical state and on its main chemical composition, essential to model surface organic chemistry.

We will complement the probe results with observations from the orbiter that will continue through the duration of the mission. Through their coverage of the entire satellite, these observations will allow us to extend some of the probe results to global scales. The instruments of special interest for our purposes are:

A) VIMS: The Visual-Infrared Mapping Spectrometer will allow an examination of Titan's surface through 'windows' between strong methane absorptions. In addition to searches for hydrocarbon lakes and aerosol drifts, this instrument can look for deposits of specific chemicals such as CO_2. It will also investigate lower atmosphere meteorology and help determine if there is an evident source for atmospheric methane (rapidly being depleted) and a hydrocarbon cycle, with clouds, rain and rivers of hydrocarbons.

B) The VIMS findings on the distribution of surface liquids will be supplemented by RADAR and Imaging Science System observations. The latter (ISS) will also help with lower atmosphere meteorology.

C) CIRS: The Consolidated InfraRed Spectrometer will search for additional trace constituents, thereby improving constraints on models of atmospheric photochemistry. It will also help define the vertical and horizontal distribution of these starting materials for prebiological chemical evolution.

The data provided by these instruments will be used, together with:

– Data from laboratory experiments simulating the evolution of models of the Titan atmosphere, carried out at low temperature. Such experiments are under development at LISA, with special emphasis on the products that have low stability at room temperature, but are stable at low temperature (Aflalaye *et al.*, 1995; Coll *et al.*, 1995; de Vanssay *et al.*, 1995; Coll *et al.*, 1997; 1999). These new experiments provide a much better simulation of conditions on Titan than the previous ones, as demonstrated by the recent detection of C_4N_2 (Coll, 1997; Coll *et al.*, 1999); this compound was, before, the only trace organic observed in Titan's atmosphere but not detected in Titan simulation experiments.

– Theoretical modeling, including photochemical modeling integrating chemistry and physics of the atmosphere.

