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Effect of Water and Formic Acid on OH + CH₄ Reaction: An Ab Initio/DFT Study

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Abstract: In this work, we used ab initio/DFT method coupled with statistical rate theory to answer the question of whether or not formic acid (HCOOH) and water molecules can catalyze the most important atmospheric and combustion prototype reaction, i.e., OH (OH radical) + CH₄. The potential energy surface for OH + CH₄ and OH + CH₄ (+X) (X = HCOOH, H₂O) reactions were calculated using the combination of hybrid-density functional theory and coupled-cluster theory with Pople basis set [(CCSD(T)/ 6-311++G(3df,3pd)]//M06-2X/6-311++G(3df,3pd)]. The results of this study show that the catalytic effect of HCOOH (FA) and water molecules on the OH + CH₄ reaction has a major impact when the concentration of FA and H₂O is not included. In this situation the rate constants for the CH₄ + HO···HCOOH (3 × 10⁻⁹ cm³ molecule⁻¹ s⁻¹) reaction is ~10⁵ times and for CH₄ + H₂O···HO reaction (3 × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ at 300 K) is ~20 times higher than OH + CH₄ (~6 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹). However, the total effective rate constants, which include the concentration of both species in the kinetic calculation has no effect under atmospheric condition. As a result, the total effective reaction rate constants are smaller. The rate constants when taking the account of the FA and water for CH₄ + HO···HCOOH (4.1 × 10⁻²² cm² molecule⁻¹ s⁻¹) is at least seven orders magnitude and for the CH₄ + H₂O···HO (7.6 × 10⁻¹⁷ cm² molecule⁻¹ s⁻¹) is two orders magnitude smaller than OH + CH₄ reaction. These results are also consistent with previous experimental and theoretical studies on similar reaction systems. This study helps to understand how FA and water molecules change the reaction kinetic under atmospheric conditions for OH + CH₄ reaction.

Keywords: methane; OH radical; catalysis; formic acid; water; ab initio/DFT; CVT/SCT

1. Introduction

The tropospheric concentration of important greenhouse gases, i.e., methane (CH₄), is steadily increasing [1–4]. In the atmosphere, OH (OH radical) plays a crucial role in removing the CH₄ [1–4]. The atmospheric lifetime of methane is due to loss by OH is ~12–17 years [1–4]. This reaction is also important in high-temperature combustion kinetics [5]. Due to large uncertainty in the rate constants data, many experimental measurements and theoretical studies have been performed [1–5]. To avoid the repetition of previous studies, only a few studies have been discussed here [1–5]. Various experimental measurements were used to estimate the rate constant for OH + CH₄ reaction into the atmosphere condition and reported its atmospheric lifetime due to loss with the OH [1–4]. Experimental measurement on OH + CH₄ reaction was done by Vaghjian et al. [2] in the temperature range of 295 to 400 K. Due to the limited number of high temperature studies, Srinivasan et al. measured the rate constants of OH + CH₄ using the reflected shock tube method [5]. The OH + CH₄ reaction has been extensively studied by using various theoretical approaches [6–9]. Most of the theoretical studies have focused on calculating the rate constants using a high-level ab initio methods and statistical rate theory [6–9]. Ellingson et al. [9] proposed the rate constants for OH + CH₄ reaction and its 12C/13C kinetic
isotopes effect using harmonic, hindered, and free rotor approaches. Their calculated rate constants were in good agreement with experimentally measurement values. Li and Gua calculated the thermal rate constants for isotopic effects for OH + CH₄ using UCCSD(T)-F12a/aug-cc-pVTZ and canonical variational transition state theory (CVT) using the free rotor approach [6,8]. In this study, we have re-calculated the rate constants for OH + CH₄ using a similar level of theories to validate our theoretical approach and compare the rate constants for the effect of HCOOH/H₂O on OH + CH₄ reaction.

It is believed that volcanic eruptions emitted various gases into the Earth’s atmosphere [10–12]. Toxic acids such as hydrochloric (HCl), formic acid (HCOOH), and sulfuric (H₂SO₄) acid in the atmosphere are produced from volcanic activities [10–12]. The source of HCOOH (FA) in atmospheric reactions has been extensively studied in recent years [10–12]. FA is mainly produced by oxidation of volatile organic compounds (VOCs), soil, burning of fossil fuels, and terrestrial vegetation [10–12]. FA also influences pH-dependent chemical reactions in clouds [11]. FA is one of the most abundant organic acid present in the atmosphere [10]. The atmospheric abundance of FA varies from 0.01 to 10 ppbv depending upon the altitudes [13–19]. FA can catalyze many important atmospheric reactions such as CH₃O + O₂ [13], OH + HCl [14], H₂O + CH₃COO [15], HO₂ + Cl [16], H₂O + CH₂O [17], and OH + CH₂O [19]. These studies suggest that FA can form ring types of complexes and transition states, which lower the barrier heights and increase the reaction rate constant under atmospheric conditions [13–19]. However, in realistic atmospheric conditions, the effective rate constants decrease and the catalytic effect does not favor the reaction [12–19]. To the best of our knowledge, the acidolysis of OH + CH₄ by a FA molecule has not been studied. Therefore, we have investigated the effect of the FA molecule on the most important atmospheric and combustion prototype of reaction, i.e., OH + CH₄. The focus of the present work is to explore the potential energy surface for the effect of FA on OH + CH₄ and calculate the rate constants under atmospheric conditions.

