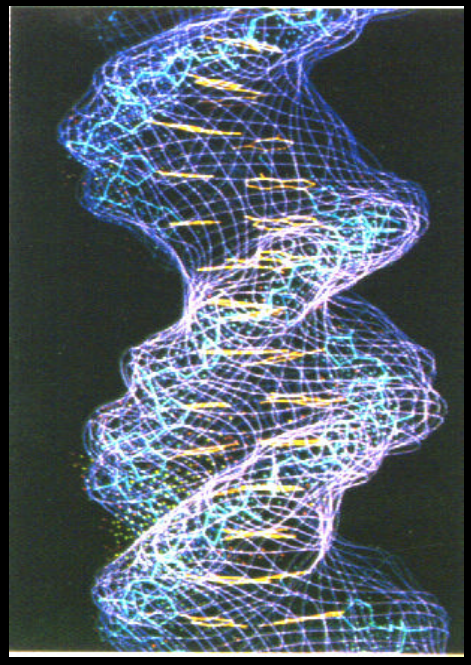

Titan’s “Bio”chemistry

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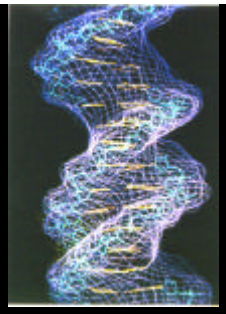


Titan: one of the most interesting bodies in the solar system for Exo/astrobiology

Exo/astrobiology: life in the universe – origins, distribution and evolution of life and of structures and processes related to life in the universe.

⇒ includes the origins of life on Earth and elsewhere
⇒ search for extraterrestrial life
⇒ search for organic compounds and organic chemistry and in particular prebiotic-like chemistry in extraterrestrial environments.

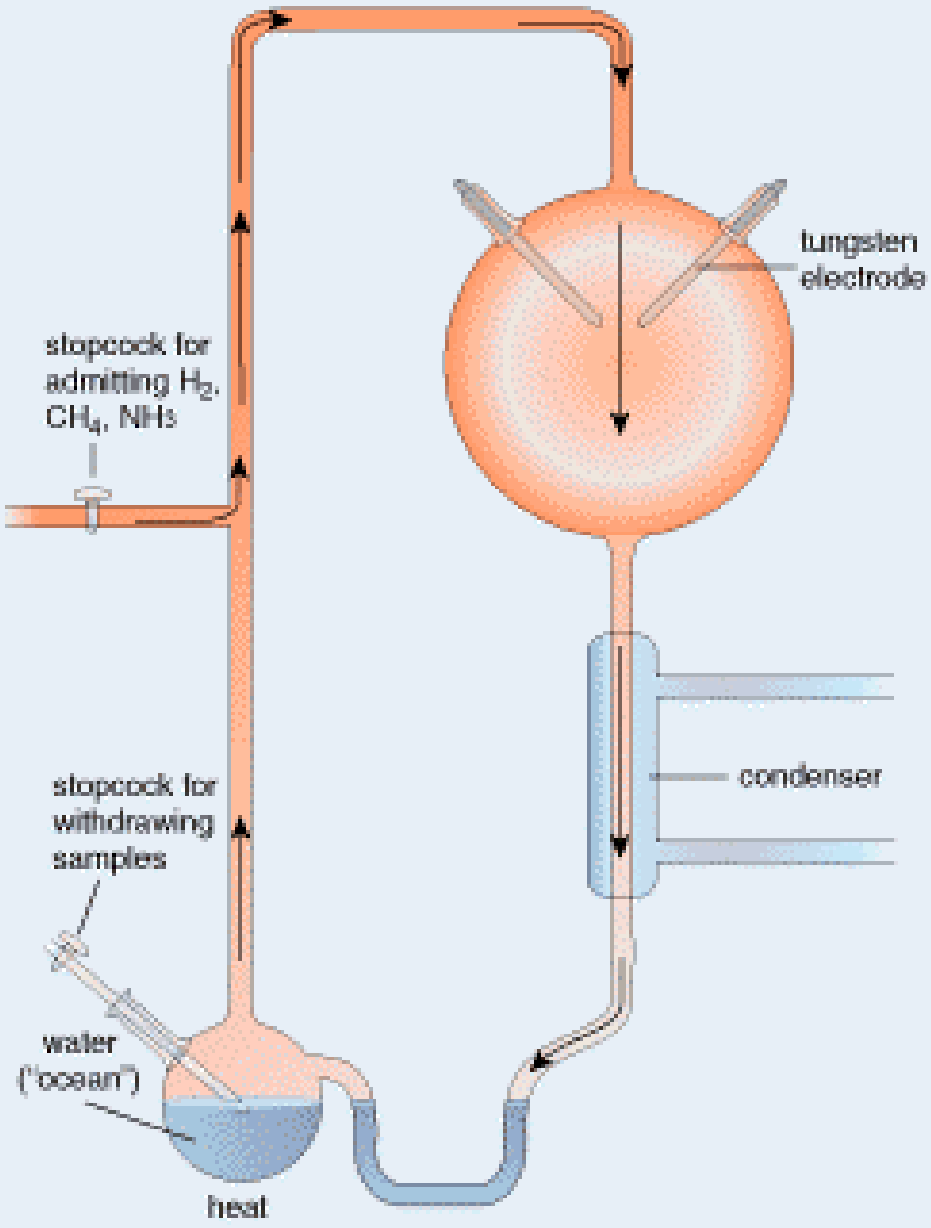
Keep in mind that terrestrial life is so far the ONLY clear case of life we have …

