High Temperature Branching Ratio of Acetaldehyde + OH Reaction

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Abstract

The reaction of acetaldehyde (CH$_3$CHO) with hydroxyl radicals (OH) plays an important role in atmospheric and combustion chemistry. The low-temperature chemistry of this reaction has been studied widely in the literature. However, the branching of this reaction at high temperatures is not well known. Aiming to deduce the branching ratio of CH$_3$CHO + OH, measurements were carried out in a shock tube by introducing deuterium into the chemical system. Overall rate coefficients for OH reactions with acetaldehyde (CH$_3$CHO), acetaldehyde-2,2,2-d$_3$ (CD$_3$CHO), acetaldehyde-d$_4$ (CD$_3$CDO) were measured over the temperature range of 950-1300 K and 1.5-3.0 bar. In addition, rate coefficients of OH radicals with acetone (CH$_3$C(O)CH$_3$) and acetone-d$_6$ (CD$_3$C(O)CD$_3$) were measured to deduce the kinetic isotopic effect of H-abstraction reaction at the methyl site. The measured rate coefficients can be represented by the following Arrhenius expressions (cm$^3$/molecule/s):

\[
k_1(\text{CH}_3\text{CHO} + \text{OH}) = 1.29 \times 10^{-10} \exp \left(-1996.5 \frac{K}{T}\right)
\]
\[
k_2(\text{CD}_3\text{CHO} + \text{OH}) = 1.06 \times 10^{-10} \exp \left(-2151.9 \frac{K}{T}\right)
\]
\[
k_3(\text{CD}_3\text{CDO} + \text{OH}) = 1.18 \times 10^{-10} \exp \left(-2554.1 \frac{K}{T}\right)
\]
\[
k_4(\text{CH}_3\text{COCCH}_3 + \text{OH}) = 7.15 \times 10^{-11} \exp \left(-2695.7 \frac{K}{T}\right)
\]
\[
k_5(\text{CD}_3\text{COCCD}_3 + \text{OH}) = 6.02 \times 10^{-11} \exp \left(-3130.5 \frac{K}{T}\right)
\]

In contrast to the low-temperature chemistry, our results indicate that H-abstraction from the methyl site of acetaldehyde is important at high temperatures and the branching fraction of this channel is $\sim 65 \%$. On per H atom basis, however, H-abstraction from the aldehydic group is faster than that of methyl group even at high temperatures.

Keywords: Acetaldehyde; Acetone; Hydroxyl radicals; Deuterium; Branching ratio.
1. Introduction

Acetaldehyde is one of the most abundant hazardous byproducts in the combustion of various fuels [1, 2]. The reaction of OH radicals with acetaldehyde is the dominant oxidation pathway in both combustion and atmospheric environments [3]. The reaction may take place via abstraction and/or addition channels in an overall exothermic process (reactions 1a – 1d):

\[
\text{CH}_3\text{CHO} + \text{OH} \rightarrow \begin{cases} \bullet \text{CH}_2\text{CHO} + \text{H}_2\text{O} & \Delta H_{\text{rxn}, 298K}^o = (-97.91 \pm 0.89) \text{ kJ mol}^{-1} \\ \text{CH}_3\text{CO}^* + \text{H}_2\text{O} & \Delta H_{\text{rxn}, 298K}^o = (-123.68 \pm 0.26) \text{ kJ mol}^{-1} \\ \text{CH}_2\text{CHO} + \text{HCOOH} & \Delta H_{\text{rxn}, 298K}^o = (-103.79 \pm 0.34) \text{ kJ mol}^{-1} \\ \text{CH}_3\text{COOH} + \text{H} & \Delta H_{\text{rxn}, 298K}^o = (-86.86 \pm 0.48) \text{ kJ mol}^{-1} \end{cases}
\]

(R1a)

(R1b)

(R1c)

(R1d)

