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Propane Oxidation at High Pressure and Intermediate Temperatures

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Motivations

- ❖ Propane: a major component in LPG
- ❖ Propane: a minor but sensitive component of natural gas
- ❖ Engines and gas turbines: need experimental data at high pressures and intermediate temperatures

Experimental: laminar flow reactor

- ❖ Quartz reactor to minimize surface reactions
- ❖ Steel pressure shell to achieve high pressures
- ❖ Temperature: 500–900 K
- ❖ Pressure: 100 bar
- ❖ Isothermal Zone Length: 42–44 cm
- ❖ Residence time: 8–11 s
- ❖ Measurement via GC

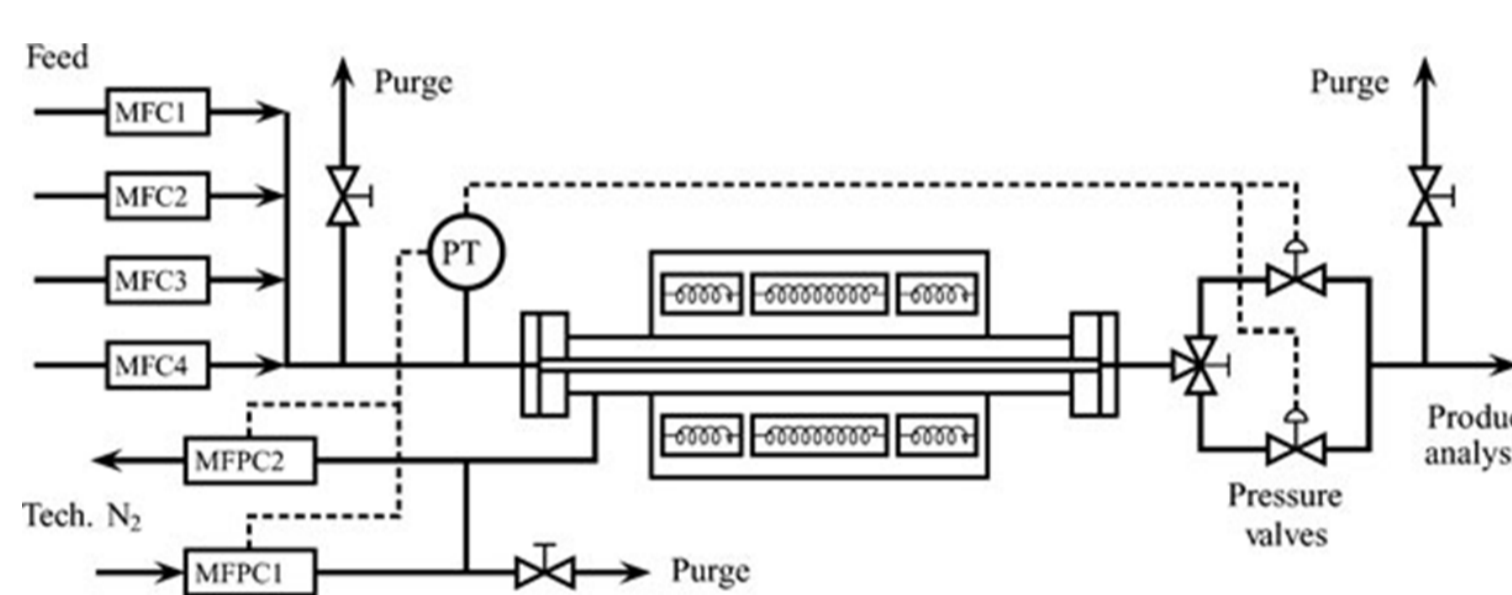


Fig 2. Schematic diagram of the high pressure laminar flow reactor

Chemical kinetics model

- ❖ H₂/CO/HC's subsets from recent work by Glarborg et al. [1–4].
- ❖ C₃ subset is reviewed and introduced in the present work.
- ❖ Low temperature sequences for propane oxidation is adopted from Goldsmith et al. [5].

