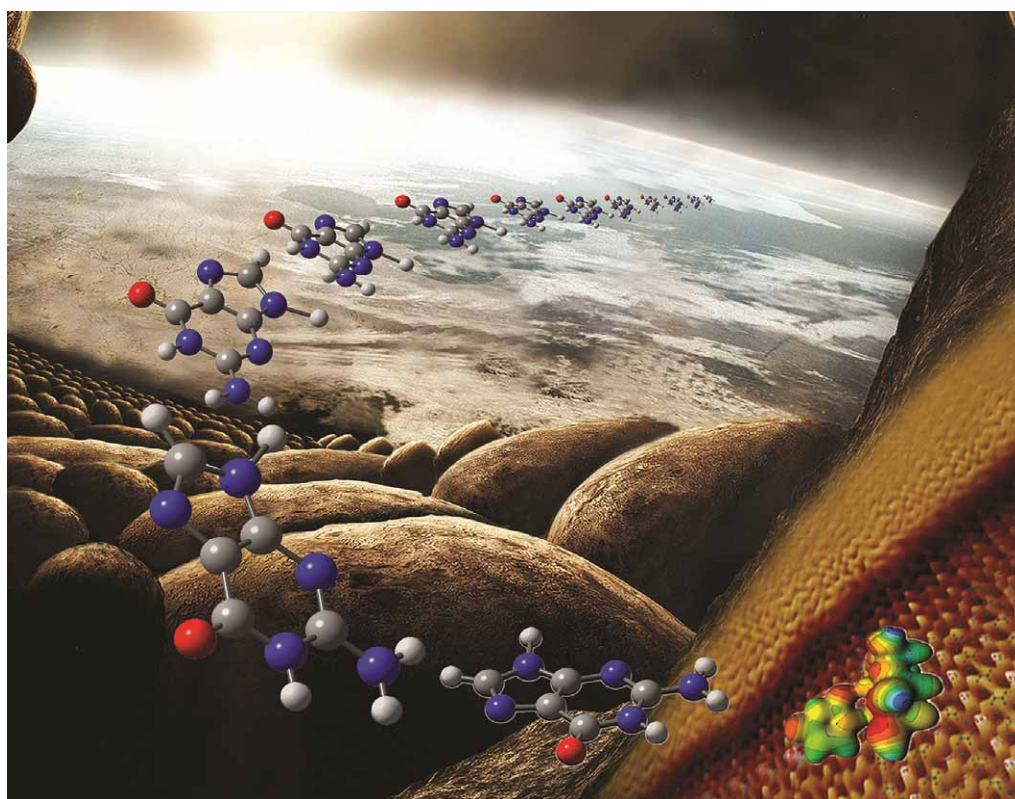


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## TUTORIAL REVIEW

# Elementary reactions of N atoms with hydrocarbons: first steps towards the formation of prebiotic N-containing molecules in planetary atmospheres†

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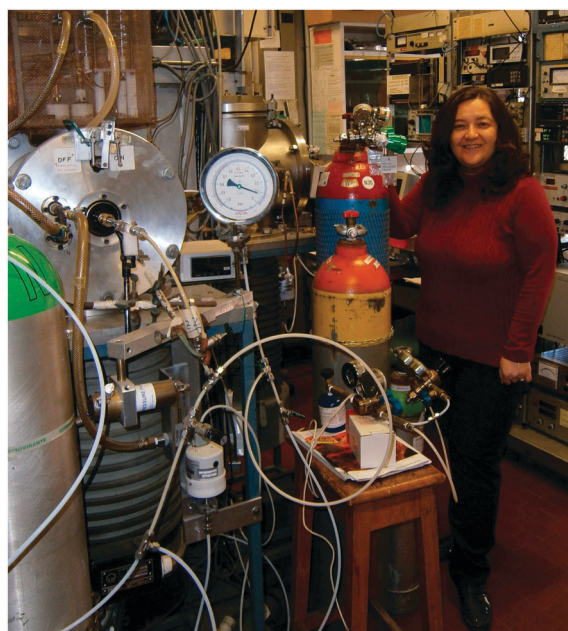
Gas-phase reactions involving atomic nitrogen in the ground  $^4\text{S}$  and first excited  $^2\text{D}$  electronic states with simple hydrocarbons or hydrocarbon radicals lead to the formation of prebiotic N-containing organic molecules. These reactions are now active in the upper atmosphere of Titan (a massive moon of Saturn) and might have played an important role in nitrogen fixation in the primitive upper terrestrial atmosphere, assuming that it is similar to the present atmosphere of Titan. The products of these reactions (nitriles, imines and radicals) are the precursors of larger N-containing molecules, which form the dense haze aerosols that completely cover the moon of Saturn. If anything similar to Titan's haze has ever existed on our planet, it is reasonable to imagine that, once deposited on the surface of the oceans, further chemical evolution might have transformed these molecules into aminoacids and nucleobases, the molecular building blocks of living entities. The experimental techniques necessary to investigate these reactions in detail are presented and the main results reviewed.

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### 1. Introduction

Nitrogen is an element essential for life as we know it. Amino acids, the building blocks of proteins, and nucleobases, included in the structures of both DNA and RNA, contain



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one or more nitrogen atoms bound to carbon. In our planet, the most abundant supply of nitrogen in the atmosphere is as  $N_2$  (dinitrogen). In some rocks, nitrogen is present as nitrate ions, but the weathering of those rocks is estimated to make a small contribution to the available nitrogen which enters into biological cycles.<sup>1</sup> The chemical inertness of the very stable gaseous dinitrogen is such that very few natural processes can convert it into its bioavailable compounds,<sup>2</sup> either in a reduced or an oxidized state, while industrial “nitrogen fixation” processes have been the subject of extended studies for the production of fertilizers and explosives for more than one century. In the present conditions of our planet, dinitrogen is naturally fixed into its compounds mainly *via* nitrogen-fixing bacteria.<sup>2</sup> Another natural source of fixed nitrogen is lightning, which converts the two major components of air into NO, followed by atmospheric oxidation to  $NO_2$  which is then converted to  $HNO_3$  and scavenged by rain.<sup>1</sup> But which were the mechanisms of nitrogen fixation in primordial Earth, before the appearance of life, when neither biogenic  $O_2$  nor nitrogen-fixing bacteria were present?

The answer to this question is difficult to achieve, because there is no geological record of what happened in our planet during the first half billion years after its formation.<sup>3,4</sup> The origin itself of  $N_2$  in its present large amount is a matter of debate. According to numerous hints, nitrogen was either outgassed from the interior of Earth as  $N_2$  and other nitrogen volatile compounds or delivered by comets/meteorites as ammonia,  $NH_3$ , which was then transformed into  $N_2$  by photolytic processes.<sup>3</sup> If prebiotic nitrogen-bearing organic compounds formed and accumulated during the preponderance of  $NH_3$  over  $N_2$ , then there is no problem in explaining nitrogen fixation into organic molecules because ammonia is quite available to chemical reactions. On the contrary, if terrestrial nitrogen was mainly supplied as molecular  $N_2$  – which is, indeed, believed to have been by far the most abundant nitrogen molecule in the proto-solar nebula<sup>4</sup> – or the conversion from  $NH_3$  to  $N_2$  was too fast for some nitrogen to be fixed in other compounds, the question of primordial dinitrogen fixation in an abiotic environment remains open.

