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EXPERIMENTAL AND KINETIC MODELLING STUDY OF THE OXIDATION OF CYCLOPENTANE AND METHYLCYCLOPENTANE AT ATMOSPHERIC PRESSURE

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Abstract
Cyclopentane and methylcyclopentane oxidation was investigated in a jet-stirred reactor at 1 atm, over temperatures ranging from 900 K to 1250 K, for fuel-lean, stoichiometric, and fuel-rich mixtures at a constant residence time of 70 ms. The initial mole fraction of both fuels was kept constant at 1000 ppm. The reactants were highly diluted by a flow of nitrogen to ensure thermal homogeneity. Samples of the reacting mixture were analyzed on-line or off-line by Fourier transform infrared spectroscopy and gas chromatography. A detailed kinetic mechanism consisting of 590 species involved in 3469 reversible reactions was developed and validated against these new experimental results and previously reported ignition delays. Reaction pathways analysis as well as sensitivity analyses were performed to get insights into the differences observed during the oxidation process of cyclopentane and methylcyclopentane.

Introduction
As compared to linear alkanes, the oxidation of cyclo-alkanes and substituted cycloalkanes, such as cyclo-pentane and methylcyclopentane, has received very little attention. However, with the growing interest on biomass-derived fuels, and fuels derived from oil sands and shale, the understanding of the combustion chemistry of these cyclic hydrocarbons becomes of major scientific and practical importance. Among cycloalkanes, cyclohexane is the most studied one. In their work on the low- and high-temperature oxidation of cyclohexane, Serinyel et al. [1] reported more than 20 previous studies on this compound. They also validated a detailed kinetic mechanism for the oxidation of cyclohexane under jet-stirred reactor conditions as well as laminar burning velocities and ignition delays in shock-tube and rapid compression machine. Furthermore, the combustion community has also shown interest to alkylated cyclohexanes, from methyl to propyl, under various experimental conditions. Despite a recent greater attention, studies on cyclopentane or methylcyclopentane oxidation are still sparse.

Tsang [2] investigated the thermal decomposition of cyclopentane using a single-pulse shock-tube. Several distinct pathways were considered and the isomerization to 1-pentene was found to be a major route of consumption under these conditions, while the formation of cyclopropane was also detected. High-temperature autoignition of cyclopentane was studied by Sirjean et al. [3] in a shock-tube. A detailed chemical kinetic mechanism was developed and used to explain the longer ignition delays observed as compared to cyclohexane. The ring opening of cyclopentyl radicals was demonstrated to be responsible for this lower reactivity. Cyclopentane ignition was also investigated at elevated pressures by Daley et al. [4] and compared to that of cyclohexane. Mechanisms from the literature were tested and, although the general trends were captured, they all predicted ignition times generally longer than those measured. Recently, Al Rashidi et al. [5-7] elucidated the different reactivity regimes in

cyclopentane oxidation by means of jet-stirred reactor experiments, computational chemistry, and kinetic modelling. Their simulations reproduced the unique reactivity trend of cyclopentane at high-pressure and they showed that this peculiar behavior may be attributed to the C-C/C-H scission branching ratio of the cyclopentyl radical.

The oxidation of methylcyclopentane was first studied by Burgoyne and Silk [8] in a quartz bulb. They determined the pressure-temperature limits for spontaneous cool- and hot-flame ignitions of methylcyclopentane-oxygen mixtures. Brown and King [9] investigated the very-low-pressure pyrolysis of methylcyclopentane. The data were interpreted in terms of ring-opening bond fission pathways and bond fission to methyl and cyclo-alkyl radicals. They proposed high-pressure rate expressions for the overall decomposition of methylcyclopentane and showed their data supported the assumption of a biradical mechanism for ring opening. More recently, Sivaramakrishnan and Michael [10] measured the high-temperature rate constants of methylcyclopentane H-abstractions by OH radicals in a shock tube and showed that these reactions are favored on ortho secondary carbons (carbon s1 in Fig. 1). Sirjean et al. [11] theoretically studied the thermal unimolecular decomposition of methylcyclopentyl radicals. For ring-opening reactions, they showed an increase of the activation energy when the double bond is formed in the ring (endo) in contrast to the cases in which the double bond is formed on the side chain (exo). Boehman and coworkers [12-14] focused on the low-temperature oxidation of cycloalkanes in engines. They observed methylcyclopentane showed little low-temperature reactivity prior to autoignition as compared to methylcyclohexane or decalin. Moreover, methylcyclopentenes were found to play an important role under their conditions, and methyl substitution on the ring was found to significantly promote the formation of propene relative to ethylene. Finally, Tian et al. [15] measured ignition delay times of cyclopentane/O_2 and methylcyclopentane/O_2 mixtures diluted in argon and developed a detailed kinetic mechanism validated against their experimental results. They observed methylcyclopentane had shorter ignition delays than cyclopentane and attributed this to the presence of the methyl group and the propensity of methylcyclopentane to produce H atoms.

