High temperature measurements for the rate constants of C₁-C₄ aldehydes with OH in a shock tube

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Abstract The overall rate constants for the reactions of hydroxyl radicals (OH) with a series of aldehydes, formaldehyde (CH₂O), acetaldehyde (CH₃CHO), propionaldehyde (C₂H₅CHO) and n-butyraldehyde (n-C₃H₇CHO), were studied behind reflected shock waves at temperatures of 950 - 1400 K and pressures of 1 - 2 atm. OH radicals were produced by rapid thermal decomposition of tert-butyl hydroperoxide (TBHP), and OH time-histories were monitored by narrow-linewidth UV laser absorption of the well-characterized R₁(5) line in the OH A-X (0, 0) band near 306.69 nm. The overall rate constants were inferred by fitting simulated OH profiles to the measured OH time histories using detailed mechanisms of Veloo et al. (2013), USC Mech-II (2007) and GRI Mech 3.0. The measured high-temperature aldehydes + OH rate constants can be expressed in modified Arrhenius equations, in units of cm³mol⁻¹s⁻¹ and K, as

$$k_{\text{CH}_2\text{O}} = 1.02 \times 10^7 T^{1.92} \exp(779/T) \pm 13\%$$

$$k_{\text{CH}_3\text{CHO}} = 4.32 \times 10^6 T^{2.02} \exp(716K/T) \pm 22\%$$

$$k_{\text{C}_2\text{H}_5\text{CHO}} = 5.94 \times 10^6 T^{1.98} \exp(823K/T) \pm 27\%$$

$$k_{\text{nC}_3\text{H}_7\text{CHO}} = 5.36 \times 10^6 T^{2.06} \exp(658K/T) \pm 25\%$$

No pressure dependence was observed in these measurements. The measured rate constant for the formaldehyde + OH reaction is consistent with previous experimental work from Vasudevan et al. (2005) within +/-25%. For C₂-C₄ aldehydes + OH, this study provides the first direct rate constant measurement at high temperatures. More general rate constant expressions covering a much wider temperature range (200 - 1400 K) were also determined by combining current measurements with existing low temperature data in the literature. These wide-range expressions were seen to be in excellent agreement with most existing experimental data.

Keywords aldehydes; OH; rate constant; high temperature; shock tube

1. Introduction

Oxygenated fuels are receiving increasing attention in combustion studies. They are attractive for their potential as either neat fuels or fuel additives in engines to enhance combustion and to reduce CO and soot formation [1-3], but their combustion has been linked to an increase in the toxic emissions of aldehydes [4]. To address the need to quantitatively predict emissions from combustors, extensive chemical kinetic reaction models for the oxidation of these fuels have been developed [5-7]. With the kinetic modeling of oxygenated fuels beginning to mature, it is pertinent to revisit the kinetics of aldehydes, particularly the larger molecular weight aldehydes, where less is known.

Of particular interest is the H-abstraction reaction of aldehydes by hydroxyl radicals (OH), which is the primary aldehydes removal pathway during combustion. For formaldehyde (CH_2O), this reaction has been relatively well studied at high temperatures. Vasudevan et al. [8] inferred the rate constant over 934 - 1670 K in shock tube experiments by monitoring OH concentration time-histories. D'Anna et al. [9] performed quantum chemical calculations for the rate constant. However, despite the richness of experimental studies and theoretical calculations, there is still large scatter in the existing data. For C_2 - C_4 aldehydes + OH, previous research has focused on the low temperature region (202 - 517 K) [10 - 19]. Experimental studies at combustion temperatures, however, are sparse. Taylor et al. [20] measured the rate constant of $\text{CH}_3\text{CHO} + \text{OH}$ by pulsed laser photolysis and LIF over 297 - 860 K, and Veloo et al. [21, 22] studied the oxidation of $\text{C}_2\text{H}_5\text{CHO}$ and $n\text{-C}_3\text{H}_7\text{CHO}$ in a jet reactor and flames. Yet no direct high temperature rate constant measurements for C_2 - C_4 aldehydes + OH have been reported, which motivates current research.

