

Low-Temperature Ignition and Oxidation Mechanisms of Tetrahydropyran

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Abstract

Cyclic ethers are relevant as next-generation biofuels and are also combustion intermediates that directly follow from unimolecular decomposition of hydroperoxyalkyl radicals. Accordingly, cyclic ether reactions are crucial to understanding low-temperature oxidation for advanced compression-ignition combustion applications where peroxy radicals are central to degenerate chain-branching pathways. Reaction mechanisms relevant to low-temperature ignition of cyclic ethers contain intrinsic complexities due to competing reactions of carbon-centered radicals formed in the initiation step undergoing either reactions with O₂ or ring-opening. To gain insight into mechanisms describing tetrahydropyran combustion, ignition delay time and speciation measurements were conducted. The present work integrates measurements below 1000 K of ignition delay times and species profiles in rapid compression machine experiments from 5 bar – 20 bar, spanning several equivalence ratios, with jet-stirred reactor experiments at 1 bar and stoichiometric conditions to provide the first set of data on tetrahydropyran combustion at temperatures where peroxy radical reactions dominate. The experiments are complemented with the development of the first chemical kinetics mechanism for tetrahydropyran that includes peroxy radical reactions, including O₂-addition to tetrahydropyranyl ($\dot{R}$), HO $\dot{O}$ -elimination from tetrahydropyranylperoxy (RO $\dot{O}$) and hydroperoxytetrahydropyranyl (QOOH), cyclic ether formation, β -scission of QOOH, and ketohydroperoxide formation.

Negative-temperature coefficient (NTC) behavior is exhibited in the experiments and is reflected in the model predictions, which were within experimental uncertainty for several conditions. Disparities between the model predictions and experiments were analyzed via sensitivity analysis to identify contributing factors from elementary reactions. The analyses examine the role of ring-opening products of tetrahydropyranyl and hydroperoxytetrahydropyranyl isomers to identify reaction mechanisms that may contribute to model uncertainties. The detection of 66 species in the JSR experiments indicates that tetrahydropyran undergoes complex reaction networks, which include alkyl radical reactions and aldehyde radical reactions. Primary radicals pentanal-5-yl and butanal-4-yl are derived from ring-opening reactions of tetrahydropyran-1-yl and undergo subsequent decarbonylation to form alkyl radicals that undergo reaction with O₂ and may contribute to chain-branching, in addition to pathways involving tetrahydropyran-derived ketohydroperoxides.

Keywords: cyclic ether, rapid compression machine, peroxy radicals, autoignition, jet-stirred reactor

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Information for Colloquium Chairs and Cochairs, Editors, and Reviewers

1) Novelty and Significance Statement

Novelty:

- We provide the first detailed chemical kinetics model for tetrahydropyran – a cyclic ether biofuel and an intermediate of *n*-alkane oxidation – that includes peroxy-radical chemistry to enable better understanding of low-temperature combustion behavior.
- Our paper provides the first ignition delay time measurements for tetrahydropyran below 1000 K.
- We also provide the first speciation measurements from low-temperature oxidation of tetrahydropyran.
- We expand the state of knowledge on cyclic ether chemistry including ring-opening reactions by uncovering connections to aldehydes and competing reactions channels with O₂.

Significance: This paper brings to light several fundamental kinetics aspects of cyclic ether oxidation, including the role of ring-opening kinetics of R and QOOH radicals, and related impact on ignition chemistry. Our findings are significant as they expand the understanding of the low-temperature chemical kinetics of a novel biofuel. Moreover, the experiments and modeling highlight clear connections of tetrahydropyran combustion to oxidation of radicals common to other fuels including *n*-butane, diethyl ether, and tetrahydrofuran. This is significant because it underscores the value of sub-mechanisms of several classes of species to the development of a detailed mechanism. Lastly, we identify important shortcomings that must be investigated in a future study to improve model accuracy for simulating tetrahydropyran oxidation and similar biofuels for the benefit of increasing the sustainability of the combustion-derived energy for the transportation sector.

2) Author Contributions

- SH: Writing/Draft, Methodology, Measurements, Modeling, Formal Analysis
- MS: Measurements, Modeling, Formal Analysis
- MP: Measurements, Formal Analysis
- RM: Measurements, Formal Analysis
- ND: Measurements
- AH: Measurements
- GV: Methodology, Writing/Editing
- YF: Kinetic Model Development, Writing/Editing
- KAH: Methodology, Formal Analysis, Writing/Editing
- BR: Conceptualization, Formal Analysis, Writing/Editing

3) Authors' Preference and Justification for Mode of Presentation at the Symposium

The authors prefer the oral presentation paper (OPP) option at the Symposium, for the following reasons:

1. We highlight fundamental kinetics questions that will spur research activities of experimentalists and theoreticians.
2. Presentation of this work will motivate the community for discussions on new experimental and modeling efforts on dicarbonyls, relevant to cyclic ethers and ketohydroperoxide chemistry.
3. Our paper produces new insight that impacts kinetics modeling approaches toward cyclic ethers.
4. We contribute to three of the four themes of the 40th Symposium: *Combustion Fundamentals*, *Combustion Research Tools*, and *Combustion Impact and Mitigation*. Our paper is not part of a broader set of work requiring extensive background for an engaging presentation.

