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Effect of ammonia and water molecule on OH + CH₃OH reaction under tropospheric condition

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The rate coefficients for OH + CH₃OH and OH + CH₃OH (+ X) (X = NH₃, H₂O) reactions were calculated using microcanonical, and canonical variational transition state theory (CVT) between 200 and 400 K based on potential energy surface constructed using CCSD(T)//M06-2X/6-311++G(3df,3pd). The results show that OH + CH₃OH is dominated by the hydrogen atoms abstraction from CH₃ position in both free and ammonia/water catalyzed ones. This result is in consistent with previous experimental and theoretical studies. The calculated rate coefficient for the OH + CH₃OH ($8.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), for OH + CH₃OH (+ NH₃) [$1.9 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$] and for OH + CH₃OH (+ H₂O) [$8.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$] at 300 K. The rate coefficient is at least 8 order magnitude [for OH + CH₃OH(+ NH₃) reaction] and 3 orders magnitude [OH + CH₃OH (+ H₂O)] are smaller than free OH + CH₃OH reaction. Our calculations predict that the catalytic effect of single ammonia and water molecule on OH + CH₃OH reaction has no effect under tropospheric conditions because the dominated ammonia and water-assisted reaction depends on ammonia and water concentration, respectively. As a result, the total effective reaction rate coefficients are smaller. The current study provides a comprehensive example of how basic and neutral catalysts effect the most important atmospheric prototype alcohol reactions.

Methanol (CH₃OH) is most abundant volatile organic compounds (VOCs) in the atmosphere. The main sources of the emission of CH₃OH are from living organisms and human activities^{1–3}. CH₃OH has been used as a fuel additive to reduce emissions of hydrocarbons from automobile^{1–3}. The reactions of CH₃OH may have elusive and indirect effects in the formation of secondary organic aerosols, therefore their impact on the tropospheric oxidizing power, disturbing air quality and adverse effect on human health^{1–3}. CH₃OH abundances are also dominated by direct emissions, but some sources also include the oxidation pathways of methane and from other volatile organic species. The oxidation of methanol forms species that includes carbon monoxide (CO), formaldehyde (HCHO), and tropospheric ozone (O₃). Because the reaction of hydroxyl radical (OH) with CH₃OH is the most important sink for this simplest alcohol; it is therefore determining the atmospheric lifetime of CH₃OH.

Many experimental and theoretical studies on the OH + CH₃OH reaction system have been performed^{1–5}. As suggested in earlier works^{1–5}, OH + CH₃OH proceeds hydrogen abstraction by the OH radical at either the methyl (–CH₃) or the hydroxyl site (–OH) of CH₃OH, assisted by the formation of a pre-reactive complex^{3,4}. It is known that hydrogen abstraction from CH₃ group is the most dominated channel than the hydrogen abstraction from OH site at temperature $\geq 200 \text{ K}$ ^{3,4}. Recently, Nguyen et al.⁵ reported reaction rate coefficients for OH + CH₃OH reaction at temperature $\leq 200 \text{ K}$. They suggested that the formation of CH₃O radical plays a more important role due to quantum mechanical tunneling.

Gaseous ammonia (NH₃) is the most abundant alkaline gas in the atmosphere. The main source of NH₃ emissions is agriculture, including animal husbandry and NH₃-based fertilizer applications^{6–8}. It has been suggested that NH₃ emissions have been increasing over the last few decades on a global scale. Besides, its concentration in atmosphere, ammonia emission is steadily increasing from the food production industries^{6–8}. It is expected that global emission of ammonia could increase by many folds in future. It is known that ammonia molecules present in the atmosphere can influence the many important atmospheric reactions^{6–10}. For this purpose, it is important to have a clear understanding of OH radical reaction with CH₃OH in presence of NH₃. NH₃ has similar efficiency as H₂O in catalyzing many hydrogen abstraction reactions. Based on that, the possibility of the NH₃-catalytic effect on the HO + CH₃OH reaction has been investigated in this work.

To the best of our knowledge, there is only one theoretical study reported by Jonas et al. on the catalytic effect of NH₃ on the OH + CH₃OH reaction⁹. They have investigated the mechanism and kinetics of the OH + CH₃OH reaction with and without the presence of H₂O, NH₃, and H₂SO₄ using ab initio/DFT. They concluded that

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participation of NH_3 on the $\text{OH} + \text{CH}_3\text{OH}$ reaction could enhance the reaction rate and change the reaction mechanism, but this process is unlikely to occur under the atmospheric conditions, due to a very weak interaction NH_3 with CH_3OH .

During the past few years, many research groups have proposed the catalytic effect of a single water molecule for many atmospheric reactions^{11–26}. The possibility of one water molecule as a catalyst in reactions of $\text{OH} + \text{CH}_3\text{OH}$, have been proposed by Jara et al.^{12,13} and Chao et al.¹¹ have measured reaction rate coefficients with water molecule and suggested that no catalytic role of water molecule was observed, which contradict the measurement of Jara-Toro et al.^{12,13} Recently, Wu et al.¹⁴ have proposed the detailed study of water-assisted pathways and predicted temperature-dependent rate coefficients for $\text{OH} + \text{CH}_3\text{OH} (+ \text{H}_2\text{O})$ using hybrid functional coupled with advanced kinetic models¹⁴. The result reported by them is in ~ 1 – 2 order magnitude smaller than reaction without water. In our previous works, we revealed that the catalytic effect of H_2O molecules is not important in the atmospheric reactions *i.e.*, $\text{OH} + \text{CH}_2\text{O}$ and $\text{OH} + \text{CH}_2\text{CH}_2$, $\text{OH} + \text{CH}_2\text{NH}$ and $\text{CH}_2\text{NH} + \text{H}_2\text{O}$ reactions^{16–19}. Experimental measurement suggested that the day-time atmospheric lifetime of methanol in presence of OH radical is ~ 2 weeks³. Because of its long lifetime, effect of ammonia and water molecules on the $\text{OH} + \text{CH}_3\text{OH}$ reaction has been re-investigated and may be useful for the benchmark performance of atmospheric models. For that purpose, the details chemical kinetic investigation was done using *ab initio*/DFT methods coupled with statistical rate theories. The comparison of reaction energies and rate coefficients for $\text{OH} + \text{CH}_3\text{OH}$, and in presence of ammonia/ water provide more confidence in our results.

Theoretical methodology

Quantum chemical calculations. All the electronic structure calculations were performed with the Gaussian 09 suite of programs²⁷. Stationary points on the PES for $\text{OH} + \text{CH}_3\text{OH}$, $\text{OH} + \text{CH}_3\text{OH} (+ \text{NH}_3)$ and $\text{OH} + \text{CH}_3\text{OH} (+ \text{H}_2\text{O})$ reactions were computed using M06-2X/6-311++G(3df,3pd) level²⁸ (see Table S1). To estimate the zero-point corrections (ZPE), normal-modes of vibrational frequency was performed at optimized geometries. The optimized transition states (TSs) have one imaginary frequency whereas reactants, complexes, and products have all positive vibrational frequencies. To improve the accuracy of energy, the single point energy calculations were performed at CCSD(T)/6-311++G(3df,3pd) level. As discussed in the previous work, the combination of CC and M06-2X with 6-311++G(3df,3pd) basis set typically gives results that are accurate to ~ 1 – 2 kcal/mol and is probably of the order of ~ 1 kcal mol^{-1} in the current study^{16–19}. The spin expectation value $\langle S^2 \rangle$ for each species was calculated and found in between ~ 0.75 – 0.85 , indicating that spin contamination was negligible. For barrierless reaction pathways, $\omega\text{B97XD}/6-311++\text{G}(3\text{df},3\text{pd})$ were used to account for the empirical dispersion correction²⁹. We have also performed the calculation using CBS-QB3 level and results are given in Supporting Information.

Chemical kinetics calculations. The two steps of the radical–molecule reactions schemes can be expressed as



where k_1 is the bimolecular forward rate coefficients ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and k_{-1} is unimolecular reverse rate coefficients (s^{-1}) and k_2 is the unimolecular rate coefficient (s^{-1}) for the second step.

According to Eq. 1, the net rate of the reaction of the complex $\text{R} \cdots \text{X}$ satisfies the following equation

$$\frac{d[\text{R} \cdots \text{X}]}{dt} = k_1[\text{R}][\text{X}] - k_{-1}[\text{R} \cdots \text{X}] - k_2[\text{R} \cdots \text{X}] \quad (2)$$

At the steady state condition

$$\frac{d[\text{R} \cdots \text{X}]}{dt} = k_1[\text{R}][\text{X}] - k_{-1}[\text{R} \cdots \text{X}] - k_2[\text{R} \cdots \text{X}] = 0 \quad (3)$$

The steady-state model leads to a rate coefficient for the overall reaction, which can be written

$$k_{\mu\text{-CVT}} = \frac{k_1 \times k_2}{k_{-1} + k_2} \quad (4)$$

where k_1 is microcanonical variational transition state theory (μVTST) rate coefficients for $\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH} \cdots \text{OH}$ were calculated using Multiwell_ktools Program^{30–32}, k_{-1} is μVTST reverse rate coefficients obtained from equilibrium constant. The thermally μVTST for $\text{CH}_3\text{OH} \cdots \text{OH} \rightarrow \text{CH}_3\text{OH} + \text{OH}$ were calculated based on our previous works and details procedure are given in the references^{30–32}. The k_2 is $k_{\text{CVT}}^{\text{unimol}}$ unimolecular rate coefficients based on CVT/SCT approach were computed using PolyRate and GaussRate suite of programs^{33,34}. The rate coefficients for $\text{CH}_3\text{OH} \cdots \text{OH} \rightarrow \text{TS}_a \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O}$ and $\text{CH}_3\text{OH} \cdots \text{OH} \rightarrow \text{TS}_b \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O}$ were calculated using PolyRate and GaussRate suite of programs^{33,34}.

