A Shock Tube Kinetic Study on the Branching Ratio of Methanol + OH Reaction

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Abstract

Methanol (CH_3OH) is the simplest alcohol and is considered to be a future fuel, produced by solar-driven reduction of carbon dioxide. The reaction of methanol and hydroxyl radicals is important in both combustion and atmospheric systems because this reaction is the dominant consumption pathway for methanol oxidation. Hydrogen abstraction at the CH_3 or OH site of CH_3OH leads to different radical intermediates. The relative importance of these two channels is critical for combustion modeling as the subsequent chemistries of the product radicals (CH_3O and CH_2OH) are markedly different. In this work, we measured overall rate coefficients for the reaction of methanol (CH_3OH), methanol- d_3 (CD_3OH) and methanol- d_1 (CH_2DOH) with OH radicals over the temperature range of 900 – 1300 K and pressures near 1.3 atm by employing shock tube / UV laser absorption technique. Combining our results with literature data, we recommend following three-parameter Arrhenius expressions ($\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$):

$$k_1(\text{CH}_3\text{OH} + \text{OH}) = 3.25 \times 10^{-13} \left(\frac{T}{300 \text{ K}} \right)^{2.55} \exp \left(297.8 \frac{\text{K}}{T} \right) \quad 210 - 1344 \text{ K}$$

$$k_2(\text{CD}_3\text{OH} + \text{OH}) = 4.69 \times 10^{-13} \left(\frac{T}{300 \text{ K}} \right)^{2.24} \exp \left(-59.8 \frac{\text{K}}{T} \right) \quad 293 - 1287 \text{ K}$$

Using our measured total rate coefficients, we determined site-specific H-abstraction rate coefficients, and, hence, branching ratios of the two abstraction channels. Our results show that abstraction at the CH_3 site is the dominant channel, contributing more than 80% throughout our temperature range. Our calculated site-specific rate coefficients (per H atom) over 900 – 1300 K are given by ($\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$):

$$k_{1a}^H(\text{CH}_2\text{OH channel}) = 2.55 \times 10^{-11} \exp(-2287.1 \text{ K}/T)$$

$$k_{1b}(\text{CH}_3\text{O channel}) = 4.30 \times 10^{-11} \exp(-3463.2 \text{ K}/T)$$

Keywords: *Methanol; Hydroxyl radicals; Shock tube; Site-specific rates; Branching ratio.*

1. Introduction

In recent years, there have been growing concerns over global warming and diminishing petroleum reserves. These concerns have led to thrusts directed at shifting from conventional fuels to renewable alternatives with low greenhouse gas emission. Methanol and ethanol have received considerable attention in combustion community as alternative fuels and/or fuel additives [1-3]. These fuels look promising from the prospective of enhanced engine performance and low pollutant emissions. Methanol is the simplest alcohol which can be industrially produced from syngas ($\text{CO} + \text{H}_2$), biomass [4] and natural gas [5]. Both methanol and hydroxyl radicals appear as important intermediates during the combustion of hydrocarbons and oxygenated fuels. Methanol can act as a sink for CH_3 and OH radicals, and the subsequent chemistry of methanol leading to various products is of crucial importance for combustion modeling. Particularly, the reaction of methanol and OH radicals is important in both combustion and atmospheric systems because this reaction is the dominant pathway for methanol oxidation. Because of its significance, this reaction has been the subject of extensive experimental [6-17] and theoretical [17-20] investigations.

Hydroxyl initiated oxidation of methanol occurs by abstraction of a hydrogen atom at either the CH_3 (Reaction 1a) or the OH site (Reaction 1b).