1. Introduction

Utilization of next-generation biofuels remains of interest for reducing the carbon intensity of the transportation sector. Continuing advances in catalysis create improved synthesis routes for lignocellulosic biofuels, such as tetrahydropyran [1, 2]. Incorporating tetrahydropyran in advanced compression-ignition technologies requires understanding of reaction pathways that describe low-temperature oxidation, which is driven by reactions of carbon-centered radicals ($\dot{R}$) with O_2 that form peroxy radicals ($RO\dot{O}$) and subsequent hydroperoxy-substituted radicals, $\dot{Q}OOH$ (**Fig. 1**). Moreover, because cyclic ether oxidation is complex due to ring-opening reactions [3, 4], detailed understanding relies on both experimental and modeling approaches.

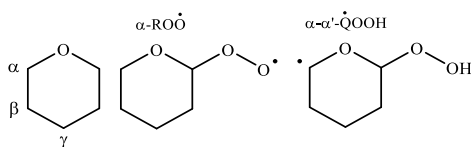


Figure 1: Molecular structures of tetrahydropyran with distinct H-abstraction sites, and example $RO\dot{O}$ and $\dot{Q}OOH$ with notation for peroxy group and localized radical sites.

Several studies on high-temperature combustion of tetrahydropyran are reported. Dagaut et al. [5] measured ignition delay times and species profiles from 800 – 1700 K and generated the first chemical kinetics mechanism. Labbe et al. [6] conducted laminar flame experiments and generated a detailed mechanism drawing analogy to cyclohexane. Tran et al. [7] developed a mechanism to compare to pyrolysis experiments, premixed flame experiments, and shock tube experiments. Despite progress on chemical kinetics mechanisms, however, none include peroxy-radical reactions necessary for describing low-temperature oxidation.

Low-temperature combustion studies of tetrahydropyran are also reported. Rotavera et al. [8] examined the effect of the ether group on chain-terminating reactions using multiplexed-photoionization mass-spectrometry (MPIMS) experiments and theoretical rate calculations. Yields of conjugate alkenes from chain-terminating pathways produced via $\dot{R} + O_2$ reactions were favorable up to ~600 K, yet diminished with increasing temperature due to ring-opening of initial $\dot{R}$ radicals. Chen et al. [9] measured time-dependent yields of $\dot{O}H$ and $HO\dot{O}$ between 500 – 750 K in tetrahydropyran and cyclohexane oxidation using multi-pass near-IR absorption spectroscopy. In addition, the presence of the cyclic ether group created additional pathways to form $\dot{O}H$ and $HO\dot{O}$ from ring-opening of $\dot{R}$ and $\dot{Q}OOH$ radicals. Davis et al. [10] studied the reaction mechanisms of tetrahydropyran and cyclohexane oxidation from 500 – 700 K via MPIMS experiments and theoretical calculations to examine the effect of the cyclic ether

on ketohydroperoxide formation. The cyclic ether group rendered ring-opening reactions more facile, leading to lower ketohydroperoxide yields direct from tetrahydropyran compared to cyclohexane, due to unimolecular decomposition of $\dot{Q}OOH$ that precludes second- O_2 -addition.

The present work provides extensive experimental measurements from multiple apparatus and the development of the first chemical kinetics mechanism for modeling low-temperature combustion of tetrahydropyran. Ignition times are reported for tetrahydropyran at low-temperatures for the first time and are measured in rapid compression machine (RCM) experiments along with time-dependent species profiles. Species profiles are measured in a jet-stirred reactor (JSR) for the first time in the low-temperature regime from 500 – 900 K. Simulations of ignition delay times and species profiles with the new model highlight the impact of the cyclic ether functional group on low-temperature combustion systems through its introduction of favorable ring-opening reactions and, critically, consequent aldehyde chemistry that links the oxidation of tetrahydropyran to the oxidation of 1-propyl and 1-butyl.

2. Experimental and Modeling Approach

The following sections concisely describe the RCM measurements at the RWTH Aachen facility (*Section 2.1*), RCM measurements at the University of Lille facility (*Section 2.2*), JSR measurements at the University of Georgia (*Section 2.3*), and the approach for the development of the chemical kinetics mechanism (*Section 2.4*).

2.1 RCM measurements (Aachen)

Ignition delay times were measured in a single, creviced-piston RCM detailed in Ramalingam et al. [11]. An adjustable endwall allows for variation of the compression ratio and therefore alteration of the end-of-compression (EOC) temperature without altering the bath gas composition (mole fractions in **Table S1a**). The creviced-piston ensures an adiabatic core by suppressing roll-up vortices. Non-reactive pressure traces (located in **S1b**) are measured with a Kistler pressure sensor (6125C-U20) and collected at each condition by replacing O_2 with N_2 . The non-reactive trace allows for a volume profile to be derived to account for facility effects [12]. Overall uncertainties in the EOC conditions are approximately ± 5 K in end of compression temperature (T_c) and $\pm 0.5\%$ in end of compression pressure (P_c) [13]. The ignition delay times, defined as the time between EOC and the highest rate of pressure increase afterwards, were measured for tetrahydropyran at 10 bar and 20 bar using equivalence ratios (ϕ) of 0.5, 1.0, and 2.0, where ϕ is defined as the ratio of tetrahydropyran: O_2 for the actual condition relative to the stoichiometric condition. T_c covered ~600 – 1000 K.