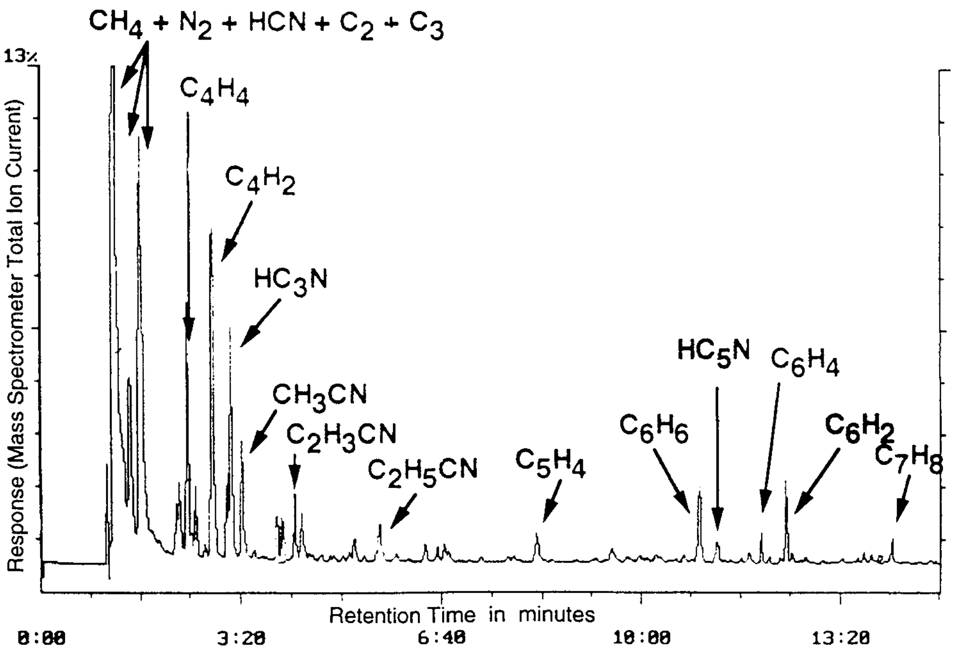

Figure 3. Total ion gas chromatogram of a sample obtained after four hours sparking of a N_2-CH_4 gas mixture (800 mbar/13 mbar, constant partial pressures) at low temperature (about 150 K). GC column; CP-Sil-5 CB, 25 m $\times$ 0.15 mm ID (1.2 mm film thickness); column temperature: isothermal 20 °C for 2 min.; 10 °C/min. up to 40 °C, isothermal at 40 °C for 6 min., 20 °C/min. up to 150 °C, isothermal 150 °C. Carrier gas: helium; inlet pressure: 30 pi; detector and peak identification: MS (ion trap).

2.2. Gas phase organic chemistry

From GC-MS data, it will be possible to obtain vertical concentration profiles of the already known atmospheric constituents, in particular CH_4, C_2H_2, C_2H_6, HCN, C_2N_2, HC_3N, CO, CO_2 and CH_3CN, but also those of many other, not yet detected organic compounds. The expected species include hydrocarbons such as butanes (C_4H_{10}), polyynes (C_6H_2, C_8H_2) and higher hydrocarbons, and nitriles such as acrylonitrile H_2C_2HCN and HC_4CN (Figure 3). Data from HASI will also be taken into account, to check the presence or absence of electric discharges in the atmosphere, which may contribute locally to additional syntheses. Data on the winds and turbulence (Doppler wind Experiment) and on the clouds (DISR) will also be taken into consideration in the model, to constrain the meteorological parameters.

Using those data, together with the T.P. vertical profiles given by HASI, and with the help of kinetic modeling software currently used at LISA (FACSIMILE numerical integrator, which 'uses fixed-step implicit backward-difference predictor-corrector formulas of orders 1 to 5' (Curtis, 1979)), we should be able to develop a detailed model of the gas phase organic chemistry occurring in Titan's atmosphere. Such modeling should allow us to verify the importance of the stratospheric photocatalytic dissociation of CH_4, and the effective coupling of UV and electrons in the primary processes of the chemistry of Titan's atmosphere. But this modeling will also have to include the data from ACP/GC-MS related to the chemical composition of the cores of the atmospheric aerosols. The accurate measurement of the relative abundances of minor species, detected or not yet detected, will also provide information on the mechanisms involved in atmospheric organic syntheses. For instance, knowledge of the ratio of branched hydrocarbon chains/linear hydrocarbon chains, and an accurate assessment of the abundances and vertical distribution of the polyynes (C_4H_2, C_6H_2,...) are important.

A particular emphasis will be given to CO and CO_2. The determination of the CO vertical concentration profile by GC-MS will provide information on the source of oxygen atoms on Titan, and, consequently, on the complexity of the satellite's organic chemistry. For instance, if it is confirmed that CO is depleted in the high stratosphere relative to the troposphere, and if it appears that this is due to the presence of a source of CO on the surface (such as dissolved oceanic CO), then we can expect that oxygen is involved in the surface organic chemistry. Such a discovery would suggest that organic chemistry is more complex than expected, and that oxygenated purines or pyrimidines bases, or even amino-acids may be present in this medium. In addition, Ar and isotopic analyses by the MS part of the GC-MS instrument will provide information on the origin and evolution of Titan's atmosphere. This will give additional indications on the possible presence of O-organics on Titan's surface, depending on the origin of atmospheric CO.

The abundance of CO_2 at the surface of Titan will provide another constraint on the oxygen chemistry. The trace of CO_2 in the atmosphere is thought to be produced from CO by the reaction:

$$CO + OH \longrightarrow CO_2 + H$$

What is the source of the OH? With the discovery of H_2O in Titan's upper atmosphere by ISO (Coustenis *et al.*, 1998), it appears that most of the OH may come in to Titan by bombardment of ice particles. However, some of it could come from the dissociation of CO with subsequent attack of CH_4 by $O(^1D)$ (Samuelson *et al.*, 1983). Widespread, thick deposits of CO_2 would imply a large initial source of CO and the potential for additional oxygen chemistry (Owen and Gautier, 1989).