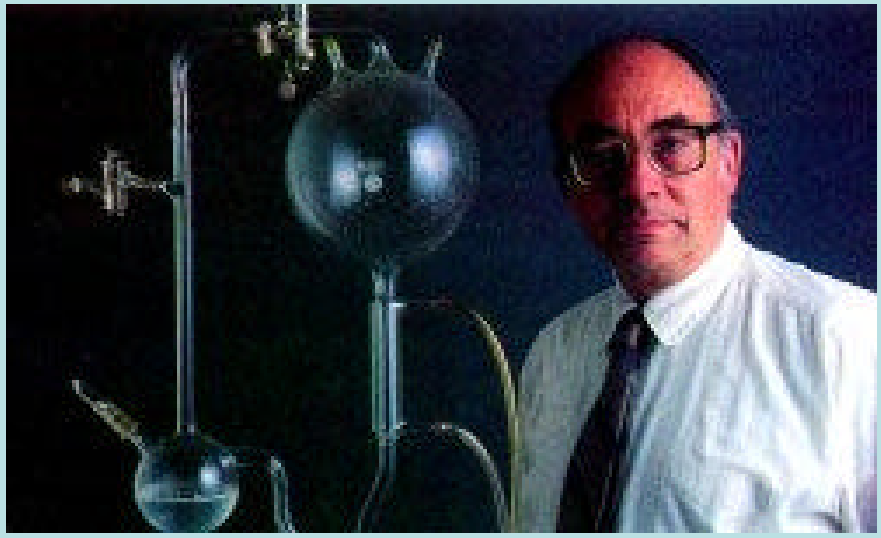
Origins of life:

Theory of Chemical Evolution (Oparin, 1924; Haldane, 1929) still the general idea

A long spontaneous (thermodynamically speaking) evolution of organics from simple molecules to complex organic matter including macromolecules capable of self-replication, preceeding biological evolution

First successful experimental test of this: the now well known and classical Stanley Miller's experiment (Science, 1953) – 50th anniversary!!


tungsten electrode
stopcock for admitting H_2, CH_4, NH_3
condenser
stopcock for withdrawing samples
water ("ocean")
heat



Historical importance of this experiment:

it induced the development of systematic researches in the field of origins of life, and in particular of prebiotic chemistry

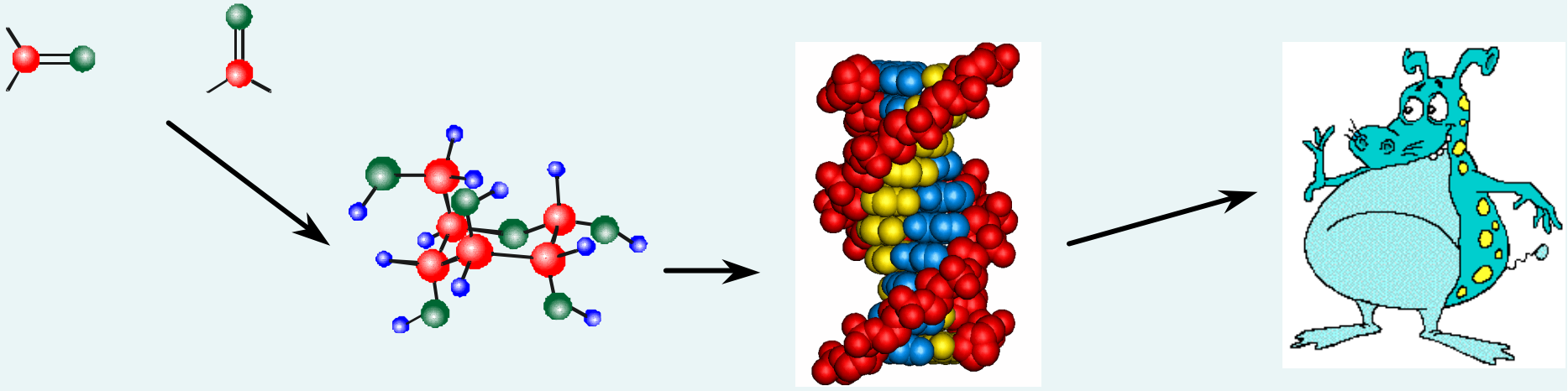
An experiment done 1000 and 1000 of times within different conditions

Best gas mixture for gas phase prebiotic synthesis : N_2-CH_4 (produces the wildest variety of organics)