Results: fuel-rich mixture

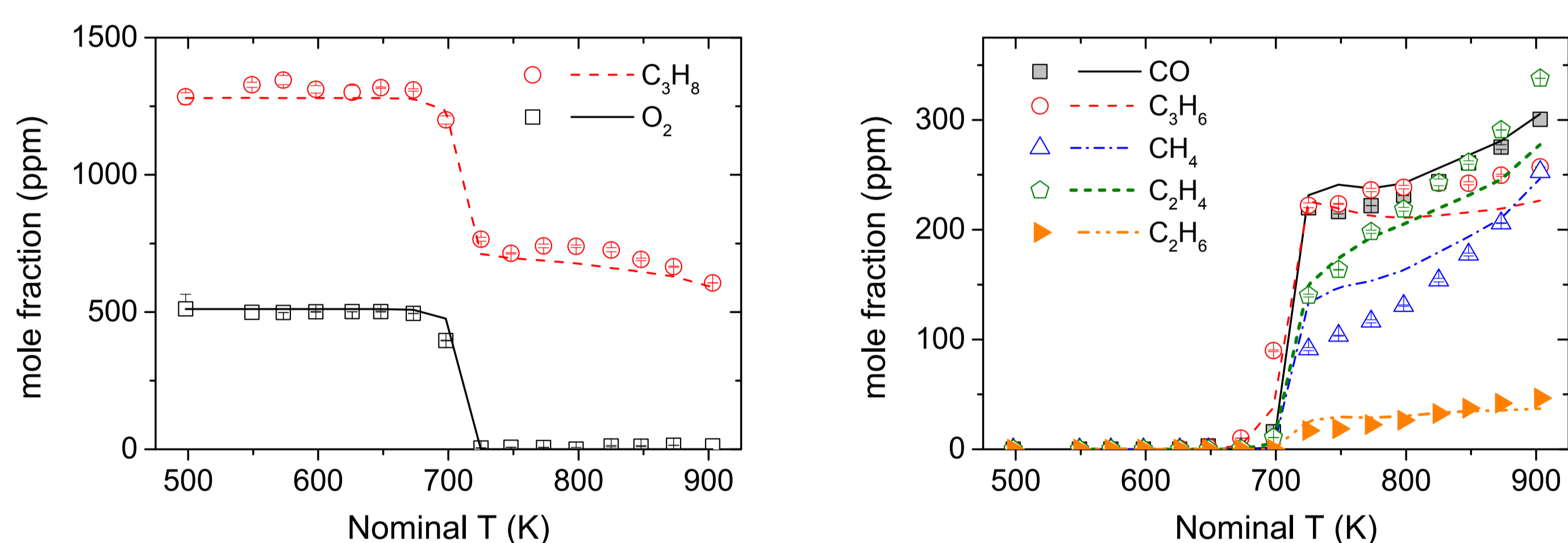


Fig 3. Results of experiments under reducing conditions (1285 ppm C₃H₈ and 511 ppm O₂ in N₂, $\Phi=12.5$) at 100 bar pressure.

The fuel oxidation started at 700–725 K for a fuel-rich mixture (reducing conditions), and the major detected products have been CO, C₃H₆, CH₄, and C₂H₄. The model was able to reproduce the onset of oxidation as well as the concentrations of intermediate components precisely.

