



Dependence of Biofuel Ignition Chemistry on OH-Initiated Branching Fractions

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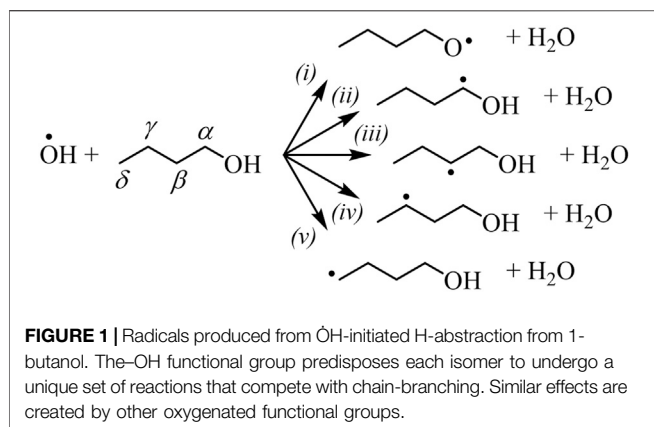
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Abstraction of hydrogen by $\dot{\text{O}}\text{H}$ is the dominant initiation step in low-temperature oxidation of biofuels. Theoretical chemical kinetics calculations for such reactions provide a direct means of quantifying rates of abstraction, which are critical to modeling biofuel combustion. However, in several cases and despite agreement on total rate coefficients, branching fractions (i.e. the distribution of initial radicals) can vary depending on the level of theory, which leads to variations in ignition delay time predictions. To examine the connection between branching fractions and ignition delay time predictions, simulations were conducted for 1-butanol, cyclopentanone, and methyl propanoate at 10 atm and from 500–1000 K. For each case, the simulations utilized recent combustion mechanisms to produce an initial set of ignition delay time trends. H-abstraction rates were then replaced using rates from the literature to examine the effects of $\dot{\text{O}}\text{H}$ -initiated branching fractions on ignition chemistry. Branching fractions were found to significantly influence ignition chemistry, specifically in the case of 1-butanol, even when total rate coefficients were relatively consistent. From comparison of site-specific rates in the literature, branching fractions for initiation of 1-butanol and methyl propanoate are not consistent, which resulted in ignition delay times differing by factors of up to 6.3 and 1.2 respectively. Conversely, in the case of cyclopentanone, for which both the total and the site-specific rate coefficients agree, ignition delay times were unaffected. From the observed dependence of ignition delay times on $\dot{\text{O}}\text{H}$ -initiated branching fractions, an intermediate step in the development of combustion mechanisms is necessary to validate site-specific rate coefficients and ensure accurate model predictions. Speciation measurements are one example that can provide a critical link to radical-specific, fundamental chemical pathways and determine accurate branching fractions.

Keywords: biofuel, low-temperature combustion, branching fraction, alcohol, ketone, ester

INTRODUCTION

Ignition delay times are an important metric necessary for the development of predictive combustion models, which depend on accurate chemical kinetics, including reaction mechanisms and rates for elementary steps including abstraction, addition, isomerization, and disproportionation. The chemistry leading to ignition, defined here as the time where the rate of change in the mole fraction of $\dot{\text{O}}\text{H}$ reaches a local maximum, results from a chain-branching step that is governed by a balance of temperature- and pressure-dependent reactions. For low-temperature combustion,



occurring below 1000 K and where ignition occurs via hydroperoxyalkyl ($\dot{\text{Q}}\text{OOH}$)-mediated chain-branching (Zádor et al., 2011; Savee et al., 2015), the initiation step is particularly important because the radical isomers formed via H-abstraction each follow a unique set of reactions that compete with chain-branching–propagating ($\dot{\text{O}}\text{H}$ forming) or inhibiting ($\text{HO}\dot{\text{O}}$ forming). The propensity of a radical isomer to react with O_2 , form $\dot{\text{Q}}\text{OOH}$, then undergo second- O_2 -addition ultimately determines the contribution of that isomer to chain-branching, which is derived from decomposition of ketohydroperoxide species and results in the net production of two radicals ($\dot{\text{O}}\text{H}$ + carbonyl-oxy radical). Understanding the connections between ignition delay times and the initiation step, particularly the branching fractions of initial radicals and species related directly to $\dot{\text{Q}}\text{OOH}$, is critical.

OH -initiated H-abstraction is the dominant step below 1000 K for all types of biofuels (Rotavera and Taatjes, 2021). Oxygenated functional groups affect branching fractions of $\dot{\text{O}}\text{H} + \text{RH} \rightarrow \text{H}_2\text{O} + \dot{\text{R}}$ due to a reduction in adjacent C–H bond energy and from hydrogen bonding in the transition state with the H atom of the hydroxyl radical (Rotavera and Taatjes, 2021); the label RH is used to designate an arbitrary biofuel, such as 1-butanol. **Figure 1** shows the radical isomers of 1-butanol formed via H-abstraction by $\dot{\text{O}}\text{H}$. As an example of the -OH functional group influence, reaction of the α isomer, formed in (ii), with O_2 exclusively produces butanal + $\text{HO}\dot{\text{O}}$ in a chain-inhibiting step, while $\dot{\text{Q}}\text{OOH}$ -mediated reactions are possible for other radicals (Rotavera and Taatjes, 2021). In part, because selectivity towards α radicals in alcohols is favored, ignition delay times of 1-butanol below 1000 K are longer when compared to *n*-butane (Rotavera and Taatjes, 2021). Similarly, radicals formed in biofuels with different functional groups, such as R–C(=O)–R (ketones) and R–C(=O)–O–R (esters) exert significant influence over the distribution of initial radicals and subsequent reaction mechanisms connected to each. In some cases, to the extent that branching fractions vary significantly, site-specific rate coefficients employed in chemical kinetics mechanisms may skew the reliability of ignition predictions.

While site-specific rate coefficient measurements are not common, for some species, theoretical rate calculations are

available from multiple studies that employ high-level methods. In such cases, the correct $k(T)$ to select for inclusion in a mechanism is often unclear, particularly when total rate coefficients are consistent with one another and with experiment. Moreover, as discussed in the present work, branching fractions can differ substantially even when total rate coefficients are similar.

