

## Detailed Mechanism of Reaction between CH<sub>3</sub> and NO A Theoretical Study

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**Abstract:** An accurate composite method, namely CBS-QB3, was performed to explore the detailed mechanism for the CH<sub>3</sub> + NO reaction, in which the addition of CH<sub>3</sub> to N site of NO can proceed through one accessible pathway, then, go to many directions. Competitively, the barrierless association of those two radicals is the most feasible pathway to form the adduct CH<sub>3</sub>NO which then leads to six main products: **P1** (NH<sub>3</sub> + CO), **P2** (H<sub>2</sub> + HNCO), **P3** (H<sub>2</sub>O + NCH), **P4** (H<sub>2</sub>O + CNH), **P5** (H<sub>2</sub> + NCOH) and **P6** (NH<sub>2</sub> + HCO) via 12 intermediates and 20 transition state. The NH<sub>3</sub> + CO (**P1**) and NCOH + H<sub>2</sub> (**P6**) channels were found to be the most and the least thermodynamically favorable products, respectively. Kinetically, H<sub>2</sub>O + NCH (**P3**) is expected to the most feasible pathway due to its low barrier height (within 12kcal/mol to 50kcal/mol) in comparison with other product channels. It is suggested that this mechanism should be used as a framework for detailed kinetic analysis in an attempt to improve the existing detailed kinetic mechanism for fuel combustion.

**Keywords:** Mechanism, Combustion, Thermodynamics, Methyl radical, Nitrogen monoxide

### I. Introduction:

Aside from being a renewable energy source, biodiesel also manifests desirable characteristic over conventional diesel, namely significant decrease in sulfates and carbon monoxides (CO) exhaustion [1]. However, a note-worthy issue is the high nitric oxide (NO) emission of biodiesel combustion, reducing its usage [2]. CH<sub>3</sub> has been shown to be the main hydrocarbon derivative of the bio-fuel surrogate [3]. Therefore, an in-depth kinetics analysis on the reaction between CH<sub>3</sub> and NO, which would provide further knowledge into fuel re-burning stage [4], is in high demand. Such knowledge is the key to efficient engine design and controlling NO pollutant gas release.

In additional to its involvement in engine powering, the importance of this system in atmospheric chemistry has for long attracted the attention of many researchers, both theoretical and experimental. In 1996, Nguyen *et al.* proposed a primitive potential energy surface for HCN + H<sub>2</sub>O formation and also calculated the high-pressure rate constant for this channel [5]. Similarly, a paper by Miler *et al.* (1997) also carried out a kinetic analysis, with an addition of channel of H<sub>2</sub>CN + OH [6]. On the other hand, Zhang and co-workers (2005) investigated this system with a sole focus on geometry and energy of the involved species, and suggested four product channels in total [7]. In general, this research only studied a part of constructing potential energy surface; a complete kinetic behaviours has not yet to be carried out.

Due to the information in the field being scattered, this study aims to provide a comprehensive study with extensively-studied reaction mechanism and complete potential energy surface. The well-defined potential energy surface (PES) constructed under high accurate method (e.g. CBS-QB3) will provide good data to study the kinetics properties of the mentioned system.

### II. Computational details:

#### Electronic structure calculation

The electronic structure calculations were carried out using Gaussian09 [8,9]. A composite method developed by Petersson and co-workers (1999) [10], namely CBS-QB3 was used to construct the molecular modelling and electronic energy calculations. The CBS-QB3 method calculated geometries and frequencies at the B3LYP/CBSB7 level of the theory; then, using CCSD(T)/6-31+G(d') and MP4SDQ/CBSB4 for single point calculations. The energy was calculated and extrapolated to reach the infinite basis set by MP2/CBSB3 method [11]. All of the reactants, intermediates and transition state were obtained with the optimized structures and the lowest energy formation. The species differed by a rotating group around and a single bond was treated with hindered rotation (HIR); therefore, conformers of the same species are implicitly included in calculating process in the most accurate manner as described hereafter. In addition, the intrinsic reaction path (IRC) was also used to verify the correction of the transition state in which the minimum energy paths (MEP) from transition state to its reactants and products would be analyzed [12].

