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Theoretical study on the mechanism of the cycloaddition reaction between ketenimine and hydrogen cyanide

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Abstract: The mechanism of the cycloaddition reaction between the interstellar molecules ketenimine and HCN was investigated employing the second-order Møller–Plesset perturbation theory (MP2) method in order to understand better the reactivity of the nitrogenous cumulene ketenimine with the carbon–nitrogen triple bond compound HCN. Geometry optimizations and vibrational analyses were performed for the stationary points on the potential energy surfaces of the system. The calculated results showed that five-membered cyclic carbene intermediates could be produced through pericyclic reaction processes between ketenimine and HCN. Through subsequent H-transfer processes, the carbene intermediates could isomerize to pyrazole and imidazole compounds. The present study is helpful in the understanding of the formation of prebiotic species in interstellar space.

Keywords: ketenimine; pericyclic reaction; interstellar molecule; pyrazole; imidazole.

INTRODUCTION

Ketenimine, $CH_2=C=NH$, has attracted a lot of attention as a reactive intermediate in organic chemistry[1] and astrochemistry.[2] Jacox *et al.* predicted in 1963 that ketenimine was tentatively identified as a product of the reaction of the imidyl radical (NH) with acetylene ($HC\equiv CH$) in solid argon.[3] In 1979, Jacox accomplished the first spectroscopic identification of ketenimine in a matrix isolation study of the products from the reaction of excited argon atoms with CH_3CN.[4] The first study of ketenimine in the gas phase by microwave spectroscopy was reported by Rodler *et al.* in 1984, in which 2-cyanoethanol ($HOCH_2CH_2CN$) was pyrolized at 800 °C to form ketenimine.[5]

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Ketenimine was detected in the absorption toward the star-forming region Sagittarius B2(N) with a radio telescope. Ketenimine is likely formed directly from its isomer methyl cyanide (CH_3CN) by tautomerization driven by shocks that pervade the star-forming region and it is a compact and relatively abundant species in Sgr B2(N).[2] Therefore, lots of theoretical and experimental investigations have been employed to study the formation of ketenimine in the interstellar medium. Balucani *et al.* reported combined crossed beam and theoretical studies of the $N(^2D)+C_2H_4$ reaction and implications for atmospheric models of Titan.[6] They verified ketenimine as one of the main products in this reaction. In consideration that nitriles were detected in Titan's atmosphere, in the cometary comae and the interstellar medium, Hudson and Moore reported laboratory investigations of the low-temperature chemistry of some nitriles. In the absence of water, ketenimine is one of the photo and radiation chemical products of these nitriles.[7] Aminoacetonitrile, a species of astrochemical interest, was detected in the interstellar medium. The reaction of aminoacrylonitrile with Ni^+ was investigated by means of mass spectrometry techniques and density functional theory calculations and ketenimine was found to be one of the main products of this reaction.[8] Using Fourier transform infrared spectroscopy, ketenimine was trapped and identified when CH_3COCN was irradiated in an argon matrix at extremely low temperatures.[9]

As an unstable nitrogenous cumulene, ketenimine can react with unsaturated compounds to form heterocyclic compounds. Song *et al.*[10] investigated the cycloaddition reaction between ketenimine and cyclopentadiene by several theoretical methods and determined that the activation energy of this reaction is 156.5 kJ mol^{-1} using the G3B3 method. Fang and Li studied the formation of four-membered compounds through stepwise cycloaddition reactions between ketenimine and olefins by an *ab initio* method.[11] In addition, Sun *et al.*[12] reported the reaction between ketenimine and water, acetamide being the final product formed by tautomerization. Kuangsen Sung *et al.*[13] reported the amination reaction of ketenimine by NMR and *ab initio* studies, which provided the formation pathways of vinylidenediamine.

The fact that organic chemistry started in space could be considered a challenge for the scientific community.[14] Among the extrasolar objects, the galactic center molecular clouds,[15] hot cores,[16] and hot corinos[17] are particularly rich in complex organic molecules (COMs). Some more complex COMs were observed in comets[18] and meteorites, where amino acids were also detected.[19] Ketenimine and hydrogen cyanide (HCN)[20] are both interstellar molecules. Accordingly, it was postulated that the reaction of ketenimine and HCN might be one of the formation pathways of prebiotic species. In the present study, a theoretical investigation of the reaction mechanism between ketenimine and HCN was performed employing the second-order Møler–Plesset perturbation theory (MP2) method in order to understand better the reactivity of ketenimine and the possible formation of prebiotic species in interstellar space.