Rate coefficients that are included in a given chemical kinetics mechanism are derived from measurements or theoretical chemical kinetics computations. In absence of both, rate rules are adopted as a means of approximation, yet are typically incapable of capturing functional group effects over broad ranges of temperature and pressure. Fenard et al. (Fenard et al., 2018) employed transition state theory to compute $\text{RO}\dot{\text{O}}$ isomerization rates in tetrahydrofuran oxidation, which differed up to 10^2 s^{-1} at 600 K compared with rates from alkane-based rate rules. Additionally, Al Rashidi et al. (Al Rashidi et al., 2015) showed that the use of rate rules predicted C–C and C–O bond-scission rates significantly lower than analogous reactions in di-*n*-butyl ether and over a broad range of temperature.

The initiation step is important because of the direct impact on the balance of chain reactions that precede ignition. Connections between the initial radical pool and ignition are described cogently in the theoretical calculations of Ji et al. (Ji et al., 2016) for alkyl radical oxidation in the context of identifying turnover states, i.e. the inflection point in the negative-temperature coefficient (NTC) region near the high-temperature regime where ignition times exhibit a local maximum. In addition, site-specific initiation reactions often appear in sensitivity analysis, such as in Jacobs et al. (Jacobs et al., 2019) for dimethoxymethane, Vranckx et al. (Vranckx et al., 2011) for 1-butanol, Burke et al. (Burke et al., 2016) for butanone, among others. The present work expands on the basic concept that bridges an initial radical pool of arbitrary composition, e.g. $\dot{\text{R}}$, $\text{RO}\dot{\text{O}}$, and $\dot{\text{Q}}\text{OOH}$ as in Ji et al. (Ji et al., 2016), with the dynamics that subsequently unfold and lead to ignition. Specifically, the dependence of ignition predictions on branching fractions of the initiation step is examined quantitatively using several sets of rate parameters for $\dot{\text{O}}\text{H} + \text{RH} \rightarrow \text{H}_2\text{O} + \dot{\text{R}}$ where total rate coefficients agree, yet site-specific rate coefficients differ.

To examine the influence of branching fractions on ignition delay times, a series of ChemKin simulations was conducted for 1-butanol, cyclopentanone, and methyl propanoate. For all three species, recent chemical kinetics mechanisms were utilized to produce an initial, baseline set of simulations. Additional ignition simulations were then conducted using all available sets of site-specific rate coefficients from the literature for OH -initiated H-abstraction, which effectively alters the branching fractions of the initiation step.

The most pronounced effects were observed for 1-butanol. As a result, additional simulations were conducted to examine the underlying details. First, to complement the simulations where branching fractions were varied, additional ignition simulations were conducted to account for uncertainties in the rate coefficients in order to quantify the impact on the model predictions. Second, rate-of-production and sensitivity analysis simulations were conducted to assess the impact on reactions involving $\dot{\text{O}}\text{H}$ from changing the branching fractions. Third,

TABLE 1 | Chemical kinetics mechanisms used for ignition delay time simulations.

Species	Mechanism
1-butanol	Sarathy et al. Sarathy et al. (2012)
cyclopentanone	Thion et al. Thion et al. (2016), Zhang et al. Zhang et al. (2019)
methyl propanoate	Felsmann et al. Felsmann et al. (2017)

TABLE 2 | References for rate coefficients for $\dot{\text{O}}\text{H}$ -initiated H-abstraction from 1-butanol, cyclopentanone, and methyl propanoate.

Reaction	Reference
$\dot{\text{O}}\text{H} + 1\text{-butanol} \rightarrow \text{H}_2\text{O} + \dot{\text{R}}$	Sarathy et al. Sarathy et al. (2012) Zhou et al. Zhou et al. (2011) Seal et al. Seal et al. (2013) McGillen et al. McGillen et al. (2013)
$\dot{\text{O}}\text{H} + \text{cyclopentanone} \rightarrow \text{H}_2\text{O} + \dot{\text{R}}$	Thion et al. Sarathy et al. (2012) Zhou et al. Zhou et al. (2016)
$\dot{\text{O}}\text{H} + \text{methyl propanoate} \rightarrow \text{H}_2\text{O} + \dot{\text{R}}$	Mendes et al. Mendes et al. (2014) Tan et al. Tan et al. (2016)

species profile simulations were conducted to assess the dependence of species produced from $\dot{\text{R}} + \text{O}_2$ reactions on branching fractions of the initiation step.

The sections below provide an overview of the approach taken for the chemical kinetics modeling, a comparison of branching fractions from several theoretical computations, and the effect of using different site-specific rates for H-abstraction by $\dot{\text{O}}\text{H}$ on ignition predictions. Basic analysis is then applied to provide some clarity on the results, interpreted in the context of the selectivity towards one radical isomer or another produced in the initiation step. Subsequent analysis is also discussed as to what experimental measurements may provide for a more reliable validation assessment to determine the most appropriate set of rate parameters to incorporate in a chemical kinetics mechanism.

Ignition delay time measurements exist for 1-butanol (Vranckx et al., 2011; Weber et al., 2011), cyclopentanone (Zhang et al., 2019), and methyl propanoate (Akih-Kumgeh and Bergthorson, 2011; Zhang et al., 2014; Kumar et al., 2018), and cover a broad range of conditions. For simplicity in examining the basic premise herein, the simulations were restricted to stoichiometric conditions, a pressure of 10 atm, and temperatures from 675–1000 K. Moreover, the objective of the present work is to quantify the effect of differences in branching fraction predictions of the initiation step on ignition delay times—for the specific case when total rate coefficients agree—rather than drawing contrast between mechanisms or proposing revised rate parameters.

