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A Comprehensive Experimental and Modeling Study of iso-Pentanol Combustion

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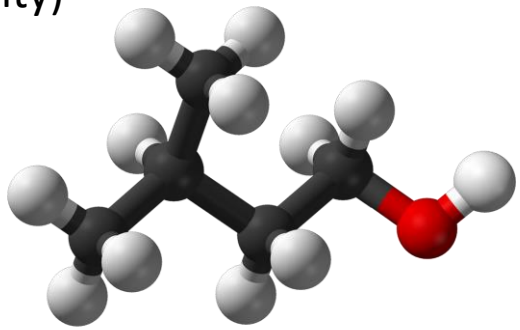
Introduction

- ✓Interest in alternative fuels and fuel additives has increased
- ✓Oxygenated fuels are being considered as alternative fuels
  - ✓potential to reduce particulate emissions
  - ✓balance emissions of greenhouse gas (CO_2) from combustion devices
- ✓Ethanol is an attractive alternative alcohol fuel extender for petroleum fuels
  - ✓can reduce the dependency upon petroleum fuels and greenhouse gas emissions
  - ✓Disadvantages (high hygroscopicity and low energy density)
- ✓Iso-Pentanol as a bio-derived gasoline substitute
  - ✓higher energy density and less hygroscopic than ethanol
- ✓The purpose of the present study
  - ✓to improve the understanding of its combustion
  - ✓to present the comprehensive detailed chemical kinetic model

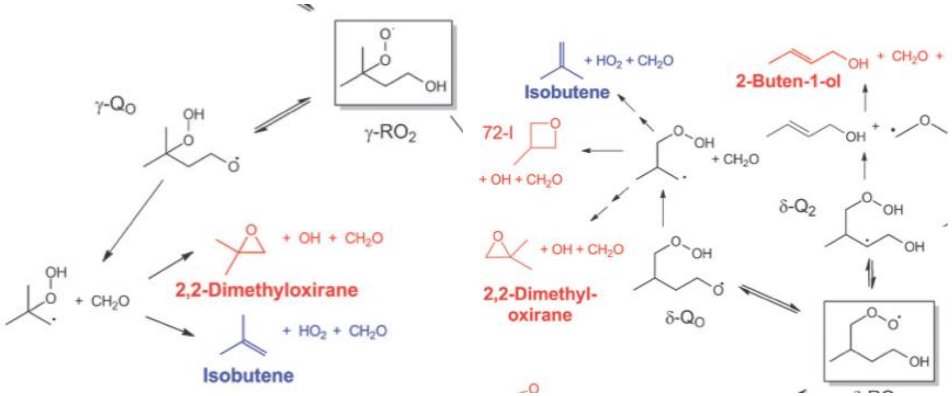


Chemical Kinetic Model

Mani Sarathy and Sungwoo Park (KAUST), Charles Westbrook and William Pitz (LLNL)

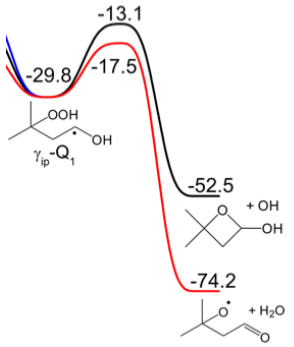
- ✓ Based on previous modeling study on C_4 and C_5 alcohols (360 species and 2072 reactions)
- ✓ High-temperature reaction classes
  - ✓ Unimolecular fuel decomposition
  - ✓ H-atom abstraction from the fuel
  - ✓ Fuel radical decomposition
  - ✓ …
- ✓ Low-temperature reaction classes
  - ✓ Addition of O_2 to fuel radicals (R + O_2 = ROO)
  - ✓ ROO radical isomerization (ROO = QOOH)
  - ✓ Concerted eliminations (ROO = enol + HO_2)
  - ✓ …
  - ✓ Included Waddington reaction pathway involving a 6-membered TST ring. Welz et al. show H transfers from the OH group are important for the γ-ROO and δ-ROO radicals via 7- and 8-membered TST rings so these are included. (paths to iso-butene)
  - ✓ Included Welz et al.'s unconventional water elimination pathway from QOOH radicals where the hydroperoxide is on the γ site and the radical is on the α site. (red line in figure)