In the absence of any information on the composition and chemical evolution of the primordial atmosphere, one of the best scientific approaches is to study the atmospheric chemistry of celestial bodies which share common characteristics with primitive Earth. Awaiting information on Earth-like exoplanets, the best neighbor to look at is Titan, the massive moon of Saturn, because its  $N_2$ -dominated, mildly reducing atmosphere can be considered somewhat reminiscent of the primeval atmosphere of Earth.<sup>5,6</sup> This is an interesting working hypothesis, which can make an important contribution to the debate concerning the synthesis of *prebiotic molecules* on Earth before the emergence of life, especially because nowadays Titan is the object of our solar system with the most active atmospheric chemistry. In this context, prebiotic molecules are defined as those organic molecules which can be naturally synthesized in abiotic processes, but are characterized by some complexity and all the appropriate “ingredients” (for instance, C–N and C–O bonds) to be the possible precursors of biological molecules<sup>4,7,8</sup> (namely sugars, amino acids, nucleobases *etc.*). The average chemical composition of our galaxy and

that of a living cell are very different and so are the types of molecules, which are mostly large and complex in a cell, rare and quite simple in space. During the formation and evolution of our solar system and in the passage from inanimate matter to living entities a chemical differentiation has clearly taken place, leading from simple to increasingly more structured molecules. Having an intermediate degree of complexity, it is reasonable to conceive that the prebiotic molecules observed in several extraterrestrial environments<sup>3,4</sup> are the link between matter in the universe and matter in living entities.

How did Earth become so rich in prebiotic molecules to have had the chance for life to spontaneously evolve from them? Two possibilities have been considered so far: endogenous or exogenous synthesis.<sup>9,10</sup> According to the endogenous synthesis vision, prebiotic species were synthesized directly on Earth from simple parent molecules (such as  $N_2$  or  $NH_3$ ,  $H_2O$  or  $H_2$ ,  $CH_4$  or  $CO_2$  and others),<sup>11–14</sup> which were trapped into the interior of Earth and then released by outgassing or volcanic eruption. The composition of the atmosphere could have been in a reduced or oxidized (or intermediate) state<sup>13,14</sup> and various sources of energy (such as intense lightning, energetic solar photons, radioactivity, intense volcanic activity, and shock waves of different kinds) could have induced its chemical transformation.<sup>13,14</sup> The ground-breaking Urey–Miller experiment,<sup>11</sup> which demonstrated that an abiotic synthesis of prebiotic molecules is possible starting from very simple gaseous parent species, has been in support of this hypothesis for more than 50 years. For completeness, we remind that there is an alternative endogenous synthesis theory, according to which the organic synthesis of prebiotic molecules has taken place in the proximity of oceanic hydrothermal vents.<sup>15</sup>

In the exogenous synthesis vision, instead, most of the organic molecules are believed to have come from space using comets, asteroids, meteorites and interplanetary dust particles as carriers.<sup>9,10</sup> This suggestion is supported by the observation of plenty of simple organic molecules in all these objects (see ref. 16–21 and references therein). According to this theory, prebiotic molecules were synthesized in the nebula from which the solar system originated and were then incorporated in the bodies of the solar system, including small ones such as comets and meteorites. Comets and meteorites were able to preserve them, being far away from the young Sun, from which intense emissions of photons and energetic particles took place, capable of destroying any complex molecule in nearby objects. Subsequently, comets and meteorites falling on our planet would have brought those molecules to the already cooled-down Earth,<sup>3,9,10</sup> where they could evolve in an aqueous medium. In support of this hypothesis, there is the observation of many prebiotic molecules in the interstellar clouds, including star-forming regions: amongst the more than 170 molecules/ions identified in the interstellar medium,<sup>22</sup> only a few tens do not contain carbon atoms and many prebiotic species (*e.g.* glycolaldehyde, cyanoacetylene, formamide) have been identified. Whether these molecules are preserved during the early phases of solar-type star formation and in the solar nebula, how they are incorporated into comets and meteorites and whether they can survive entering the terrestrial atmosphere remain open questions to be addressed.<sup>16,23</sup>



As we are going to see, the case of Titan seems to support the endogenous synthesis theory, because prebiotic molecules as well as N-rich organic aerosols (which form the haze layers that completely cover this moon) are efficiently synthesized locally, in the gaseous environment of the upper atmosphere. After the Voyager missions, the atmosphere of Titan has attracted considerable attention, because of the detection of gas-phase nitriles in trace amounts. Nitriles are thought to be key intermediates in the formation of biologically relevant molecules.<sup>7,8</sup> The surface temperature of Titan is  $\sim 95$  K and even in the upper stratosphere the temperature does not exceed  $\sim 180$  K. At this temperature, water is tough ice (the surface of Titan is actually made of water ice) and the absence of liquid water inevitably prevents the evolution of life as we know it. Paradoxically, however, the absence of a biosphere and the frozen satellite surface make Titan an ideal candidate as a chemical environment probably close enough to the primitive terrestrial atmosphere before the appearance of life drastically altered its composition.<sup>3</sup> In conclusion, the study of the chemical evolution of Titan's atmosphere can help us to understand how biologically active N-containing molecules and their nitrile precursors can be synthesized in a mildly reducing atmosphere,<sup>5</sup> possibly resembling that of our planet before the emergence of life.

What is, then, the status of our comprehension of the chemical composition and evolution of the atmosphere of Titan? Similarly to the atmosphere of Earth, the atmosphere of Titan can be regarded as a giant photoreactor, where the energy deposited mainly by solar photons, but also by cosmic rays and other energetic particles, drives a complex gas-phase chemistry.<sup>24–28</sup> Laboratory simulations of the chemical evolution of the atmosphere of Titan have been widely performed in experimental setups similar, in their basic aspects, to that of Urey–Miller (without liquid water).<sup>29</sup> When using a percentage of nitrogen and methane similar to the one encountered on Titan, not only has the formation of nitriles and other N-containing organic molecules been observed, but a solid yellow/brown sticky residue (tholins) is also formed.<sup>5,29</sup> The relation between synthetic tholins and the orange aerosols forming the haze of Titan, as well as some other materials observed in other celestial bodies, is evident. However, the analogy between a planetary atmosphere and a small laboratory reactor should not be brought too far. Large scale phenomena cannot be reproduced in laboratory experiments: the composition of a planetary atmosphere is neither homogeneous nor constant and vertical/horizontal transport or temperature and pressure gradients cannot be simulated. In addition, in a laboratory vessel, wall collisions, not occurring in a gaseous environment with the dimension of a planetary atmosphere, can strongly influence the chemical outcome by favoring radical recombination.<sup>29</sup> Recent experimental setups have tried to reduce the wall effects and to measure the chemical products *in situ*.<sup>30,31</sup> Nevertheless, as recently pointed out, these experiments and their results should only be taken as indicative of the chemistry and aerosol composition of Titan.<sup>29</sup>

The best way to account for the chemistry of the atmosphere of Titan, as well as that of solar and extrasolar planets, remains a multidisciplinary approach where the observations

are reproduced by photochemical models (the models are referred to as photochemical as the main source of energy that drives the chemical processing are solar photons) that consider the physical conditions with their variations and complex networks of interconnected elementary chemical reactions (unimolecular, bimolecular and, in denser atmospheric regions, trimolecular). Numerous molecular processes are involved, including radiative association and recombination, photon- or particle-induced ionization and ion–molecule reactions, photon- or particle-induced dissociation and radical–molecule reactions, heterogeneous or multiphase processes involving the aerosols.<sup>32</sup> For the modeling of these complex networks of elementary reactions, a number of experimental parameters are needed and, therefore, the molecular processes necessary to construct an accurate model have to be fully characterized in laboratory experiments. Numerous photochemical models of increasing complexity<sup>24–28</sup> have attempted to describe the atmospheric composition of Titan and important improvements have been achieved after the results of the Cassini–Huygens mission.<sup>32,33</sup>