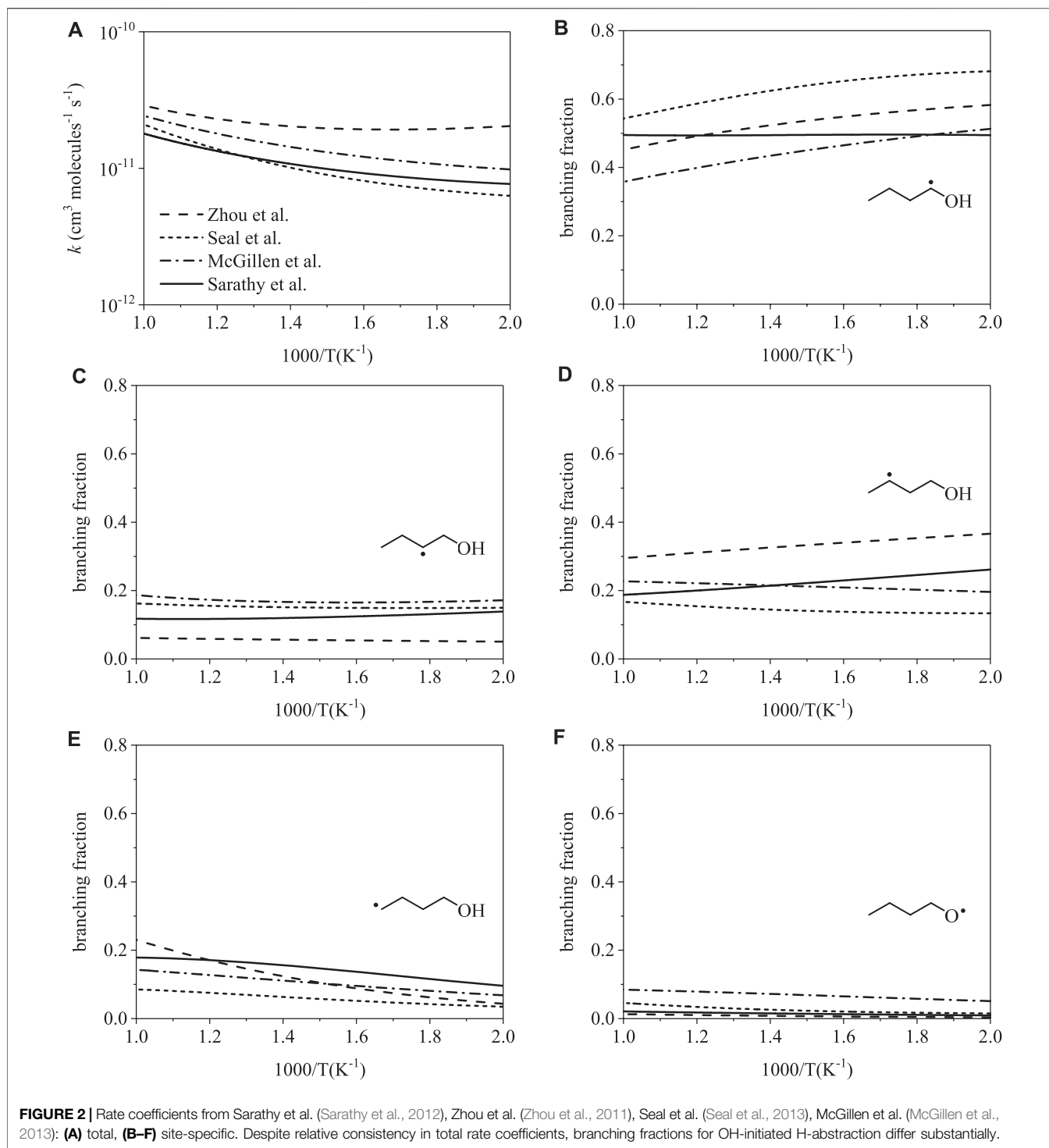
APPROACH

Using ChemKin (v19.0), simulations were conducted using the closed 0-D homogenous batch reactor module to determine ignition delay times under isobaric conditions at 10 atm over a temperature range of 650–1000 K at an equivalence ratio of $\phi = 1$ and with $\sim 76\%$ N_2 to represent practical combustion conditions.

Ignition delay times were defined from the model simulations using $\dot{\text{O}}\text{H}$ time profiles; a representative example is shown in the **Supplemental Material S1**. Ignition delay times were defined as the time where the rate of change in the mole fraction of $\dot{\text{O}}\text{H}$ reaches a local maximum, indicating chain-branching, and times longer than $\sim 1,000$ ms were neglected. **Table 1** lists the chemical kinetics mechanisms used for each species. In the case of cyclopentanone, two mechanisms that contain peroxy radical chemistry exist in the literature. To examine the effects of differing branching fractions for site-specific H-abstractions, initiation steps of $\text{RH} + \dot{\text{O}}\text{H}$ were replaced using all sets of rate parameters available in literature (**Table 2**). Importantly, for 1-butanol and methyl propanoate, the total rate coefficients are similar, yet the site-specific branching fractions differ as discussed in *Chemical Kinetics Modeling*.

In addition to ignition delay time modeling, ChemKin simulations were also conducted on 1-butanol oxidation to examine the effects of differing branching fractions on combustion intermediates. Using the perfectly-stirred reactor module, simulations were conducted under stoichiometric conditions with $\sim 95\%$ N_2 , 0.71% (7,100 ppm) 1-butanol and 4.29% O_2 . The conditions of the simulations were a 2000 ms residence time, pressure of 10 atm, and temperature range of 500–1000 K where peroxy radical chemistry is dominant. Four sets of simulations were conducted using the detailed chemical kinetics mechanism of Sarathy et al. (Sarathy et al., 2012). Subsequent modifications to the Sarathy et al. (Sarathy et al., 2012) mechanism employed site-specific rates for $\dot{\text{O}}\text{H} + 1\text{-butanol} \rightarrow \dot{\text{R}} + \text{H}_2\text{O}$ from Zhou et al. (Zhou et al., 2011), McGillen et al. (McGillen et al., 2013), and Seal et al. (Seal et al., 2013). Vranckx et al. (Vranckx et al., 2011) also developed a mechanism for 1-butanol, yet low-temperature peroxy chemistry is treated with a simplified model that includes a lumped approach for $\dot{\text{Q}}\text{OOH}$ reactions, as opposed to Sarathy et al. (Sarathy et al., 2012) in which radical-specific pathways are defined explicitly.