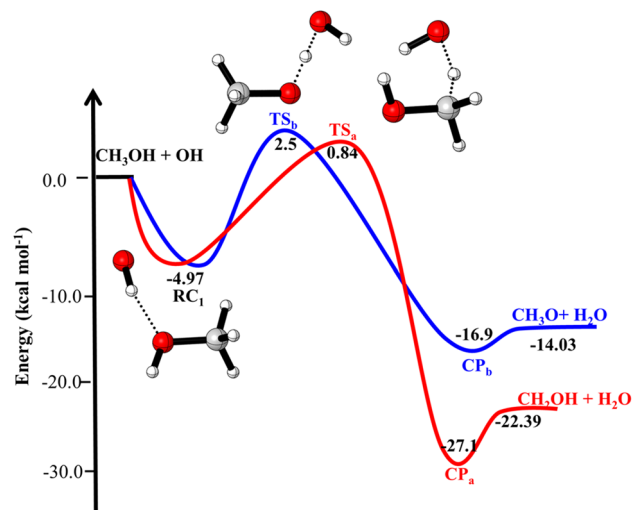


Figure 1. Zero-point corrected potential energy surface for OH + CH₃OH reaction obtained using CC//M06-2X with 6-311++G(3df,3pd) basis set.

The generalized rate coefficients were calculated by minimizing the transition state dividing surface along the reaction coordinate to get the canonical variational transition state theory (CVT) rate coefficients, which is given by Eq. (5) and Eq. (6):

$$k^{GT}(T, s) = \Gamma L^{\ddagger} \times \frac{k_B T}{h} \frac{Q_{TS}^{\ddagger}(T, s)}{Q_R(T)} \exp\left(-\frac{V_{MEP}(s)}{k_B T}\right) \quad (5)$$

$$k^{CVT}(T) = \min_s k^{GT}(T, s) = k^{GT}(T, s^{CVT}(T)) \quad (6)$$

where $k^{GT}(T, s)$ and $k^{CVT}(T)$ are the rate coefficients of generalized and canonical variational,

transition state theory, respectively, V_{MEP} is the classical barrier height, Γ is the small curvature tunneling (SCT) correction as implemented in Polyrate³³, h is Planck's constant, k_B is the Boltzmann constant, and Q_{TS}^{\ddagger} and Q_R are the total partition functions for the transition state and the reactants, respectively. The rate coefficients were calculated using a dual dynamic approach with CVT and the interpolated single point energies (ISPE) correction.

Results and discussion

Reaction pathways for OH + CH₃OH. The zero-point corrected PES for the water-free OH + CH₃OH reaction is shown in Fig. 1. The energies of complexes, transition states (TSs) and products are shown relative to the energy of the reactants. The optimized structures of complexes and TSs are shown in Fig. 2. As shown in the figure, reaction channel a is more exothermic and has lower barrier heights (5.8 kcal/mol,) than channel b (7.5 kcal/mol); the former is therefore predicted to be both kinetically and thermodynamically more favorable.

The reaction proceeds via the formation of a pre-reactive complex (RC₁) with C₁ point group of symmetry in which the H of OH group is directed towards O of CH₃OH. The energy of RC₁ is 4.97 kcal mol⁻¹ lower than the reactants and is in good agreement with the previous theoretical values^{4,5,12}. To abstract the hydrogen atom from CH₃ and OH group, OH of RC₁ rotate in the plane until O atom come closer to the CH₃ and OH group of CH₃OH to pass via the geometry of TS_a and TS_b. The barrier heights for hydrogen abstraction from CH₃ group is 5.8 kcal/mol. This value is in good agreements with the value reported by Nguyen et al.⁵, Gao et al.⁴ and Jara et al.¹² The barrier heights for H-abstraction reaction from OH group (~7.5 kcal/mol) is also in good agreement with previously reported values^{4,5,12}.

Reaction pathways for OH + CH₃OH (+NH₃). In the presence of ammonia, the simultaneous collision of CH₃OH, OH, and NH₃ molecules are most unlikely, therefore, the reaction will occur through the formation of a two-body complex, and then this complex collides with a third species to form the three-body complexes. As discussed in our earlier studies^{16,17}, we believe the formation of CH₃OH...NH₃ or OH...NH₃ formed first, followed by an attack of the third molecule to these complexes. The complexes CH₃OH...NH₃ and OH...NH₃ are assumed to be more important than CH₃OH...OH. This assumption is based on our previous studies on the similar reaction OH + CH₂CH₂ (+H₂O), OH + CH₂O (+H₂O) and OH + CH₂NH (+H₂O)^{16,17}. Because the atmospheric concentration of CH₃OH...OH is smaller than the OH...NH₃ and CH₃OH...NH₃. Therefore, CH₃OH...OH + NH₃ is not considered in this work. In those two cases, most probable reaction pathways consist of two consecutive bimolecular elementary steps followed by unimolecular pathways:

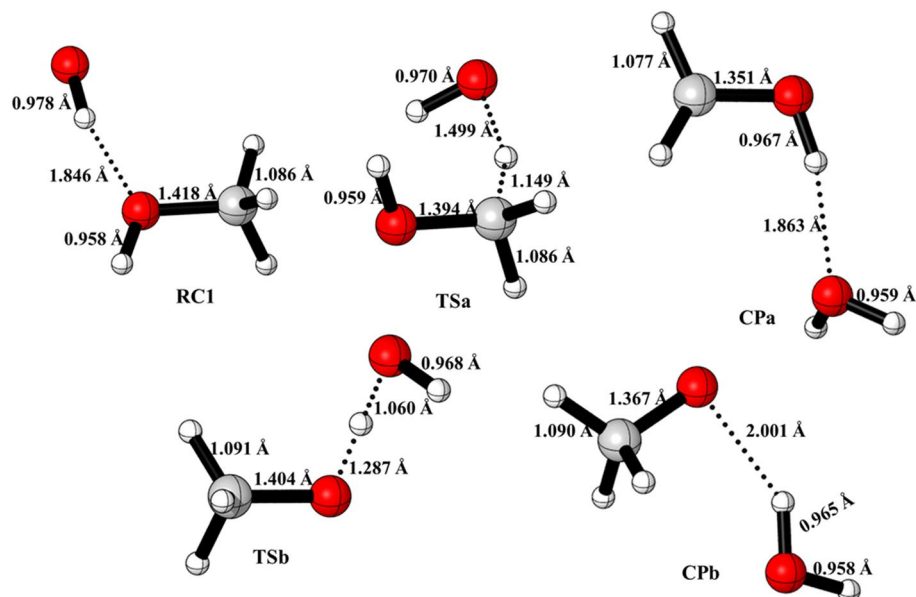


Figure 2. Structural and geometrical changes during OH + CH₃OH reaction calculated using M06-2X/6-311++G(3df,3pd). These structures were generated from CYLview software.

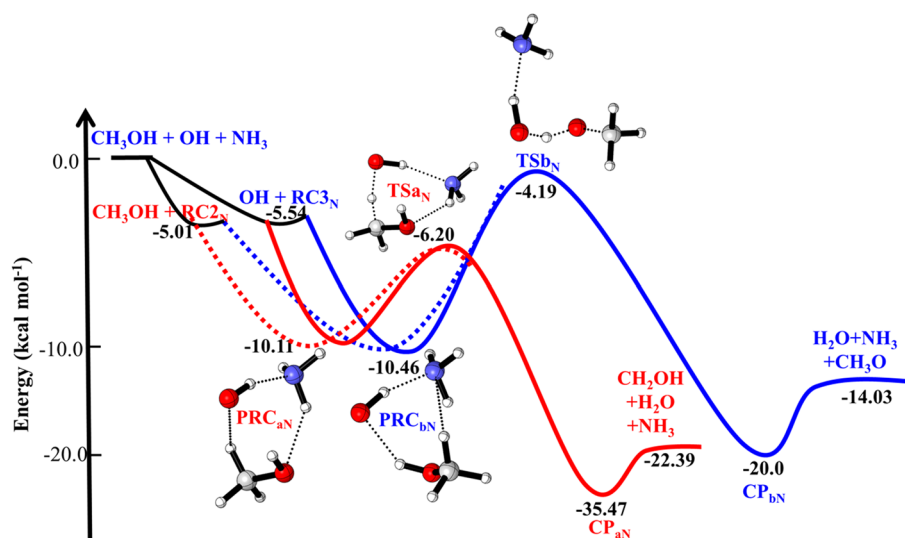
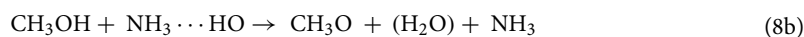
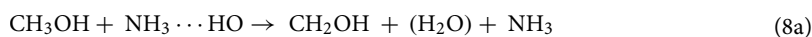
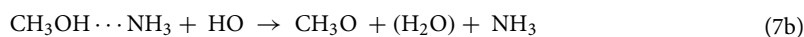
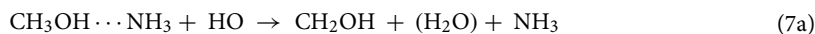


Figure 3. Potential energy surface for ammonia-assisted OH + CH₃OH reaction obtained using CC//M06-2X with 6-311++G(3df,3pd) basis set. The relative energies include zero-point corrections.



