Atmospheric chemistry of CH$_3$O: its unimolecular reaction and reactions with H$_2$O, NH$_3$, and HF

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We have investigated the hydrogen atom transfer processes of CH$_3$O to CH$_2$OH without catalyst and with water, ammonia, and hydrofluoric acid as catalysts using ab initio methods, density functional theory (DFT) methods, and canonical variational transition state theory with small curvature tunneling (CVT/SCT). Herein, we have performed the benchmark barrier heights of the title reactions using W3X-LI/CCSD(T)-F12a/VDZ-F12 methods. We have also performed the calculations of the combination of MPW-type, PBE-type exchange, M05-type, M06-type functional, and composite theoretical model chemistry methods such as CBS-QB3 and G4. We found that the M05-2X/aug-cc-pVTZ, mPW2PLYP/MG3S, M05-2X/aug-cc-pVTZ, and M06-2X/MG3S methods are performed better in different functionals with the unsigned errors (UEs) of 0.34, 0.02, 0.05, and 0.75 kcal mol$^{-1}$ for its unimolecular reaction and reactions with H$_2$O, NH$_3$, and HF, respectively. The calculated results show that NH$_3$ exerts the strongest catalytic role in the isomerization reaction of CH$_3$O to CH$_2$OH, compared with H$_2$O and HF. In addition, the calculated rate constants show that the effect of tunneling increases the rate constant of the unimolecular reaction of CH$_3$O by $10^2$–$10^{12}$ times in the temperature range of 210–350 K. Moreover, the variational effects of the transition state are obvious in CH$_3$O + NH$_3$. The calculated results also show that the direct unimolecular reaction of CH$_3$O to CH$_2$OH is dominant in the sink of CH$_3$O, compared with the CH$_2$OH + H$_2$SO$_4$, CH$_2$OH + HCOOH, CH$_2$OH + H$_2$O, CH$_2$OH + NH$_3$, and CH$_2$OH + HF reactions in the atmosphere. The present results provide a new insight into catalysts that not only affect energy barriers, but have influences on tunneling and variational effects of transition states. The present findings should have broad implications in computational chemistry and atmospheric chemistry.

1. Introduction

Alkoxy radicals have received a great amount of attention because they play a key role in both combustion and atmospheric chemistry.¹ The methoxy radical (CH$_3$O) is one of the simplest alkoxy radicals.² CH$_3$O is produced from OH-initiated oxidation of CH$_4$.³ In the atmosphere, CH$_3$O undergoes unimolecular isomerization and decomposition and bimolecular reaction.⁴ While CH$_3$O dominantly reacts with O$_2$, responsible for the formation of HCHO and HO$_2$, the CH$_3$OH + O$_2$ reaction is 10¹ times faster than the CH$_2$OH + O$_2$ reaction, where CH$_2$OH is formed through the hydrogen atom transfer of CH$_3$O.⁵ Therefore, Radford stated that the isomerization reaction of CH$_3$O could be an important process for the loss of CH$_3$O.⁶

Exploring the unimolecular isomerization of CH$_3$O is required to estimate the fate of CH$_3$O in the atmosphere. The reaction kinetics and dynamics of methoxy radicals (CH$_3$O) has been extensively investigated for both experimental and theoretical methods in the literature.¹⁷–¹⁹ However, the kinetics of the unimolecular isomerization reaction of CH$_3$O remains unclear. With regard to the unimolecular reaction of CH$_3$O, the energy barrier is very high, in the range of 26–36 kcal mol$^{-1}$, depending on different theoretical methods.¹⁴,¹⁶,²⁰–²² For example, Batt et al.¹⁶ estimated an energy barrier of 26.1 kcal mol$^{-1}$, Tachikawa et al.²² reported an energy barrier of 32.88 kcal mol$^{-1}$ calculated by CCSDST4/D95V**, Saibo et al.²¹ reported an energy barrier of 36 kcal mol$^{-1}$ calculated by MP3/6-31G**. This uncertainty of energy barrier of CH$_3$O unimolecular isomerization leads to the difficulty in quantitatively estimating the rate constant of CH$_3$O unimolecular isomerization reaction. In addition, CH$_3$O unimolecular isomerization is a hydrogen atom transfer (HAT) reaction. In particular, tunneling effects play a critical role in reaction kinesics for hydrogen transfer reactions,²³,²⁴ such as the unimolecular reactions of Criegee intermediates,²⁵–²⁸ CH$_2$OH + OH,²⁹ HO + H$_2$SO$_4$–NH$_2$,²⁰ unimolecular rearrangement of Rh(PH$_3$)$_2$ClCH$_4$,³¹ H/D + CO,³²,³³ H/D + CH$_3$OH,³⁴ and Al

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+ 3H₂O. Therefore, it is necessary to reevaluate kinetics of the unimolecular isomerization reaction of CH₃O.