The enthalpy of reaction (ΔH_{0K}°) values are taken from a recent theoretical work of Xu and Lin [20]. Both reactions (1a) and (1b) are not single step reactions, but occur by addition-elimination mechanism in an overall exothermic process, with activation barriers of 4.2 and 15.0 kJ mol^{-1} , respectively [20]. For both reactions, complexes are formed at the entrance as well as exit channels. However, the hydrogen-bonded complex, $\text{OH} \cdots \text{O}(\text{H})\text{CH}_3$, formed at the entrance channel is weakly bound ($\sim 20 \text{ kJ mol}^{-1}$), hence it will rapidly re-dissociate back to

reactants at high temperatures. As the hydrogen-bonded complex has no kinetic relevance at high temperatures, these reactions (1a and 1b) behave as single step processes, leading to products *via* well-defined transition states. The transition state for reaction (1a) lies about 11 kJ mol⁻¹ lower than that of reaction (1b). As a result, the CH₃O forming channel, reaction (1b), appears to be a minor channel as predicted by the *ab initio*/RRKM calculations of Xu and Lin [20]. Their calculated branching ratio, $\phi_{1b} = k_{1b}/(k_{1a} + k_{1b})$, is less than 10% over the entire temperature range (200 – 3000 K) of their work. At room temperature, their theoretical value for ϕ_{1b} is found to be somewhat lower than that determined experimentally ($\phi_{1b} = 0.1 - 0.25$) by several groups [9, 21, 22]. The branching ratio for CH₃O forming channel predicted by a recent master equation study of Shannon et al. [17] is somewhat large ($\phi_{1b} = 0.36$ at 298 K). Furthermore, Shannon et al. [17] reported that the channel (1b) becomes increasingly important below 250 K, and that it contributes almost exclusively ($\phi_{1b} = 0.99$) at 70 K due to quantum tunneling of the hydrogen-bonded complex that has relatively long-life time at low temperatures.

Although most previous works agree that methoxy (CH₃O) forming channel is minor at room temperature, yet the temperature dependence of the branching ratio is not well established. Hägele et al. [21] reported branching ratios (ϕ_{1b}) of 0.11 and 0.22 at 298 K and 393 K, respectively, and suggested that the contribution of channel (1b) increases to ~ 50% near 780 K. Along the same line, Dóbbé et al. [16] reported methoxy yield of 0.1 and 0.3 at 298 and 600 K, respectively, and predicted that the formation of CH₃O dominates over 1000 K. In another work, Hess and Tully [11] reported that channel (1b) remains inactive at room temperature, but estimated that both channels become equally important near 880 K. The authors observed a sharp decrease in the ratio of the rate coefficients of OH + CH₃OH reaction and OH + CD₃OH reaction above 625 K. They attributed this unusual behavior to the increasing relative importance of channel (1b) at high temperatures. [In a very recent work, Olm et al. \[23\]](#)

optimized methanol combustion mechanism and found that their optimization favored strong temperature dependence of the branching ratios with methoxy channel (1b) emerging dominant at higher temperatures ($T \geq 1300$ K). In contrast, recent theoretical works by Xu and Lin [20] and Jodkowski et al. [19] predict that the branching ratios virtually remains constant with temperature, and that the methoxy channel (1b) does not contribute more than ~10% to the total rate coefficients even at 3000 K. In the same spirit, Gao et al.[24] very recently showed through *ab initio*/competitive canonical unified statistical (CCUS) model that reaction (1a) is dominant, and the branching ratios change much less with temperatures above 500 K. However, unlike earlier theoretical results [19, 20], their prediction of branching fraction for methoxy channel (1b) is as high as 30% at high temperatures. These theoretical results thus do not support the earlier speculations about the increasing relative importance of channel (1b) at high temperatures.

As for the total rate coefficients ($k_1 = k_{1a} + k_{1b}$) of methanol + OH reaction, most of the previous low-temperatures studies [9-11, 14, 17, 21, 25, 26] concur well with the recommended value of $9.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [27] at 298 K. However, large discrepancies were observed among experimental [8, 9, 11-13, 15] and theoretical results [18-20] at high temperatures. While *ab initio*/RRKM calculations of Xu and Lin [20] agree reasonably well with Tsang's BEBO (bond-energy bond order) calculations [18], their values are lower by a factor of 2 as compared to Jodkowski et al. [19] theoretical results above 1000 K. A recent shock tube / laser absorption study of Zaczek et al. [13] ($T = 961 - 1231$ K and $P = 1.18 - 1.48$ atm) showed excellent agreement with the results of Vandooren and Van Tiggelen [8], and also with the calculated values of Xu and Lin [20] and Tsang [18]. Moreover, these high-temperature experimental data showed a smooth transition in a non-linear Arrhenius plot with low-temperature data of Hess and Tully [11] ($T = 293 - 866$ K and $P = 700$ Torr). However, Zaczek et al. [13] shock tube data were found to be 40% higher than the single data point of Bott and

