

The Reaction of the Methylidyne Radical (CH X²Π) with the Hydrogen Cyanide (HCN X¹Σ⁺) Molecule in Cold Molecular Clouds and Planetary Atmospheres

Lubov I. Krikunova^{1,2*}, Anatoliy A. Nikolayev^{1,2}, Denis P. Porfirev^{1,2}, and Alexander M. Mebel³

¹Lebedev Physical Institute, 221 Novo-Sadovaya str., Samara 443011, Russia

²Samara National Research University, 34 Moskovskoe shosse, Samara 443086, Russia

³Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th str., Miami, Florida 33199, USA

* e-mail: lubov13markova@gmail.com

Abstract. The reaction of the methylidyne (CH; X²Π) radical with hydrogen cyanide (HCN; X¹Σ) molecule was studied at a collision energy of 4.0 kJ/mol with ab initio calculations of the potential energy surface (PES). Geometries and potential energies of reactants, products, intermediates and transition states (TS) for the reaction were found by means of ab initio quantum chemical method ωB97xd/cc-pVTZ and the higher-level corrections were evaluated at the CCSD(T)-F12 level of theory with the cc-pVQZ-f12 (*E*₁) and cc-pVTZ-f12 (*E*₂) basis sets. The calculated values then were used for extrapolation to the complete basis set (CBS) limit using the two-point expression $E(CBS) = E_1 + 0.69377 \times (E_1 - E_2)$. Analysis of the found energies, structural and kinetic characteristics of the involved compounds allowed us to determine the reaction paths leading to the formation of linear and cyclic intermediates, as well as to the formation of atomic and molecular hydrogen. Those results were utilized in Rice–Ramsperger–Kassel–Marcus calculations of the product branching ratios at the zero pressure limit – common approach in modelling of the cold molecular clouds chemistry. Mechanism identified emphasizes importance of the CH+HCN reaction as an important supplier of the initial bricks for building heterocyclic hydrocarbons in extreme environments. © 2022 Journal of Biomedical Photonics & Engineering.

Keywords: potential energy surface; rate constants; density functional theory; methylidyne; hydrogen cyanide; cyanomethylidyne; cyanomethylene.

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1 Introduction

A wide variety of chemical elements and even complex molecular compounds, including organic ones, were found in space using spectroscopy methods [1]. Carbon, nitrogen, and hydrogen atoms are common constituents of interstellar clouds and planetary atmospheres. Among the complex molecules there are “prebiotic” compounds, such as aminoacetonitrile, which can participate in the formation of glycine, the simplest amino acid. Ribose, the basis of organic life, can also be formed in molecular clouds [2]. If such compounds fall into favorable

conditions, this will already be precursors for the emergence of life.

The methylidyne radical (CH, X²Π) represents the simplest organic radical, highly reactive and able to interact with neutral molecules [3]. It plays an important role in various chemical environments ranging from the hydrocarbon combustion, dense interstellar clouds, and in planetary atmospheres. Since the very first detection of the methylidyne radical in the interstellar medium in 1937, methylidyne has been dubbed “ubiquitous” in deep space and has been observed toward diffuse clouds namely ζ Per [4], molecular clouds like TMC-1 [5, 6],

and star forming regions such as SgrB2 [7–10]. Reactions involving the CH radical provide one of the ways to synthesize long hydrocarbons and complex organic molecules in dense interstellar clouds and planetary atmospheres [11].

Methylidyne is the result of the photodissociation of methane in the Lyman series Ly- α line. Methane is known to be present in appreciable amounts in interstellar clouds. The decay of methane, either by absorbing photons or colliding with energetic particles, begins a complex chemical evolution that can form cyclic and linear organic molecules. The fact that low-temperature experimental rate constants for various reactions of CH with organic molecules are typically on the order of 10^{-10} cm³ mol⁻¹ s⁻¹ suggests that the CH radical is indeed sufficiently reactive for its reactions with the hydrogen cyanide molecule to be significant both in cold molecular clouds, and in the planetary atmospheres [12]. Thus, the experimental temperature dependence of the total rate constants of the reactions of methylidyne with unsaturated organic molecules suggests that these reactions proceed without any barriers. Since the CH radical has a high enthalpy of formation, 596.40 kJ/mol, there are many thermodynamically accessible channels for the reactions of the methylidyne radical with unsaturated organic molecules. The identification of products and the determination of their branching factors are particularly important for obtaining reliable simulations of complex chemistry such as interstellar chemistry [11].