CALCULATION METHOD

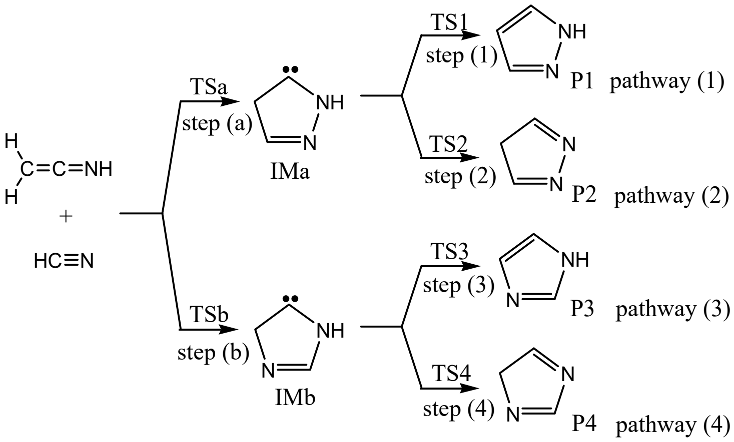
The second-order Møller–Plesset perturbation theory (MP2) method in combination with the aug-cc-pVTZ basis set was employed to locate all the stationary points along the reaction pathways without the imposition of any symmetry constraints. To evaluate the validity of the basis set, the basis set superposition error (*BSSE*) was calculated for the first-formed intermediate, **IMa**, employing the Boys–Bernardi counterpoise technique.[21] As a result, the calculated *BSSE* of 10.4 kJ mol^{-1} is much smaller than that of the interaction energy of 73.7 kJ mol^{-1} in **IMa**. Therefore, the aug-cc-pVTZ basis set should be valid for the present study.

Based on the optimized geometries, frequency analyses were performed to confirm the nature of the minima and the transition states. Moreover, intrinsic reaction coordinate (*IRC*) calculations were performed to validate further the calculated transition states connecting the reactants and products. Additionally, the relevant energy quantities, such as the reaction energies and barrier heights, were corrected with zero-point vibrational energy (*ZPVE*) corrections.

To explain the changes in the hybridization of some atoms in chemical reactions, the natural bond orbital (NBO) method based on the optimized structures[22] was employed.

The calculated energy parameters were further refined by single point energy calculations for pathways (1)–(4), Scheme 1, using the coupled cluster with single, double, and triple excitations method (CCSD(T)) in combination with the aug-cc-pVTZ basis set based on the optimized geometries at the MP2/aug-cc-pVTZ level of theory. All the energy parameters are summarized in Table I. For the sake of simplicity, the energetic results at the CCSD(T)/ /aug-cc-pVTZ level of theory are mainly discussed below if not otherwise stated.

All the calculations have been performed using the Gaussian 98 program.[23]



Scheme 1. The four proposed pathways for the cycloaddition reaction between ketenimine and HCN.

TABLE I. Relative energies (in kJ mol^{-1}) of the isolated reactants calculated at the MP2/ /aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels of theory; ZPVE corrections were considered using the results of the MP2/aug-cc-pVTZ level of theory

Species	MP2/aug-cc-pVTZ	CCSD(T)/aug-cc-pVTZ
TSa	103.8	142.9
IMa	84.9	73.7
TS1	131.7	119.6
P1	–149.3	–144.3
TS2	256.7	251.9
P2	–40.6	–41.7
TSb	137.0	157.4
IMb	36.5	26.0
TS3	75.5	81.4
P3	–192.0	–170.1
TS4	200.8	201.6
P4	–111.4	–109.9

RESULTS AND DISCUSSION

As displayed in Scheme 1, four possible pathways for the reaction between ketenimine and HCN were proposed. The geometric parameters for the reactants (R1 – ketenimine and R2 – HCN), transition states (TS), intermediates (IM), and products (P) involved in the pathways (1)–(4) are displayed in Fig. 1. The cal-