The oxidation of CH₄ in the stratosphere is an important source of water vapor in this region. Over the last few years, many experimental and theoretical studies have been conducted on the catalytic effect of a single water molecule on many important atmospheric reactions, such as OH + CH₂O, OH + CH₂CH₂, OH + CH₂NH, OH + CH₂CHO, OH + CH₃OH, OH + HCl, O₂ + CH₂O, and O₂ + CH₂OH [20–32]. Experimental measurements on some of the reactions, i.e., OH + CH₃OH (+H₂O) [20] and OH + CH₃CHO (+H₂O) [22], have been performed. Jara et al. [20] and Vöhringer-Martinez [22] have measured reaction rate constants and suggested that the catalytic role of water molecules dominated at lower temperatures. Recently, Wu et al. [21], have proposed reaction kinetic data using a high-level ab initio method and an advanced kinetic model for OH + CH₃OH. Their calculated rate constants were in good agreement with the experimentally measured values of Jara et al. [20]. Most of the theoretical studies suggest that a single water molecule formed a water-bounded ring type of pre-reactive complexes (PRCs) and transition states (TSs), which reduces the energy barrier but does not increase the rate constant under atmospheric conditions. In 2012, Thomsen et al. [23], proposed the effect of a single water molecule on OH + CH₄ using ab initio/DFT method [23]. They suggested that the role of water molecules in OH + CH₄ reaction is less important under atmospheric conditions. To the best of our knowledge, the detailed kinetics analysis of this reaction is still not known, and the effect of temperature-dependent water concentration on OH + CH₄ has not been reported. In our previous works, we proposed the catalytic effect of H₂O molecules in the atmospheric reactions, i.e., OH + CH₃O, OH + CH₂CH₂, OH + CH₂NH, OH + CH₂OH, CH₂NH + H₂O, and CH₂OH + O₂ reactions [25–28]. We have also suggested that the catalytic role of water is less important under atmospheric conditions.

Because of CH₄ long lifetime and a good model for the most important atmospheric and combustion reaction prototype molecule, the effect of FA and water molecules was investigated. The rate constant for the effect of FA and water molecules on OH + CH₄ were investigated at different atmospheric concentrations of FA and water molecules at different temperatures. The results of this study may be useful for the benchmark performance for
other higher chain alkanes. The comparison of reaction energies and rate constants with the literature values provides more confidence in our results.

2. Theoretical Methodology

2.1. Computational Method

All the electronic structure calculations were done with the Gaussian 09 suite of programs (Revision A.02, Gaussian, Inc., Wallingford, CT, USA, 2009) [33]. Optimized geometries for the species involved in \( \cdot \text{OH} + \text{CH}_4 \), \( \cdot \text{OH} + \text{CH}_4 (+\text{HCOOH}) \), and \( \cdot \text{OH} + \text{CH}_4 (+\text{H}_2\text{O}) \) reactions were computed using M06-2X/6-311++G(3df,3pd) level [34] (see Table S1). The harmonic vibrational frequency of all the species was calculated to obtain the zero-point corrections (ZPE). The frequency analysis shows that all the reactants, complexes and products have all positive values whereas all the transition states (TSs) have a single imaginary (see Table S2). Intrinsic reaction coordinate (IRC) calculations were performed to confirm the identity of pre-reactive complex and post-reactive complex for every TS. The single point energies were calculated using CCSD(T)/6-311++G(3df,3pd) (CC) level of theory at optimized geometries of M06-2X/6-311++G(3df,3pd)(M06-2X). As discussed in the previous works, the combination of CC//M06-2X typically provides results that are accurate to \( \sim 1–2 \) kcal/mol [23–26]. Therefore, we believe the CC//M06-2X provides accurate energies for rotational vibrational parameters for \( \cdot \text{OH} + \text{CH}_4 \), \( \cdot \text{OH} + \text{CH}_4 (+\text{HCOOH}) \), and \( \cdot \text{OH} + \text{CH}_4 (+\text{H}_2\text{O}) \) reactions. The ZPE, electronic energies, thermal correction, enthalpy correction, and free energy correction for all the species are tabulated in Table S3.

2.2. Chemical Kinetics Calculations

The temperature-dependent rate constants were calculated by Equations (1) and (2):

\[
l_k^{GT}(T, s) = \Gamma L^2 \times \frac{k_B T}{h} \frac{Q_{TS}^{\neq}(T, s)}{Q_R(T)} \exp \left( - \frac{V_{MEP}(s)}{k_B T} \right)
\]

\[
l_k^{CVT}(T) = \min_s \kappa^{GT}(T, s) = \kappa^{GT} \left( T, s^{CVT}(T) \right)
\]

where \( k_k^{GT}(T, s) \) is generalized rate constants and \( k_k^{CVT}(T) \) are the temperature dependent rate canonical variational transition state theory (CVT) rate constants, \( V_{MEP} \) is the barrier height without zero-point correction, \( L^2 \) is a reaction path degeneracy, \( h \) is Planck’s constant, \( k_B \) is the Boltzmann constant, and \( Q_{TS}^{\neq} \) and \( Q_R \) are the total partition functions for the transition state and the reactants, respectively, \( \Gamma \) is the small curvature tunneling (SCT) correction as implemented in Polyrate [35]. The rate constants were calculated using a dual dynamic approach with CVT and the interpolated single point energies (ISPE) correction calculated using dual level direct dynamic approach CVT/SCT with interpolated single point energies (ISPE) as discussed in the reference [35,36]. PolyRate and GaussRate suite of programs were used to calculate the temperature-dependent bimolecular and unimolecular rate constants based on CVT/SCT (Table S4) approach [35,36].