2 Computational methods

The long-range corrected hybrid density functional ω B97xd [13, 14] with the cc-pvtz [15] basis set was used for geometry optimization of different species on the C₂H₂N potential energy surface (PES) accessed by the methylidyne plus hydrogen cyanide molecule reaction, including the reactants, products, intermediates, and transition states (TS). The same ω B97xd/cc-pvtz level of theory was then employed to compute vibrational frequencies for each stationary structure. The frequencies were utilized in the evaluation of zero-point vibrational energy corrections (ZPE) and in the calculations of rate constants. In order to obtain chemically accurate relative energies of various species on the C₂H₂N PES, the explicitly correlated couple clusters method with single and double excitations and with perturbative treatment of triple excitations CCSD(T)-F12 [16, 17] in conjunction with Dunning's correlation-consistent cc-pVTZ-f12 and cc-pVQZ-f12 basis sets was used to refine single-point energies of all optimized structures. The final energies of all structures were extrapolated to the complete basis set (CBS) [18] limit using the two-point expression:

$$E(\text{CSB}) = E_1 + 0.69377 \times (E_1 - E_2), \quad (1)$$

where

$$E_1 = E(\text{CCSD}(T) - \text{F12} / \text{cc} - \text{pVTZ} - f12), \quad (2)$$

$$E_2 = E(\text{CCSD}(T) - \text{F12} / \text{cc} - \text{pVQZ} - f12).$$

Relative energies are anticipated to be accurate within 1 kcal/mol or even better [19]. The GAUSSIAN 09 [20] and MOLPRO 2010 [21] quantum chemistry software codes were used for the *ab initio* calculations.

The Rice–Ramsperger–Kassel–Marcus (RRKM) approach utilizing the energetic and molecular parameters from the electronic structure calculations was employed to evaluate energy-dependent rate constants for all unimolecular reaction steps taking place on the C₂H₂N PES following the initial bimolecular association stage [22]. In the calculations of the energy-dependent rate constants, the internal energy for each C₂H₂N intermediate or transition state was assumed to be equal to the sum of the collision and chemical activation energies, where the chemical activation energy is a negative of the relative energy of the species relative to the separated methylidyne plus hydrogen cyanide reactants. Rate constants were evaluated as functions of the available internal energy of each intermediate or transition state within the harmonic approximation using ω B97xd/cc-pVTZ frequencies and employing our in-house code Unimol [23, 24]. Unimol is an updated version of our previous software code on energy dependent RRKM calculations of rate constants for multiwell and multichannel unimolecular reactions under single-collision conditions and for solving a system of first-order kinetic equations. Unimol automatically processes GAUSSIAN 09 log files to compute numbers of states for transition states and densities of states for local minima employing the direct count method. The internal energy is assumed to be equal to the sum of the collision energy and the chemical activation energy, that is, negative of the relative energy of a species with respect to the reactants. Only one energy level is considered throughout as at a zero-pressure limit corresponding to crossed molecular beams conditions. RRKM rate constants are then used to compute product branching ratios by solving first-order kinetic equations within steady-state approximation.

3 Results & Discussion

3.1 Initial adducts

Initial adducts are listed in Fig. 1.

The barrierless reactions are initiated through addition of the methylidyne radical to the nitrogen atom of the hydrogen cyanide molecule with the intermediate w1 (−41.8 kcal/mol) formation. An alternative way is methylidyne radical addition to the carbon atom of the hydrogen cyanide molecule with the intermediate w2 (−53 kcal/mol) formation. As a result of the methylidyne radical addition to the triple C–N bond of the hydrogen cyanide molecule the cyclic intermediate w3 is formed

(-50.4 kcal/mol). The intermediate w4 (-104.5 kcal/mol) can be formed if the methylidyne radical inserts into the C–H bond of the hydrogen cyanide molecule.