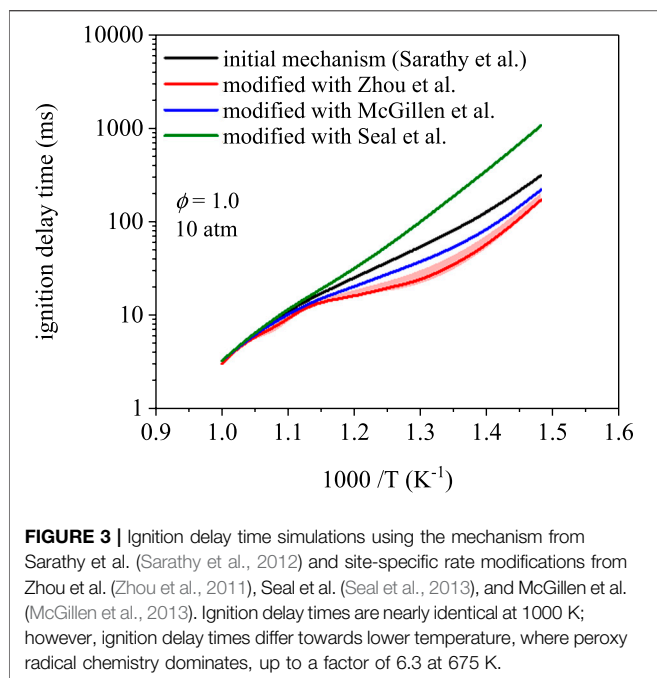
For 1-butanol, simulations were conducted using rate parameters from Zhou et al. (Zhou et al., 2011), McGillen et al. (McGillen et al., 2013), and Seal et al. (Seal et al., 2013) to replace the parameters in the base mechanism of Sarathy et al. (Sarathy et al., 2012). Seal et al. (Seal et al., 2013) utilized a four-parameter non-Arrhenius equation for fitting calculated rates over the temperature range 200–2400 K. To obtain the format necessary for ChemKin, the rates computed in Seal et al. (Seal et al., 2013) were fit to a conventional three-parameter modified Arrhenius equation over the temperature range of 500–1000 K **Supplemental Material S2**. To make the modifications for the cyclopentanone simulations, initiation rates were switched between the two mechanisms, i.e. the Thion et al. (Thion



et al., 2016) modification employed rates from the mechanism of Zhang et al. (Zhang et al., 2019) and vice versa. The Zhang et al. (Zhang et al., 2019) mechanism uses OH-initiation rates from Zhou et al. (Zhou et al., 2016). For methyl propanoate, one modification was made using rates from Mendes et al. (Mendes et al., 2014). The mechanism of Felsmann et al. (Felsmann et al., 2017) uses rates from Tan et al. (Tan et al., 2016). A complete list

of the rate parameters used for each simulation is in **Supplemental Material S3**.

To assess the influence of uncertainty in site-specific rate coefficients on ignition times, simulations were conducted for 1-butanol using the upper and lower bounds provided in Zhou et al. (Zhou et al., 2011), McGillen et al. (McGillen et al., 2013), and Seal et al. (Seal et al., 2013). Zhou et al. (Zhou et al., 2011)



utilized the G3 method for the potential energy surface computations, which inherit an uncertainty of ~ 1 kcal/mol (Curtiss et al., 1998). The rate parameters in McGillen et al. (McGillen et al., 2013) were produced from fits to experimental product yields (Cavalli et al., 2002; Hurley et al., 2009), which were reported with an uncertainty of $\pm 10\%$. Barrier heights in Seal et al. (Seal et al., 2013) were reported with a mean unsigned error of ± 0.28 kcal/mol. All site-specific rate parameters with upper and lower bounds of uncertainties are listed in **Supplemental Material S3** along with a tabulation of the resultant effects on ignition delay times **Supplemental Material S4**.

CHEMICAL KINETICS MODELING

Total rate coefficients and branching fractions for site-specific H-abstraction of each reaction in **Table 2** are compared in the sections below for 1-butanol (*Butanol*), cyclopentanone (*Cyclopentanone*), and methyl propanoate (*Methyl Propanoate*). Subsequently, results from the ignition delay time simulations using modified versions of the mechanisms in **Table 1** are compared. The most salient observation from the results is that variation in branching fractions for $\text{OH} + \text{RH} \rightarrow \text{H}_2\text{O} + \dot{\text{R}}$ leads directly to non-negligible variations in ignition delay times for two species. Significant effects are shown for 1-butanol and moderate effects for methyl propanoate. Conversely, variations are negligible in the branching fractions for cyclopentanone, which resulted in negligible effects on ignition delay times. Consistency in the dependence on branching fractions across the three species underscores the importance of site-specific rate coefficients on accurately predicting ignition delay times, as well as species profiles (*Discussion*).