For ammonia-assisted reaction PES was carefully searched and all possible stationary points were identified. The zero-point corrected energies for ammonia-assisted OH + CH₃OH reaction is shown in Fig. 3 and optimized structure of RCs, PRCs and TSs are shown in Fig. 4. The difference of binding energies between two-body complex CH₃OH⋯NH₃ (− 5.54 kcal/mol) and OH⋯NH₃ (− 5.01 kcal/mol) is 0.5 kcal/mol. This BE is 1 kcal/mol higher than the value of OH⋯H₂O¹⁶. This result is due to fact that the N–H hydrogen bond is stronger than

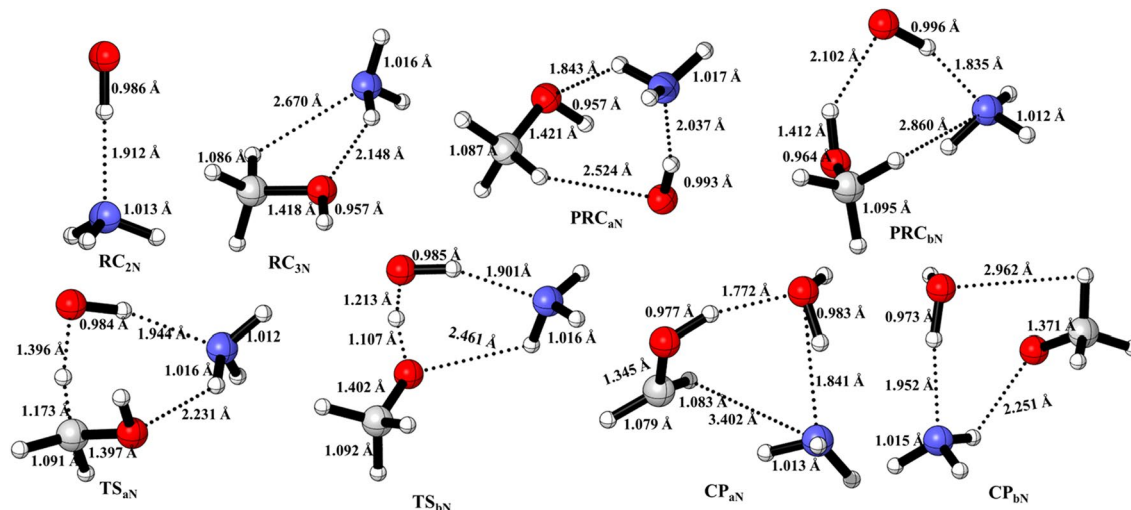
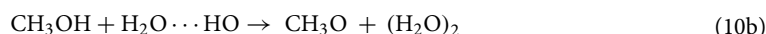
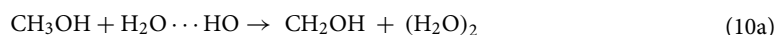
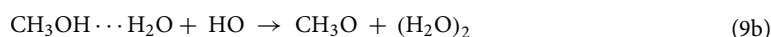
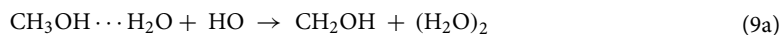


Figure 4. Optimized structures of ammonia-assisted pre-reactive complexes, transition states and post-reactive complexes were obtained using M06-2X/6-311++G(3df,3pd).

O–H hydrogen bond. When CH_3OH added to $\text{RC}_{2\text{N}}$, and OH radical added to $\text{RC}_{3\text{N}}$, five pre-reactive complexes were formed in which N of ammonia is acting as a proton donor and proton acceptor. Out of five PRC_{N} , only two PRC_{aN} and PRC_{bN} are the most stable, therefore, other PRCs will not be considered in the kinetic calculations. As shown in Fig. 3, in both cases $\text{CH}_3\text{OH} + \text{RC}_{2\text{N}}$ and $\text{OH} + \text{RC}_{3\text{N}}$ formed PRC_{aN} and PRC_{bN} with a BE of $-10.1 \text{ kcal mol}^{-1}$ and -10.46 kcal/mol , respectively. The seven-membered ring structure of PRC_{aN} and its binding energy of $-10.1 \text{ kcal mol}^{-1}$ are due to the combined effects of the N–H and O–H hydrogen bonds. The structure of these complexes is similar to the complexes found in water-assisted reaction^{12,16}. The energies of these complexes are closer to the water-assisted complexes as discussed in earlier¹² and later in “Reaction pathways for $\text{OH} + \text{CH}_3\text{OH} (+\text{H}_2\text{O})$ ” section. Starting from PRC_{aN} , we have identified hydrogen abstraction by OH radical leading to CH_2OH and CH_3O . Transition state ($\text{TS}_{1\text{aN}}$) corresponds to H abstraction reaction from methyl position. The calculated barrier height for this pathway ($\sim 4 \text{ kcal/mol}$), which is lower than the barrier height for $\text{OH} + \text{CH}_3\text{OH}$ (5.7 kcal/mol) reaction. The barrier heights of TS_{bN} is $\sim 6.2 \text{ kcal/mol}$, which is $\sim 1 \text{ kcal}$ lower than the TS_{bN} of $\text{OH} + \text{CH}_3\text{OH}$ reaction. As suggested in $\text{OH} + \text{CH}_3\text{OH}$ reaction, the H-abstraction pathway from CH_3 position is thermodynamically more favorable than the H-abstraction from OH bond. Addition of more ammonia *i.e.*, $(\text{NH}_3)_{n>1}$ may be further reduced the energies and become more thermodynamically favorable, but such reaction is not considered in the gas phase.

Reaction pathways for $\text{OH} + \text{CH}_3\text{OH} (+\text{H}_2\text{O})$. We have applied a similar approach for the water-assisted reactions as discussed in the case of ammonia and earlier studies^{16–26}. Because the simultaneous collisions of OH, CH_3OH and H_2O , are very unlikely, the termolecular reaction probability is very small under true conditions either a $\text{CH}_3\text{OH}\cdots\text{H}_2\text{O}$ or $\text{OH}\cdots\text{H}_2\text{O}$ is expected to form first, followed by an attack of the third molecule OH or CH_3OH to this complex. In these two cases, most probable reaction pathways consist of two consecutive bimolecular elementary steps followed by unimolecular pathways:



When a water molecule is added to the $\text{OH} + \text{CH}_3\text{OH}$, the reaction proceeds via similar reaction channels *i.e.*, pathway a and pathway b but reaction mechanism becomes quite complex, yielding different isomers of pre-reactive complexes and transition states. As discussed in earlier studies¹⁴, we have also found different isomers of pre-reactive complex and transition states. The zero-point corrected energies of complexes, transition states, and products are shown in Fig. 5 using CCSD(T)//M06-2X/with 6-311++G(3df,3pd) basis set. The optimized structure of complexes and TSs are shown in Fig. 6. We have found multiple structures of transition states and pre-reactive complex. For the simplicity, we have used only the minimum energy structure as discussed in earlier work^{12,14}.

The calculated binding energy (BE) between CH_3OH and H_2O (-4.06 kcal/mol) is in very good agreement with value (-4 kcal/mol) reported previously^{12,14}. The BE of $\text{H}_2\text{O}\cdots\text{OH}$ (-4.0 kcal/mol) is nearly same the BE of $\text{CH}_3\text{OH}\cdots\text{H}_2\text{O}$ (-4.0 kcal/mol). This is due to fact that the hydrogen bond (O \cdots H) in $\text{H}_2\text{O}\cdots\text{OH}$ is very similar to the C–O \cdots H interaction in $\text{CH}_3\text{OH}\cdots\text{H}_2\text{O}$.

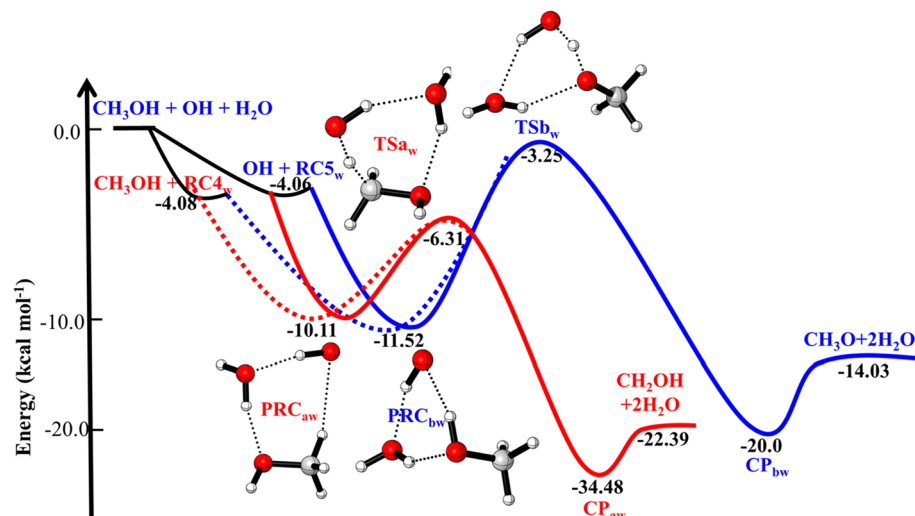


Figure 5. Potential energy surface for water assisted OH + CH₃OH reaction obtained using CC//M06-2X with 6-311++G(3df,3pd) basis set. The relative energies include zero-point corrections.

