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Full-Length Article

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Abstract:

Cyclopentane (C_5H_{10}) and tetrahydrofuran (C_4H_8O) are both 5-membered ring compounds. The present study compares the auto-ignition of cyclopentane and tetrahydrofuran in a high-pressure shock-tube (20 atm). 12 different mixtures were investigated at two different fuel initial mole fractions (1% and 2%): at X_{fuel} = 1%, three equivalence ratios, kept constant between cyclopentane and tetrahydrofuran, were studied (0.5, 1, and 2), whereas three X_{fuel}/X_{O2} were investigated when X_{fuel} = 2%. A detailed kinetic mechanism was developed to reproduce cyclopentane and tetrahydrofuran auto-ignition. The agreement between our experimental results and the modeling is very good. This mechanism was used to explain the similarities and differences observed between cyclopentane and tetrahydrofuran auto-ignition.

Keywords: Ignition delay time; shock tube; cyclopentane; tetrahydrofuran; kinetic mechanism

1. Introduction

Cyclopentane (CPT) is one of the simplest cycloalkanes with five membered carbon ring, which has high-octane and knock-resistant characteristics, and it is commonly found in commercial gasoline [1]. Nowadays, the shift from fossil fuels to bio-fuels is an interesting project for decreasing the dependence of petroleum-based fuels, and limiting the total CO_2 emission. Tetrahydrofuran (THF) is a saturated cyclic ether compound, and has been shown to be as a promising bio-fuel for internal combustion engines [2–4]. THF has a lower heating value (30.96 MJ L^{-1}) [3,4] which is close to that of CPT (33.50 MJ L^{-1}) [5], both are in the vicinity of that of gasoline (~31.60 MJ L^{-1}) [2]. As seen in Figure 1, molecular structures of CPT and THF are similar excluding the oxygen heteroatom in THF ring. Therefore, it is critical to compare the ignition kinetics of these two molecules.

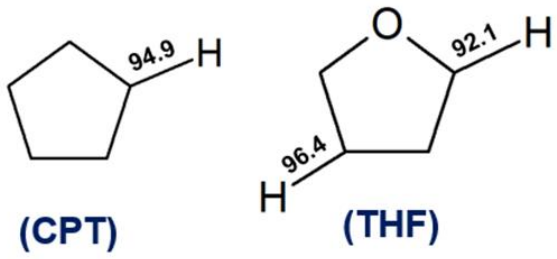


Figure 1: Structures of CPT and THF with bond dissociation energies (in kcal mol^{-1}) calculated using ALFABET webtool [6].

The main numerical and experimental studies on CPT and THF auto-ignition in shock tubes are summarized in Table 1.

Table 1: Main studies of the combustion of CPT and THF in shock tubes

Reference	Fuel	Composition	Conditions
Orme et *al.*[7]	CPT	1% CPT/O_2/Ar φ = 0.577 – 2.0	P_5 = 1 atm T_5 = 1370 – 1820 K

Sajid et *al.* [8]	CPT	1% CPT/O_2/Ar φ = 2.0 1.38 – 5.30 % CPT/Air φ = 0.5 – 2.0	P_5 = 10, 20 and 40 atm T_5 = 900 – 1650 K
Al Rashidi et *al.*[9]	CPT	1.4 – 5.4 % CPT/Air φ = 0.5 – 2.0	P_5 = 20 and 40 bar T_5 = 920 – 1320 K
Dagaut et *al.* [10]	THF	0.5, 1% THF/O_2/Ar φ = 0.5 – 2.0	P_5 = 2.5, 3.5 and 5 bar T_5 = 1000 – 1800 K
Uygun et *al.* [11]	THF	THF/Air φ = 1.0	P_5 = 20 and 40 bar T_5 = 691 – 1100 K
Fenard et *al*. [12]	THF	THF/O_2/Inert mixture (N_2, Ar) φ = 1.0	P_5 = 0.64, 0.77, 0.91 MPa T_5 = 691 – 1100 K
Tran et *al*. [2]	THF	0.25, 0.5, 1% THF/O_2/Ar φ = 0.5 – 2.0	P_5 = 811 – 932 kPa T_5 = 691 – 1100 K

Many studies focusing on the comparison of the autoignition of cyclopentane with other hydrocarbons have been reported in the literature [13–16]. Sirjean et *al*. [13] measured the ignition delay times of CPT/oxygen/argon and cyclohexane/oxygen/argon mixtures in a shock tube, these mixtures contained 0.5 or 1% of fuel with equivalence ratios ranging from 0.5 to 2.0. Temperatures and pressures behind the reflected shock waves were between 7.3–9.5 atm and 1230–1840 K, respectively. These experimental data showed that the reactivity of CPT was much lower than that of cyclohexane. Authors explained this observation by the difference of stability of the corresponding cycloalkyl radicals. Ignition delay times of CPT/air and cyclohexane/air mixtures were measured by Daley et *al.*[14] in a shock tube at pressure of 11–61 atm, between 847–1379 K, and with equivalence ratios of 0.25, 0.5, 1.0. The comparison of the reactivity between CPT and cyclohexane in this study was similar to

that observed in the study of Sirjean et *al*.[13]. Tian et *al*.[15] measured ignition delay times of 1% cyclopentane/O_2/ and 0.833% methylcyclopentane/O_2 mixtures diluted in argon behind reflected shock waves at 1.1 and 10 atm, between 1150 to 1850 K and with equivalence ratios of 0.577, 1 and 2.0. Their experimental results showed that ignition delay time of cyclopentane is longer than that of methylcylopentane, especially for the fuel-lean mixture. This observation was explained by the presence of the methyl group, which weakened the C-C bonds of the cycle, and favored the unimolecular decomposition of methylcyclopentane. Lokhachari et *al*. [16] investigated the impact of dimethyl ether on the ignition delay time of CPT in a shock tube and a rapid compression machine. A temperature range of 650–1350 K at elevated pressures of 20 and 40 bar for two mixtures (30/70 and 70/30%mol cyclopentane/dimethyl ether mixture) in air were studied at equivalence ratios of 0.5, 1.0 and 2.0. The blending of dimethyl ether to CPT increased the reactivity of the mixture at relatively lower temperatures (650–1000 K), while the reactivity was very similar at high temperatures (1000–1350 K). A detailed kinetic mechanism was developed to validate the experimental results.

Based on this literature review, the comparison of the auto-ignition of cyclopentane and tetrahydrofuran has never been investigated before. Therefore, this study aims at comparing the ignition delay times of CPT/O_2/Ar and THF/O_2/Ar mixtures at a pressure of 20 atm, equivalence ratios ranging from lean to rich conditions (0.5, 1.0, 2.0) and with X_{fuel}/X_{O2} ratios of 0.08, 0.16, 0.32. A detailed kinetic mechanism describing the oxidation of CPT and THF is used in order to explain the observed differences and similarities in terms of the ignition behaviors between CPT and THF.