Cohen [12] near 1200 K. The data of Vandooren and Van Tiggelen [8] and the extrapolation of Zaczek et al. [13] lie roughly 60% higher than the shock tube / OH multi-pass absorption data ($T = 1591 - 1710$ K) of Srinivasan et al. [15]. The results of indirect determination of Bowman [6], Westbrook and Dryer [7] and high-temperature data obtained by Meier et al. [9] ($T = 300 - 1000$ K) using discharge flow / LIF technique are inconsistent with the existing high-temperature data from other groups [7, 8, 13, 18-20, 28]. These discrepancies clearly warrant an additional kinetic study at high temperatures for this very important reaction.

Due to the importance of the branching ratio of methanol + OH for combustion modeling and due to the discrepancies at high temperatures in previous works, we aim to investigate the branching ratios for reactions (1a) and (1b) by providing new high-temperature experimental data for the reaction of OH with methanol (Reaction 1) and deuterated methanol (Reactions 2 and 3) using shock tube / laser absorption technique.

2. Experimental Method

All experiments were carried out behind reflected shock waves over the temperature range of 900 – 1300 K and pressures near 1.3 atm using the low-pressure shock tube (LPST) facility at King Abdullah University of Science and Technology (KAUST). As the details are provided in our earlier works [29, 30], we describe the facility very briefly here. This is a stainless-steel tube that has an inner diameter of 14.2 cm, a 9 m long driven section and a variable length

driver section. In this work, we used 3 m long driver section to achieve a test time of ~ 1.5 ms behind reflected shock wave. We used polycarbonate diaphragms of thickness 5 mm to divide the driven section from the driver section and to achieve reflected shock pressures of ~ 1.5 atm. We employed a series of five PCB 113B26 piezoelectric pressure transducers placed in the last 1.3 m of the driven section to measure the incident shock speed. We calculated temperatures and pressures behind reflected shock waves by using measured incident shock speed, initial temperature/pressure and by employing shock-jump relations [31] embedded in the Frosh code [32].

Hydroxyl radicals were generated *via* fast thermal decomposition of *tert*-butyl hydroperoxide (TBHP) which is known to be a clean source of OH radicals [33]. We generated a UV light beam near 307 nm by the external frequency doubling of red light (614 nm) produced by a ring-dye cw laser, which was pumped by an Nd:YAG laser at 532 nm. In the current work, the UV light was tuned to the center (306.6868 nm) of the well-characterized R1(5) absorption line in the (0, 0) absorption band of $A^2\Sigma^+ \leftarrow X^2\Pi$ electronic system of OH. We used two quartz optical windows at 2 cm away from the end wall to guide the UV light through the shock tube for OH detection. We employed two modified Thorlab PDA36-EC photodetectors (spectral range 305 -1100 nm) to measure the laser intensity before and after the shock tube. The noise of the laser beam after common-mode-rejection was less than 0.1% of the signal. Using Beer-Lambert law, absorbance (A) = $\ln(I_0/I) = X_{OH}k_{OH}PL$, we quantitatively converted laser intensity time-profile into OH mole fraction (X_{OH}) time-profile. Here, I and I_0 are the transmitted and incident laser intensities, k_{OH} ($\text{atm}^{-1}\text{cm}^{-1}$) is the OH absorption coefficient at 306.68 nm, P is the total pressure, and L is the optical path-length (14.2 cm).

The chemicals used were: 70% solution of TBHP in water from Sigma Aldrich, argon and helium (Linde Company, 99.999%), methanol (99.9%), methanol-d3 (CD_3OH , 99.8% D) from Sigma Aldrich, and methanol-d1 (CH_2DOH , 98% D) from Cambridge Isotope

Laboratories (CIL). The concentrations of methanol and TBHP were chosen such that OH decay follows pseudo-first-order behavior. Gas mixtures were prepared manometrically in a 24-l Teflon-coated stainless-steel vessel, equipped with a magnetically-driven stirrer, and left for at least two hours for homogeneity. Prior to gas mixture preparation, we turbo-pumped the mixing tank down to $<10^{-5}$ Torr. We measured the partial pressures of methanol and TBHP accurately using 0 – 20 Torr MKS Baratron pressure gauge.

