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Previsão de Novos Canais de Reação para o CN + C_2H_2

Resumo: Neste trabalho, apresentamos um estudo da reação do ciano (CN) com a molécula C_2H_2. Mais precisamente, determinamos as geometrias, frequências e energias eletrônicas para as diferentes espécies envolvidas nos caminhos de reação do processo CN + C_2H_2 usando o nível de cálculo M06L/ 6-311++G(d,p). A partir deste estudo, foi possível propor três novos caminhos de reação para este importante processo colisional.

Palavras-chave: Superfície de Energia Potencial; CN; C_2H_2; Reação CN + C_2H_2.

Abstract

In this work, we present a study of the reaction of cyano (CN) with C_2H_2 molecule. More precisely, we determined the geometries, frequencies, and electronic energies for the various species involved in the CN+C_2H_2 reaction pathways at the M06L/6-311++G(d,p) level. From this study, it was possible to propose three new pathways for this important reactive scattering process.

Keywords: Potential Energy Surface; CN; C_2H_2; CN + C_2H_2 Reaction.

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Predicting New Pathways for the Reaction CN + C_2H_2

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1. Introduction

The study of the reaction involving molecules, such as H_2C_2 and CN radical, has been explored over last years in Chemistry.[1-7] Some species, like H_2C_2 and HC_3N, have been found in Titan's stratosphere by photochemistry.[1] Reactions involving CN radical with small unsaturated hydrocarbons are very important in several gaseous media, for instance combustion systems, interstellar clouds and planetary atmospheres rich in N_2/hydrocarbon.[8,9] As an example of their importance in terrestrial environments, there is the role of the CN radical in the complex formation and destruction processes of polluting NO_x species in combustion systems.[10,11] Reactions involving an open-shell atom and a neutral molecule are quite analogous to radical-neutral reactions; these have been studied in the laboratory at, and above, room temperature with mixed results. Among the best studied rapid low-temperature reactions in the laboratory are processes involving the radical CN, a known interstellar molecule, although it is not obvious why these reactions avoid short-range barriers. One such reaction, the CN-acetylene system

$CN + C_2H_2 \rightarrow HC_3N + H$ (1)

$\rightarrow$ C=CNHC +H (2)

$\rightarrow$ HCCNC + H (3)

$\rightarrow C_2H + HCN$ (4)

$\rightarrow C_2H + HNC$ (5)

is possibly an important interstellar reaction because it is assumed to lead to the simplest cyanopolyyne, HCCCN.

1.1 Complexes derived from HC_3N: HC_2NC and C=CNHC Isomers

The ab initio methods are applied to explore the possibility that neutral-neutral reactions lead to the formation of cyanoacetylene **HC_3N** and its isomers **HC_2NC** (HCCNC) and **C=CNHC** (HNCCC) in interstellar space.[7] Even though HCCCN (cyanoacetylene) is known since the beginning of the last century,[12] its isomers are studied experimentally for more than a decade. The rotational transitions of two carbine species: HCCNC (isocyanoacetylene), was detected in interstellar gas clouds[13,14] and in the laboratory.[15,16] These discoveries were followed by the detection of vibrational spectra in the gas phase (HCCNC) and in rare gas matrices.[17,18]

According to Fukuzawa and Osamura the HNCCC and HCCNC molecules are thought to be mainly produced by ion-molecule reactions because of their low abundances. These results have given support to the observed abundance ratio between HCCCN and HNCCC. These reactions contribute to the formation HC_3N interstellar clouds. The researchers concluded that neutral-neutral reactions are very important in the formation of HCCCN but not in that of its isomers.[7]

Experimental work on this system by Sims *et. al.*[19] and previous authors shows that it is quite rapid at room temperature, becomes somewhat more rapid as the temperature is reduced to ≈50 K, and then becomes only slightly less rapid as the temperature is reduced further. The large range indicates that there is no barrier in the potential surface in excess of the zero-point energy of reactants, yet the puzzling temperature dependence indicates something unusual.[5]

