# Nitrogen gas-phase prebiotic chemistry in planetary atmospheres: the lesson of Titan

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**Abstract.** We explore the rich organic chemistry of Titan, in particular chemical pathways leading to nitrogen containing organic molecules such as nitriles and imines, both known to be molecules of high prebiotic potential. Such chemistry is driven by solar UV photons and it is conceivable that similar processes occurring in the upper atmosphere of Earth have given rise to chemistry that preceded life.

**Key words.** Astrobiology – Planets and satellites: atmospheres – Molecular processes

## 1. Introduction

The question of the emergence of life out of nonliving matter is a central one in science. In particular, from a chemical point of view, the key feature of living organisms are large organic macromolecules, whose origin from simple species abundant in the cosmos needs to be accounted for in any meaningful theory on life's origin. Unfortunately, the geological record of our planet holds little information on the chemical processes leading to life. The establishment of the existence of liquid water reservoirs, as well as the discovery of possible chemofossils, can approximately pinpoint the time range for the abiotic origin of life to ca. 4 billion years ago (Bella et al. 2015). This means that the formation of prebiotic molecules, organic molecules of considerable molecular mass that can play the role of building blocks of life, was relatively fast after the formation of Earth. This posits a challenging problem, because the existence of large amounts of liquid water would appear to pre-

clude the formation of organic molecules of any significant length. Such molecules must nevertheless have been formed in an abiotic environment from much simpler precursors (as shown, for example, in the Urey-Miller experiment). Even though the first guess would be that they were synthesized on Earth (the *endogenous* theory), in recent years extraterrestrial environments have been theorized as possible origins of prebiotic molecules (the *exogenous* theory) (Chyba & Sagan, 1992). Studying Earth-like objects can shed light on possible mechanisms of such synthesis. In this respect, it is of particular interest the case of Titan, because of its active atmospheric chemistry capable of generating really complex organic molecules, with a mass up to 8000 Da, in the upper layers (Vuitton et al. 2019). Titan is a massive moon of Saturn and is a particularly interesting case where the study of an extraterrestrial object can furnish information on the chemical evolution of early Earth. The detection of methane ($CH_4$) in its upper atmosphere has triggered hypotheses of the formation of

higher hydrocarbons there. Moreover, since the first detection by Voyager of trace amounts of nitriles, the interest for this moon has increased, as nitriles are considered important precursors of biologically relevant molecules. The extremely low temperatures of Titan preclude the existence of water in the liquid state (and therefore the evolution of life as is known to us). However, it is precisely for this reason that Titan offers us the unique possibility of studying chemical evolution at an early stage, whithout the contribution given by hydrolysys of nitriles. There are several compelling pieces of evidence for such evolution, such as the presence of high molecular mass species in the upper part of the atmosphe and the composition of the haze aerosols, that is, nitrogen-rich organic macromolecules according to the Huygens aerosol analyser (Israel et al., 2005). Therefore, it follows that the study of the photochemical evolution of Titan can at least confirm the possibility of prebiotic molecule synthesis starting from materials as simple as $CH_4$ and $N_2$ and a sufficient amount of energy.

## 2. Photochemical models and the quest of accurate laboratory data

In general, we can say that planetary atmospheres can be regarded as large-scale photoreactors, where the energy transferred through UV radiation, cosmic rays and solar winds can trigger chemical reactions by dissociating the stable molecules therein contained. In particular, laboratory simulations of the atmosphere of Titan have demonstrated clearly the formation of nitriles and N-containing organic macromolecules, as well as a yellow-brown solid residue for which the term *tholin* was coined (Sagan et al., 1992). It is conceivable that the orange haze of Titan is formed by similar macromolecules. However, the analogy between a planetary atmosphere and a laboratory should not be taken too far. For example, temperature and pressure gradients are difficult to simulate in a laboratory. Conversely, effects such as wall collisions are absent from the chemistry of atmospheres. In order to fully describe the chemistry of planetary atmospheres, the collaboration of many disciplines is re-