112 2.2 RCM measurements (Lille)

113 Ignition delay times were also measured in a
114 single, creviced-piston RCM with a right-angle design
115 detailed in Mergulhão et al. [14]. The right-angle
116 design maintains the combustion chamber volume
117 constant after EOC and T_C is controlled through
118 changing the bath gas composition (mole fractions in
119 **Table S1c**). From Bourgeois et al. [15], a 45-ms
120 compression time is used in conjunction with the
121 creviced-piston to minimize piston roll-up vortex
122 formation. Pressure traces are measured using a
123 Kistler pressure transducer (6052) and charge
124 amplifier (5018). Uncertainties in T_C and P_C are ± 5 K
125 and ± 0.1 bar respectively. Non-reactive pressure
126 traces are measured through substitution of N_2 for O_2
127 in the bath gas (located in **S1d**). Ignition delay times
128 were measured at stoichiometric conditions for P_C of
129 5, 10, and 15 bar.

130 Time-dependent species profiles are measured by
131 sampling the reactive mixture at different times
132 between the EOC and total ignition, in a series of
133 RCM experiments at the same condition. Sampled
134 gases were quenched via expansion cooling into a
135 heated chamber ~ 40 times the volume of the
136 combustion chamber. Gas-sampling was conducted
137 when EOC conditions were 730 K and 10 bar using a
138 diluted stoichiometric mixture (mole fractions of
139 1.41%, 9.86%, and 88.77% for tetrahydropyran, O_2 ,
140 and N_2 respectively) that led to an extended ignition
141 delay (53.4 ms) against which time is normalized for
142 the reported species concentrations. Following gas
143 chromatographic separation, O_2 and CO are
144 quantified using a thermal conductivity detector
145 (TCD) while all other species are analyzed with a
146 flame ionization detector (FID). The results were
147 corrected from crevice volume dilution as described
148 in [14]. The uncertainty of the measured species mole
149 fractions is $\pm 10\%$ for calibrated species with TCD and
150 FID, and $\pm 20\%$ for species quantified using the
151 effective carbon number with FID [16].

153 2.3 JSR measurements – (Georgia)

154 Species profiles were measured using a 33.5 cm³
155 jet-stirred reactor following the design in Dagaut et al.
156 [17] described in Hartness et al. [18] and Koritzke et
157 al. [19]. Thermal-based mass flow controllers deliver
158 O_2 and N_2 to the reactor. Gas-phase tetrahydropyran
159 is delivered with N_2 through a separate capillary by a
160 temperature-programmed vapor delivery system
161 maintained at 60 ± 1 °C, which uses a Coriolis liquid
162 flow controller. Experiments were conducted at a
163 residence time of 4.0 ± 0.1 s and covered 500 – 900 K
164 in 25 K increments at stoichiometric conditions.
165 Reactor pressure was maintained at 835 ± 4 Torr via
166 PID control. The concentrations of tetrahydropyran
167 and oxygen were maintained at 0.5% and 3.5% by
168 volume with N_2 as the balance.

169 Temperature gradients, measured across the
170 ~ 3.2 cm reactor centerline with a K-type
171 thermocouple, are at most $\pm 0.8\%$ of the nominal
172 temperature due to PID control of four heating plates.

173 Sampling occurs through a quartz sonic probe,
174 positioned at 1.5 cm from the center of the reactor that
175 quenches the sample and sends cooled extracted gases
176 into a quartz cell via inert-coated lines maintained at
177 70 °C. The quartz cell is connected to an inert-coated
178 compression cell maintained at 70 °C which supplies
179 the gases to a GC.

180 H_2 , O_2 , CO, CH_4 , and CO_2 are quantified via
181 packed column separation and a TCD. The remaining
182 gas is split into two equal volumes and injected onto
183 separate, identical columns that follow the same
184 temperature programming, one leading to a 70-eV
185 electron-impact ionization mass spectrometer (EI-
186 MS) and the other to a vacuum-ultraviolet absorption
187 cell (VUV) maintained at 110 ± 1 °C and 800 ± 8 Torr.

188 Reference measurements are conducted on
189 calibration mixtures produced manometrically,
190 typically at 500 ppm, and injected onto the GC
191 columns leading to the EI-MS and VUV detectors
192 along with a 1% N_2O internal standard. MS and VUV
193 spectra for all species are in **S2**. The use of the two
194 detectors in tandem with GC allows for cross-
195 validation of species quantification, at concentrations
196 as low as 1 ppm, via several methods explained in **S3**
197 and for identification of stereoisomers and
198 constitutional isomers. Uncertainties in
199 concentrations were calculated by species from repeat
200 experiments and are $<10\%$ except in the case of
201 pentanediol (**S3**). The method used to measure a
202 reference spectrum for pentanediol relied on injection
203 of an aqueous pentanediol solution into the GC. The
204 variance between the reference spectra was $\sim 7\%$. The
205 calculated experimental uncertainty is $\pm 20\%$ on
206 average when comparing repeat experiments, likely
207 due to the low vapor pressure (~ 15 mTorr at 20 °C).