Probably, from the point of view of a chemist, the most remarkable achievements of the Cassini–Huygens mission are the discovery of an unexpectedly rich ionosphere,<sup>34</sup> with large positive<sup>35</sup> and negative<sup>36</sup> ions (the negative ions have masses as large as several thousand Daltons), and the analysis of the aerosol composition by means of the Aerosol Collector and Pyrolyser (ACP) on-board Huygens.<sup>37</sup> The entire satellite, in fact, is completely covered by thick haze layers and the nature of the aerosols which compose them has been another challenge to our comprehension of this exotic celestial body. According to the ACP results and consistently with the chemical composition of laboratory tholins,<sup>29</sup> the aerosols are nitrogen-rich organic macromolecules. The new photochemical models of Titan have now several challenges to face: (i) the ion chemistry cannot be considered separately from the neutral chemistry occurring in the stratosphere and *vice versa*; on the contrary, there appears to be a strong coupling between neutral and ion chemistry;<sup>28,32,38,39</sup> (ii) the ‘chemical factory’ of trace constituents is now more extended towards the thermosphere, rather than the stratosphere, as believed in the past;<sup>32</sup> species like benzene, ammonia or simple imines have been identified in the ionosphere and not in the stratosphere;<sup>34,38,39</sup> (iii) haze formation mechanisms from the gaseous phase in the upper part of the atmosphere must be envisaged and a mechanism for significant incorporation of nitrogen into organic macromolecules has to be conceived.<sup>29,31,32</sup>

In this Review, neutral chemistry involving nitrogen atoms and simple hydrocarbons that leads to compounds with a novel C–N bond will be critically presented, with particular attention on the formation of prebiotic compounds, such as simple nitriles and imines, in the atmosphere of Titan and, possibly, in the earlier terrestrial atmosphere. This Review is not meant to treat comprehensively either the chemical evolution of the atmosphere of Titan or the chemistry of all the forms of active nitrogen which play a role in the atmosphere of Titan or have played it in the primordial terrestrial atmosphere. In particular, neither ion–molecule reactions, which are assuming an increasingly higher importance after the new results from the Cassini–Huygens mission, nor aerosol

heterogeneous processes will be discussed and the focus will be only on bimolecular neutral–neutral reactions up to the formation mechanism of aerosols. Readers interested in the other aspects are referred to ref. 31, 32 and 40 and references therein.

## 2. Nitrogen atoms in the upper atmosphere of Titan

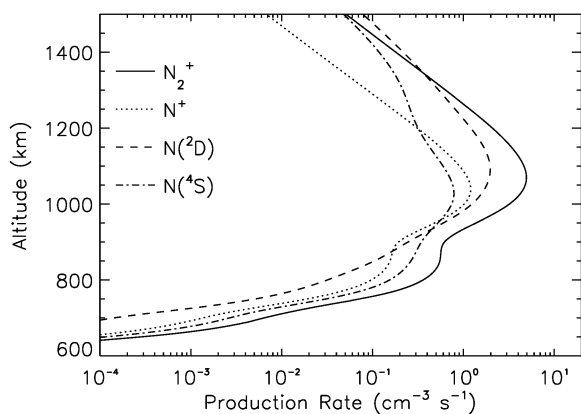
The observation of nitriles and of N-rich organic aerosols is a solid proof that nitrogen chemistry is active in the upper atmosphere of Titan leading to N-containing molecules and macromolecules. Since there are practically no radicals able to react with  $N_2$  (dinitrogen is one of the most strongly bound molecules in nature) at the temperature of Titan, the formation of nitriles must be initiated by the reactions of active forms of nitrogen, such as nitrogen atoms or ions, which can be formed in the upper atmosphere. In particular, atomic nitrogen can be produced by  $N_2$  dissociation induced by electron impact, extreme ultra-violet photolysis and dissociative photoionization, galactic cosmic ray absorption, and  $N_2^+$  dissociative recombination.<sup>41</sup> These processes lead to atomic nitrogen in the ground,  $^4S_{3/2}$ , and first electronically excited,  $^2D_{3/2,5/2}$ , states with comparable yields. In Fig. 1 are shown the production rates of  $N(^4S)$  and  $N(^2D)$  as a function of the altitude, together with those of nitrogen ions. These profiles are those obtained by Lavvas *et al.* in their recent work<sup>41</sup> on the energy deposition processes and primary photo-products in the upper atmosphere of Titan. As visible from Fig. 1, the production rate of  $N(^2D)$  is larger than that of  $N(^4S)$  above 900 km. The radiative lifetimes of the metastable states  $^2D_{3/2}$  and  $^2D_{5/2}$  are quite long (13.6 h and 36.7 h,<sup>32</sup> respectively), because the  $^2D$ – $^4S$  transition is both spin- and orbital-forbidden. In addition, collisional deactivation of  $N(^2D)$  by  $N_2$  is a slow process<sup>42</sup> and, therefore, the main fate of  $N(^2D)$  above 800 km is chemical reaction with other constituents of Titan's atmosphere. The production of N atoms in the  $^2D$  state is very important, because  $N(^4S)$  atoms exhibit very low reactivity with closed-shell molecules and the probability of collision with another open-shell species is small. On the contrary the reactions of  $N(^2D)$  with several molecules identified in the atmosphere of Titan (including the relatively abundant  $CH_4$  and  $C_2H_6$ ) can make an important contribution to the

chemical evolution of the atmosphere. As already commented on, nitrogen ions can also play an important role in the nitrogen chemistry of Titan. The interested readers are referred to ref. 32 and 40.

## 3. Laboratory experiments addressing neutral bimolecular reactions of relevance in the atmospheric chemistry of Titan

A scrutiny of the available photochemical models of the atmosphere of Titan, including the latest ones,<sup>26–28</sup> reveals that many elementary steps which play or might play a significant role in the chemical evolution of Titan's atmosphere have never been studied in laboratory experiments and are included in the models with parameters estimated by analogy with 'similar' ones. Other elementary reactions have been included with laboratory parameters measured under different conditions (particularly temperature), but the extrapolation of the experimental data to temperatures different from those actually used in the experiments is not warranted,<sup>43,44</sup> while the analogy with similar systems can lead to completely erroneous evaluations (see, for instance, the cases illustrated below on the apparently similar reactions  $N(^2D) + CH_4$  and  $N(^2D) + C_2H_6$ ).