quired. Photochemical models must be constructed that take into account both physical and chemical processes, and these latter ones need to be characterized in laboratory experiments. In a photochemical model, the evolution of the concentration of each species with time is modelled taking into account all possible processes (both physical and chemical) serving as sources or sinks for it. In order for the model to be reliable, several parameters need to be determined experimentally. After the Cassini-Huygens mission, it was understood that ion chemistry and neutral chemistry in Titan's atmosphere are strongly coupled (see Vuitton et al. 2019, and references therein). Moreover, the discovery of molecules such as benzene and imines in the ionosphere has displaced the presumed chemical factory towards the thermosphere. Unfortunately, much information is still lacking in this respect as many reactions have not been characterized in laboratory experiments and their presumed contribution in the models is, at best, tentative. In order to be a good candidate for inclusion in a photochemical model a reaction needs to be both thermodynamically feasible and kinetically fast. It is obvious that the faster reactions will be the most important ones in chemical models. Exothermicity can be a fallacious guide, as there are cases where the most exothermic channel is not the dominant one from a kinetic point of view. In addition, the branching ratios of all products of a reaction need to be known with a high precision as these products will subsequently participate in further reactions. This is particularly true where relatively complex molecules are concerned since typically there are many product channels involved. Given the need for experimental characterization of chemical reactions under the appropriate conditions (for instance, the T of the upper atmosphere does not exceed 180 K), several techniques have been developed to this purpose. One of these is the CRESU technique (acronym from the French *Cinetique de Reaction en Ecoulement Supersonique Uniforme*), which permits measuring bimolecular rate constants at temperatures as low as 10-15 K. Its main disadvantage is its lack of product specificity, as it only

measures the decay rate of the reactants. An complementary method is the crossed molecular beam (CMB) method, whereby two molecular beams collide in a vacuum and the products fly towards the detector without undergoing any subsequent collisions. In this way, what is observed is the outcome of many identical collisions. Mass spectrometric (MS) detection permits identification of the products. Therefore, the CMB-MS technique has the advantage of determining, in principle, all product channels with their respective branching ratios, as well as the partitioning of energy. In many cases, the experimental study of chemical reactions is very difficult or even impossible, for example when the reactants are two unstable species. In such cases, theoretical calculations are the only way of establishing the kinetic behaviour of chemical reactions. In order to calculate rate constants for a chemical reaction system, the potential energy surface (PES) of the system needs to be constructed either by resolving the Schrödinger equation for various nuclear configurations or through the use of density functional theory (DFT). Such calculations permit to identify the various *intermediates* and *transition states* along the reaction path of interest, as stationary points of the potential energy. Once the PES has been determined, the energies and dynamical and geometrical characteristics of each species (vibrational frequencies and rotational constants) are calculated and rate constants are calculated for each elementary reaction through the Rice-Ramsperger-Kassel-Marcus (RRKM) scheme in the *microcanonical ensemble* (i.e. at a constant total energy). The assumptions implicit in this scheme are 1) each transition state (TS) satisfies the "no recrossing" assumption, i.e. reactants crossing a TS will certainly end up as products and 2) in each species, the available energy is completely randomized among the available degrees of freedom, with no dynamical preferences. Within the RRKM scheme, the microcanonical rate constant of an elementary chemical step is given by the formula $k(E) = \frac{N(E)}{h\rho(E)}$ where $N(E)$ stands for the number of available microstates in the transition state, $h$ is Planck's constant and $\rho(E)$ stands for the density of states of the reactants.

In an ordinary laboratory chemical environment, the *canonical ensemble* is used (at a constant temperature), as the frequency of collisions with external particles ensures an efficient energy exchange. However, in modelling astrochemical reaction, the microcanonical approach is justified by the fact that the reactions of interest occur in an almost collision-free environment, where no energy is exchanged with the surroundings. After the rate constants pertaining to the whole of the reaction system have been determined, the overall rate constants for the formation of each possible product are calculated through the resolution of an appropriate master equation. At the end, once rate constants for each product are available for a sufficiently wide range of energies, such rate constants are Boltzmann averaged to yield rate coefficients as functions of temperature.