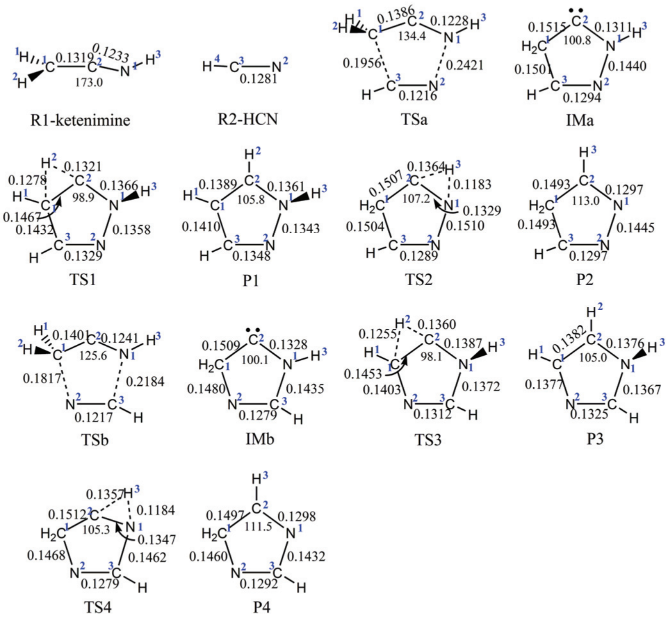


Fig. 1. Optimized structures of the reactants (ketenimine and HCN), transition states (TS), intermediates (IM), and products (P) in the four reaction pathways at the MP2/aug-cc-pVTZ level of theory. The bond lengths and bond angles are in nm and degree, respectively.

culated relative energies for the available stationary points and reaction profile are illustrated in Fig. 2. All the reactants and products are in the singlet state.

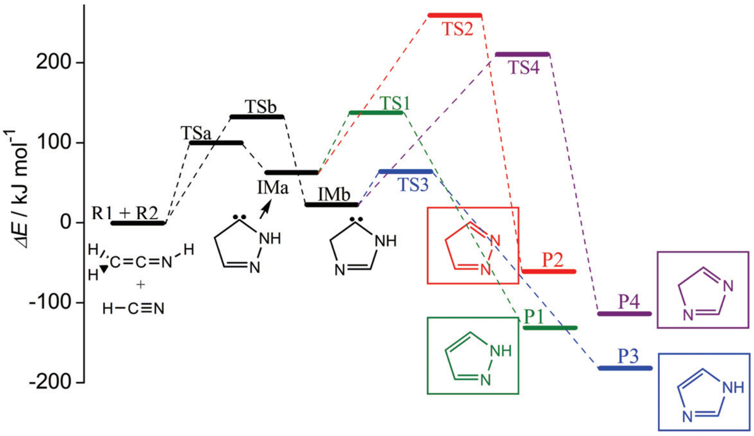


Fig. 2. Reaction profile for the reaction between ketenimine and HCN at the MP2/aug-cc-pVTZ level of theory.

Step (a): pericyclic reaction process to form the five-membered cyclic carbene intermediate ***IMa***

The first intermediate **IMa** was formed along reaction pathways (1) and (2) *via* a barrier of 142.9 kJ mol^{-1}. The calculated unique imaginary frequency of the transition state, **TSa**, in step (a) of the pericyclic reaction process was 476*i* cm^{-1} at the MP2/aug-cc-pVTZ level of theory.

As shown in Fig. 1, in **TSa**, the distances C1–C3 and N1–N2 are 0.1962 and 0.2368 nm, respectively. Thus, in the transition state **TSa**, two new bonds C1–C3 and N1–N2 are to be formed. At the same time, the distance C3–N2 in the R2 fragment of **TSa** reaches 0.1213 nm, which is longer by 0.0046 nm than that in HCN. Therefore, based on the bond length data, the triple bond C3–N2 in HCN is to be transformed into a double bond in **TSa**. Moreover, the bond angle C1–C2–N1 decreased continuously. The formation of the new σ bonds C1–C3 and N1–N2 and the cleavage of the π bond of C3–N2 occur simultaneously. Therefore, step (a) is a concerted reaction process. As shown in Fig. 3, these changes of bond length and bond angle could be further validated by *IRC* calculations based on **TSa**.