2. Experiment methods

2.1. Mixture preparation

The 12 tested mixtures of CPT/O_2/Ar and THF/O_2/Ar reported in Table 2 were prepared into two stainless-steel tanks (T1 and T2 in Figure 2) based on the partial pressure method, and left to homogenize for at least 3 hours. The liquid fuels CPT with a purity of 98% and THF with a purity of 99.9% were provided by Sigma-Aldrich. High purity gases dioxygen and argon were delivered by Air-Liquide.

Two stainless-steel tanks are connected to the tube and vacuum system (a roughing pump and a turbo-molecular pump) through a manifold. To avoid any contamination, the vacuum system pumps down the tanks below 3 Pa prior to mixture preparation. The partial pressure of fuel in the stainless-steel tanks was 50 mbar for the case of 1% of fuel in the mixture and 100 mbar for 2% of fuel. Thus, in order to avoid any condensation of the fuels, the tanks and the manifold were heated up to 40-50 °C to allow the partial pressures of CPT and THF to be at least four times lower than their vapor pressures [17]. For sake of comparison, the choice was made to maintain the equivalence ratio constant between CPT and THF experiments when 1% of fuel was used, and the X_{fuel}/X_{O2} ratio constant when 2% of fuel was used. The estimated uncertainties for the mole fractions of fuel, O_2, and Ar are 0.81%, 0.56%, and 0.2% respectively.

Table 2: Summary of the mixture composition used in this study. φ is the equivalence ratio, X_{fuel}/X_{O2} is the ratio of fuel and oxygen mole fractions in the mixture.

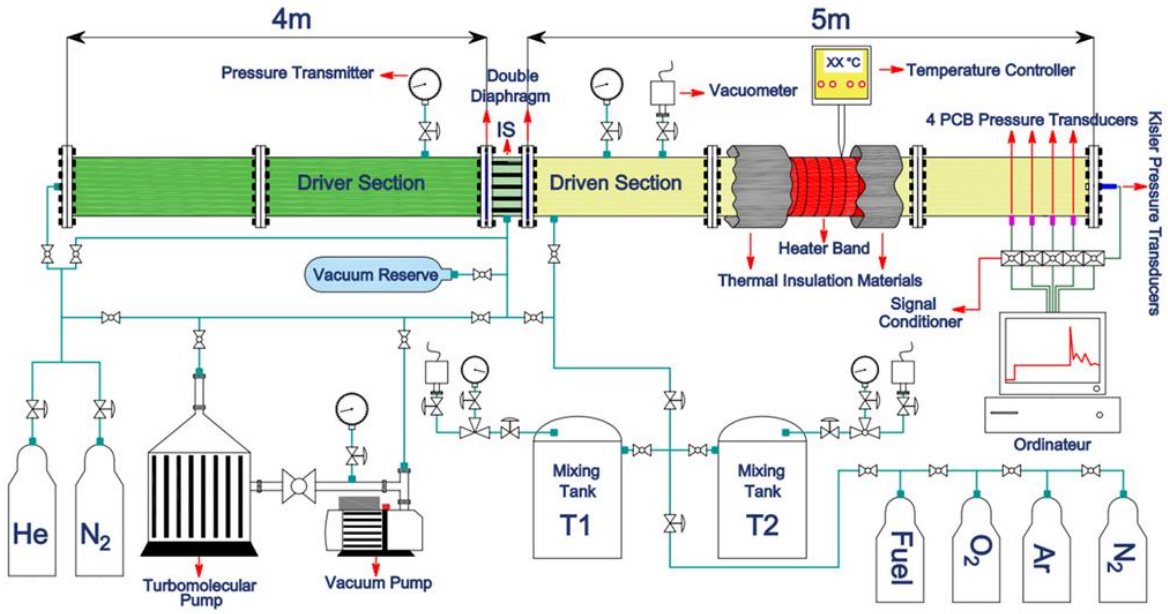
Mixture	Mixture composition (mole fraction)				φ	X_{fuel}/X_{O2}
	CPT	THF	O_2	Ar		
mix.1	0.010	0.000	0.150	0.840	0.50	0.067
mix.2	0.010	0.000	0.075	0.915	1.00	0.033
mix.3	0.010	0.000	0.038	0.952	2.00	0.017
mix.4	0.000	0.010	0.110	0.880	0.50	0.091
mix.5	0.000	0.010	0.055	0.935	1.00	0.046
mix.6	0.000	0.010	0.027	0.963	2.00	0.023

mix.7	0.020	0.000	0.250	0.730	0.60	0.080
mix.8	0.020	0.000	0.125	0.855	1.20	0.160
mix.9	0.020	0.000	0.063	0.917	2.40	0.320
mix.10	0.000	0.020	0.250	0.730	0.44	0.080
mix.11	0.000	0.020	0.125	0.855	0.88	0.160
mix.12	0.000	0.020	0.063	0.917	1.76	0.320

2.2. Ignition delay time measurements

The ignition delay times of the CPT/O_2/Ar and THF/O_2/Ar mixtures are measured in a high-pressure shock tube in DRIVE [18] over a temperature range of 865–1700 K at 20 atm. As presented in Figure 2, the tube consists of a stainless-steel tube (inner diameter of 50 mm) and separated into two parts (driver section 4 m and driven section 5 m) by a double stainless-steel diaphragm. The position of the shock wave is measured using four piezoelectric pressure transducers (PCB 113B22) located in the last part of the driven section. The post-shock pressure is recorded by using an additional piezoelectric pressure transducer (Kistler 603B1) positioned at the end-wall.

Helium was used as the driver gas. The driven section was heated up to 40–50 °C to avoid any condensation of CPT or THF during the measurements. The diaphragm thickness ranging from 200 to 300 µm are used. The rupture of both diaphragms, creating the shock wave, was performed using the vacuum reserve leading to an immediate pressure decrease in the intermediate section. To prevent any contamination of the tested mixture during the experiment, the tube is pumped down below 5 Pa.



125 Figure 2: Schematic diagram of the high-pressure shock tube apparatus in DRIVE laboratory.

126

127 The method used to identify the ignition delay time in this study is explained in more detail in
128 [18]. Pressure profiles recorded by the pressure transducers (PCB 113B22) are used to
129 determine the ignition delay time as presented in Figure 3. The ignition delay time is inferred
130 by the crossing between the horizontal line at p_5 and the tangent line to the pressure trace at
131 the maximum pressure increase. The post-shock pressure, p_5 and post-shock temperature T_5,
132 were calculated from the shock wave velocity and the initial conditions based on the 1-D
133 shock relations and the species thermodynamics using the chemical equilibrium software
134 Gaseq [22]. The difference between the post-shock pressure p_5 calculated by Gaseq and that
135 of the experimental pressure trace is below ± 4%. The accuracy of the post-shock temperature
136 T_5 is ± 1% which corresponds to ± 8–15 K. The estimated uncertainty for the measured
137 pressure p_5 is approximately 1.5%.