209 2.4 chemical kinetics mechanism development

210 Unimolecular reactions, H-abstraction, and β -
211 scission reactions and corresponding rate parameters
212 from Tran et al. [7] were utilized along with some
213 modifications (*vide infra*) and integrated into a base
214 mechanism, NUIGmech1.1 [20]. H-abstraction
215 reactions by $\dot{O}H$ from Tran et al. [7], which were
216 developed using the correlation of Dean and Bozzelli
217 [21], were adopted. H-abstraction reactions by $HO\dot{O}$
218 are of moderate sensitivity in high-temperature
219 experiments, as in Tran et al. [7], yet are of elevated
220 importance at low-to-intermediate temperatures for
221 tetrahydropyran oxidation, where $HO\dot{O}$ production
222 and H-abstraction are more facile due to the cyclic
223 ether group [8, 9]. The rate coefficient measured for
224 $HO\dot{O}$ + cyclohexane [22] was adopted. The activation
225 energy is decreased by 1.5 kcal·mol⁻¹ for abstraction
226 of hydrogen from the α -position of tetrahydropyran,
227 which yields the radical $\alpha\text{-}\dot{R}$ (cf. **Fig. 1**), to account
228 for the effects of the cyclic ether group. As $\alpha\text{-}\dot{R}$ is the
229 most abundant tetrahydropyranyl isomer, β -scission
230 reactions were updated following theoretical
231 calculations in Rotavera et al. [8]. Given the absence
232 of rate coefficients for tetrahydropyranyl reactions, $\dot{R}$
233 + O_2 rate parameters for cyclohexyl + O_2 [23] were

234 adopted because of the similarity in the number of
 235 conformers and related axial and equatorial hydrogen
 236 atoms. Other reaction classes considered to describe
 237 low-temperature combustion are similar to alkanes
 238 [24]. To account for the existence of the three R
 239 isomers for tetrahydropyran, pre-exponential factors
 240 for $\text{R} + \text{O}_2$ were lowered by a factor of ~ 3 for each
 241 such that the total rate of $\text{R} + \text{O}_2$ is similar to Zou et
 242 al. [23]. Pre-exponential factors for isomerization
 243 reactions of ROO into QOOH were divided by a factor
 244 of 2 compared to analogous reactions of
 245 cyclohexylperoxy [23]. In addition, elementary
 246 reactions of the conjugate alkene isomers were
 247 defined in detail following the approach for pentene
 248 isomers in NUIGmech1.1 where the most influential
 249 reactions were OH-addition to the C=C bond, the
 250 Waddington mechanism, hydroxy-alkylperoxy
 251 radical reactions, HOO -addition to allylic radicals,
 252 and alkenyl-peroxy radical reactions. Polynomial
 253 coefficients for thermodynamic properties of species
 254 related to tetrahydropyran that are absent in Tran et al.
 255 [7] were estimated via group additivity using reaction
 256 mechanism generator (RMG) [25, 26]. Mechanism
 257 files and a species glossary are in S4.

258 3. Results

259
 260 The following sections describe the ignition delay
 261 time measurements (Section 3.1) at 10 bar and 20 bar
 262 for lean and stoichiometric conditions along with
 263 RCM-measured species profiles (Section 3.2). JSR
 264 species profiles (Section 3.3) are described at
 265 stoichiometric conditions from 500 – 900 K.
 266 Modeling predictions for ignition delay times and
 267 species profiles are included throughout. Sensitivity
 268 analysis at the time of ignition is also included to
 269 investigate model discrepancies.

270 Section 3.1 – ignition delay times

271 **Figure 2a** compares ignition delay times of
 272 tetrahydropyran measured at stoichiometric
 273 conditions between 5 bar and 20 bar. The raw,
 274 unaveraged data for the ignition delay time
 275 measurements are in S1 along with measurements at
 276 other conditions that highlight repeatability in the
 277 experiments. Starting around 700 K, NTC behavior is
 278 observed at both 5 bar and 10 bar noted from the non-
 279 linear trend in the logarithm of ignition delay times
 280 with increasing temperature. The model captures
 281 trends qualitatively in **Fig. 2a**, yet shows quantitative
 282 discrepancies below 700 K for 5 bar and 10 bar, where
 283 total ignition delay times are overpredicted. First stage
 284 ignitions are overpredicted at 5 bar, yet are
 285 reproduced more accurately at 10 bar. In the same
 286 temperature region at 20 bar, however, the model
 287 predicts ignition at stoichiometric conditions within
 288 experimental uncertainty. The NTC behavior is
 289 exaggerated in the experiments at the lower
 290 equivalence ratio (**Fig. 2b**), which coincides with
 291 more pronounced discrepancies in the model between
 292 770 K and 900 K. The model predictions of ignition
 293 770 K and 900 K. The model predictions of ignition
 294 are consistent with the experiments below 730 K at