7m and 8m Waddington-like reactions



Welz et al, Phys. Chem. Chem. Phys., 2012, 14, 3112–3127

Water elimination

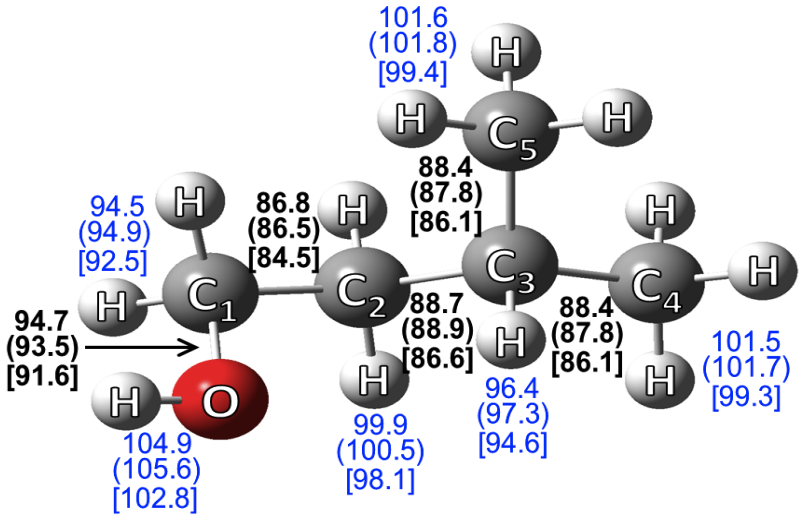


Welz et al, J. Phys. Chem. Lett. 2013, 4, 350–354

Quantum Chemistry Calculations

Alex Davis and Mani Sarathy (KAUST)

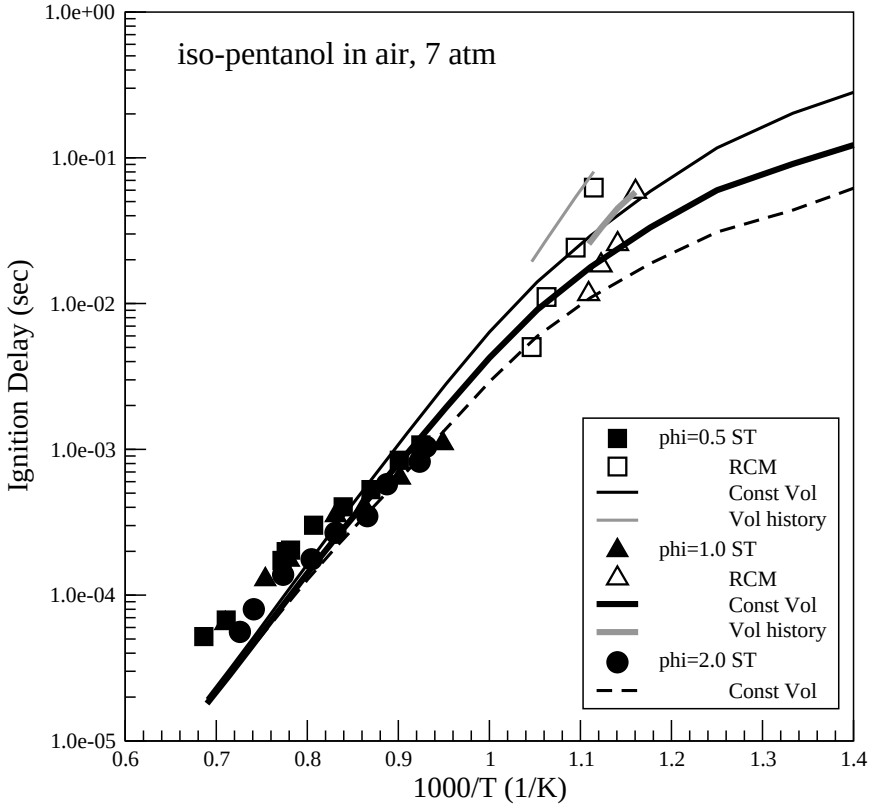
- Gaussian calculations used to determine most stable conformer and BDEs
- G3, G4 and CBS-QB3 levels of theory
- trans CCCC conformation, with the branching methyl and OH groups in gauche configurations on opposite sides of the backbone, is the most stable structure
- The α-C-H BDE for iso-pentanol and n-pentanol are very similar at 93.6 and 94.0 kcal mol^{-1}, respectively, suggesting that the methyl group has minimal influence on the strength of this bond
- iso-Pentanol displays the alkane-like and alcohol-specific portions of the molecule, which forms the basis for the allocation of reaction rate constants.