Experimental

The JSR experimental setup has been described in previous studies [16, 17]. Briefly, it consists of a 4 cm diameter fused silica sphere with four 1 mm i.d. nozzles. High purity nitrogen (< 100 ppm H_2O, < 50 ppm O_2, < 1000 ppm Ar, < 5 ppm H_2, Air Liquide) was used as a diluent and mixed with the reactants before reaching the mixing point at the entrance of the injectors. High dilution (0.1 % mol. of fuel) was used to reduce temperature gradients and heat release inside the reactor. High-purity reactants were used: oxygen 99.995 % pure was provided by Air Liquide, while cyclopentane (CAS 287-92-3) > 98 % pure and methylcyclopentane (CAS 96-37-7) > 97 % pure were both obtained from Aldrich. 1.2 % of n-pentane was measured within cyclopentane and 0.7 % of n-hexane within methylcyclopentane. These impurities were taken into account for the simulations. To reduce temperature gradients inside the reactor, the reactants were preheated before injection. The fuel was delivered to a vaporizer assembly maintained at 473 K by means of a HPLC pump and an online degassing unit (Shimadzu LC10 AD VP and DGU-20 A3). Small temperature gradients (~ 1 K/cm) were measured along the vertical axis of the reactor using a thermocouple located inside a thin-wall fused-silica tube (0.1 mm Pt-Pt/Rh-10 %) to prevent catalytic reactions on the metallic wires. A fused-silica low-pressure sonic probe was used to sample the reacting mixtures and send samples to the analyzers via a Teflon heated line (393 K). Gas samples were analyzed online by FTIR. A resolution of 0.5 cm^{-1} was used. The sample cell had a 10 m optical path length and samples were analyzed at 200 mbar. Off-line GC analyses following collection and storage at ~ 50 mbar in 1L Pyrex bulbs were also

performed. Gas chromatographs operating with capillary columns (a 0.32 mm i.d. DB-624, a 0.32 mm i.d. CP-Al_2O_3-KCl, a 0.53 mm i.d. CP-Carboplot-P7, and a 0.32 mm i.d. CP-SIL 5CB coupled to a 0.53 mm i.d. DB1-ms), a TCD (thermal conductivity detector), and a FID (flame ionization detector). Two GC-MS (Varian CP3800-V1200 and Shimadzu GC-MS 2010 Plus) operating with electron impact ionization (70 eV) were used for products identification. Thanks to this analytical equipment, it was possible to measure several species with different techniques or columns, giving high confidence into our measurements. The measured species were: CO, CO_2, water, H_2, O_2, methane, formaldehyde, ethane, ethylene, acetylene, propene, allene, propyne, acroleine, 1-butene, 1,3-butadiene, vinylacetylene, 1-pentene, 1-hexene, benzene, cyclopentene, cyclopentadiene, methylcyclopentene, methylcyclopentadiene, cyclopentane and methylcyclopentane.

All the experiments were performed at a mean residence time, τ, of 70 ms and a pressure of 1 atm. The reactants were constantly flowing into the JSR, while the reactor temperature was increased stepwise from 900 to 1250 K. A good repeatability of the measurements and a reasonably good carbon balance (typically 100 ± 10%) were obtained.

Kinetic Modelling

The kinetic modelling of cyclopentane and methylcyclopentane oxidation in jet-stirred reactor was performed using the PSR computer code [18] while ignition delays were computed thanks to the SENKIN code [19], both from the CHEMKIN-II package. The detailed kinetic reaction mechanism consisting of 590 species involved in 3469 reversible reactions and the thermochemical properties are available upon request from the authors.

The kinetic reaction mechanism used here is based on a previously proposed mechanism for the oxidation of a variety of fuels up to C_6 [20, 21]. It was extended by including the chemistry of cyclopentane and methylcyclopentane oxidation. Cyclopentene, cyclopentadiene, hex-1-ene and hex-2-ene sub-mechanisms were also revisited to improve our predictions. For the new species, the thermochemical properties were computed using group and bond additivity methods [22]. The chemical structure, the name used in the mechanism as well as the heat of formation and entropy at 298 K of the most important species in C_5 cyclic species sub-mechanism are gathered in Table 1.

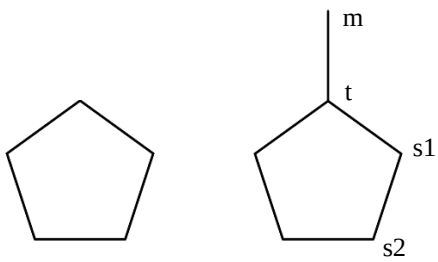
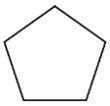
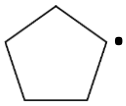
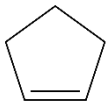
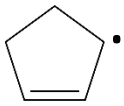
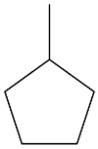
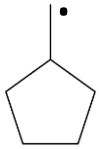
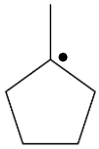
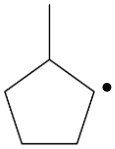
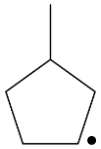
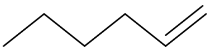
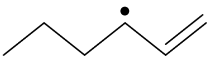
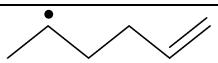
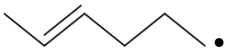
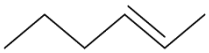
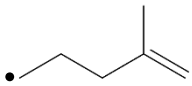
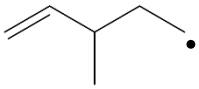
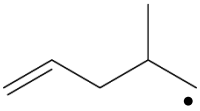
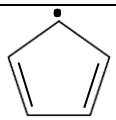