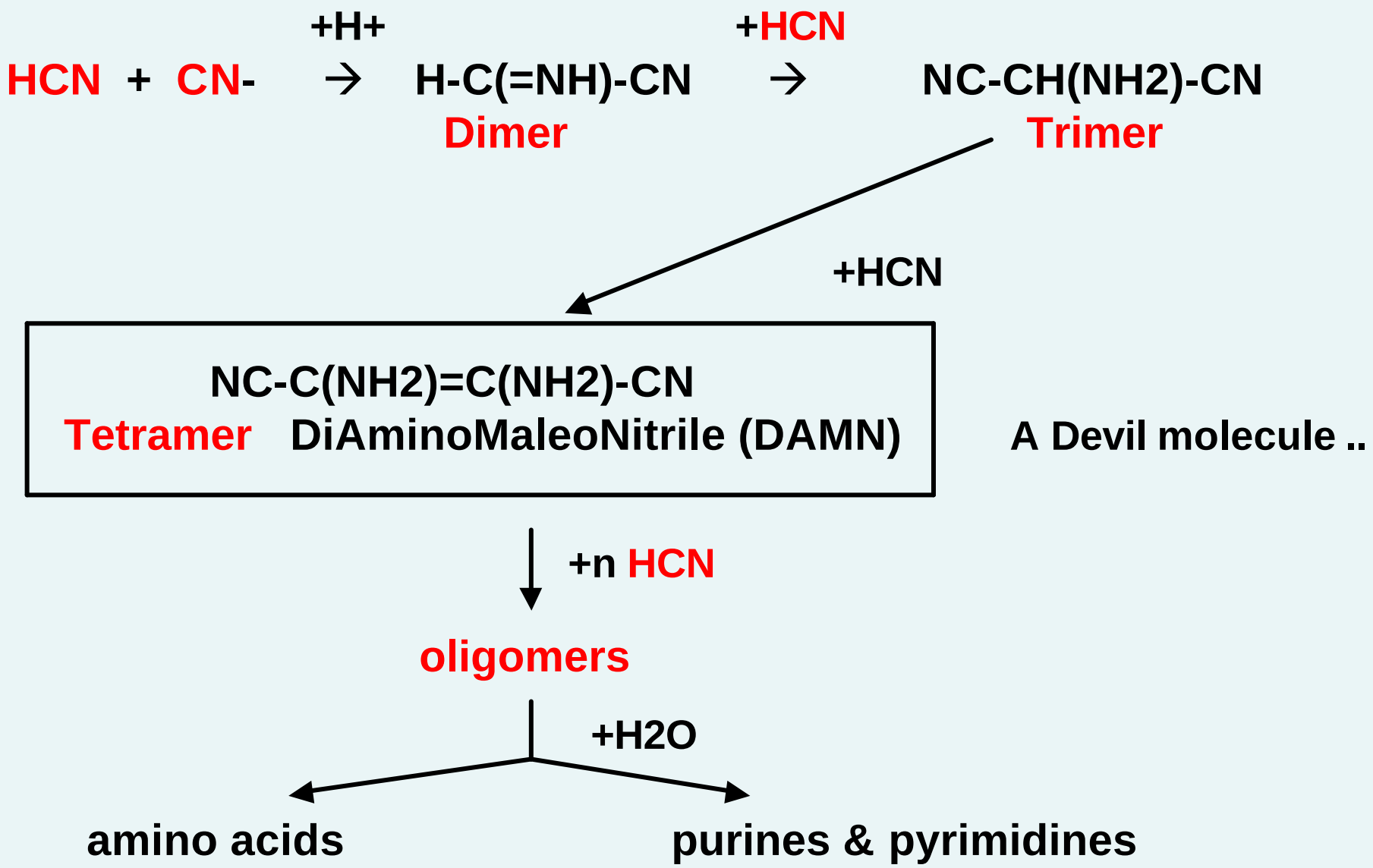
Oxidized gas mixture (CO_2-N_2-H_2O) very poor for gas phase prebiotic synthesis

Basic prebiotic chemistry

Prebiotic chemistry is organic chemistry in aqueous solution, under plausible conditions of the primitive terrestrial environment, leading to compounds of biological interest. Elementary prebiotic chemistry uses simple and reactive organic compounds, such HCN, HC3N, HCHO or their oligomers.



Prebiotic chemistry of HCN



Of course, within 50 years of research in this field, the detailed scenario of terrestrial chemical evolution – still very tentative – has drastically evolved itself!!

The primitive atmosphere of the Earth was probably not the starting point of the prebiotic processes.

The main sources of organics are currently believed to be :

- **Extraterrestrial importations (comets, meteorites – macro and micro -)**
- **Possible syntheses of organic matter from inorganic molecules in the vicinity of submarine hydrothermal vents**

However, the general idea and ingredient are still the same:

Organic matter
Liquid water
Energy

Titan

On Titan, liquid water speculative,
but organics indeed are present :
very abundant in the gas phase and probably in the aerosol phase

Prime exobiological interest :
presence of a complex organic chemistry
many analogies with the Earth (atmosphere, physical & chemical couplings, ..)