Results: stoichiometric mixture

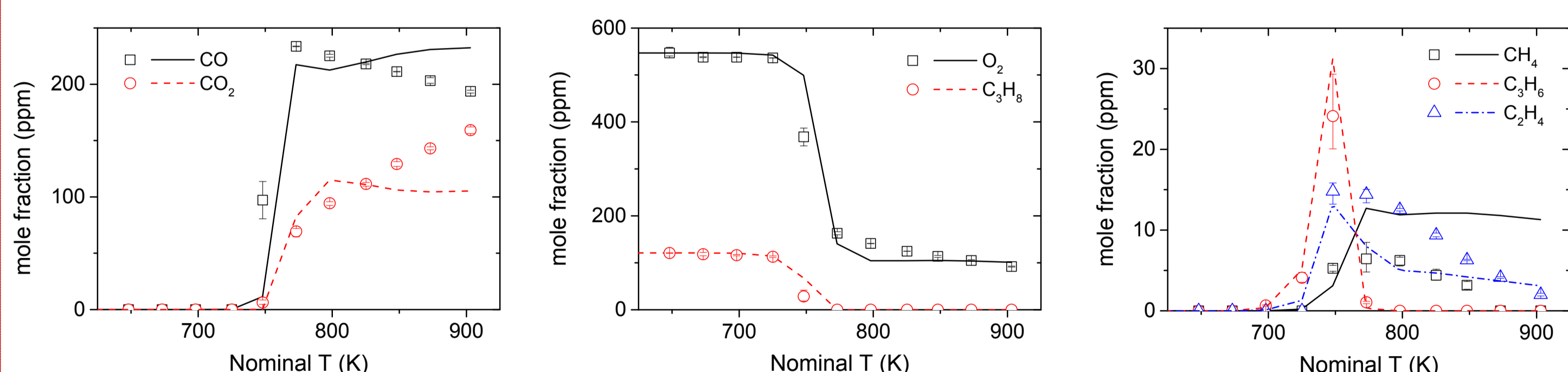


Fig 4. Results of experiments under stoichiometric conditions (121 ppm C₃H₈ and 547 ppm O₂ in N₂, $\Phi=1.1$) at 100 bar pressure.

For a stoichiometric mixture, the fuel conversion started around 725 K. At T>750 K, propane was oxidized almost completely. The major products of the oxidation were CO and CO₂ and the concentration of propene and ethene decreased sharply at T>775 K. The model captured the onset temperature of ignition accurately but it seems that CO oxidation to CO₂ at high temperatures was not precisely captured by the model.

Results: fuel-lean mixture

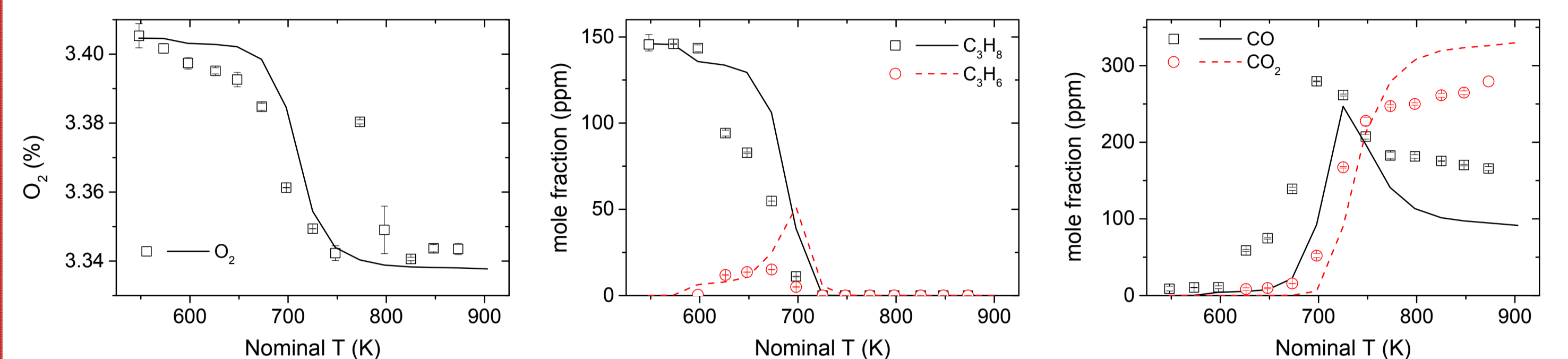


Fig 5. Results of experiments under oxidizing conditions (146 ppm C₃H₈ and 3.405% O₂ in N₂, $\Phi=0.02$) at 100 bar pressure.