In this work, we present a new potential energy profile for the $CN+C_2H_2$ reaction at the M06L/6-311++G(d,p) level. This new finding provides three new pathways for this reaction. The values of the energies showed in SEP are in good agreement compared to Huang *et. al.*[2] and Balucani *et. al.*[3] Moreover, Huang *et. al.*[2] showed in their work an intermediate path in the SEP where they presented the isocyano vinyl molecule, HCCHNC, which participates in the reaction in the *cis* or *trans* forms. In our research, one of the new paths that we found include the HCCHNC molecule as an intermediate product. This evidence about HCCHNC gives us support to believe in the existence of this new path. In the two new pathways we found the presence of the isocyanoacetylene - HCCNC. This molecule participates with complex reactant and complex product. Theoretical and experimental studies[13,14] have confirmed the existence of HCCNC. This leads us to believe in the possibility of the occurrence of reaction of these new channels.

2. Computational Methods

2.1 Ab Initio Calculations

The hybrid density functional M06L method[20] combined with the 6-311++G(d,p) basis set has been employed in our work to optimize the geometries of the reactant, complex reactants, transition states, complex products and products of the $CN+C_2H_2$ reaction.

The M06L is a local functional and its location allows the use of highly efficient algorithms to reduce the cost in computation time for large systems. The M06L functional is very suitable for application in thermochemistry, transition metal and has a better performance than B3LYP for main-groups in thermochemical, large barriers and non-covalent interactions.[21]

Vibrational frequencies calculated at M06L level were used for characterization of stationary points as minima and transition states, for zero-point energy (ZPE) corrections, because it is known that the ZPE value is significant in hydrogen-bonded systems.[22] The number of imaginary frequencies (0 or 1) indicates whether a minimum or a transition state has been located. To confirm that the transition state really connects with designated intermediates along the reaction path, the intrinsic reaction coordinate (IRC) calculations were performed. Also, the intrinsic reaction coordinate (IRC)[23] calculations were used to confirm the connection between the designated transition states and the reactants or products. All quantum chemistry calculations were performed with Gaussian 09 program. The relative energies (the total energy of the reactants is set to zero for reference) of all species involved at the M06L (pure functional) level are summarized in Figure 1.

3. Results and Discussion

3.1. Potential Energy Profile and Reaction Mechanism

Figure 1 shows the potential energy profile of the $CN+C_2H_2$ reaction, while the optimized geometries of the species involved in this profile are presented in Figure 2. These results are in close agreement with Huang *et. al.*[2] and Balucani *et. al.*[3] Huang *et. al.* display a simplified doublet C_3H_2N potential energy profile and feasible exit channels to C_3HN isomers. The CN radical attacks the electron density of two perpendicular molecular orbitals without an entrance barrier to form a cis and trans cyanovinyl radicals HCCHCN.[3] Following, we make a discussion of the possible reaction pathways presented in Figure1.

In Figure 1, we show the $CN+C_2H_2$ reaction with the following products: HC_3N + H, C=CNHC+H, HCCNC + H, C_2H + HCN and C_2H + HNC. For the HC_3N + H we have some possible pathways. The first candidate for this product is CN + C_2H_2 → cys – HCCHCN → TS3 → HC_3N + H. In this pathway the cys – HCCHCN participates as reactant with energy of -240 kJ mol^{-1}. The other channel that forms the same product is $CN+C_2H_2$ → cys – HCCHCN → TS1 → trans – HCCHCN → TS4 → HC_3N + H. The cyanovinyl radical, trans - HCCHCN, participates like an intermediate product of the channel with -240 kJ mol^{-1}. Finally, the last candidate to form HC_3N + H CN + C_2H_2 → cys–HCCHCN → TS1→ trans – HCCHCN → H_2CCCN → TS5 → HC_3N + H. In this pathway, the trans – HCCHCN participates as reactant and for the complex product we have H_2CCCN with -291 kJ mol^{-1} of energy. For the product C=CNHC we have the following: CN + C_2H_2 → cys – HCCHCN → TS1→ trans – HCCHCN → TS6 → HCCHNC → C=CNHC + H with an energy of 5 kJ mol^{-1} for the HCCHNC and 389 kJ mol^{-1} for the hydrogen abstraction, C=CNHC + H. In the construction of the product HCCNC + H two pathways can be taken. The first one is CN + C_2H_2 → cys – HCCHCN → TS1 → trans – HCCHCN → TS8 → HCCNC + H and the second CN + C_2H_2 → cys–HCCHCN → TS1 → trans – HCCHCN → TS6 → HCCHNC → TS7 → HCCNC + H. Both pathways lead to the same product with energy of 10 kJ mol^{-1}. Finally, for the last two channels of the potential energy profiles we have: CN + C_2H_2 → TS9 → C_2H + HCN and CN + C_2H_2 → C2H + HNC. For these pathways we have energy of 34 kJ mol^{-1} for the product