3. Results and Discussion

3.1 Measurements of overall rate coefficients

Overall rate coefficients for the hydrogen abstraction reaction of methanol and deuterated methanol by OH radicals were measured by conducting shock tube experiments for post-reflected-shock temperatures of 900 – 1300 K and pressures ~ 1.3 atm. In our experiments, test gas mixtures containing ~ 500 ppm of methanol (CH_3OH , CD_3OH or CH_2DOH) and 20 – 40 ppm of TBHP in argon were shock-heated to generate OH radicals that reacted with methanol by following pseudo-first-order kinetics. To account for the role of secondary chemistry, a detailed kinetic model was used to iteratively fit the experimentally measured OH time-profiles while treating the rate coefficient of target reaction ($\text{methanol} + \text{OH} \rightarrow \text{products}$) as a variable. Our kinetic model consisted of the base mechanism of Sarathy et al. [34] and TBHP sub-mechanism of Pang et al. [35]. Chemkin Pro [36] was used to perform [constant internal energy and volume constrains \(constant UV\)](#) zero-dimensional kinetic simulations. Representative measured OH time-history and simulated profiles are shown in Fig. 1. The best-fit simulated profile resulted in a rate coefficient of $k_1 = 1.33 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (1) at 1159 K and 1.37 atm. Hydroxyl decay obeyed first order kinetics, as illustrated by the exponential decrease of OH concentration (see inset of Fig. 1). It should be noted that experiments carried

out with two different mixtures, 20 or 40 ppm TBHP with 500 ppm methanol, gave very similar rate measurements.

Figure 1. Hydroxyl time-history for $\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{products}$ at 1159 K and 1.37 atm. Mixture composition: 500 ppm methanol and 39 ppm TBHP (~ 91 ppm H_2O) diluted in argon.

The reliability of k_1 was assessed by observing the effect of $\pm 50\%$ perturbation in the best-fit k_1 during kinetic modelling. These perturbations are also plotted in Fig. 1 and show strong sensitivity of OH mole fraction to k_1 . Furthermore, sensitivity analyses were performed for a range of conditions to study the influence of secondary reactions. A representative hydroxyl sensitivity analysis is shown in Fig. 2. As expected, the secondary chemistries have negligible effect on hydroxyl time-history over the time window of our experiments. Only the target reaction is found to be the most sensitive reaction towards OH decay. However, at late reaction times, $\text{CH}_3 + \text{OH} = \text{CH}_2\text{OH} + \text{H}$ becomes increasingly important. The rate coefficient of this reaction is quite well established in the literature and we use the mechanism-fitting methodology, as opposed to pseudo-first-order analysis, to account for small contributions of secondary chemistry. Furthermore, we varied the branching ratio ($\phi_{1b} = k_{1b}/k_1 \sim 0.1$ to 0.5) by a factor of 5, and found negligible influence on the extracted value of k_1 .

Figure 2. Hydroxyl sensitivity analysis for $\text{CH}_3\text{OH} + \text{OH}$ reaction at 1159 K and 1.37 atm. The OH sensitivity is defined as $S_{\text{OH}} = (\partial X_{\text{OH}} / \partial k_i) \times (k_i / X_{\text{OH}})$, where k_i is the rate coefficients of the i^{th} reaction and X_{OH} is the local OH mole fraction.

Detailed uncertainty analysis was performed at a representative condition of 1159 K and 1.37 atm. Root-mean-square method was used to calculate the overall uncertainty. The overall uncertainty (2σ) was estimated to be $\pm 17\%$ that transpired from various sources of errors, such as temperature ($\pm 0.7\%$), determination of time zero ($\pm 0.5 \mu\text{s}$), gas composition ($\pm 5\%$), OH absorption coefficient ($\pm 3\%$), detection wavelength ($\pm 0.002 \text{ cm}^{-1}$), fitting the measured OH profile ($\pm 5\%$), and the accuracy of the rate coefficients of secondary reactions. Our reported values of all rate coefficients have roughly the same estimated uncertainty of $\sim \pm 20\%$.