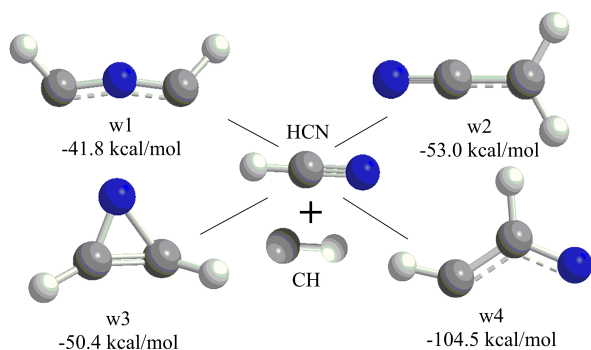


Fig. 1 Initial adducts in the barrierless reaction.

Studied reactions of the methylidyne radical with organic molecules demonstrate that a ratio in the entrance channels of multiple bond addition and C–H bond insertion of about 85:15, which can be understood in terms of a reduced cone of acceptance of the C–H σ -bond compared to the π electrons of the multiple bond [25]. There are the similar reaction dynamics mechanisms in the CH+HCN reaction, suggesting that methylidyne radical addition to the carbon or nitrogen atom or C–N triple bond of HCN is likely the dominant entrance channel [12].

3.2 Potential energy surface

Simplified complete PES diagram (Fig. 2) demonstrates the most energetically favorable reaction paths. Detailed molecular structures are presented in Fig. 3. The PES could be partitioned into two branches leading towards linear or cyclic structures. The first one mostly stems

from w4 (-104.5 kcal/mol) intermediate and its predecessor w2 (-53.0 kcal/mol), which are connected through transition state b2 with relative to reagents energy of -9.9 kcal/mol. There are three possible paths from w4. The first two ones are direct hydrogen atom/molecule losses. Elimination of H-atom is barrierless and results in formation of cyanomethylene (product p1: -0.6 kcal/mol). Hydrogen molecule separation requires to overcome b2 barrier, which relative energy is 3.6 kcal/mol less than that of p1, and leads to cyanomethylidyne (product p2: -12.2 kcal/mol). The third way includes additional step – bend of the CCN chain $w4 \rightarrow b6 \rightarrow w6$, with barrier of -52.8 kcal/mol in forward and -2.1 kcal/mol in backward directions. Then the nitrogen atom could be inserted between carbon atoms through low energy barrier b8: only -1.1 kcal/mol to form w9 (-81.1 kcal/mol) and -28.6 kcal/mol to activate reverse transformation. The second branch of the PES starts in w1 (-41.8 kcal/mol) which precedes cyclic intermediate w3 (-50.4 kcal/mol). That triangular structure could be transformed into aforementioned w9 by shifting of H-atom from one carbon to another and simultaneous cleavage of CC-bond, which possesses moderate for the PES barrier b5 of -41.9 kcal/mol in $w3 \rightarrow w9$ direction and relatively high one of -72.6 kcal/mol for the reverse step. Path to another cyclic molecule w7 (-25.9 kcal/mol) branches off after hydrogen jump from one of the carbon atoms to nitrogen $w3 \rightarrow b3 \rightarrow w5$. Barrier for that isomerization is of 33.5 kcal/mol, which is more than 4 times higher than for the reverse step (8.1 kcal/mol). Two paths lead to w7. The first one is immediate cycle reclosure $w5 \rightarrow b7 \rightarrow w7$ with low barrier of 6.1 kcal/mol to overcome. The second transformation includes additional NH-group shift $w5 \rightarrow b4 (-13.1$ kcal/mol) $\rightarrow w8 (-72.6$ kcal/mol) $\rightarrow b9 (-10.3$ kcal/mol) $\rightarrow w7$.