Initial steps of this chemistry relatively well understood

Starts with CH4 + N2 photon and electron impact dissociation

Key role of C2H2 and HCN :

- **Formation in the high atmosphere**
- **Diffusion to the lower levels where they allow the**
- **Formation of higher hydrocarbons and nitriles**

Additional CH4 dissociation in the low stratosphere through photocatalytic process involving C2H2 and polyynes

Titan's organic chemistry is well mimicked in the laboratory with simulation experiments:

Last experiments produce :

- **ALL organic species already detected in gas phase**
- **With right orders of magnitude of relative concentration**
- **+ many other**

⇒ validation of such experimental simulation

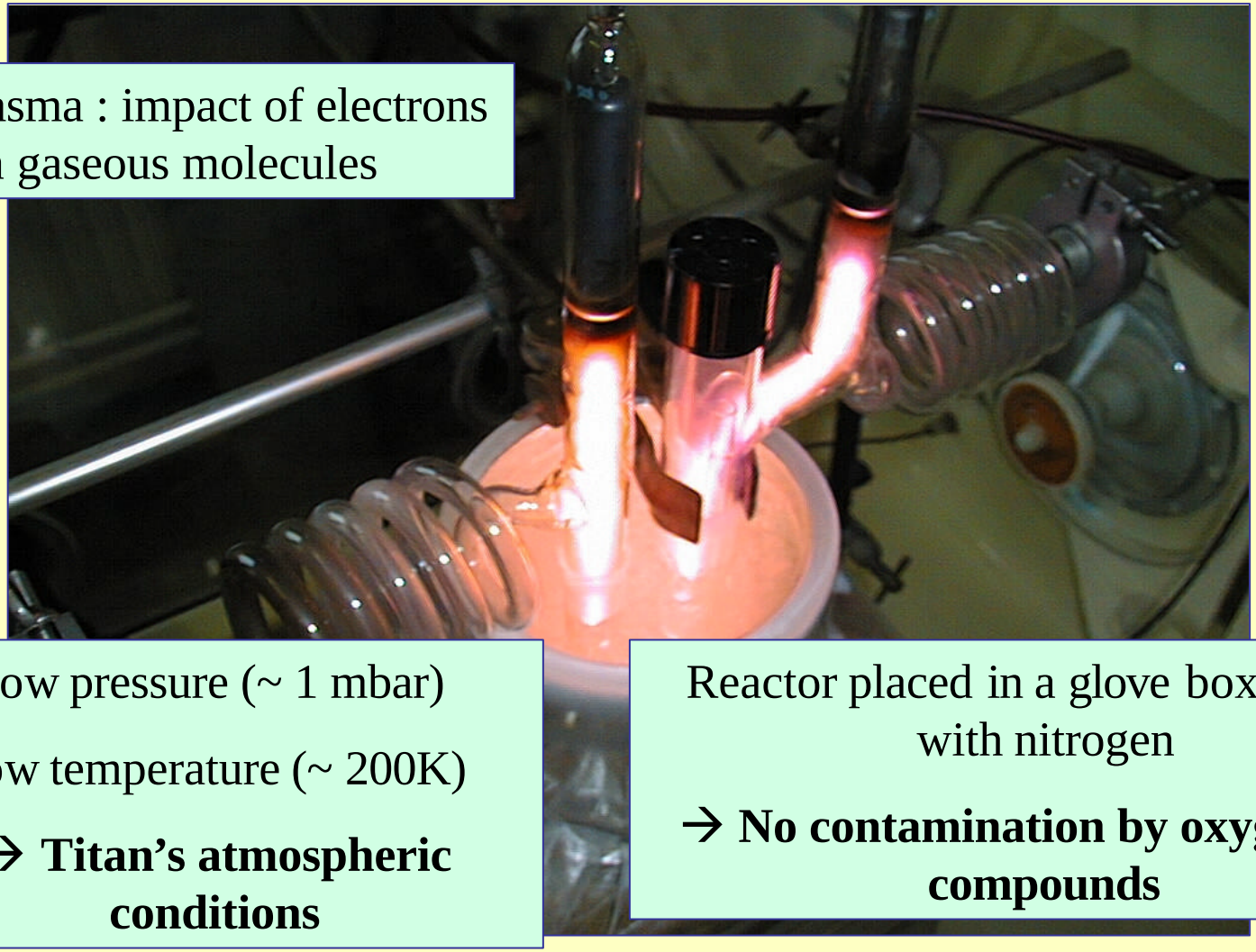
⇒ one can extrapolate these results and assume that the others are also present

⇒ very useful guide for further searches (both by remote sensing & in situ observations)

⇒ This includes the gas AND the aerosol phases

The experimental setup for global simulation at LISA

Cold plasma : impact of electrons on gaseous molecules



low pressure (~ 1 mbar)

low temperature (~ 200K)

→ **Titan's atmospheric conditions**

Reactor placed in a glove box purged with nitrogen

→ **No contamination by oxygenated compounds**

GAS PHASE

- More than 150 organic molecules detected

- Mainly hydrocarbons and nitriles (absence of amines at a noticeable level, except ammonia)

- Detection of all gaseous organic species observed on Titan

- Including the first detection of C4N2, unstable at room temperature (Coll et al. 1999)

- Detection of polyynes (C4H2, C6H2, C8H2) and probably cyanopolyyne HC4-CN

- And formation of organic compounds with asymmetric carbon

  hydrocarbons : CH3 – C*H (C2H5) – CH=CH2

  nitriles : CH3 – C*H (CN) - CH=CH2

Recent experiments on N2-CH4 mixtures including CO at the 100 ppm level (Bernard et al, PSS 51, 1003, 2003; Coll et al, ApJ 598, 700, 2003) :