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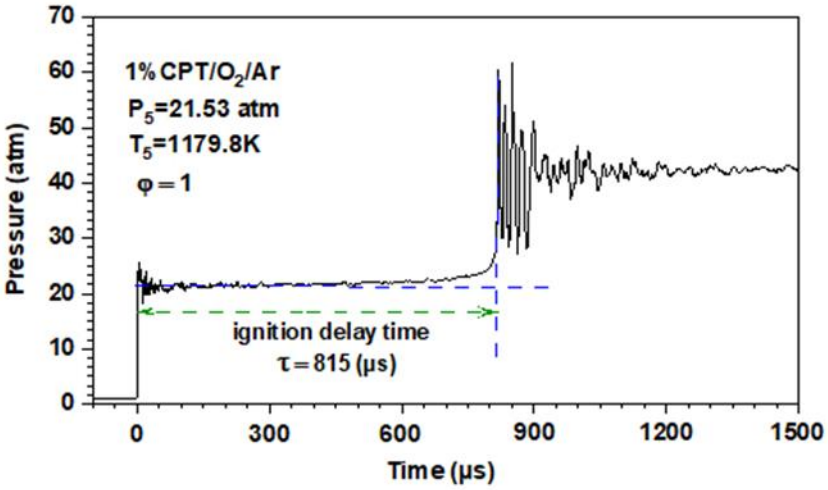


Figure 3: Definition of ignition delay time

In the shock tube experiment, several non-ideal effects influence the measurement of ignition delay time. The displacement of the reflected shock wave creates a boundary layer behind it, affecting the pressure and temperature p_5 and T_5. The overall uncertainty in ignition delay time was influenced by multiple factors, including uncertainties in reflected shock conditions, variations in mixture preparation, and the precision of ignition delay determination from measured signals. This uncertainty is approximately ±20%.

3. Kinetic modeling and simulation method

Shock tube simulations were performed using ANSYS Chemkin 2022 R2 [23] with the constant volume assumption. Computed ignition delay times were determined from calculated pressure profiles by the method presented in section 2.2. For the longest ignition delay times, a pressure rise was observed between the reflected shock and the auto-ignition. The impact of the pressure rise on ignition delay times has been discussed elsewhere [24, 25]. A negative heat loss (i.e. a heat gain) of -20 cal s^{-1} < $\dot{Q}$ < -50 cal s^{-1} was introduced as an input in Chemkin in order to account for the pressure rise experimentally observed (2.4% /ms < dp/dt < 7.5% /ms). For a given mixture, the same heat gain is used. For each of the 12 tested mixtures the value of the heat gain was adapted in order to reproduce the experimental

pressure rise. The longest ignition delay times of CPT and THF were clearly influenced by the heat gain while this impact was not observed for shorter ignition delay times (see Figures S1 and S2 in the Supplementary Material).

The kinetic mechanism used in the simulations was developed by merging a mechanism for THF from Fenard et *al.* [12] and a mechanism for CPT from Lokhachari et *al.* [16]. The kinetic and thermodynamic data of the common reactions and species in both mechanisms were taken from Fenard et *al.* [12]. The list of common species and reactions is presented in the Supplementary Material. Indeed, doing so has no impact on the performance of Lokhachari et *al.* sub-mechanism to model CPT auto-ignition and preserve the capability of Fenard et *al.* sub-mechanism to reproduce THF ignition delays (see Figures S3 and S4 in the Supplementary Material). On the contrary, keeping the kinetic and thermodynamic data from Lokhachari et *al.* for common reactions and species yield an overprediction of the ignition delay times of THF. The origin of this discrepancy would be interesting to investigate but is beyond the scope of this study.

The present mechanism contains 1322 species and 6709 reactions and is available with its thermodynamic data in Chemkin format in supplementary material.

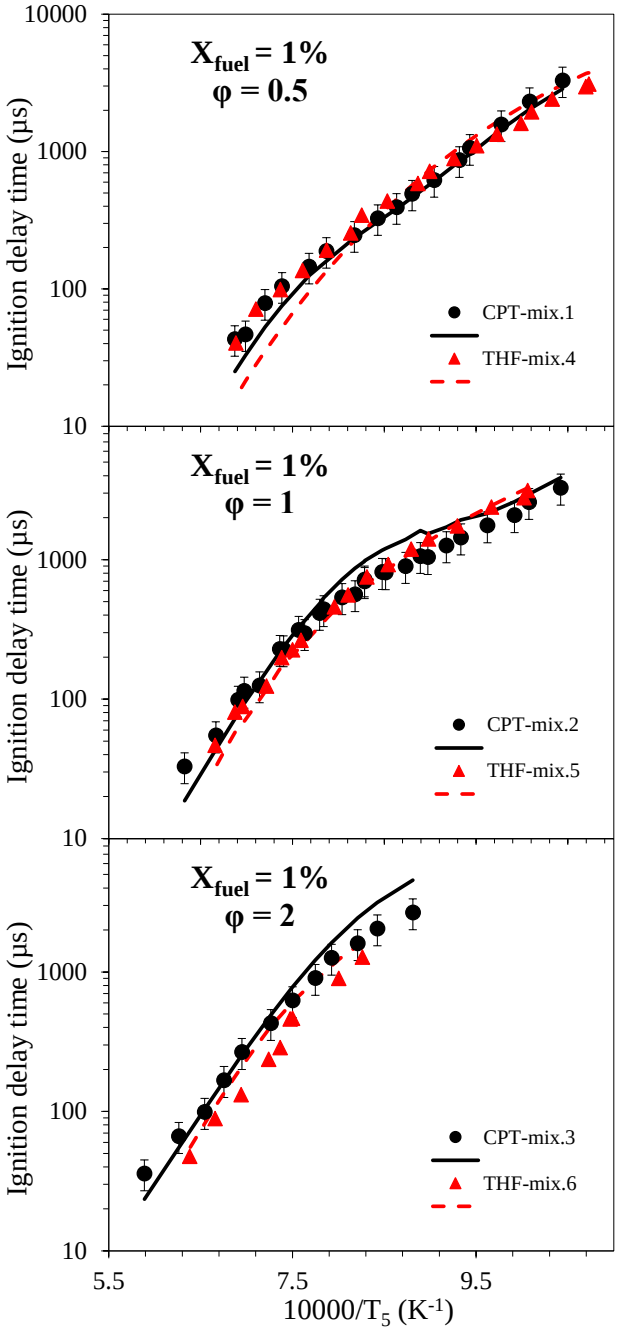
4. Results and discussion

A vertical error bar of 25% was applied to present experimental data, accounting for uncertainties of our experimental set-up and mixture preparation. The shortest and the longest ignition delay times are the measurement limits with these two molecules for each condition in our experimental device.

4.1 X_{Fuel} = 1 %

Figure 4 presents the comparison of reactivity between CPT and THF for different mixtures in shock tube at 20 atm. As can be seen in this figure, cyclopentane (CPT) and

tetrahydrofuran (THF) have very similar ignition delay times with 1% of fuel, THF being slightly more reactive at $\varphi = 2$. It can also be seen that the proposed kinetic mechanism is very well able to capture the observed trends, the ignition delay times of THF being underestimated under fuel-lean conditions at high-temperature. This mechanism was thus used to identify the reaction pathways involved in the auto-ignition of CPT and THF in order to highlight the reason why they behave similarly despite weaker C-H bond dissociation energies on the α-carbons of THF.