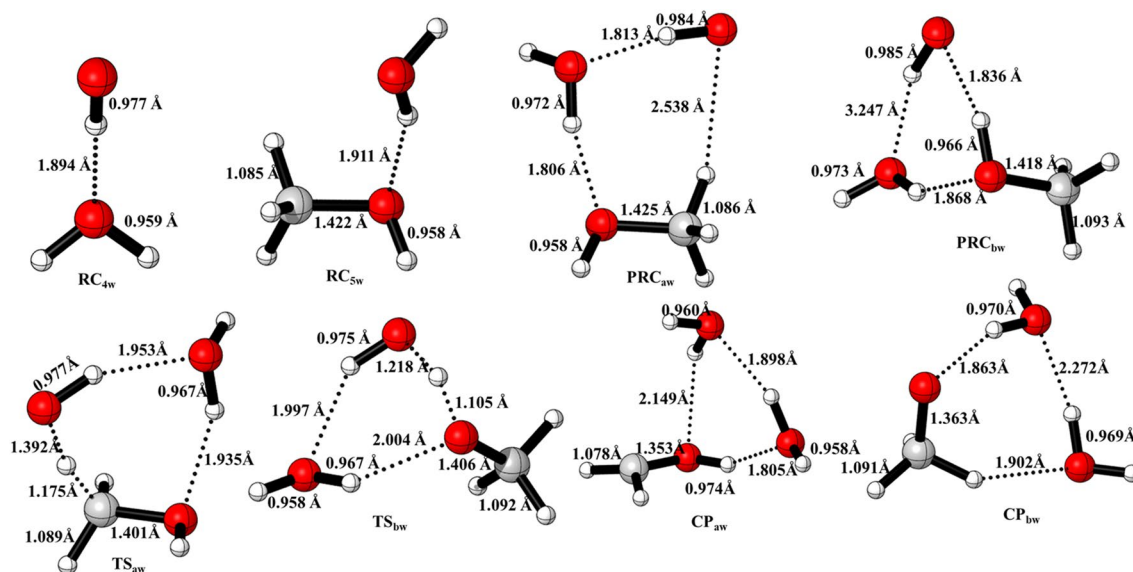


Figure 6. Structures of water-assisted pre-reactive complexes, transition states and post-reactive complexes were optimized using M06-2X/6-311++G(3df,3pd).

When a third molecule (CH₃OH or OH radical) attacked to these complexes *i.e.*, H₂O...OH, CH₃OH...H₂O, different pre-reactive complexes isomers were observed. Out of these PRCs, we have chosen only most stable PRCs, *i.e.*, PRC_{aw} and PRC_{bw} in the current study. The BE of PRC_{aw} (−10.8 kcal/mol) is the combined effect of O...H and C...H interactions. Starting from PRC_{aw}, we have identified one reaction pathway, *i.e.*, hydrogen abstraction by OH radical on methyl carbon. Transition state (TS_{1aw}) corresponds to H abstraction reaction from methyl position. The calculated barrier height for this pathway (~4 kcal/mol), which is lower than the barrier height for water-free reaction (~6 kcal/mol). The hydrogen abstraction from O–H bond leads to form a product via transition state (TS_{2bw}) correspond to H-abstraction reaction. The barrier height of TS_{2bw} (~6 kcal/mol) is lower than value the value of TS_{2b} (~7.5 kcal/mol). The PRC_{bw} has different structure than PRC_{aw} and energetically 1 kcal/mol higher.

Enthalpies of reactions. The enthalpies relative to the reactants for OH + CH₃OH, and ammonia/water assisted reaction are given in Table 1. This table also includes enthalpies values from the literature values^{5,12,14,35–37}. The enthalpies of reaction of OH + CH₃OH → CH₂OH + H₂O and OH + CH₃OH → CH₃O + H₂O agree with the ATcT thermochemical data base^{35–37} within ~1 kcal/mol, respectively and are in excellent agreement with previous theoretical calculations¹². As shown in Fig. 4, the formation of the complex in OH...CH₃OH...NH₃ (PRC_{aN}) and OH...CH₃OH...NH₃ (PRC_{bN}), structurally and energetically they are different (see Fig. 4 and Table 1). The

OH + CH ₃ OH →	This work	Literature ^{a,b,c}
OH...CH ₃ OH (RC1)	-4.97	-4.37, -4.47, 4.90, 4.82 ^a
HO...HCH ₂ OH (TS _a)	-0.84	0.1, 0.36 ^a
HO...HOCH ₃ (TS _b)	2.50	1.91, 3.29 ^a
CH ₂ OH + H ₂ O	-22.39	-23.13, 23.1, 23.09 ^b
CH ₃ O + H ₂ O	-14.03	-13.66, 13.73 ^b
OH + CH ₃ OH + NH ₃ →	This work	Literature
OH...CH ₃ OH...NH ₃ (PRC _{aN})	-10.11	-
OH...CH ₃ OH...NH ₃ (PRC _{bN})	-10.45	-
OH...HCH ₂ OH...NH ₃ (TS _{aN})	-6.2	-
OH...HO...HOCH ₃ ...NH ₃ (TS _{bN})	-4.19	-
CH ₂ OH + H ₂ O + NH ₃	-22.39	-
CH ₃ O + H ₂ O + NH ₃	-14.03	-
OH + CH ₃ OH + H ₂ O →	This work	Literature ^a
OH...CH ₃ OH...H ₂ O (PRC _{aw})	-10.80	-10.80 ^c
OH...CH ₃ OH...H ₂ O (PRC _{bw})	-11.52	-12.03 ^c
OH...HCH ₂ OH...H ₂ O (TS _{aw})	-6.31	-4.98 ^c
OH...HO...HOCH ₃ ...H ₂ O (TS _{bw})	-3.25	-2.74 ^c
CH ₂ OH + 2H ₂ O	-22.39	-23.09 ^b
CH ₃ O + 2H ₂ O	-14.03	-13.73 ^b

Table 1. Enthalpies of reaction (ΔH_{rxn} (0 K) in kcal mol⁻¹ of OH + CH₃OH reaction. ^aNguyen et al.⁵, ^bATCT³⁵⁻³⁷, ^cJara et al.¹².

different BE of PRC_{aN} (-10.1 kcal/mol) and PRC_{bN} (-10.5 kcal/mol) is due to the different orientation of OH and NH₃ molecules.

The calculated BE of PRC_{aw} (-10.1 kcal/mol) and PRC_{bw} (-11.5 kcal/mol) are in very good agreements with the value (-9.3 kcal/mol) reported by Jara-Toro et al.¹² The energies of PRCs and transition states of reaction systems were also compared with the theoretically available value () and products energies were compared with the most accurate set of experimental value from Active Thermochemical Tables. The PRC_{aN} and (PRC_{bN}), are structurally similar to those of PRC_{aw} and PRC_{bw}. The energy difference between these complexes is due to the presence of N-H bond.

On the basis of the energetics summarized in Table 1, it is clear that barrier height for the abstraction from CH₃ group is small compared to abstraction from OH group in all the cases discussed here. The effect of ammonia and water leads to the lower barrier height and makes the reaction more thermodynamically favorable.

As suggested by the reviewer, we have used another level of quantum chemical method to justify the accuracy of the calculations. We have re-done the calculation using CBS-QB3 level as suggested by the reviewer. The results are given in supporting information Table S5 and rate coefficient plots are shown in Supporting Information Figure S4 and Figure S5. The calculated energies for both the transition state is 0.5 kcal/mol difference than the CC/M06 level and rate coefficients for CH₃OH + OH reaction is nearly factor of 5 higher than the experimental measurement. Therefore, we believe the results of CBS-QB3 did not improve as we expected. As suggested in Nguyen et al.⁵ study, the TSs of CH₃OH + OH are very sensitive to the quantum chemical methods, even they used HEAT Protocol for the energies calculation, and their results are off by factor of 2 from the experimental measurement. Nguyen et al.⁵ also adjusted their barrier heights to get accurate results. In our earlier work³⁸ on CH₂NH + OH, we used CCSDT/aug-cc-pvtz for optimization and energies calculation, due to sensitive nature of barrier height, we adjusted the barrier height by 0.3 kcal/mol, and adjusted value agreed with the experimentally measure value. This adjustment is well within the estimated accuracy of the theoretical methods (~2 kcal/mol) as suggested in the earlier studies³⁸.

Rate coefficients. *OH + CH₃OH reaction.* To the best of our knowledge until now, the details of interaction between OH and CH₃OH in the temperature range of 200–400 K had not been investigated, despite the large rate coefficient recommended in the literature for OH + CH₃OH leading to CH₃O/CH₂OH + H₂O^{4,5,12,14}. The CH₃OH...HO that assume to play important roles in the HO + CH₃OH reaction system is formed via the entrance channels which have the well depth of ~5 kcal/mol. Figure 7 shows the zero-point corrected potential energy for the entrance channel forming CH₃OH...HO.

To locate the transition state of dissociation of CH₃OH...HO, the potential energies (including zero-point energies) were computed in a series of constrained optimizations as a function of the R_{O...O} bond distance (from 3 to 7 Å). The optimized geometries at some points along with the reaction pathways are shown in Fig. 8.

The CVTST "trial" rate coefficients were computed in the temperature range of 200–400 K along the reaction path is shown in Supporting Information Figure S1. At each temperature, the plot shows a single minimum between 5.5 and 6.0 Å. The rate coefficients for dissociation and association reaction were computed using microcanonical approaches and values are tabulated in Table 2.

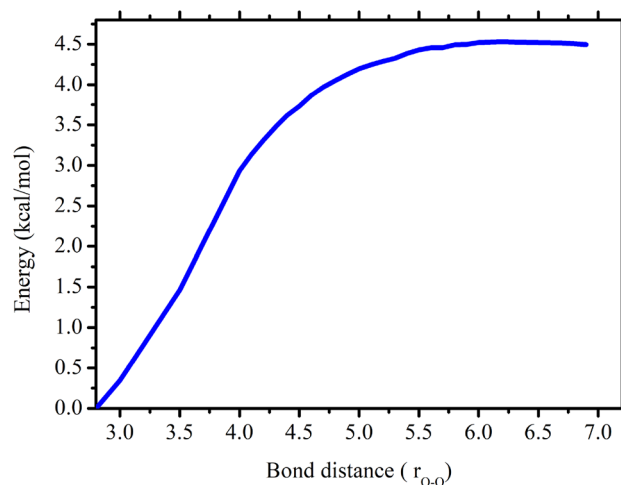


Figure 7. Zero-point corrected potential energy profile dissociation of the $\text{CH}_3\text{OH}\cdots\text{HO}$ as functions of $R_{\text{O-O}}$ distances computed at the CCSD(T)/6-311++G(3df,3pd)// ω B97XD/6-311++G(3df,3pd) level.