The given enthalpies of reactions are based on the enthalpies of formation provided by Ruscic and Bross in their 1.22g version of the thermochemical network [4]. Acetaldehyde + OH reaction rate coefficients exhibit a strong curvature on an Arrhenius plot, and it has the slowest rate coefficient near 600 K [5]. This unusual temperature dependence of the rate coefficient appears to stem from the complex kinetics of competing channels. The hydroxyl radical may abstract H-atoms either at the methyl or the aldehyde site to produce formyl methyl radical (CH₂CHO), reaction (R1a), or acetyl radical (CH₃CO), reaction (R1b), respectively. The chemistry of these radicals is of particular interest because their subsequent reactions lead to different radical pool which govern the oxidation kinetics of acetaldehyde. For example, CH₃CO decomposes to CH₃ and CO, whereas CH₂CHO may lose an H atom to produce ketene (CH₂=C=O). The relative importance of these channels plays a central role in describing the oxidation of acetaldehyde.

Reaction of acetaldehyde with OH has been the subject of several studies (see a comprehensive review in Table S3 of Supplementary Materials). Over the span of 50 years, most of the kinetic
studies focused on understanding the low-temperature reactivity of this reaction. Most results are consistent with $k_1 = (1.53 \pm 0.1) \times 10^{-11}$ cm$^3$/molecule/s at 298 K, and agreed that the addition channels (R1c+R1d) are kinetically irrelevant at low temperatures. By using time-resolved UV spectroscopy, Cameron et al. [6] directly monitored CH$_3$CO and CH$_3$ radicals and confirmed reaction (R1b) to be the dominant pathway, contributing $\sim 93 \pm 18\%$, while the upper limit for the two addition-elimination channels (R1c + R1d) was found to be $\sim 5\%$. Using tunable IR spectroscopy, Wang et al. [7] deduced a yield of $\sim 100\%$ for H$_2$O, and an upper limit of $5 \pm 5\%$ was assigned to the addition channels. Vandenberk and Peeters et al. [8] employed a flow reactor coupled to a molecular-beam mass spectrometer to determine the product branching at room temperature. They deduced a yield of $89 \pm 6\%$ for H$_2$O, but could not detect HCOOH (reaction (R1c)). They concluded that reaction (R1) predominantly undergoes H-abstraction to produce CH$_3$CO and H$_2$O (reaction (R1b)). Butkovskaya et al. [9] determined H$_2$O yield of $98 \pm 5\%$ by utilizing a flow reactor coupled to a chemical ionization/mass spectrometry technique. By detecting CH$_2$CHO, the contribution of reaction (1a) was determined to be $5 \pm 2\%$.

These observations are in line with the experimental and theoretical study of D’Anna et al. [10] who showed that the reaction of OH radicals with acetaldehyde takes place exclusively via H-abstraction at the aldehyde group. In contrast to the plethora of studies at low temperatures, the branching ratios of these channels (R1a-R1d) have not been measured previously at high temperatures. A few studies [3, 11-13] have predicted high-temperature branching ratios with widely varying results (discussed in Section 3.4).

The aim of this work is to discern the branching ratio of reactions (R1a) and (R1b) at high temperatures where the addition-elimination pathways (R1c+R1d) are kinetically insignificant. To achieve our objectives, we selected deuterated isotopes of acetaldehyde and acetone. Rate
coefficients for reactions (R1-R5) were determined by employing a shock tube and laser diagnostics technique.

\[
\begin{align*}
\text{CH}_3\text{CHO}+\text{OH} & \rightarrow \text{Products} \quad \text{(R1)} \\
\text{CD}_3\text{CHO}+\text{OH} & \rightarrow \text{Products} \quad \text{(R2)} \\
\text{CD}_3\text{CDO}+\text{OH} & \rightarrow \text{Products} \quad \text{(R3)} \\
\text{CH}_3\text{COCH}_3+\text{OH} & \rightarrow \text{Products} \quad \text{(R4)} \\
\text{CD}_3\text{COCD}_3+\text{OH} & \rightarrow \text{Products} \quad \text{(R5)}
\end{align*}
\]

2. Experimental Methods

Absolute rate coefficients for the reactions of OH radicals with acetaldehyde, acetone and their isotopomers were measured over 950 – 1300 K and 1.5 – 3.0 bar.