The Multiwell Thermo code [37] was used calculate the equilibrium constant \( (K_{eq}) \) for the formation of complexes as given in Equation (3):

\[
K_{eq} = \frac{Q_{RC}^{\neq} \exp \left( - \frac{E_{RC} - E_R}{k_B T} \right)}{Q_R}
\]

The equilibrium constants \( (K_{eq}) \) for the formation complexes calculated by Equation (3) were tabulated in Tables S5 and S6.

3. Results and Discussion

3.1. Reaction Pathways for \( \cdot \text{OH} + \text{CH}_4 \)

The potential energy surface (PES) for \( \cdot \text{OH} + \text{CH}_4 \) reaction is shown in Figure 1. The rotational vibrational parameters of \( \text{CH}_4 \), \( \cdot \text{OH} \) and TS and products are given in Table S2. As shown in Figure 1, the reaction proceeds via the formation of a pre-reactive complex.
RC₁) whose energy is higher than the reactants. This is due to the fact that the orientation of H of ·OH is toward the carbon atom of CH₄. The role of complex in ·OH + CH₄ reaction is unimportant as suggested in earlier studies [8]. The barrier height for ·OH + CH₄ is ~5.0 kcal/mol is in very good agreement with the value reported by earlier theoretical studies (5–6 kcal/mol) [6–9].

3. Results and Discussion

3.1. Reaction Pathways for OH + CH₄

The potential energy surface (PES) for ·OH + CH₄ reaction is shown in Figure 1. The optimized geometries and rotational vibrational parameters of CH₄, ·OH, and TS and products are given in Tables S1 and S2. The calculated binding energy (BE) between ·OH and FA1 (−3.85 kcal/mol) is in very good agreement with the value (−3.59 kcal/mol) reported previously [19]. The BE of FA2···OH (−2.83 kcal/mol) is 1 kcal/mol higher than the BE of FA1···OH (−3.85 kcal/mol). This is due to the fact that the cis and trans orientation of FA. The trans form of FA with ·OH leading to more strong hydrogen bonding than the cis form. The B.E. of CH₄···HCOOH (+0.3 kcal/mol) and CH₄···HCOOH

Figure 1. Potential energy surface for the ·OH + CH₄ reaction leading to form methyl radical and water. The stationary point was computed at the CC//M06-2X level and ZPE correction obtained from vibrational analysis using M06-2X.

3.1.1. Reaction Pathways for ·OH + CH₄ (+HCOOH)

As discussed in the earlier studies, [13,14,25–28], under true conditions, it is very unlikely that ·OH, CH₄, and HCOOH collide simultaneously, therefore the probability of a termolecular reaction is negligible. It is expected that either a CH₄···HCOOH or ·OH···HCOOH and CH₄···HO will form first, followed by an attack on this complex by third molecule ·OH or CH₄ or HCOOH. In these three cases, the probable reactions are shown in Equations (4)–(6):

\[
\begin{align*}
\text{CH}_4 \cdots \text{HCOOH} + \text{OH} & \rightarrow \text{CH}_3 + (\text{H}_2\text{O}) + \text{HCOOH} & (4) \\
\text{CH}_4 \cdots \text{HO} + \text{HCOOH} & \rightarrow \text{CH}_3 + (\text{H}_2\text{O}) + \text{HCOOH} & (5) \\
\text{CH}_4 + \text{HCOOH} \cdots \text{HO} & \rightarrow \text{CH}_3 + (\text{H}_2\text{O}) + \text{HCOOH} & (6)
\end{align*}
\]

The potential energy surface (PES) for the effect of FA on ·OH + CH₄ reaction is shown in Figure 2. The optimized geometries and rotational vibrational parameters of CH₄, OH, and TS and products are given in Tables S1 and S2. The calculated binding energy (BE) between ·OH and FA1 (−3.85 kcal/mol) is in very good agreement with the value (−3.59 kcal/mol) reported previously [19]. The BE of FA2···OH (−2.83 kcal/mol) is 1 kcal/mol higher than the BE of FA1···OH (−3.85 kcal/mol). This is due to the fact that the cis and trans orientation of FA. The trans form of FA with ·OH leading to more strong hydrogen bonding than the cis form. The B.E. of CH₄···HCOOH (+0.3 kcal/mol) and CH₄···HCOOH
(+0.3 kcal/mol) is very small compared to B.E. of HCOOH···OH, therefore, we have neglected these complexes. As shown in Figure 2, beginning with the CH₄ + HCOOH···OH, two three-body complexes PRC₉A-1 and PRC₉A-2 were formed due to the trans and cis orientation of FA (Figure 2). The relevant TS structures connected to these PRCs are shown in Figure 2. The other PRC₉A was also optimized and found that they are less stable than PRC₉A-1 and PRC₉A-2, therefore not included in the PES of CH₄ + OH···HCOOH reaction (see Figure S1).