Figure 1: Cyclopentane (left) and methylcyclopentane (right) with carbon labels.

The fuel (either cyclopentane or methylcyclopentane) can react via thermal decomposition involving C-C, and C-H bond breaking. Previous authors have shown that ring opening for cycloalkanes proceeds through the formation of biradical intermediates [23-25]. In the case of cyclopentane, homolytic C-C bond scissions yield either 1-pentene or propene and ethylene. In the literature [2, 23], this second pathway produces cyclopropane and ethylene, but taking into account that cyclopropane was not considered in our mechanism and that, at 1000 K, this pathway is more than 100 times lower than that yielding 1-pentene, propene replaced cyclopropane. Rate constants for both of these pathways were taken from [2]. For methylcyclopentane, hexenes or methylpentenes can be produced through five distinct pathways in addition to cyclopentyl and methyl radicals. The rate constants for the formation

of alkenes was adapted from Tsang [2] while that for the formation of cyclopentyl and methyl radicals was taken from Zhang et al. [25] from methylcyclohexane decomposition. The rate constant for C-H bond breaking leading to cyclopentyl was adopted from [5] while the formation of the four primary radicals of methylcyclopentane was taken from Tian et al. [15]. Cyclopentane may react through bimolecular initiations with O_2, the rate constant of which was taken from [5]. Methylcyclopentane may also react through bimolecular initiations with O_2, yielding the four primary radicals: again, rate constants proposed by Tian et al. [15] were adopted. Propagation reactions proceed via H-abstractions by small radicals (H, O, OH, HO_2, CH_3). For cyclopentane, H-abstractions by OH were taken from Sivaramakrishnan and Michael [10], while for H-abstractions by H and HO_2 rates from Handford-Styring and Walker [26, 27] were selected. For H-abstractions by O and CH_3, no direct measurements were available and rates from [28] were chosen. For methylcyclopentane, H-abstractions by H, O, OH, CH_3, and HO_2 on the four secondary carbons were taken equal to that for cyclopentane. In the case of the primary and the tertiary carbons (m and t), rate constants used in our previous studies were chosen [29, 30].

Table 1: Chemical structures, names used in the kinetic mechanism, and heat of formation (kcal/mol) and entropy (cal/K/mol) at 298 K of the most important species in cyclopentane and methylcyclopentane sub-mechanisms.

 cyc5h10 $\Delta_f H°$ = -18.4 S° = 70.0	 cyc5h9 $\Delta_f H°$ = 26.6 S° = 71.4	 cyc5h8 $\Delta_f H°$ = 8.9 S° = 68.1	 cyc5h7 $\Delta_f H°$ = 41.3 S° = 70.8	 cpd $\Delta_f H°$ = 24.2 S° = 65.5
 mcp $\Delta_f H°$ = -25.6 S° = 81.1	 mcpm $\Delta_f H°$ = 22.5 S° = 83.3	 mcpt $\Delta_f H°$ = 17.9 S° = 82.9	 mcps1 $\Delta_f H°$ = 20.4 S° = 83.8	 mcps2 $\Delta_f H°$ = 20.4 S° = 83.8
 c6h12-1 $\Delta_f H°$ = -10.1 $\Delta S°$ = 91.6	 c6h1116 $\Delta_f H°$ = 38.7 $\Delta S°$ = 93.6	 c6h1113 $\Delta_f H°$ = 21.4 $\Delta S°$ = 90.2	 c6h1115 $\Delta_f H°$ = 36.5 $\Delta S°$ = 93.8	 c6h1126 $\Delta_f H°$ = 38.8 $\Delta S°$ = 92.8
 c6h12-2 $\Delta_f H°$ = -12.8 S° = 90.7	 pent2m1d5 $\Delta_f H°$ = 35.4 S° = 92.5	 pent3m1d5 $\Delta_f H°$ = 37.6 S° = 92.7	 pent4m1d5 $\Delta_f H°$ = 36.4 S° = 91.7	 c5h5 $\Delta_f H°$ = 63.1 S° = 64.0