Following a similar methodology to that described for methanol + OH rate measurements, overall rate coefficients were measured for $\text{CD}_3\text{OH} + \text{OH}$ (Reaction 2) and $\text{CH}_2\text{DOH} + \text{OH}$ (Reaction 3). For each molecule, experiments were conducted with two separate mixtures and these produced very similar rate coefficient results.

Our experimentally measured rate coefficients for the reaction of OH with methanol, methanol- d_1 and methanol- d_3 , along with the experimental conditions, are compiled in Table S1 (Supplementary Material) and plotted in Fig. 3. As expected, replacement of H atoms with D atoms lowers the rate coefficients, thereby making methanol- d_1 to have intermediate reactivity between methanol and methanol- d_3 .

Figure 3. Measured rate coefficients for reaction of OH with three methanol molecules. Symbols indicate experimental data and solid lines represent two-parameter Arrhenius fit to the data.

Our measured overall rate coefficients for $k_1 = k_{1a} + k_{1b}$, and $k_2 = k_{2a} + k_{2b}$ are compared with literature data in Fig. 4. For the sake of clarity, only some selective data from literature are plotted. As can be seen, our rate data for methanol + OH (k_1) show excellent agreement with the most recent shock tube data of Zaczek et al [13]. Our measurements for k_1 and k_2 provide smooth transition from the low-temperature data of Hess and Tully data [11], resulting into non-linear Arrhenius behavior over the wide temperature range. Moreover, our data compliment the earlier determination of k_1 by Vandooren and Van Tiggelen [8], Xu and Lin [20] and Tsang [18] (not shown in Fig. 4) for the overlapping temperature region. The data reported by Srinivasan et al. [15] at higher temperatures are roughly 2 times slower than our extrapolated values. The single-point rate reported by Bott and Cohen [12] at 1205 K for k_1 is roughly 2 times slower than ours, whereas the *ab initio* results of Jodkowski et al. [19] overestimate our data by at least 30%. As discussed earlier, high-temperature data of Bowman [6], Westbrook and Dryer [7] and Meier et al. [9] are too slow and remain inconsistent with other literature data including our results.

Figure 4. Arrhenius plots for the total rate coefficients (k_1 and k_2) of methanol + OH and methanol_d3 + OH. Some selected data from earlier studies are also shown for comparison. Solid lines represent the recommended 3-parameter Arrhenius expression from this work.

At 1000 K, the rate coefficient for $\text{CH}_3\text{OH} + \text{OH}$ reaction is found to be $\sim 1 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$. This value is about 5 times faster than that of $\text{CH}_3\text{OH} + \text{H}$ ($\sim 1.9 \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$) and several orders of magnitude faster than $\text{CH}_3\text{OH} + \text{CH}_3$ reaction ($\sim 2.4 \times 10^{-14} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$) [19]. Hydrogen abstraction of methanol by OH radicals is both kinetically and thermodynamically more favorable than that of the abstraction by other combustion radicals, e.g., H and CH_3 (see the potential energy surfaces in ref. [19]). Therefore, the reaction $\text{CH}_3\text{OH} + \text{OH}$ clearly appears to be the dominant oxidation pathway for CH_3OH under combustion conditions.

The rate coefficients of $\text{CH}_3\text{OH} + \text{OH}$ reaction exhibited strong temperature dependence / strong curvature in the Arrhenius plot (see Fig. 4). Because the barrier heights for both reactions (1a) and (1b) are small, 4.2 and 15.0 kJ/mol, respectively [20], and reaction (1b) is expected to have a small contribution to the overall $\text{CH}_3\text{OH} + \text{OH}$ reaction (see our results for branching ratios below), this non-linear Arrhenius behavior appears to be the effect of entropic contribution (A factor). For the bimolecular reactions like methanol + OH, the pre-exponential factor (A) depends on $\sqrt{T^{-3}}$ at low temperatures, whereas at high temperatures, $A \propto \sqrt{T^5}$, thereby causing severe curvature in the Arrhenius plot.