The other issue is that there are some reports that water and atmospheric acids can remarkably decrease the energy barrier of hydrogen atom transfer reaction. More over water, sulfuric acid, and formic acid have been reported to reduce the isomerization of methoxy to 25.7, 2.3, and 4.2 kcal mol⁻¹, respectively. In particular, the calculated results are 25.7 kcal mol⁻¹ by Buszek et al. and 22.9 kcal mol⁻¹ by Kumar et al. at the CCSD(T)/aug-cc-pVTZ/QCISD/6-31G(d) and CCSD(T)/aug-cc-pVTZ/MP2/aug-cc-pVTZ, respectively. It is noted that the reported water catalytic CH₃O isomerization of the energy barrier has difference of 2–3 kcal mol⁻¹. This results lead to the inaccuracy of evaluating the kinetics of the methoxy unimolecular isomerization reaction. In addition, the catalytic effect of ammonia is better than in the literature. Hydrofluoric acid is an important inorganic acid in the atmosphere. So, we calculated the H₂O, NH₃, and HF as catalysts in the unimolecular isomerization reaction of CH₃O.

In this work, we investigated the hydrogen atom transfer processes of CH₃O to CH₂OH catalyzed by water, ammonia, and hydrofluoric acid using ab initio methods and density functional theory (DFT) methods, and canonical variational transition state theory with small curvature tunneling (CVT/SCT). We studied following reactions:

\[
\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{OH} \quad (1)
\]

\[
\text{CH}_3\text{O} + M \rightarrow \text{CH}_2\text{OH} + M \quad (2)
\]

where M stands for H₂O, NH₃, and HF. The purpose of this work is to determine which functional is best for every specific reaction studied here and estimate the catalytic capability of these catalysts, explore the tunneling effects, and obtain the quantitative rate constants. Herein, we also present definitive examples how to use theoretical methods to predict the quantitative rate constants for hydrogen atom transfer reactions.

2. Computational methods

2.1. Benchmark calculation

It is of great necessity for studying the atmospheric reactions with high-accurate electronic structure methods to obtain quantitative results. We used the CCSD(T)-F12a/VDZ-F12 (ref. 38–40) and QCISD/VTZ** methods for optimizing the reactants, pre-reactive complexes, transition states, post-reactive complexes, and products and calculating their corresponding frequencies. Single point energy calculations were carried out using the W2X** and W3X-L** methods at the CCSD(T)-F12a/VDZ-F12 and QCISD/VTZ optimized geometries, respectively. We have obtained the benchmark barrier heights of hydrogen atom transfer reactions for CH₃O to CH₂OH by different catalysts at the W3X-L/CCSD(T)-F12a/VDZ-F12 level as our best estimate. It is worth noting that W3X-L composite methods have been used in the reactions of Criegee intermediates with water, SO₂ with OH, and HO₂ with XCHO to obtain rate constants with experimental accuracy.

2.2. Composite method calculation

Quantum chemical composite methods have developed because they approach CCSD(T)/CBS.** We used G4, unrestrained coupled cluster spin contamination corrected [UCCSD(T)], and unrestricted Brueckner doubles [UBD(T)] variations of the Weizmann-1 theory (W1), named as W1U and W1BD, and the CBS-QB3 (ref. 47) method.

2.3. Density functional theory (DFT) calculation

We studied different functionals: (1) the generalized gradient approximation (GGA) such as B98 ref. 48 and BP86 (ref. 49–51); (2) depending on the density of Laplace or kinetic energy density of meta-GGA such as M11-L; (3) hybrid GGA with the addition of Hartree–Fock (HF) exchange to non-local information of occupied orbital such as BKM; (4) global hybrid meta-GGA: B3LYP, M05-2X, M06-HF, and M06-2X; (5) range-separated hybrid meta GGA such as M11 (ref. 66) and range-separated meta-NGA such as MN12-SX; and (6) double hybrid density functional using from both occupied and virtual orbital such as B2PLYP, B2PLYPD, and MPW2PLYP. These computations were finished using aug-cc-pVTZ, aug-cc-pVTZ, and ma-TZVP basis sets.