C_2H + HCN and 99 kJ mol^{-1} for the product C_2H + HNC.

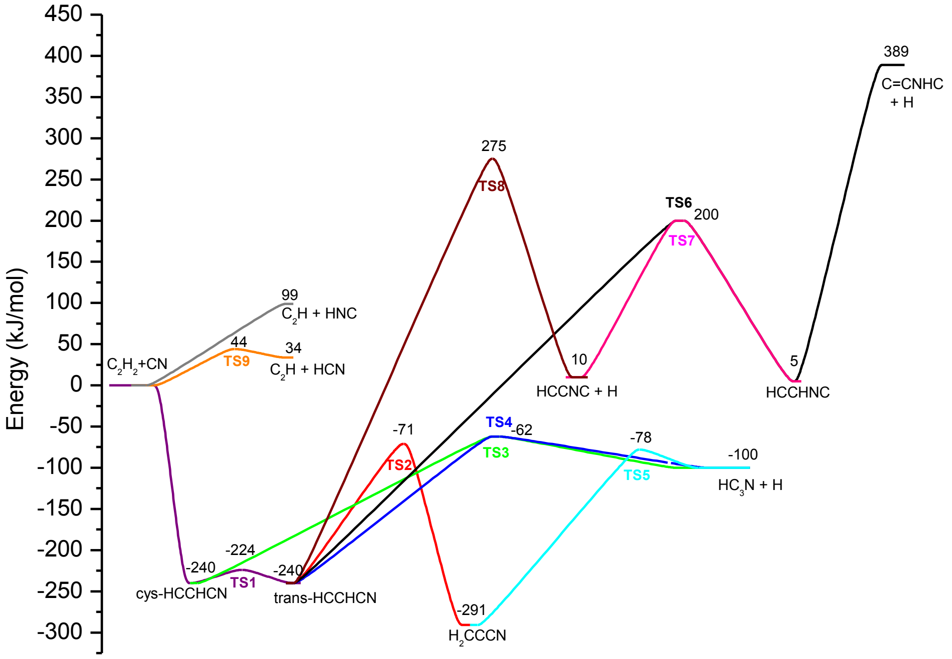

Figure1. Potential energy diagram for decomposition of CN+C_2H_2 reaction at the M06L/6-311++G(d,p) level

3.2. CN + C_2H_2 → HC_3N + H

In this channel both initial collision complexes are stabilized by 240 kJ mol^{-1} in relation to the separated reactants. Balucani *et. al.*[3] found 242 kJ mol^{-1} for this pathway. Both complexes show a C-H bond separate to form cyanoacetylene, HCCCN, and a hydrogen atom.

The product of channel 1, trans form, participates as reactant in the pathway 2 to form H_2CCCN. In this channel we have a barrier of 169 kJ mol^{-1}. RRKM calculations show that 15% of the collision complexes depict an H atom migration via barrier of 177 kJ mol^{-1} forming the doublet H_2CCCN radical.[3] For Balucani[3], this intermediate is stabilized by 288 kJ mol^{-1} in relation to the reactants – which represents the global minimum of the C_3H_2N potential energy profile - and decays via H atom emission to the HCCCN isomer. In our work, this intermediate is stabilized by 291 kJ mol^{-1}. Our result for production of HC_3N + H (100 kJ mol^{-1}) are agreement with Balucani *et. al.*[3] (94 kJ mol^{-1}).