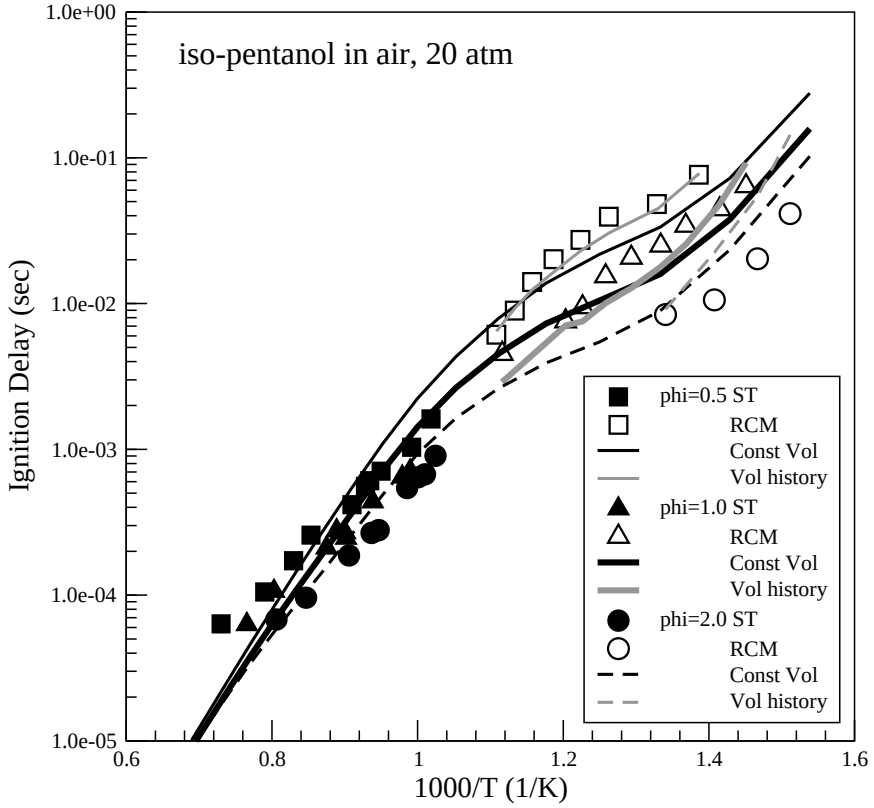


Bond dissociation energies for iso-pentanol.
[] G4 values
() G3 values
no brackets CBS-QB3 values.
Blue values are C–H
Black are C–C BDEs
(kcal mol^{-1} at 298 K).