2.4. Reaction kinetics

The rate constants were calculated using canonical variational transition-state theory with small curvature tunneling (CVT/SCT). We selected the best functional for every specific reaction to do direct dynamics calculations by comparing with our best estimate. The unimolecular rate constants of CH₃O to CH₂OH was calculated by M05-2X/aug-cc-pVTZ, while the bimolecular rate constants of the CH₃O + H₂O, CH₃O + NH₃, and CH₃O + HF reactions were calculated using MPW2PLYP/MG3S, M05-2X/aug-cc-pVTZ, and M06-2X/MG3S, respectively. Scale factors were used to scale all directly calculated harmonic vibrational frequencies, which are 0.964, 0.972, 0.964, and 0.970 for M05-2X/aug-cc-pVTZ, MPW2PLYP/MG3S, M05-2X/aug-cc-pVTZ, and M06-2X/MG3S, respectively.

The optimization and frequency calculations of all geometries including reactants, transition states, and products calculated were carried out with the Gaussian 09 (ref. 83) suites of programs. The high level geometry optimization calculations are performed using the Molpro 2012 (ref. 84) suites of programs. Rate constants were calculated using the Polyrate 2010A and Gausssrate 2009 (ref. 86) dynamics codes.

3. Results and discussion

We have obtained the benchmark barrier heights of CH₃O to CH₂OH without catalyst and with water, ammonia, and hydrofluoric acid as catalysts using W3X-L/CCSD(T)-F12a/VDZ-F12 methods. We defined the unsigned error (UE) to determine which is the best functional, and UE is the absolute value of the difference between the computed barrier heights by different methods and the benchmark barrier heights calculated by W3X-L/CCSD(T)-F12a/VDZ-F12.
3.1. The unimolecular isomerization of CH$_3$O

The unimolecular isomerization of CH$_3$O into CH$_2$OH occurs via the transfer of the hydrogen atom of CH$_3$ group to the oxygen atom in CH$_3$O responsible for the formation of CH$_2$OH as shown in Fig. 1. The unimolecular isomerization of CH$_3$O into CH$_2$OH has been extensively studied using different theoretical methods; the previous calculated results indicated that the barrier heights of the unimolecular isomerization of CH$_3$O into CH$_2$OH are varies between 26.1 and 36.0 kcal mol$^{-1}$

Therefore, higher-level theoretical methods are required to obtain quantitative results. Herein, we use the benchmark calculation of beyond-CCSD(T) to obtain reliable results. The main results are summarized in Table 1 and Fig. 1, while all the results are provided in Table S1 (ESI).

The calculated results by W3X-L//CCSD(T)-F12a/VDZ-F12 indicate that the barrier height of the reaction is 29.56 kcal mol$^{-1}$ in Table 1. Fig. 2 shows that the results are calculated by various density functional methods and *ab initio* methods, where the UEs are 0.13, 0.18, 0.32, and 0.34 kcal mol$^{-1}$ using W1U, CBS-QB3, W1BD, and M05-2X/aug-cc-pVTZ, respectively; this results reflect slight changes for different theoretical methods. Therefore, the barrier height of the unimolecular isomerization of CH$_3$O into CH$_2$OH is computed to be 29.56 kcal mol$^{-1}$ (W3X-L//CCSD(T)-F12a/VDZ-F12), which should be reliable. The W2X//CCSD(T)-F12a/VDZ-F12 result is 29.64 kcal mol$^{-1}$, which agrees well with the value of 29.56 kcal mol$^{-1}$; this shows that the electronic

![Fig. 1](image)

*Fig. 1* Variation in potential energy surface for the reactants, intermediates, transition states, and products of the CH$_3$O isomerization into CH$_2$OH in the without catalysis and catalyzed by water, ammonia, and hydrofluoric acid reactions at the W3X-L//CCSD(T)-F12a/VDZ-F12 level.