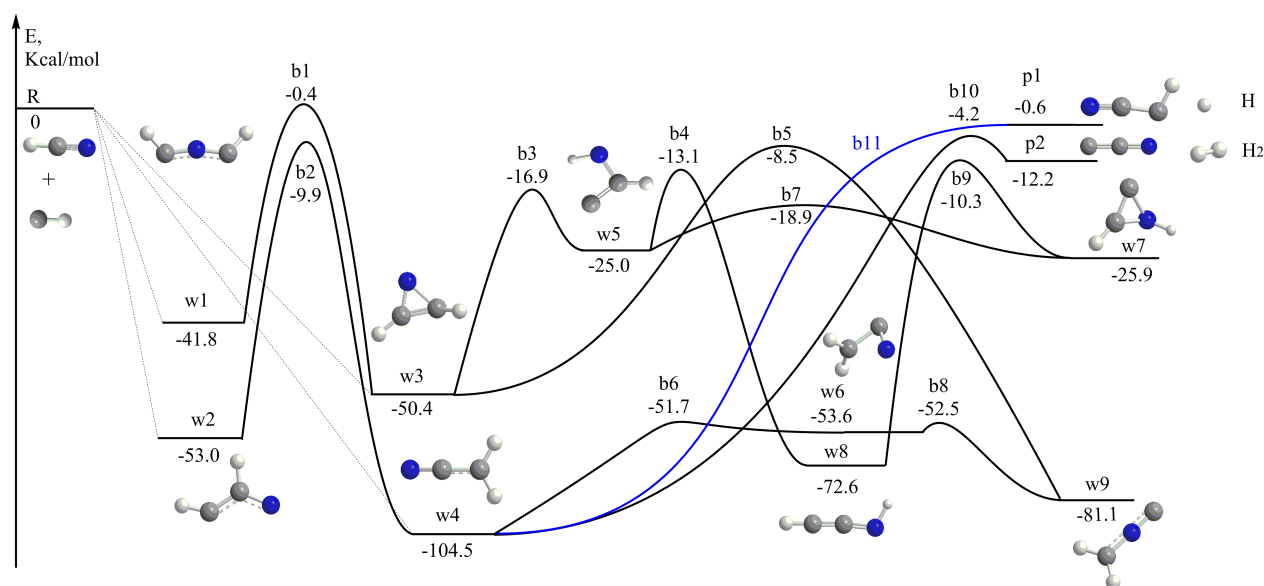


Fig. 2 The HCN+CH reaction potential energy surface.