![Figure 2. Potential-energy surface for the effect of FA on ·OH + CH₄ reaction leading to form methyl radical, water, and formic acid. The stationary point was computed at the CC//M06-2X level and ZPE correction obtained from vibrational analysis using M06-2X.](image)

The BE of PRC₉A-1 (−6.96 kcal/mol) and PRC₉A-2 (−4.32 kcal/mol) is the result of C···H and O···H interactions. Starting from PRC₉A-1 and PRC₉A-2, we have identified two reaction pathways, i.e., hydrogen abstraction by ·OH on two different orientations of FA. Transition state (TS₉₁) corresponds to H-abstraction reaction from methane hydrogen via PRC₉A-1. The calculated barrier heights for this pathway (~3.76 kcal/mol), which are lower than the barrier height for ·OH + CH₄ reaction (~5 kcal/mol). The transition state (TS₉₂) corresponds to the H abstraction reaction from methane hydrogen via PRC₉A-2. The calculated barrier height TS₉₂ (~ 5.32 kcal/mol) which leads to form a product FA-2 (cis-Hydrogen). The barrier height of TS₉₁ (~4 kcal/mol,) is ~1 kcal/mol lower than the value of TS₉₂ (~5 kcal/mol) expected to play a more important role in the kinetic calculations [13,14,19].
3.1.2. Reaction Pathways for `OH + CH₄ (+H₂O)

As suggested in the FA case, the simultaneous collisions of `OH, CH₄, and H₂O, are very unlikely, therefore the termolecular reaction probability is negligible under real conditions. It is expected that either a CH₄···H₂O or `OH···H₂O or CH₄···OH will form first, followed by an attack on this complex by the third molecule `OH or CH₄ or H₂O to this complex. In these three cases, the most probable reactions are given in Equations (7)–(9):

\[
\begin{align*}
\text{CH}_4 \cdot \cdot \cdot \text{H}_2\text{O} + \text{OH} &\rightarrow \text{CH}_3 + (\text{H}_2\text{O})_2 \\
\text{CH}_4 \cdot \cdot \cdot \text{HO}' + \text{H}_2\text{O} &\rightarrow \text{CH}_3 + (\text{H}_2\text{O})_2 \\
\text{CH}_4 + \text{H}_2\text{O} \cdot \cdot \cdot \text{HO}' &\rightarrow \text{CH}_3 + (\text{H}_2\text{O})_2
\end{align*}
\]

Out of three, only one OH···H₂O (−4.1 kcal/mol) as a two-body complex is found to be more stable than CH₄···H₂O (−0.3 kcal/mol) and CH₄···OH (+0.3 kcal/mol), therefore the reactions (7) and (8) are not considered in the potential energy surface plot. The potential energy surface (PES) for the effect of water on `OH + CH₄ reaction is shown in Figure 3. As shown in Figure 3, beginning with the CH₄ + `OH···H₂O reaction, the three-body complex i.e., PRCₖ was formed depending on the approach of the hydrogen atom in the `OH towards the water oxygen or the hydrogen of `OH (Figure 3). We tried different way of projecting OH and H₂O in the reaction, which led to two different PRCₖs, i.e., PRCₖ-1 (−4.3 kcal/mol) and PRCₖ-2 (−3.1 kcal/mol). The optimized structure is given in the supporting information Figure S1. As suggested in earlier work on a similar reaction system [21], only stable PRCₖ was considered for the rate constant calculations. Therefore, we restricted our discussion to only stable PRCₖ-1.

![Figure 3. Potential energy surface profile for the effect of water molecules on `OH + CH₄ reaction leading to form methyl radical and water molecules. The stationary point was computed at the CC//M06-2X level and ZPE correction obtained from vibrational analysis using M06-2X.](image)

3.2. Enthalpies of Reactions (∆H_rxn (0 K))

The enthalpies (∆H(0 K)) relative to the reactants for `OH + CH₄, `OH + CH₄ (+HCOOH) and `OH + CH₄ (+H₂O) reactions are given in Table 1. The calculated ∆H(0 K) of `OH + CH₄

\[
\begin{align*}
\text{CH}_4 + \text{OH} + \text{H}_2\text{O} &\rightarrow \text{CH}_3 + (\text{H}_2\text{O})_2 \\
\text{CH}_4 + \text{RC}_2\text{w} &\rightarrow \text{CH}_3 + (\text{H}_2\text{O})_2 \\
\text{Post-PRC} &\rightarrow \text{CH}_3 + 2\text{H}_2\text{O}
\end{align*}
\]
→CH₃ + H₂O (−14.4 kcal/mol) is in excellent agreement with the ATcT thermochemical data (−14.3 kcal/mol) base [38–40] and is in very good agreement with previous theoretical calculation (−13.9 kcal/mol) [7,9]. As shown in Figure 2, the formation of the complex in OH···CH₄···HCOOH (PRCFA1) and OH···CH₄···HCOOH (PRCFA2), are in trans- and cis orientation of HCOOH. Due to the different orientations of OH and HCOOH molecules, the BE of PRCFA1 (−6.96 kcal/mol) and PRCFA2 (−4.32 kcal/mol) are different (see Figure 2 and Table 1). The orientation of the H-atom of HCOOH makes a strong hydrogen bond between OH···CH₄···HCOOH leading to more stable PRCFA1. The calculated BE of OH···CH₄···H₂O (PRCw) (−4 kcal/mol) is lower than BE of PRCFA (−6.96 kcal/mol) due to the presence of weak hydrogen bonds. It is clear from Table 1 that barrier height for the effect of FA and water molecules on OH + CH₄ reaction is smaller than the barrier height of the free OH + CH₄ reaction, which gives the indication of catalytic behavior of FA and water on OH + CH₄ reaction.