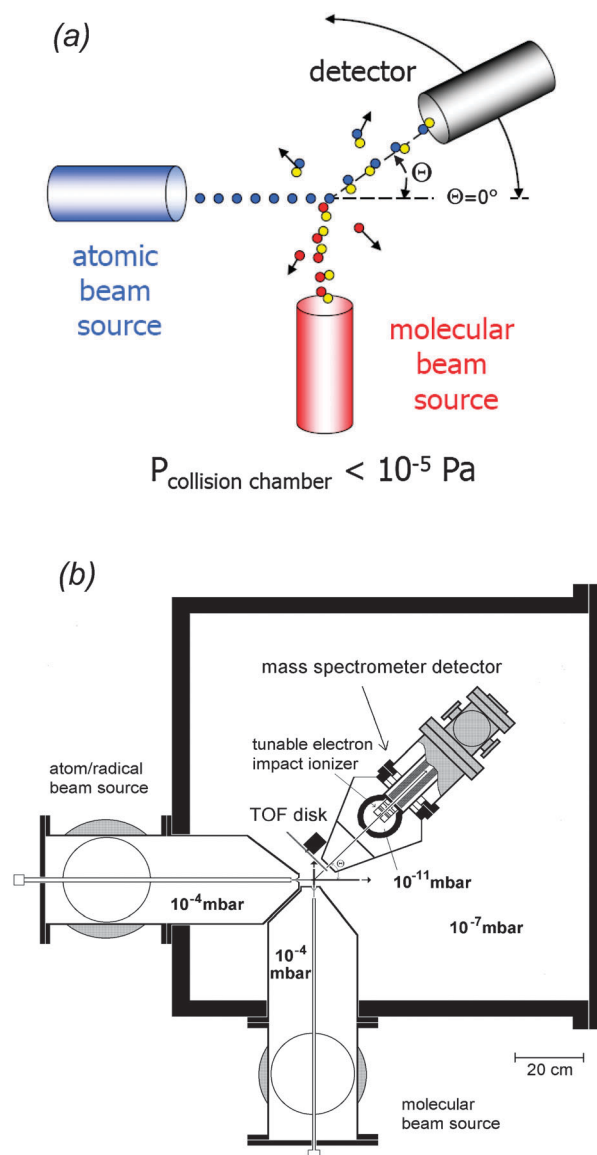
In recent years, the interest in planetary sciences has induced the community of physical chemists to apply new experimental techniques to the study of the elementary reactions of relevance in the atmospheric chemistry of Titan.<sup>8</sup> In particular, the CRESU technique (a French acronym for *Cinétique de Reaction en Ecoulement Supersonique Uniforme*), able to measure the rate coefficients at temperatures as low as 10–15 K, has allowed measuring the rate constants of many reactions at the temperatures typical of Titan.<sup>43,45</sup> Quite interestingly, in many cases the CRESU results pointed out that the extrapolation at very low temperatures of the Arrhenius dependence of the rate constant outside the range of temperatures investigated is not warranted and important deviations (in some cases of several orders of magnitude) have been observed.<sup>43</sup> The CRESU technique is now used in several laboratories and a new database of rate constants at very low temperatures is becoming available.<sup>46</sup> However, this kinetics technique, as well as others, follows the decay rate of one of the reactants, providing no information on the nature of the reaction primary products. This piece of information is also very important, because the products of one elementary reaction are going to be the reactants of a subsequent one in the complex network of elementary steps that describes the chemical evolution of planetary atmospheres. In addition, as pointed out by Krasnopolsky,<sup>28</sup> reaction products should always be specified in the models because unidentified products correspond to irreversible loss of the reactants in the models, while they can circulate back in reaction cycles, as seen for many species in the present terrestrial atmosphere. In conclusion, in the light of the new challenges for an accurate description of the chemical evolution of Titan's atmosphere, the need to establish the nature of the primary products and their branching ratios (BRs) in laboratory experiments has become compelling. When relatively complex molecules



**Fig. 1** Production rate of active nitrogen species in the upper atmosphere of Titan as a function of the altitude. Reprinted from ref. 41 with permission from Elsevier.

(such as C2 or C3 hydrocarbons like those observed on Titan) are involved, there are several open channels which compete with each other and it is not easy to establish *a priori* which is (are) the dominant one(s) simply on the basis of chemical intuition or enthalpy variations. There are actually numerous systems where the most exothermic channels have been found not to be the most relevant ones, because it is the reaction dynamics along the underlying potential energy surface (PES) that controls whether a specific reaction pathway is accessible by the system or not, and to which extent competing pathways occur.<sup>47,48</sup>

For this reason, in the last few decades, another experimental technique, the crossed molecular beam (CMB) method with mass-spectrometric (MS) detection, has joined and complemented the more traditional kinetics approach.<sup>48–54</sup> The CMB technique in its ‘universal’ arrangement making use of MS detection is a convenient experimental method for the investigation of polyatomic multi-channel elementary reactions under single collision conditions.<sup>48–53</sup> This technique, originally developed to address fundamental aspects on reaction mechanisms at the microscopic level by 1986 Nobel Laureates Y. T. Lee and D. R. Herschbach, has recently been improved to a level that allows one to study polyatomic multi-channel reactions including those of relevance in astrochemistry.<sup>48–53</sup> The CMB-MS technique is very convenient to establish the nature of the primary products. In CMB experiments, in fact, the two reactants are not simply mixed together, but are confined into distinct well-defined supersonic molecular beams which cross each other at a specific angle (see Fig. 2(a)). Therefore, the reactant of each beam collides only with that of the other beam, the products are formed only at the collision centre and, then, are free to fly towards the detector (see Fig. 2(a)) without secondary or wall collisions (the pressure of the collision chamber is maintained at  $\sim 10^{-5}$  Pa, so that the mean free path of the products is much larger than the dimensions of the collision chamber). In other words, in CMB experiments the outcome of numerous identical, well-defined bimolecular reactions under single collision conditions is observed. The collision-free conditions are very important in establishing the nature of the primary products, because they are often transient species which, in bulk experiments, could undergo either secondary collisions capable of altering their nature or recombination on the vessel walls. In CMB experiments, product detection can be realized *via* spectroscopic techniques, which are both sensitive and selective.<sup>47</sup> However, when the identity of the primary products is not known, which is rather common for polyatomic multichannel reactions, the use of universal MS detection is crucial because it allows determining the mass (and also the gross formula) of the possible products.<sup>48,52</sup> every species can be ionized and then detected at the high electron energy normally used in the ionizer preceding a quadrupole mass filter. Another beneficial factor with respect to common MS flow reactors is the possibility to measure product angular and velocity distributions: from the analysis of those functions it is possible to infer the reaction mechanism and to determine the amount of the total energy available to the products. In this way, the energetics of the various reaction channels can be derived and isomeric products with different enthalpies of formation



**Fig. 2** (a) Block diagram of a crossed molecular beam experiment for a reaction involving an atomic species and a diatomic molecule. Adapted from ref. 56 with kind permission from Springer Science + Business Media. (b) A schematic view of the Perugia crossed molecular beam apparatus with soft-ionization mass spectrometric detection. Reprinted from ref. 52 by permission of the publisher (Taylor & Francis Ltd.) (1 mbar = 100 Pa).

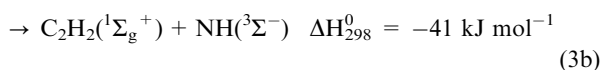
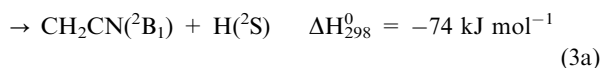
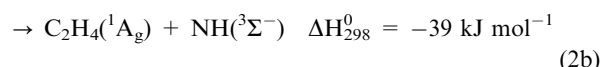
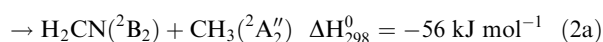
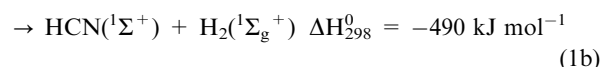
distinguished.<sup>52,54,55</sup> Ultimately, as the ionization cross sections of many molecules and radicals are known or can be reliably estimated,<sup>48,52</sup> the BR can be obtained from the observed product densities. Summarizing, the CMB-MS technique allows determining (a) the identity of the primary reaction products, (b) the BRs of the open reaction channels, (c) the reaction mechanisms at the microscopic level for each channel, and (d) the product energy release. Information on the reaction mechanism and product energy release can also be of help in the modelling of dense atmospheres, because in those conditions intermediate long-lived complexes can be collisionally stabilized, whereas vibrationally hot radicals produced by exothermic reactions can react more easily than