Propane concentration dropped sharply at T>600 K for a fuel-lean mixture (oxidizing conditions), and propane vanished from the exhaust at T>725 K. The model predicted slower reactivity compared to the experiments, so the fuel conversion was slightly underpredicted by the model.

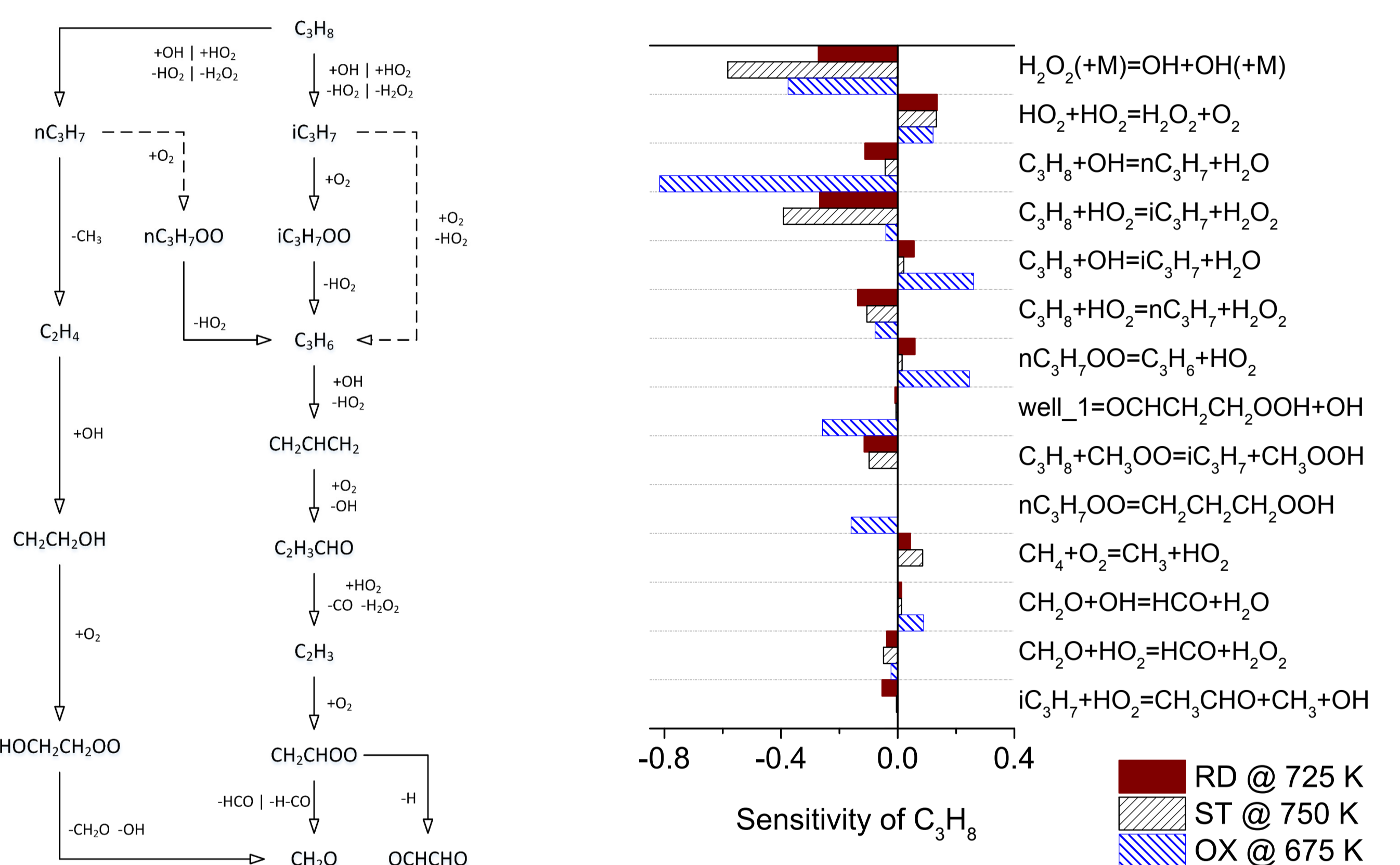
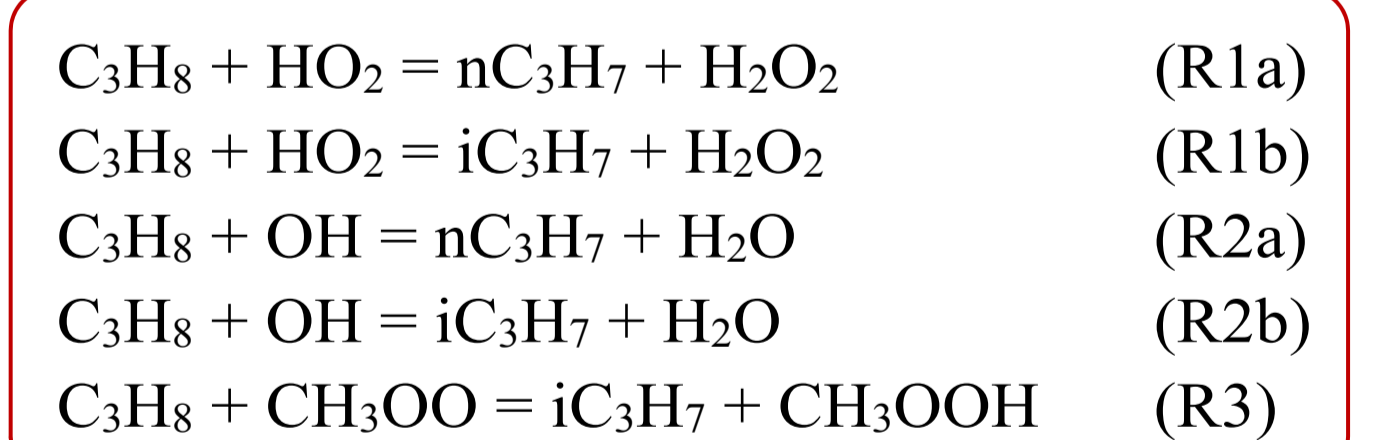