Table 1. Enthalpies of reaction (ΔH_rxn (0 K)) in kcal mol⁻¹ of OH + CH₄ reaction.

| Reaction | This Work | Literature a,b,c |
|----------|-----------|------------------|
| OH···CH₄ (RCl) | 0.30 | −14.3 a, −13.9 b, −13.4 c |
| HO···HCH₃ (TS) | 4.93 | |
| CH₃ + H₂O | −14.4 | |
| OH + CH₄ + HCOOH | This Work | |
| OH···CH₄···HCOOH (PRCFA1) | −6.96 | |
| OH···CH₄···HCOOH (PRCFA) | −4.32 | |
| OH···HCH₃···HCOOH (TPFA1) | −3.2 | |
| OH···HCOOH···HCH₃ (TPFA2) | +1.0 | |
| H₂O···HCOOH···CH₃ (Post-PRCFA1) | −17.4 | |
| H₂O···HCOOH···CH₃ (Post-PRCFA2) | −22.7 | |
| CH₃ + H₂O + FA | −14.4 | |
| OH + CH₄ + H₂O | This Work | |
| OH···CH₄···H₂O (PRCw) | −4.32 | |
| OH···HCH₃···H₂O (TSP) | +1.6 | |
| H₂O···H₂O···CH₃ (Post-PRCw) | −18.42 | |
| CH₃ + 2H₂O | −14.4 | |

a ATcT thermochemical data [38–40]. b [9]. c [7].

3.3. Rate Constants

OH + CH₄ Reaction

The CVT/SCT rate constant for OH + CH₄ reaction is calculated and tabulated in Table 2 and shown in Figure 4. The calculated value using harmonic oscillator (HO) approximation is a factor of ~2 lower than experimentally measured values over the entire temperature range (Table 2). The rate constant calculated using HO approximation (2.3 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ at 300 K) is in very good agreement with the HO approximation of Ellingson et al [9] (2.3 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ at 300 K).

As suggested by Ellingson et al. [9], the free-rotor approximation is the correct choice, which is consistent with our study. The calculated value using free-rotor approximation at 300 K (6.1 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹) is in excellent agreement with the experimentally measured [2,41] value (6.7 × 10⁻¹⁵ and 6.9 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹) and good agreement with theoretically calculated ones (4 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ and 6 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹) [7,9]. Our value is in very good agreement over the entire temperature range with the experimentally measured values. The calculated value is also in very good agreement with Srinivasan et al. (Figure 4) [5]. The calculations of rate constant for OH + CH₄ reaction provide more confidence in our theoretical approach CC//M06-2X with CVT/SCT method. To avoid the repetition of the OH + CH₄ reaction, we have restricted our comparison to only a few experimental and theoretical values [2,5,7,9,41].
Table 2. Comparison of calculated rate constants (cm$^3$ molecule$^{-1}$ s$^{-1}$) and literature rate constants for the OH + CH$_4$ → CH$_3$ + H$_2$O.

| Temp (K) | $k_{HO}$ | $k_{FR}$ | Exp [2,39] | Exp [5] | Theory [9] |
|----------|-----------|-----------|-------------|---------|------------|
| 200      | $1.7 \times 10^{-16}$ | $4.6 \times 10^{-16}$ | $3.6 \times 10^{-16}$ | $3.7 \times 10^{-16}$ | $1.5 \times 10^{-16}$ |
| 225      | $3.4 \times 10^{-16}$ | $8.9 \times 10^{-16}$ | $9.5 \times 10^{-16}$ | $9.5 \times 10^{-16}$ | $4.2 \times 10^{-16}$ |
| 250      | $7.0 \times 10^{-16}$ | $1.8 \times 10^{-15}$ | $2.0 \times 10^{-15}$ | $2.1 \times 10^{-15}$ | $9.8 \times 10^{-16}$ |
| 275      | $1.3 \times 10^{-15}$ | $3.5 \times 10^{-15}$ | $3.9 \times 10^{-15}$ | $4.0 \times 10^{-15}$ | $2.0 \times 10^{-15}$ |
| 300      | $2.3 \times 10^{-15}$ | $6.1 \times 10^{-15}$ | $6.6 \times 10^{-15}$ | $6.9 \times 10^{-15}$ | $3.8 \times 10^{-15}$ |
| 325      | $3.9 \times 10^{-15}$ | $1.0 \times 10^{-14}$ | $1.0 \times 10^{-14}$ | $1.1 \times 10^{-14}$ | $6.4 \times 10^{-15}$ |
| 350      | $6.1 \times 10^{-15}$ | $1.6 \times 10^{-14}$ | $1.5 \times 10^{-14}$ | $1.8 \times 10^{-14}$ | $1.0 \times 10^{-14}$ |
| 375      | $9.2 \times 10^{-15}$ | $2.4 \times 10^{-14}$ | $2.2 \times 10^{-14}$ | $2.6 \times 10^{-14}$ | $1.6 \times 10^{-14}$ |
| 400      | $1.3 \times 10^{-14}$ | $3.5 \times 10^{-14}$ | $2.9 \times 10^{-14}$ | $3.6 \times 10^{-14}$ | $2.3 \times 10^{-14}$ |

$k = A \times 10^{-28} \exp(-B/T)$

Figure 4. Rate constants for OH + CH$_4$ reaction. The rate constants were calculated using harmonic oscillator and free-rotor approximation.