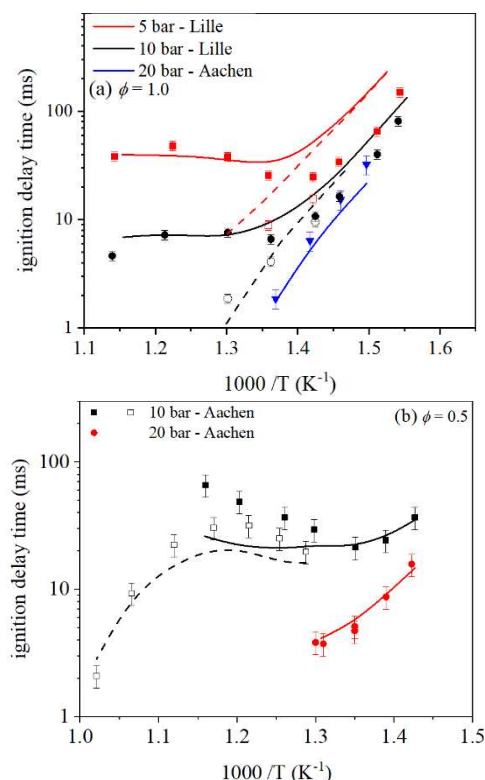


Figure 2. (a) Stoichiometric ignition delay times at 5 bar and 10 bar (Lille), and 20 bar (Aachen); hollow points and experiments denote first-stage ignition. (b) Lean ignition delay times at 10 bar and 20 bar; open symbols and dashed lines denote experiments where Ar is present in the bath gas.

295 lean conditions for 10 bar and 20 bar, yet are shorter
 296 in the NTC region; the opposite discrepancy is
 297 observed at stoichiometric conditions. Model
 298 discrepancies reach a factor of up to ~ 2.5 near 860 K
 299 for lean conditions at 10 bar (**Fig. 2b**).

300 Section 3.2 –RCM species profiles

301 Species profiles (S5) for 14 intermediates were
 302 measured in the Lille RCM. The time profile for
 303 tetrahydropyran is in **Fig. 3**. The conjugate alkenes of
 304 tetrahydropyran, produced by HOO -elimination from
 305 QOOH or by chain-terminating reactions of ROO
 306 isomers [8], and propene, which may arise from
 307 several pathways, including β -scission reactions of
 308 radicals formed via ring-opening, are also in **Fig. 3**.
 309 The model qualitatively reproduces the
 310 tetrahydropyran profile, yet predicts higher
 311 consumption rates after the normalized time of ~ 0.50 .
 312 The shape of the time profiles of the alkene
 313 intermediates are similar, yet are not well captured by
 314 the model, quantitatively. For example, the
 315 concentration of 3,4-dihydro-2H-pyran decreases at a
 316 normalized time of 0.50 in the experiment versus 0.25
 317 in the model. The amount of 3,4-dihydro-2H-pyran
 318 formed at the inflection points are, however,
 319 comparable between the experiment and model with

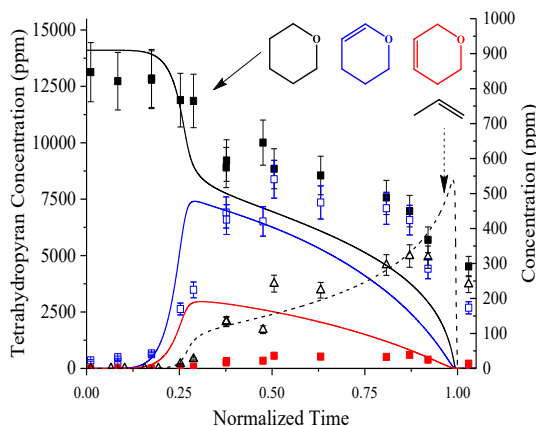


Figure 3: Species time profiles for tetrahydropyran (solid black), 3,4-dihydro-2H-pyran (blue), 3,6-dihydro-2H-pyran (red), and propene (dashed black and hollow triangles) collected from RCM measurements. Time is normalized to the ignition delay time of 53.4 ms at sampling conditions.

concentrations of 540 ppm and 480 ppm respectively. In contrast, 3,6-dihydro-2H-pyran concentrations are overestimated up to a factor of 5. The concentration of propene follows a different time profile than the conjugate alkenes of tetrahydropyran and is well-captured by the model.

Section 3.3 – JSR Species Profiles

Analysis of tetrahydropyran oxidation resulted in the detection of 66 species, 30 of which were quantified and 7 were identified qualitatively (S6). Mass spectra for unidentified intermediates include several which are of parent m/z 98 and m/z 100, and are likely connected to QOOH-mediated pathways (S6). In addition, species were detected in the narrow temperature range of $\sim 575 - 625$ K, which coincides with ketohydroperoxide formation [10]. From analysis of VUV spectra and mass spectra, 2-methyl-1,3-dioxolane and propyl formate were identified. The formation mechanisms are unclear, yet the temperature profile and molecular structures may arise from second- O_2 -addition reactions or decomposition products of ketohydroperoxides (S6). Species profiles for the 30 quantified intermediates are in S7. The following describes the temperature dependence of intermediates in three sections: tetrahydropyran and conjugate alkene isomers (Section 3.3.1); 1-butyl-derived cyclic ethers (Section 3.3.2); pentanedial and propene (Section 3.3.3).