1-Butanol

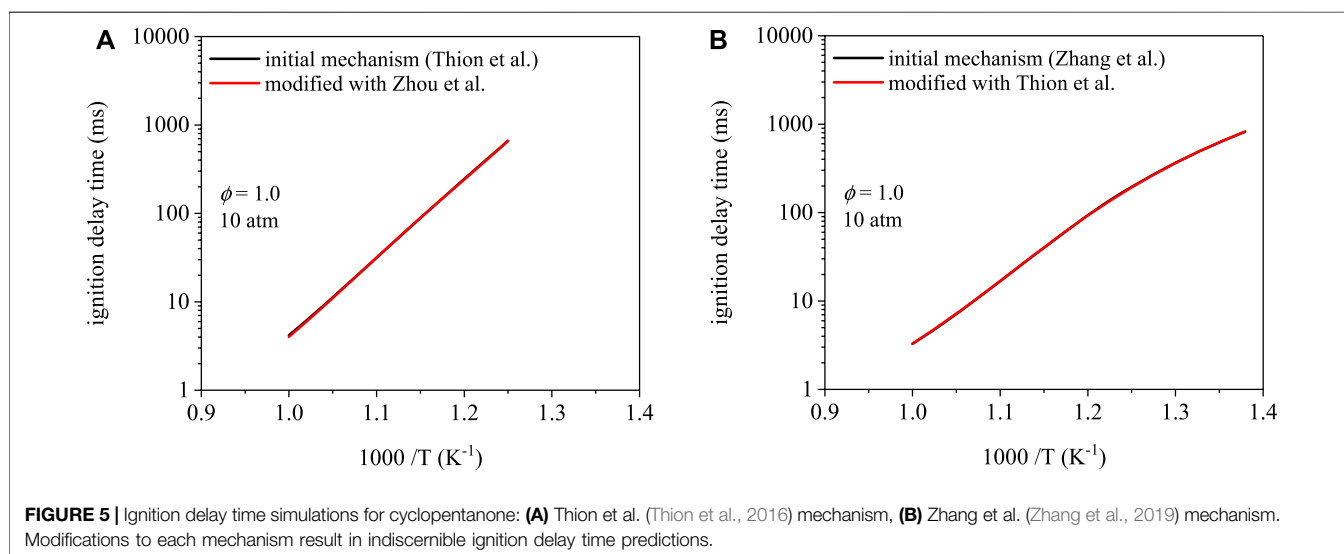
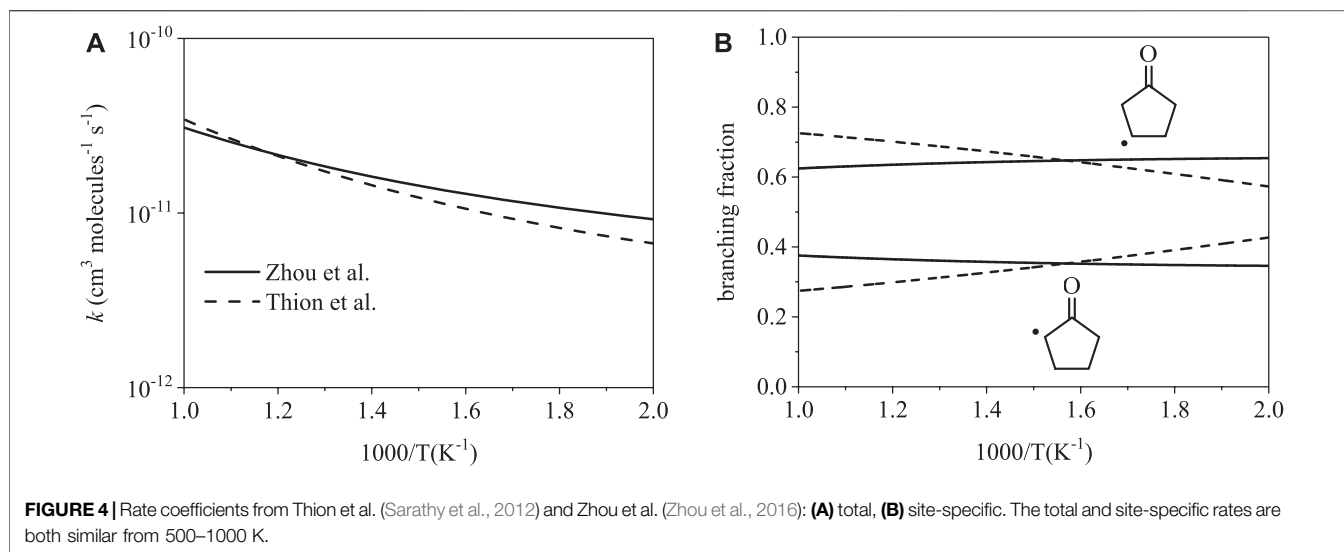
Total rate coefficients for H-abstraction from 1-butanol by hydroxyl are shown in **Figure 2A** from 500 to 1000 K. The largest disparity, occurring at 500 K, is a factor of 3.2 between rates from Seal et al. (Seal et al., 2013) and Zhou et al. (Zhou et al., 2011). At 1000 K, disagreement decreases to a factor of 1.6. Despite the relative agreement in the total rates, site-specific rates vary considerably (**Figure 2B,F**). At 500 K, branching fractions vary up to factors of 1.4 for α radicals, 3.4 for β radicals, 2.7 for γ radicals, 2.7 for δ radicals, and 12.8 for RO radicals. At 1000 K, branching fractions vary up to factors of 1.5 for α radicals, 3.0 for β radicals, 1.8 for γ radicals, 2.7 for δ radicals, and 6.5 for RO radicals. Predictions of branching fractions as a function of temperature vary considerably as well. Branching fractions follow either a weak or strong dependence on temperature, as illustrated in **Figure 2B**, where Sarathy et al. (Sarathy et al., 2012) predicts weak temperature dependence for the α radical while the other three rates do not.

Figure 3 compares ignition delay times as a function of temperature for the mechanism of 1-butanol from Sarathy et al. (Sarathy et al., 2012) and the rate modifications in **Table 2**. Three of the mechanisms predicted 675 K as the first temperature to yield an ignition delay time below 1,000 ms. The modification using rates from Seal et al. (Seal et al., 2013) predicted an ignition delay time of 1,070 ms at 675 K. Disagreement between the four mechanisms is highest at 675 K—a factor of 6.3 difference between predictions using rates from Zhou et al. (Zhou et al., 2011) and Seal et al. (Seal et al., 2013). The predictions converge at 1000 K to ~ 3.2 ms with a maximum difference of 0.20 ms, which indicates that low-temperature chemistry is more sensitive to branching fractions. In addition, for a given mechanism, the effects of uncertainty in site-specific rate coefficients increases towards lower temperatures (**S4**). However, for the simulations in **Figure 3** produced using the modifications, uncertainties in the rate coefficients translated to negligible differences in ignition delay times from 675–1000 K ($< 5\%$ in nearly all cases). The latter observation indicates that uncertainty in branching fractions does not explain the appreciable differences towards lower temperatures, which implies that the composition of the initial radical pool is the main driver.

Cyclopentanone

Total rate coefficients for cyclopentanone initiation by $\dot{\text{O}}\text{H}$ are shown in **Figure 4A**. The two rates are remarkably consistent with one another, with the largest difference being a factor of 1.5 at 500 K. Branching fractions for cyclopentanone are shown in **Figure 4B**. While the difference appears large at the extrema, the branching fractions are similar. Branching fractions reach the largest disagreement of factors of 1.4 and 1.2 at 1000 K for the α radical and β radical respectively. The average disagreement from 500–1000 K is only 1.2 for the α radical and 1.1 for the β radical.

Ignition delay time predictions as a function of temperature are shown in **Figure 5** for cyclopentanone and are mechanism-dependent. The mechanism of Zhang et al. (Zhang et al., 2019) predicts shorter ignition delay times overall. However,

