Theoretical study of the addition and hydrogen abstraction reactions of the methyl radical with formaldehyde and hydroxymethylene

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Abstract: The mechanism, thermochemistry and kinetics of the addition and hydrogen-atom abstraction reactions of the methyl radical with formaldehyde and hydroxymethylene were investigated by ab initio calculations. The potential energy surface (PES) of the reactions were calculated by single point calculations at the CCSD(T)/6-311++G(3df,2p) level based on geometries at the B3LYP/6-311++G(3df,2p) level. The rate constants of various product channels were estimated by the variational transition state theory (VTST) and are discussed for the seven reactions in the temperature range of 300–2000 K and at 101325 Pa pressure. The calculated results showed that all the hydrogen abstraction reactions are more favorable than the addition ones.

Keywords: rate constants; hydrogen abstraction reactions; CCSD(T); B3LYP.

INTRODUCTION

Free radicals play a crucial role in chemical reactions. Most of the reactions in the fuel system, the earth's atmosphere and planets have involved free radicals. In fact, their mechanisms have been intensively studied recently.1–4 The methyl radical CH₃, one of the most important free radicals due to its high reactive activity, is favored in combustion research. Recent results showed that it also participates in chemical vapor deposition (CVD) and chemical vapor infiltration (CVI) routes.5–7 Among alkyl radicals, CH₃ shows an imperviable characteristic to thermal decomposition.8 Formaldehyde H₂C=O, the first polyatomic organic compound observed in the interstellar medium and in dark nebulae, was predicted to be present in the Titan atmosphere. The H₂C=O molecule is among the most abundant aldehyde molecules in the terrestrial lower atmosphere, where it is

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emitted, among other sources, from the combustion of fossil fuels and from biomass burning. In combustion systems, it lies on the primary oxidation pathway of natural gas and other alkane-based hydrocarbon fuels, i.e., \( \text{H}_2\text{CO} \) emission from fuel engines increases with the use of oxygenated fuels, including methanol, ethanol, and methyl tertiary butyl ether blended fuels.\(^9\) On the unimolecular rearrangement of formaldehyde, \textit{ab initio} calculations proved that formaldehyde can isomerize to form \textit{trans-} and \textit{cis-}HCOH. However the isomerization barrier of \( \sim 78.87 \text{ kcal mol}^{-1} \) and a reaction endoergicity of \( \sim 47.80 \text{ kcal mol}^{-1} \) means that the formation of these isomers are less favorable.\(^10\) Hence, the study of the reactions \textit{CH}_3 radicals with formaldehyde and alkanes is important to understand the process of hydrocarbon combustions. Many experimental and theoretical studies of the \textit{CH}_3 + \textit{CH}_2\text{O} reaction system were performed\(^11\)–\(^18\) and the general consensus was that hydrogen abstraction is an important channel. Li \textit{et al.} located stationary points on the \textit{CH}_3 + \textit{CH}_2\text{O} potential energy surface at the QCISD(T)/6-311++G(3df,2p)//MP2/6-311++G(d,p) levels of theory in a recent theoretical study.\(^15\) However, their computed rate constant at 600 K was about two times slower than the recommended value which was based on the work of Choudhury \textit{et al.}\(^16\) By using a shock tube and modeling method, the reaction was studied over a large range of high temperatures. The modeling study was well fitted by quantum mechanical tunneling over the entire experimental range 300–1700 K.

To the best of our knowledge, no work on the mechanism of the reaction of the methyl radical with hydroxymethylene has ever been performed, neither by experiment nor by theory. In this paper, we investigated the mechanism of the addition and hydrogen abstraction for reactions between formaldehyde and its isomers with methyl radical in the gas phase. The temperature dependence of rate constants from these reactions were verified and clarified.