The decomposition reactions by β-scissions and reactions with O_2 of the primary radicals of both fuels were also considered. Seven different C-C β-scissions were considered in the case of methylcyclopentane for which rate expressions calculated by Sirjean et al. [11] and by Gong et al. [24] were adopted. For the ring opening of cyclopentyl yielding pent-1-en-5-yl, the rate calculated by Sirjean et al. was divided by two to reproduce the reactivity observed

under rich conditions at 10 atm. For C-H β-scissions, rate constants proposed in our previous works [29, 30] were used except for the formation of methylene cyclopentane for which we used the rate constant calculated by Gong et al. [24]. For the oxidation reactions by O_2 yielding methylcyclopentenes or methylcyclopentadienes, the rate constants proposed by Battin-Leclerc [31] were selected. Finally, the methylcyclopentadiene sub-mechanism was taken from Herbinet et al. [32] with the decomposition yielding methyl and cyclopentadienyl radicals coming from Sharma and Green [33] at atmospheric pressure. Fulvene formation was also considered. Submechanisms for the oxidation and pyrolysis of cyclopentene and cyclopentadiene were taken from our previous works [21, 34] and updated using the work by Vermeire et al. [35] on 1,5-hexadiene.

Results and Discussion

For the sake of comparison, experiments were performed at a constant mean residence time of 70 ms and constant atmospheric pressure for both fuels. The equivalence ratio, φ, was varied from fuel-lean to fuel-rich conditions (0.5, 1, and 2); the fuel initial mole fraction was 1000 ppm for all experiments. The temperature ranged from 900 to 1250 K. A good repeatability was observed in the experiments and a reasonably good carbon balance of 100±10% was achieved.

Figure 2 presents the evolution of the mole fraction of cyclopentane (left) and methylcyclopentane (right) at three different equivalence ratios (0.5, 1, and 2) together with our simulations. It can be noticed from this figure that the conversion of cyclopentane is more affected by the equivalence ratio than that of methyl cyclopentane. Half of the initial cyclopentane is consumed at T = 1150 K, T = 1165 K, and T = 1180 K for the fuel-lean, the stoichiometric and the fuel-rich mixtures respectively, while half of the initial methylcyclopentane is consumed at T = 1135 K, T = 1140 K, and T = 1145 K for the fuel-lean, the stoichiometric and the fuel-rich mixtures respectively. Moreover, the calculations performed with our detailed kinetic mechanism are in good agreement with our experimental data for both fuels at the three equivalence ratios.

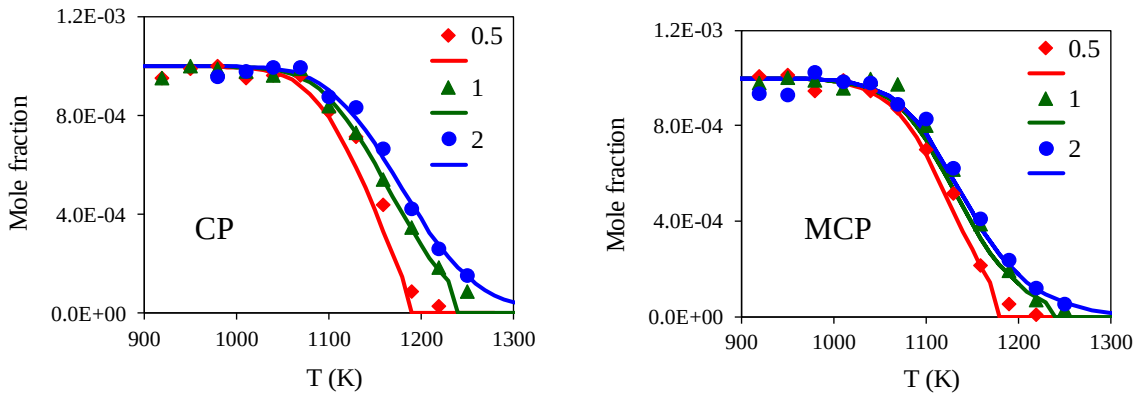


Figure 2: Experimental (symbols) and computed (lines) mole fraction profiles obtained from the oxidation of cyclopentane (left) and methylcyclopentane (right) in a JSR at p = 1 atm, τ = 0.07s, and φ = 0.5 (blue), φ = 1 (red), and φ = 2 (green).

Figure 3 shows the results obtained for a fuel-lean mixture of cyclopentane (empty triangles and dashed line) and methylcyclopentane (filled circles and full line). Under these conditions, methylcyclopentane consumption starts at a slightly lower temperature than the conversion of cyclopentane. These experiments were indeed performed starting at 710 K, but no evidence of reactivity below 1000 K was observed for both fuels under these conditions.

