A Theoretical Investigation of the Reactions of N(^{2}D) and CN with Acrylonitrile and Implications for the Prebiotic Chemistry of Titan

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Abstract. The reactions between acrylonitrile and two different reactive species, namely N(^{2}D) and the CN radical were investigated by performing accurate electronic structure calculations with the aim to unveil the most important aspects of the Potential Energy Surfaces. For each reaction, several product channels involving the elimination of H atoms were identified, allowing the formation of different radical species, depending on the initial site of attack. Both reactions appears to be exothermic and without an entrance barrier, suggesting their possible efficient role in the nitrogen-rich chemistry of the atmosphere of Titan.

Keywords: Ab initio calculations · Astrochemistry · Planetary atmosphere · Titan

1 Introduction

Chemical reactions involving molecular species containing nitrogen appears to be pivotal in several extraterrestrial environments, including the atmosphere of Titan [1–3]. After the appearance of life, the geomorphology and the characteristic of our planet have undergone massive modifications. As a consequence, in order to have a clear picture of the first stages of our prebiotic chemistry, the study of planets and moons, similar to the primitive Earth, can be of great help. In particular, the main focus of astrobiological studies is Titan, the largest moon of Saturn, as well as one of the few moons of the Solar System, which possess a thick atmosphere. Interesting data about Titan and its unique atmosphere became available with different exploratory missions, including the two Voyager missions [4–7] and, much later, the fascinating Cassini-Huygens mission [8]. According to the different analysis, the main component of Titan's atmosphere appears to be molecular nitrogen (N_2) [6], together with other species, present in

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lower amount, including methane, the second most abundant molecule, and several hydrocarbons (e.g. ethane, ethylene, acetylene, etc.) [5]. The best strategy for the understanding of the chemistry of Titan's atmosphere is characterized by a multidisciplinary approach, which culminates in accurate photochemical models [9–11] that include physical and chemical parameters, derived through theoretical and/or experimental investigations, allowing to obtain the rate constants for the most relevant elementary reactions [12]. Considering the high stability of the N_2 molecule, one of the initial steps for the chemistry of N-bearing molecules is considered to be the impact of molecular nitrogen with high energy free electrons, leading to the formation of the "active nitrogen", including nitrogen atoms in their ground and excited states N(^{4}S) and N(^{2}D), respectively. The first electronically excited state of atomic nitrogen, N(^{2}D), is metastable with a relatively long radiative lifetime [13]. It is 230.0 kJ/mol higher than the ground state and appears to be very reactive [14,15]. The second excited metastable state of atomic nitrogen, N(^{2}P), can be present simultaneously with N(^{2}D). Nevertheless, its reactivity appears to be lower and it can be easily converted into N(^{2}D) [13]. Several theoretical and experimental studies have been performed to study the reactivity of N(^{2}D) with different hydrocarbons, with possible applications in the atmosphere of Titan (namely, N(^{2}D)+ C_2H_2; C_2H_4; C_2H_6; C_6H_6; CH_3CCH; HC_3N; C_7H_8) [16–26]. Another abundant reactive species in the atmosphere of Titan appears to be the cyano (CN) radical. According to the last refinements of photochemical models, the main formation pathway for the CN radical is the photodissociation of HCN, which is very abundant [27]. The aforementioned process appears to be particularly efficient between 800 km and 1000 km of altitude [28]. In the same regions, namely at altitudes above 600 km [13],the interaction between EUV photons and N_2 leads to the formation of N(^{2}D) with high efficiency. A particularly important N-containing molecule detected on Titan's atmosphere appears to be acrylonitrile (CH_2CHCN). In the last years this molecule received a great deal of attention because it was found to be the best candidate for the formation of membrane-like structures in apolar solvents [29], such as the methane-rich lakes, peculiars on Titan's surface. The presence of acrylonitrile was initially inferred by the detection of the CH_2CHCNH^+ cation using the INMS (Ion and Neutral Mass Spectrometer) [30–33] onboard the Cassini orbiter, while the definitive proof of the presence of neutral CH_2CHCN came from the analysis of the data coming from the ALMA facilities (Atacama Large Millimeter/Submillimeter Array) [34]. A follow-up study using higher sensitivity data from the ALMA archive, presented the very first spatially resolved map of the distribution of acrylonitrile in Titan's atmosphere [35]. The main formation mechanism for acrylonitrile is the reaction between the cyano radical and the ethylene molecule (C_2H_4). Different theoretical and experimental investigations on this reaction [36–43] revealed a rate coefficient of the order of 10^{-10} cm^3 molec^{-1} s^{-1} and demonstrated that the main reaction pathway is