Combining the high-temperature data from this work and Zaczek et al. [13] with the low-temperature data from Hess and Tully [11], Dillon et al. [14] and Jiménez et al.[25], the following three-parameter Arrhenius expression, Eq. (1), is recommended for k_1 over a wide temperature range of 210 – 1344 K. Similarly for k_2 ($\text{CD}_3\text{OH} + \text{OH}$), our high-temperature data are combined with low-temperature data of Hess and Tully[11], Greenhill and O’Grady [10] and MacCaulley et al. [22] to get the three-parameter Arrhenius expression, Eq. (2), over the temperature range of 293 – 1287 K. As shown in Fig. 4, Eqs. (1) and (2) reproduce the experimental data remarkably in the entire temperature range with an average deviation of 7% for k_1 and 13% for k_2 .

$$k_1(T) = 3.25 \times 10^{-13} \left(\frac{T}{300 \text{ K}} \right)^{2.55} \exp \left(297.8 \frac{\text{K}}{T} \right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (210 - 1344 \text{ K}) \quad (1)$$

$$k_2(T) = 4.69 \times 10^{-13} \left(\frac{T}{300 \text{ K}} \right)^{2.24} \exp \left(-59.8 \frac{\text{K}}{T} \right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (293 - 1287 \text{ K}) \quad (2)$$

Comparing k_1 and k_2 , it is found that the isotopic substitution at the methyl site inhibits the reactivity of methanol causing a significant drop in the rate coefficients. Unlike the reports of Hess and Tully [11] who observed a sharp fall from the linear trend of $\log(k_1/k_2)$ vs $1/T$ plot beyond 625 K, similar plot from our recommended values for k_1 and k_2 does not show sign of such a break at high temperatures. Instead, the plot of k_1/k_2 varied exponentially with $1/T$, as is usually seen for the deuterated kinetic isotopic effect (DKIE) for hydrogen abstraction reaction of $\text{RH} + \text{OH} \rightarrow \text{R} + \text{H}_2\text{O}$ reactions. Furthermore, the DKIE (k_1/k_2) for $\text{CH}_3\text{OH} + \text{OH}$ shows a weak temperature dependence as compared to $\text{C}_2\text{H}_6 + \text{OH}$ reaction (see Fig. S1 of Supplementary Material). This can be understood by the difference of their corresponding activation barriers which are 4.2 kJ/mol [20] for $\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}$ (major channel) and 9.3 kJ/mol [37] for $\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O}$. For hydrogen abstraction reactions, a stronger C-H bond displays much steeper temperature dependence of DKIE (k_1/k_2) than a weaker C-H bond [30, 38]. As in our earlier work for ethane + OH reaction system [37],

the DKIE (k_1/k_2) for methanol + OH is found to asymptote to a value of ~ 1.4 at high temperatures (see Fig. S1). Arguably, these findings may lead to a conclusion that the hydrogen abstraction reaction of methanol + OH dominates at the methyl site even at the high temperatures of our experiments.

3.2 Site-specific rate coefficients and branching ratios

The overall rate constant for methanol + OH reaction can be expressed as the sum of site-specific rate coefficients. This can be done because i) the reaction of methanol and OH is a single step reaction at high temperatures, as discussed in the Introduction section, ii) the isotopic substitution in a chemical environment does not affect the reaction kinetics at a neighboring site [11]. Therefore, the total rate coefficients measured in this work can be partitioned into site-specific rates as follows:

$$k_1 = k_{1b} + 3 \times k_{1a}^H = 1.23 \times 10^{-10} \exp\left(-2573.4 \frac{K}{T}\right) \quad (919 - 1344 \text{ K}) \quad (3)$$

$$k_2 = k_{1b} + 3 \times k_{1a}^D = 7.08 \times 10^{-11} \exp\left(-2351.6 \frac{K}{T}\right) \quad (879 - 1327 \text{ K}) \quad (4)$$

$$k_3 = k_{1b} + 2 \times k_{1a}^H + k_{1a}^D = 9.76 \times 10^{-11} \exp\left(-2452.4 \frac{K}{T}\right) \quad (933 - 1260 \text{ K}) \quad (5)$$