2.3. Organic chemistry in Titan's aerosols

Using the data directly related to the gas phase, coupled with the temperature (T) and pressure (P) vertical profiles from HASI, it will be possible to model very accurately the condensation processes occurring in the stratosphere and troposphere.

ACP/GC-MS data will provide information on the bulk chemical composition of the stratospheric and tropospheric particles, with a discrimination between the cores of these particles and the outer layers of condensates. The chemical analysis of the cores of the particles, by pyrolysis techniques, is of major importance for the scientific objectives.

The pyrograms obtained either with Pyr-MS or Pyr-GC-MS, give essential information on the nature of the pyrolysis fragments. This can be used to infer the chemical structure of the sample and as a guide to perform calibrations (by direct comparison of the pyrograms of standard samples with those of the unknown, using identical conditions of pyrolysis, and with the help of similarity coefficients, which can allow a secure identification). This technique has already been used successfully to analyze models of Titan's aerosol oligomers (Khare *et al.*, 1981; 1984). Similar studies are developed by Raulin's team (Coll, 1997; Coll *et al.*, 1997; Coll *et al.*, 1999), using up-to-date gas chromatographic columns. Applied to Titan's aerosols, it will allow us to check if the core of the particle, assumed to be composed of oligomers formed in the high atmosphere, is constituted of only carbonaceous oligomers free of heteroatoms, or includes C+N oligomers. Such a measurement will have very important implications for our understanding of the primary processes occurring in the high atmospheric regions. It will be a way to determine the relative contributions of the photopolymerization and co-polymerization processes of CH_4, C_2H_2, C_2H_4 and HCN.

In addition, the use of an analytical pyrolysis cycle with several temperatures will allow evaporation and analysis of the volatile part of the collected aerosols without pyrolyzing either this part, or the core. With such analyses, it will be possible to detect minor atmospheric constituents undetectable in the gas phase, because they can be highly concentrated in the aerosol compared to the gas phase. It will also be possible to get information on the absolute quantity of aerosol collected in the atmosphere, and on the ratio of the core to the condensate parts. This will provide a major constraint for microphysical modeling of Titan's organic aerosol. Cloud structure data from DISR, and P,T vertical profiles, winds and turbulence data from HASI and DWE will also be used to constrain the models.

2.4. Organic Chemistry on Titan's Surface

2.4.1. *Organic Liquids*

If there are lakes, ponds, rivers, etc. on the surface, it will be possible to derive their main composition from that of the atmosphere just above the surface, knowing temperature and pressure at the interface. This will be done by coupling the data related to the gas phase composition near the surface (GC-MS) with the data from HASI (T,P), assuming chemical equilibrium between the liquids and the atmosphere, provided the probe descent occurs over one of the ponds or lakes. The assumption of thermodynamic equilibrium will be checked by looking at the wind data (HASI and DWE), and at the atmospheric near surface mole fraction of C_2H_6 (GC-MS).

If the probe survives only a few seconds after impact into a liquid, the GC-MS will quickly provide information on the composition. We expect mostly semiquantitative measurements because of the possible selective vaporization of the samples and vapor transfer in the MS. Nevertheless, we will certainly be able to identify the main constituents. SSP will provide quantitative measurement of the index of refraction of the liquid, which is directly connected by an almost linear relationship to the CH_4/C_2H_6 ratio if these are the only two main constituents (Badoz *et al.*, 1992). Comparisons of the values of primary liquid composition deduced from thermodynamical modeling of the liquid/atmosphere interface and the direct analyses from SSP and GC-MS will also allow us to check whether or not there is a quasi thermodynamic equilibrium between surface liquids and the atmosphere. The amplitude of the difference between model and observation can be correlated with the amplitude of the surface turbulence. This will provide information on the turbulence (zonal winds, temperature gradients, etc.) at the interface between ocean and atmosphere.