related to the elimination of hydrogen atoms, with the subsequent formation of CH_2CHCN. Not much is known about the possible destruction mechanisms of acrylonitrile. The main loss mechanisms are indeed a proton transfer process from $HCNH^+$ (or alternatively $C_2H_5^+$), followed by electron recombination of HC_3NH^+ [44,45]. According to the previously reported photochemical models, the reaction of $N(^2D)$ and CN radical with the CH_2CHCN molecule could represent a feasible destruction mechanism on Titan's atmosphere. Unfortunately the only data available in the models for the title reactions derive from extrapolation processes [12,27,28,46] or comes from analogies with similar systems [28], without considering the presence of different isomers. In the present contribution we report a theoretical characterization of the main reaction pathways for the $N(^2D)$+CH_2CHCN and CN+CH_2CHCN reactions, with particular attention on the different mechanism for the initial bimolecular attack.

2 Computational Methods

The overall doublet Potential Energy Surface (PES) for the two $N(^2D)$+ CH_2CHCN and CN+CH_2CHCN reactions was investigated adopting a computational strategy previously used with success in several cases [16,17,23,47–49]. A first exploration of the Potential Energy Surface was performed using of Density Functional Theory (DFT) calculations, with the B3LYP [50,51] functional, together with with the correlation consistent valence polarized set aug-cc-pVTZ [52–54]. The same level of theory was used for the analysis of harmonic vibrational frequencies, in order to determine the nature of each stationary point, i.e. minimum if all the frequencies are real and saddle point if there is one, and only one, imaginary frequency. Intrinsic Reaction Coordinates (IRC) calculations [55,56] were performed to assign each identified stationary point to the corresponding reactants and products. The calculation of the harmonic vibrational frequencies allowed us to derive the zero-point energy, to correct the energy to 0 K. In order to obtain a better estimation of the energy of $N(^2D)$, we added 230 kJ/mol (related to the experimental separation [57] $N(^4S)$-$N(^2D)$) to the calculated energy of $N(^4S)$. All calculations were carried out using GAUSSIAN 09 [58], while the graphical analysis of the calculated stationary points was performed using MOLDEN [59,60].

3 Results

3.1 The CN+CH_2CHCN Reaction

The first step of the CN+CH_2CHCN reaction is the addition of CN to the terminal carbon of the CH_2CHCN molecule, leading, in a barrierless process, to the formation of the MIN1 intermediate. The global exothermicity of the process

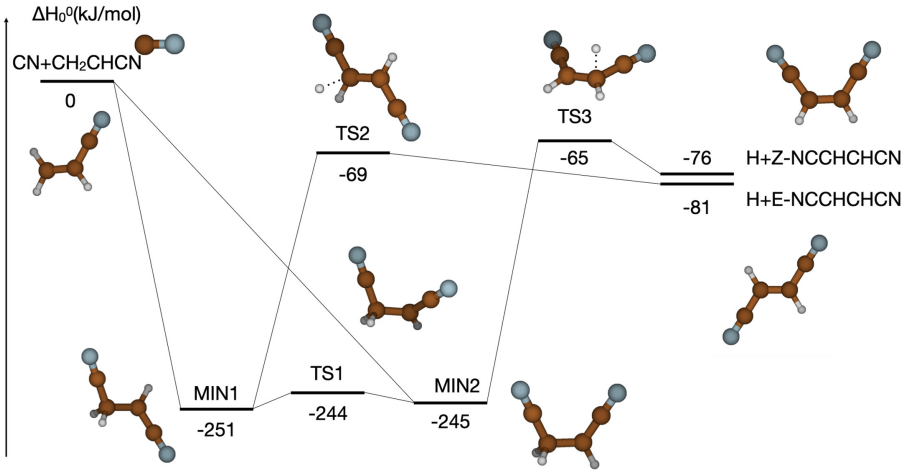

Fig. 1. Two-dimensional representation of the Potential Energy Surface for the reaction CN+CH_2CHCN with the energies evaluated using the B3LYP functional and the aug-cc-pVTZ basis set.