| Methods               | TS1   | UE    | TS2   | UE    | TS3   | UE    | TS4   | UE    |
|-----------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| W3X-L//CCSD(T)-F12a/VDZ-F12 | 29.56 | 0.00  | 24.17 | 0.00  | 15.21 | 0.00  | 23.82 | 0.00  |
| W2X//CCSD(T)-F12a/VDZ-F12 | 29.64 | 0.08  | 24.26 | 0.09  | 15.26 | 0.05  | 24.30 | 0.48  |
| W2X//QCISD/cc-pVTZ     | 29.07 | 0.49  | 23.82 | 0.35  | 14.65 | 0.56  | 23.86 | 0.04  |
| W3X-L//QCISD/cc-pVTZ   | 28.99 | 0.57  | 23.74 | 0.43  | 14.62 | 0.59  | 23.32 | 0.50  |
| W1U                   | 29.69 | 0.13  | 24.72 | 0.55  | 15.32 | 0.11  | 25.39 | 1.57  |
| W1BD                  | 29.88 | 0.32  | 24.88 | 0.71  | 15.47 | 0.26  | 25.11 | 1.29  |
| mPW2PLYP/MG3S         | 31.33 | 1.77  | 24.15 | 0.02  | 15.48 | 0.27  | 22.92 | 0.90  |
| M06-2X/MG3S           | 30.39 | 0.83  | 23.19 | 0.98  | 15.71 | 0.50  | 23.07 | 0.75  |
| G4                    | 30.09 | 0.53  | 25.87 | 1.70  | 15.97 | 0.76  | 25.55 | 1.73  |
| CBS-QB3               | 29.74 | 0.18  | 25.24 | 1.07  | 15.06 | 0.15  | 27.62 | 3.80  |
| M05-2X/aug-cc-pVTZ    | 29.90 | 0.34  | 21.35 | 2.82  | 15.16 | 0.05  | 20.41 | 3.41  |
| M05-2X/maug-cc-pVTZ   | 30.04 | 0.48  | 21.65 | 2.52  | 15.40 | 0.19  | 20.80 | 3.02  |

*Table 1* The energy barriers of the CH$_3$O isomerization into CH$_2$OH, the CH$_3$O + H$_2$O, CH$_3$O + NH$_3$, and CH$_3$O + HF reactions with zero-point energy involved at 0 K (kcal mol$^{-1}$).

* †*Unsigned error (UE) obtained via the absolute value of the difference between the computed barrier heights and the benchmark barrier heights.
The unimolecular isomerization of CH$_3$O into CH$_2$OH with water as a catalyst using W3X-L//CCSD(T)-F12a/VDZ-F12 theoretical method. The computed energy barrier is 24.17 kcal mol$^{-1}$ in Table 1. Additionally, Fig. 3 shows that the UEs are 0.02, 0.55, and 0.71 kcal mol$^{-1}$ for the mPW2PLYP/MG3S, W1U, and W1BD theoretical methods, respectively, comparing with the barrier height of TS2 calculated by W3X-L//CCSD(T)-F12a/VDZ-F12.

Previous investigations have shown that ammonia has remarkably catalytic role in hydrogen transfer processes in the H$_2$SO$_4$...NH$_3$+OH, CF$_3$OH+NH$_3$, SO$_3$+H$_2$O+NH$_3$ (ref. 87) reactions. Herein, we investigate the CH$_3$O+NH$_3$ reaction, resulting in the formation CH$_2$OH and NH$_3$, where NH$_3$ is acted as a catalyst. The optimized geometries of the transition state TS3 are provided in Fig. 1. The energy barrier of the CH$_3$O+NH$_3$ reaction is 15.21, 15.26 kcal mol$^{-1}$ using the best W3X-L//CCSD(T)-F12a/VDZ-F12 method, W2X//CCSD(T)-F12a/VDZ-F12 method in Table 1, which shows that the beyond-CCSD(T) calculations are not necessary for obtaining quantitative results; this shows that there are not multireference features in the CH$_3$O+NH$_3$ reaction. In addition, the QCISD-optimized geometries and frequency calculations are still not adequate to obtain quantitative results because the UE of W3X-L//CCSD/T/VTZ is 0.59 kcal mol$^{-1}$, comparing with the results calculated by W3X-L//CCSD(T)-F12a/VDZ-F12 in Table 1. The calculated results also shows that NH$_3$ has much stronger catalytic ability in the isomerization reaction of CH$_3$O to CH$_2$OH than H$_2$O because the energy of the CH$_3$O+NH$_3$ reaction is about 9 kcal mol$^{-1}$ lower than that of the CH$_3$O+H$_2$O reaction, which also agree with the previous investigation in the CF$_3$OH+NH$_3$ reaction. It is noted the UE of M05-2X/aug-cc-pVTZ is only 0.05 kcal mol$^{-1}$ in Table 1 and Fig. 4. Thus, the M05-2X/aug-cc-pVTZ theoretical method is chosen to do direct dynamics calculations in the CH$_3$O+NH$_3$ reaction.