## 3. The reactions of N($^2$D) with aliphatic and aromatic hydrocarbons

The presence of N-rich organic molecules in the upper atmosphere of Titan suggests that the $N_2$ molecule can be activated. Active forms of $N_2$ include its ions (both monatomic and biatomic), the electronically excited states of $N_2$ and atomic N. Various processes (such as solar UV radiation or cosmic rays) can form N in both its ground $^4S_{3/2}$ state and its excited $^2D_{3/2,5/2}$ ones (Vuitton et al. 2019). Whereas the former is little reactive, the latter will react in the atmosphere of Titan with other species given its metastability with respect to relaxation. In particular, it can react with hydrocarbons such as $CH_4$, $C_2H_6$, $C_2H_4$ and $C_2H_2$, furnishing the first step towards the formation of N-containing organic molecules. Very little was known on the kinetics of these reactions at low temperatures until recently, when a series of CRESU measurements were performed (Hickson et al. 2020; Nunez-Reyes et al. 2019a,b). Thus, for the reaction with $CH_4$ no significant differences were found with the rate constants already used in the models. On the other hand, the reactions with $C_2H_6$ and $C_3H_8$ were found to be significantly slower at low temperatures than had been hitherto as-

sumed. The situation is different with respect to the reactions with $C_2H_2$ and $C_2H_4$. Both of them were found to be substantially faster than their previously used values suggest. This has had a profound effect on models, whereby the reactions with ethylene and acetylene are now the main paths of $N(^2D)$ consumption rather than methane, despite the latter's higher abundance. In all these cases, no product channels are determined as it is only the decay rate of reactants that is measured.

In our laboratory, we have systematically investigated a series of chemical reactions involving $N(^2D)$ by means of the CMB-MS method, coupled with electronic structure and RRKM calculations (crucial in extending the results to lower temperatures). In a first series of experiments, we verified that the reaction with $CH_4$ leads to $CH_2NH$ as the main product, contrarily to what believed before (the main products were assumed to be $CH_3+NH$; Balucani et al. 2009). The reaction with $C_2H_6$ was found to produce mainly $CH_2NH$ and $CH_3CHNH$ rather than $NH + C_2H_5$, as previously assumed (Balucani et al. 2010). The reaction with $C_2H_2$ was, instead, confirmed to produce mainly HCCN, thus accounting for its formation in the conditions of Titan (Balucani et al. 2000). The reaction with $C_2H_4$ produced mainly $CH_2NCH$ and $CH_2(N)CH$ and these latter results have precluded this reaction from being a possible precursor of acetonitrile (Balucani et al. 2012). More recently, we have extended the same combined experimental and theoretical approach to the investigation of the $N(^2D)$ reactions with aromatic species (benzene, toluene and pyridine, which have been detected or supposed to be present in the upper atmosphere of Titan) and other highly unsaturated hydrocarbons (propyne, allene, cyanoacetylene). These last studies have been conducted within the frame of the Italian National Project of Astrobiology (Onofri et al., 2020). Remarkably, the reaction with benzene has been found to destroy the 6-atom aromatic ring, which is, instead, preserved in the case of toluene (Balucani et al., 2018, Rosi et al., 2020 and in preparation). The reaction with pyridine also bring to a ring contraction (Recio, PhD thesis, 2021). In all cases, however, a nitrogen atom is included in the final products which exhibit some complexity. The reactions with allene and propyne indicated a significant difference in the chemical behaviour of the two isomers, thus underlying the necessity to treat them separately in photochemical models. Finally, the reaction between $N(^2D)$ and the widely observed cyanoacetylene species clearly indicate that additional nitrogen atoms can be included in the final products when the co-reactant in an unsaturated nitrile. In conclusion, in all reactions investigated, the reactive processes lead to an enrichment of the nitrogen content in the final products. Given the special nature of nitriles and other N-containing species like imines in prebiotic chemistry, the present results confirm that if chemistry such as the one we observe in the atmosphere of Titan nowadays was active in the primitive terrestrial atmosphere, the subsequent contact with water of the formed products and their hydrolysis could have brought to a plethora of complex organic molecules, the further evolution of which could lead to the building blocks of life.

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