Ignition Delay Time

P=7, 20 atm



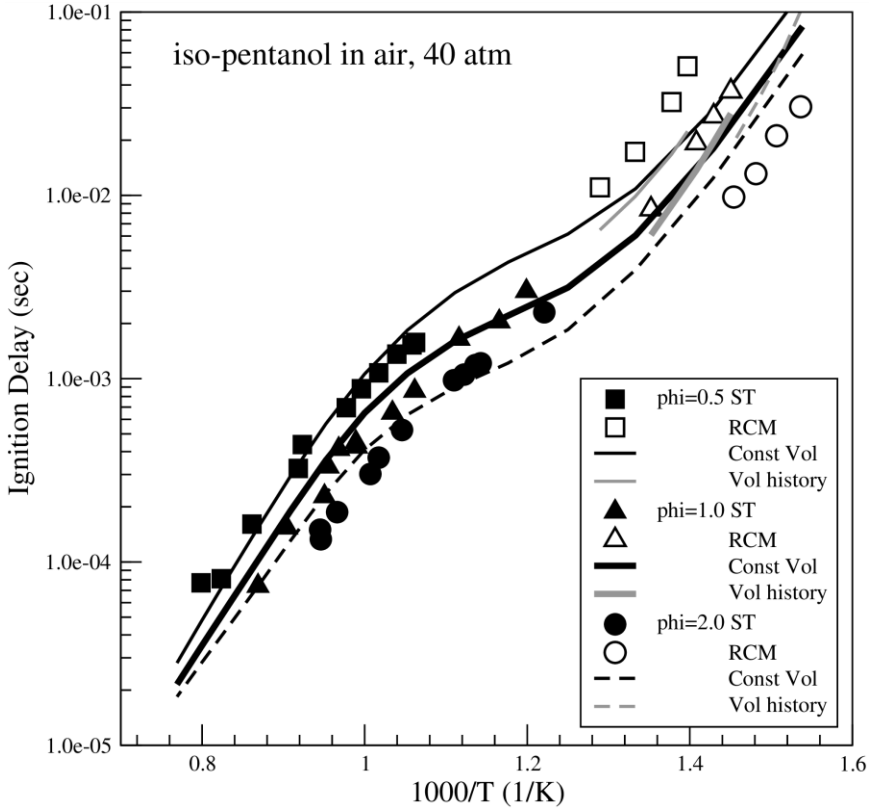


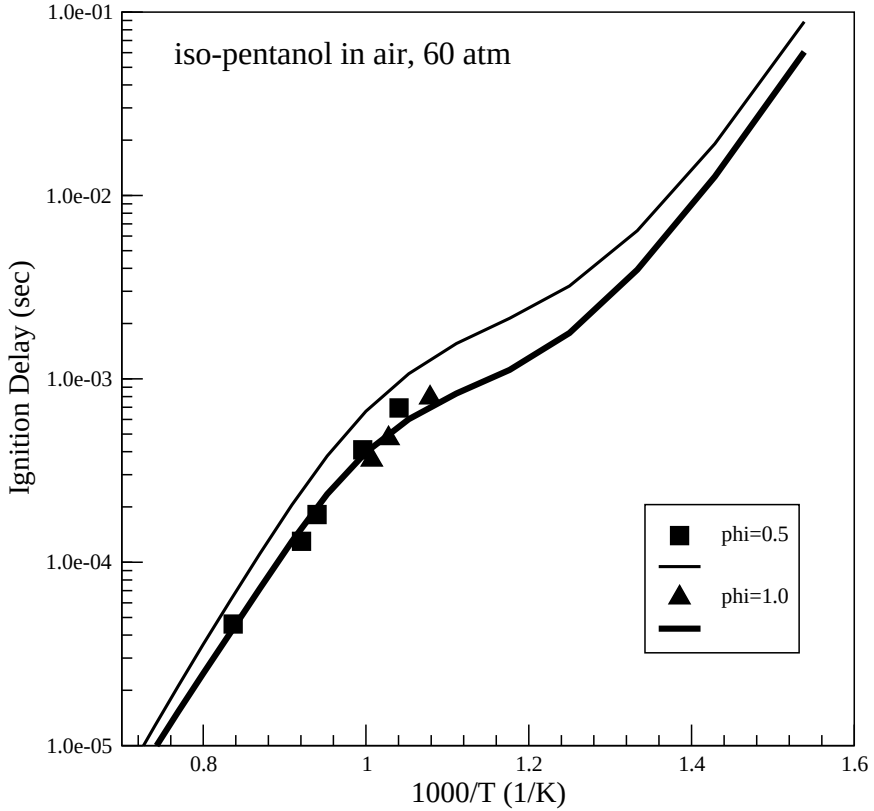
Tsujimura *et al*. "Development of Isopentanol Reaction Mechanism Reproducing Autoignition Character at High and Low Temperatures" Energy & Fuels (2012)