### III. Results and discussions

#### Potential Energy Surface (PES)

In the singlet PES at 0 K, the reaction scheme and the energy for stable species and transition state at CBS-QB3 are shown below (cf. Figure 1). To display the related energy between the species of the system, the reactants' energy was considered as equal to zero. Those channels with transition state energy higher than 15kcal/mol, thus contribute insignificantly to the combustion reaction, were excluded. Only 12 intermediates, 20 transition states and six main products

were discussed and taken into account for further calculations. Approaching high accurate computational thermo-chemistry scheme, Sirjean [11] has mentioned that CBS-QB3 was considered as a relevant calculation when the yield of Mean Absolute Deviation within 1.1 kcal/mol.

There is only one accessible pathway from initial reactants lead to the formation of  $\text{CH}_3\text{NO}$  species (barrierless reaction of N-end attacks to forms a  $\text{CH}_3\text{ON}$  conformer). There is no NO- $\pi$ -Bond attack could be found on the **IM1** formation pathway. The barrierless reaction of N-end attacks between  $\text{CH}_3\cdot$  and  $\text{NO}\cdot$  lead to the formation of the adduct nitrosomethane:  $\text{CH}_3\text{NO}$  (**IM1**) at -38.4kcal/mol below the entrance level. Subsequently, **IM1** is then isomerised into  $\text{CH}_2\text{NHO}$  (**IM2**) by crossing the barrier **TS1** lying at 12.4kcal/mol and from **IM2**, three possible pathways can take place:

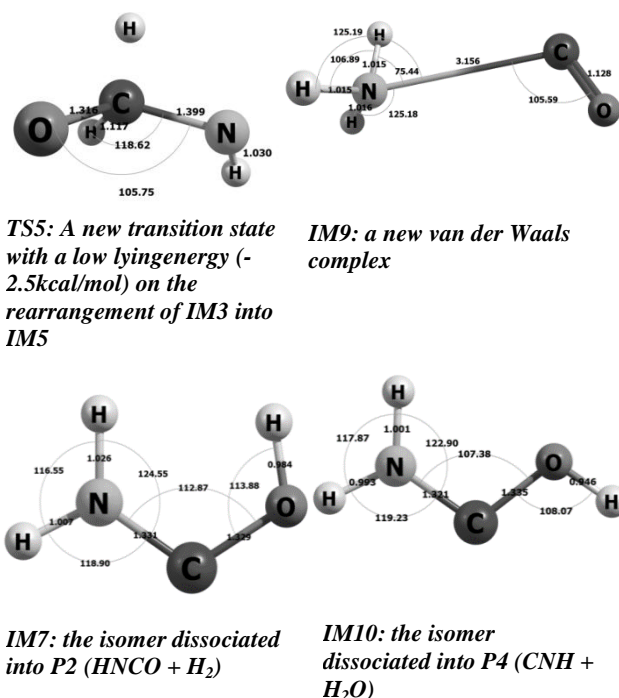
**CH<sub>2</sub>NOH (IM4) isomerization:** A H-shift from N to O with the low energy barrier of 42.2kcal/mol give a rise to intermediate **IM4**, which can be followed by the dissociation into  $\text{HCN} + \text{H}_2\text{O}$  (**P3**) lying at -82.6kcal/mol via the 57.9kcal/mol energy barrier. This direction is predicted as the most favourable pathway based on the low of accessing barrier height and the short of converting isomerizations process into final products.

**CHNHOH (IM6) isomerization:** **IM2** can rearrange into **IM6** by a 1,5-H migration whose energy barrier is 51kcal/mol. Similar to the previous pathway, **P3** can be subsequently formed with the reaction barrier of 13.1kcal/mol, where the broken bond between O-N atoms and N-H atoms were substituted by H-O attacks for water formation.