Section 3.3.1 – tetrahydropyran, alkene isomers

The temperature dependence of tetrahydropyran and conjugate alkenes products, 3,4-dihydro-2H-pyran and 3,6-dihydro-2H-pyran, are in Fig. 4. Clear NTC behavior is exhibited from 600 – 775 K. The trend is reproduced qualitatively by the model, although not quantitatively due as the predictions show increased consumption and a narrower NTC region, which is predicted to end near 725 K. Both

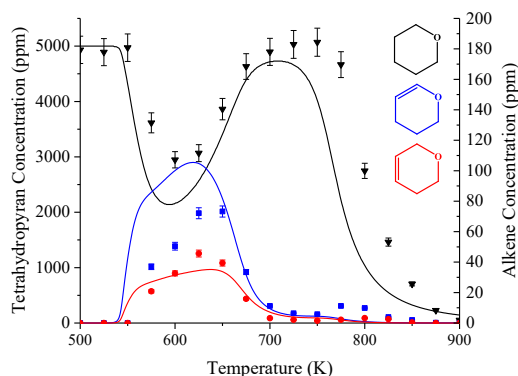


Figure 4: Temperature dependence of tetrahydropyran (black), 3,4-dihydro-2H-pyran (blue), and 3,6-dihydro-2H-pyran (red) at stoichiometric conditions from 500 – 900 K from JSR measurements.

3,4-dihydro-2H-pyran and 3,6-dihydro-2H-pyran reach local maxima in concentration at 625 K and 775 K. Steady-state concentrations of 3,4-dihydro-2H-pyran are higher than that of 3,6-dihydro-2H-pyran, which is consistent with [8]. Prior to the NTC region, the model predicts the magnitude of 3,4-dihydro-2H-pyran and 3,6-dihydro-2H-pyran concentrations within experimental uncertainty (Fig. 4), yet the temperature dependence of the two alkenes is not captured. The model predicts alkene formation at lower temperatures during first-stage ignition and predicts negligible formation in the second stage potentially due to increased rates of tetrahydropyranyl ring-opening reactions.

Section 3.3.2 – 1-butyl-derived cyclic ethers

The cyclic ether group in tetrahydropyran enables ring-opening of α -R into pentanal-5-yl ($H_2C(CH_2)_3C(=O)H$), which undergoes facile isomerization and subsequent decarbonylation to form 1-butyl + CO [10]. No other species that could form from pentanal-5-yl, such as 4-pentenal, were observed. The production of 1-butyl radicals is confirmed by the detection of all three cyclic ethers formed upon reaction with O_2 : 1,2-epoxybutane, 2-methyloxetane, and tetrahydrofuran (Fig. 5).

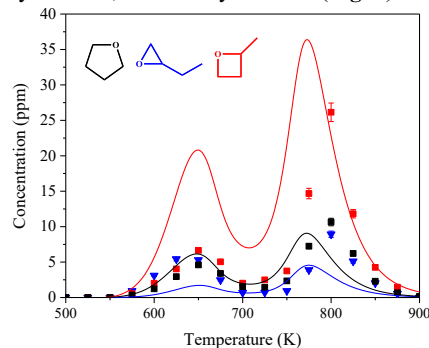


Figure 5: Temperature dependence of 1-butyl-derived cyclic ethers: 1,2-epoxybutane, 2-methyloxetane, and tetrahydrofuran. Modeling results divided by a factor of 10.

The reactions in the model describing the formation and consumption of cyclic ethers comes from the base mechanism, NUIGmech1.1. For all cyclic ethers, the model overpredicts the steady-state concentration by an order of magnitude, which may arise from uncertainties in the preceding reaction steps of tetrahydropyran-1-yl leading to 1-butyl.

Section 3.3.3 – pentanediol and propene

Steady-state concentrations of pentanediol, which forms only from ring-opening of α - α' -QOOH (cf. Fig. 1) and subsequent loss of OH, reaches local maxima at 650 K and 775 K (Fig. 6). Increased flux towards ring-opening of α - α' -QOOH coincides with increasing temperature into the NTC region from 600 – 650 K, which is also observed for the analogous species in tetrahydrofuran oxidation, butanediol [19]. At 700 K, pentanediol concentration reaches a steady-state concentration of ~ 100 ppm, indicating that nearly all of the tetrahydropyran is consumed (cf. Fig. 4) via the chain-propagating pathway. The model incorrectly predicts the temperature dependence of pentanediol, by the 60-K difference in peak concentrations, and quantitatively by a factor of ~ 2.5 . Similar model discrepancies were observed for tetrahydrofuran oxidation for the analogous reaction at nearly the reaction conditions [19].

Figure 6 also shows the temperature dependence of propene, which is qualitatively captured by the model. However, quantitative discrepancies up to a factor of 4 exist below 700 K. Propene is formed at temperatures as low as 575 K, where C–C β -scission reaction rates of 1-butyl to form propene are unfavorable compared to reaction with O₂ (*vide infra*) while a direct pathway from pentanediol exists via successive decarbonylation steps. Additional formation pathways to propene may exist that are not included in the present chemical kinetics mechanism.

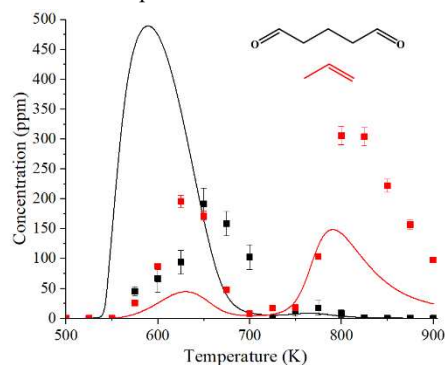


Figure 6: Temperature dependence of pentanediol (black) and propene (red) compared to model predictions (lines).