When HF is acted as a catalyst in the CH$_3$O+HF reaction responsible for the formation of CH$_2$OH, the energy barrier is decreased to 23.82 kcal mol$^{-1}$ in the CH$_3$O+HF reaction from 29.56 kcal mol$^{-1}$ in the unimolecular reaction of CH$_3$O to CH$_2$OH at the W3X-L//CCSD(T)-F12a/VDZ-F12 level in Table 1. In addition, it is particularly noted that the difference in the energy of the CH$_3$O+HF reaction between W3X-L//CCSD(T)-F12 and W2X//CCSD(T)-F12a/VDZ-F12 is about 0.5 kcal mol$^{-1}$.
which shows that there are certain multireference features for the transition state TS4; this reveals that different catalyst may lead to the variation of nature of electronic structures in the transition states. Also, the W3X-L/CCISD/VTZ energy barrier is estimated to be 23.32 kcal mol$^{-1}$, which is about 0.5 kcal mol$^{-1}$ different from the W3X-L/CCISD(T)-F12a/VDZ-F12 in TS4; this shows that the QCISD/VTZ-optimized geometries and calculated frequencies still present unreliable results in estimating rate constants quantitatively for hydrogen transfer systems. It is noted that the CBS-QB3 result is 27.62 kcal mol$^{-1}$ and the M05-2X/aug-cc-pVTZ result is 20.41 kcal mol$^{-1}$ as listed in Table 1. The difference between CBS-QB3 and M05-2X/aug-cc-pVTZ is about 7.21 kcal mol$^{-1}$. However, compared with the benchmark result of 23.82 kcal mol$^{-1}$, the CBS-QB3 method overestimates the barrier height, while the M05-2X/aug-cc-pVTZ method underestimates the barrier in TS4. The UE of M06-2X/MG3S is about 0.75 kcal mol$^{-1}$, which is the best functional for the CH$_3$O + HF reaction as shown in Table 1 and Fig. 5.

3.3. Rate constants

The calculated rate constants are presented in Table 2, where lists that the rate constants of the four reactions investigated herein are calculated using canonical variational transition-state theory with small curvature tunneling (CVT/SCT) in the temperature range of 210–350 K. Tunneling transmission coefficients are listed in Table 2, which shows that the tunneling transmission coefficients are very large for the hydrogen atom transfer process at 210 K. Furthermore, the tunneling transmission coefficient in the unimolecular isomerization of CH$_3$O to CH$_2$OH is even larger than the other reaction; in particular it is 3.29 $\times$ 10$^{-12}$ at 210 K (Table 2). It is also noted that tunneling effects are very remarkable in the CH$_3$O unimolecular isomerization into CH$_2$OH, CH$_3$O + H$_2$O, and CH$_3$O + HF reactions, while the CH$_2$O + NH$_3$ reaction is not remarkable. For example, the tunneling coefficients are 4.71 $\times$ 10$^4$, 6.46 $\times$ 10$^5$, and 9.18 $\times$ 10$^5$ remarkable in the CH$_3$O unimolecular isomerization into CH$_2$OH, CH$_3$O + H$_2$O, and CH$_3$O + HF reactions, while the tunneling coefficient in the CH$_3$O + NH$_3$ reaction is only 5.85 at 298 K (Table 2). It is particular noted that the energy barrier in the CH$_3$O + NH$_3$ reaction is the lowest of the four reactions; this shows that although NH$_3$ exerts the strongest catalytic role in the CH$_3$O unimolecular isomerization into CH$_2$OH for three different catalysts, NH$_3$ also reduces tunneling and consequently that the rate constants of the CH$_3$O + NH$_3$ reaction is still slow.

The variational effects are also different from each other in Table 2. Of particular interest is the obvious variational effects in the CH$_3$O + NH$_3$, leading in further decreasing the rate constants of the CH$_3$O + NH$_3$ reaction. Thus, the catalyst not only has influences on the energy barriers, but affects on tunneling and variational effects of transition states.