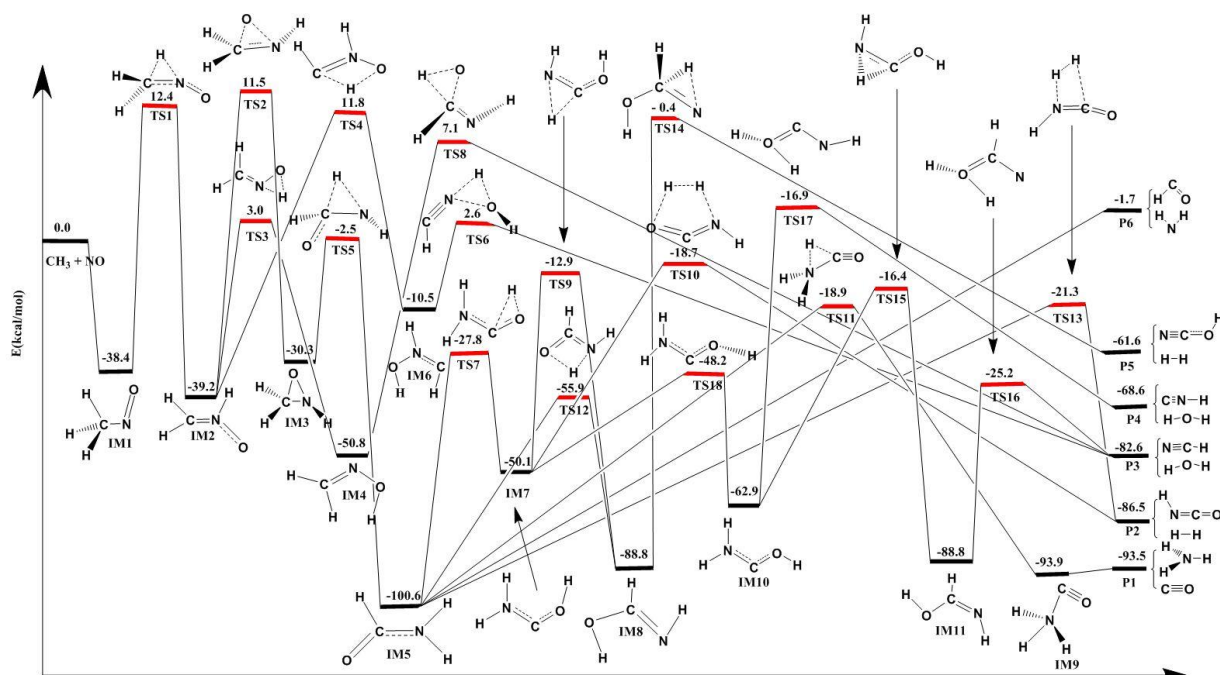
**OCH<sub>2</sub>NH (IM3) isomerization and subsequential reaction:** C-O bond formation produces the ring-structured **IM3** with the barrier height is higher than those of previous pathway (50.7 kcal/mol). It then isomerizes into the global minima  $\text{OCHNH}_2$  (**IM5**) via **TS5** lying at -2.5 kcal/mol. Comparably, **IM5** is the most stable intermediates when lying out at the energy of -101.3kcal/mol. In addition, the **TS5** obtained by this method is greatly more accessible than the TS located at MC-QCISD//B3LYP/6-311g(d,p)+ZPE of Zhang et al. [7], whose relative energy is 15.4 kcal/mol and structure was not shown. From the thermodynamically favoured **IM5**, the reaction can go on to a variety of directions:

a.  $\text{CO} + \text{NH}_2$  (**P6**) uni-molecular reaction: The C-N bond fission can lead to the biradical product **P6** at -1.7 kcal/mol with no barrier and it was evaluated as the least feasible yielding product.

b.  $\text{H}_2 + \text{HNCO/HONC}$  (**P2, P5**) formation: The H atom can migrate from C atom to O atom to form **IM7** and its conformer **IM10** (cf. Figure 2). Since the energy difference between these conformers is 12.8 kcal/mol. For the simplicity of illustration, they should be grouped together; however, these isomers were treated separately because each conformer plays a role in processing different yielding products. From **IM5**,  $\text{H}_2$  can be formed together with HNCO for bimolecular products lying at -86.5kcal/mol; in which, intermediate **IM5** is rearranged into **IM7** before reaching **P2** by a barrier of 72.8 and 31.4kcal/mol, respectively. Besides, **IM5** itself can go through **TS13**, with 79.3kcal/mol barrier height along the reaction coordinate, to lead to the product **P2**. Alternatively, HOCN can be the accompanying product when the route **IM5**  $\rightarrow$  **IM7**  $\rightarrow$  **IM8**  $\rightarrow$  **P5** is taken. On the final reaching step, **IM8** had to pass a very high energy barrier (89.2kcal/mol) before breaking down into NCOH and  $\text{H}_2$  radicals. Due to the complex accessing channels and high barriers, this pathway may be less contributed to the yielding product at the end.