**COMPUTATIONAL DETAILS**

All calculations were realized using the Gaussian 09 program.\(^19\) Since the studied systems, methyl radical with formaldehyde and hydroxymethylene, are open-shell species, the density functional theory (DFT) method was superior in using the precise electron density to calculate the molecular characteristics. For calculations relating to open-shell systems using the DFT method, spin contamination does not affect the molecular properties.\(^20,21\) The hybrid density functional method (B3LYP), Becke’s three parameter nonlocal exchange functional\(^22-24\) with the nonlocal correlation functional of Yang \textit{et al.}\(^25\) with 6-311++G(3df,2p) basis set\(^26\) was used to optimize the geometries of the reactants, transition states (TS), and products. Frequencies calculations were performed at the same level to check whether the obtained stationary points are local minima or saddle points. Local minima and saddle points were confirmed to have all real frequencies and only one imaginary frequency, respectively. Then, vibrational frequencies of all species were scaled by a standard factor of 0.9679.\(^27\) To achieve more reliable energies of various species, the CCSD(T)/6-311++G(3d,2p) method was employed to obtain the single point energy based on the optimized geometries.\(^28\) Following the researches,

\[^*\] 1 kcal = 4184 J
the use of calculated data from the CCSD(T)/B3LYP method with 6-311++G(3df,2p) basis set in estimating the rate constants of the gas phase reactions gave the good results.29-33

At 101325 Pa pressure, temperature dependent rate constants were collected using the variational transition state theory (VTST) with Eckart tunneling correction34 and the KisThelp program.35

RESULTS AND DISCUSSION

In all systems, both addition and abstraction reaction paths were investigated:

\[
\begin{align*}
\text{CH}_3 + \text{H}_2\text{C}=\text{O} & \rightarrow \text{TS}-k_1 \rightarrow \text{CH}_3-\text{CH}_2-\text{O} & \text{(R1)} \\
\text{CH}_3 + \text{H}_2\text{C}=\text{O} & \rightarrow \text{TS}-k_2 \rightarrow \text{CH}_3-\text{O}-\text{CH}_2 & \text{(R2)} \\
\text{CH}_3 + \text{H}_2\text{C}=\text{O} & \rightarrow \text{TS}-k_3 \rightarrow \text{CH}_4 + \text{HCO} & \text{(R3)} \\
\text{CH}_3 + \text{cis-}\text{HCOH} & \rightarrow \text{TS}-k_4 \rightarrow \text{CH}_4 + \text{HOC} & \text{(R4)} \\
\text{CH}_3 + \text{cis-}\text{HCOH} & \rightarrow \text{TS}-k_5 \rightarrow \text{cis-CH}_3-\text{OH}-\text{CH} & \text{(R5)} \\
\text{CH}_3 + \text{trans-}\text{HCOH} & \rightarrow \text{TS}-k_6 \rightarrow \text{trans-CH}_3-\text{OH}-\text{CH} & \text{(R6)} \\
\text{CH}_3 + \text{trans-}\text{HCOH} & \rightarrow \text{TS}-k_7 \rightarrow \text{CH}_4 + \text{HOC} & \text{(R7)} \\
\text{CH}_3 + \text{trans-}\text{HCOH} & \rightarrow \text{TS}-k_8 \rightarrow \text{CH}_4 + \text{HCO} & \text{(R8)}
\end{align*}
\]

Details of barrier heights and enthalpy changes of reactions are presented in the section Barrier height and enthalpy changes of the reactions, and the rate constants in the section Rate constants.

Barrier height and enthalpy changes of the reactions

Eight transition states were found in the reaction of methyl radicals with formaldehyde and hydroxymethylene. The geometries of the eight transitional structures are presented in Fig. 1. The potential energy surface (PES) is shown in Fig. 2 in which the energy of reactants (\(\text{CH}_3 + \text{H}_2\text{C}=\text{O}\)) was considered as zero energy. There were three transition states in the reaction of methyl radicals with formaldehyde, i.e., addition to atom C of the molecule \(\text{H}_2\text{CO}\) via \(\text{TS}-k_1\) (7.87 kcal mol\(^{-1}\)), addition to atom O via \(\text{TS}-k_2\) (20.29 kcal mol\(^{-1}\)) and abstraction of atom H via \(\text{TS}-k_3\) (9.89 kcal mol\(^{-1}\)). Thus, the barrier of the addition reaction to atomic C was slightly lower than that of the abstraction reaction and much lower than that of the addition to atomic O. These values are in good agreement with those from previous works by Che and Liu.17,18

For \(\text{trans-}\text{HCOH}\) molecules, three transitional structures were obtained, i.e., \(\text{TS}-k_6\) (86.94 kcal mol\(^{-1}\)) from the addition reaction, and \(\text{TS}-k_7\) (58.70 kcal mol\(^{-1}\)) and \(\text{TS}-k_8\) (50.95 kcal mol\(^{-1}\)) from abstraction reactions. The calculated values for the geometrical parameters of the compounds and a comparison to experimental references are presented in Table I. The geometrical parameters estimated from the B3LYP/6-311++G(3df,2p) method agree more with experimental values.
Fig. 1. Optimized geometries of the transition states obtained at the B3LYP/6-311++G(3df,2p) level of theory. Bond lengths are shown in Å, and angles are in degrees.