This set of data will also provide information on:

– The present and initial total volume of the lakes and ponds, since the current CH_4/C_2H_6 liquid ratio can be directly connected to the evolution of the liquid bodies;

– The average depth of the organic deposit at the bottom of the lakes and ponds, since that quantity is closely related to the temperature and main composition of the liquid;

By coupling the data characterizing the atmospheric aerosols to the data related to the main characteristics of the liquids, it is possible to deduce information on the minor constituents of the liquids. In particular, from an estimate of the flux of aerosols down to the surface, knowing their chemical composition, it will be possible to derive the downward flux of several of the minor atmospheric constituents to the surface. Then, knowing their solubility which can be estimated from thermodynamic calculations (Raulin, 1987; Dubouloz *et al.*, 1989 ; Thompson *et al.*, 1992), one can deduce for each of these solutes whether saturation is reached or not. In that case, their concentration should be equal to their solubility. Otherwise, if their downward flux is not high enough, their concentration is controlled by the flux. With a very fast surface sample analysis, GC-MS can also provide information on the nature and range of concentration of minor constituents. Comparison between the values given by thermodynamical calculations, and observed concentrations will give some indication about the presence of sinks or sources of minor constituents in Titan's lakes and pounds. This will also provide some clue about the occurrence of chemical reactions still going on in these liquids.

2.4.2. *Solid Surface*

Assuming the lander touches down on a solid surface, several different scenarios can be envisaged. The surface can have regions consisting of:

(a) A thick layer of fluffy material, consisting of aerosols that have 'rained out' of the atmosphere, accumulating as drifts in low-lying areas protected from near-surface winds.

(b) Exposed deposits of CO_2 ice, or terrains frosted by CO_2.

(c) Exposed H_2O ice, 'bedrock' possibly sculpted by rains and rivers of liquid hydrocarbons.

(d) Accumulations of debris impacting objects. In particular they could be dark carbon-rich icy fragments from Hyperion

(e) Combinations of the above, such as drifts of aerosols cemented by hydrocarbon rains, overlying impact debris and frosted by CO_2.

The recent HST and ground-based observations of Titan's surface (Smith *et al.*, 1996; Combes *et al.*, 1997) suggest that we may obtain some better information about these various possibilities before the Huygens probe is deployed in 2005. Observations of Titan with the Arecibo radar that will become possible in the next few years will add to this knowledge. However, all of these data will be obtained at resolutions that are far too coarse to predict exact conditions at the landing site.

If the probe survives the impact of landing, the GC-MS should be able to provide a chemical analysis of any of the candidate materials we have described. This could be one of the most important sets of data returned by the Cassini-Huygens mission. The GC-MS has a heated inlet tube that extends several mm beyond the probe's outer skin. A landing in a fluffy drift of aerosols would therefore provide access to an unusually concentrated sample of the organic compounds that the atmosphere of Titan has produced during many hundreds of millions of years. Even a successful touchdown on water ice could provide useful information. The value D/H in crustal H_2O on Titan will provide a fundamental constraint on hypotheses for the origin of Titan's methane: Was this gas formed on the satellite by impacts during accretion or was it formed in the Saturn sub-nebula and trapped in the icy grains from which Titan was subsequently made?

In addition to the GC-MS measurements SSP, DISR and Radar data may also provide some indications on the chemical nature of the landing point. And, by subsurface sounding with the Radar, Cassini may be able to detect the presence of liquids or solids below the layer of fluffy material.