2.1 Low-Pressure Shock Tube (LPST) Facility

The low-pressure shock tube (LPST) facility has been detailed previously [14]. The stainless-steel shock tube is comprised of a 9 m driven section and a variable length driver section with an inner diameter of 14.2 cm. Pressure bursting of polycarbonate diaphragms generated shock waves with helium as the driver gas. A series of five piezoelectric transducers (PCB 113B26) were placed along the last 1.5 m of the driven section to measure incident shock speed. Temperature and pressure behind reflected shock waves, \(T_5\) and \(P_5\), were calculated by employing Rankine-Hugoniot relationship embedded in the Frosh code [15]. Uncertainties in \(T_5\) and \(P_5\) were \(~\pm 1\%\) which mainly came from the uncertainty of the measured incident shock velocity.

2.2 Hydroxyl Laser Diagnostic

Hydroxyl radicals were generated via fast thermal decomposition (half-life \(\leq 1\mu s\) for \(T \geq 1000\text{K}\)) of a well-known clean OH precursor, \(\text{tert}\)-butyl hydroperoxide (TBHP) [16]. Reaction kinetics was
followed by monitoring OH radicals near the center (306.6868 nm) of the well-characterized $R_1(5)$ absorption line in the $(0, 0)$ vibrational band of the $A^2 \Sigma^+ \leftarrow X^2 \Pi$ electronic system of OH. A narrow linewidth cw laser system, comprising of an Nd:YAG 532 nm pump laser, a ring-dye visible laser and a frequency doubler, was used to generate UV light. The laser beam was guided through the shock tube via two quartz windows, installed 2 cm away from the shock tube end wall. Two modified Thorlab PDA36-EC photodetectors (spectral range 190-1100 nm) were used to measure the laser intensity before and after the shock tube. A common-mode-rejection (CMR) scheme was employed to account for laser intensity fluctuations. After CMR, the laser noise was less than 0.1% of the signal. Incident and transmitted laser intensities were quantitatively converted to OH mole fraction ($X_{OH}$) using Beer-Lambert law. To infer $X_{OH}$, the line strength at a reference temperature $T_0$, $S_{OH}(T_0)$, and line shape function, $\Phi_v$, must be known. In order to calculate the absorption coefficients of OH radicals for the particular electronic excitation of OH radical at 306.6868 nm, the spectral data for line strength and line shape were taken from Rea et al. [17].

2.3 Mixture Preparation

The purity of the used chemicals are: 70 % TBHP solution in water, acetaldehyde (99.5%), acetaldehyde-2,2,2-d$_3$ (≥98 atom% D), acetaldehyde-d$_4$ (≥99 atom% D), acetone (99.5%), and acetone-d$_6$ (99.9 atom% D) obtained from Sigma-Aldrich; the driver gas, helium (99.99%) and the dilution gas, argon (99.999%) were purchased from AH Gases. Mixtures were prepared manometrically in a 24-litre teflon-coated stainless-steel vessel which is equipped with a magnetically-driven stirrer. For mixture preparation, MKS Baratron pressure gauges of various ranges were employed to accurately measure partial pressures of gases. Prior to mixture preparation, several cycles of freeze-pump-thaw were employed to remove the dissolved gases,
e.g., O2, N2 and CO2. The mixing vessel was turbo-pumped to ~ 10^-6 mbar. The mixtures were left for at least two hours to ensure homogeneity.

3. Results and Discussion

3.1 Measurements of Rate Coefficients

Rate coefficients were measured at the conditions listed in Table S1 and S2 (Supplementary Material). Various mixture compositions (~ 400-600 ppm fuel and 20-60 ppm TBHP) were employed so that OH radical decay follows first-order kinetics. Figure 1 displays a representative OH time-history recorded at 1073 K and 2.64 bar for CH3CHO + OH \( \rightarrow \) products (R1). As seen, OH decayed exponentially with time; therefore, the pseudo-first order kinetic analysis can be applied to extract the total rate coefficient (see inset of Fig. 1 and Fig. S1 in SM). However, to account for minor influence of secondary chemistries, a detailed assembled kinetic model (provided in Supplementary Material) comprising of GRI 3.0 [18] and TBHP mechanism of Pang et al. [16] was used to iteratively fit the experimentally measured OH time-profiles by treating the target reaction as variable. An illustrative example of the best-fit is shown in Fig. 1 with the red line, and perturbations of ± 50% from the best-fit value \( (k_1 = 1.99 \times 10^{-11} \text{ cm}^3/\text{molecule/s}) \) are also shown. Figure S2 shows hydroxyl sensitivity analysis which indicates that the secondary chemistry has negligible effect on the measured OH time-history over the first tens of microseconds. For the other reactions (R2 – R5), similar methods were employed to determine the total rate coefficients. Measured rate coefficients are listed in Tables S1 and S2 (Supplementary Material).