Fig 6. Left: Reaction pathways for propane oxidation under stoichiometric conditions (750 K, 100 bar). Right: Sensitivity of C₃H₈ prediction under flow-reactor conditions (RD: reducing, ST: stoichiometric, OX: oxidizing conditions) at 100 bar. The component HOOCH₂CH₂CH₂OOH is named “well_1” in above.

According to the results of sensitivity analyses, propane oxidation is largely controlled by H-abstraction by HO₂ from propane (R1). The branch leading to iC₃H₇ shows a larger sensitivity compared to the other one (except for oxidizing conditions). The reaction between C₃H₈ and OH (R2) is also sensitive. While the branch to nC₃H₇ promotes the oxidation, the other branch to iC₃H₇ inhibits the fuel conversion. The H-abstraction by CH₃OO from propane (R3) is also sensitive for reducing and stoichiometric conditions.



Analysing the reaction pathway of propane oxidation revealed that for stoichiometric conditions and at 750 K, the major path for propane oxidation begins with H-abstraction by OH and HO₂ (R1 & R2). If the H-abstraction results in an iC₃H₇ radical, it will add to molecular oxygen to give iC₃H₇OO, which later decomposes to propene. If R1 and R2 yield nC₃H₇, then decomposition to ethene is favoured compared to addition of nC₃H₇ to molecular oxygen.

Summary

Propane oxidation at intermediate temperatures (500–900 K) and high pressure (100 bar) has been characterized by conducting experiments in a laminar flow reactor over a wide range of stoichiometries. The onset of fuel oxidation was found to be 600–725 K, depending on mixture stoichiometry. The model agreed well with the measurements of fuel-rich and stoichiometric mixtures while the model underpredicted the fuel conversion for fuel-lean conditions. Sensitivity analyses revealed the importance of H-abstraction reactions by HO₂, OH, and CH₃OO in controlling propane oxidation at 750 K.

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