Based on the aforementioned considerations, the current study is targeted at overall rate constants of the following reactions at $T > 1000$ K:

with the goal of providing the first set of high temperature rate constant data for C_2 - C_4 aldehydes + OH and complementing the low temperature data found in previous studies.

2. Experimental Setup

By pyrolyzing TBHP/aldehyde mixtures behind reflected shock waves, the current study yields accurate rate constant values from OH concentration time-histories monitored by laser absorption. Experimental details are elaborated in the following three sections.

2.1. Shock Tube

Experiments were carried out in a 14.13-cm diameter high-purity shock tube at Stanford. The shock tube has a driven section of 8.5 m, and a driver section of 3.3 m, allowing for steady test time of more than 2 ms at standard test conditions. Measurement are taken behind the reflected shock waves, where the gas temperatures and pressures were determined from the incident shock speed at the endwall location, using ideal shock relations. The uncertainties in temperatures and pressures (less than $\pm 1\%$) were mainly due to uncertainties in the measured shock velocities ($\pm 0.2\%$). The incident shock velocities were calculated from the time intervals between the arrivals of incident shock waves at 5 PCB piezoelectric pressure transducers located on the sidewall over the last 1.5 m of the shock tube, and then linearly extrapolated to the endwall location. A pair of fused silica windows, located 2 cm from the endwall, enabled optical access for the OH laser absorption diagnostic.

2.2. Laser absorption diagnostic for OH

The concentration of OH radical was monitored using UV laser absorption near 306.69nm, targeting the $R_1(5)$ transition in the OH A-X (0,0) band. This strong and isolated transition had been well-characterized by Herbon et al. [23], and successfully used in many previous OH studies [24, 25]. To access this UV transition, a Spectra-Physics 380A tunable ring dye laser was used. Inside the laser cavity, a rhodamine 6G dye jet was excited by the CW output of a 5W Coherent Verdi pump laser at 532 nm, creating visible laser light at 613.4 nm; the visible light was then intra-cavity frequency-doubled by a temperature-tuned AD*A crystal to generate about 1mW of UV light at 306.69 nm. Laser light was captured with Thorlabs PDA36A detectors (bandwidth = 1MHz, active area = 3.6 x 3.6 mm). Due to the intrinsic jittering of the dye jet, the laser output power had rapid fluctuations (up to about 10% peak-to-peak changes), but the wavelength remained stable. A common-mode-rejection scheme was used to remove these fluctuations in the detected laser signal, allowing a minimum absorption of 0.1% to be measured. This was equivalent to 0.3 ppm OH at typical shock conditions of 1200 K and 2 atm. The OH species concentration was calculated from the Beer-Lambert law, $I / I_0 = \exp(-k_{OH}X_{OH}PL)$, where I and I_0 were the transmitted and incident laser intensities, respectively, k_{OH} the OH absorption constant, P the total gas pressure, L the

diameter of the shock tube (14.13 cm), and X_{OH} the OH mole fraction to be determined. The overall uncertainty in the measured OH mole fraction was estimated to be less than $\pm 5\%$, mainly governed by the uncertainty in k_{OH} . Measurements were also conducted to verify that there was no significant interference absorption or emission by repeating the experiments with the laser tuned off the OH transition and with the laser beam blocked. All data were sampled at 2 MHz and recorded with a 14-bit National Instrument digital data acquisition system.