As shown in Fig. 1, **IMa** is characterized by a carbene structure. Here, the calculated hybridization of the C2 atom in **IMa** is sp$^{2.73}$ within the framework of the NBO method. The first two hybrid orbitals are bonded with C1 and N1, respectively. The third one contains lone pair electrons, and the fourth one is an empty orbital. The carbene is usually unstable. Along the reaction profile, **IMa** is endothermic with a value of 73.7 kJ mol^{-1} compared with that of the reactants. In general, **IMa** will be isomerized to the stable species by bonding its lone electrons. Therefore, the next step of the reaction is a H-transfer process, followed by the formation of the products **P1** and **P2**, respectively.

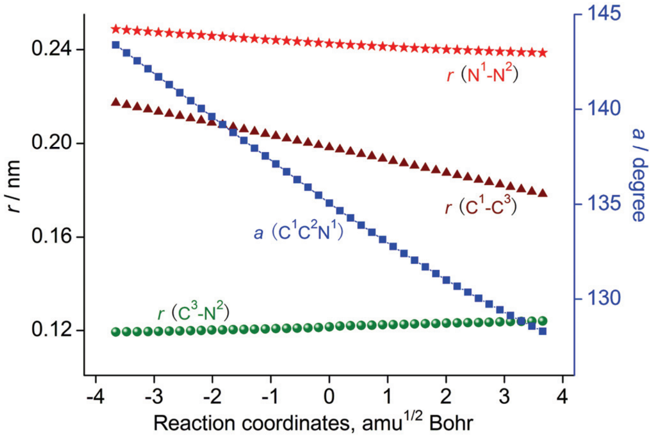


Fig. 3. Selected bond lengths and bond angle changes along the reaction coordinates of step (a) between ketenimine and HCN.

*Step (1): H-transfer process to form 1*H*-pyrazole*

The reaction step (1) is the transfer of hydrogen H2 from C1 to the adjacent C2, resulting in the isomerization of **IMa** into **P1** *via* **TS1**. Here, the calculated barrier is 45.9 kJ mol^{-1} and the imaginary frequency of **TS1** is 950*i* cm^{-1}. In details, as shown in Fig. 1, the distance of C1–H2 in **TS1** is elongated to 0.1258 nm, and the distance of C2–H2 reached 0.1332 nm, which indicate that the H2 atom can transfer from C1 to C2. At the same time, the bond length of C1–C2 in **TS1** decreases to 0.1468 nm (the bond length of C1–C2 in **IMa** is 0.1511 nm), suggesting the single bond configuration of C1–C2 in **IMa** will transfer into a double bond one in **P1**. As shown in Fig. 4, these changes of bond length could be further validated by IRC calculations based on **TS1**.

P1 is 1*H*-pyrazole. In **P1**, all of the cyclized atoms are in the same plane. Along the reaction profile, **P1** is a relatively stable species, which is exothermic with a value of 144.3 kJ mol^{-1} in comparison with the reactants.

*Step (2): H-transfer process to form 4*H*-pyrazole*

Similar to reaction step (1), step (2) is also a hydrogen transfer process. In step (2), the H3 atom in **IMa** migrates from N to C2, and **IMa** converts to **P2** *via* **TS2**, with a reaction barrier of 178.2 kJ mol^{-1}. **P2** is 4*H*-pyrazole. **P2**, is more stable than **IMa**, exothermic with a value of 41.7 kJ mol^{-1} in comparison with the reactants.

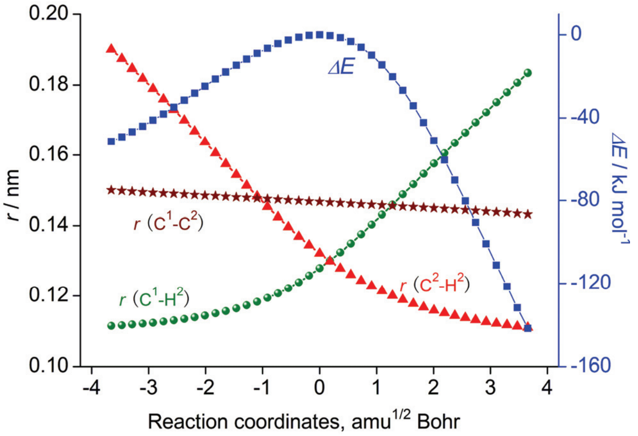


Fig. 4. Selected bond lengths and energy changes along the reaction coordinates of step (1) between ketenimine and HCN.