189

190 Figure 4: CPT (black) and THF (red) ignition delay times vs. 10000/T_5 for X_{fuel} = 1%, p_5 = 20

191 atm, and three different equivalence ratios.

192 Although CPT and THF have very similar ignition delay times with 1% of fuel, it turns out

193 that the chain of reactions eventually leading to the ignition of the mixtures is significantly

194 different. Reaction pathway analyses were performed at φ = 0.5, T_5 = 1110 K, at φ = 1, T_5 =

195 1250 K, and at φ = 2, T_5 = 1425 K, for both CPT and THF, when the temperature increase

reaches 5% of the initial T_5. The choice of this criterion was made in order to compare cyclopentane and tetrahydrofuran reactivity for a given mixture composition at the same temperature, since temperature is a key parameter in kinetics. On the other hand, because of this choice, it is not possible to compare these analyses for a same fuel at different equivalence ratios. Here, the focus is on the differences and similarities between CPT and THF reactivity for each condition.

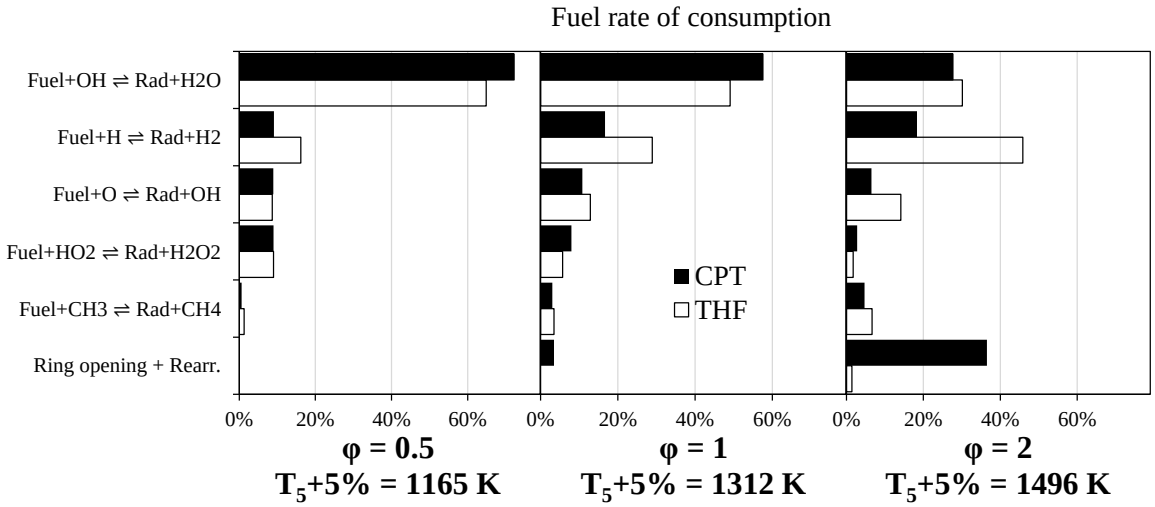


Figure 5: Main pathways of CPT and THF consumption at φ = 0.5, 1, and 2 for X_{fuel} = 1%, and P_5 = 20 atm. *Rad is cyclopentyl for CPT and the sum of α- and β-tetrahydrofuranyl for THF - Rearr. stands for rearrangement.*

Figure 5 shows that, under fuel-lean and stoichiometric conditions, both CPT and THF are mostly consumed by H-abstraction reactions by OH, CPT being slightly more consumed by OH than THF. On the contrary, THF is more consumed than CPT by H-abstraction reactions by H atoms. It means that, under these conditions, both fuels are able to generate enough radicals to be consumed approximately at the same pace. Under fuel-rich conditions, among H-abstraction reactions, OH still dominates CPT consumption, but cyclopentane is more consumed by the ring opening reaction followed by a rearrangement yielding 1-pentene. Under the same conditions, THF is mostly consumed by H-abstraction reactions by H,

followed by OH. Unlike CPT, ring opening, has virtually no role as an initiation step in the case of THF. It shows that the radical pool has less influence on the ignition process in the case of CPT than for THF under fuel-rich conditions.

The fate of the fuel radicals is presented by Figure 6. It turns out that, regardless of the conditions, ring opening is always the dominant pathway for THF, the formation of dihydrofurans (mostly by C-H β-scission) being rather limited. As far as cyclopentyl radical is concerned, ring opening reaction is also dominant for fuel-rich and stoichiometric mixtures, however since ring dehydrogenation and oxidation preserve the ring structure, ring opening is not dominant under fuel-lean conditions. Therefore, the radical pool necessary to consume THF is obtained from ring opening and subsequent reactions whereas, for CPT, the ring structure indeed participates to the formation of the small radicals.