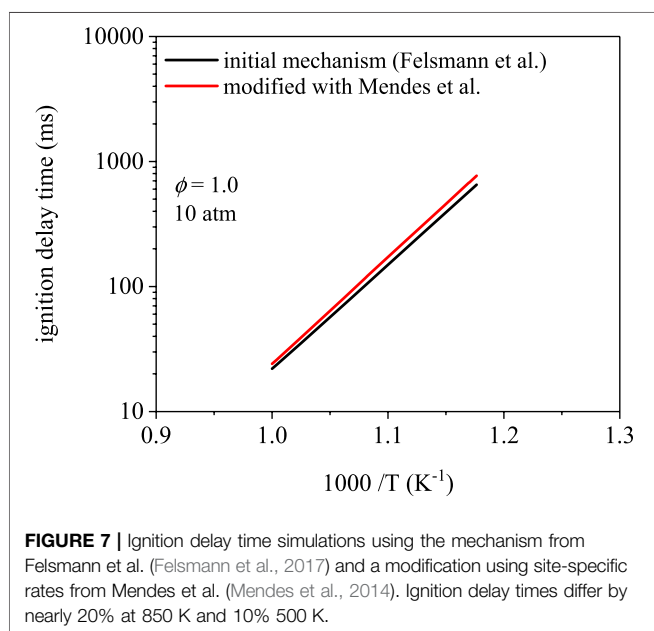
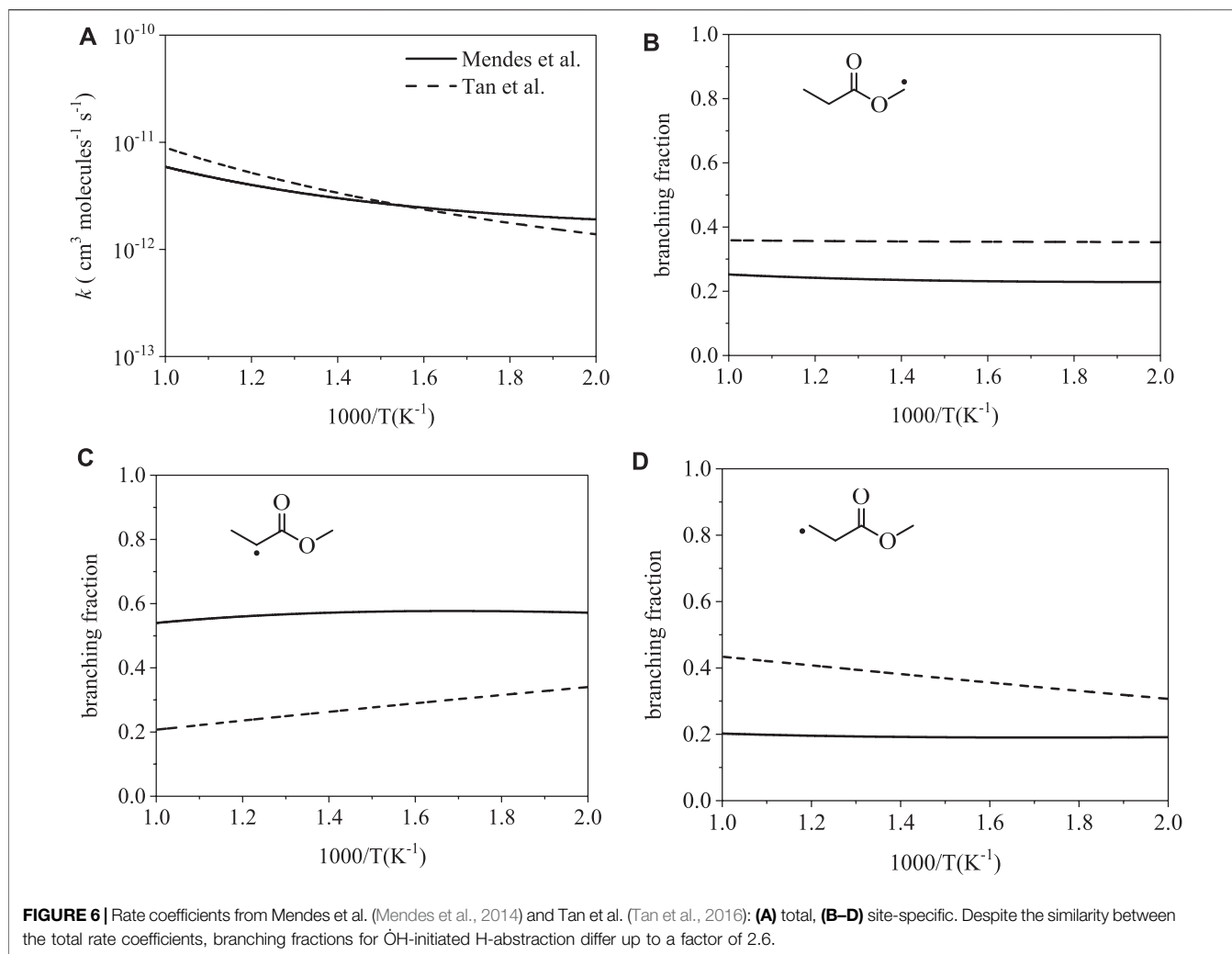


modifications made to each mechanism did not affect ignition delay times. To reiterate, modification to the mechanism of Thion et al. (Thion et al., 2016) involved replacing initiation rate parameters with those from Zhou et al. (Zhou et al., 2016). The Zhang et al. (Zhang et al., 2019) mechanism uses initiation rates from Zhou et al. (Zhou et al., 2016). Modification of the mechanism from Zhang et al. (Zhang et al., 2019) involved replacing its initiation rate parameters with those of the mechanism from Thion et al. (Thion et al., 2016). As shown in **Figures 5A,B**, predictions using the initial and modified mechanism overlap each other. Despite the relative difference in ignition delay times between the two mechanisms, interchanging the initiation rates resulted in no effect on the predictions, which is potentially due to the similarity in branching fractions between the α and β isomers.

Methyl Propanoate

Figure 6A shows total rate coefficients of $\dot{\text{O}}\text{H}$ -initiation for methyl propanoate. The calculations of Mendes et al. (Mendes et al., 2014) and Tan et al. (Tan et al., 2016) are largely consistent; disparities of factors 1.5 and 1.4 occur at 500 and 1000 K. Despite agreement on the total rate coefficient, branching fractions vary significantly: radical isomers α (**Figure 6B**), α' (**Figure 6B**), and β' (**Figure 6C**) differ by factors of up to 1.5, 1.7, and 1.6, respectively, at 500 K and by factors of up to 1.4, 2.6, and 2.1, respectively, at 1000 K. The prime notation (α' and β') is used to indicate abstraction sites on the ethyl group, the carboxylic acid side of the ester, while α is used to indicate the methyl group on the alcohol-derived side of the ester.

Figure 7 shows the ignition delay times for methyl propanoate using the Felsmann et al. (Felsmann et al., 2017) mechanism, which uses rates from Tan et al. (Tan et al., 2016). Low-



temperature chain-branching is limited in methyl propanoate oxidation in part because of resonance-stabilization of the α and α' sites, which inhibits O_2 -addition (Rotavera and Taatjes, 2021). As a result, ignition delay times below 1,000 ms were only observed at temperatures higher than 850 K. Over the temperature range covered, the differences in ignition delay times are within typical experimental uncertainty. The two trends are within 20% at 850 K (651 ms for the initial mechanism, 769 ms for the modification). At higher temperature, the difference decreases to $\sim 10\%$ at 1000 K (22 vs 24 ms).