is 251 kJ/mol. Once formed, MIN1 can directly undergo a H-elimination process, forming the E-NCCHCHCN radical. The global exothermicity of the process is 81 kJ/mol, while a barrier of 182 kJ/mol is present in the product channel. The frequency analysis of the transition state, TS2, shows the breaking of a C-H σ bond, with a bond distance of 2.092 Å. Alternatively, the aforementioned MIN1 can isomerize to MIN2, through a rotation around the central C-C bond. A small barrier of 7 kJ/mol is represented by the TS1 transition state. Once formed, MIN2 can lead to the formation of atomic hydrogen, together with the Z-NCCHCHCN radical, located 76 kJ/mol under the energy of the CN+CH_2CHCN reagents. A transition state, TS3, located 65 kJ/mol below the energy of the reactants, was identified for the H-elimination process. A schematic diagram, representing the PES derived for the CN+CH_2CHCN reaction is reported in Fig. 1, while in Fig. 2 are reported the geometry (bond distances in Å) of the most important stationary points, including the CH_2CHCN reactant, evaluated through the previous described DFT calculations. A list of enthalpy changes and barrier heights (in kJ/mol, corrected at 0 K) computed at the same level of theory is reported in Table 1.

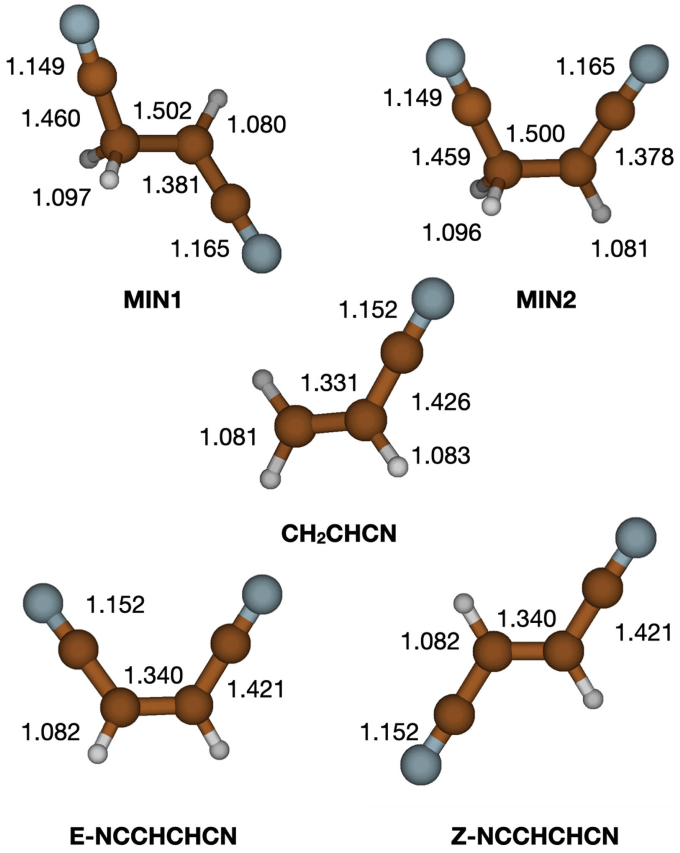

Fig. 2. Bond distances (reported in Angstroms) for some of the most important stationary points identified in the PES for the CN+CH_2CHCN reaction.