2.3. OH source and gas mixture preparation

Tert-butyl hydroperoxide (TBHP) was used as the OH precursor. Upon shock-heating at temperatures above 1000 K and atmospheric pressure, TBHP decomposed almost instantaneously (less than 1 μ s) into OH, CH_3 and acetone. On the other hand, as a result of the relatively low gas temperature (< 900 K) and pressure (< 0.5 atm), the decomposition of TBHP is generally negligible during the short time interval between the incident and the reflected shock waves. Gas-phase TBHP, vaporized from a 70% TBHP/water solution, was mixed with aldehyde (or precursor) vapor, and diluted in argon for use as test gas in the shock tube experiments. Gas mixtures were prepared manometrically in a 14-L stainless steel mixing tank, which was pre-heated to 50 $^{\circ}C$ to prevent wall condensation. The mixing tank was also equipped with a magnetic stirrer, which ensured mixture homogeneity and accelerated mixing. To allow for more accurate control of the mixture compositions, a double-dilution method was employed [24]. A highly concentrated mixture was first prepared and mixed for at least 2 hours, and the mixture was then further diluted with argon and mixed for an additional 2 hours prior to the experiments. To confirm the composition of the test mixtures, small portions of the mixtures were sampled from the endwall location of the shock tube, and analyzed external to the shock tube in a 29.9 m Herriott type multi-pass cell using DFG laser absorption. Fuel concentrations were calculated using the aldehydes cross-sections obtained from the PNNL database [26]. Measured mixture compositions were consistent for various fuel concentrations, and agreed within $\pm 5\%$ from expected values of the manometrical preparation.

The aldehyde liquids used in the experiments were: acetaldehyde (ACS reagent, $>99.5\%$ purity), propionaldehyde (reagent grade, $>97\%$ purity), and n-butyraldehyde ($>99.7\%$ purity), all supplied by Sigma Aldrich. Pure formaldehyde was not commercially available. Instead, 1,3,5-Trioxane ($> 99\%$ purity), also supplied by Sigma Aldrich, was used as a neat CH_2O precursor at $T > 900K$. More details about the chemistry of 1,3,5-trioxane can be found in Wang et al. [27]. Prior to the mixture preparation, these chemicals were purified using a freeze-pump-thaw procedure to remove dissolved air. The bath gas argon utilized in this study ($> 99.999\%$ purity), was supplied by Praxair and used without further purification. Between

experiments, the shock tube and mixing assembly were routinely evacuated with a turbo-molecular pump to $\sim 6 \mu$ torr to prevent contamination of the test mixture from any residual impurity inside the shock tube; the subsequent leak-plus-outgassing rate was negligible.

3. Kinetic Measurements

Reaction rate constants of OH + aldehydes were determined from OH concentration time-histories. By designing experiments with aldehydes in excess of the TBHP, the measured OH concentration time-history decayed exponentially in time, and a pseudo-first order kinetic analysis could be used to determine the rate constant. A simple exponential fitting, however, would neglect secondary reactions, which in total may contribute up to about 18% of the OH decay rate under the experimental conditions of the current study, especially at low TBHP to aldehydes ratios. Hence, for more accurate rate constant determinations, detailed reaction mechanisms were used to account for secondary reactions. USC-Mech II [28] and GRI-Mech 3.0 [29] were chosen as the base mechanism for studies of CH_2O and CH_3CHO , and recent kinetics models from Veloo et al. [21, 22] were used for $\text{C}_2\text{H}_5\text{CHO}$ and $\text{n-C}_3\text{H}_7\text{CHO}$. Also included in the kinetics modeling was a TBHP sub-mechanism comprising the following reactions:

where the rate constants for reactions 5 were obtained from Pang et al. [30], and for reaction 6 from Choo and Benson [31]. The thermodynamic parameters for TBHP and tert-butoxy radical were taken from the thermodynamic database from Goos et al. [32], and the thermodynamic parameters for OH were updated with the values from Herbon et al. [23]. The rate constants of the following reactions were updated with more recent values:

where the rate constants for reaction 7 were obtained from Wooldrige et al. [33], for reaction 8 from Lam et al. [24], and for reaction 9 from Vasudevan et al. [34]. The effects of other reactions, such as TBHP + OH, were found negligible and therefore not discussed here. The measured aldehydes + OH rate constants were found insensitive between different base reaction mechanisms used in the study.