A detailed uncertainty analysis was conducted for reaction (R1) at a representative condition of 1073 K and 2.64 bar. Various sources of errors were considered, such as uncertainty in temperature (±0.7%), determination of time zero (±0.5 µs), fitting of the measured OH time-history profile (±6
%, mixture composition (±5%), target wavelength (±0.001 cm⁻¹), and OH absorption-cross section (±3%). While estimating the uncertainty stemming from each individual error source, the variable corresponding to the error source was perturbed to its lower and upper bounds, and the rate coefficient of the target reaction was varied to get best-fit with the measured OH profile. By doing so, uncertainty in the rate coefficients from each error source was quantified at a particular temperature and pressure, and these uncertainties were then combined, using the root-mean-square method, to get the overall uncertainty in the measured rate coefficient. Our reported values of the rate coefficients for all reactions have roughly the same value of estimated uncertainty ~ ±20%.

**Figure 1.** Measured OH time-history for CH₃CHO + OH → products (R1) at 1073 K and 2.64 bar. Mixture composition: 513 ppm CH₃CHO / 47 ppm TBHP (~120 ppm H₂O) diluted in Ar.

### 3.2 Kinetics of OH Radicals with Acetaldehyde

Figure 2 displays the temperature dependence of the rate coefficients for acetaldehyde reaction with OH radicals. The reaction exhibits a complex behavior showing a negative temperature dependence of the rate coefficients at low temperatures, but positive temperature dependence at high temperatures. The data of Taylor et al. [5] shows a strong curvature with slowest reactivity ($k_1 \sim 9.5 \times 10^{-12}$ cm³/molecule/s) near 600 K. This hints towards the differences in the relative importance of competing channels at different temperatures.
The reaction of acetaldehyde with OH radicals is known to take place via an addition-elimination mechanism in an overall exothermic process, resulting in a complex kinetic behavior [10, 11, 22, 23]. The initial process involves the formation of a hydrogen-bonded pre-reaction complex, resulting from the interaction of OH radical with the lone pair electrons of the oxygen atom of the carbonyl group (>C=O). The stabilization energy of the complex is ~ 5 kcal/mole [10, 11]. Similar stability has been reported for the complexes comprising of OH radicals and other aldehydes [11]. At low temperatures, these complexes play an important role and exhibit complex temperature dependence. The appearance of pre-reaction complexes prior to the corresponding transition states of the abstraction pathways makes such channels to deviate from elementary bimolecular behavior. Their importance and relevance in the low-temperature kinetics have recently been highlighted by Alvarez-Idaboy et al. [23] and D’Anna et al. [10].

Interestingly, theoretical studies revealed that the transition state responsible for the abstraction of hydrogen atom from the aldehyde group, leading to CH₃CO and H₂O, lies below the reactants’ energy by ~ 2.3 kcal/mol [10, 11]. Similar values of the negative energy barriers for aldehydic H-
abstraction are found for higher aldehydes + OH reactions [11]. However, for formaldehyde + OH reaction, the corresponding transition state lies almost thermoneutral. This difference in the relative energy of the transition states results in the higher reactivity of OH reaction with acetaldehyde compared to that of formaldehyde [24] despite the fact that formaldehyde has twice the number of aldehydic hydrogen atoms. The inductive effect of the methyl group in acetaldehyde appears to stabilize the corresponding transition state, thus lowering its energy more than that of formaldehyde.