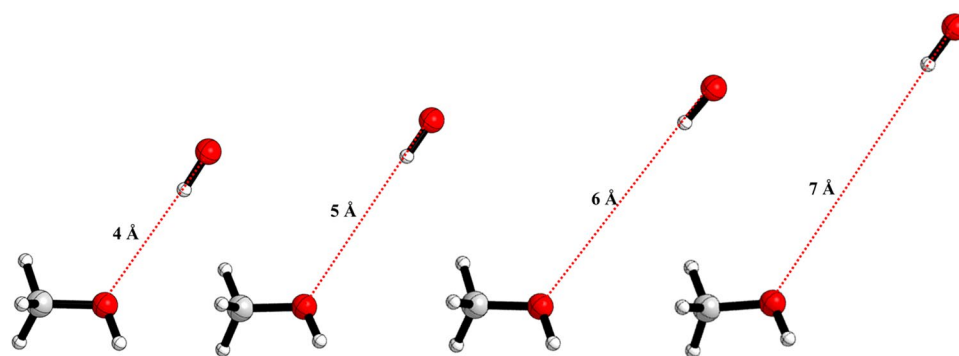


Figure 8. Dissociation of $\text{CH}_3\text{OH}\cdots\text{OH}$ at several $R_{\text{O-O}}$ distances along the reaction of $\text{OH} + \text{CH}_3\text{OH}$.

Temp	k_1	k_{-1}	k_{2-a}	k_{2-b}	$k_{\mu\text{-CVT}}$ (this work) ^a	Exp.value ²
200	1.16×10^{-11}	2.01×10^8	6.72×10^5	9.58×10^5	3.50×10^{-13}	5.70×10^{-13}
225	1.23×10^{-11}	7.78×10^8	2.51×10^6	3.01×10^5	3.60×10^{-13}	6.40×10^{-13}
250	1.29×10^{-11}	2.29×10^9	7.79×10^6	2.57×10^6	4.10×10^{-13}	7.22×10^{-13}
275	1.36×10^{-11}	5.50×10^9	2.03×10^7	6.82×10^6	4.68×10^{-13}	8.13×10^{-13}
300	1.43×10^{-11}	1.14×10^{10}	4.63×10^7	1.62×10^6	5.42×10^{-13}	9.15×10^{-13}
325	1.50×10^{-11}	2.09×10^{10}	9.09×10^7	3.47×10^7	6.07×10^{-13}	1.03×10^{-12}
350	1.57×10^{-11}	3.52×10^{10}	1.62×10^8	6.81×10^7	6.76×10^{-13}	1.15×10^{-12}
375	1.64×10^{-11}	5.51×10^{10}	2.67×10^8	1.24×10^8	7.48×10^{-13}	1.28×10^{-12}
400	1.72×10^{-11}	8.15×10^{10}	4.13×10^8	2.11×10^8	8.24×10^{-13}	1.42×10^{-12}
$k = AT^n \exp(-B/T)$	$A = 5.09 \times 10^{-14}$ $n = 0.93$ $B = -101.52$	$A = 1.62 \times 10^{15}$ $n = -0.58$ $B = 2566.5$	$A = 1.53 \times 10^7$ $n = 1.47$ $B = 2188.4$	$A = 4.7 \times 10^{-40}$ $n = 17.28$ $B = -2536.4$	$A = 1.01 \times 10^{-20}$ $n = 2.86$ $B = -431.03$	$A = 3.82 \times 10^{-19}$ $n = 2.4$ $B = 300$

Table 2. Calculated rate coefficients for the $\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH}/\text{CH}_3\text{O} + \text{H}_2\text{O}$ calculated at CC/M06 level. k_1 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is microcanonical VTST rate coefficient, k_{-1} (s^{-1}) microcanonical reverse rate coefficient, k_{2-a} (s^{-1}) is $k^{\text{CVT}}(T)$ rate coefficient for pathway a, k_{2-b} (s^{-1}) is $k^{\text{CVT}}(T)$ rate coefficient for pathway b, $k_{\mu\text{-CVT}}$ is total rate coefficient without adjustment ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

The rate coefficients for the formation of $\text{CH}_3\text{OH}\cdots\text{HO}$ is almost independent of temperature. The calculated value is also compared with similar type of reaction system and the values were very close to each other^{16,26}. The calculated lifetime of the complex at 225 K, which is near to the altitude of 10–12 km is ~ 1 ns. This lifetime of the complex is too short to undergoes secondary reaction. In fact, 1 ns is very rapid, which could be negligible in the $\text{CH}_3\text{OH} + \text{OH}$ reaction and direct abstraction reaction could lead the products⁵. To the best of our knowledge the microcanonical VTST calculation for the forming the $\text{CH}_3\text{OH}\cdots\text{HO}$ in the temperature range of 200–400 K

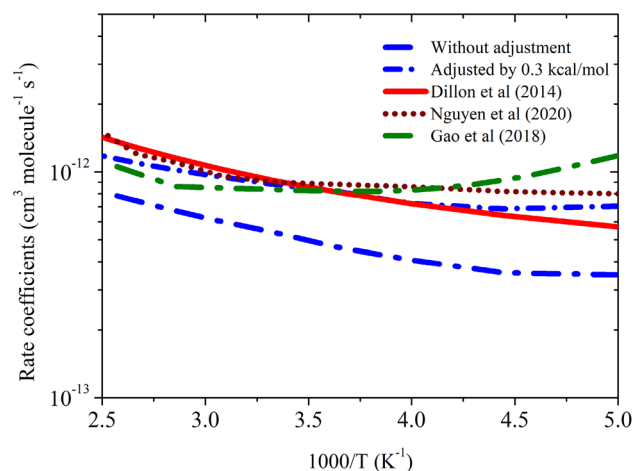


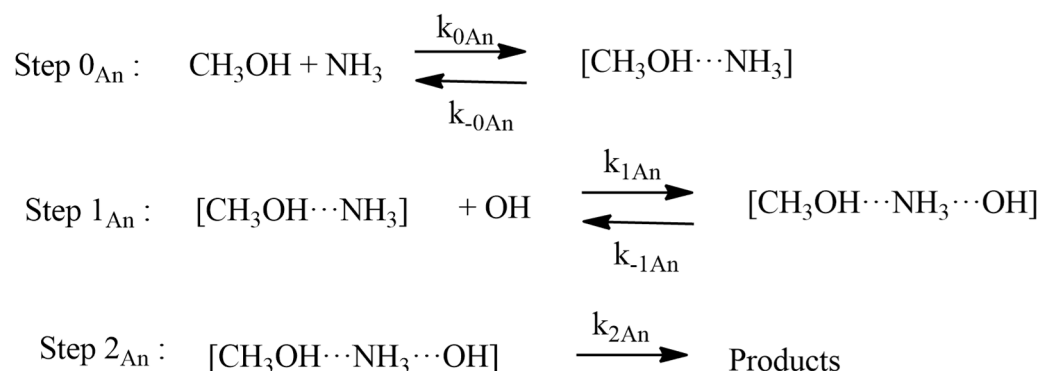
Figure 9. Rate coefficients for OH + CH₃OH reaction.

is not known and were not discussed in earlier studies. As suggested in earlier studies⁵ that at high-pressure limit complex CH₃OH⋯HO will completely be stabilized by the collisions with another atmospheric molecule and will be rapidly re-populated thermally. Once it re-populated, the complex decomposes to give the CH₂OH + H₂O and CH₃O + H₂O. We believe that rate coefficients calculation for the barrierless reaction using microVTST is better choice than the use of equilibrium approach for calculation of the total rate coefficient (see Eq. 3), which can reduce the error in the kinetic calculation at least by factor of 2.

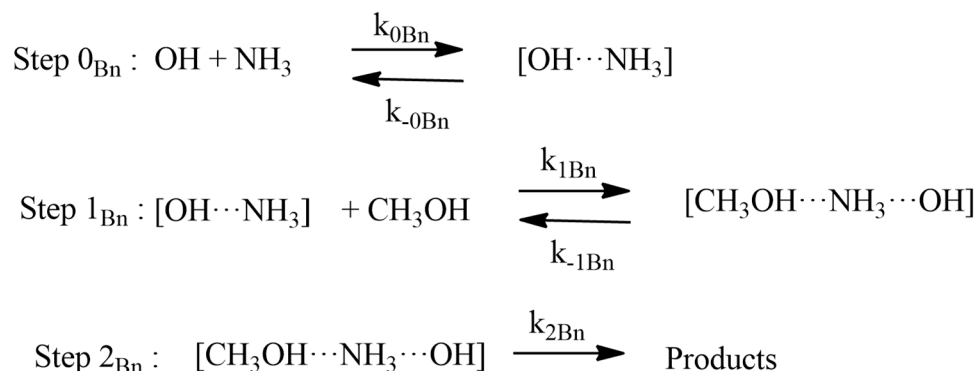
The rate coefficients calculated using CC//M06-2X are shown in Fig. 9. Our Calculated value at 300 K ($5.42 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is in good agreement with the experimentally measured² value ($9.15 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and theoretically^{4,5} calculated ones (6.2×10^{-13} , 8.2×10^{-13} and $9.13 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)^{4,5,12}. The calculated value is factor of ~2 lower than experimental values over the entire temperature range. This level of accuracy is sufficient for the present purposes, considering the expected errors in the computed thermochemistry. In the recent work Nguyen et al.⁵ suggested that the barrier heights of OH + CH₃OH reaction is very sensitive to the quantum chemical calculation. They suggested that it is very challenging to calculate accurate energy using ab initio method for OH + CH₃OH reaction even using HEATs protocol⁵. To match the calculated value with experimentally measured values, they adjusted the barrier heights by 0.4 kcal/mol⁵. We have also applied same approach and adjusted the barrier height of TS_a and TS_b by -0.3 kcal/mol. This adjustment is well within the estimated accuracy of the theoretical methods (< 1 kcal/mol), which brings the computed rate constants into almost exact agreement with the experimental values over 200–400 K. Similar adjustment was done in earlier research work to correct the reaction energies³⁸. We have also calculated the percentage contribution of Pathway a (CH₂OH + H₂O, > 95%) and for Pathway b (CH₃O + OH, < 5% in the temperature range of 200–400 K. This result is in very good agreement with the experimentally measured percentage contribution in the same temperature range³.