suggested by the average temperature of the surrounding environments. The significant advantages of the CMB-MS technique have motivated its extension to the study of reactions of interest in astrochemistry, making it a valuable complementary experimental approach to kinetics experiments. For years, indeed, the CMB-MS method has been employed to study bimolecular reactions of relevance in astrochemistry in numerous laboratories. In this way some reactions of atomic species – such as O and C atoms<sup>48,50,51,57</sup> – and simple radicals<sup>49,58–63</sup> – such as OH, CN, CH, C<sub>2</sub>H, C<sub>6</sub>H<sub>5</sub> – or other transient species, such as C<sub>2</sub> and C<sub>3</sub>,<sup>64–66</sup> have been characterized. A limit of the CMB-MS method has been imposed by the dissociative ionization of products and interfering species, which have complicated the detection of all the channels of multichannel polyatomic reactions in many cases. To reduce this problem, the technique of soft ionization by tunable low-energy electrons or tunable VUV synchrotron radiation has been implemented in several CMB machines.<sup>48,52,67</sup> Such a novel approach in CMB experiments has shown to be of success in characterizing all the channels of multi-channel reactive systems.<sup>48,52,68</sup> Another improvement has been the set-up of a variable beam crossing angle configuration in a CMB-MS machine<sup>48,52,57</sup> which allows lowering the experimental collision energy ( $E_c$ ) so that the low temperature environment of the atmosphere of Titan can be better simulated. In Fig. 2(b) a schematic view of the CMB-MS machine with a tunable electron impact ionizer of Perugia is shown.<sup>52</sup> In this experimental set-up, use is made of continuous supersonic beams of reactant species. The transient species beam is produced by means of a radiofrequency discharge beam source.<sup>60,65,69</sup>

#### 4. The reactions of atomic nitrogen in the ground electronic state with hydrocarbon radicals

Since the first global photochemical model developed by Yung *et al.*,<sup>24</sup> the reactions of atomic nitrogen in both ground and first electronically excited states have been recognized to play an important role in the chemistry of the atmosphere of Titan. The reactions of ground state atomic nitrogen, N(<sup>4</sup>S), with closed-shell molecules, including unsaturated hydrocarbons such as C<sub>2</sub>H<sub>4</sub> or C<sub>2</sub>H<sub>2</sub>, are extremely slow.<sup>70,71</sup> This might seem surprising if one considers that unsaturated hydrocarbons offer their  $\pi$  electrons to the electrophilic attack of electron-deficient radical species such as N(<sup>4</sup>S). The reason for that resides in the correlation rules: reactants in quartet and singlet states can correlate only with quartet intermediates, which are very rare in chemistry. In addition, many reactions of N(<sup>4</sup>S) with simple molecules are strongly endothermic. Few reactions involving N(<sup>4</sup>S) have been found to be fast and they always involve another open-shell species.<sup>72–74</sup> Therefore, the low reactivity of N(<sup>4</sup>S) with closed-shell species limits its role to the reactions with hydrocarbon radicals, which are relatively abundant, being produced by either the photolysis of methane and higher hydrocarbons or their reactions with radicals. The most important hydrocarbon radical is the methyl radical (CH<sub>3</sub>) which is mostly produced by photolysis of methane at high altitudes or by CH<sub>4</sub> photosensitized dissociation *via* photodissociation of acetylene to C<sub>2</sub>H at lower altitudes.<sup>24–28</sup>

Bimolecular reactions involving two open-shell species are quite difficult to investigate in laboratory experiments. To the best of my knowledge, the only reactions investigated in laboratory experiments are those involving CH<sub>3</sub> (methyl), C<sub>2</sub>H<sub>5</sub> (ethyl) and C<sub>2</sub>H<sub>3</sub> (vinyl).<sup>72–74</sup>



(The enthalpies of reactions are those reported in ref. 72–74). Rate coefficients and product branching ratios for the reactions (1)–(3) at 298 K were determined several years ago in the same research group by means of a discharge flow tube coupled to MS detection.<sup>72–74</sup> In particular, the dominant channel for reaction (1) is channel (1a) with a BR of *ca.* 90%, for reaction (2) it is channel (2b) with a BR of *ca.* 65% and for reaction (3) it is channel (3a) with a BR of *ca.* 80%. Therefore, considering the 298 K rate coefficients close to the gas kinetics limit ( $k_{(1)} = 8.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ,  $k_{(2)} = 1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and  $k_{(3)} = 7.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ), we can consider reactions (1) and (3) efficient pathways for the formation of a compound with a novel C–N bond in the atmospheric conditions of Titan. In particular, reaction (1) has always been considered to be the main step in the production of the observed HCN molecule, as CH<sub>3</sub> is the most abundant radical species in the atmosphere of Titan (the primary product H<sub>2</sub>CN can easily react with other species, such as H atoms, thus producing HCN). It should be noted, however, that, in spite of the meticulous work done by the authors, MS detection in a flow tube experiment has left some uncertainty on the BR especially because of the possible effect of secondary and wall collisions and of the presence of isomeric species, such as cyano and isocyano isomers (*e.g.* HCN/HNC in reaction (1)), as well as products at the same mass-to-charge ( $m/z$ ) ratio (*e.g.* C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>CN in reaction (2)). Experimental tricks (such as the use of isotopically labeled reactants)<sup>72–74</sup> and VUV synchrotron radiation at the ionization threshold<sup>73</sup> were used to increase the accuracy of the BR. Nevertheless, some uncertainty has remained. For instance, the use of synchrotron radiation in the study of reaction (2) has limited the detection to the species with an ionization energy less than 10.9 eV, thus excluding detection of other possible products such as NH, HCN, CH<sub>3</sub>CN, H<sub>2</sub> and CH<sub>4</sub>.<sup>73</sup>



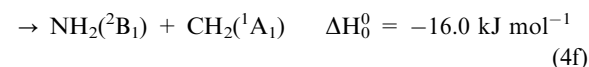
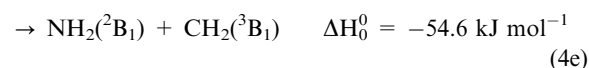
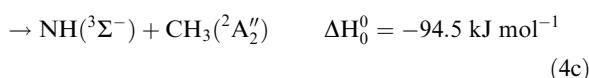
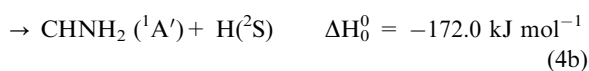
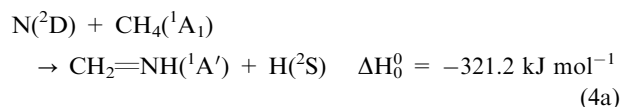
## 5. The reactions of atomic nitrogen in the first electronically excited state with hydrocarbons

The reactions of  $N(^2D)$  with the closed-shell hydrocarbons  $CH_4$  and  $C_2H_2$  have been considered to be important steps towards the formation of HCN and  $C_2N_2$  – both observed in the atmosphere of Titan during the Voyager mission – since early models.<sup>24,75</sup> Another  $N(^2D)$  reaction, the one with ethylene, was later invoked to explain the formation of acetonitrile detected in ground-based observations.<sup>25</sup> As a matter of fact, very little was known about  $N(^2D)$  reactions until recently and reliable laboratory experiments have become available only since the late 1990s, because of the experimental difficulties in studying those systems. The room temperature rate constants for the reactions  $N(^2D) + CH_4$  and  $N(^2D) + C_2H_2$  have been found to be slightly larger than those originally used in the models.<sup>42</sup> The kinetics of other relevant  $N(^2D)$  reactions were also investigated,<sup>42</sup> in some cases also considering the temperature dependence of the rate coefficients. Once again, however, those kinetics experiments were only able to follow the  $N(^2D)$  decay rate and no information was provided on the nature of the primary products.