3.2 The $N(^2D)$+CH_2CHCN Reaction

The potential energy surface for the $N(^2D)$+CH_2CHCN reaction shows four different minima (MIN1, MIN2, MIN3, and MIN4) linked by three possible transition states (TS4 connecting MIN1 and MIN4; TS1 connecting MIN1 and MIN3, and TS5, connecting MIN3 and MIN2). The first step of the reaction is represented by the barrierless attack of $N(^2D)$ to the C_1=C_2 double bond of the acrylonitrile molecule, leading to the formation of the cyclic intermediate MIN1, located 444 kJ/mol below the reactant energy asymptote. Once formed, MIN1 can directly undergo a H-elimination process. In details, the elimination of a hydrogen atom from the terminal (C_1) carbon atom leads to the formation of the cyclic c-CH(N)CHCN co-fragment, located 255 kJ/mol below the reactant energy asymptote through a barrier of 199 kJ/mol. Alternatively, the cyclic c-CH_2(N)CCN cofragment can be formed through the fission of the C_2-H σ bond, overcoming a barrier of 215 kJ/mol. The global exothermicity of the process is

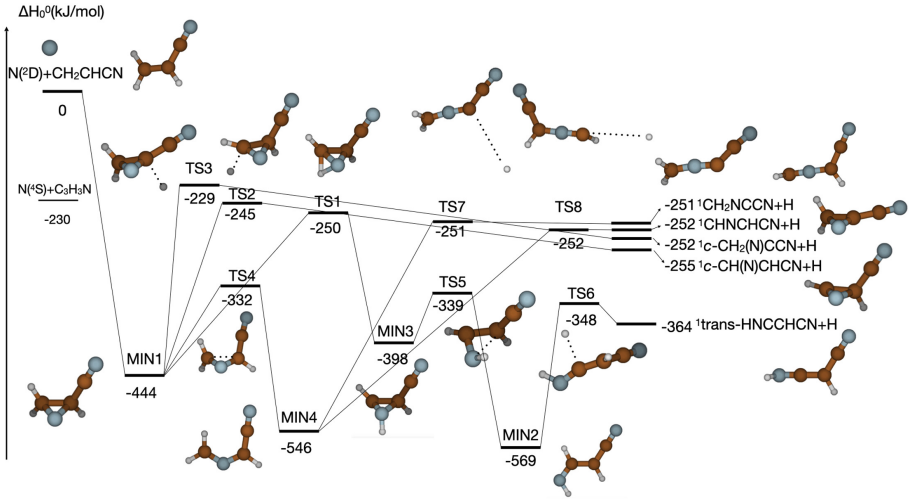

Fig. 3. Two-dimensional representation of the Potential Energy Surface for the reaction N(^{2}D)+CH_2CHCNN with the energies evaluated using the B3LYP functional and the aug-cc-pVTZ basis set.

252 kJ/mol. A different fate for the MIN1 intermediate is represented by isomerization processes. A migration of an H atom leads to the formation of the MIN3 intermediate, through the TS1 transition state. Once formed, the MIN3 intermediate, located 398 kJ/mol below the reactant energy asymptote, can directly isomerize leading to the formation of the MIN2 intermediate, in which the nitrogen atom is inserted in the C_1-H bond of the acrylonitrile molecule. The global exothermicity of the process is 171 kJ/mol, while a barrier of 59 kJ/mol must be overcome. The related transition state, TS5, located 339 kJ/mol below the energy of the reactants, clearly shows the breaking of the C_2-N bond. The elimination of a hydrogen atom from the new formed MIN2 intermediate leads to the formation of the linear co-fragment trans-HNCCHCN, with a relative energy of −364 kJ/mol. A different isomerization process identified starting from the aforementioned MIN1 intermediate is characterized by a ring opening process. The breaking of the C_1-C_2 σ bond of MIN1, indeed, leads to the formation of the linear intermediate MIN4, showing a relative energy of −546 kJ/mol. A barrier of 112 kJ/mol must be overcome during the process, while the related transition state, TS4, clearly shows the breaking of the C_1-C_2 σ bond, with a bond distance of 1.905 Å. Finally two possible H-elimination processes can take place starting from MIN4, leading to the formation of two different combination of products, H+CHNCHCN and H+CH_2NCCN, located 252 kJ/mol and 251 kJ/mol below the reactant energy asymptote, respectively, depending on whether the H-elimination process takes place from the terminal C_1 carbon or from the internal C_2 carbon. Two different transition states were located in the PES for the H-elimination processes, representing a barrier almost equal to

Table 1. List of Enthalpy variations and computed energy barriers (reported in kJ/mol, 0 K) for the CN+CH_2CHCN reaction.