It is worth noting that the rate constants of these reactions are increased with the increase of temperature. At 298 K, the rate constants of the CH$_3$O isomerization into CH$_2$OH, CH$_3$O + H$_2$O, CH$_3$O + NH$_3$, and CH$_3$O + HF reactions are 9.15 $\times$ 10$^{-1}$ s$^{-1}$, 3.27 $\times$ 10$^{-28}$ cm$^3$ per molecule per s, 6.14 $\times$ 10$^{-24}$ cm$^3$ per molecule per s, and 5.17 $\times$ 10$^{-26}$ cm$^3$ per molecule per s, respectively. In addition, note that $k_3$ is estimated to be 6.89 $\times$ 10$^{-27}$–4.09 $\times$ 10$^{-25}$ cm$^3$ per molecule per s between 230 and 350 K, while $k_3$ is estimated to be 0.20 $\times$ 10$^{-26}$–1.78 $\times$ 10$^{-22}$ cm$^3$ per molecule per s between 230 and 350 K; this shows $k_3$ is larger than $k_4$. However, in 210 K $k_4$ is calculated to be 4.53 $\times$ 10$^{-27}$ cm$^3$ per molecule per s, which is slightly larger than that of $k_3$ (3.11 $\times$ 10$^{-27}$ cm$^3$ per molecule per s) because the tunneling of TS4 is 6.87 $\times$ 10$^3$, which is much larger than that of TS3 (1.73 $\times$ 10$^3$).

3.4. Atmospheric implications

The calculated atmospheric lifetimes are provided in Table 3. With regard to the unimolecular reaction, $\tau_{TS1}$ is calculated by $\tau_{TS1} = \frac{1}{k_1}$, where $k_1$ is the unimolecular rate constant of the reaction TS1, while for bimolecular reactions, $\tau_{TS2}$, $\tau_{TS3}$, and $\tau_{TS4}$ are calculated by $\tau_{TS2} = \frac{1}{k_2[H_2O]}$, $\tau_{TS3} = \frac{1}{k_3[NH_3]}$, and $\tau_{TS4} = \frac{1}{k_4[HF]}$, where $k_2$, $k_3$, and $k_4$ are the bimolecular rate constants of the reactions TS2, TS3, and TS4, respectively, and [H$_2$O] is the concentration of H$_2$O is 4.4 $\times$ 10$^{16}$ molecule per cm$^3$, [NH$_3$] is the concentration of NH$_3$ is 1.32 $\times$ 10$^{12}$ molecule per cm$^3$, and [HF] is the concentration of HF is 1.8 $\times$ 10$^7$ molecule per cm$^3$. 

![Fig. 4 The unsigned error for the energy barrier of CH$_3$O + NH$_3$.](image1)

![Fig. 5 The unsigned error for the energy barrier of CH$_3$O + HF.](image2)
The calculated unimolecular rate constants \( k_a \) and the bimolecular reaction rate constants \( k_{ab} \) and \( k_{ac} \) cm\(^3\) per molecule per s for the reactions of CH\(_3\)O with H\(_2\)O and HF are mPW2PLYP/MG3S and M06-2X/MG3S, respectively.

| \( T/K \) | \( r_{TS1}^a \) | \( r_{TS2}^b \) | \( r_{TS3}^b \) | \( r_{TS4}^b \) |
|---|---|---|---|---|
| 210 | \( 3.4 \times 10^3 \) | \( 1.7 \times 10^{12} \) | \( 2.4 \times 10^{14} \) | \( 1.2 \times 10^{19} \) |
| 230 | \( 1.9 \times 10^3 \) | \( 5.4 \times 10^{11} \) | \( 3.8 \times 10^{13} \) | \( 8.1 \times 10^{18} \) |
| 250 | \( 9.4 \times 10^3 \) | \( 1.6 \times 10^{11} \) | \( 6.1 \times 10^{12} \) | \( 4.9 \times 10^{18} \) |
| 270 | \( 4.1 \times 10^4 \) | \( 4.4 \times 10^{10} \) | \( 1.1 \times 10^{12} \) | \( 2.8 \times 10^{18} \) |
| 290 | \( 1.6 \times 10^4 \) | \( 1.2 \times 10^{10} \) | \( 2.2 \times 10^{11} \) | \( 1.4 \times 10^{18} \) |
| 298 | \( 1.1 \times 10^4 \) | \( 7.0 \times 10^9 \) | \( 1.2 \times 10^{11} \) | \( 1.1 \times 10^{18} \) |
| 310 | \( 5.8 \times 10^4 \) | \( 3.1 \times 10^9 \) | \( 5.3 \times 10^{10} \) | \( 6.9 \times 10^{17} \) |
| 330 | \( 1.9 \times 10^5 \) | \( 8.4 \times 10^8 \) | \( 1.4 \times 10^{10} \) | \( 3.1 \times 10^{17} \) |
| 350 | \( 5.8 \times 10^5 \) | \( 2.3 \times 10^8 \) | \( 4.3 \times 10^9 \) | \( 1.4 \times 10^{17} \) |