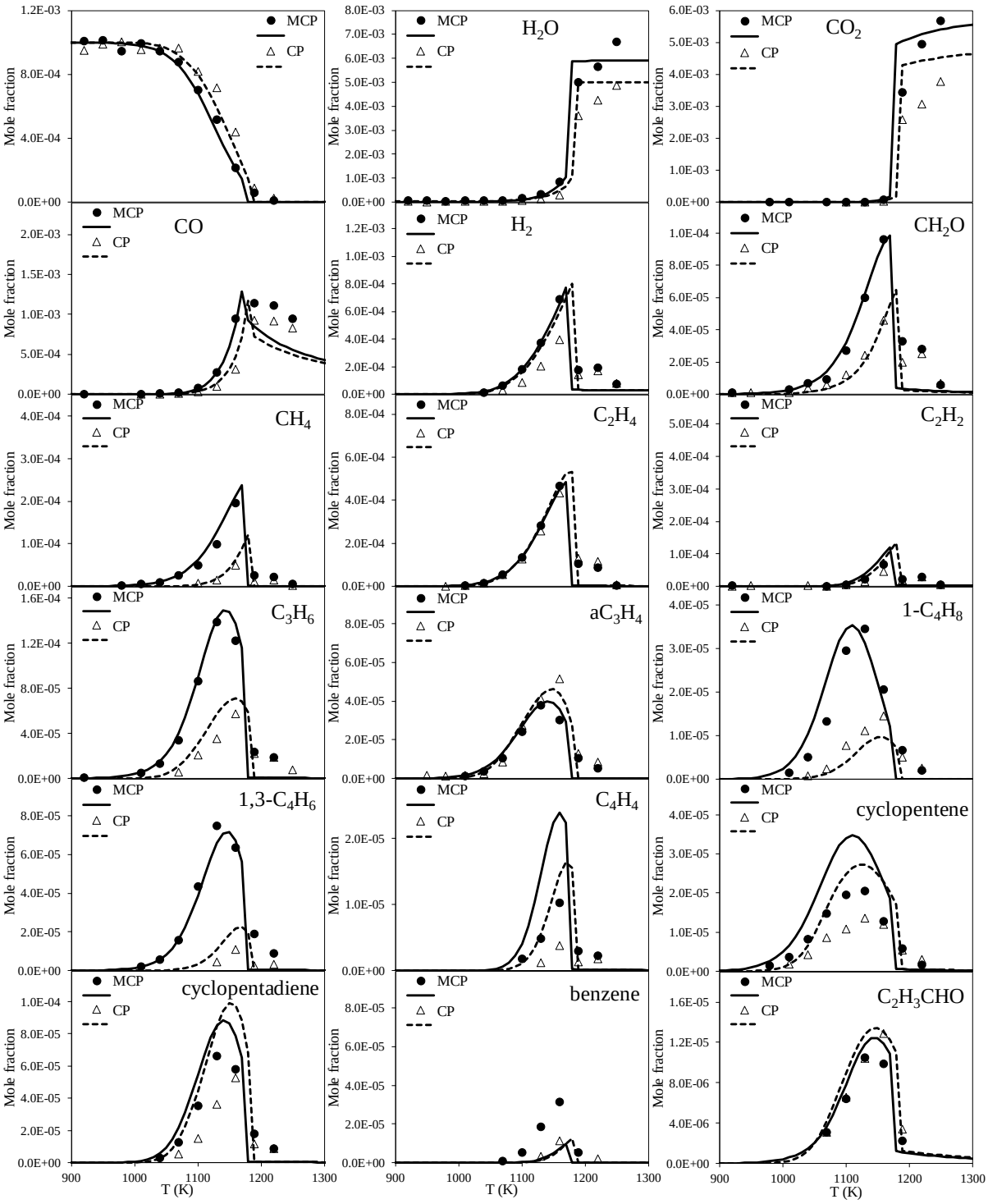


Figure 3: Experimental and computed mole fraction profiles obtained from the oxidation of cyclopentane (empty triangles and dashed line) and methylcyclopentane (filled circles and full line) in a JSR at $\varphi = 0.5$, p = 1 atm, $\tau = 0.07$s.

The observed intermediates are mainly unsaturated compounds (C_2H_2, C_2H_4, C_3H_6, 1,3-C_4H_6, cyclopentene, cyclopentadiene, and benzene) regardless to the equivalence ratio. Except for water, CO, and CO_2, formaldehyde and acrolein were the only oxygenates identified. It should be noticed that 12 ppm of n-pentane and 7 ppm of n-hexane were introduced into the JSR together with cyclopentane and methylcyclopentane, respectively.

This small amount of impurity was taken into account in our simulations but it was observed it had no impact on the reactivity or the species mole fractions. Also, less than 2 ppm of pent-1-ene and 1 ppm of hex-1-ene was measured either under fuel-lean, fuel-rich or stoichiometric conditions with cyclopentane and methylcyclopentane, respectively.