DISCUSSION

Despite the relative consistency among total rate coefficients, ignition delay times can vary substantially when branching fractions differ. At 675 K, ignition delay time predictions for 1-butanol range from roughly 170–1,070 ms depending on the choice of rate parameters. At 850 K, the lowest temperature included for methyl propanoate, ignition delay times varied

from 651 to 769 ms. As shown for 1-butanol and methyl propanoate, changes in branching fractions clearly affected ignition delay times. Variations of branching fractions led to differences of up to ~20% for methyl propanoate, which is within the typical range of experimental error. Conversely, variations in branching fractions led to differences of over 600% for 1-butanol. The effects were more pronounced for 1-butanol than for methyl propanoate most likely due to the limited role of peroxy radicals in oxidation of the latter species owing to resonance-stabilization of the initial radical. As shown in *1-butanol*, ignition delay time predictions are not always a reflection of differences in the total rate coefficient for 1-butanol, which implies that branching fractions play a significant role in the simulation results.

As shown in **Figure 2B**, Seal et al. (Seal et al., 2013) predicts the largest flux of 1-butanol towards α radicals, and the modification of the Sarathy et al. (Sarathy et al., 2012) mechanism using rates from Seal et al. (Seal et al., 2013) produced the longest ignition delay times in **Figure 3**. As the α isomer exclusively reacts with O_2 in a chain-inhibiting step to form butanal and $HO\dot{O}$, the prediction of higher flux towards the α isomer is consistent with longer ignition delay times as a result of using the Seal et al. (Seal et al., 2013) rates.

Ignition delay time simulations for cyclopentanone provide additional confirmation on the effects of branching fractions on ignition predictions. Within the low-temperature region, branching fractions were remarkably similar, reaching the largest disagreement of factors of 1.4 and 1.2 at 1000 K for the α radical and β radical, respectively. With notable agreement from both the total rate coefficients and the site-specific rate coefficients, both mechanisms yielded nearly identical ignition delay times when rates from Zhou et al. (Zhou et al., 2016) and Thion et al. (Thion et al., 2016) were switched between the mechanisms listed in **Table 1**.

The results herein indicate that branching fractions of $\dot{O}H$ -initiated H-abstraction reactions are of significant importance, which is because each initial radical follows unique oxidation chemistry, some of which directly influences the degree to which low-temperature chain-branching occurs. To the extent that a functional group affects the rate and mechanism of reaction with $\dot{O}H$, branching fractions are potentially most important for molecules in which more distinct sites for H-abstractions exist. As an example, in the present work the disparity between ignition delay times was negligible for cyclopentanone, yet within typical experimental uncertainty in the case of methyl propanoate, and pronounced for 1-butanol.

Accordingly, direct and radical-specific experimental measurements of species profiles are needed to provide benchmark validation targets for site-specific rate coefficients and to bridge the gap in model sensitivity between initiation steps and ignition delay times. Ideally, such targets must form from a specific isomer of the initial radical pool to accurately develop a connection between the predicted yield of that radical, i.e. the calculated branching fraction, and products formed via subsequent oxidation. Species produced via chain-propagation from $\dot{R} + O_2 \rightarrow$ products and $\dot{Q}OOH \rightarrow$ products are examples of validation targets that are often isomer-dependent and may serve

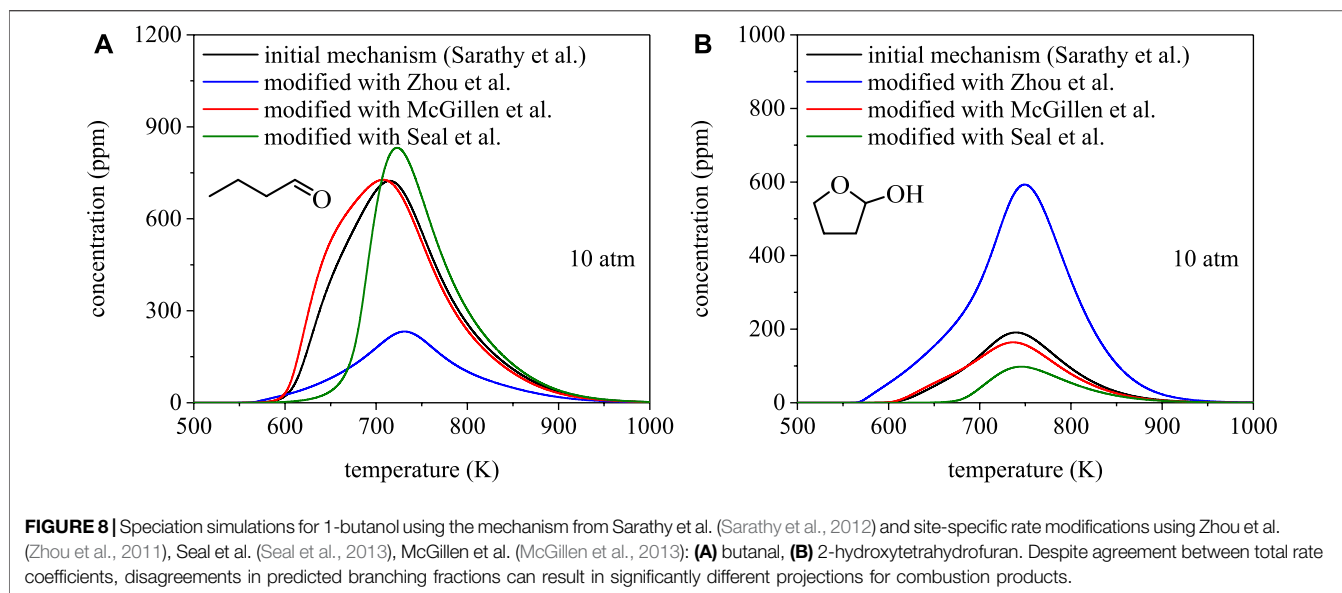
as unique identifiers for determining correct branching fractions to utilize in combustion models.

Validation targets for 1-butanol include butanal, 3-hydroxybutanal, and 2-hydroxytetrahydrofuran, among other species. Because of the impact of the alcohol group, butanal is a validation target exclusively for the α radical isomer of 1-butanol, $CH_3CH_2CH_2\dot{C}HOH$. Similarly, 3-hydroxybutanal is a validation target for the γ radical isomer of 1-butanol, $CH_3\dot{C}HCH_2CH_2OH$. The peroxy radical formed via O_2 -addition, $\gamma-RO\dot{O}$, can isomerize to form $\dot{Q}OOH$ via a favorable six-membered transition state. 2-hydroxytetrahydrofuran is a validation target for the δ isomer of 1-butanol. $\delta-RO\dot{O}$ follows a similar reaction sequence to $\gamma-RO\dot{O}$, yet involving a seven-membered ring transition state to form 2-hydroxytetrahydrofuran.

