



Kinetic mechanisms of hydrogen abstraction reactions from methanol by methyl, triplet methylene and formyl radicals



Jun Shi, Jing-yu Ran*, Chang-lei Qin, Wen-jie Qi, Li Zhang

Key Laboratory of Low-grade Energy Utilization Technologies and Systems (Chongqing University), Ministry of Education, Chongqing 400030, China

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ABSTRACT

Although H-abstraction reactions from methanol by methyl radical (CH_3), triplet methylene radical ($^3\text{CH}_2$) and formyl radical (HCO) are important for methanol pyrolysis and combustion, the kinetic mechanisms of those reactions are indistinct and need to be better understood. Ab initio calculations were performed to optimize geometries of transition states using Gaussian 09W package with the B3LYP density functional at the 6-311++G (3df, 3pd) basis set. Energy barrier and minimum energy path (MEP) on the reaction potential energy surface were calculated with MP2 method at the same basis set. The canonical variational transition state theory (CVT) with Eckart tunneling correction were employed to compute rate constants over the temperature range 298–2000 K. Results show that, for reaction $\text{CH}_3\text{OH} + \text{CH}_3$, barrier height for hydroxymethyl channel (R1a) is 12.59 kcal/mol and for methoxy channel (R1b) is 13.82 kcal/mol. Rate constants for channels R1a and R1b are $k_{1a} = 3.635 \times 10^{-31} T^{5.58} \exp(-1962/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{1b} = 4.342 \times 10^{-28} T^{4.61} \exp(-4284/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. For reaction $\text{CH}_3\text{OH} + ^3\text{CH}_2$, barrier heights for hydroxymethyl channel (R2a) and methoxy channel (R2b) are 7.68 kcal/mol and 9.19 kcal/mol, respectively. Rate constant for channel R2a is $k_{2a} = 5.885 \times 10^{-28} T^{4.19} \exp(-1813/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and for channel R2b is $k_{2b} = 2.266 \times 10^{-28} T^{4.26} \exp(-2833/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For reaction $\text{CH}_3\text{OH} + \text{HCO}$, barrier heights for hydroxymethyl channel (R3a) and methoxy channel (R3b) are 21.88 kcal/mol and 28.83 kcal/mol, respectively. Rate constant for channel R3a is $k_{3a} = 8.156 \times 10^{-38} T^{7.37} \exp(-4900/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and for channel R3b is $k_{3b} = 2.007 \times 10^{-27} T^{4.34} \exp(-11,605/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This study is beneficial for improving the kinetic mechanism of methanol pyrolysis and combustion.

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1. Introduction

As the shortage of fossil energy, alcohol fuels are regarded as hopeful, renewable and clean energy and are widely used in many fields [1–4]. For instance, alcohol fuels are used as an additive in the gasoline to reduce soot and particulates [5–11]. Methanol and ethanol have been used as alternative of gasoline for decades [12]. Recently, the methanol fuel is increasingly used as a cheap energy resource in the industry of aluminum metallurgy and ceramic by an efficient combustion technology [13]. Therefore, the pyrolysis and combustion are major methods for converting alcohol fuels into energy, and the study on the kinetic mechanism of pyrolysis and combustion of alcohol fuels is necessary for facilitating the utilization of this renewable fuel. Moreover, the

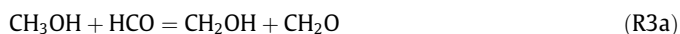
combustions of heavy alcohols are very complex. So a systematic approach was adopted to achieve reliable kinetic data of simple alcohols and hydrocarbons, which can build the kinetic mechanisms of higher alcohols through a hierarchical procedure [14]. Methanol is regarded as the simplest alcohol fuel, therefore, the study on kinetic mechanism of methanol pyrolysis can provide beneficial insights for revealing kinetic mechanisms of pyrolysis and combustion of higher alcohols.

In the past several decades, the thermal decomposition of methanol has been investigated extensively [15–26], but the kinetic mechanism for predicting the methanol pyrolysis is indistinct, and many elementary reactions still need to be improved. Hydrogen abstraction reaction for the process of pyrolysis and combustion of methanol is very important, because a large amount of methanol is consumed through hydrogen abstraction reaction with many radicals [27], such as atomic hydrogen (H), methyl radical (CH_3 , reaction R1), triplet methylene radical ($^3\text{CH}_2$, reaction R2) and formyl radical (HCO, reaction R3) and hydroxide radical (OH).

* Corresponding author at: No. 174 Shazheng St, Shapingba, Chongqing 400044, PR China. Tel.: +86 23 6510 2107; fax: +86 23 6511 1832.

E-mail address: ranjy@cqu.edu.cn (J.-y. Ran).

As a large number of methyl radical, triplet methylene radical and formyl radical would be produced at the high temperature, the hydrogen abstraction reactions of methanol with those radicals cannot be ignored. However, the study of kinetic mechanism of those reactions is very limited, especially for the reaction of methanol with triplet methylene radical and formyl radical.