GC-MS + FTIR analysis:

200 compounds identified

Detection of NH3

The main O-organic product is not methanol,
nor formaldehyde
but oxirane
(ethylene oxide)

-oxirane a good candidate to search for in Titan's atmosphere

SOLID PHASE

Supposed to be laboratory analogues of Titan's aerosols

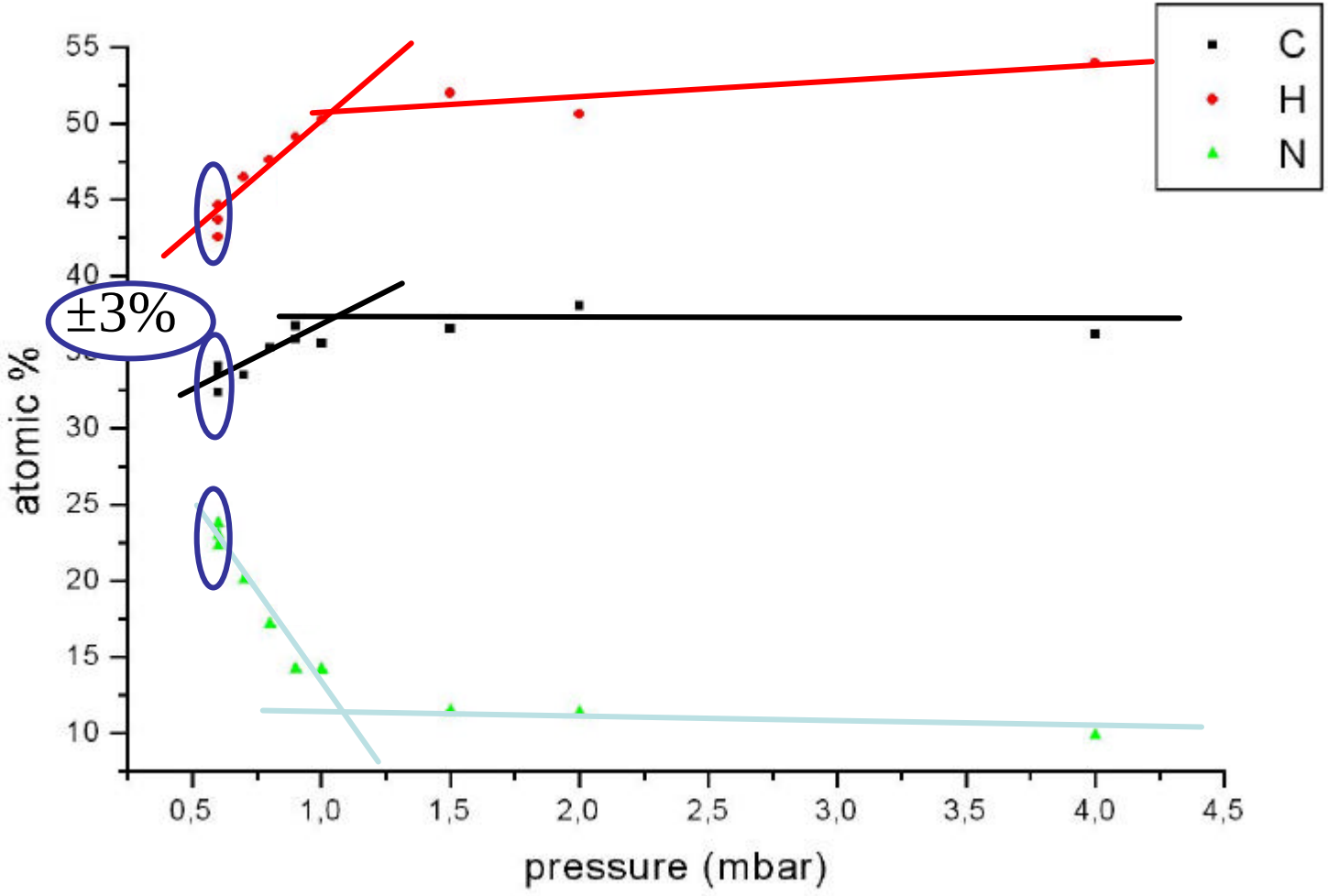
Generic name (introduced by Carl Sagan in the late 70ties)
Tholins.

Titan's tholins largely studied since the first studies by Carl Sagan & Bishun Khare 25 years ago.