Reaction path	B3LYP/aug-cc-pVTZ	
	ΔH_0^0	Barrier heights
CN+CH_2CHCN → MIN1	−251	–
CN+CH_2CHCN → MIN2	−245	–
MIN1 → MIN2	6	7
MIN1 → H + E-NCCHCHCN	170	182
MIN1 → H + Z-NCCHCHCN	169	180

the energy of the products, related to a weak C-H interaction as can be seen from the bond distances of 4.599 Å and 4.731 Å respectively. A schematic representation of the Potential Energy Surface derived for the N(^{2}D)+CH_2CHCN reaction is reported in Fig. 3, while in Figs. 4, 5 and 6 are reported the geometry (bond distances in $\mathring{A}$) of the most important stationary points evaluated at the B3LYP/aug-cc-pVTZ level of theory. A list of enthalpy changes and barrier heights (in kJ/mol, corrected at 0 K) computed at the B3LYP/aug-cc-pVTZ level of theory is reported in Table 2.

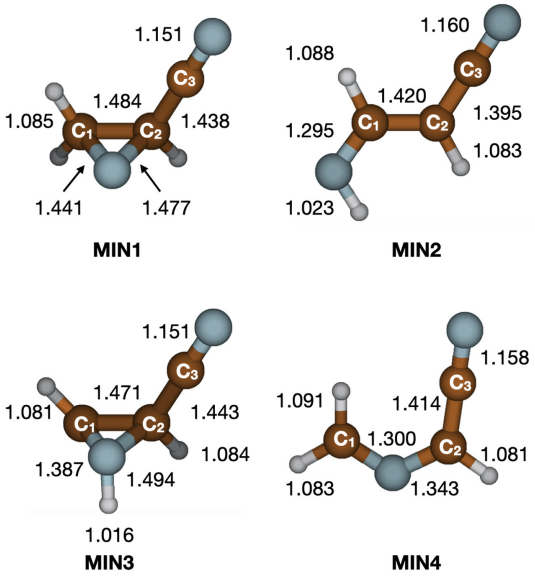

Fig. 4. Bond distances (reported in Angstroms) for the minimum points identified in the PES for the N(^{2}D)+CH_2CHCN reaction.

Table 2. List of Enthalpy variations and computed energy barriers (reported in kJ/mol, 0 K) for the N(^{2}D)+CH_2CHCN reaction.

Reaction path	B3LYP/aug-cc-pVTZ	
	ΔH_0^0	Barrier heights
N(^{2}D)+CH_2CHCN → MIN1	−444	–
MIN1 → MIN4	−102	112
MIN1 → MIN3	46	194
MIN1 → H + ^{1}c-CH_2(N)CCN	192	215
MIN1 → H + ^{1}c-CH(N)CHCN	189	199
MIN4 → H + $^1CH_2NCCN$	295	295
MIN4 → H + ^{1}CHNCHCN	294	294
MIN3 → MIN2	−171	59
MIN2 → H + ^{1}trans-HNCCHCN	205	221

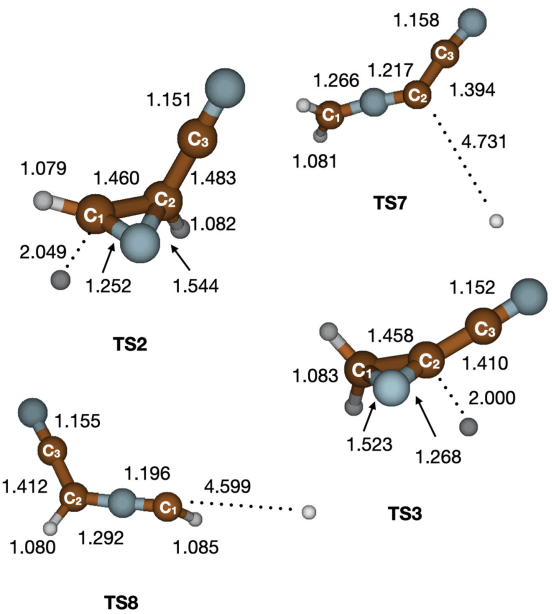

Fig. 5. Bond distances (reported in Angstroms) for transition states identified in the PES for the N(^{2}D)+CH_2CHCN reaction.