The study on the H-abstraction reaction from methanol by H and OH has been investigated extensively [12,28–34] by using experimental and computational methods. For instance, Jodkowski et al. [35] studied the reaction of methanol with H atom and OH by using theoretical computation at MP2 and MP4 level and G2 methodology. Recently, Meana-Pañeda and co-workers [27] also reported the investigation of H-abstraction reaction from methanol by H atom using high-level computation at the MC3BB level together with direct dynamics calculations CVT/ μ OMT. However, the study on the H-abstraction reaction from methanol by CH_3 , ${}^3\text{CH}_2$ and HCO is very limited. Jodkowski et al. [35] studied the reaction of methanol with CH_3 and obtained a similar energy height for reactions R1a and R1b is 14.0 kcal/mol and 13.6 kcal/mol, respectively. Alecu and Truhlar [36,37] studied the H-abstraction reaction from methanol by CH_3 numerically, and recommended the best energy height for R1a and R1b is 12.93 kcal/mol and 12.58 kcal/mol, respectively. The rate constant for R1a and R1b in the study of Jodkowski et al. [35] is higher than that obtained by Alecu and Truhlar [36,37] and Tsang [38] in the temperature of 298–2000 K. Recently, Peukert and Michael [39] investigated rate constants for R1a and R1b using experimental method, they obtained the rate constants for reactions R1a and R1b in the temperature range of 1138–1270 K, which are lower than those obtained by Jodkowski et al. [35], Alecu and Truhlar [36,37] and Tsang [38]. Although the H-abstraction reaction of methanol with CH_3 has been widely studied, its kinetic mechanism still needs to be further studied. The H-abstraction reaction of methanol with ${}^3\text{CH}_2$ is not found except for the data recommended by Tsang [38], which was obtained on the base of energy height of H-abstraction reaction from methanol by CH_3 . Except for the rate constants of reactions R3a and R3b recommended by Tsang [38,40], which the uncertainty factors is 10 and 3, respectively, there is little information about the H-abstraction reaction from methanol by HCO. In addition, a large amount of CH_3 , ${}^3\text{CH}_2$ and HCO radicals are produced at the later time of methanol pyrolysis at high temperature. Therefore, studies on the H-abstraction reactions from methanol with CH_3 , ${}^3\text{CH}_2$ and HCO radicals are necessary for improving the kinetic mechanism of methanol pyrolysis and combustion.

In this study, we firstly studied the potential energy surface of H-abstraction from methanol by CH_3 , ${}^3\text{CH}_2$ and HCO radicals using Gaussian 09W computer program [41], including the geometrical structure of reactants, transition states, stationary points and products, energy height and minimum energy path (MEP). And then we calculated the rate constants for reactions with canonical variational transition state theory (CVT) and Eckart tunneling correction using Kinetic and Statistical Thermodynamic Package

(KiSTheLP) computer code [42] based on the results of quantum chemistry calculations.

2. Computational methodology

2.1. Quantum chemistry calculation

Ab initio calculations were performed to build the potential energy surfaces of reactions R1 and R2 by using the commercial packages of Gaussian 09W and GaussView 5.0 [41]. Firstly, the geometric structures of reactants, intermediates, transition states and products were optimized by using the B3LYP density functional [43–45] and the 6-311++G (3df, 3pd) basis set. And then the vibrational frequencies were calculated using Moller–Plesset many-body perturbation theory [46] of second order (MP2) at the 6-311++G (3df, 3pd) basis set for the energies with zero-point energy correction. The calculation with the B3LYP density functional was also conducted by at the same basis set, which was used as a comparison. Finally, the IRC calculations were conducted to verify the transition states and to obtain the MEP for rate constant calculations. The energies of reaction coordinate points along the MEP were calculated by using MP2 method with the 6-311++G (3df, 3pd) basis set. Those results were used for the calculation of rate constant with canonical variational transition state theory.

2.2. Rate constant calculation

The molecular thermodynamic properties of reactants, stationary points, transition states and products can be calculated according to the results of quantum chemistry calculations by using the Kinetic and Statistical Thermodynamical Package (KiSTheLP) [42]. This computer code also can predict kinetic properties of gas-phase chemical reaction, just as the frequently used program POLYRATE. In this study, a scaling factor was used to correct the system error in the prediction of vibrational frequency by a quantum chemistry software [47]. The canonical variational transition state theory (CVT) was used to calculate rate constants for reactions R1, R2 and R3. Based on the transition state theory (TST) [48,49], the rate constants at different positions of the reaction coordinate $k_{\text{TST}}(T, s)$ [42] was obtained by Eq. (1).

$$k_{\text{TST}}(T, s) = \sigma \frac{k_b T Q_{\text{TS}}(T, s)}{h N_A Q_{\text{R}}(T)} e^{-\frac{V^\ddagger(s)}{k_b T}} \quad (1)$$

$$\sigma = \frac{n^\ddagger \times \sigma^{\text{R}}}{n^{\text{R}} \times \sigma^{\ddagger}} \quad (2)$$

where σ is the reaction path degeneracy [50,51] which can be computed by Eq. (2). n^\ddagger and n^{R} are the number of isomers of transition state and reactant, respectively, and σ^{\ddagger} and σ^{R} are the rotational symmetry number which is given in the result of frequency calculation. k_b is the Boltzmann's constant, T is the temperature, h is the Planck's constant, and N_A is Avogadro's number. $V^\ddagger(s)$ is barrier height corrected by zero-point energy at different positions of the reaction coordinate. $Q_{\text{TS}}(T, s)$ is the total partition function of transition states at different positions of the reaction coordinate. $Q_{\text{R}}(T)$ is the total partition function of reactants. s is the distance along the MEP on the reaction coordinate. The rate constant $k_{\text{CVT}}(T)$ was calculated via the CVT theory by minimizing $k_{\text{TST}}(T, s)$ respect to s along the MEP, as Eq. (3).

$$k_{\text{CVT}}(T) = \min_s k_{\text{TST}}(T, s) \quad (3)$$

$$k_{i,\text{CVT}/\text{ECK}}(T) = \chi_i(T) k_{i,\text{CVT}}(T) \quad (4)$$

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