The hydrogen abstraction reaction from the methyl group of acetaldehyde, leading to CH₂CHO and H₂O, occurs via a distinct energy barrier (ΔE₀ ~ 3.3 kcal/mol relative to reactants [10, 11]). Hence, it is clear why reaction (R1a) is kinetically insignificant at low temperatures. This fact is also reinforced by the experimental [8, 9] and theoretical results [10]. The barrier height for OH addition reaction leading to HCOOH (reaction (R1c)) or CH₃COOH (reaction (R1d)) was calculated to be ~7.6 kcal/mol, and the corresponding transition state was found to be much tighter [10, 23]. Therefore, the addition channels, (R1c) and (R1d), are found to have negligible importance at atmospheric conditions.

The observed unusual negative temperature dependence for H-abstraction reaction of acetaldehyde + OH at low temperatures is the consequence of a negative activation barrier for the process. Most of the earlier reports [24-29] for the room-temperature coefficients appear to be consistent with an average value of \( k_1 (298±2 \text{ K}) = (1.53±0.1) \times 10^{-11} \text{ cm}^3/\text{molecule/s} \) (see Table S3 for the summary of previous works). Only the reports of Taylor et al. [22] and Semmes et al. [20] are somewhat slower by ~20%, whereas the result of Niki et al. [19] is faster by ~30% compared to the average literature values. The low-temperature data of Sivakumaran and Crowley [30], Zhu et al. [31], and Michael et al. [32] exhibited a clear negative temperature dependence. At higher temperatures (\( T \))
> 700 K), Taylor et al. [5] reported that H-abstraction predominantly occurs at the methyl group, displaying a positive temperature dependence. Our rate coefficient data agree very well with the only previous high-temperature work of Wang et al. [33] (see Fig. 2). Our data can be best described (R² ~ 0.96) by the following Arrhenius expression in unit of cm³/molecule/s over the temperature range of 950-1300 K:

\[
k_1(\text{CH}_3\text{CHO} + \text{OH}) = 1.29 \times 10^{-10} \exp\left(-1996.5 \frac{K}{T}\right) \quad \text{Eq. (1)}
\]

Theoretical rate coefficients of Mendes et al. [11] severely underpredict our data by at least a factor of five. AramcoMech 3.0 [34] employs a rate expression that is too fast at low temperatures and too slow at high temperatures with an onset of transition temperature higher than that shown by the experimental data. Excluding some problematic literature data sets [19-22], all remaining data are combined with ours to generate the following bi-exponential rate expression, Eq. (2). The below expression (cm³/molecule/s) reproduces the experimental data with an adjusted R² of 0.94 over the temperature range of 202 – 1327 K.

\[
k_1(\text{CH}_3\text{CHO} + \text{OH}) = 1.42 \times 10^{-10} \exp\left(-2631.44 \frac{K}{T}\right) + 4.69 \times 10^{-12} \exp\left(348.74 \frac{K}{T}\right) \quad \text{Eq. (2)}
\]

### 3.3 Kinetic Isotope Effect (KIE) of Acetaldehyde + OH

Figure 3 displays high-temperature rate coefficients measured in this work for acetaldehyde isotopomers + OH reactions. Isotopic substitution caused inhibition in the reactivity of acetaldehyde with OH radicals. CD₃CHO + OH (R2) showed a significant drop (~ 20%) in the rate coefficient and exhibited somewhat stronger temperature dependence than its non-deuterated counterpart. This clearly shows that H-abstraction from the methyl group (R1a) becomes an active channel at high temperatures. Our experiments gave a value of ~1.45 (k₁/k₂) for KIE near 950 K which compared reasonably well with the value of 1.64 reported by Taylor et al. [5] at 861 K.
According to Taylor et al. [5], KIE ($k_1/k_2$) dropped to 1.1 at 600 K; however, the isotopic substitution at the aldehyde group resulted in KIE, $k(\text{CH}_3\text{CHO}+\text{OH})/k(\text{CH}_3\text{CDO}+\text{OH})$, of 1.39 and 1.68 at 600 and 298 K, respectively [5]. The isotopic substitution at the aldehydic hydrogen atom resulted in decreased rate coefficients at low temperatures, which indicates that H-abstraction from the aldehyde group becomes the dominant channel at low to intermediate temperatures (see Figure S3). Our measured rate coefficients for acetaldehyde isotopomers + OH reactions may be described by the following Arrhenius expressions (cm$^3$/molecule/s) with $R^2$ of 0.90 and 0.96, respectively.