Fig. 2. Details of stationary points on PES (kcal mol⁻¹) of the CH₃ + H₂CO and CH₃ + HCOH reactions obtained at the CCSD(T)/B3LYP/6-311++G(3d,2p) level. The calculation values in italic¹⁷ and underlined¹⁸ were taken from theoretical papers. The value in parentheses was the experimental value from the literature.³⁶
TABLE I. Geometrical parameters of the species

<table>
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<tr>
<th>Species</th>
<th>Experimental</th>
<th>B3LYP/6-311++G(3df,2p)</th>
<th>MP2/6-311++G(3df,2p)</th>
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</thead>
<tbody>
<tr>
<td>H₂C=O</td>
<td>d(C–H) = 1.111 Å</td>
<td>d(C–H) = 1.106 Å</td>
<td>d(C–H) = 1.101 Å</td>
</tr>
<tr>
<td></td>
<td>d(C–O) = 1.205 Å</td>
<td>d(C–O) = 1.199 Å</td>
<td>d(C–O) = 1.209 Å</td>
</tr>
<tr>
<td></td>
<td>∠(HCH) = 116.13°</td>
<td>∠(HCH) = 116.08°</td>
<td>∠(HCH) = 116.44°</td>
</tr>
<tr>
<td></td>
<td>∠(HCO) = 121.91°</td>
<td>∠(HCO) = 121.96°</td>
<td>∠(HCO) = 121.78°</td>
</tr>
<tr>
<td>CH₃</td>
<td>d(C–H) = 1.079 Å</td>
<td>d(C–H) = 1.078 Å</td>
<td>d(C–H) = 1.074 Å</td>
</tr>
<tr>
<td></td>
<td>∠(HCH) = 120.00°</td>
<td>∠(HCH) = 120.00°</td>
<td>∠(HCH) = 120.00°</td>
</tr>
<tr>
<td>CH₄</td>
<td>d(C–H) = 1.0870 Å</td>
<td>d(C–H) = 1.0881 Å</td>
<td>d(C–H) = 1.0855 Å</td>
</tr>
<tr>
<td></td>
<td>∠(HCH) = 109.471°</td>
<td>∠(HCH) = 109.471°</td>
<td>∠(HCH) = 109.471°</td>
</tr>
</tbody>
</table>

than those of the MP2/6-311++G(3df,2p) method. Therefore, when using the database from the results of the CCSD(T)/B3LYP/6-311++G(3df,2p) method, a fault was found that the relative energy of TS-k₈ in R₈ was lower by about 1.35 kcal mol⁻¹ than that of reactants (CH₃ + trans-HCOH). Therefore the geometry of these structures in this reaction path were optimized at the MP2/6-311++G(3df,2p) level and the single point energy at CCSD(T)/6-311++G(3d,2p) level was calculated. As a result, the relative energy of TS-k₈ was slightly higher than that of the reactants (CH₃ + trans-HCOH) by 0.26 kcal mol⁻¹. After considering the results from both methods, it was confirmed that, in reality, the barrier height of this process was too low to distinguish them by the calculation methods.

For cis-HCOH molecules, only two transition states, i.e., TS-k₄ (60.15 kcal mol⁻¹) of the H-abstraction reaction (R₄) and TS-k₅ (92.56 kcal mol⁻¹) of the addition reaction (R₅) were found. The calculation did not reveal a transition state for the abstraction reaction of H atom in the –CH group of the cis-HCOH molecule at the B3LYP/6-311++G(3d,2p) level, as opposed to the one for trans-HCOH via TS-k₈.

In the case of trans/cis-HCOH, all the barriers of the abstraction reactions were much lower than those of the addition reactions.