Because of the importance of  $N(^2D)$  reactions with the hydrocarbons present in the atmosphere of Titan, a systematic investigation of  $N(^2D)$  reactions with simple hydrocarbons by means of the CMB-MS technique has been performed in the Perugia laboratory. The experimental results have been complemented by electronic structure calculations of the relevant PES (stationary points) and statistical (*via* the Rice–Ramsperger–Kassel–Marcus, RRKM, method) calculations of the BRs. This combined theoretical and experimental approach has been applied so far to the multichannel reactions  $N(^2D) + CH_4$ ,  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$ .<sup>54,55,76–78</sup>

### 5.1 The reaction $N(^2D) + CH_4$

For this reaction, which is the most important one involving  $N(^2D)$  as methane is the second most abundant species in the atmosphere of Titan, there are several thermodynamically allowed channels:

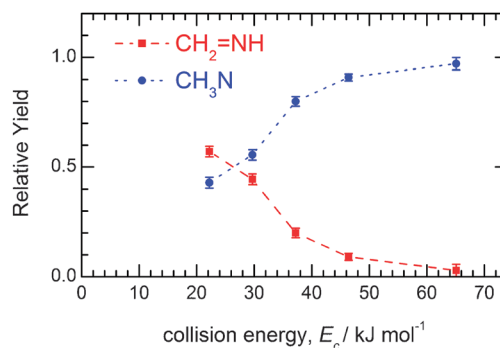


where the enthalpies of the reaction channels reported are those derived at the CCSD(T) level of calculations.<sup>54</sup>

A first collision-free investigation with spectroscopic detection established that the H-forming channels are dominant over the channel (4c) leading to NH with an absolute yield of  $0.3 \pm 0.1$  for the NH formation channel and  $0.8 \pm 0.2$  for the H-displacement channel, which, however, can be associated to three different molecular isomers.<sup>79</sup> No further information was given on the nature of the molecular co-product, even though the most probable candidate was believed to be methanimine ( $CH_2=NH$ ) formed in channel (4a). In our laboratory we have investigated the dynamics of the H-displacement channels at five different collision energies (from 22.2 up to 65.1 kJ mol<sup>-1</sup>).<sup>54,55</sup> The CMB-MS has led to the identification of two distinct isomers as primary reaction products, methanimine (from channel (4a)) and methylnitrene (from channel (4d)), the yield of which significantly varies with the total available energy, as summarized in Fig. 3, where the  $CH_2=NH$  and  $CH_3N$  relative yield is reported as a function of the experimental  $E_c$ .

From the derived center-of-mass product angular and translational energy distributions the reaction micromechanisms, the product energy partitioning and the relative branching ratios of the competing reaction channels leading to the two isomers have been obtained.<sup>55</sup> The interpretation of the scattering results has been assisted by electronic structure calculations of stationary points and product energetics for the  $CH_4N$  ground state doublet potential energy surface.<sup>55</sup> A comparison between experimental results of the two isomer branching ratios and RRKM estimates, based on the electronic structure calculations, was performed. Unfortunately, this system is highly nonstatistical, because the production of the less stable  $CH_3N$  isomer is dominated by *dynamical* effects which cannot be accounted for in statistical calculations.<sup>55</sup> And, in fact, RRKM calculations failed to reproduce the experimental relative yield of channel (4a) *vs.* channel (4d).

The implications for the modeling of the atmosphere of Titan are as follows. The early assumption that only NH and  $CH_3$  are the products of the  $N(^2D) + CH_4$  reaction<sup>24</sup> is not correct: that reactive channel accounts only for about 30% in the room temperature laboratory experiment by Umemoto *et al.*<sup>79</sup> and, by analyzing the trend of the BR as a function of the available energy for the dynamically similar  $CH_3N + H$



**Fig. 3** Relative yields of the isomeric products  $CH_2=NH$  (red squares) and  $CH_3N$  (blue diamonds) as a function of collision energy,  $E_c$ , derived from crossed molecular beam studies of the  $N(^2D) + CH_4$  reaction. The dashed and dotted lines joining the data points are drawn to guide the eye only. Adapted from ref. 80 with permission from the The Royal Society of Chemistry.

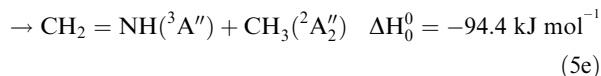
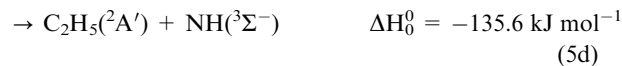
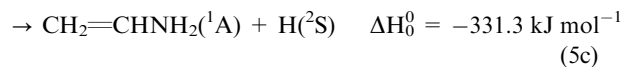
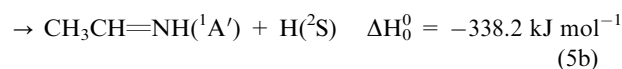
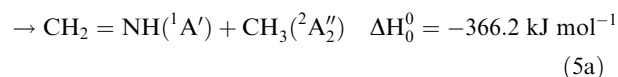
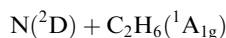


channel, we can presume that it will be even lower under the low temperature conditions of Titan's atmosphere. Unluckily, since this reactive system deviates remarkably from statistical behavior, we cannot refer to our RRKM calculations performed at the energy of relevance to the atmosphere of Titan to evaluate the product BRs. Anyway, even though the experiments have been performed at collision energies higher than those achievable at the low temperature typical of the atmosphere of Titan, our results confirm that the reaction  $\text{N}(^2\text{D}) + \text{CH}_4$  is an active route to the formation of methanimine, a closed-shell molecule containing a novel C–N bond. That demonstrates that such a bond can be generated directly by a reaction involving an active form of nitrogen, the main constituent of the atmosphere of Titan, and  $\text{CH}_4$ , the second most abundant species, and that nitrogen fixation can be achieved in abiotic conditions.  $\text{CH}_2=\text{NH}$  has not been observed directly in Titan's atmosphere so far, but its protonated form,  $\text{CH}_2\text{NH}_2^+$ , has been invoked to reproduce the peak at  $m/z = 30$  recorded by the ion neutral mass spectrometer (INMS) on the Cassini spacecraft.<sup>34</sup> The presence of a double CN bond renders  $\text{CH}_2=\text{NH}$  a very reactive molecule, and similarly to the entire family of imines, methanimine easily undergoes polymerization, oxidation, and hydrolysis.<sup>81</sup> This compound is so reactive that its characterization in the laboratory has been possible only by producing it *in situ* from the pyrolysis of amines, methyl azide and other azido compounds. Therefore, it is reasonable to assume that, in a relatively dense medium such as the upper atmosphere of Titan (collision time  $\sim 1$  s),<sup>32</sup> methanimine quickly reacts with radicals or undergoes polymerization and copolymerization. Alternatively, it could photodissociate to  $\text{HCNH}/\text{H}_2\text{CN} + \text{H}$  or  $\text{HCN}/\text{HNC} + \text{H}_2$ . The absorption cross section of  $\text{CH}_2\text{NH}$  has been measured in the 235–260 nm range,<sup>82</sup> but the photodissociation product yield has not been characterized. Nevertheless, it is known that activated  $\text{CH}_2=\text{NH}$  can dissociate to  $\text{HCNH}/\text{H}_2\text{CN} + \text{H}$  or  $\text{HCN}/\text{HNC} + \text{H}_2$  along the ground state PES *via* quite large energy barriers,<sup>83</sup> which can certainly be overcome after UV absorption to an excited state and internal conversion to the ground electronic state. Interestingly, the above-mentioned processes have been included in the recent photochemical model of Titan by Lavvas *et al.*,<sup>26,27</sup> who were the first to consider the possible transformation that  $\text{CH}_2=\text{NH}$  undergoes after its formation. Because of the lack of experimental parameters, the effect of some processes, such as the formation of  $\text{CH}_2=\text{NH}$  dimer or the copolymerization with other nitriles, could only be estimated. Nevertheless, several interesting considerations have been made. For instance, if the main photolysis product is assumed to be the  $\text{H}_2\text{CN}$  radical rather than HCN, there are no significant changes in the HCN profile, since  $\text{H}_2\text{CN}$  is readily converted to HCN by reaction with H. As a matter of fact, the model by Lavvas *et al.*<sup>27</sup> appears to predict a larger quantity of  $\text{CH}_2=\text{NH}$  than necessary to reproduce the INMS observation,<sup>34</sup> implying that there is an overestimate of  $\text{CH}_2=\text{NH}$  production or, more probably, an underestimate of  $\text{CH}_2=\text{NH}$  loss (in this respect, the use of the CMB-MS results could be of help, as Lavvas *et al.* have used for channel (1a) a yield of 0.8 in accord with the suggestion of Umemoto *et al.*, while also methylnitrene is formed in the H-displacement channels). As a growing amount