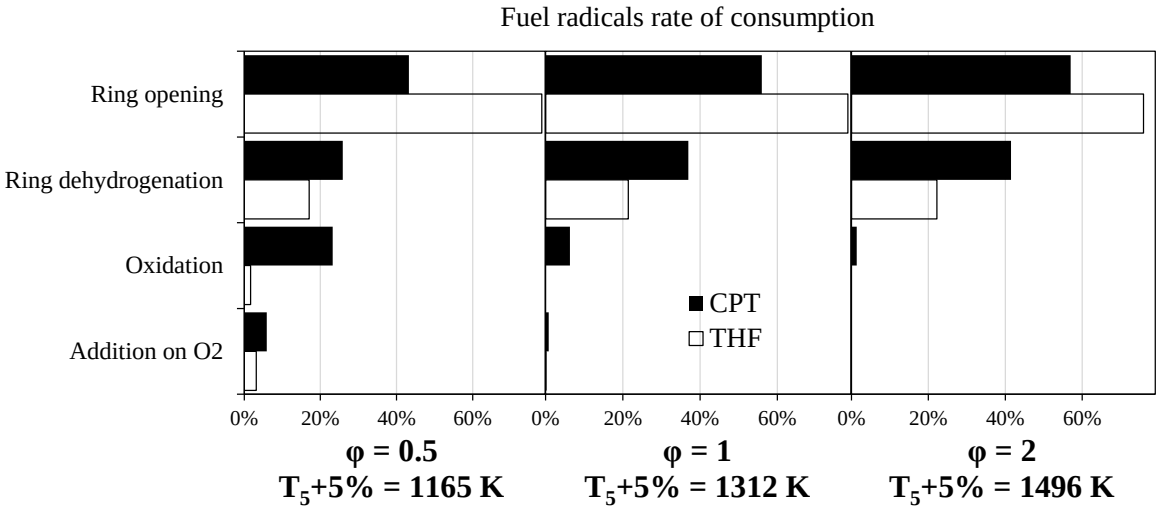
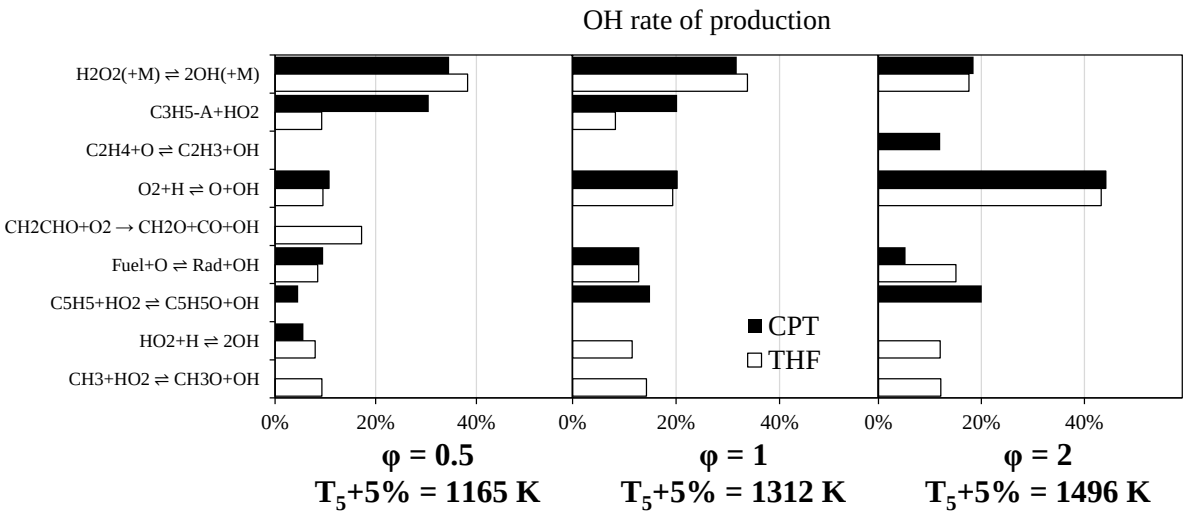


Figure 6: Main consumption pathways for cyclopentyl, and α- and β-tetrahydrofuranyl radicals at φ = 0.5, 1, and 2 for X_{fuel} = 1%, and p_5 = 20 atm.

- Role of OH:

As commonly observed, under fuel-lean conditions, OH is a key radical to consume both CPT and THF. Figure 7 shows that, for both fuels, the decomposition of H_2O_2 is a major

OH provider However, while in the case of CPT the second most important OH providers are the reactions C_3H_5-a + HO_2 ⇌ C_3H_5O + OH and C_3H_5OOH ⇌ C_3H_5O + OH, almost 20% of OH comes from $CH_2CHO + O_2 \rightarrow CH_2O + CO + OH$. In the case of THF, vinoxy radicals are essentially formed from α-tetrahydrofuranyl after ring opening. The reaction $CH_2CHO + O_2 \rightarrow CH_2O + CO + OH$ makes THF less dependent on HO_2 to produce OH than CPT. The share of $H + O_2$ ⇌ $OH + O$ and Fuel + O ⇌ Rad + OH, (Rad: cyclopentyl for CPT, and the sum of α- and β-tetrahydrofuranyl for THF), in OH production is almost the same for both fuels. Finally, the role of allyl radical in OH production is less important for THF than for CPT because when cyclopentyl opens, it only yields allyl after β-scission, while β-tetrahydrofuranyl is the only radical able to produce allyl, the α-tetrahydrofuranyl, the most abundant one, producing mainly vinoxy radicals. In addition, it can be noticed that the sum of the contributions of vinoxy and allyl radicals produces relatively less OH for THF than allyl alone for CPT. Although the temperatures of the analyses are different, more or less the same picture can be drawn for the stoichiometric mixture except that the role of vinoxy + O_2 decreases for THF and $H + O_2$ increases for both fuels. Under fuel-rich conditions, OH is mostly produced from $H + O_2$ ⇌ $OH + O$ for both fuels with the same share. The role of H_2O_2 dissociation is also very similar between CPT and THF. The difference lies on $C_5H_5 + HO_2$ and the H-abstraction from C_2H_4 by O atoms, which are respectively the third and fourth most important OH production routes for CPT, whereas OH is produced by THF + O H-abstraction reactions, $HO_2 + H$ ⇌ 2 OH, and $CH_3 + HO_2$ ⇌ CH_3O + OH in addition to $H + O_2$ ⇌ $OH + O$ and H_2O_2 dissociation for THF.



252

253 Figure 7: Main pathways of OH production for CPT and THF at φ = 0.5, 1, and 2 for X_{fuel} =
254 1%, and p_5 = 20 atm. *Rad is cyclopentyl for CPT and the sum of α- and β-tetrahydrofuranyl for THF, and*
255 *C3H5-A + HO₂ stands for the sum of C_3H_5-a + HO_2 ⇌ C_3H_5O + OH and C_3H_5OOH ⇌ C_3H_5O + OH.*

256 To summarize the role of OH, H_2O_2 dissociation and H + O_2 ⇌ OH + O have similar shares
257 for CPT and THF regardless of the equivalence ratio, and this flux represents between 45 %
258 and 62 % of the total OH rate of production. This appears to be sufficient for cyclopentane
259 and tetrahydrofuran to ignite after a similar delay in addition to:

260 - under fuel-lean conditions, the production of OH from C_3H_5-a + HO_2 in CPT oxidation is
261 compensated by CH_2CHO + O_2 → CH_2O + CO + OH and CH_3 + HO_2 ⇌ CH_3O + OH in THF
262 oxidation.

263 - for a stoichiometric mixture, the additional OH comes from C_3H_5-a + HO_2 and C_5H_5 + HO_2
264 for CPT, whereas H + HO_2 ⇌ 2 OH and CH_3 + HO_2 ⇌ CH_3O + OH produce the additional
265 OH for THF, showing again the strong influence of HO_2 on the ignition of both fuels, and the
266 role of allylic radicals for CPT and small radicals for THF.

- under fuel-rich conditions, H + HO_2, CH_3 + HO_2, and THF + O are responsible for the extra OH production for THF while, in the case of CPT, it relies on C_5H_5 + HO_2 and C_2H_4 + O ⇌ C_2H_3 + OH.

- Role of HO_2:

H_2O_2, which plays a significant role in the production of OH for CPT as well as for THF for the fuel-lean and stoichiometric mixtures, mostly comes from the H-abstraction reaction on the fuel by HO_2 and the dismutation of HO_2 with itself. It is therefore ultimately HO_2 which has a preponderant role in the production of OH under these conditions. As can be seen in Figure 8, H + O_2 (+M) ⇌ HO_2 (+M) has a very similar share in terms of HO_2 production between CPT and THF regardless of the equivalence ratio (and the temperature). However, under fuel-lean conditions, 38% of HO_2 comes from the oxidation of cyclopentyl radicals (including direct oxidation by O_2 and concerted elimination of HO_2 after O_2 addition), and 26% from HCO + O_2, whereas for THF, HCO + O_2 dominates the production of HO_2 (56%), C_2H_5 + O_2 playing a minor role (9%). For the stoichiometric mixture, more HO_2 is produced from HCO + O_2 in the case of THF, but CPT compensate with the oxidation of cyclopentyl radicals. Finally, under fuel-rich conditions, almost two third of the HO_2 comes from HCO + O_2 for CPT, which is more than THF, but THF compensate producing also HO_2 from CH_2OH + O_2 ⇌ CH_2O + HO_2.