3.4. Formic Acid Assisted ·OH + CH$_4$ Reaction

As suggested in the thermochemistry section, the binding energy of CH$_4$···HCOOH, and CH$_4$···OH smaller than that of HCOOH···HO' which will result in a shorter lifetime. Therefore, the formation of CH$_4$···HCOOH, CH$_4$···OH is almost negligible compared to HCOOH···HO' and only one channel, i.e., CH$_4$ + HCOOH···HO' is considered for the rate constants calculations.

$$\text{OH} + \text{HCOOH} \rightarrow \text{HCOOH} \cdot \cdot \cdot \text{HO} + \text{CH}_4 \quad \text{~}$$

$\frac{k_{0j}}{k_{0j}}$ $\text{HCOOH} \cdot \cdot \cdot \text{HO} + \text{CH}_4 \rightarrow \text{HCOOH} \cdot \cdot \cdot \text{HO} + \text{CH}_4 \rightarrow \text{Products}$

The temperature-dependent rate constants for the reactions of OH + CH$_4$ (+HCOOH) were calculated based on the high-pressure limit condition. Locating the TS of backward reaction, i.e., PRGF$A \rightarrow$ ‘OH···HCOOH + CH$_4$ is complicated, in that case, to account for the presence of forward and backward reactions ($k_{FA} = K_{eq} k_{2f}$) equilibrium approach was used. This kinetic model is reasonably correct as discussed in our earlier studies [25–28]. The rate constants (s$^{-1}$) ($k_{2f}$) were computed using the CVT/SCT approach are presented in supporting information, Table S4. The equilibrium constants ($K_{eq}$) are shown in Tables S5 and S6.
The rate constants \( k_{2FA1} = K_{eq(FA1)} \times k_{T5F1} \) and \( k_{2FA2} = K_{eq(FA2)} \times k_{T5F2} \) for \( \cdot \text{OH} + \text{CH}_4 \) (+HCOOH) were calculated in the temperature range of 200 to 400 K and are shown in Figure 5. \( k_{2FA1} \) are bimolecular rate constants of Pathway FA-1 and \( k_{2FA2} \) are bimolecular rate constants for Pathway FA-2, where \( K_{eq(FA1)} \) and \( K_{eq(FA2)} \) are equilibrium constants for \( \text{CH}_4 + \cdot \text{OH} \cdots \text{HCOOH} \rightarrow \text{PRC}_{FA1} \) and \( \text{CH}_4 + \cdot \text{OH} \cdots \text{HCOOH} \rightarrow \text{PRC}_{FA2} \), respectively (see Table S6). The rate constant of Pathway FA-1 \((3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 300 K) is higher than Pathway FA-2 \((6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 300 K), which shows that Pathway FA-1 is more kinetically favorable than Pathway FA-2.

\[
k_{eff} = \left\{ K_{eq(FA1)} \times k_{T5F1} \right\} + \left\{ K_{eq(FA2)} \times k_{T5F2} \right\} \times [\text{HCOOH}]
\]  

(11)

where \( K_{eq(FA1)} \) and \( K_{eq(FA2)} \) are equilibrium constants of \( \cdot \text{OH} + \text{HCOOH} \rightarrow \text{RC}_{4F1} \) and \( \cdot \text{OH} + \text{HCOOH} \rightarrow \text{RC}_{4F2} \), respectively (see Table S5) and [HCOOH] is FA concentration used at 10 ppbv and 0.01 ppbv are based on previous studies [13,14]. The total effective rate constant for \( \cdot \text{OH} + \text{CH}_4 \) (+HCOOH) \((4 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 300 K) is ~7 order magnitude lower than \( \cdot \text{OH} + \text{CH}_4 \) reaction \((6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 300 K). This result is similar to FA-assisted reaction \( \cdot \text{OH} + \text{HCHO} \) (+HCOOH): \(7 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 300 K) as reported in the earlier study [19]. The rate constants show positive temperature-dependent (Figure 5). The similar kind of behavior was observed in the literature on the effect of FA on atmospheric reactions [13].
3.5. Water-Assisted \( \cdot \text{OH} + \text{CH}_4 \) Reaction

As discussed in the case of FA assisted reaction, only one \( \text{CH}_4 + \cdot \text{OH} \cdots \text{H}_2\text{O} \) channel is considered for the rate constants calculations. The other channels, i.e., the formation of \( \text{CH}_4 \cdots \text{H}_2\text{O}, \text{CH}_4 \cdots \cdot \text{OH} \), are almost negligible.

The reaction pathways for the effect of a water molecule on \( \cdot \text{OH} + \text{CH}_4 \) starting with \( \cdot \text{OH} \cdots \text{H}_2\text{O} \) are presented in Equation (12):

\[
\begin{align*}
\text{OH} + \text{H}_2\text{O} & \overset{k_{\text{tw}}}{\rightleftharpoons} \text{H}_2\text{O} \cdots \cdot \text{HO} + \text{CH}_4 & \overset{k_{1w}}{\rightleftharpoons} \text{H}_2\text{O} \cdots \cdot \text{HO} \cdots \cdot \text{CH}_4 \overset{k_{2w}}{\rightarrow} \text{Products}
\end{align*}
\]

The rate constants (s\(^{-1}\)) for \( \cdot \text{OH} + \text{CH}_4 (+\text{H}_2\text{O}) \) \((\text{PRC}_w \rightarrow \text{TS} \rightarrow \text{P})\) were tabulated in Table S4. The rate constants \((\text{cm}^3\text{molecule}^{-1}\text{s}^{-1})\) were calculated using \(k_{2w} = K_{\text{eq}(A)} \times k_{\text{TSaw}}\), where \(K_{\text{eq}(A)}\) is in equilibrium constants involved in the \( \cdot \text{OH} \cdots \text{H}_2\text{O} + \text{CH}_4 \) reaction. The rate constants in the temperature range of 200 K to 400 K for with and without water concentration are shown in Figure 6. The rate constants for \( \text{CH}_4 + \text{H}_2\text{O} \cdots \cdot \text{OH} \) reaction \((3 \times 10^{-14} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \text{ at } 300 \text{ K})\) is ~20 times higher than \( \cdot \text{OH} + \text{CH}_4 \) reaction \((6 \times 10^{-15} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \text{ at } 300 \text{ K})\). As shown in Figure 6, the water-catalyzed reaction has higher rate constants than a water-free reaction in the entire temperature range 200–400 K.