\( a \) For the unimolecular reaction, \( r_{TS1}^b = \frac{1}{k_b} \), where \( k_b \) is the unimolecular rate constant of the reaction TS1. For bimolecular reactions, \( r_{TS2}^b = \frac{1}{k_2[H_2O]} \), \( r_{TS3}^b = \frac{1}{k_3[NH_3]} \), and \( r_{TS4}^b = \frac{1}{k_4[HF]} \), where \( k_2, k_3, \) and \( k_4 \) are the bimolecular rate constants of the reactions TS2, TS3, and TS4, respectively, and [H\(_2\)O] is the concentration of H\(_2\)O is 4.4 \times 10\(^7\) molecules per cm\(^3\); [NH\(_3\)] is the concentration of NH\(_3\) is 1.32 \times 10\(^8\) molecules per cm\(^3\); and [HF] is the concentration of HF is 1.8 \times 10\(^7\) molecule per cm\(^3\).}

The atmospheric lifetime of the direct unimolecular reaction of CH\(_3\)O to CH\(_2\)OH at 298 K, which shows that the direct unimolecular reaction of CH\(_3\)O to CH\(_2\)OH can compete well with the corresponding bimolecular reaction of CH\(_3\)O + H\(_2\)SO\(_4\) and CH\(_3\)O + HCOOH.

4. Concluding remarks

The unimolecular reaction of CH\(_3\)O to CH\(_2\)OH catalyzed by different catalysts has been investigated by combining with W3X-L/CCSD(T)-F12a/VDZ-F12 benchmark calculations, the validated density functional, and canonical variational transition-state theory with small curvature tunneling. The main conclusions are extracted from the results as follows.

1. We considered significant pathways for the isomerization of CH\(_3\)O to CH\(_2\)OH via the reactions with water, ammonia, and hydrofluoric acid. The results show that different catalysts can decrease the energy barrier of the unimolecular isomerization of CH\(_3\)O to CH\(_2\)OH. The reductions of energy barriers for the isomerization of CH\(_3\)O to CH\(_2\)OH catalyzed by water, ammonia, and hydrofluoric acid are 5.39, 14.35, and 5.74 kcal mol\(^{-1}\) respectively, comparing with the energy barrier of the isomerization of CH\(_3\)O to CH\(_2\)OH without catalyst. Thus, the result shows that ammonia has the best catalytic ability among the three catalysts.

2. We tabulate the unsigned error (UE) of the tested methods as listed in Table 1. The calculated results also show that the different functionals with basis sets have different accuracy. Among the functionals, the best method for the unimolecular isomerization of methoxy to hydroxymethyl and the bimolecular reaction of CH\(_3\)O with NH\(_3\) are M05-2X/aug-cc-pVTZ. And, the best method for the bimolecular reactions of CH\(_3\)O with H\(_2\)O and HF are mPW2PLYP/MG3S and M06-2X/MG3S, respectively.

3. The calculated rate constants show that catalysts can affect variational effects of transition states and tunneling. In addition, we show that the atmospheric lifetime of CH\(_3\)O is mainly determined by the direct unimolecular reaction of CH\(_3\)O to CH\(_2\)OH due to tunneling, which has not been previously considered.
Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research is supported by National Natural Science Foundation of China (41775125 and 41615007), Science and Technology Foundation of Guizhou Province & Guizhou Minzu University, China[(2015)7211], Science and Technology Foundation of Guizhou Provincial Department of Education, China [(2015)350).

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