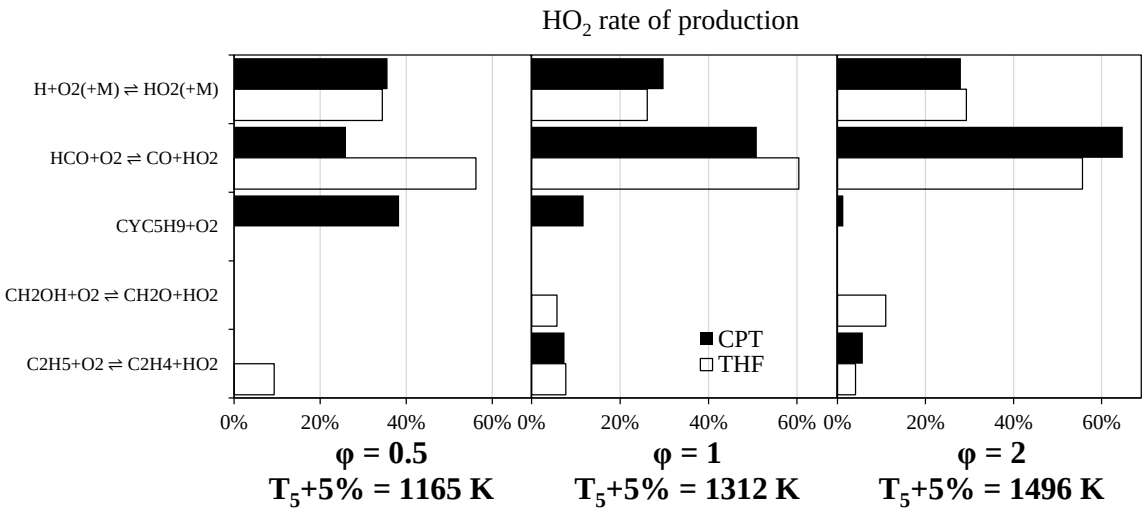


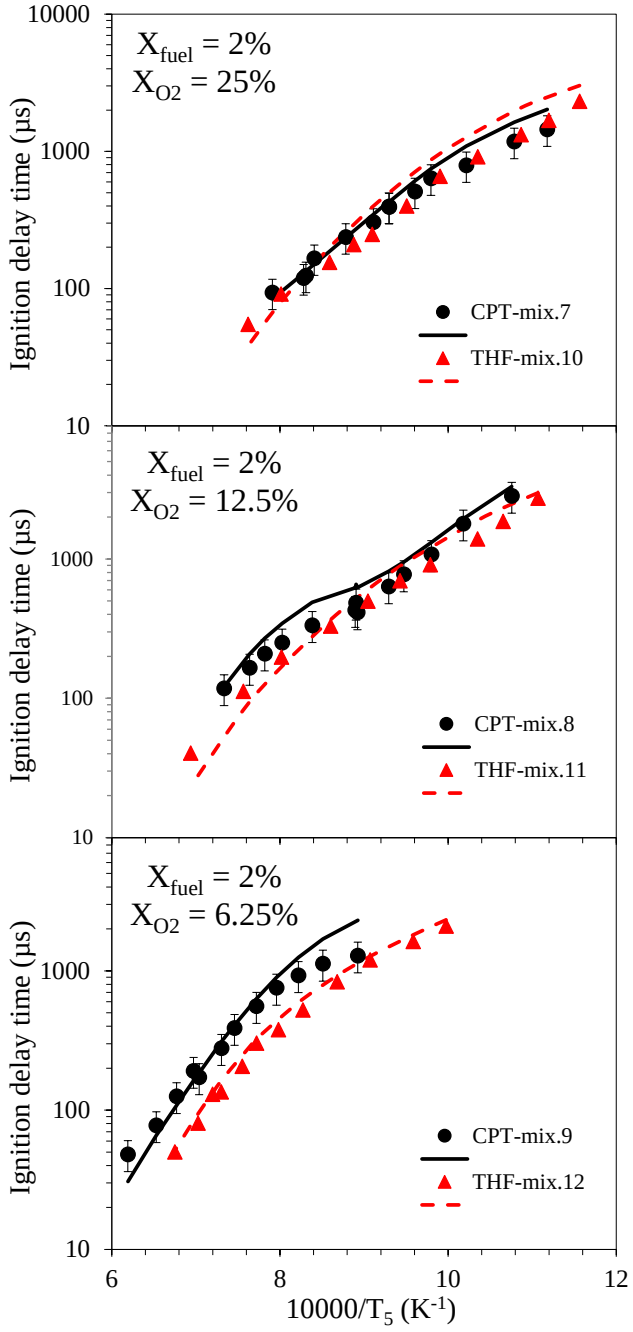
Figure 8: Main pathways of HO_2 production for CPT and THF at φ = 0.5, 1, and 2 for X_{fuel} = 1%, and p_5 = 20 atm. *CYC5H9 + O2 stands for the sum of the direct oxidation by O_2 and the concerted elimination of HO_2 after O_2 addition.*

To summarize on the role of HO_2, ring opening is a very important pathway in the consumption of THF. It is made easier as compared to CPT by the presence of the O atom. It finally yields high amounts of formyl radicals which in turn produce HO_2, strongly related to OH formation, and thus THF consumption (and ignition) under the explored conditions. For CPT, the picture is more complicated. Under fuel-lean conditions and lower temperature, the ring is preserved and HO_2 is formed by oxidation of cyclopentyl radicals. This, however, takes a similar time to occur as in the case of THF. For stoichiometric and fuel-rich mixtures, where ring opening dominates cyclopentyl consumption, HO_2 is formed, as for THF, mostly from HCO which comes from the regular pathway for alkanes through CH_2O, C_2H_3, and C_2H_4 making CPT to auto-ignite like THF does.