A representative OH concentration time-history trace from a TBHP/CH₃CHO experiment is shown in Fig. 1. The initial TBHP concentration in the mixture (23.5 ppm in Fig. 1) is inferred from the measured OH concentration extrapolated to time zero, and the balance water concentration is inferred from the total partial pressure of TBHP and water in the manometrically-prepared mixture. The distortion in the OH signal at early times is due to deflection of the laser beam at shock passage. Note, however, under the condition of near pseudo-first-order reaction (fuel:OH > 10:1), the measured reaction rates have been found insensitive to the initial TBHP concentration. The aldehyde + OH rate constant is inferred from best-fitting the model prediction to the measured OH time-history by changing the target reaction rate constant. The RMS error in the best fit was less than 1%. Also shown are the simulated OH time-histories at the target rate modified by +/- 30%, which indicate very high sensitivity of the rate constant measurement. A formal sensitivity analysis including both target reaction and secondary reactions has also been conducted.

Shown in Fig. 2a is the OH sensitivity plot of the CH₃CHO + OH system. OH sensitivity is usually defined as the ratio of the percentage change in the local OH mole fraction (X_{OH}) and the percentage change in the reaction rate under investigation (k_i) :

$S_{OH} = (\partial X_{OH} / \partial k_i) / (X_{OH} / k_i)$. This analysis has clearly revealed that the target reaction CH₃CHO + OH is the dominant reaction during the test time of the experiment. However, conventional sensitivity analysis may yield the counterintuitive result that while the target rate constant is mainly determined from the slope near time zero, all the reaction sensitivities are close to zero. This is because the initial OH mole fraction is a fixed number independent of reaction rates. Alternatively, we can introduce the ΔOH sensitivity, defined as $S_{\Delta OH} = (\partial \Delta X_{OH} / \partial k_i) / (\Delta X_{OH} / k_i)$, where $\Delta X_{OH}(t) = X_{OH}(t) - X_{OH,0}$ is the mole fraction of OH that has been consumed in the reactions. As shown in Fig. 2b, the ΔOH sensitivity analysis more clearly indicates that the target reaction is directly related to the OH consumption and is the dominant channel of OH removal.

A detailed uncertainty analysis (Fig. 3) suggested that the overall uncertainty limits of the measured rate constant of CH₃CHO + OH at 1176 K, 2.025 atm were -20.4%/+11.8%. The primary contributions to this uncertainty were 1) uncertainty in the rate constant of CH₃ + OH = CH₂(s) + H₂O (obtained from Vasudevan et al. [34]), 2) uncertainty in the rate constant of CH₃ + OH (+M) = CH₃OH (+M) (obtained from GRI-Mech 3.0 [29]), and 3) uncertainty in the mixture composition. Three major sources of CH₃ were identified: decomposition of TBHP, decomposition of the aldehyde fragment after H-abstraction by OH, and the thermal decomposition of CH₃CHO. In this study we focused on the very first 50 microseconds where the effect of CH₃CHO thermal decomposition was small (according to the USC-Mech II [28] model, less than 1% CH₃CHO decomposition occurred during the first 50 microsecond even at the highest test temperature). Noticing that the

amount of CH₃ is roughly proportional to the initial TBHP mole fraction, we could reduce the uncertainty from these interfering reactions by increasing the initial aldehyde/TBHP ratio. We made use of different mixtures to cross-validate our determination of the target rate constant.

4. Summary of Results

A total of 61 reflected shock wave experiments were performed to determine the overall rate constants for the reactions of OH with four aldehydes (CH₂O, CH₃CHO, C₂H₅CHO and n-C₃H₇CHO) at near-pseudo-first-order conditions. Experiments were carried out over the temperature range of 950-1400 K at pressures of 1-2 atm using different initial fuel and TBHP concentrations. Results are summarized in Table 1.