3.2. CN + C_2H_2 → C=CNHC +H and CN + C_2H_2 → HCCNC + H

In our study, we found for this reaction the product C=CNHC (HNC_3) + H and the isomer isocyanoacetylene, HCCNC, with energy of 10 kJ mol^{-1} for the product HCCNC + H and 389 kJ mol^{-1} for the C=CNHC + H. The HCCNC + H has two different possible reactants, HCCHCN and HCCHNC, with the energies of -240 kJ mol^{-1} and 5 kJ mol^{-1} respectively. The HCCHNC isomer also participates as a reactant in the formation of C=CNHC + H. Balucani *et. al.* in their detailed investigation about CN + C_2H_2 argument that the isocyanoacetylene isomer is not formed, as its formation is endothermic by 13 kJ mol^{-1} and their investigation did not show this isomer.[3] Detection of HCCNC originating from the CSE surrounding IRC10216 has important implications for the chemistry producing HC_3N and its isomers.[24] A number of chemical reaction schemes has been proposed for producing HC_3N and the other cyanopolyynes in the CSE surrounding IRC10216.[24] Kawaguchi et. al. detected HCCNC and HNCCC, two isomers of HC_3N, in TMC-1.[13,14] Models of circumstellar chemistry a search was made for the HCCNC isomer of HC_3N toward IRC10216.[16]

3.3. CN + C_2H_2 → C_2H + HCN and CN + C_2H_2 → C_2H + HNC

In this reaction, an H atom is abstraction by CN to form HCN plus C_2H or HNC plus C_2H. According to Balucani, this abstraction of H atom by CN is energetically feasible in cold molecular clouds, as both reactions are endothermic by 23 and 83 kJ mol^{-1} and must pass barriers of 41 and 96 kJ mol^{-1} and that in the outer atmosphere of old dying carbon stars such as IRC + 10216 the enhanced kinetic energy of the reactants in the of the Maxwell-Boltzmann distribution might be sufficient to overcome the barriers to form the HCCNC isomer or HNC/HCN in these high-temperature enviroments[3].

We can find two products, C_2H + HCN and C_2H + HNC, in the Huang investigation with the energies of 23 kJ mol^{-1} and 83 kJ mol^{-1} respectively.[2] In our work, we have shown only the path C_2H + HCN and our calculation show a barrier of 10 kJ mol^{-1} with energy of 33 kJ mol^{-1} for the product C_2H + HCN. We did not find barrier to formation of the C_2H + HNC.

Table 1 shows the values of the frequencies and zero-point energy (ZPE) of the reactant, transition states and products of species studied and they are also compared with the experimental and theoretical reference data.

Table1. Frequencies (cm^{-1}) and zero-point energy (kJ/mol) for the species involved in the reaction of C_2H_2 +CN, calculated at the M06L/6-311++G(d,p)

Species	Vibrational wavenumbers (cm^{-1})	References	ZPE (kJ/mol)
C_2H_2	580.3,580.3, 801.1, 801.1, 2075.2151, 3399.7822, 3508.2	(612, 730, 1974,3289, 3374)[25]	70.26
CN	1957.4	2069[26]	11.71
TS1	1016.1□, 264.1, 221.1, 334.2, 422.6, 569.6, 844.4, 905.0, 2005.7, 2339.9, 3033.6, 3540.7		77.13
TS2	778.8□, 236.8, 367.3, 580.7, 681.1, 792.6, 980.7, 1295.6, 1690.4, 2388.1, 3075.0, 3467.6		93.05
TS3	862.4□, 270.9, 271.9, 452.9, 565.7, 570.1, 631.1, 694.6, 912.3, 2069.0, 2336.2, 3436.8		73.94
TS4	862.6□, 271.1, 272.0, 453.0, 565.8, 569.7, 631.1, 694.7, 912.1, 2069.0, 2336.1, 3436.7		73.94
TS5	195.5□, 112.2, 162.1, 403.9, 425.9, 598.8, 705.4, 825.3, 936.7, 1998.2, 3463.5, 6610.1		97.15
TS6	850.9□, 187.9, 193.9, 544.4, 598.1, 763.4, 993.8,		87.65