Pathways (3) and (4)

Analogous to the description above, ketenimine could also react with HCN to form the C1–N2 and N1–C3 σ bonds, the formed intermediate **IMb** could be isomerized to **P3** and **P4** through hydrogen transfer processes, which are indicated as reaction pathways (3) and (4). The geometric parameters for the reactants, transition states, intermediates, and products involved in the reaction pathways (3) and (4) are displayed in Fig. 1. The calculated relative energies for the available stationary points and reaction profile of pathways (3) and (4) are illustrated in Fig. 2.

The barrier in the first step (*i.e.*, step (b), a concerted reaction process to form the carbene intermediate **IMb**) of pathways (3) and (4) is 157.4 kJ mol^{-1}, which is higher by 14.5 kJ mol^{-1} than that of pathways (1) and (2). Subsequently, the further processes of pathways (3) and (4) are similar to those of pathways (1) and (2), *i.e.*, hydrogen transfer processes to form **P3** (step (3)) and **P4** (step (4)), which are 1*H*-imidazole and 4*H*-imidazole, respectively.

Comparisons of the four reaction pathways

For the concerted reaction steps (a) and (b), which formed carbene pyrazole and imidazole intermediates, the barriers are 142.9 and 157.4 kJ mol^{-1}, respectively. Therefore, the carbene pyrazole intermediate is easier to generate. For the formations of **P1** and **P2** in steps (1) and (2), the corresponding barriers are 45.9 and 178.2 kJ mol^{-1}, respectively. Therefore, from the kinetic viewpoint, reaction pathway (1) is the most favorable channel. For the final products (**P1** and **P2**) in the pathways (1) and (2), their energies are –144.3 and –41.7 kJ mol^{-1}, respectively. Therefore, from the point of view of thermodynamics, **P1** (1*H*-pyrazole) is the dominant product.

CONCLUSIONS

In this study, the cycloaddition reaction mechanisms between ketenimine and HCN were investigated employing the MP2 method in combination with the aug-cc-pVTZ basis set. The calculated results showed that five-membered cyclic carbene intermediates could be produced through pericyclic reaction processes between ketenimine and HCN. Through the following H-transfer processes, the carbene intermediates could isomerize to pyrazole and imidazole products, respectively. Four possible pathways, namely (1)–(4), lead to four ultimate products **P1** (1*H*-pyrazole), **P2** (4*H*-pyrazole), **P3** (1*H*-imidazole) and **P4** (4*H*-imidazole), respectively. From the kinetic viewpoint, reaction pathway (1) is the most favorable channel. The reactions of ketenimine with HCN through the pericyclic reaction step in pathways (3) and (4) are difficult. Most organic molecules with physiological activity have heterocyclic constituent. Therefore, the heterocyclic products (pyrazole and imidazole) of reaction between ketenimine and HCN in interstellar space may play important roles in the origin of prebiotic species.

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ИЗВОД

ТЕОРИЈСКА СТУДИЈА МЕХАНИЗМА ЦИКЛОАДИЦИОНЕ РЕАКЦИЈЕ ИЗМЕЂУ КЕТЕНИМИНА И ЦИЈАНОВОДОНИКА

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Механизам циклоадиционе реакције између кетенимина и HCN истраживан је помоћу Møller–Plesset теорије поремећаја другог реда (MP2) да би се боље резумела реактивност азотног кумулена кетенимина са једињењем које има троструку везу угљеник–азот – HCN. Урађена је оптимизација геометрије и вибрациона анализа стационарних тачака на површини потенцијалне енергије система. Израчунавања показују да се могу произвести петочлани циклични карбенски интермедијери перицикличном реакцијом између кетенимина и HCN. Накнадним процесом преноса водоника карбенски интермедијери се могу изомеризовати у пиразолска, односно имидазолска једињења. Ова студија може помоћи у разумевању формирања пребиотичких молекулских врста у међузвезданом простору.

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