where k_1 , k_2 , and k_3 are the total rate coefficients for the reaction of OH radicals with methanol, methanol-d₃, and methanol-d₁. For simplicity, the superscripts H or D are used to identify the type of atom undergoing abstraction reaction, whereas the subscripts a and b refer to the abstraction at the methyl and hydroxyl sites, respectively. Here, we have three unknowns (k_{1a}^H , k_{1a}^D and k_{1b}) and three equations, but only two of these equations are independent. For the third needed equation to solve the system, we used the theoretical results of Xu and Lin [20] as reference values to construct an optimization scheme. As initial input, we chose the results of Xu and Lin [20] because their theory predicts the high-temperature data remarkably and their

branching ratios have been used in AramcoMech 2.0 and Sarathy et al. [34] recent kinetic models for methanol oxidation. An optimization method is adopted here to extract the three unknowns (k_{1a}^H , k_{1a}^D and k_{1b}). The genetic algorithm function (Ga) embedded in Matlab was used to minimize the differences between measured rate coefficients and calculated rate coefficients from the derived site-specific values. We varied the input values of k_{1a}^H/k_{1b} and confirmed that our final results were not sensitive to the initial values. Our results are plotted in Fig. 5, and expressed in the following Arrhenius equations ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$k_{1b} = 4.30 \times 10^{-11} \exp\left(-3463.2 \frac{K}{T}\right) \quad (900 - 1300 \text{ K}) \quad (6)$$

$$k_{1a}^H = 2.55 \times 10^{-11} \exp\left(-2287.1 \frac{K}{T}\right) \quad (900 - 1300 \text{ K}) \quad (7)$$

$$k_{1a}^D = 1.91 \times 10^{-11} \exp\left(-2336.6 \frac{K}{T}\right) \quad (900 - 1300 \text{ K}) \quad (8)$$

Figure 5. Site-specific (per H or D atom) rate coefficients for abstraction from methanol.

Figure 5 compares our site-specific abstraction rate coefficients (per H or D atom) with theoretical results of Xu and Lin [20] and Jodkowski et al. [19], wherever applicable. Not surprisingly, our results show that k_{1a}^D is slower than k_{1a}^H . As expected, hydrogen abstraction

from the hydroxyl site (k_{1b}) shows stronger temperature dependence, reflecting higher activation barrier than that of abstraction from the CH_3 site (k_{1a}^H). Abstraction from the methyl site (k_{1a}^H) is found to be at least 1.7 times faster than k_{1b} under our experimental conditions. Our values for k_{1a}^H match excellently with those of Xu and Lin [20], but their values for k_{1b} are lower than our results by a factor of ~ 2.7 . On the other hand, Jodkowski et al. [19] predict k_{1a}^H to be about a factor of 2 larger than our results, but their k_{1b} prediction is only $\sim 30\%$ slower than our values.

Figure 6 displays the branching ratios determined in this work, and compares with theoretical branching ratios of Xu and Lin [20], Jodkowski et al. [19] and Gao et al.[24]. Interestingly, although two of the theoretical works [19, 20] differ in their site-specific abstraction rate coefficients (see Fig. 5), both predict identical branching ratios for the two channels of methanol + OH reaction. Our experimental results agree with these theoretical predictions to the extent that hydrogen abstraction of methanol at the methyl site i.e. channel (1a) is the dominant channel over the entire temperature range of our study. For example, both Xu and Lin [20] and Jodkowski et al. [19] predict the branching fraction for methoxy channel (1b) to be less than 10% even up to 3000 K; whereas Gao et al. [24] predicts a branching fraction for this channel as high as 30% at high temperatures (see Fig. 6). Our experimental results suggest that branching fraction for the channel (1b) reaches $\sim 20\%$ at 1300 K, and this channel may become increasingly important at higher temperatures as seen by the slopes of our branching ratios in Fig. 6. We further carried out additional experiments by investigating the reactions of CH_3OD and CD_3OD with OH radicals. Our aim was to discern the effect of deuteration at the hydroxyl site and hence to verify the relative importance of channel (1b). We found that our measured rate coefficients for the hydrogen abstraction from CH_3OD and CD_3OD by OH radicals were found to be non-statistically significant as compared to the reactions of OH with CH_3OH and CD_3OH , respectively (see Fig. S2 and Table S2 in the