4.2 X_{Fuel} = 2 %

Figure 9 presents a comparison of the ignition delay times of CPT and THF for different mixtures in shock tube at 20 atm. As can be seen from this figure, cyclopentane (CPT) and tetrahydrofuran (THF) have again very similar ignition delay times with 25% of

303 O_2, and 12.5% of O_2 at low temperature. However, cyclopentane ignites later than
304 tetrahydrofuran with 12.5% of O_2 at high temperature and with 6.25% of O_2. It can also be
305 seen in Fig. 9 that the kinetic mechanism is still well able to capture the observed trends, and
306 particularly the ignition delay of CPT. Therefore, this mechanism was used to identify the
307 reaction pathways involved in the auto-ignition of CPT and THF in order to highlight the
308 reason of the delay observed for CPT. Four reaction pathway analyses were performed at X_{O2}
309 = 25%, T_5 = 1000 K, at X_{O2} = 12.5%, T_5 = 1000 K and 1335 K, and at X_{O2} = 6.25%, T_5 =
310 1335 K, both for CPT and THF, with the same criterion on the temperature increase of 5% as
311 when X_{fuel} = 1%. With this choice of T_5, comparisons can also be done between X_{O2} = 25%
312 and X_{O2} = 12.5% at 1000 K, and also between X_{O2} = 12.5% and X_{O2} = 6.25% at 1335 K.



313

314 Figure 9: CPT (black) and THF (red) ignition delay times vs. 10000/T_5 for X_{fuel} = 2%, p_5 = 20

315 atm, and three different O_2 initial mole fractions.

316 Figure 10 shows that, when X_{O2} = 25%, THF is mostly consumed by OH while CPT is half

317 consumed by OH and half by HO_2. The share of HO_2 in the consumption of CPT decreases

318 with the mole fraction of O_2 while that of H increases. It can also be noticed that the reaction

319 producing 1-pentene from cyclopentane (ring opening + rearrangement) consumes 18% of

CPT when X_{O2} = 6.25% while such a reaction does not occur for THF. OH is again of major importance in the consumption of both CPT and THF, HO_2 playing a non-negligible role for CPT with high O_2 content as well as H atoms for THF with low O_2 content.

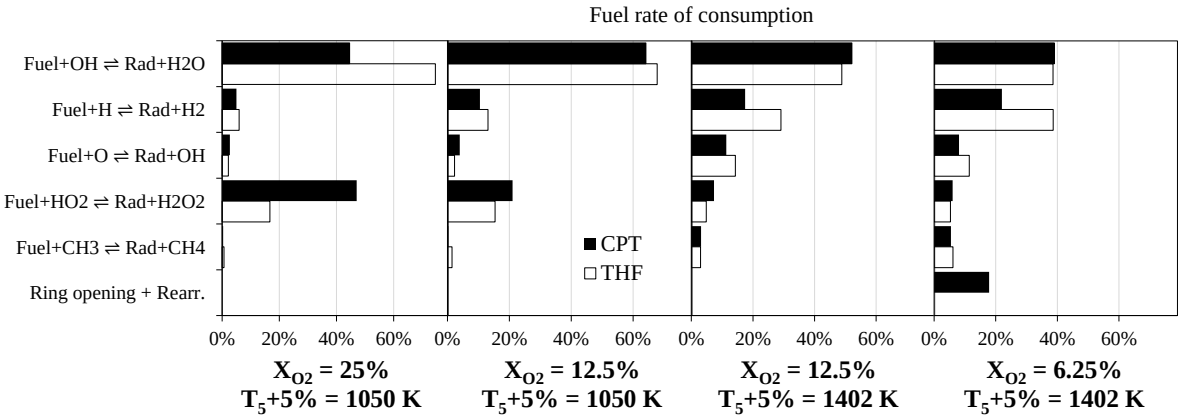


Figure 10: Main pathways of CPT and THF consumption at X_{O2} = 25%, 12.5%, and 6.25% for X_{fuel} = 2%, and p_5 = 20 atm. *Rad is cyclopentyl for CPT and the sum of α- and β-tetrahydrofuranyl for THF - Rearr. stands for rearrangement.*

Under these conditions, the relative rates of consumption of the fuel radicals are presented in Figure 11. It turns out that the fate of cyclopentyl and tetrahydrofuranyls is very similar to what was observed when X_{fuel} = 1%, tetrahydrofuranyls being mostly consumed by ring opening whereas the C5 ring is maintained at lower temperature and opens at higher temperature, when CPT is delayed as compared to THF.

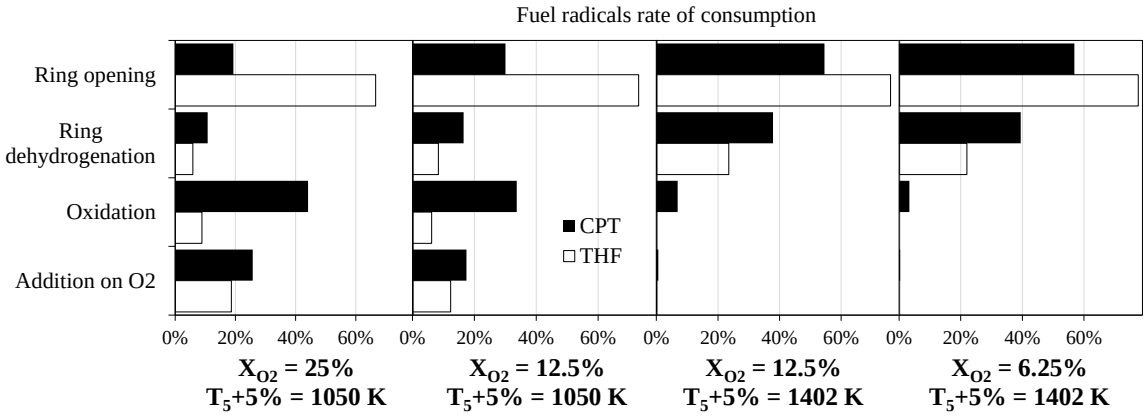


Figure 11: Main consumption pathways for cyclopentyl, and α- and β-tetrahydrofuranyl at X_{O2} = 25%, 12.5%, and 6.25% for X_{fuel} = 2%, and p_5 = 20 atm.

- Role of OH:

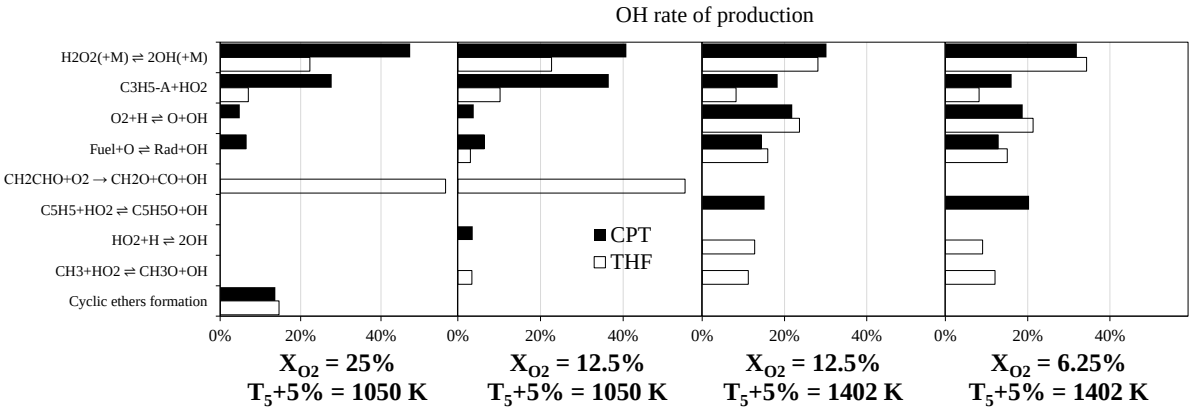


Figure 12: Main pathways of OH production for CPT and THF at X_{O2} = 25%, 12.5%, and 6.25% for X_{fuel} = 2%, and p_5 = 20 atm. *Rad is cyclopentyl for CPT and the sum of α- and β-tetrahydrofuranyl for THF, and C3H5-A + HO2 stands for the sum of* C_3H_5*-a +* $HO_2 \rightleftharpoons C_3H_5O + OH$ *and* $C_3H_5OOH \rightleftharpoons C_3H_5O + OH$.