More sophisticated experimental protocols allowing a simulation closer to the real conditions:
glove box
low Pressure
low temperature

Very different properties depending on the conditions :
C/N from <1 to > 10 !!

parameter	C	H	N
pressure ↗	↗	↗	↘

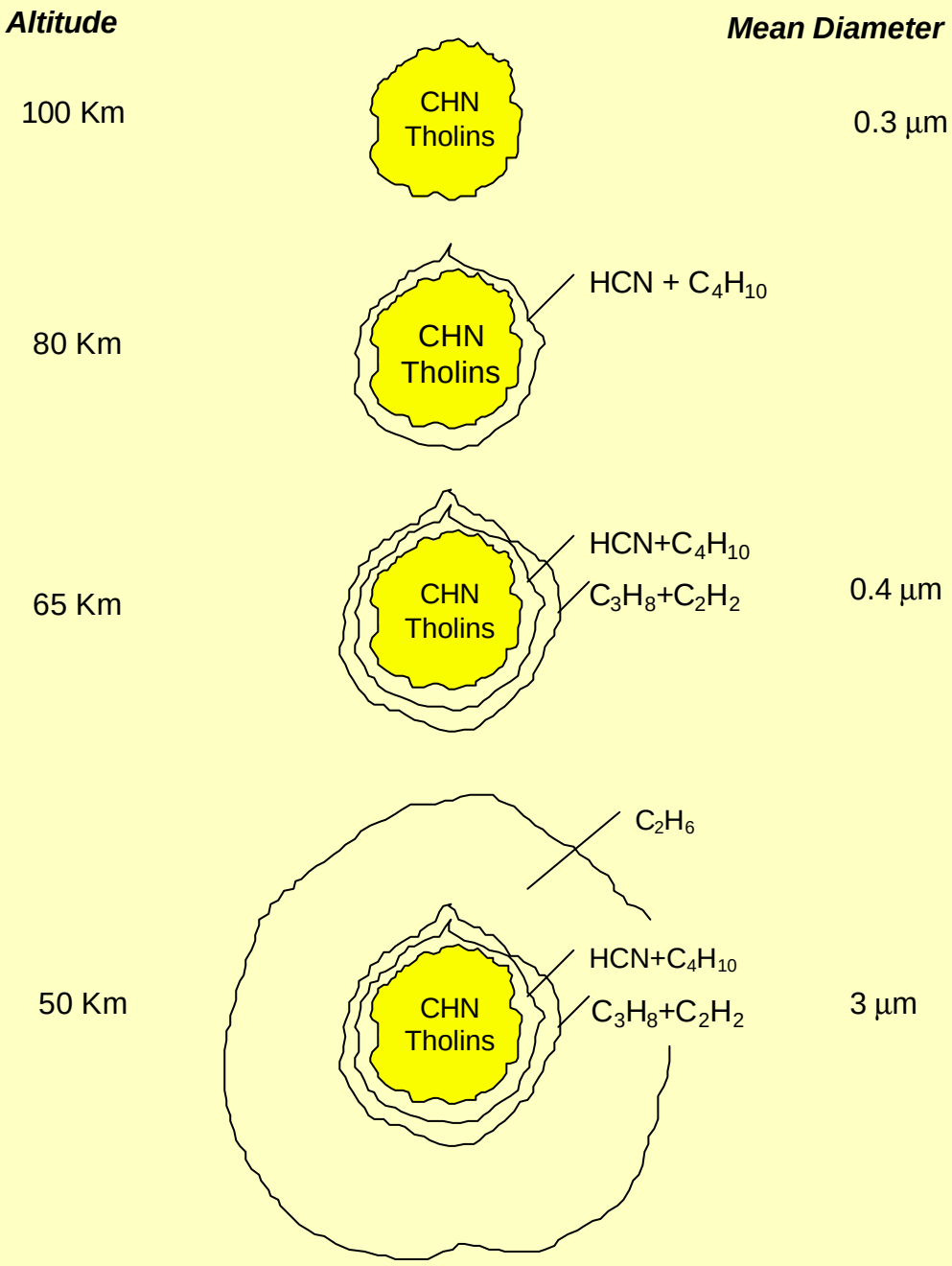


Molecular composition : still very badly known

- HCN polymers or oligomers,
- HCN-C2H2 co-oligomers
- HC3N polymers,
- HC3N-HCN co-oligomers
- Macromolecule of largely irregular structure

What is known

- Optical properties: refractive indices
- C/H, C/N
- IR and UV spectra + pyrolysis-GC-MS: aliphatic & benzenic hydrocarbon groups, CN, NH2 & C=NH groups,
- Direct analysis by chemical derivatization techniques before and after hydrolysis: amino-acid or their precursors
- Gel filtration chromatography of the water soluble fraction : molecular mass ~ 500 to 1000 Dalton ((McDonald et al., 1994)
- And even : nutritious properties (for terrestrial bacteries …) (Khare/Sagan tholins, Stocker et al., 1990)


Altitude
Mean Diameter
100 Km
CHN Tholins
0.3 μm
80 Km
CHN Tholins
HCN + C4H10
65 Km
CHN Tholins
HCN+C4H10
C3H8+C2H2
0.4 μm
50 Km
C2H6
CHN Tholins
HCN+C4H10
C3H8+C2H2
3 μm

Organic chemistry may be even, more complex on Titan

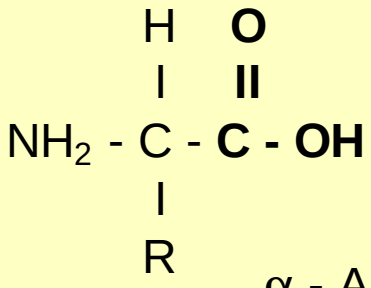
Liquid bodies very likely but of hydrocarbons
=> Low solubility of tholins and most organics of prebiotic interest
=> However chemistry induced by cosmic rays + interface solid/liquid