**Figure 2.** The singlet geometries parameters of some new molecules as well as the two  $\text{NH}_2\text{COH}$  isomers computed at CBS-QB3 level. The values of angle are in degrees and of distance are in Angstroms.



**Figure 1.** The simplified potential energy surface for CH<sub>3</sub> + NO system at 0K, calculated at the composite method CBS-QB3. Numbers are the energies relative to that of the reactants and channels (having energy higher than 17 kcal/mol above the entrance channel are not included). Value are in kcal/mol

c. H<sub>2</sub>O + HNC/HCN (**P3**, **P4**) formation: H<sub>2</sub>O can be formed along with HNC (**P5**) when **IM7** transform into **IM10** and then under goes a 5, 4-H migration via the barrier height of 46kcal/mol. On the other hand, HCN is the byproduct via the pathway **IM7** → **IM10** → **IM11** → **P3** with the barriers in relative with reactants being -48.2, -16.4 and -25.2kcal/mol, respectively.

d. NH<sub>3</sub> + CO (**P1**) formation: **IM5** crossed 81.7kcal/mol barrier of energy to form the thermodynamically favoured **P1** which is the most stabilized species among dissociation products. Although, there is a van der Waals complex **IM9** (cf. Figure 2), since the energy difference between this complex and the dissociated product (**P1**) is not significant (0.4 kcal/mol), we would exclude **IM9** in further calculations. This is a new channel that has not been described in previous studies on CH<sub>3</sub> + NO system. Although, it has been mentioned as a reverse reaction in a PES research [14] via an experimental study, to the best of our knowledge, there has been no theoretical thermodynamics calculation for this channel.

**Isomers and hindered treatment:** The different arrangement of NH<sub>2</sub>COH (**IM7/IM10**) molecule led to different products formation was evident for the effects of atom distributions into molecular interaction and rearrangement. Therefore, only isomers, which contributed insignificantly to the system, were excluded in this system. All species was carefully analyzed and considered HIR to achieve optimal results.

Overall, most of the intermediates lie below the entrance level and have a low-lying energy. In term of Zero-point-corrected electronic energy, **P1** is the most stabilized product formation; however, to determine and conclude the most abundant products, we need more analysis on the kinetics mechanism for the whole system. As discussed above, from **IM2**, there are three possible pathways; in which, **P3** is the most competitive yielding product by the low of lying transition states and simple transformations pathway.

#### IV. Conclusions:

A detailed potential energy surface was characterized for CH<sub>3</sub> and NO reaction at the CBS-QB3 level of theory. There are six main products of this system have been found **P1** (NH<sub>3</sub> + CO), **P2** (H<sub>2</sub> + HNCO), **P3** (H<sub>2</sub>O + NCH), **P4** (H<sub>2</sub>O + CNH), **P5** (H<sub>2</sub> + NCOH) and **P6** (NH<sub>2</sub> + HCO); in which, **P1** (NH<sub>3</sub> + CO) is the most feasible one with the -93.5kcal/mol energy of formation on the studied condition. Whereas, **P6** (NH<sub>2</sub> + HCO) is the least competitive yielding product when lying at -1.7kcal/mol. However, considering kinetic behaviours, **P3** (H<sub>2</sub>O + NCH), as discussed in previous studies [15-19], is the dominated product. The transition states involved in **P3** pathway is more competitive with other channels due its low barriers (e.g. 13.1 kcal/mol from **IM6**), then neglect the other pathways. The well constructed potential energy surface of CH<sub>3</sub> + NO system from this study is recommended to be used as a framework for characterizing thermodynamic and kinetics later on.

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