If the surface is made of solid rocks, (considered highly improbable), it is likely that the main information on the surface will be given by DISR data, just before the impact. If that information is unambiguous and clearly shows the presence of such a solid surface, then we will be faced with a number of tough questions: What is the source of those rocks? Where is the expected liquid ethane? Where is the methane reservoir?

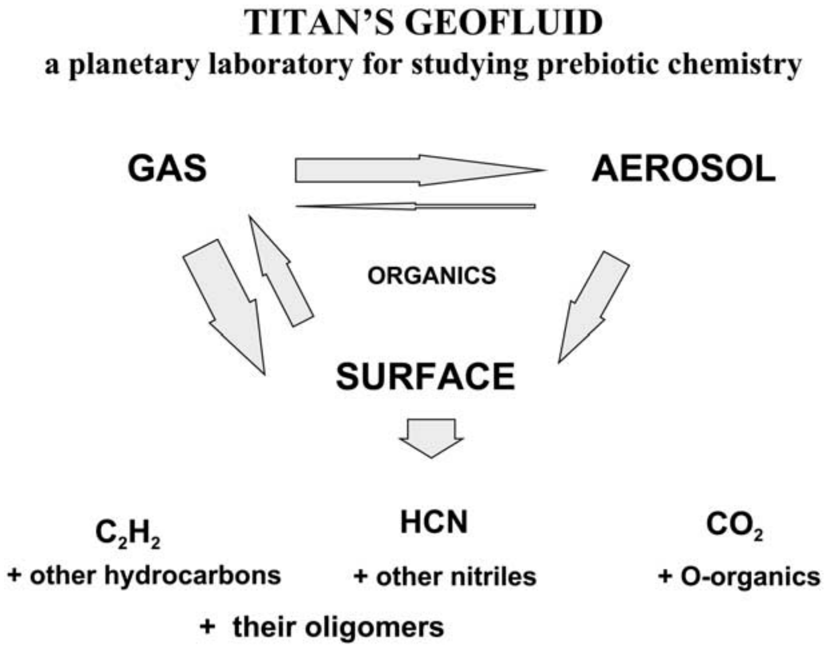

Figure 4. The strong couplings between the different parts of Titan's 'geofluid'.

3. Exobiological Conclusions

The Cassini-Huygens mission offers a unique opportunity to study the origin, nature and evolution of organic compounds as well as their distribution in the different parts of what could be called Titan's 'geofluid'. This includes the gas phase, liquid phase (seas, lakes), solid phase (sedimentary deposits) and condensed atmospheric phases (aerosols). All the instruments planned on board the probe, (and many of the instruments on the orbiter) will collect data of crucial importance for our understanding of Titan chemistry, especially organic chemistry.

By coupling these observational data with experimental (laboratory simulation) and theoretical (photochemical, microphysical and thermodynamical modeling) data, it will be possible to study and model:

– organic chemistry in Titan's atmosphere, using kinetics and thermodynamics, and with the help of laboratory simulation experiments: nature, mechanisms of formation, relative abundances, distribution and level of complexity of the organic compounds in the gas phase.

– Titan's aerosols: their formation, their chemical composition and structure, their vertical distribution, their possible chemistry, and evolution on the surface of Titan.

– Titan's lakes and ponds: their physical characteristics, chemical composition, the possible organic chemistry which can occur in this cold liquid medium under the action of high energy cosmic rays.

– the interactions between the different parts of Titan's 'geofluid' (Figure 4).

– the consequences of these results for our theories of the origin of life on the Earth, and more generally for chemical evolution throughout the universe.

These approaches will be developed in a complementary way. The Cassini-Huygens mission through its development, has already induced a large increase in the number of research programs devoted to Titan's organic chemistry. Such current studies strongly demonstrate the importance of the implications of Titan's organic chemistry in the field of exobiology and the origins of Life. They also show that many research groups want to contribute to the development of the mission, and to preparing the scientific community to use the mission data in an optimized way as soon as the Cassini-Huygens data will be available.

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