DFT Study on the Mechanisms of C_4H_2 + CN Reaction

Yizhen Tang, Hao Sun, Yaru Pan, and Rongshun Wang*
Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University,
Renmin Road 5268, Changchun, Jilin 130024, P. R. China

(Received January 29, 2007; CL-070101; E-mail: wangrs@nenu.edu.cn)

A detailed theoretical survey on the potential energy surface for the CN + C_4H_2 reaction is carried out at the QCISD(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p) level. The geometries, vibrational frequencies, and energies of all stationary points involved in the reaction are calculated at the B3LYP/6-311+G(d,p) level. The results suggest that there are two different mechanisms and six pathways in the title reaction. Six products are yielded, and P3: H + HC_5N is the dominant product from the view of energy.

The reactions of CN radical with various compounds are strongly relevant to combustion in N-containing fuel system, and Titan's atmosphere. Studies of the kinetics of CN reactions with numerous species such as H_2, hydrogen halides, nitrogen oxides, hydrocarbons, etc.[1–8] have been reported. Since cyanoacetylene (HC_3N) and cyanopolynes had been found in interstellar clouds, Titan's atmosphere and circumstellar enveloped of carbon rich stars, many researchers begun to focus their attention on them.[9–14] In 1993, Smith and Sims proposed that the reactions of CN radicals with alkynes could provide a route to synthesis of cyanopolyynes. Seki et al. studied the rate constant of CN + C_4H_2 reaction experimentally, and they referred to that HC_5N + H was the main products.[15] To the best of our knowledge, no theoretical research has been attempted on this reaction yet.

Density functional theoretical calculations are carried out for the title reaction using the Gaussian 98 program.[16] The geometries of reactants (R), transition states (TS), intermediates (IM), and products (P) are optimized using the B3LYP/6-311+G(d,p) level. The vibrational frequencies are obtained at the same level. Connections of the transition states and products are verified by the intrinsic reaction coordinate (IRC) calculations. In order to obtain more reliable information of potential energy surface (PES), the single point energy calculations are performed at the higher level of QCISD(T)/6-311+G(d,p). According to the different methods to deal with the electrons of the current system, the relative energies are different, but the change trends are accordant. Figure 1 exhibits the potential energy surface at the QCISD(T)/6-311+G(d,p) level, and Figure 2 shows the geometries of the transition states. The ZPE corrections, relative energies, reaction enthalpies, and imaginary frequencies of transition states are listed in the Table 1.

According to the site of the initial attack, the reaction is described as two mechanisms: direct hydrogen abstraction mechanism and acetylenic carbon addition–elimination mechanism. Because of the approximate electrophilic reactivity of the C and N atom, they both exhibit strong attack activity to C and H atoms of C_4H_2. Therefore, C-dominated and N-dominated attack involving six channels exist in the title reaction.

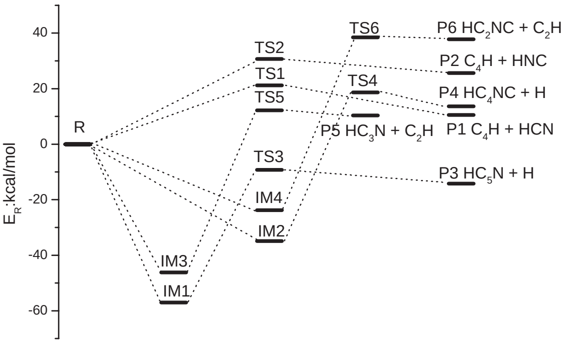

Figure 1. The profile of potential energy surface for the CN + C_4H_2.

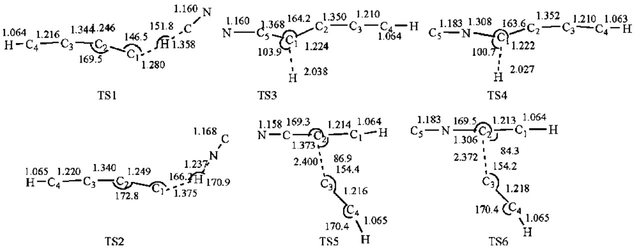

Figure 2. The optimized geometries of transition states in the CN + C_4H_2 reaction at the B3LYP/6-311+G(d,p) level (Bond lengths are in angstroms and angles in degrees).

The direct abstraction of one H atom in C_4H_2 molecule can produce C_4H + HCN (P1) and C_4H + HNC (P2) via TS1 and TS2, respectively. The geometries of both transition states are approximate. With the energy barriers of 21.2 and 30.8 kcal/mol, P1 and P2 are yielded. And the two pathways are endothermic by the heat of 8.4 and 22.5 kcal/mol. With the lower barrier and more stable product, channel P1 predominates over P2.

The barrier-less addition of the CN radical to the acetylenic π bond leads to four different adduct intermediates. IM1 and IM2 are the result of CN binding to the terminal C atom, while IM3 and IM4, from the attack on the middle C atom.