Supplementary Materials). That being said, deuteration of the hydroxyl group had no discernible effect on the measured rate coefficients. In contrast, deuteration of the methyl group greatly caused the kinetic isotopic effect by suppressing the rate coefficients. From these results, one can unarguably conclude that hydrogen abstraction of CH₃OH by OH radical predominantly happens at the –CH₃ site even at high temperatures though there is a little scatter in the values for the temperature dependence of the branching fraction. Current findings of the branching ratios, however, do not support the earlier predictions of Dóbé et al. [16], Hägele et al. [21] and Hess and Tully et al. [11] that hydrogen abstraction of methanol at the hydroxyl site contributes > 50% at temperatures higher than about 1000 K.

Figure 6. Branching ratios for H-abstraction at the hydroxyl site (k_{1b}) and the CH₃ site (k_{1a}) of methanol.

4. Conclusions

This work presents the first experimental determination of the branching ratios for the hydrogen abstraction reaction of methanol by OH radicals. We conducted shock tube experiments to measure the total rate coefficients for the reaction of hydroxyl with CH₃OH, CD₃OH and CH₂DOH over 900 – 1300 K. These measurements allowed us to elucidate the branching ratios of CH₃OH + OH reaction. We found that hydrogen abstraction of methanol at the CH₃ site is dominant and contributes over 80% in the entire temperature range of our study. Our result

further showed that hydrogen abstraction at the hydroxyl site becomes increasingly important at high temperatures. The results of this work will be very important for improving the prediction of methanol oxidation mechanisms.

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List of figure captions

Figure 1. Hydroxyl time-history for $\text{CH}_3\text{OH} + \text{OH} \rightarrow$ products at 1159 K and 1.37 atm. Mixture composition: 500 ppm methanol and 39 ppm TBHP (~ 91 ppm H_2O) diluted in argon.

Figure 2. Hydroxyl sensitivity analysis for $\text{CH}_3\text{OH} + \text{OH}$ reaction at 1159 K and 1.37 atm. The OH sensitivity is defined as $S_{\text{OH}} = (\partial X_{\text{OH}} / \partial k_i) \times (k_i / X_{\text{OH}})$, where k_i is the rate coefficients of the i th reaction and X_{OH} is the local OH mole fraction.

Figure 3. Measured rate coefficients for the three methanol molecules and OH. Symbols indicate experimental data and solid lines represent two-parameter Arrhenius fit to the data.

Figure 4. Arrhenius plots for the total rate coefficients (k_1 and k_2) of methanol + OH and methanol-d3 + OH. Some selected data from earlier studies are also shown for comparison. Solid lines represent the recommended 3-parameter Arrhenius expression from this work.

Figure 5. Site-specific (per H or D atom) rate coefficients for abstraction from methanol.

Figure 6. Branching ratios for H-abstraction at the hydroxyl site (k_{1b}) and the CH_3 site (k_{1a}) of methanol.

485 **List of supplementary file:**

486 **Supplementary Material I:**

487 **Table S1:** Determined rate coefficients for the reaction of methanol+OH with corresponding
488 pressure and temperature. All bath gas argon.

489 **Table S2:** Determined rate coefficients for the reaction of methanol_OD and OH with
490 corresponding pressure and temperature. Bath gas is argon.

491 **Figure S1.** Temperature dependence of DKIE (k_H/k_D) for the reaction of methanol and ethane
492 with OH radicals. The steeper DKIE of ethane + OH reaction reflects that the barrier height
493 for the abstraction of hydrogen atom from ethane by OH radicals is higher than that of
494 methanol + OH reaction. DKIE for both reaction appear to asymptote to a value of ~1.4.

495 **Figure S2.** Measured rate coefficients for reaction of OH with five methanol molecules.
496 Symbols indicate experimental data and solid lines represent two-parameter Arrhenius fit to the
497 data.
498