$$k_2(\text{CD}_3\text{CHO} + \text{OH}) = 1.06 \times 10^{-10} \exp\left(-2151.9 \frac{K}{T}\right)$$  \hspace{1cm} \text{Eq. (3)}

$$k_3(\text{CD}_3\text{CDO} + \text{OH}) = 1.18 \times 10^{-10} \exp\left(-2554.1 \frac{K}{T}\right)$$  \hspace{1cm} \text{Eq. (4)}

![Figure 3](image)

**Figure 3.** Rate coefficients for the reactions of OH with acetaldehyde isotopomers. Solid symbols: our experimental data; dash lines: Arrhenius fits of the experimental data.

### 3.4 Site-specific Rate Coefficients and Branching Ratios

As discussed earlier, addition pathways (R1c + R1d) are irrelevant at combustion conditions because such processes occur via high energy barriers ($\Delta E_0 \sim 7.7$ kcal/mol) and are also not entropically favored as opposed to the abstraction channels [10]. D’Anna et al. [10] reported the pre-exponential factor for the addition pathways to be $\sim$20 times smaller than that of the abstraction
channels which led them to conclude that the addition channel is kinetically irrelevant. Therefore, we can express the experimentally measured total rate coefficients into site-specific rate coefficients as follows:

\[
k_1(T) = k_{1b}^H + 3 \times k_{1a}^H = 1.29 \times 10^{-10} \exp \left( -1996.5 \frac{K}{T} \right) \quad \text{Eq. (5)}
\]

\[
k_2(T) = k_{1b}^H + 3 \times k_{1a}^D = 1.06 \times 10^{-10} \exp \left( -2151.9 \frac{K}{T} \right) \quad \text{Eq. (6)}
\]

\[
k_3(T) = k_{1b}^D + 3 \times k_{1a}^D = 1.18 \times 10^{-10} \exp \left( -2554.1 \frac{K}{T} \right) \quad \text{Eq. (7)}
\]

In doing so, we have assumed that i) the reaction of OH radical with acetaldehyde is quasi single step reaction at high temperatures and the pre-reaction complex has not much kinetic relevance, ii) the isotopic substitution in a chemical environment does not affect the reaction kinetics at the neighboring site. In Eqs. 5-7, \( k_1 \) to \( k_3 \) are the total rate coefficients for the reactions of OH radicals with CH\(_3\)CHO, CD\(_3\)CHO, and CD\(_3\)CDO, respectively. The superscripts, H and D, are used to identify the type of atom undergoing abstraction reaction, and the subscripts, \( a \) and \( b \), stand for abstraction at the methyl or aldehydic site, respectively. We have four unknowns but three equations only. Therefore, we need an additional equation to solve for the site-specific rate coefficients. Here, we postulate a similarity between the KIE of H-abstraction from the methyl groups of acetaldehyde and acetone.

We conducted an additional high-temperature study to discern KIE of OH reactions with acetone (R4) and acetone-d6 (R5). The reaction of OH and acetone has been extensively studied previously (see Lam et al. [35] and the references cited therein). Our measured rate coefficients, plotted in Figure 4 and represented by Eq. (8), agree excellently with Lam et al. [35].

\[
k_4(\text{CH}_3\text{COCH}_3 + \text{OH}) = 7.15 \times 10^{-11} \exp \left( -2695.7 \frac{K}{T} \right) \quad \text{(R}^2 \sim 0.99) \quad \text{Eq. (8)}
\]

13
High-temperature studies for the kinetic isotopic effect of OH reaction with acetone do not exist in the literature. Earlier studies [36-41] are confined to temperatures lower than 830 K. In Fig. 4, our measured rate coefficients are plotted along with available literature data. Yamada et al. [36] data show a smooth transition to our high-temperature rates, and they showed an excellent accord between their measured and theoretical KIE. They concluded that the addition pathway is negligibly small while the direct H-abstraction pathway dominates above 450 K, and below this temperature the abstraction reaction proceeds via a hydrogen bonded pre-reaction complex. This finding is reinforced by a recent theoretical study of Zhou et al. [42] who reported that the direct abstraction dominates over the entire temperature range of 500 – 2000 K, and the abstraction via pre-reaction complex does not contribute more than 15%. They further reported that OH addition channel is not significant for acetone (branching ratio less than 1%).