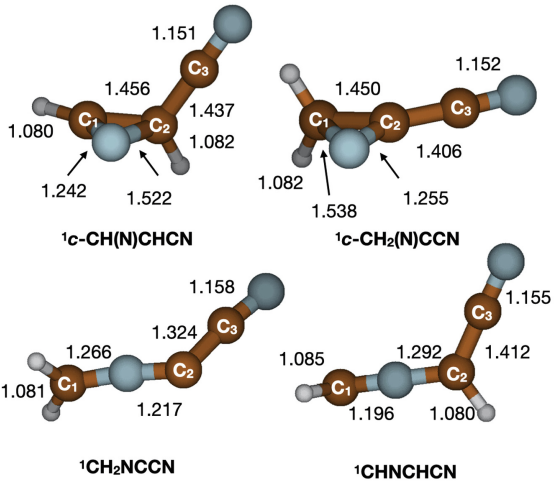

Fig. 6. Bond distances (reported in Angstroms) for the most important products identified in the PES for the $N(^2D)+CH_2CHCN$ reaction.

4 Discussion

The two reactions $N(^2D)+CH_2CHCN$ and $CN+CH_2CHCN$ show some differences, especially considering the initial bimolecular approach. The attack of $N(^2D)$ to the double bond of the acrylonitrile molecule is driven by the high electrophilicity of the nitrogen, attracted by the electron density of the double bond. As a result the $N(^2D)+CH_2CHCN$ reaction, leads to the formation of a cyclic intermediate, characterized by the presence of two C-N bond, involving the two ethylenic carbon atoms, in a cyclic structure. The formation of two main cyclic species is possible, thanks to a H-elimination process directly after the initial attack, depending on wether the hydrogen atom is eliminated from the terminal or internal C atom. Alternatively the C(N)C ring opening process was identified as the responsible of the formation of a linear intermediate, MIN4, which can directly undergo a H-elimination process. A comparison with the reaction of $N(^2D)$ with ethylene (C_2H_4), previously investigated with the same theoretical approach [21], shows several similarities. Nevertheless, in the case of acrylonitrile, the presence of a CN group removes the symmetry of ethylene, leading to an increased number of possible reactive channels and products. Differently, when the co-reactant is the cyano radical, the first step of the reaction is the attack of the CN radical to the terminal carbon of acrylonitrile, leading to the formation of a new C-C σ bond, as shown also from the C-C bond distance of 1.502 Å. Also in this case, several similarities can be noticed with the $CN+C_2H_4$ reaction [37], with the main differences driven by the loss of the symmetry in the acrylonitrile molecule. In general, a complete analysis of the global potential energy surface, including additional channels for the two reactions is needed and will be the focus of future works, including a more accurate

analysis of the energies at the CCSD(T) level of theory [61,62]. The data will be validated considering a comparison with the experimental results, obtained through the such as crossed molecular beams (CMB) apparatus, with the aim to unveil the global reaction mechanism.

5 Conclusions

The present contribution is related to the theoretical investigation of the potential energy surface for the two N(^{2}D)+CH_2CHCN and CN+CH_2CHCN reactions, that are important for the chemistry of planetary atmospheres, in particular in the atmosphere of Titan. Both the N(^{2}D) and the CN addition processes to the CH_2CHCN molecule have been found to be barrierless.

The low temperatures of the atmosphere of Titan represent a harsh chemical environments, where only reactions characterized by the absence of an entrance barrier, together with the presence of stationary points below the reactant energy asymptote, can take place. Following this formalism, the two N(^{2}D)+CH_2CHCN and CN+CH_2CHCN reactions, appears to be feasible and important pathways to add information about the chemistry of nitrogen bearing molecules on Titan's atmosphere. A complete understanding of the overall PES will allow a kinetic analysis in order to derive the rate constants and branching ratios of the two processes. Subsequently, the derived kinetic parameters for the title reactions will be used to improve the chemical models of the atmosphere of Titan.

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