Ammonia-assisted OH + CH₃OH reaction. As discussed in “Reaction pathways for OH + CH₃OH (+ H₂O)” section and given in Eq. (7) and (8), only two entry channels CH₃OH⋯NH₃ + HO (Pathway A_n) and CH₃OH + NH₃⋯HO (Pathway B_n) are considered for the rate coefficient calculations.

Pathway A_n



Pathway B_n



The rate coefficients for the reactions of OH + CH₃OH (+ NH₃) were calculated based on high-pressure limit condition. Because of the presence of two or more hydrogen bonds in PRC_N, locating the TS of backward reaction *i.e.*, PRC_N → CH₃OH⋯NH₃ + OH and PRC_s → CH₃OH + NH₃⋯OH using constrained optimization technique is more complicated than locating the TS for CH₃OH⋯HO → OH + CH₃OH, the latter has a single hydrogen bond. In that case, we have used the equilibrium approach to account for the presence of forward and backward reactions. The total rate coefficients in Eq. 4: $k_{\mu\text{-CVT}} = \frac{k_1 \times k_2}{k_{-1} + k_2}$ were assumed that $k_{-1} > k_2$, $k = K_{eq}k_2$. This kinetic model is reasonably correct at the high-pressure limit and for the three-body complex, where the pre-reactive complex can be stabilized by collisions with other atmospheric species^{18–25}.

The unimolecular rate coefficients (k_2) were computed using CVT/SCT method and the rate coefficient (k_2) values are tabulated in supporting information, Table S2. The equilibrium constants (K_{eq}) for the formation of two-body and three-body complexes were calculated based and the results are tabulated in Table S3 and Table S4.

The rate coefficients for HO + CH₃OH (+ NH₃) were calculated in the temperature range 200 to 400 K using CVT/SCT methods are shown in Fig. 9. The rate coefficients of Pathway A_n and Pathway B_n were calculated using the approach given in Eq. 11:

$$k_{AN}^{CVT} = k_{1N} + k_{2N} \text{ and } k_{BN}^{CVT} = k_{1'} + k_{2'}. \quad (11)$$

$k_{1N} = K_{eq(E)} \times k_{TSaN}$, $k_{2N} = K_{eq(G)} \times k_{TSaN}$, $k_{1'} = K_{eq(F)} \times k_{TSbN}$, $k_{2'} = K_{eq(H)} \times k_{TSbN}$ and are bimolecular rate coefficients of each reaction pathway involved in the OH + CH₃OH reaction. The total rate coefficients for OH + CH₃OH (+ NH₃) are expressed by Eq. 12:

$$k_{total-N} = k_{AN}^{CVT} + k_{BN}^{CVT} \quad (12)$$

The total rate coefficients in the temperature range of 200–400 K of Pathway A_N and Pathway B_N are also shown in Fig. 10. Our results show that the rate coefficients of Pathway B_N are higher than Pathway A_N. In general, the rate coefficients of ammonia-assisted reaction is higher than the OH + CH₃OH reaction in the temperature range of 200–400 K (see Fig. 10). Our calculations suggest that the catalytic effect takes place if step 0 is not included in the reaction mechanism. Ignoring step 0 is equivalent to assuming that all the methanol is complexed with ammonia, which is not true.

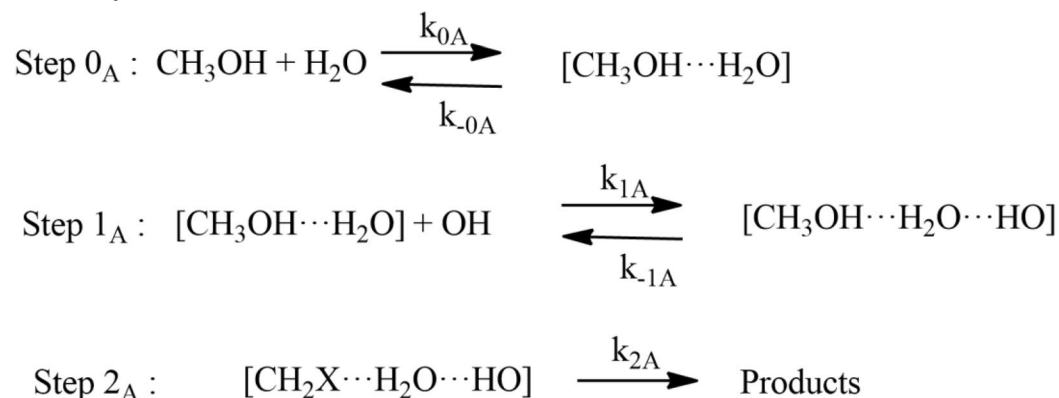
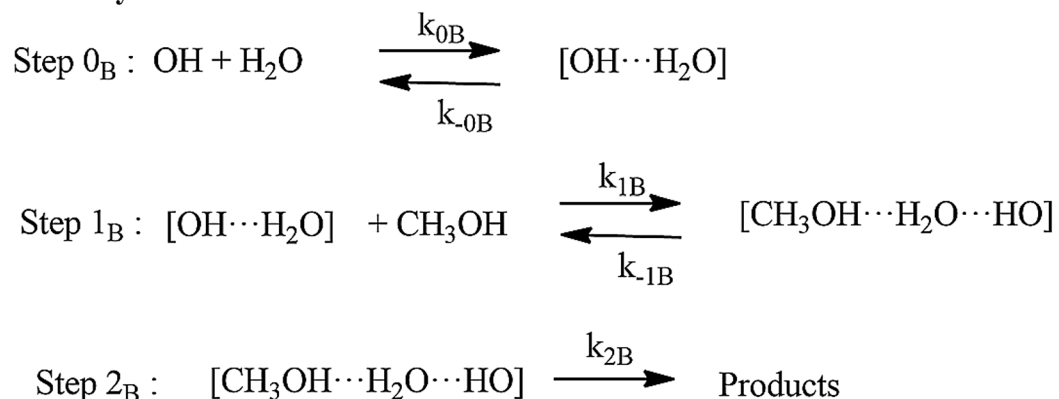
The correct expression to calculate the total effective rate coefficients by Eq. 13:

$$k_{total-N}^{eff} = \left[\left\{ K_{eq(5)} \times k_{AN}^{CVT} \right\} + \left\{ K_{eq(4)} \times k_{BN}^{CVT} \right\} \right] \times [NH_3]. \quad (13)$$

where $K_{eq(5)}$ and $K_{eq(4)}$ are equilibrium constants of CH₃OH + NH₃ → RC₅, and NH₃ + HO → RC₄, reactions, respectively (see Table 2) and [NH₃] is ammonia concentration used at 10 ppbv based on previous studies^{6,8}.

The total effective rate coefficient for OH + CH₃OH (+ NH₃) (2.7×10^{-21} cm³ molecule⁻¹ s⁻¹ at 300 K) is ~ 8 order magnitude lower than OH + CH₃OH reaction (8.8×10^{-13} cm³ molecule⁻¹ s⁻¹). This result is due to fact that the ammonia-assisted pathway depends on ammonia concentration (see Table 2). As discussed in dry OH + CH₃OH reaction, without adjustment, the agreement with experiments was good, but adjustment gave in excellent agreement with the experimental data. Therefore, we adjusted the barrier height of the PRC_{A_n} → TSA_n and PRC_{B_n} → TSB_n channel by – 0.3 kcal/mol. The calculated rate coefficients are nearly same even after the adjustment of the (see Fig. 10) and show negative temperature-dependent, such behavior has also been observed for similar reactions system in the literature^{7,8}. The rate coefficient at different NH₃ concentration is shown in Fig. 10b. The calculated values are consistent with the previous studies of similar type of reaction⁸.

Water-assisted OH + CH₃OH reaction. The reaction mechanisms for OH + CH₃OH in presence of a single water molecule are presented. To get more confidence in the predicted rate coefficients, we compared our results with previously published results^{12,14}.

Pathway A_w**Pathway B_w**

The rate coefficients for $\text{OH} + \text{CH}_3\text{OH} (+ \text{H}_2\text{O})$ were calculated in the temperature range 200 to 400 K using CVT/SCT methods (see Table S2). The rate coefficients of Pathway A_w and Pathway B_w were calculated using the approach given in Eq. 14

$$k_{A_w}^{CVT} = k_3 + k_4 \text{ and } k_{B_w}^{CVT} = k_3' + k_4'. \quad (14)$$

where $k_3 = K_{eq(A)} \times k_{TSaw}$, $k_4 = K_{eq(C)} \times k_{TSaw}$, $k_3' = K_{eq(B)} \times k_{TSbw}$, $k_4' = K_{eq(D)} \times k_{TSbw}$, and are bimolecular rate coefficients of each reaction pathway involved in the $\text{OH} + \text{CH}_3\text{OH}$ reaction. The total rate coefficients for $\text{OH} + \text{CH}_3\text{OH} (+ \text{H}_2\text{O})$ are expressed by Eq. 15:

$$k_{total-w} = k_{A_w}^{CVT} + k_{B_w}^{CVT}. \quad (15)$$

The rate coefficients in the temperature range of 200 K to 400 K for Pathway A_w, Pathway B_w and total effective rate coefficients are shown in Fig. 11. In both pathways, $\text{OH} + \text{CH}_3\text{OH} (+ \text{H}_2\text{O})$ is dominated over the H-abstraction pathway. Our results show that the rate coefficients of Pathway A_w are higher than Pathway B_w. It can be seen that, if step 0 is ignored, the rate coefficient of $\text{CH}_3\text{OH} + \text{H}_2\text{O}\cdots\text{OH}$ reaction ($1.12 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K) is ~2 times higher than $\text{CH}_3\text{OH} + \text{OH}$ reaction ($6.45 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K). In general, the rate coefficients of water-catalyzed reaction are higher than the water-free reaction at the temperature < 300 K (see Fig. 6).