![Figure 4](image.png)

**Figure 4.** Comparison of rate coefficients for CD₃C(O)CD₃ + OH reaction from this work and literature. Also plotted are our rate coefficients for CH₃C(O)CH₃ + OH reaction and recommended expression from Lam et al. [35]. See also Fig. S4 (Supplementary Material) for zoomed-in view of our measured rate coefficients.

Our measured rates are described by Eq. (9) with $R^2 \sim 0.98$, while all literature data can be represented by the three-parameters Arrhenius expression, Eq. (10), with $R^2 \sim 0.98$:

$$k_5(\text{CD}_3\text{COCD}_3 + \text{OH}) = 6.02 \times 10^{-11} \exp\left(-3130.5 \frac{K}{T}\right)$$  \hspace{1cm} \text{Eq. (9)}
\[ k_5(\text{CD}_3\text{COCD}_3 + \text{OH}) = 5.55 \times 10^{-16} \times T^{1.43} \exp\left(-1408.5 \frac{K}{T}\right) \quad \text{Eq. (10)} \]

Combining Eqs. (9) and (10), we get:

\[ \frac{k_5}{k_4}(T) = \frac{k_{1a}^D}{k_{1a}^H}(T) = 0.842 \times \exp\left(-434.8 \frac{K}{T}\right) \quad \text{Eq. (11)} \]

The kinetic isotope effect \((k_d/k_5)\), is assumed to be equal to \(\frac{k_{1a}^H}{k_{1a}^D}\) while solving for the unknowns \((k_{1a}^H, k_{1a}^D, k_{1b}^H, k_{1b}^D)\) of acetaldehyde + OH system. This may be a valid assumption because i) the transition states responsible for H-abstraction from the methyl site of acetone and acetaldehyde lie \(~3.3 \text{ kcal/mol}\) above the reactants’ energy at the CCSD(T)/CBS level of theory [11, 42], and at high temperatures the pre-reaction complex does not play a significant role in either case, ii) the variation in the pre-exponential factor would largely cancel out while taking the ratio of \(k_d/k_5\) and \(\frac{k_{1a}^H}{k_{1a}^D}\). The solutions for the site-specific rate coefficients are plotted in Fig. 5, and have the following Arrhenius expressions (cm\(^3\)/molecule/s) over 950 – 1300 K:

\[ k_{1a}^H = 3.38 \times 10^{-11} \exp\left(-2182.8 \frac{K}{T}\right) \quad \text{Eq. (12)} \]

\[ k_{1a}^D = 2.85 \times 10^{-11} \exp\left(-2619.1 \frac{K}{T}\right) \quad \text{Eq. (13)} \]

\[ k_{1b}^H = 3.11 \times 10^{-11} \exp\left(-1631.4 \frac{K}{T}\right) \quad \text{Eq. (14)} \]

\[ k_{1b}^D = 3.30 \times 10^{-11} \exp\left(-2414.9 \frac{K}{T}\right) \quad \text{Eq. (15)} \]

As expected, the deuteration effect was observed at both methyl and aldehydic sites. The temperature dependence of H-abstraction from the methyl group exhibits a steeper slope indicating a higher energy barrier process. The site-specific rate coefficient for H-abstraction at the methyl site, \(k_{1a}^H\), is around 30 – 40 % slower than that of the aldehydic site, \(k_{1b}^H\). However, the relative importance of \(k_{1a}^H\) increases with temperature.
**Figure 5.** Site-specific H/D-atom abstraction rate coefficients of acetaldehyde isotopomers + OH reactions on per H/D atom basis.