As expected, the uncertainties in the rate constant measurement were seen to decrease at higher aldehyde/TBHP ratio (Fig. 4). However, though it was tempting to use even higher aldehyde/TBHP ratio, the increased uncertainties from the thermal decomposition of aldehydes at very high temperatures and from the manometric preparation of very dilute TBHP mixtures eventually limited the measurement accuracy. The current choices of aldehyde/TBHP had already accounted for the tradeoff between these different uncertainty sources. Despite the variations in uncertainty limits, all data points followed the same trend and were seen to be very consistent. Experiments at a higher pressure (~ 4 atm) were included, and no pressure dependence was observed, which suggested that the overall OH + aldehydes rates measured in the current study were probably dominated by H-abstraction.

The measured overall rate constants for aldehydes + OH were then fitted to modified Arrhenius form over the high temperature region: $k_{\text{CH}_2\text{O}+\text{OH}} = 1.02 \times 10^7 (T/K)^{1.92} \exp(779K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, valid over 1096 – 1391 K; $k_{\text{CH}_3\text{CHO}+\text{OH}} = 4.32 \times 10^6 (T/K)^{2.02} \exp(716K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, valid over 999 – 1388 K; $k_{\text{C}_2\text{H}_5\text{CHO}+\text{OH}} = 5.94 \times 10^6 (T/K)^{1.98} \exp(823K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, valid over 958 – 1288 K; and $k_{\text{nC}_3\text{H}_7\text{CHO}+\text{OH}} = 5.36 \times 10^6 (T/K)^{2.06} \exp(658K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, valid over 1013 – 1315 K. The highest valid temperatures were selected to ensure less than 5% aldehydes thermal decomposition within the 1/e decay time of OH. The overall uncertainties in these expressions were estimated to be +/-13%, +/- 22%, +/- 27% and +/- 25%, respectively.

A cross-comparison of the rate constants for the four aldehydes + OH indicates that the activation energies of these reactions are similar, whereas the pre-exponential factors are different. It is observed in the current study that, in general, the rate constants are higher for aldehydes with longer carbon chains, which is probably due to the increased number of H-abstraction

sites. The only exception is CH₂O, for which the + OH rate constants are similar to that of C₂H₅CHO. This can possibly be explained by the different activities of H-abstraction sites: CH₂O has two α -sites, a type of site that is usually more active than the others, whereas the other aldehydes only have one.

5. Comparison with Previous Studies

Fig. 5 summarizes the reaction rate constant for CH₂O + OH from different studies at temperatures from 200 - 2000 K. In the high temperature region, the earlier shock tube measurements by Vasudevan et al. [8] agree well with the current study, within their respective error bars. Small differences between the two studies were possibly due to the larger mixture composition uncertainties in the previous study. Now with a more accurate mixture-preparation technique, as confirmed by the multi-pass cell measurement, the current study has reduced the uncertainty in the rate constant measurement by almost a half. The recommended rate expression from Tsang and Hampson [35], currently used in GRI Mech 3.0, agrees well with the current study to within 20%, significantly below their original uncertainty limit (a factor of 2). The recommended values from Baulch et al. [36] and the studies by Vandooren et al. [37] and Xu et al. [38] also agree with current measurement within their uncertainty limit (a factor of 2). Recent quantum chemistry calculations from D'Anna et al. [9] agree less well.

At lower temperatures, the reaction with OH is one of the major atmospheric sinks of aldehydes, especially in the lower troposphere. Sivakumaran et al. [39] measured the absolute rate constant of CH₂O + OH over 202 - 399 K using pulsed laser photolysis and LIF, and Atkinson et al. [40] over 299 - 426 K using flash photolysis and resonance fluorescence. Using the low temperature data from these two studies, together with the current measurements at high temperatures, a modified Arrhenius fit covering 200 K - 1400 K is proposed: $k_{\text{CH}_2\text{O}+\text{OH}} = 2.39 \times 10^7 (T/\text{K})^{1.83} \exp(562\text{K}/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$, which agrees with most experimental data in the entire temperature range of interest. The uncertainty in this expression is estimated to be +/-15%.