of evidence suggests that nitrogen chemistry contributes to the formation of the haze aerosols in the Titan upper atmosphere,<sup>31</sup>  $\text{CH}_2=\text{NH}$  is an excellent candidate to account for the formation of nitrogen-rich aerosols *via* polymerization or copolymerization with other unsaturated species or radical reactions. Finally, it should be mentioned that other  $\text{CH}_2=\text{NH}$  formation routes have been envisaged, such as the one based on a combination of ion–neutral and neutral–neutral reactions.<sup>38</sup>

## 5.2 The reaction $\text{N}(^2\text{D}) + \text{C}_2\text{H}_6$

Ethane is the second most abundant hydrocarbon in the atmosphere of Titan. Its reaction with  $\text{N}(^2\text{D})$  is very complex, as there are 22 thermodynamically allowed channels that correlate with the reactant asymptote directly or through one or more isomerization steps.<sup>78</sup> The large variety of products that can be generated is the result of the versatility of carbon and nitrogen in forming bonds, of the relatively large number of atoms involved and of the high energy content of the reactants (some products can also be formed either in the ground singlet or excited triplet states). Among the 22 open channels, those which have been found to make a contribution to the overall reaction are:



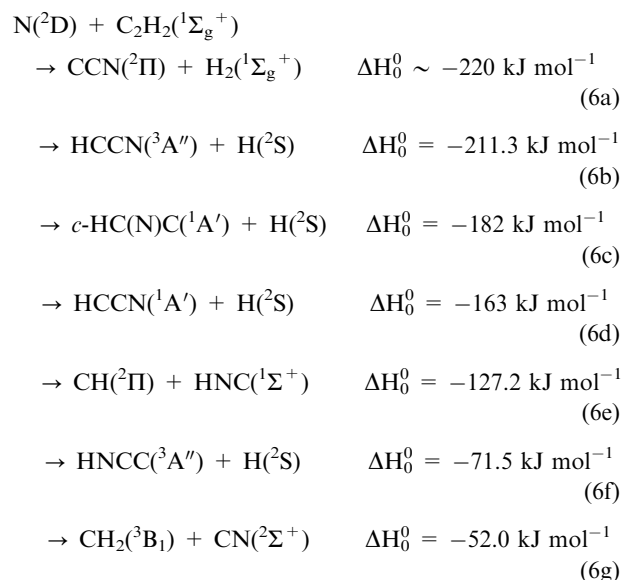
where the enthalpies of the reaction channels reported are those derived at the CCSD(T) level of calculations.<sup>78</sup>

For this system we have investigated the dynamics of the H-displacement channels by the CMB-MS method at different collision energies and from the derived center-of-mass product angular and translational energy distributions the reaction micromechanisms and the product energy partitioning have been obtained.<sup>78</sup> Contrarily to the apparently similar reaction (4), reaction (5) was found to behave in a markedly statistical way: all the dynamical observables are consistent with the formation of a bound intermediate, the lifetime of which is long enough to allow energy randomization. This is the ideal case to apply RRKM estimates of product BRs. According to these estimates, which have been performed also at the temperature relevant to the stratosphere of Titan, the C–C bond breaking channel leading to methanimine and  $\text{CH}_3$  (channel (5a)) is by far the dominant channel (BR = 79%), with the channel leading to ethanimine and H (channel (5c)) accounting for 12.4% of the global reactions. The other indicated channels make a minor (few percent) contribution.<sup>78</sup>

Interestingly, in the photochemical models of Titan reaction (5) was either assumed<sup>25,28</sup> to produce only  $\text{NH} + \text{C}_2\text{H}_5$  (which is, instead, only a minor channel) or aziridine,  $c\text{-CH}_2(\text{NH})\text{CH}_2 + \text{H}$ .<sup>27</sup> None of these suggestions is correct. Methanimine from channel (5a) is also produced by the reaction  $\text{N}(^2\text{D}) + \text{CH}_4$ . Methane is more abundant than ethane by roughly three orders of magnitude, but the rate constant (at room temperature) of the reaction  $\text{N}(^2\text{D}) + \text{C}_2\text{H}_6$  is one order of magnitude larger than that of methane. Therefore, the reaction of  $\text{N}(^2\text{D}) + \text{C}_2\text{H}_6$  should contribute by a few percent to the global budget of methanimine. As already commented on, the model by Lavvas *et al.* derived a larger quantity than that inferred by INMS and, therefore, there is no need of an additional source of  $\text{CH}_2=\text{NH}$ , as the results of reaction (5) suggest. However, as already noted, there is a lot of uncertainty on the possible fate of  $\text{CH}_2=\text{NH}$  in the upper atmosphere of Titan, because of a severe lack of knowledge on the possible chemical loss pathways of this species. Finally, it should be mentioned that the production of  $\text{CH}_3$  from a reaction destroying ethane partially recycles it, as ethane is formed by three-body recombination of  $\text{CH}_3$ . Ethanamine, the second most important molecular product of reaction (5), can also be a source of nitrogen-rich molecules and aerosols *via* addition reactions, polymerization and copolymerization. Alternatively, it might undergo UV photodissociation, thus forming reactive radicals that can further enhance the formation of nitrogen-rich complex species. A theoretical study has suggested that activated ethanimine can directly decompose into  $\text{CH}_3\text{CN} + \text{H}_2$  and  $\text{CH}_4 + \text{HCN}/\text{HNC}$ .<sup>84</sup> In this respect, activated ethanimine could be a source of acetonitrile and  $\text{HCN}/\text{HNC}$ .