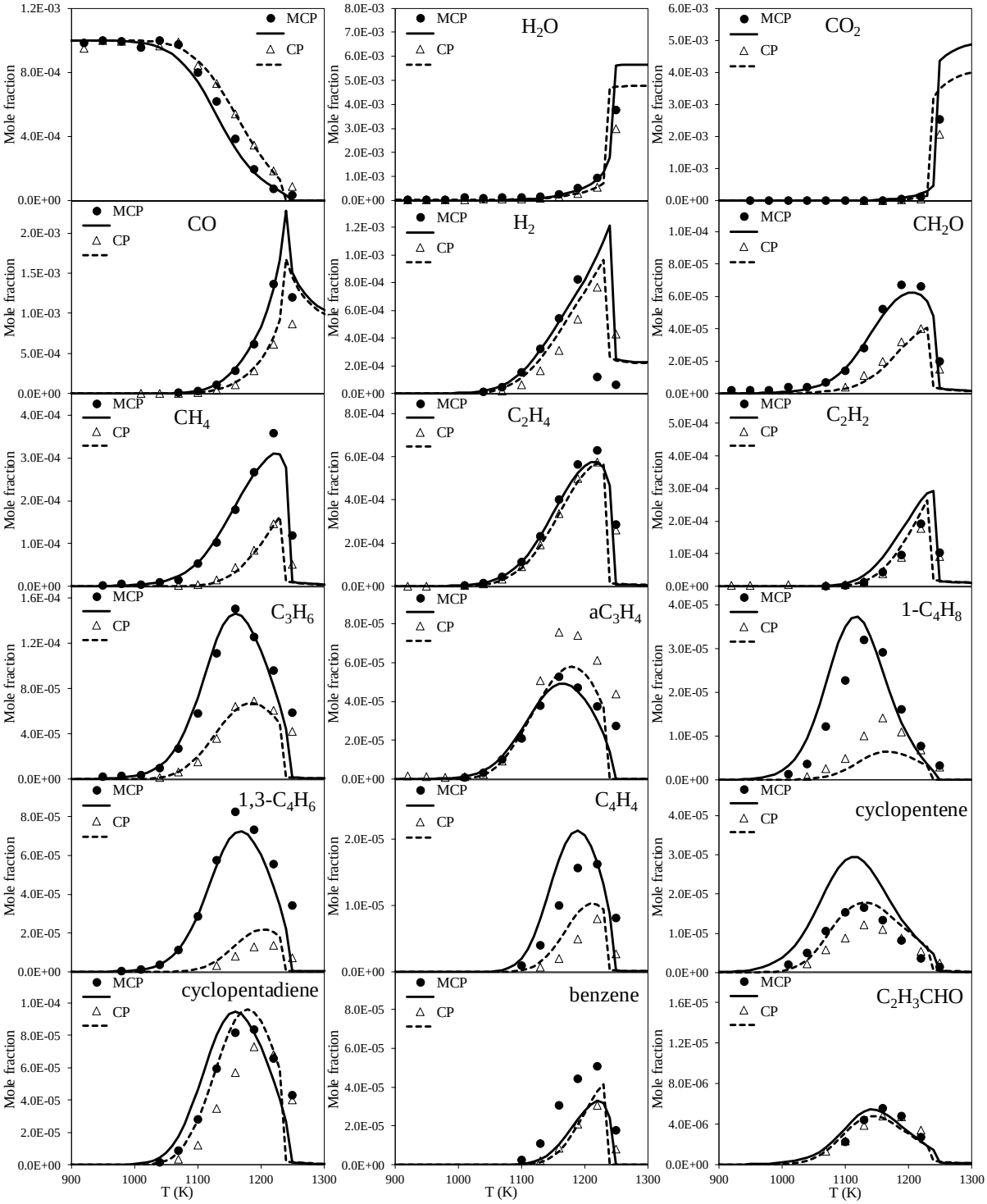


Figure 4: Experimental and computed mole fraction profiles obtained from the oxidation of cyclopentane (empty triangles and dashed line) and methylcyclopentane (filled circles and full line) in a JSR at $\varphi = 1$, $p = 1$ atm, $\tau = 0.07$s.