As discussed in previous studies¹⁶⁻¹⁸, the importance of step 0 cannot be neglected for the reaction under tropospheric conditions. Ignoring step 0 is equivalent to assuming that all the CH_3OH is formed a complex with H_2O , which is not true. If step 0 is taken into account, there is a negligible amount of $\text{CH}_3\text{OH}\cdots\text{H}_2\text{O}$ and $\text{H}_2\text{O}\cdots\text{OH}$ and thus it is the water-free gas-phase pathway that determines the rate of the reaction. Under pseudo-first-order conditions, the relative equilibrium concentrations depend strongly on the concentration of the excess of water and the correct expression to calculate the total effective rate coefficients is given by Eq. 16:

$$k_{total-w}^{eff} = \left[\left\{ K_{eq(2)} \times k_{A_w}^{CVT} \right\} + \left\{ K_{eq(3)} \times k_{B_w}^{CVT} \right\} \right] \times [\text{H}_2\text{O}]. \quad (16)$$

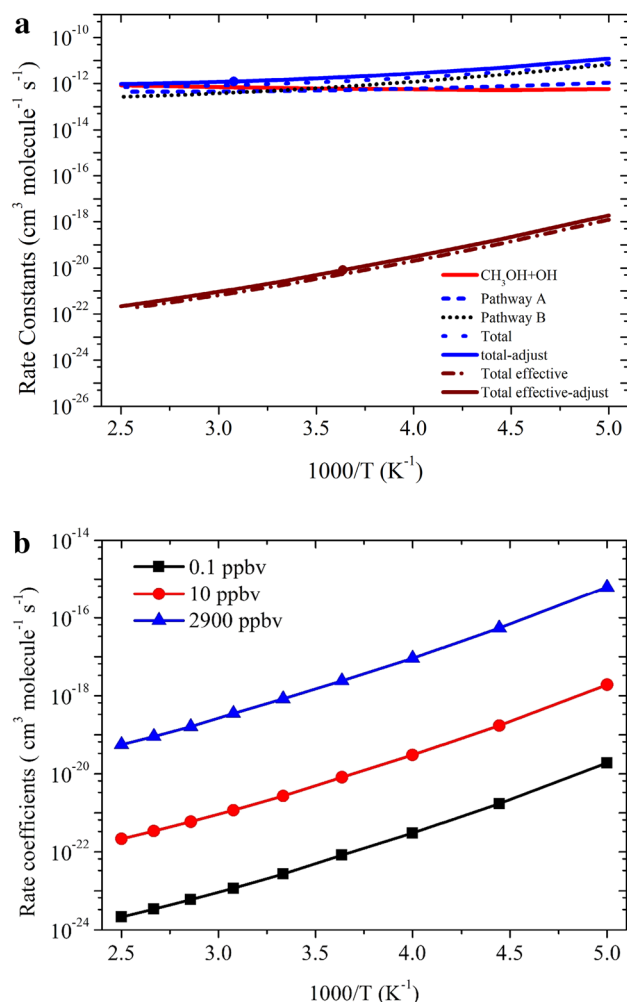


Figure 10. Rate coefficients for $\text{CH}_3\text{OH} + \text{OH}$ and $\text{CH}_3\text{OH} + \text{OH} (+\text{NH}_3)$ reactions at (a) 10 ppbv, (b) 0.1, 10 and 2900 ppbv.

where $K_{eq(2)}$ and $K_{eq(3)}$ are equilibrium constants of $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH}\cdots\text{H}_2\text{O}$, and $\text{H}_2\text{O} + \text{HO} \rightarrow \text{RC}_{2w}$ reactions, respectively (see Table S2) and $[\text{H}_2\text{O}]$ is temperature-dependent water concentration based on literature value as discussed in Wu et al.¹⁴ The water concentration is calculated using a typical temperature-dependent water concentration, which corresponds to 100% humidity³². The value of $[\text{H}_2\text{O}]$ concentration decreases with the height of altitude. This value is in good agreement with the value of Chao et al.¹¹ ($8.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Our calculated value is at least one order magnitude lower than the value reported by Wu et al.¹⁴ This is due to fact that they used different functional and different kinetic models. The effective rate coefficient calculated based on Eq. 16 ($1.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K) is ~ 3 order of magnitude lower than water-free $\text{OH} + \text{CH}_3\text{OH}$ reaction ($\sim 9.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K). This is due to the water-assisted pathway depends parametrically on water concentration. Our result is also consistent with previously reported values on similar atmospheric reactions *i.e.*, $\text{OH} + \text{CH}_2\text{NH}$, $\text{OH} + \text{CH}_3\text{CHO}$ and $\text{OH} + \text{CH}_2\text{O}$ ^{16,31,32}. Using the rate coefficients considering the water catalytic effect could decrease the atmospheric lifetime of CH_3OH by a factor of 3 in a tropical region with high RH, which would have a non-negligible effect on the global CH_3OH budget. It is interesting to mention that the reaction between CH_3OH and OH in the presence of $(\text{H}_2\text{O})_n$, $n > 1$ has been studied previously and found no impact on the rate coefficients^{9,12,14}. The rate coefficients were also calculated using different water concentration as shown in Fig. 11b. The effect of relative humidity from 20 to 100% on calculated rate coefficients are in ~ 1 order magnitude difference, which is consistent with the previously reported value¹⁴.

The total rate coefficients and effective rate coefficients for reactions systems $\text{OH} + \text{CH}_3\text{OH} (+\text{NH}_3)$ and $\text{OH} + \text{CH}_3\text{OH} (+\text{H}_2\text{O})$ are tabulated in Table 3 and shown in Fig. 12. The total rate coefficients for $\text{OH} + \text{CH}_3\text{OH} (+\text{NH}_3)$ ($2.7 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K) and $\text{OH} + \text{CH}_3\text{OH} (+\text{H}_2\text{O})$ ($1.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K).

This value is at 8 order magnitude (in the case of ammonia) and 3 order higher (in the case of water) than $\text{OH} + \text{CH}_3\text{OH}$ reaction ($8.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Our calculations suggest that the catalytic effect of ammonia and water takes place if step 0 is ignored in the reaction mechanism. This result is also consistent with previous report on a similar reaction system^{16–32}. If we ignore step 0, which means all the ammonia and

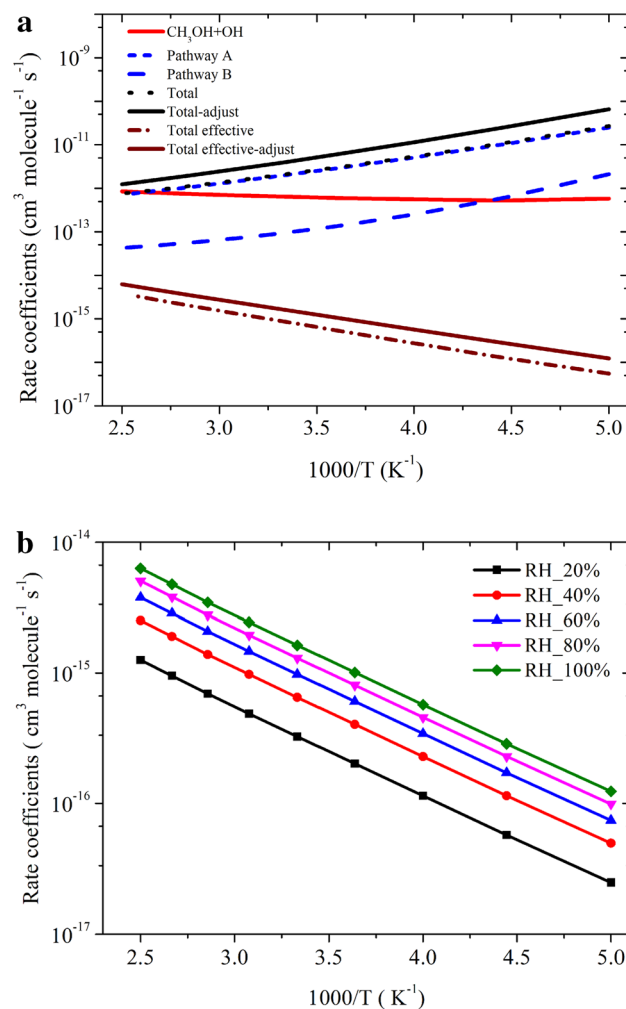


Figure 11. Rate coefficients for $\text{CH}_3\text{OH} + \text{OH} (+\text{H}_2\text{O})$ (a) 100% relative humidity (RH), (b) at different RH of H_2O .

water will be complexed with the methanol, which is not true in realistic conditions. Therefore, the correct reaction rate coefficient calculation must include the concentration of NH_3 and H_2O in the rate coefficient calculations. In that situation, our calculation demonstrates that the total effective rate coefficients for systems $\text{OH} + \text{CH}_3\text{OH} (+\text{NH}_3)$ (~ 6 – 10 order) and $\text{OH} + \text{CH}_3\text{OH} (+\text{H}_2\text{O})$ (2 – 3 order) magnitude smaller than the dry situation. This result is consistent with an earlier reports on similar reaction systems^{16–18}. It is clear that geometries of PRC_N , and TSs are different in $\text{OH} + \text{CH}_3\text{OH} (+\text{NH}_3)$ reaction systems compared to its isoelectronic analogous $\text{OH} + \text{CH}_3\text{OH} (+\text{H}_2\text{O})$ reactions, resulting in different computed enthalpies and rate coefficients. Because of this, the kinetics of $\text{OH} + \text{CH}_3\text{OH} (+\text{NH}_3)$ is quite different from those $\text{OH} + \text{CH}_3\text{OH} (+\text{H}_2\text{O})$ reaction systems. In the case of ammonia, the rate coefficients show negative temperature-dependence and in the case of water positive temperature-dependence was observed. This result may be due to that the water concentration depends highly on temperature and ammonia concentration is nearly independent of temperature.