4. Discussion

The first detailed chemical kinetics mechanism to incorporate peroxy-radical reactions was created and compared with ignition delay time and species profile measurements. Ignition delay times of tetrahydropyran are shorter and demonstrate weaker NTC behavior when compared to cyclohexane

ignition at similar conditions [27]. The difference in ignition delay indicates increased reactivity caused by the presence of the cyclic ether functional group, which is also observed for tetrahydrofuran, 2-methyltetrahydrofuran, and 3-methyltetrahydrofuran when compared to respective alkane analogues [4]. Discrepancies in first-stage ignition predictions of the RCM experiments were observed (Fig. 2) and in the time profiles given the overpredicted consumption of tetrahydropyran near 0.30 on the x-axis in Fig. 3. Disagreements between the model and total ignition delay times were most apparent in the NTC region at lean conditions and 10 bar pressure (Fig. 2), although the same region is captured well by the model at stoichiometric conditions. Sensitivity analysis at the time of ignition was conducted on OH concentration at 825 K and 10 bar for stoichiometric, lean, and RCM sampling conditions (S8). The OH concentration was chosen for the sensitivity analysis given the radical directly reflects the predicted reactivity. In all cases, OH shows positive sensitivity to H-abstraction from tetrahydropyran by OH and HO₂ to form α -R, 1-butyl formation from ring-opening of α -R, and chain-branching reactions stemming from 1-butyl + O₂. In contrast, OH sensitivity is negative for H-abstraction by OH to form β -R, which may undergo ring-opening to form an alkoxy radical via C–O bond-scission along with propagation reactions from 1-butyl to form 2-methyloxetane and 1-butene. To model tetrahydropyran oxidation effectively, the sensitivity analysis highlights the necessity of not only capturing the overall rate for OH + tetrahydropyran $\rightarrow$ products but also accurately capturing the branching fraction for the distribution of initial radicals, which imposes significant effects on ignition delay time simulations for biofuels when total rate constants are similar. As the H-abstraction reaction rates prescribed in the current mechanism are estimates, an important aspect of model improvement is an accurate set of theoretical calculations.

Given the propensity of α -R to undergo ring-opening and form pentanal-5-yl, the connection between tetrahydropyran and *n*-butane oxidation becomes clear and shows that fundamental understanding of peroxy-radical reactions in alkanes is also important for modeling cyclic ether combustion. Branching fractions for H-abstraction from linear aldehydes almost exclusively favor the aldehydic carbon site [28]. In the case of pentanal-5-yl, favorable intramolecular H-transfer forms pentanal-1-yl, which is then most likely to decompose into 1-butyl + CO via decarbonylation [29]. To the extent that O₂-addition to pentanal-5-yl occurs instead, the same reaction mechanism involving intramolecular H-transfer of the aldehydic H-atom to the peroxy group and subsequent decarbonylation may occur and result in hydroperoxy-but-4-yl, which ties directly to the peroxy-radical reactions explaining the oxidation of 1-butyl. No intermediates that arise exclusively from O₂ + pentanal-5-yl, namely 4-pentenal, were observed, which suggests that the

primary consumption pathway for pentanal-5-yl leads to the formation of 1-butyl + CO. Flux through the aldehyde-radical pathway allows for the formation of the three cyclic ether intermediates of 1-butyl (cf. Fig. 5). The model overpredicts concentrations of the cyclic ethers by nearly an order of magnitude, which from Dewey and Rotavera [30] is attributable in part to inadequate description of consumption mechanisms. Uncertainties in the preceding reaction steps leading to 1-butyl likely also contribute to the model discrepancies. Applying the aldehyde-radical pathway to ring-opening of α -tetrahydrofuranyl yields butanal-4-yl and, subsequently, propene + CO [19]. The inclusion of these reactions into the mechanism may reduce the overprediction of tetrahydrofuran concentrations. As the current mechanism is sensitive to chain-branching reactions from 1-butyl oxidation, accurately capturing the profiles for chain-propagating species from 1-butyl is likely crucial to modeling tetrahydropyran.

As evident by the relatively high concentration of pentanediol observed in the JSR experiments, ring-opening of α - α' -QOOH is yet another pathway that is important to accurately model tetrahydropyran oxidation. The current mechanism prescribes pentanediol consumption to occur exclusively through abstraction of one of the two aldehydic H atoms followed by decarbonylation to form butanal-4-yl. Given the experimental conclusion that the primary pathway for pentanal-5-yl consumption is 1-butyl formation, a reasonable expectation is that butanal-4-yl follows the same pathway to yield 1-propyl + CO. However, the latter reaction is not currently prescribed in the mechanism. Oxidation of 1-propyl overwhelmingly favors the formation of propene [31]. JSR experiments appear to corroborate the presence of 1-propyl as propene is observed even at 575 K where C-C β -scission is unfavorable, which could otherwise account for a portion of propene formation. However, at 575 K, the rate of C-C β -scission of 1-propyl is $6.7 \cdot 10^1 \text{ s}^{-1}$ [32, 33] while the pseudo-first-order rate of O_2 addition, assuming a lower limit of $k(T)$ of $10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, is $4.9 \cdot 10^5 \text{ s}^{-1}$ at stoichiometric conditions and 1 atm.