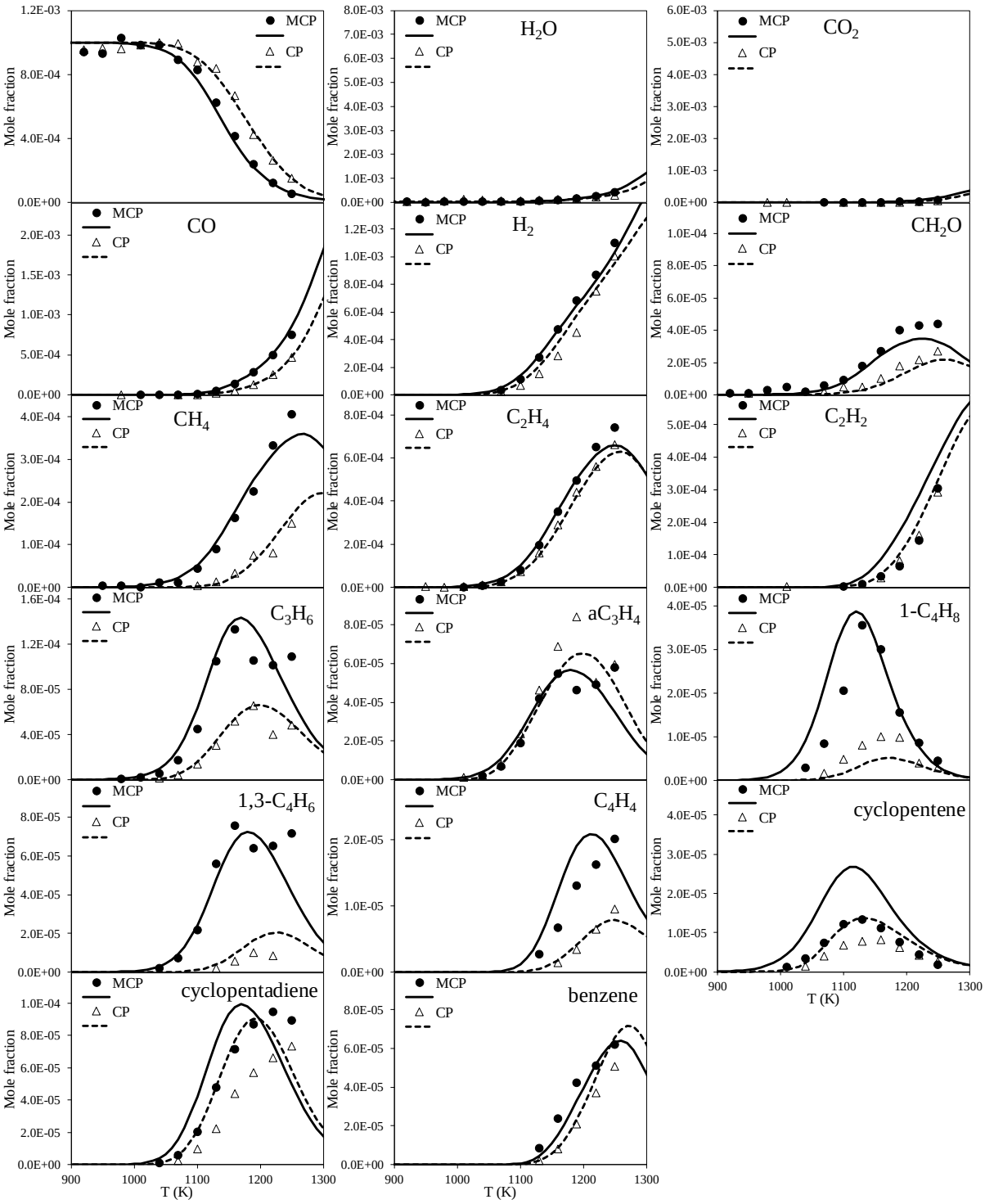


Figure 5: Experimental and computed mole fraction profiles obtained from the oxidation of cyclopentane (empty triangles and dashed line) and methylcyclopentane (filled circles and full line) in a JSR at $\varphi = 2$, $p = 1$ atm, $\tau = 0.07$s.

As can be seen from Figures 3-5, methylcyclopentane oxidation produces more formaldehyde, methane, propene, but-1-ene, buta-1,3-diene, vinylacetylene, cyclopentene, cyclopentadiene, and benzene than cyclopentane oxidation. However, similar amounts of H_2, ethylene, acetylene, allene, and acrolein are observed for both fuels.

The kinetic mechanism reproduces reasonably well the experimental data. Fuel consumption is well reproduced under all the conditions investigated. Nevertheless, some discrepancies between the simulations and the experimental data can be observed for vinylacetylene (C_4H_4), cyclopentene, cyclopentadiene or benzene, although these discrepancies are different depending on the fuel and the experimental conditions. For instance, benzene is well reproduced for cyclopentane oxidation regardless to the equivalence ratio while benzene is under-estimated for methylcyclopentane under fuel-lean and stoichiometric conditions and quite well predicted under fuel-rich conditions.

