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## メタンイミン内水素マイグレーションの反応経路解析

(東大院理) 高 翔、中井 克典、山内 薫

Reaction pathway analysis of hydrogen migration in methanimine

(School of Science, The University of Tokyo) Sho Koh, Katsunori Nakai, Kaoru Yamanouchi

### 1. Introduction

When hydrocarbon molecules are exposed to an intense laser field, a variety of characteristic phenomena are induced such as multiple ionization, chemical bond rearrangement, and ejection of  $H_3^+$  [1,2,3]. It has been revealed from *ab initio* molecular dynamics calculations that a neutral  $H_2$  moiety appearing for a relatively long period of time ( $\sim 1$  ps) within a dication molecule plays a central role in the ejection of  $H_3^+$  [4]. In the present study, in order to understand the mechanism of the  $H_3^+$  ejection from hydrocarbon molecular species, we performed theoretical calculations of hydrogen migration in methanimine  $CH_2NH$  having only three hydrogen atoms, which can be considered as one of the simplest molecular species from which  $H_3^+$  is to be ejected, using the method of global reaction route mapping (GRRM) [5,6,7].

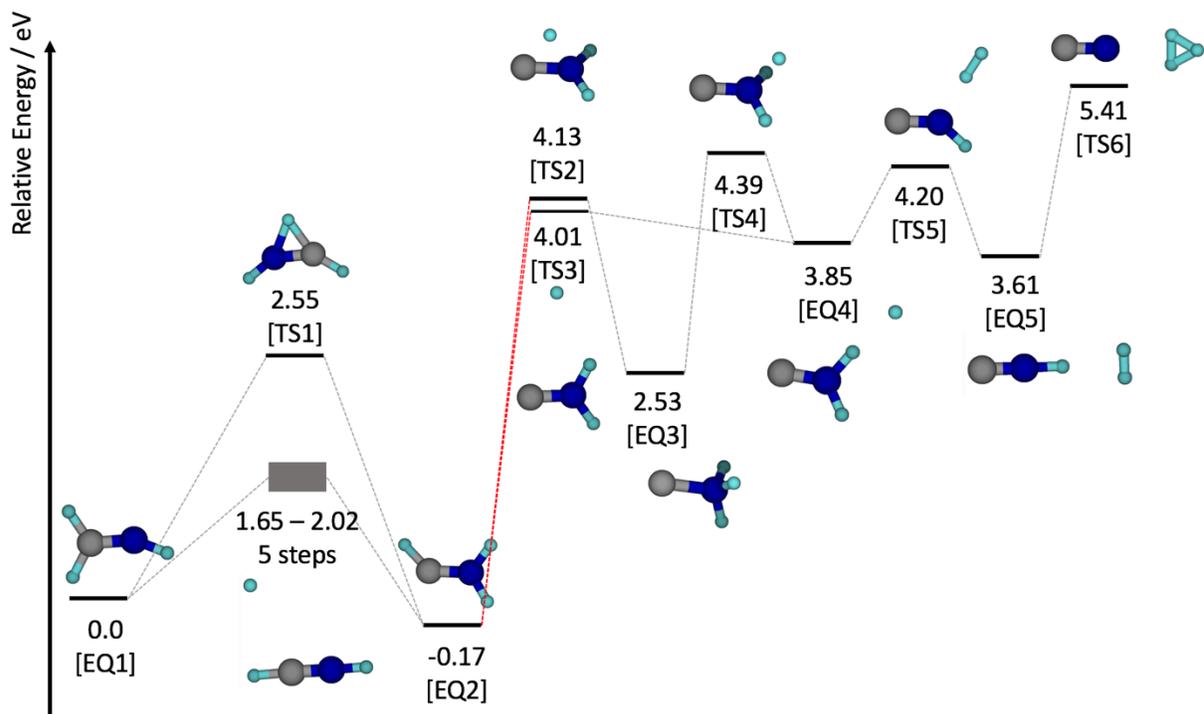
### 2. Method

Reaction pathways in the manifolds of neutral  $CH_2NH$ ,  $CH_2NH^+$  and  $CH_2NH^{2+}$  were explored by searching intrinsic reaction coordinates by the scaled hypersphere search method using GRRM (ver. 1.20) and Gaussian 09 at the B3LYP/6-31G level. The initial structures of  $CH_2NH$ ,  $CH_2NH^+$  and  $CH_2NH^{2+}$  were optimized by Gaussian 09.

### 3. Results and Discussion

The numbers of equilibrium structures (EQs), transition structures (TSs) and dissociation channels (DCs) identified in  $CH_2NH^+$  are 10, 24, and 13, respectively. We found TS6 of  $CH_2NH^+$  in which a  $H_3^+$  moiety is formed is connected from EQ5 composed of a neutral  $H_2$  moiety and  $CNH^+$ . As shown in Fig. 1, in order that  $H_3^+$  is to be produced, the isomerization reaction in  $CH_2NH^+$  proceeds in multiple steps. First, one hydrogen atom in  $CH_2$  group moves to the N atom side to form  $CHNH_2^+$  (EQ2), and then, through the pathway of EQ2-TS3-EQ4,  $CNH_2^+$  and H are formed, or through the pathway of EQ2-TS2-EQ3,  $CNH_3^+$  can be formed. It is found that the migration of a hydrogen atom from CH group to  $NH_2$  group exhibits a relatively high energy barrier larger than 4 eV for both of the two reaction routes, as

represented by the two red dotted lines in Fig. 1. It is true that an  $\text{H}_3^+$  moiety can be formed in the transition state, TS6, which may be represented as  $[\text{CN}\cdots\text{H}_3]^+$ , and that the motion of neutral  $\text{H}_2$  plays a key role in the formation of TS6, but the height of the energy barrier, 5.41 eV, measured from the equilibrium structure, EQ1, to produce TS6 is significantly large, which implies that the ejection of  $\text{H}_3^+$  may not be an abundant dissociation channel.



**Figure 1.** Reaction pathway from EQ1 to TS6 of  $\text{CH}_2\text{NH}^+$  from which  $\text{H}_3^+$  can be ejected: C, N, and H atoms are represented by gray, blue, and cyan spheres, respectively. The zero-point vibrational energies are not taken into account.

## References

- [1] K. Yamanouchi, *Science*, **295**, 1659 (2002).
- [2] T. Okino, Y. Furukawa, P. Liu, T. Ichikawa, R. Itakura, K. Hoshina, K. Yamanouchi, H. Nakano, *Chem. Phys. Lett.* **419**, 223 (2006).
- [3] K. Hoshina, Y. Furukawa, T. Okino, K. Yamanouchi, *J. Chem. Phys.* **129**, 104302 (2008).
- [4] K. Nakai, T. Kato, H. Kono, K. Yamanouchi, *J. Chem. Phys.* **139**, 181103 (2013).
- [5] K. Ohno, S. Maeda, *Chem. Phys. Lett.* **384**, 277 (2004)
- [6] S. Maeda, K. Ohno, *J. Chem. Phys.* **109**, 5742 (2005)
- [7] K. Ohno, S. Maeda, *J. Chem. Phys.* **110**, 8933 (2006)