Figure 6 compares branching ratios determined in this work with literature values for H-abstraction at the methyl site of acetaldehyde + OH reaction. Branching ratio of the methyl channel is ~ 65-68%, whereas H-abstraction from the aldehydic site contributes ~ 32-35% under our experimental conditions. On the contrary, the latter channel makes more than 90% near room temperature, as described earlier. Calculated values by Zhang et al. [13] and Mevel et al. [12] agree well with our data near 1100 – 1250 K, but their values underestimate the methyl branching ratio at lower temperatures. Theoretical branching ratio predictions of Mendes et al. [11] and Tao et al. [3] are too low. The results of our work, therefore, will help to resolve the discrepancy in the branching ratio of this very important reaction.
Figure 6. Comparison of the branching ratios for H-abstraction at the methyl site: \( \text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_2\text{CHO} + \text{H}_2\text{O} \) (R1a).

4. Conclusions

We investigated the kinetic isotope effect for the reactions of acetaldehyde and acetone with OH radicals at high temperatures. Total rate coefficients for the reactions of OH radicals with \( \text{CH}_3\text{CHO}, \text{CD}_3\text{CHO}, \text{CD}_3\text{CDO}, \text{CH}_3\text{C(O)CH}_3 \) and \( \text{CD}_3\text{C(O)CD}_3 \) were measured over 950 – 1300 K and 1.5 – 3.0 bar. Our measurements did not exhibit pressure dependence. Unlike at low temperatures, the reaction of OH radicals with acetaldehyde isotopomers clearly showed a positive temperature dependence in the investigated temperature range. From this study, we were able to discern the relative importance of the two key H-abstraction channels of acetaldehyde. Our result showed the dominance (65-68\%) of methyl hydrogen abstraction at the high temperatures of this work. On the basis of per H-atom, however, the aldehydic H-atom was still found to react faster than that of the methyl group. To our knowledge, this work presents the first experimental determination of the branching ratios of acetaldehyde + OH reaction under combustion relevant conditions. The rate parameters reported in this study are recommended for implementation in the future kinetic modeling of chemical systems involving acetaldehyde.

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References

List of Supplementary Material:

**Table S1:** Measured rate coefficients for the reactions of OH radical with CH3CHO, CD3CHO and CD3CDO. The bath gas is argon.

**Table S2:** Measured rate coefficients for the reactions of OH radical with acetone and acetone-d6. The bath gas is argon.

**Table S3:** Summary of the experimental results of OH + CH3CHO reaction.

**Figure S1.** Measured OH time-history for CD3OCD3 + OH \( \rightarrow \) products recorded at 1005 K and 2.35 bar. Mixture composition is provided in Table S2.

**Figure S2.** OH radical sensitivity analysis for the reaction of acetaldehyde + OH at 1073 K and 2.64 bar. The definition of sensitivity is: \( S_{OH}=(\partial X_{OH}/\partial k)\times(k_i/X_{OH}) \), where XOH is the OH mole fraction and \( k_i \) is the rate coefficient of the \( i \)th reaction.

**Figure S3.** Comparison with literature rate coefficients [5, 10, 22] for the acetaldehyde-2,2,2-d3 and acetaldehyde-d4. The dashed line represent the 4-parameter Arrhenius expression which can be given by equations 1-2, in the unit of cm\(^3\) molecule\(^{-1}\) s\(^{-1}\):

\[
k_2(\text{CD}_3\text{CHO} + \text{OH}) = 2.73 \times 10^{-10} \exp(-3786.9 \frac{K}{T}) + 4.18 \times 10^{-12} \exp(391.8 \frac{K}{T}) \tag{1}
\]

\[
k_3(\text{CD}_3\text{CDO} + \text{OH}) = 3.38 \times 10^{-10} \exp(-4364.2 \frac{K}{T}) + 4.10 \times 10^{-12} \exp(250.2 \frac{K}{T}) \tag{2}
\]

**Figure S4.** Measured rate coefficients for OH radical reactions with acetone isotopomers. Solid symbols represent the experimental data from the current study; whereas the dash lines represent Arrhenius fit of the experimental data.