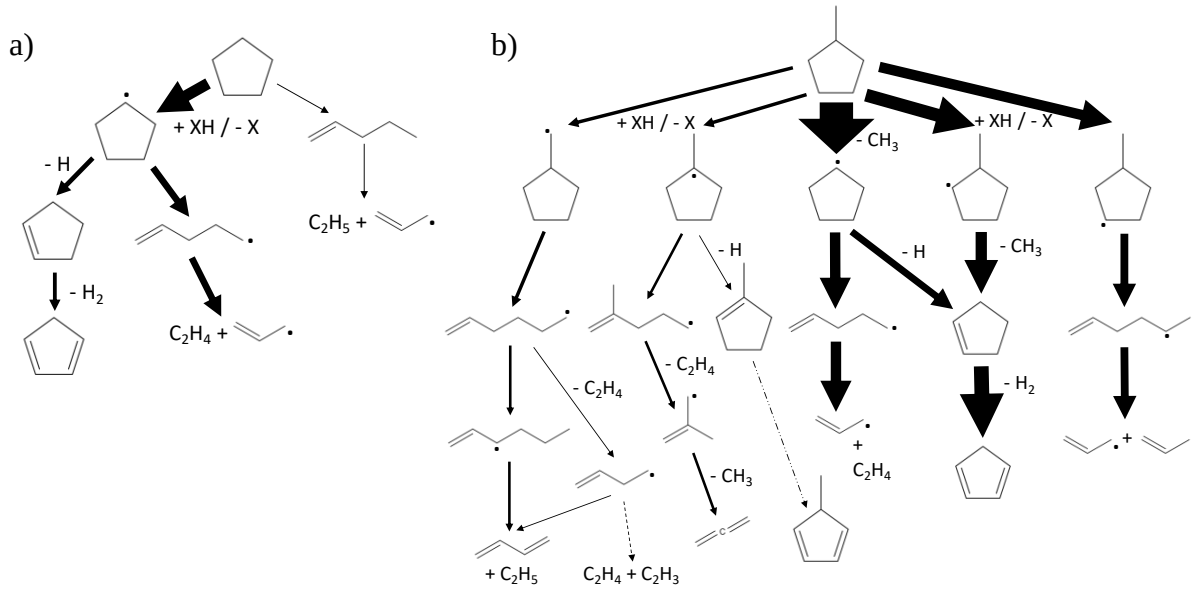


Figure 6: Reaction pathway analysis of the oxidation of cyclopentane a) and methylcyclopentane b) in a JSR at T = 1150 K, p = 1 atm, τ = 0.07s, and φ = 1 (the size of the arrows is proportional to the flow rate).

Figure 6a) depicts the reaction pathway analysis performed under stoichiometric conditions, at atmospheric pressure and 1150 K (the temperature at which ca. half of the fuel is consumed) of the oxidation of cyclopentane. Under these conditions, the oxidation of cyclopentane is quite simple: 90% of cyclopentane yields cyclopentyl radicals (H: 56.3%, OH: 21.3%, O: 6.7%, CH_3: 2.8%, a-C_3H_5: 1.5%) which in turn undergo a C-H β-scission (40%) yielding cyclopentene, or a C-C β-scission (60%) producing pent-1-en-5-yl. According to our mechanism, 99% of pent-1-en-5-yl gives ethylene and allyl radicals while 84% of pent-1-ene unimolecularly decomposes into ethyl and allyl radicals. Hydrogen is the most important radical as far as cyclopentane consumption is concerned. These H atoms are mostly produced by C-H β-scissions from cyclopentyl, allyl, and ethyl radicals. Allyl is also a key radical in the oxidation of cyclopentane: half of the allyl produced gives allene after a hydrogen departure and 17.5% of allyl also produces propene by recombination with hydrogen atoms.

Methylcyclopentane oxidation pattern is much more complicated. Figure 6b) illustrates the reaction pathways analysis of methylcyclopentane under stoichiometric conditions, at atmospheric pressure and 1150 K, the temperature at which ca. half of the fuel is consumed. Under these conditions, almost one third (31.6%) of the fuel is consumed through the decomposition yielding methyl and cyclopentyl radicals. The other unimolecular decompositions only account for few percentages of the total flow rate. Other important pathways for fuel consumption are H-abstractions by H (33.1%), OH (15.9%), and CH_3 (6.4%) yielding the four methylcyclopentyl radicals. Among these methylcyclopentyl radicals

mcps1 is the most abundant (23.6%), followed by mcps2 (21.2%) slightly less produced because of the difference in the rate constants of the H-abstraction by OH proposed by Sivaramakrishnan and Michael [10], then mcpm (7.4%) and mcpt (6.6%) are produced in smaller quantities. Cyclopentyl radicals are consumed by ring opening (61.1%) yielding pent-1-en-5-yl or C-H β-scissions (38.7%) yielding cyclopentene+H. Cyclopentene then produces cyclopentadiene by dehydrogenation (82%) or 1,3-pentadiene (8%) while pent-1-en-5-yl produces allyl and ethylene as observed for cyclopentane. Cyclopentene is mainly produced by C-C β-scission from mcps1 (89.8%) for which ring opening is a minor channel (10.2%). On the contrary, the other secondary methylcyclopentyl radical (mcps2) undergoes ring opening, mostly to form hex-1-en-5-yl (90.1%). Finally, mcpm and mcpt are much less produced and participate to the production of 1,3-C_4H_6 or allene.

Summary

Oxidation of cyclopentane and methylcyclopentane was studied in a jet-stirred reactor at atmospheric pressure, a residence time of 70 ms and for various equivalence ratios (φ = 0.5, 1, and 2). A detailed kinetic mechanism was developed in this work based on our previous studies which is well able to reproduce our experimental results in JSR. Thanks to this mechanism, the main consumption pathways for the oxidation of cyclopentane and methylcyclopentane under our experimental conditions were identified. It was found that methylcyclopentane was more reactive, under these conditions, than cyclopentane mostly because of the initiation step producing cyclopentyl and methyl radicals. Cyclopentyl radicals as well as hex-1-en-6-yl radicals are key intermediates during the oxidation process of methylcyclopentane. However, experimental data under higher pressures and in different set-ups would be of importance to fully validate our detailed kinetic mechanism.

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