The time profile of propene is captured well during RCM sampling at 10 bar, indicating that the prescribed mechanism for propene formation is more accurate at higher pressures due to the increase in collision frequency facilitating rates of β -scission reactions. The model currently overpredicts the peak concentration of pentanediol and predicts peak temperature of formation 50-K below the JSR experimental trend. Similar to Dewey and Rotavera for cyclic ethers [30], the addition of an accurate consumption mechanism for butanal-4-yl that includes the pathway to 1-propyl may result in more accurate model predictions at lower pressures for both tetrahydrofuran and pentanediol. Such discrepancies in pentanediol predictions are also observed for butanediol in tetrahydrofuran oxidation [19], at almost the exact same combustion conditions, which may

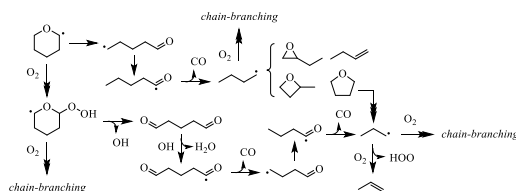


Figure 7: Reaction mechanism describing fate of tetrahydropyran-1-yl ring-opening pathways leading via decarbonylation to 1-butyl and 1-propyl radicals. Subsequent reaction of the alkyl radicals with O_2 may contribute to chain-branching during tetrahydropyran oxidation.

indicate modeling of other biofuels or hydrocarbons might benefit from a similar approach.

Figure 7 summarizes reaction pathways significant to tetrahydropyran combustion, which are elevated in importance due to the favorability of H-abstraction at α sites forming $\dot{\text{R}}$ and analogous reactions for ROO isomerization to QOOH. The ability for α -radicals to ring-open aids in identifying two deficiencies in the current model, which partially account for the discrepancies in predicted ignition delay times. First, ring-opening of α -R creates additional chain-branching pathways from O_2 -addition to QOOH radicals formed from oxidation of 1-butyl [34] and 1-propyl [35, 36]. Accurate modeling of the balance of QOOH-mediated pathways remains important, specifically rates for unimolecular pathways, $\text{QOOH} \rightarrow \text{products}$, relative to rates for bimolecular pathways, $\text{QOOH} + \text{O}_2 \rightarrow \text{products}$. For example, an imbalance in the model predictions of concentrations of cyclic ethers that stem from a lack of consumption mechanisms in the model impacts the flux to chain-propagation. For the case where chain-propagation rates are artificially lower, increased flux toward chain-branching via 1-butyl-derived or 1-propyl-derived QOOH may result. Secondly, the ring-opening step of α - α' -QOOH is chain-propagating, yet the most likely consumption mechanism for the stable co-product, pentanediol, is more complex and may lead to chain-branching via second- O_2 -addition reactions of QOOH derived from 1-propyl [35, 36]. The net effect of the two deficiencies originating from ring-opening is ultimately an increase in the predicted amount of OH and, therefore, increased reactivity (and decreased ignition times).

5. Conclusions

Ignition delay times and species profiles were measured in rapid compression machines from 5 bar – 20 bar, spanning several equivalence ratios. Species profiles were also measured in JSR experiments at 1 bar and stoichiometric conditions, providing the first set of data on the low-temperature combustion of tetrahydropyran. The measurements were then compared against the first chemical kinetics mechanism for tetrahydropyran developed herein that includes peroxy radical reactions. RCM experiments at lean conditions and 10 bar show the largest difference in predicted reactivity from the first-

generation model. Species profiles and sensitivity analysis indicate that direct calculation of rates for abstraction reactions from tetrahydropyran by both $\dot{\text{O}}\text{H}$ and $\text{HO}\dot{\text{O}}$, which are currently estimated from analogy, is required. In addition, rates for competing reactions of tetrahydropyranyl radicals (ring-opening versus O_2 -addition) are also required.

Species profiles from the JSR experiments indicate that $\alpha\text{-}\dot{\text{R}}$ and $\alpha\text{-}\alpha'\text{-}\dot{\text{Q}}\text{OOH}$ are major radicals and highly susceptible to ring-opening due to the cyclic ether group. Ring-opening reactions lead to aldehyde radical reactions becoming influential, particularly decarbonylation, which connects the combustion of tetrahydropyran to alkyl radicals – because 1-butyl and 1-propyl consumption may contribute to the chain-branching sequence of tetrahydropyran. In aggregate, multiple direct and indirect ketohydroperoxide channels may contribute to chain-branching during tetrahydropyran oxidation. Understanding the balance between ring-opening and oxygen addition to both $\dot{\text{R}}$ and $\dot{\text{Q}}\text{OOH}$ is therefore critical. In addition to prescribing accurate rates for intermediate formation and related thermochemical properties, the addition of detailed consumption mechanisms for the combustion intermediates, such as pentanedial and the conjugate alkene isomers, is also important.

626

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646 Supplementary material

- 647 S1 – Mole Fractions and Ignition Delay Times
- 648 S2 – Mass and Absorbance Reference Spectra
- 649 S3 – Quantification Methods for JSR Experiments
- 650 S4 – Kinetics Model Glossary
- 651 S5 – RCM Sampling Species Profiles
- 652 S6 – Extra Information for Observed JSR Products
- 653 S7 – JSR Species Profiles
- 654 S8 – Sensitivity Analysis Results

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