### 5.3 The reaction $\text{N}(^2\text{D}) + \text{C}_2\text{H}_2$

Also the reaction of  $\text{N}(^2\text{D})$  with acetylene is an interesting multichannel reaction leading to the formation of new species containing a C–N bond. The possible reaction channels are

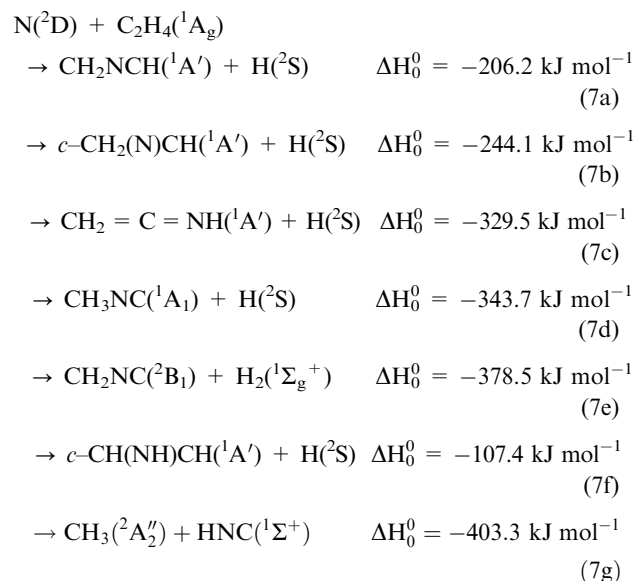


where the enthalpies of the reactions are those reported in ref. 76. In this case, CMB-MS experiments, combined with electronic structure and RRKM calculations, have established that channel (6b) is by far the dominant one,<sup>76</sup> thus supporting the mechanism of  $\text{C}_2\text{N}_2$  formation suggested by Yung.<sup>75</sup>

In addition, HCCN radical has been recently suggested to be an important precursor for nitrogenated organic solid obtained in the EUV irradiation of  $\text{N}_2/\text{CH}_4$  mixtures.<sup>31</sup>

### 5.4 The reaction $\text{N}(^2\text{D}) + \text{C}_2\text{H}_4$

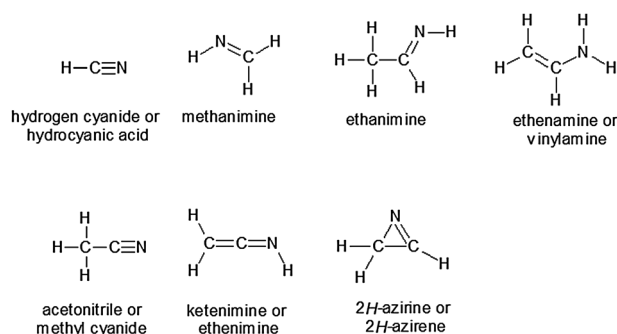
This reaction is also very complex, with 13 open channels leading to interesting species containing novel C–N bonds. According to our more recent electronic structure and RRKM calculations, the channels with a non-negligible yield are:



where the enthalpies of the reaction channels reported are those calculated at the CCSD(T) level of calculations.<sup>85</sup> This reaction has been the subject of a previous publication from our group,<sup>77</sup> where 2*H*-azirine and ketenimine were suggested to be the main molecular products produced in the H-displacement channels (7b) and (7c). We have recently repeated the experiment with an improved CMB machine and an additional species has been observed (work in progress). More specifically, we have been able to observe (with a yield of 2–3%) the formation of isoacetonitrile + H, in addition to the already identified 2*H*-azirine + H. The formation of ketenimine seems to be less important than previously inferred. Quite interestingly, from the shape of the product translational energy distribution and with the help of RRKM calculations on a new PES we have established that roughly 60% of the 2*H*-azirine molecules are formed with enough internal energy to tautomerize to the most stable acetonitrile isomer, and 90% of them do so in less than 10 ns. Therefore, it is confirmed that reaction (7) is a source of acetonitrile, even though with a yield smaller than 1 as assumed in previous models.<sup>25–27</sup> This reaction has also been the subject of another CMB-MS study using VUV synchrotron radiation. Unfortunately, in this case, because of the numerous possible reaction channels in the same *m/z* range, the results have not given a clear picture of the nature of the  $\text{CH}_3\text{CN}/\text{CH}_2\text{CN}$  product isomers.<sup>67</sup>

## 6. Exotic N-containing molecules and their destiny in the atmosphere of Titan

Detailed laboratory studies on the  $\text{N}(^4\text{S})$  reactions with  $\text{CH}_3$  and  $\text{C}_2\text{H}_3$  radicals, as well as on the  $\text{N}(^2\text{D})$  reactions with



**Fig. 4** Structures of several N-containing closed-shell molecules formed in the reactions (1)–(7).

methane (the second most abundant species in the atmosphere of Titan after  $N_2$ ) and higher hydrocarbons present in trace amounts ( $C_2H_6$ ,  $C_2H_2$  and  $C_2H_4$ ), indicate that in the atmosphere of Titan interesting species containing a novel C–N bond can easily be formed in neutral–neutral bimolecular reactions. Most of the products of reactions (1)–(7) should be produced in an amount high enough to allow their observations in the upper atmosphere of Titan. To date, only HCN and  $CH_3CN$  have been actually observed, while the presence of  $CH_2=NH$  has been inferred from its protonated form. Clearly, with a collision time of  $<1$  s in the region of interest of the atmosphere of Titan, open-shell (such as  $H_2CN$ ,  $CH_3N$  and  $HCCN$  radicals) or highly unstable unsaturated N-compounds (such as  $CH_2=NH$ ,  $CH_3CH=NH$ ,  $CH_2=C=NH$  or  $CH_2=CH-NH_2$ ) are expected to undergo reactions with other species present in the atmosphere of Titan. In addition, some other species, such as the highly strained cyclic molecule 2H-azirine, can spontaneously isomerize to their most stable tautomer acetonitrile. The structures of the closed-shell molecules formed in reactions (1)–(7) are shown in Fig. 4.

## 7. Conclusions

In this contribution, gas-phase reactions that involve atomic nitrogen and simple hydrocarbons or hydrocarbon radicals leading to the formation of nitrogen containing organic molecules have been reviewed, with reference to the role that they play in the upper atmosphere of Titan and might have played in the primitive upper terrestrial atmosphere, under the reasonable assumption that it was similar to the present atmosphere of Titan. Nitrogen must have entered into organic compounds in order to be subsequently transformed into the biologically relevant molecules that, together with others, allow life to exist. Aminoacids and nucleobases are reduced compounds of nitrogen and it is extremely important to understand how the formation of these species evolved starting from simple parent molecules in the absence of living organisms. The illustrated reactions are the first step towards the formation of nitrogen complex organic macromolecules starting from a purely gas-phase environment. On Titan, the macromolecules composing the aerosols eventually are deposited on the surface of the satellite, where they simply accumulate because the low temperature does not allow further chemical evolution. Nonetheless, it is well-known that tholins

(laboratory analogs of the Titan aerosols) in the presence of liquid water are able to hydrolyze<sup>3,4,29</sup> and give different products (including aminoacids) as a function of the pH. Therefore, if anything similar to Titan's haze has ever existed on our planet, it is reasonable to imagine that, once deposited on the surface of the oceans, further chemical evolution might have transformed these molecules into the first building blocks of living entities.

In a way, these results reinforce the endogenous synthesis theory, as in the present conditions of Titan prebiotic N-containing compounds are constantly formed and contribute to the build-up of the N-macromolecules constituting the haze aerosols. But a new endogenous theory vision is emerging from the comparison with Titan, because the organic synthesis occurs in the upper, low density part of the atmosphere starting from a purely gaseous environment (and, eventually, continues on the surface of the particles of the aerosols).

Further investigation is desirable on missing pieces of the puzzle which, when finally composed, will provide a complete description of the chemical evolution and composition of the atmosphere of Titan. In particular, reliable experimental data on the processes of polymerization/copolymerization of the above mentioned N-containing molecules accompanied by their inclusion in accurate photochemical models will finally clarify if these species are really responsible for the haze formation. More experimental information on the reactions involving open-shell radicals and ions relatively abundant in the upper atmosphere of Titan will also be very important in judging the role played by these species.

## Acknowledgements

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