Possible presence of an internal water-ammonia ocean
⇒ Efficient to convert simple organics into complex molecules,
⇒ Reprocessing chondritic organic matter into prebiotic compounds
⇒CHNO prebiotic chemistry evolving to compounds of terrestrial biological interest

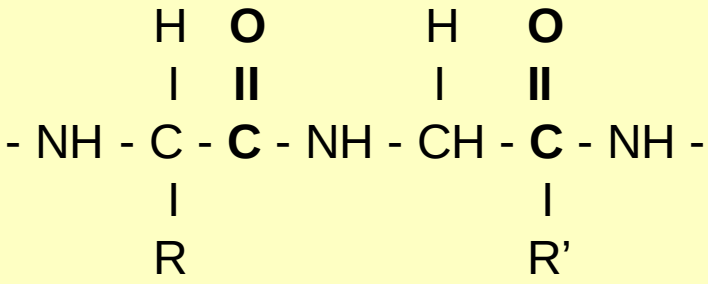
Possible occurrence of some of these processes at the surface, in the episodic liquid water formed by melting of water ice by impactors

Even if this “O”model is wrong, the possibility of a pseudo biochemistry, evolving in absence of a noticeable amount of O atoms cannot be ruled out:
=> with N chemistry replacing O-chemistry

Terrestrial Biomolecules

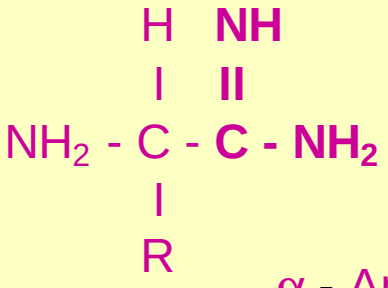


α - Aminoacids

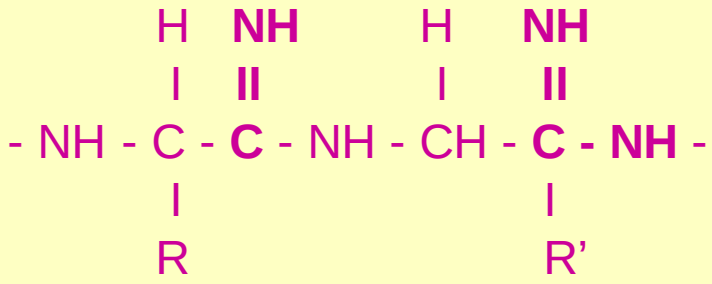


Peptide

"Ammono" Analogues



α - Aminoamidine



"Amono" peptide

Thus several ways can be envisaged to drive chemistry to prebiotic chemistry and even to biotic systems on Titan
But if life emerged on Titan, are Titan's conditions compatible with the sustaining of life ?

Life on Titan ?

Surface too cold and not energetic enough to provide the right conditions.
However, the (hypothetical) subsurface ocean, may be suitable to life.

Fortes (Icarus, 2000) shows that there are no insurmountable obstacle:

=> with a possible temperature of this ocean as high as about 260 K and the occurrence of cryovolvanic hotspots allowing 300 K

=> pressure : even at depth of 200 km, the expected pressure of about 5 kbar is not incompatible with life

=> pH : 15 % wt NH_3 is equivalent to a pH of 11.5. Some bacteria can grow on Earth at pH 12

=> energy : (mainly radiogenic heat flow ~ 5×10^{11} W) : if 1% of that is used for volcanic activity and if 10% of the later is available for living systems metabolism : this gives about 5×10^{8} W

5 x 10^8 W corresponds to the production of about 4 10^{11} mol of ATP per year and about 2 10^{13} g of biomass per year
If we assume a turn over of the order of a year : the biomass density would be 1g /m2 : 1000 times lower than Earth, but not negligeable

Which life ?

Methanogenic microorganisms ? source of CH4 in the atmosphere ? Or even of the atmospheric N2 ?

Cannot be (so far) ruled out :

But several other sources for CH4 are possible, including cometary impact chemistry !!

The origin of CH4 is a key question

It shows the whole complexity of the Titan system.