The formation of IM1 and IM2 is exothermic by 57.0 and 34.9 kcal/mol, respectively. Thereafter, IM1 and IM2 undergo C–H bond dissociation to yield P3 (H + HC_5N) and P4 (H + HC_4NC). Those processes involve two transition states, TS3 and TS4, and the activation energy heights are 47.8 and 53.6 kcal/mol, respectively. With the relevant broken C–H bonds are 2.038 and 2.027 Å, TS3 and TS4 are more product-like transition states. The heat released in pathway P3 is 23.2 kcal/mol, whereas it is endothermic by 3.3 kcal/mol in pathway P4. P3 and P4 are −14.2 and 13.6 kcal/mol on the PES. It is obvious that path P3 is more feasible than path P4. Attack of C and N atoms in CN to the middle C atom generate IM3 and IM4,

Table 1. ZPE corrections, relative energies (E_R) for all species involved in the C_4H_2 + CN reaction and reaction enthalpies (ΔH) (Energy unit: kcal/mol) and imaginary frequencies (Imag freq) of transition states (in cm^{-1})

Species	ZPE	E_R/B3LYP	E_R/QCISD(T)	ΔH	Imag freq
R	0.0425	0	0		
IM1	0.0456	−68.0	−57.0		
IM2	0.0453	−45.2	−34.9		
IM3	0.0464	−47.6	−46.2		
IM4	0.0457	−25.5	−23.8		
TS1	0.0380	6.7	21.2		i1502.2
TS2	0.0378	10.2	30.8		i1724.7
TS3	0.0381	−20.0	−9.2		i700.4
TS4	0.0375	6.4	18.7		i727.1
TS5	0.0424	8.3	12.2		i204.4
TS6	0.0417	32.8	38.5		i238.5
P1	0.0443	8.6	10.5	8.4	
P2	0.0436	22.6	25.6	22.5	
P3	0.0376	−23.5	−14.2	−23.2	
P4	0.0368	2.8	13.6	3.3	
P5	0.0406	8.8	10.4	9.1	
P6	0.0399	34.2	37.8	34.6	

respectively. By the effect of CN radical, the length of C≡C bond is 0.121 and 0.117 Å shorter than that in C_4H_2, correspondingly. Subsequently, the C≡C bond is elongated gradually, and TS5 and TS6 are formed. With the energy barrier of 58.4 and 62.3 kcal/mol, C_2H radical is eliminated, and HC_3N and HC_2NC molecules generated. P5 stands nearly at the same height with P1, while P6 is 37.8 kcal/mol on the PES. Those processes are endothermic by the heat of 9.1 and 34.6 kcal/mol. Pathway P6 is less favourable than pathway P5 because of the highest energy barrier and the least stable product.

The generation of IM1 releases the heat of 57.0 kcal/mol, which impulses the subsequent rearrangements easily. P3 and TS5 are more stable than reactant, and P3 is the lowest product on the PES, so channel P3 is the most important one. IM2, IM3, and IM4 are energy-rich intermediates whose generation are accompanied with heat releasing. But with the higher energy products and higher barrier heights, these paths in the acetylenic carbon addition–elimination mechanism are considered less important. The results are consistent with the experimental research.

In the present study, the reaction of CN with C_4H_2 is theoretically investigated at the level of QCISD(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p). Our computational results suggest that the title reaction proceed via two mechanisms (direct hydrogen abstraction mechanism and acetylenic carbon addition–elimination mechanism) involving six channels. Our calculations show that the pathway involving addition–elimination process to yield HC_5N + H (P3) dominates the title reaction. And it is concluded that the reaction of CN with C_4H_2 may do some contribution to the generation of HC_5N in interstellar clouds and Titan's atmosphere.

This work is supported by the Science Foundation for Young Teachers of Northeast Normal University. We are greatly thankful for the referees' helpful comments.

References

1 B. Atakan, A. Jacobs, M. Wahl, R. Weller, J. Wolfrum, *Chem. Phys. Lett.* **1989**, *154*, 449.
2 J. L. Durant, Jr., F. P. Tully, *Chem. Phys. Lett.* **1989**, *154*, 568.
3 D. Carty, V. L. Page, I. R. Sims, I. W. M. Smith, *Chem. Phys. Lett.* **2001**, *344*, 310.
4 B. N. Du, Z. Y. Zhou, *J. Mol. Struct (THEOCHEM)* **2005**, *713*, 71.
5 Z. W. Qu, H. Zhu, Z. S. Li, *Chem. Phys. Lett.* **2002**, *353*, 304.
6 N. Choi, M. A. Blitz, K. Mckee, P. W. Pilling, *Chem. Phys. Lett.* **2004**, *384*, 68.
7 T. Ochimizu, K. Seki, M. Yagi, J. B. Halpern, H. Okabe, *Chem. Phys. Lett.* **1999**, *313*, 451.
8 J. Park, J. F. Hershberger, *J. Chem. Phys.* **1993**, *99*, 3488.
9 J. Wang, Y. W. Zhang, L. S. Sheng, *Acta Chim. Sin.* **2002**, *60*, 1981.
10 N. Sayah, X. Li, W. M. Jackson, *J. Photochem. Photobiol., A* **1988**, *45*, 177.
11 D. L. Yang, T. Yu, N. S. Wang, M. C. Lin, *Chem. Phys.* **1992**, *160*, 317.
12 I. R. Sims, B. R. Rowe, L. B. Herbert, I. W. M. Smith, *Chem. Phys. Lett.* **1993**, *211*, 461.
13 F. Stahl, P. V. R. Schleyer, H. E. Schaefer, R. I. Kaiser, *Plan. Spac. Sci.* **2002**, *50*, 685.
14 N. Balucani, O. Asvany, Y. T. Lee, R. I. Kaiser, *Plan. Spac. Sci.* **2000**, *48*, 447.
15 K. Seki, M. Yagi, M. He, J. B. Halpern, H. Okabe, *Chem. Phys. Lett.* **1996**, *258*, 657.
16 J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. C. M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98, Revision A.9*, Gaussian, Inc., Pittsburgh, PA, **2001**.

Published on the web (Advance View) April 14, 2007; doi:10.1246/cl.2007.644