Surprisingly enough, the reaction pathways producing OH are significantly different between CPT and THF when they have similar ignition delay times (X_{O2} = 25%, and X_{O2} = 12.5% at T_5 = 1000 K) whereas they are less different when CPT ignition is delayed as compared to THF (X_{O2} = 12.5% at T_5 = 1335 K, and X_{O2} = 6.25%), as can be seen from Figure 12. For CPT, the dominant pathways for OH production lie on HO_2, either directly by reaction with allyl radicals or through H_2O_2 formation. For THF, H_2O_2 dissociation accounts only for a quarter of OH production, more than half of it coming from the reaction of vinoxy radicals and O_2 ($CH_2CHO + O_2 \rightarrow CH_2O + CO + OH$). Thus, when CPT and THF ignite after equivalent times, OH production pathways are significantly different, CPT relying more on HO_2 and THF directly on the O_2 content. However, when CPT is delayed, it comes out that

resonantly stabilized allylic radicals (allyl and cyclopentadienyl radicals) are involved in OH production for CPT while H and CH_3 are involved in the case of THF.

- Role of HO_2:

HO_2 is thus a key intermediate in the production of OH under all tested conditions for CPT, and at high-temperature and low O_2 content for THF. With a doubled initial amount of fuel, the oxidation of cyclopentyl, either directly or through addition on O_2 and concerted elimination of HO_2, gained in importance to produce HO_2 for CPT at low temperature and high O_2 content. Under the same conditions, a third of the HO_2 production for THF relies on H + O_2 (+M), another third on HCO + O_2, and the last third comes from tetrahydrofuranyl radicals oxidation. At higher temperature and lower O_2 content, when CPT is delayed compared to THF, the reaction pathways yielding HO_2 are very similar between cyclopentane and tetrahydrofuran, HCO + O_2 producing slightly more HO_2 in the case of THF than for CPT.

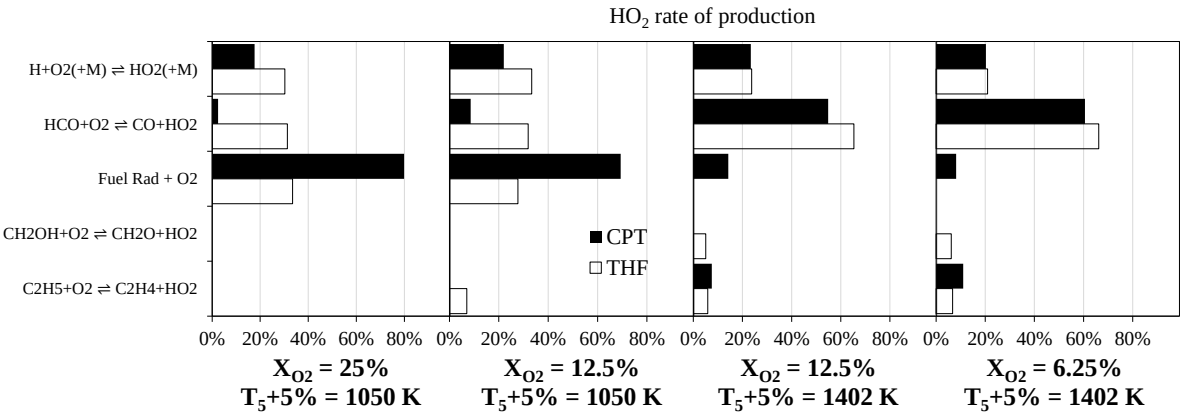


Figure 13: Main pathways of HO_2 production for CPT and THF at X_{O2} = 25%, 12.5%, and 6.25% for X_{fuel} = 2%, and p_5 = 20 atm. *Fuel Rad + O2 stands for the sum of the direct oxidation by O_2 and the concerted elimination of HO_2 after O_2 addition.*

It turns out that ring opening seems to be responsible for cyclopentane to be delayed as compared to tetrahydrofuran. As far as THF is concerned, the ring opening from the α-tetrahydrofuranyl radical, the most abundant one, produces vinoxy radicals, which in turn produce OH by reaction with O_2, at low temperature and high O_2 content, or produce H atoms (+ ketene) and CH_3 (+ CO) at high temperature and low O_2 content. This sequence of reactions generates the OH required for the consumption of THF by different, but efficient, pathways. For CPT, at low temperature and high O_2 content, the ring is preserved allowing HO_2 to be produced by reaction between cyclopentyl radicals and O_2, generating OH radicals to consume CPT as fast as THF is. However, ring opening produces allyl radicals which are most likely to be consumed by HO_2, but the ring opens at high temperature, where HO_2 is much less produced. Therefore, resonantly stabilized allyl radicals, with less partners to react with, stifle the reactivity, and cyclopentane ignition is delayed as compared with tetrahydrofuran.

5. Conclusion

This study reports the comparison between cyclopentane and tetrahydrofuran auto-ignition in a high-pressure shock tube. New ignition delay times were measured at 20 atm and various equivalence ratios and initial fuel mole fractions. A detailed kinetic mechanism was developed in order to reproduce the experimental observations. Since the agreement was found to be good, this mechanism was used to explain the similarities and differences between cyclopentane and tetrahydrofuran in terms of auto-ignition. It turns out that cyclopentane and tetrahydrofuran exhibit very similar behaviors under most of the tested conditions, only at high-temperature and low O_2 content, cyclopentane ignition is delayed. Reaction pathway analyses were performed and showed that, in the case of tetrahydrofuran, the ring is made easier to open by the presence of the oxygen atom, and the subsequent reactions of vinoxy

radicals support the production of HO_2, H, and OH radicals. In the case of cyclopentane, higher temperatures are required to open the ring but the production of HO_2 is supported by the oxidation of cyclopentyl radicals and that of OH by the reactions between resonantly stabilized allyl and cyclopentadienyl radicals with HO_2. On the contrary, when temperature increases and O_2 content decreases, ring opening is favored, increasing the production of allyl radicals but, HO_2, a key intermediate in allyl consumption, formation decreases, thus delaying the ignition of cyclopentane.

Acknowledgements

Authors gratefully acknowledge funding received from The Bourgogne Franche-Comté Council and Labex Caprysses (convention ANR-11-LABX-0006-01).

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