![Figure 6](image.png)

Figure 6. Rate constants for \( \cdot \text{OH} + \text{CH}_4 + (\text{H}_2\text{O}) \) with different relative humidity. \( \text{CH}_4 + \text{H}_2\text{O} \cdots \cdot \text{OH} \) is the rate constants without water concentration. The water concentration at this humidity is taken from our earlier studies [21,27]. The presented rates are the relative humidity of water from 20% to 100%.

As suggested in our earlier studies [25–27], the concentration of water at varying humidity levels must be used to estimate the accurate rate constant. Therefore, the correct expression to calculate the total effective rate constants is given by Equation (13)

\[
k_{\text{eff}} = \left[ \left\{ K_{\text{eq}(2)} \times k_{\text{CVT}} \right\} \right] \times [\text{H}_2\text{O}]
\]

where \(K_{\text{eq}(2)}\) are equilibrium constants of \( \text{H}_2\text{O} + \cdot \text{OH} \rightarrow \text{RC}_{2w} \) reactions, \([\text{H}_2\text{O}]\) is water concentration as discussed in earlier studies [21,27]. The effective rate constant
(7 × 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K}) is factor of ~100 lower than the water-free OH + CH₄ reaction (~6 × 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K}) at 100% humidity. The result is also consistent with similar atmospheric reactions, i.e., OH + CH₂NH, OH + CH₂CH₂, OH + CH₂O, and OH + CH₃OH [25–27].

In order to gain correct insight into the effect of FA/water on OH + CH₄ reaction, the free energy profiles for all the channels were computed and shown in supporting information Figure S2. Due to the high entropy of activation of (∆S) of FA/H₂O assisted reaction than free OH + CH₄ reaction, rate constants are higher. It is also important to point out that, in the gas phase reaction, the barrier height ∆E and ∆G are calculated as the energy difference between the transition state and those of the two-body complex, i.e., RCs. Thus, if step 0 is ignored and the rate constant is calculated as \kappa_{\text{eff}} = \kappa_{\text{eq}} \times k_2 and the reaction rate constant is higher in the presence of FA/H₂O and catalytic effect is favorable for OH + CH₄.

The total rate constants for OH + CH₄ and effective rate constants for OH + CH₄ (+HCOOH) and OH + CH₄ (+H₂O) reactions are tabulated in Table 3 and shown in Figure 7.

| Temp (K) | \kappa_{\text{CH₄+OH}} | \kappa_{\text{eff FA}} | \kappa_{\text{eff W}} |
|---------|----------------|----------------|----------------|
| 200     | 4.6 × 10^{-16} | 1.4 × 10^{-19} | 3.5 × 10^{-19} |
| 225     | 8.9 × 10^{-16} | 1.8 × 10^{-20} | 4.9 × 10^{-18} |
| 250     | 1.8 × 10^{-15} | 3.7 × 10^{-21} | 8.2 × 10^{-18} |
| 275     | 3.5 × 10^{-15} | 1.1 × 10^{-21} | 2.8 × 10^{-17} |
| 300     | 6.1 × 10^{-15} | 4.2 × 10^{-22} | 7.6 × 10^{-17} |
| 325     | 1.0 × 10^{-14} | 2.0 × 10^{-22} | 1.8 × 10^{-16} |
| 350     | 1.6 × 10^{-14} | 1.1 × 10^{-22} | 3.8 × 10^{-16} |
| 375     | 2.4 × 10^{-14} | 7.4 × 10^{-23} | 7.1 × 10^{-16} |
| 400     | 3.5 × 10^{-14} | 5.4 × 10^{-23} | 1.3 × 10^{-15} |

\begin{align*}
\kappa &= A \exp(-B/T) \\
\exp(-B/T) &= n \\
B &= 134 \\
B &= -5872 \\
B &= 2717 \\
\end{align*}