It is possible to extend our finding on the effect of an ammonia and water molecule to gas-phase $\text{OH} + \text{CH}_3\text{OH}$, reactions. In this reaction if the concentration of the $\text{CH}_3\text{O}\cdots\text{X}$ ($\text{X} = \text{NH}_3, \text{H}_2\text{O}$) the complex formed in step 0 is very low, as is the case of $\text{CH}_3\text{O}\cdots\text{X}$, the reduction of barrier height in step 2 is not expected to be large enough to increase the rate coefficients *i.e.*, a catalytic effect. As a result, the rate coefficients with ammonia (6 to 10 order) and water molecules are 2 to 3 order magnitude smaller than the reaction $\text{OH} + \text{CH}_3\text{OH}$ reaction under tropospheric conditions. Our computations demonstrate that ammonia and water have the potential to accelerate a gas phase reaction but exhibits no enhancement under tropospheric conditions as the water-and ammonia assisted reaction is slower than the $\text{OH} + \text{CH}_3\text{OH}$ reaction.

Atmospheric implications. In general, the effective rate coefficients of the ammonia and water-assisted reaction is smaller than the $\text{OH} + \text{CH}_3\text{OH}$ reaction system in the temperature range of 200 – 400 K. As a result, the effect of $\text{OH} + \text{CH}_3\text{OH}$ catalyzed by $\text{NH}_3/\text{H}_2\text{O}$ is minor importance for the sink of CH_3OH in gas-phase atmospheric chemistry. This result is consistent with experimental measurement and theoretically calculated reaction^{11–14}. The current study of methanol in the upper troposphere has important repercussions for budget

Temp	$k_{\text{CH}_3+\text{OH}}$	k_{effN}	k_{effW}
200	7.0×10^{-13}	1.9×10^{-18}	1.2×10^{-16}
225	6.8×10^{-13}	1.7×10^{-19}	2.8×10^{-16}
250	7.2×10^{-13}	3.0×10^{-20}	5.7×10^{-16}
275	8.2×10^{-13}	8.2×10^{-21}	1.0×10^{-15}
300	8.8×10^{-13}	2.7×10^{-21}	1.6×10^{-15}
325	9.5×10^{-13}	1.2×10^{-21}	2.4×10^{-15}
350	1.0×10^{-12}	5.9×10^{-22}	3.5×10^{-15}
375	1.1×10^{-12}	3.4×10^{-22}	4.7×10^{-15}
400	1.2×10^{-12}	2.2×10^{-22}	6.3×10^{-15}
$k = AT^n \exp(-B/T)$	$A = 6.66 \times 10^{-20}$ $n = 2.59$ $B = -488.82$	$A = 3.80 \times 10^{-52}$ $n = 8.90$ $B = -6082.2$	$A = 3. \times 10^{-15}$ $n = 0.69$ $B = 1390.90$

Table 3. Calculated rate coefficients for the OH + CH₃OH, OH + CH₃OH + H₂O and OH + CH₃OH + NH₃.

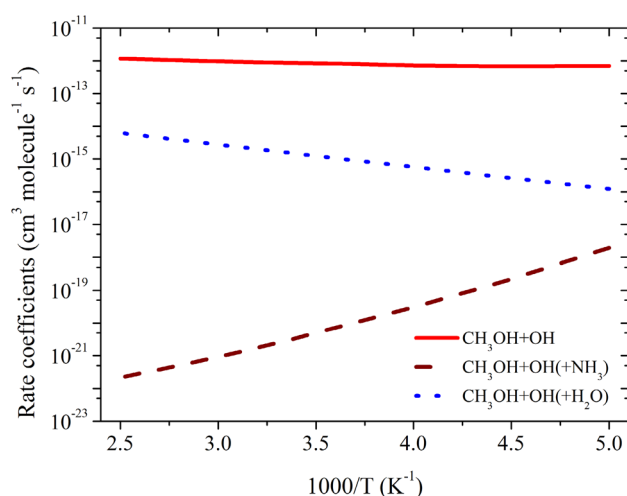
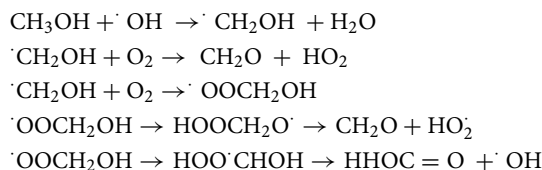


Figure 12. Comparison between rate coefficients for CH₃OH + OH, CH₃OH + OH (+NH₃) and CH₃OH + OH (+H₂O).

calculations. For that purpose, we have calculated the atmospheric lifetime of methanol at 225 K and (*i.e.*, at an altitude of ~10–11 km) taking an averaged concentration of HO radicals in the upper troposphere of OH concentration of [HO] ~ 1×10^6 molecule cm⁻³. The rate coefficient at 225 K of 6.8×10^{-13} cm³ molecule⁻¹ s⁻¹. The lifetime for methanol of 17 days is in good agreement with the experimental value of Dillon et al. (14 days)³.

In the tropospheric condition, the main radical product of the reaction is CH₂OH, which can further react with molecular ³O₂ to form formaldehyde. The formation of formaldehyde may increase the budget of formaldehyde. The degradation mechanism of the loss of CH₃OH with OH is follow as given below;



The atmospheric lifetime of CH₂OH is ~ 17 ms suggest that the formation of formaldehyde is fast under atmospheric conditions. The theoretical calculation for the formation of formic acid is not known, further study is necessary to investigate possible reactions in both atmospheric and combustion reaction. Based on this study, we believe that effect of ammonia and water on CH₂OH + O₂ will be even slower and future study is required to understand this mechanism. In general rate coefficients for the ammonia /water-assisted reaction to form CH₂O and CH₃O is negligible under tropospheric condition. Therefore, the reaction in presence of water ammonia/water cannot produce CH₃O and CH₂O radicals under tropospheric conditions. Based on current and previous studies, we propose a rule that a single ammonia /water molecule does not catalyze the reaction of OH radicals with alcohol. If there is an exception to this rule, it remains to be found. We believe the present results provide

insights into a better understanding of the gas phase catalytic effect of an ammonia and water molecule on the most important atmospheric and combustion reaction prototype molecule.

Conclusions

In the present work, the effect of single water and ammonia molecule on the gas-phase reactions of OH + CH₃OH has been investigated. The rate coefficients for two important reaction pathways OH + CH₃OH...X (X = H₂O, NH₃) and CH₃OH + HO...X (X = H₂O, NH₃) were computed calculated using CCSD(T)/6-311++G(3df,2p)//M06-2X/6-311++G(3df,2p) level with CVT/SCT approach and results were compared with previously published data.

In the presence of ammonia, the dominated reaction pathway is the H-abstraction reaction from the O–H bond. In the case of the water-assisted OH + CH₃OH reaction system, the dominated reaction pathway is the hydrogen abstraction from the CH₃ site. This result is true for both water-free and water-assisted reactions. Under the atmospheric condition, the kinetics of OH + CH₃OH (+ NH₃) is quite different from those of both OH + CH₃OH(+ H₂O). This catalytic difference between catalyst NH₃ and H₂O is possibly due to a much lower concentration of NH₃ relative to H₂O. Our results demonstrate that a single ammonia/water molecule has the potential to accelerate a gas phase reaction if step 0 is not included in the reaction mechanism. Ignoring step 0 is equivalent to assuming all the CH₃OH are complexed with water, which is not true. Therefore, the correct reaction pathways should have ammonia/water concentration in the rate coefficient calculations. This result is consistent with previous studies on similar reaction systems. Despite the fact that OH + CH₃OH reaction with the catalyst NH₃ and H₂O is not so efficient to shift the overall formation rate, the present study provides a comprehensive model of how basic and neutral catalysts assisted the gas-phase reactions. The atmospheric degradation mechanism suggests that the lifetime of CH₃OH is 17 days, which can further react with O₂ molecules to form the formaldehyde and formic acid under atmospheric and combustion conditions. The effect of ammonia and water molecules could slow the formation of formaldehyde and formic acid. Such results are interesting can be used to understand the other alcohol and similar species.

Data availability

All data generated through this study are given in Supporting Information file. Supporting Information: Tables of optimized geometries of all the species involved in the OH + CH₃OH, OH + CH₃OH (+ NH₃) and CH₃OH (+ H₂O). Tables of Equilibrium Constants and Figure of trail rate coefficients. Energies and rate coefficients calculation using at CBS-QB3 level.

Received: 21 December 2020; Accepted: 5 May 2021

Published online: 09 June 2021

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Acknowledgements

Mohamad Akbar Ali (MAA) gratefully acknowledges the Deanship of Scientific Research at King Faisal University, Saudi Arabia for financial support under Nasher Track (206163.). MAA thanks the computational support by Department of Chemistry at King Faisal University, Saudi Arabia and supercomputer facility at department of Chemistry National Taiwan University.

Author contributions

M.A.A. prepared figures and tables and draft of the paper. Balaganesh done all the gaussian and chemical kinetic calculations as discussed in the paper. Dr. Faisal A. Al-Odail and Dr. K.C. Lin provided the suggestion to improve the paper.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1038/s41598-021-90640-6>.

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