Methane Cycle

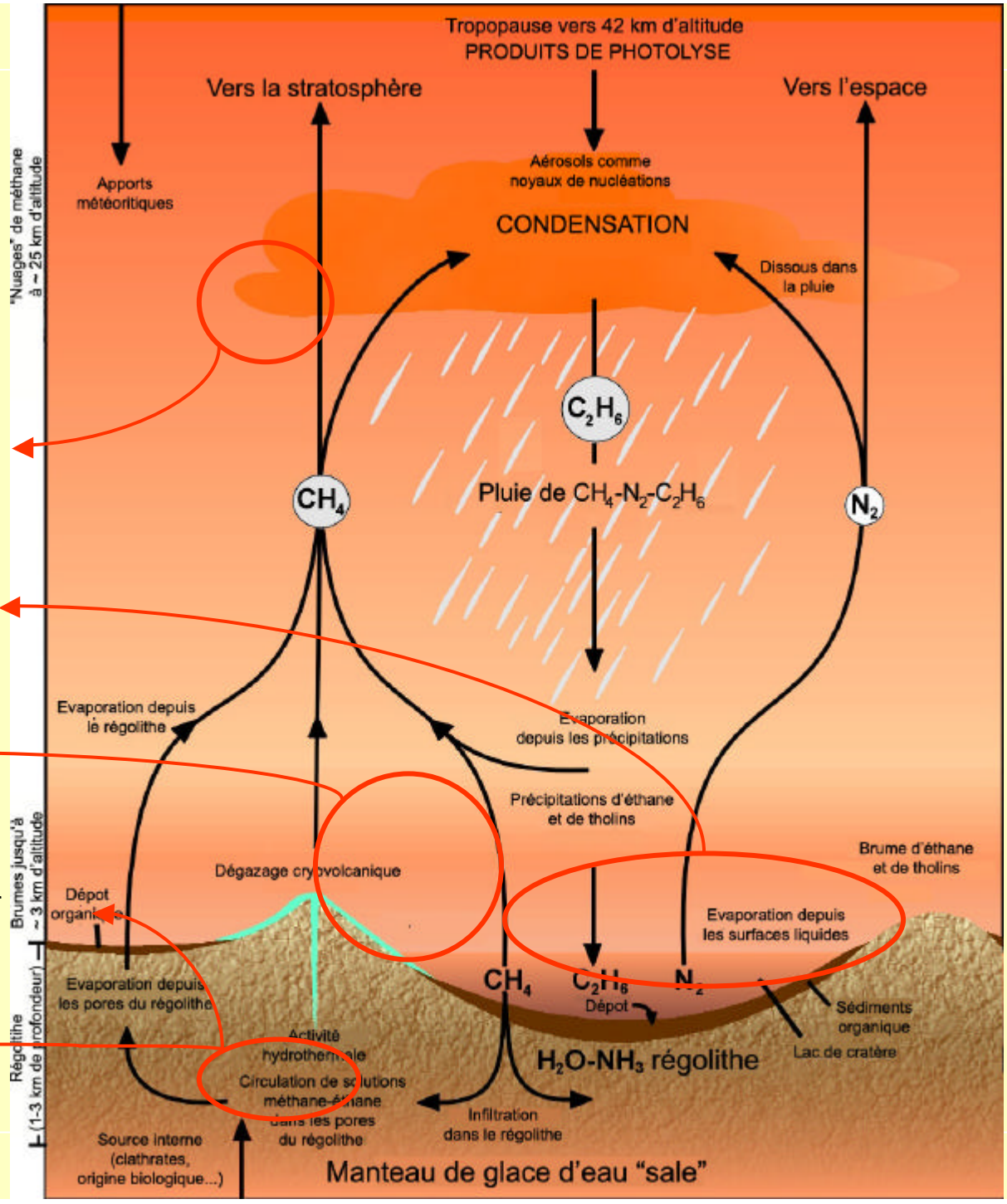
? **Meteoritic input**

? **Seas or lakes of liquid methane-ethane**

? **Cryovolcanism**

? **Methane hydrates from internal structure**

? **Biomethanogenesis**



Several of these questions could get answers from Cassini-Huygens Will bring many data of great importance for Exo/astrobiology:

⇒ **Discovery of additional atmospheric molecules, including many other organics (GC-MS, CIRS, …)**

⇒ **Determination of their vertical profils essential to constrain the (photo)chemical models (GC-MS, CIRS, …)**

⇒ **First determination of the chemical composition of Titan's aerosols (ACP+GC-MS)**

⇒ **Determination of the surface states and composition : chemical nature and complexity of the surface**

⇒ **Confirmation of the presence of the liquid bodies and determination of their composition**

⇒ **Quantification of the energy sources**

⇒ **Possible detection of tropospheric lighning**

⇒ **Possible detection of cryovolcanism**

⇒ **Information on the methane sources**

⇒ **Information on the origins of the atmosphere**

⇒ **Determination of 13C/12C ➔ if of biological origin must be much lower than solar value**

⇒ **Same with 15N/14N**

⇒ **And many other answers**

⇒ **+ many unexpected questions**

But several questions will still remain unsolved :

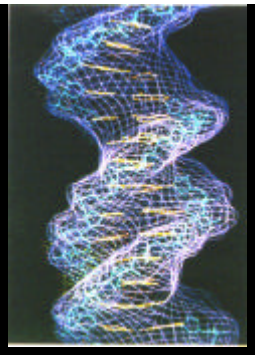
Chirality in the gas and solid phase atmospheric chemistry ?

Complexity in the surface organic chemistry

Complexity in the subsurface organic chemistry

Requesting some post Cassini-Huygens in situ exploration of Titan

Conclusions



Titan: a prebiotic-like chemistry

- **But in the quasi-absence of liquid water**
- **Emergence of life although not very likely (temperature) cannot be ruled out**
- **But the level of chemical complexity which can be reached in such an environment still fully unknown**
- **Cassini-Huygens should be able to tell us much more**
- **In particular on the complexity of this chemistry**
- **And on the origin of its main source : methane**