As shown in Table II, the enthalpy changes of the addition reactions of cis/trans-HCOH were positive and their reaction barriers were high and thus, the occurrence of these processes are unlikely. The enthalpy changes of the remaining reactions were negative, especially in the hydrogen-atom abstraction reactions of cis/trans-HCOH, which are very likely to occur. In the three reactions of formaldehyde, the barrier of the abstraction reaction was higher than that of the carbon-atom addition reaction. However, the enthalpy change of the abstraction reaction (−16.39 kcal mol⁻¹) was much lower than that of the carbon-atom addition reaction (−7.82 kcal mol⁻¹). This value is close that determined by Liu et al. (−16.53 kcal mol⁻¹) and the experimental value (−14.63 kcal mol⁻¹).
TABLE II. Expression of the rate constant and enthalpy changes of reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant, cm$^3$ mol$^{-1}$ s$^{-1}$</th>
<th>$\Delta H_{298 K}^0$ / kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This study</td>
<td>from data$^{42}$</td>
</tr>
<tr>
<td>(R1)</td>
<td>$k_1 = 4.394 \times 10^{-22} T^{2.76} \exp(-5.71 \text{ kcal mol}^{-1}/RT)$</td>
<td>$-11.38$</td>
</tr>
<tr>
<td>(R2)</td>
<td>$k_2 = 4.137 \times 10^{-22} T^{2.90} \exp(-18.13 \text{ kcal mol}^{-1}/RT)$</td>
<td>$-7.82$</td>
</tr>
<tr>
<td>(R3)</td>
<td>$k_3 = 2.644 \times 10^{-25} T^{4.22} \exp(-5.56 \text{ kcal mol}^{-1}/RT)$</td>
<td>$-16.39$</td>
</tr>
<tr>
<td>(R4)</td>
<td>$k_4 = 1.064 \times 10^{-21} T^{5.08} \exp(-1.66 \text{ kcal mol}^{-1}/RT)$</td>
<td>$-31.14$</td>
</tr>
<tr>
<td>(R5)</td>
<td>$k_5 = 7.136 \times 10^{-23} T^{2.91} \exp(-33.00 \text{ kcal mol}^{-1}/RT)$</td>
<td>$13.97$</td>
</tr>
<tr>
<td>(R6)</td>
<td>$k_6 = 8.567 \times 10^{-23} T^{2.38} \exp(-31.82 \text{ kcal mol}^{-1}/RT)$</td>
<td>$18.10$</td>
</tr>
<tr>
<td>(R7)</td>
<td>$k_7 = 1.174 \times 10^{-22} T^{3.58} \exp(-3.90 \text{ kcal mol}^{-1}/RT)$</td>
<td>$-26.73$</td>
</tr>
<tr>
<td>(R8)</td>
<td>$k_8 = 1.174 \times 10^{-22} T^{3.58} \exp(-3.90 \text{ kcal mol}^{-1}/RT)$</td>
<td>$-68.71$</td>
</tr>
</tbody>
</table>

Rate constant

Resulting rate constant calculation values of (R3) are shown in Fig. 3 and Table III in the temperature range 300–2000 K. The obtained rate constant of (R3) agreed with experimental results,$^{16}$ and is better than the calculations in the work of Li et al.$^{15}$ At 600 K, the presented calculation showed that the rate constant of (R3) was $1.24 \times 10^{-15} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is close to the experimental value (1.20 $\times 10^{-15} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$.\textsuperscript{16}

Fig 3. Plot of the calculated rate constants, $k_3$ / cm$^3$ mol$^{-1}$ s$^{-1}$, by the CCSD(T)/6-311++G(3d,2p) method and available experimental data versus 1000/T for (R3) at a pressure of 101325 Pa.

As mentioned above, the calculation for barrier height of TS-$k_8$ was faulty and hence, CCSD(T)/B3LYP/6-311++G(3df,2p) methods were not used to calculate the rate constant for the reaction via TS-$k_8$. The rate constants for seven reactions (R1)–(R7) are given in Table IV. These rate constant expressions were presented in Table II. These results have showed that rate constant of each abstraction reaction was higher than that of the addition one. Although the barrier of H-abstraction reaction of CH$_3$ with H$_2$C=O was higher than that of C-addition of H$_2$C=O, the H-abstraction rate constant was higher. The rate constants of addi-
tion of trans/cis-HCHO molecules were quite small. These values are in agreement with the positive enthalpy changes of these reactions.