The result of this study suggests that the catalytic effect of FA and water takes place if the concentration of these molecules were not included, which is unrealistic. Therefore, to calculate the correct reaction rate constants we must include the concentration of HCOOH and H₂O in the final rate constant calculations. In that situation, the results explain that the total effective rate constants for systems OH + CH₄ (+HCOOH) (~7 order) and OH + CH₄ (+H₂O) (2 order) are magnitudes smaller than the free situation. The total effective rate constants OH + CH₄ (+HCOOH) (~4 × 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K}) and OH + CH₄ (+H₂O) (~7 × 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K}) are smaller than OH + CH₄ (~6 × 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K}). Similar results were reported in an earlier study [13,25–28]. It is clear from geometries of PRCs and TSs, which are different in OH + CH₄ (+HCOOH) than reaction OH + CH₄(+H₂O) resulted in different computed enthalpies and rate constants. Because of that, the kinetics of OH + CH₄ (+HCOOH) are quite different from those OH + CH₄ (+H₂O) reaction systems. In the case of the FA, the rate constants show positive temperature dependence, and in the case of water, the rate constants show negative temperature dependence. This is due to water concentration varying greatly with temperature, whereas HCOOH concentration is nearly temperature independent.
In the case of FA-assisted reaction, the PRC_{FA} has the larger stability than that of PRC_{W}, which results in a larger equilibrium constant of CH\textsubscript{4} + HCOOH···HO (4 × 10\textsuperscript{-21} at 300 K) than CH\textsubscript{4} + H\textsubscript{2}O···HO (1 × 10\textsuperscript{-21} at 300 K). The barrier height for FA-assisted reaction is lower than water-assisted reaction results larger rate constants for FA-assisted reaction (3 × 10\textsuperscript{-11} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}) than water-assisted reaction (3.3 × 10\textsuperscript{-14} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}). However, the concentrations of the FA are much lower than H\textsubscript{2}O in the atmosphere, which then makes the rate constants smaller for FA case (4.2 × 10\textsuperscript{-22} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} 300 K) than water (7.6 × 10\textsuperscript{-17} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} at 300 K).

In general, the effective rate constants of the FA and water-assisted reaction is smaller than the ‘OH + CH\textsubscript{4} reaction system. As a result, the catalytic effect of FA/H\textsubscript{2}O on ‘OH + CH\textsubscript{4} reaction is of minor importance in gas-phase atmospheric reaction chemistry. This result is consistent with previously reported results on similar reaction system \[13,25–28\]. To understand the upper troposphere consequences of CH\textsubscript{4}, we have calculated the lifetime of CH\textsubscript{4} at 250 K at an altitude of \(\sim\)11 km. The averaged concentration of [ OH] \(\sim 1 \times 10^6\) molecule cm\textsuperscript{-3} and the rate constant (2 × 10\textsuperscript{-15} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} at 250 K) were used to calculate the lifetime of CH\textsubscript{4} as \(\tau = 1/[\text{[OH]} \times k]\). The calculated lifetime of CH\textsubscript{4} (16 years) is in good agreement with the value reported by Kulogoski et al. (16 years) [42].

As discussed in this study, the rate constants for the effect of FA and water are almost negligible as compared to the naked reaction. It is important to mention that the comparison of effective rate constant with naked reaction does not provide the complete picture for the degradation mechanism of CH\textsubscript{4}. Experimental measurement is required to validate the current study. Based on this study, we believe that the effect of FA and water on the formation of formaldehyde will even be slower. We believe the current finding provides better insights into the gas-phase catalytic activity of FA and water molecules on ‘OH + CH\textsubscript{4}.

4. Conclusions

The effect of FA and water molecules on ‘OH + CH\textsubscript{4} was explored. The potential energy surfaces for OH + CH\textsubscript{4}, CH\textsubscript{4} + H\textsubscript{2}O··· HCOOH, and CH\textsubscript{4} + H\textsubscript{2}O···H\textsubscript{2}O have been
explored using CC//M06-2X. The rate constants for these reactions were computed using CVT/SCT approach.

In the presence of FA, the two different channels of the hydrogen abstraction reaction were identified. In the case of the water reaction, only one reaction pathway was identified. Under the atmospheric condition, the kinetics of \( \text{OH} + \text{CH}_4 (+\text{HCOOH}) \) is quite different from those of \( \text{OH} + \text{CH}_4 (+\text{H}_2\text{O}) \). This difference is possibly due to the FA concentrations being much lower than \( \text{H}_2\text{O} \). Our results demonstrate that a FA and water molecule has the potential to catalyze the gas-phase reaction if the atmospheric concentration of these species is not included in the kinetic calculations. However, as suggested, the total effective rate constant must include the concentration of FA and water. In that situation, the total rate is constants for the effect of FA and water than the \( \text{OH} + \text{CH}_4 \) reaction is lower. The present study provides a comprehensive model of how the acidic nature of these catalysts affects the gas-phase reaction kinetics. The atmospheric degradation mechanism suggests that \( \text{CH}_3 \) can further react with \( \text{O}_2 \) molecules to form the formaldehyde under atmospheric and combustion conditions. The effect of FA and water molecules could be even slower in the formation of formaldehyde. These kinds of results are interesting and can be used to identify the effect of FA and water on higher chain alkane compounds.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12020133/s1, Figure S1: Three body complexes for the effect of FA/H\(_2\)O on OH + CH\(_4\) reaction; Figure S2: Free energy profiles for the CH\(_4\) + OH (___), CH\(_4\) + OH + H\(_2\)O (___) and CH\(_4\) + OH + HCOOH (___) reactions; Table S1: Optimized geometries of reactants, complexes, products and transition states obtained using M06-2X/6-311++G(3df,3pd); Table S2: Rotational -vibrational parameters obtained from vibrational analysis; Table S3: Electronic Energies (Eo), Zero-point correction (ZPE), Thermal Correction (ET), Thermal Correction to Enthalpy (HT), Free energy correction (G), Entropy (cal/mol-K) of all the species involved in the reactions; Table S4: Calculated CVT unimolecular rate constant (k\(_{\text{unimolec}}\) in s\(^{-1}\)) for the formation of two-body complex; Table S5: Calculated equilibrium constants (\( K_{\text{eq}} \) in cm\(^3\) molecule\(^{-1}\)) for the formation of three-body complex.

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**Data Availability Statement:** All data generated through this study are given in Supporting Information file.

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