To illustrate the dependence of species profiles on branching fractions, **Figure 8** shows mole fractions of butanal and 2-hydroxytetrahydrofuran from PSR simulations using the mechanism of Sarathy et al. (Sarathy et al., 2012) and the three mechanism modifications discussed in *Approach*. The PSR module in ChemKin is the most common and appropriate model for simulating steady-state homogeneous reacting systems from which species profiles are measured, e.g. jet-stirred reactors (Herbinet et al., 2013). Despite being a major product of 1-butanol combustion, the predicted yields of butanal from the four simulations vary significantly. Notably, the differences are consistent with the ignition delay time results, in terms of a dependence on branching fractions, and stem from differences in predictions of selectivity towards α radicals. The rates from Seal et al. (Seal et al., 2013) predict the largest branching fraction towards α radicals and, consistent with that result, the simulation in **Figure 8A** produced from modifying the Sarathy et al. (Sarathy et al., 2012) mechanism with the rates from Seal et al. (Seal et al., 2013) predicts the highest yield of butanal.

Cyclic ethers, such as 2-hydroxytetrahydrofuran, are also major chain-propagation products of 1-butanol combustion. As shown in **Figure 8B**, the four simulations predict comparable concentrations of 2-hydroxytetrahydrofuran to butanal and, similarly, the temperature dependence varies with the set of site-specific rate coefficients used in the mechanism. Despite being predicted to form in comparable concentrations to butanal, no experimental measurements of 2-hydroxytetrahydrofuran (or any other OH-substituted cyclic ethers from 1-butanol), exist. The lack of such measurements highlights a need for speciation measurements in order to provide a direct connection to validating site-specific rate coefficients used in biofuel combustion mechanisms to ultimately enable robust ignition delay time predictions.

Rate-of-production calculations **Supplemental Material S5** were conducted on $\dot{O}H$ using each of the four 1-butanol mechanisms at 675 K, the temperature at which the largest observable change occurred. Radical-specific pathways were unchanged despite variations in branching fractions of the initiation step. Instead, changes in the flux towards specific initial radicals only affected the rate of $\dot{O}H$ formation/consumption through a common set of oxidation pathways, which in turn controlled the overall yield of $\dot{O}H$. As reflected



in the ignition delay time trends (cf. **Figure 3**), the Zhou et al. (Zhou et al., 2011) modification yielded the highest net production rate of $\dot{\text{O}}\text{H}$ ($\sim 10^{-2} \text{ mol cm}^{-3} \text{ s}^{-1}$) at the predicted ignition time, 170 ms, while the Seal et al. (Seal et al., 2013) modification produced the lowest ($\sim 10^{-12} \text{ mol cm}^{-3} \text{ s}^{-1}$) at the predicted ignition time, 1,070 ms. The only outlier is the dissociation reaction $\dot{\text{O}}\text{H} + \text{M} \rightarrow \ddot{\text{O}} + \dot{\text{H}} + \text{M}$ in the modification using the Seal et al. (Seal et al., 2013) rate parameters **Supplemental Material S5**, which replaces $\text{CH}_2\text{O} + \dot{\text{O}}\text{H} \rightarrow \text{HCO} + \text{H}_2\text{O}$ that appears in the results using the other mechanisms. However, the predicted rate of dissociation is the lowest of the ten reactions for $\dot{\text{O}}\text{H}$.

Sensitivity analysis calculations were also conducted to determine the ten reactions to which $\dot{\text{O}}\text{H}$ is most sensitive **Supplemental Material S6**. The reactions are mostly categorized into five classes: initiation/H-abstraction, first- O_2 -addition, second- O_2 -addition, $\text{ROO} \rightarrow \text{QOOH}$ isomerization, or HOO -elimination. The relative importance of one reaction over another varies depending on the mechanism and no clear trend is apparent. However, the dominance of peroxy radical chemistry mediating $\dot{\text{O}}\text{H}$ underscores the role that isomer-resolved speciation measurements may play in identifying proper branching fractions of initial radical isomers.

CONCLUSION

Several sets of ignition delay times simulations were conducted at 10 atm for 1-butanol, cyclopentanone, and methyl propanoate using recent combustion mechanisms in the literature. Results were produced from the initial, unmodified mechanisms, followed by additional simulations wherein site-specific rates for $\dot{\text{O}}\text{H}$ -initiated H-abstraction were replaced in each mechanism using rates from the literature. The main objective of the simulations was to determine the impact of varying branching fractions in the initiation step on ignition delay time simulations for the specific case when total rate coefficients agree.

For both 1-butanol and methyl propanoate, branching fractions in the literature vary non-negligibly and, when incorporated into chemical kinetics mechanisms, led to appreciable differences in ignition delay times below 1000 K for 1-butanol. Relatively minor differences were shown for methyl propanoate predictions. Conversely, site-specific abstraction rates for $\dot{\text{O}}\text{H} + \text{cyclopentanone} \rightarrow \dot{\text{R}} + \text{H}_2\text{O}$ are similar and ignition delay time predictions show no dependence on the choice of rates. In the case of 1-butanol, for which multiple rate coefficient studies exist, no significant effects on ignition delay time predictions were observed from uncertainties in the site-specific rate coefficients.

The effects of varying branching fractions were analyzed on three different biofuels for which multiple sets of rate coefficients are available along with detailed chemical kinetics mechanisms that include peroxy radical chemistry. Incidentally, for the present conditions, none of the three biofuels exhibit significant NTC behavior. The dependence of ignition predictions on branching fractions shown herein may also apply in a more general sense to biofuels that undergo NTC behavior, such as diethyl ether, 2-pentanone, or 3-pentanone. To more accurately model combustion of biofuels at low temperature, more stringent and direct validation targets are needed to determine proper branching fractions for initiation reactions. One example of such a target are speciation profiles that provide a direct connection to quantifying isomer-dependent products of combustion reactions, particularly $\dot{\text{R}} + \text{O}_2 \rightarrow \text{products}$ and $\text{QOOH} \rightarrow \text{products}$.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

SH contributed computational modeling, analysis, and manuscript preparation; BR contributed analysis and manuscript review.

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SUPPLEMENTARY MATERIAL

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