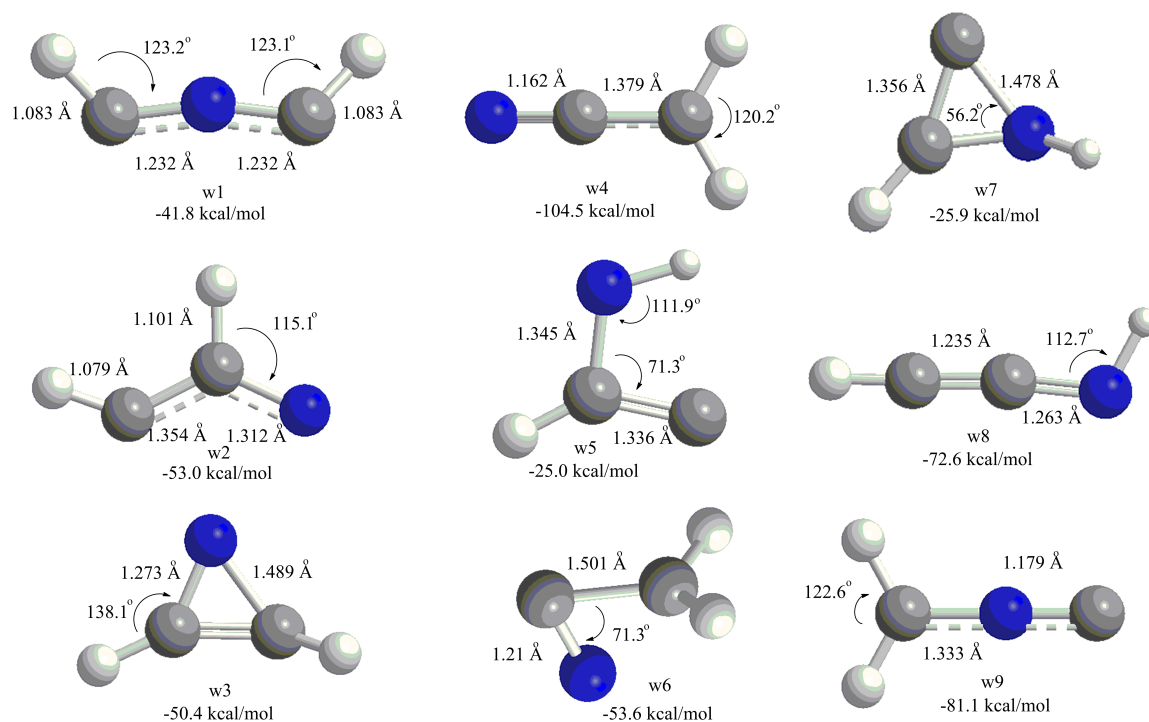


Fig. 3 Detailed molecular structures of intermediates of interest.

From the PES, we can infer that stabilization in the w8-well should not play an important role in the whole dynamics, because of energetically favorable direct step $w5 \rightarrow w7 \rightarrow w8$, which also possesses significantly lower barriers to proceed. Regarding products, entropically factors play in favor of cyanomethylene production, whereas it requires slightly more energy. Thus, the final answer about relative yields of those molecules could be given only after kinetic calculations.

3.3 Rate constants

Rate constants evaluated are listed in Table 1. As predicted, steps $w8 \rightarrow w5$ and $w8 \rightarrow w7$ are one of the slowest. However, stabilization still could make some impact, because the rate constants for $w5 \rightarrow w8$ and $w5 \rightarrow w7$ isomerizations are of the same order. The rate constant of p1-formation from w4 adduct is more than two times higher than one for p2.

Table 1 Rate constant.

Step	k , s^{-1}	Step	k , s^{-1}
$w4 \rightarrow p1$	$5.08E+10$	$w3 \rightarrow w9$	$6.44E+10$
$w4 \rightarrow p2$	$2.37E+10$	$w9 \rightarrow w3$	$3.04E+09$
$w8 \rightarrow w7$	$2.35E+09$	$w5 \rightarrow w8$	$2.30E+12$
$w7 \rightarrow w8$	$1.89E+12$	$w8 \rightarrow w5$	$4.22E+09$
$w9 \rightarrow w6$	$9.73E+11$	$w3 \rightarrow w5$	$2.53E+11$
$w6 \rightarrow w9$	$3.26E+13$	$w5 \rightarrow w3$	$3.03E+12$
$w5 \rightarrow w7$	$3.95E+12$	$w2 \rightarrow w4$	$8.88E+09$
$w7 \rightarrow w5$	$5.82E+12$	$w4 \rightarrow w2$	$6.40E+09$
$w6 \rightarrow w4$	$2.65E+13$	$w1 \rightarrow w3$	$3.39E+09$
$w4 \rightarrow w6$	$7.61E+11$	$w3 \rightarrow w1$	$5.23E+09$

Corresponding statistical yields were determined using RRKM theory. Since the initial adducts w1–w4 can rearrange to each other via barriers that are lower than dissociation barriers, the resulting product branching ratios from RRKM calculations appear to be practically independent of the initial intermediate. RRKM theory predicts the HCCN product (p1) along with atomic hydrogen to be the most likely product (~68.2%) followed by the CCN (p2) product along with molecular hydrogen (~31.8%).

4 Conclusion

The reaction of the unsaturated hydrogen cyanide molecule HCN with the methylidyne radical CH was studied. Because of the highly reactive nature of methylidyne, the reaction does not have entry barriers. Moreover, the relative energy of every intermediate, product and transition state on the presented PES is lower than that of reactants. Moreover, relative energy of every intermediate, product and transition state on the presented PES is lower than that of reagents. Which allows us to state, that proposed mechanism is feasible even in cold interstellar media. Simple one- or two-step paths leading towards the growth of linear molecules are revealed. Formation of the first one, cyanomethylene, significantly outstrips that of the runner-up, cyanomethylidyne, with relative yields ~68.2% and ~31.8% respectively. Investigated reaction could be treated as the first step of chemical evolution resulting in the formation of organic compounds from the simplest molecules. These organic species can in turn trigger reactions that generate polycyclic organic compounds, which can be considered as an initial stage of abiogenesis leading to the synthesis of the most basic amino acids.

Disclosures

All authors declare that there is no conflict of interests in this paper.

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