	1333.2, 1462.9, 1988.7, 3270.9, 3316.4		
TS7	850.9□, 187.9, 193.9, 544.4, 598.1, 763.4, 993.8, 1333.2, 1462.9, 1988.7, 3270.9, 3316.4		87.65
TS8	1244.6□, 240.9, 250.2, 646.8, 670.1, 949.4, 994.5, 1239.3, 1489.6, 1819.5, 2032.2, 3487.7		82.66
TS9	1701.9□, 52.3, 194.6, 194.8, 438.0, 487.5, 487.9, 807.2, 807.3, 2093.1, 2268.2, 3420.3		67.29
cys – HCCHCN	225.9, 364.7, 534.6, 708.1,885.6, 894.5, 1028.9, 1292.2, 1683.8, 2386.8, 3168.4, 3294.7		98.50
H$_2$CCCN	189.4, 287.5, 486.4,585.1, 855.6, 917.5, 1009.0, 1444.1, 1749.9, 2199.2, 3120.2, 3225.7		96.12
trans – HCCHCN	241.7, 355.1, 558.7, 698.9, 806.3, 850.3, 1015.7, 1273.8, 1657.1, 2389.9, 3135.9, 3280.3		97.28
HC$_3$N	223.2, 490.3, 491.1, 683.6, 694.3, 883.1, 2147.5, 2384.1, 3486.9	(1852.8, 2175.8, 3196.5)[27,a] (715,893,1852,2169,3208)[27,b] (241, 551, 715,910, 2191,2398, 3472)[28,c]	68.69 67.66[12,d]
HCCHNC	222.6, 366.6, 560.7, 620.8, 684.2, 687.2, 989.0, 1331.5, 1455.2, 2238.8, 3278.4, 3472.1		95.15
HCCNC	235.4, 368.1, 492.2, 638.9, 643.2, 977.1, 2087.2, 2287.8, 3455.9	(203, 424, 634, 945, 2093, 2286, 3472)[29]	66.90 66.32[12]
C=CNHC	173.1, 278.9, 364.1, 644.9, 883.6, 1023.6, 1516.5, 1867.1, 3527.9	(180, 191, 461, 593, 596, 965, 1958, 2293, 3715)[18,e]	61.48
C$_2$H	1300.3, 2069.5, 3420.6	(1846, 3611)[30,a] (570, 1975, 3346) [31]	48.48
HCN	768.0, 768.1, 2165.1, 3404.7	(712,2097, 3311)[26]	42.50
HNC	537.5, 537.4, 2084.7, 3767.5	(462.72,2023.86, 3652.65)[32,33]	41.43

[a] Experimental Data. [b]B3LYP/6-311++G(3d,3pd). [c]PBE0/aug-cc-pVTZ. [d]B3LYP/aug-cc-pVTZ (see Ref. 12). [e] B3LYP/6-311++G(d,p) with scaling factor 0.96.