The current study provides the first direct rate constant measurement of C₂ - C₄ aldehydes + OH at high temperatures, shown in Fig. 6. The recommended rate expressions by Baulch et al. [36] and Warnatz [41] agree with the current study within their uncertainty limits (a factor of 1.58 and 2.51, respectively). It is worth noting that while the Baulch et al. recommendation is specified up to only 1000 K, our experiment has explored much higher temperatures. At lower temperatures, there have been overall rate constant measurements from Dobe et al. [10], Sivakumaran et al. [11] and Zhu et al. [12].

We have fitted the reaction rate constant as a smooth function of temperature in the following form: $k_{\text{CH}_3\text{CHO}+\text{OH}}(202 - 1388 \text{ K}) = [8.49 \times 10^{13} \exp(-2674\text{K}/T) + 2.76 \times 10^{12} \exp(357\text{K}/T)] \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$, with the overall uncertainty estimated to

be +/- 25%. This expression not only reconciles most low temperature data with our high temperature measurement, but also fits reasonably well to the recent experimental data from Taylor et al. (2006) [20] at intermediate temperatures.

Fewer studies have been conducted for the other two aldehydes, either theoretically or experimentally. Most previous experimental studies are in the low temperature range [13-19, 42]. Combining these data with our measurements (see Fig. 7 and 8), the following overall rate constant expressions can be obtained:

$$k_{\text{C}_2\text{H}_5\text{CHO}+\text{OH}} (240 - 1288 \text{ K}) = [6.83 \times 10^{13} \exp(-2240\text{K}/T) + 3.00 \times 10^{12} \exp(417\text{K}/T)] \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}, \text{ and}$$

$$k_{\text{nC}_3\text{H}_7\text{CHO}+\text{OH}} (258 - 1315 \text{ K}) = [1.19 \times 10^{14} \exp(-2343\text{K}/T) + 2.90 \times 10^{12} \exp(481\text{K}/T)] \text{ cm}^3\text{mol}^{-1}\text{s}^{-1},$$

with their overall uncertainties estimated to be +/- 30% and +/- 28%, respectively. These expressions are seen to agree with most experimental data over the entire temperature range, and are in close accord with the recent jet reactor and flame studies of Veloo et al. [21, 22], as shown in Fig. 7 and 8.

6. Concluding Remarks

Reactions between OH radicals and C₁-C₄ aldehydes were studied behind reflected shock waves at elevated temperatures. The use of TBHP as an OH precursor, in conjunction with a sensitive OH absorption diagnostic, yielded accurate OH concentration time-histories, which were employed to extract overall reaction rate constants for OH + aldehydes over 950 – 1400 K. The uncertainties in these rate constant measurements were low (around +/-20%), as confirmed by detailed uncertainty analyses accounting for both experimental and mechanism-induced contributions. Comparison with previous work for CH₂O + OH showed good agreement at high temperatures. For C₂ - C₄ aldehydes + OH, our study provides the first direct rate constant measurements at high temperatures. By combining our high temperature data with low temperature data from previous studies, best-fit expressions over 200 K – 1400 K were also obtained, providing excellent agreement with most existing experimental data.

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Table 1. Aldehydes + OH = Products: Rate Constant Data