TABLE III. Rate constants for R3 and R1 in the temperature range 300–2000 K, at 101325 Pa pressure

<table>
<thead>
<tr>
<th>$T / K$</th>
<th>$k_3$ / cm$^3$ mol$^{-1}$ s$^{-1}$</th>
<th>$k_1$ / cm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>$7.96 \times 10^{-19}$</td>
<td>$1.20 \times 10^{-19}$</td>
</tr>
<tr>
<td>400</td>
<td>$2.13 \times 10^{-17}$</td>
<td>$5.92 \times 10^{-18}$</td>
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<tr>
<td>500</td>
<td>$1.24 \times 10^{-15}$</td>
<td>$3.97 \times 10^{-16}$</td>
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<td>600</td>
<td>$1.41 \times 10^{-14}$</td>
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<td>700</td>
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<tr>
<td>1200</td>
<td>$5.13 \times 10^{-12}$</td>
<td>$1.15 \times 10^{-12}$</td>
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TABLE IV. Rate constants, cm$^3$ mol$^{-1}$ s$^{-1}$, for reactions R1–R7

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<tr>
<th>$T / K$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_3$</th>
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<td>$1.09 \times 10^{-13}$</td>
<td>$1.13 \times 10^{-14}$</td>
<td>$3.90 \times 10^{-12}$</td>
<td>$8.99 \times 10^{-12}$</td>
<td>$4.10 \times 10^{-17}$</td>
<td>$5.10 \times 10^{-17}$</td>
<td>$2.33 \times 10^{-11}$</td>
</tr>
<tr>
<td>2000</td>
<td>$1.33 \times 10^{-13}$</td>
<td>$1.64 \times 10^{-14}$</td>
<td>$5.13 \times 10^{-12}$</td>
<td>$1.06 \times 10^{-11}$</td>
<td>$7.39 \times 10^{-17}$</td>
<td>$9.00 \times 10^{-17}$</td>
<td>$2.93 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

Figures 3 and 4, and Table III, show that the rate constants of (R1) and (R3) were in good agreement with experimental results at high temperatures. For example, at 2000 K, in cm$^3$ mol$^{-1}$ s$^{-1}$ units, the calculations in this study were $k_3 = 5.13 \times 10^{-12}$ and $k_1 = 1.33 \times 10^{-13}$, in comparison to the experimental results of $k_3 = 5.05 \times 10^{-12}$ and $k_1 = 1.01 \times 10^{-13}$. 

Available on line at www.shd.org.rs/JSCS/
The temperature dependence of the branching ratios is illustrated in Fig. 5. In all temperature regions, the branching ratio of CH$_3$–O–CH$_2$ was negligibly small. At the highest temperature in this study, 2000 K, CH$_3$–O–CH$_2$ was 0.3%. The pathway leading to product (CH$_4$+HCO) dominated over the entire studied temperature range. In the temperature range 300–2000 K, the branching ratio of CH$_4$+HCO increased gradually from 80.4 to 97.2% while the branching ratio of CH$_3$–CH$_2$–O decreased gradually from 19.6 to 2.5%.

CONCLUSIONS

In this work, chemically accurate \textit{ab initio} CCSD(T)/B3LYP/6-311++G(3df,2p) calculations of PES for the addition and hydrogen-atom abstraction reactions (CH$_3$ + H$_2$=CO) and (CH$_3$ + HCOH) were performed, followed by calculations of the rate constants by the VTST method. Enthalpy change values of reactions were estimated by the CCSD(T)/6-311++G(3df,2p) method. The calculated results showed that the hydrogen abstraction reactions were the primary pathway in the temperature range from 300 to 2000 K. Three-parameter fittings of the calculated rate constants induced expressions for these reactions.
The rate constants of abstraction reactions for hydroxymethylene were much greater than those for formaldehyde. Moreover, the calculation results showed better agreement than previous works on rate constants of the addition and hydrogen abstraction reactions of the methyl radical with formaldehyde. This research may shed light on experimental studies and knowledge of the reaction mechanism of the methyl radical and hydroxymethylene.

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