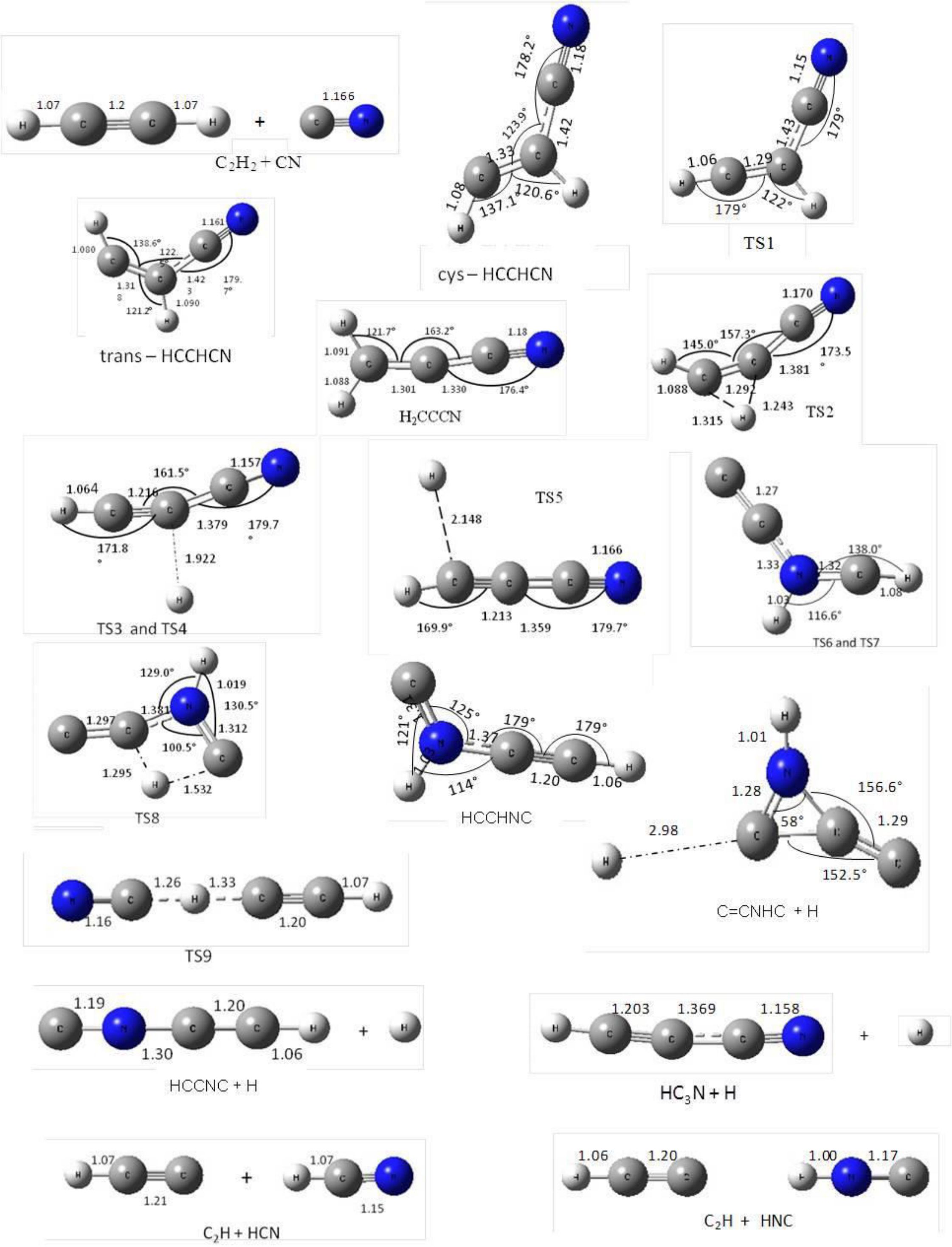

Figure 2. Optimized geometries for the various species involved in the C_2H_2 +CN reaction pathways at the M06L/6-311++G(d,p) level. The units for bond lengths and bond angles are Å and degrees, respectively

4. Conclusions

In this work, the CN+C_2H_2 reaction potential energy profiles were determined based on the geometrical optimization, frequency and energy calculations at the M06L/6-311++G(d,p) level. Our results predicted three new pathways for the CN + C_2H_2 reaction, two of them given by CN + C_2H_2 → cys – HCCHCN → TS1 → trans – HCCHCN → TS8 → HCCNC + H and the other pathway to same product is given by CN + C_2H_2 → cys – HCCHCN → TS1 → trans – HCCHCN → TS6 → HCCHNC → TS7 → HCCNC + H. The third pathway is given by CN + C_2H_2 → cys – HCCHCN → TS1 → trans – HCCHCN → TS6 → HCCHNC → C=CNHC + H. The same HCCNC product was found in Huang's potential energy profile, but with a different pathway. Huang's product energy value was about 13 kJ mol^{-1} at B3LYP/6-311G(d,p). This value is in good agreement with the value found in the present work (about 10 kJ mol^{-1}). The C=CNHC + H product was not predicted by Huang's potential energy profile and Balucani's work but it was found in the present work. Finally, our study found no barrier for the CN + C_2H_2→ C_2H + HNC channel. This is in disagreement with the Huang's results that found a barrier c.a of 13 kJ mol^{-1}.

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