T [K]	P [atm]	k [cm ³ mol ⁻¹ s ⁻¹]	T [K]	P [atm]	k [cm ³ mol ⁻¹ s ⁻¹]
100 ppm trioxane / 100 ppm TBHP (and water) / Ar			958	1.250	1.13×10^{13}
1391	1.332	1.95×10^{13}	1279	0.945	1.60×10^{13}
1201	1.311	1.60×10^{13}	1104	1.144	1.35×10^{13}
1096	1.348	1.45×10^{13}	500 ppm C ₂ H ₅ CHO / 150 ppm TBHP (and water) / Ar		
1249	1.265	1.70×10^{13}	958	1.243	1.12×10^{13}
1333	1.112	1.85×10^{13}	1143	1.087	1.39×10^{13}
50 ppm trioxane / 30 ppm TBHP (and water) / Ar			1241	1.011	1.57×10^{13}
1127	0.943	1.47×10^{13}	300 ppm n-C ₃ H ₇ CHO / 100 ppm TBHP (and water)/ Ar		
1161	0.880	1.55×10^{13}	1202	2.109	2.00×10^{13}
1242	0.838	1.69×10^{13}	150 ppm n-C ₃ H ₇ CHO / 50 ppm TBHP (and water) / Ar		
500 ppm CH ₃ CHO / 100 ppm TBHP (and water) / Ar			1199	2.102	1.98×10^{13}
1367	1.943	1.55×10^{13}	1267	2.014	2.15×10^{13}
1216	2.143	1.30×10^{13}	1125	2.123	1.80×10^{13}
1085	2.208	1.10×10^{13}	500 ppm n-C ₃ H ₇ CHO / 250 ppm TBHP (and water)/ Ar		
1327	1.888	1.50×10^{13}	1209	2.129	2.00×10^{13}
300 ppm CH ₃ CHO / 100 ppm TBHP (and water) /Ar			1140	2.172	1.85×10^{13}
1252	1.966	1.35×10^{13}	1004	2.319	1.55×10^{13}
1101	2.158	1.15×10^{13}	200 ppm n-C ₃ H ₇ CHO / 100 ppm TBHP (and water)/ Ar		
1029	2.214	1.05×10^{13}	1196	2.093	2.00×10^{13}
1342	1.920	1.52×10^{13}	1124	2.121	1.78×10^{13}
1176	2.025	1.28×10^{13}	250 ppm n-C ₃ H ₇ CHO / 125 ppm TBHP (and water)/ Ar		
1354	2.072	1.54×10^{13}	1069	1.188	1.67×10^{13}
200 ppm CH ₃ CHO / 100 ppm TBHP (and water) / Ar			1114	1.160	1.78×10^{13}
1152	2.201	1.21×10^{13}	1135	1.077	1.80×10^{13}
1366	1.942	1.53×10^{13}	1167	1.004	1.90×10^{13}
999	2.293	1.00×10^{13}	1235	0.965	2.10×10^{13}
100 ppm CH ₃ CHO / 100 ppm TBHP (and water) / Ar			1315	0.916	2.30×10^{13}
1388	1.990	1.58×10^{13}	250 ppm n-C ₃ H ₇ CHO / 83 ppm TBHP (and water) / Ar		
1248	3.914	1.36×10^{13}	1307	0.909	2.27×10^{13}
300 ppm C ₂ H ₅ CHO / 100 ppm TBHP (and water) / Ar			1295	0.957	2.25×10^{13}
1208	2.130	1.49×10^{13}	1274	0.986	2.18×10^{13}
1093	2.247	1.31×10^{13}	1240	0.999	2.10×10^{13}
985	2.237	1.16×10^{13}	1203	1.010	2.00×10^{13}
300 ppm C ₂ H ₅ CHO / 50 ppm TBHP (and water) / Ar			1013	1.179	1.55×10^{13}
1195	2.091	1.45×10^{13}	500 ppm n-C ₃ H ₇ CHO / 100 ppm TBHP (and water)/ Ar		
1288	2.059	1.60×10^{13}	1015	1.184	1.57×10^{13}
1244	0.990	1.55×10^{13}	1086	1.107	1.70×10^{13}
1189	1.042	1.46×10^{13}	1177	1.014	1.95×10^{13}
			1237	0.965	2.10×10^{13}

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Figure 1. Example OH time-history of $\text{CH}_3\text{CHO} + \text{OH}$

(a)

(b)

Figure 2. (a) OH sensitivity analysis, $S_{OH} = (\partial X_{OH} / \partial k_i) / (X_{OH} / k_i)$.

(b) ΔOH sensitivity, $S_{\Delta OH} = (\partial \Delta X_{OH} / \partial k_i) / (\Delta X_{OH} / k_i)$

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