Ignition Delay Time

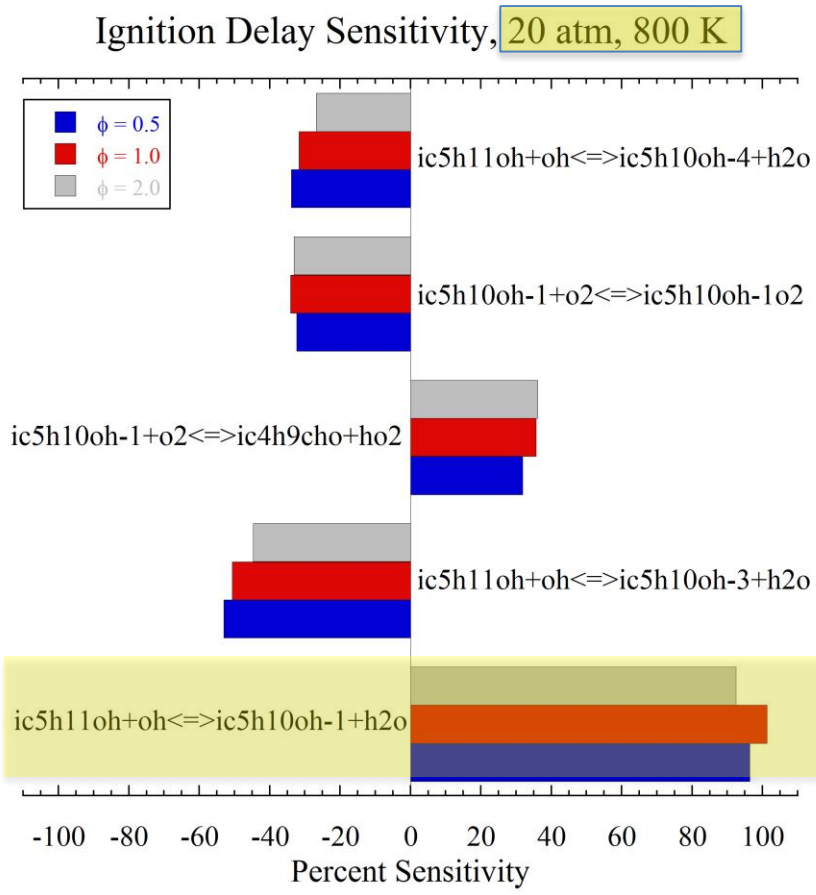
P=40, 60 atm

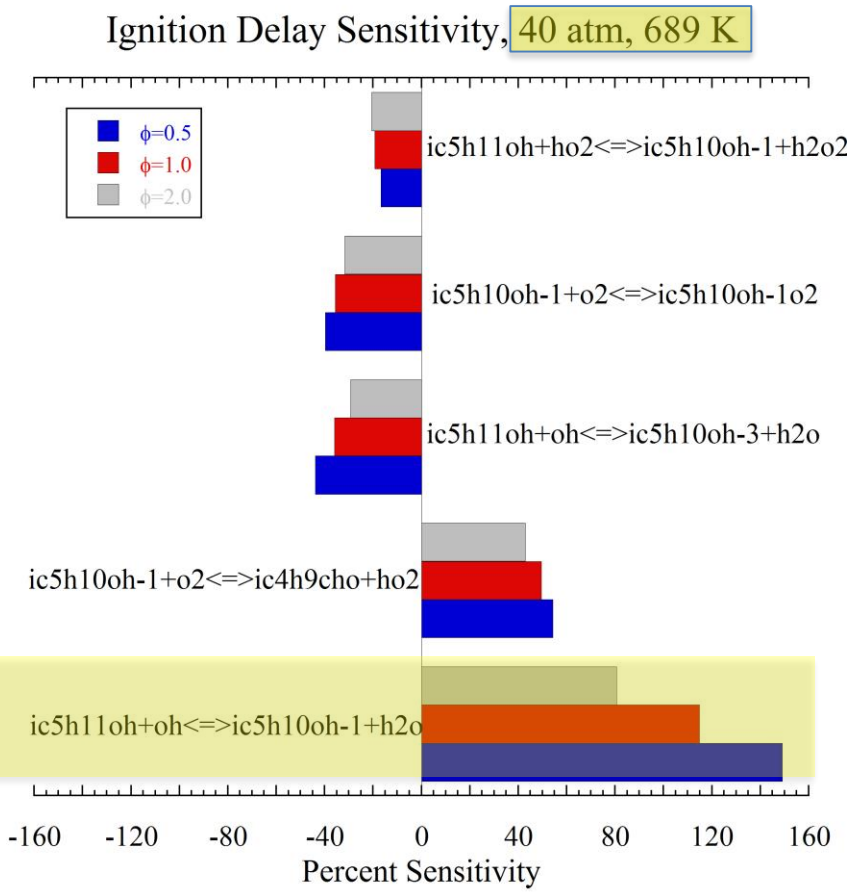
RCM from Bryan Weber and Chih-Jen Sung (UCONN)
ST from Weijing Wang and Matthew Oehlschlaeger (RPI)





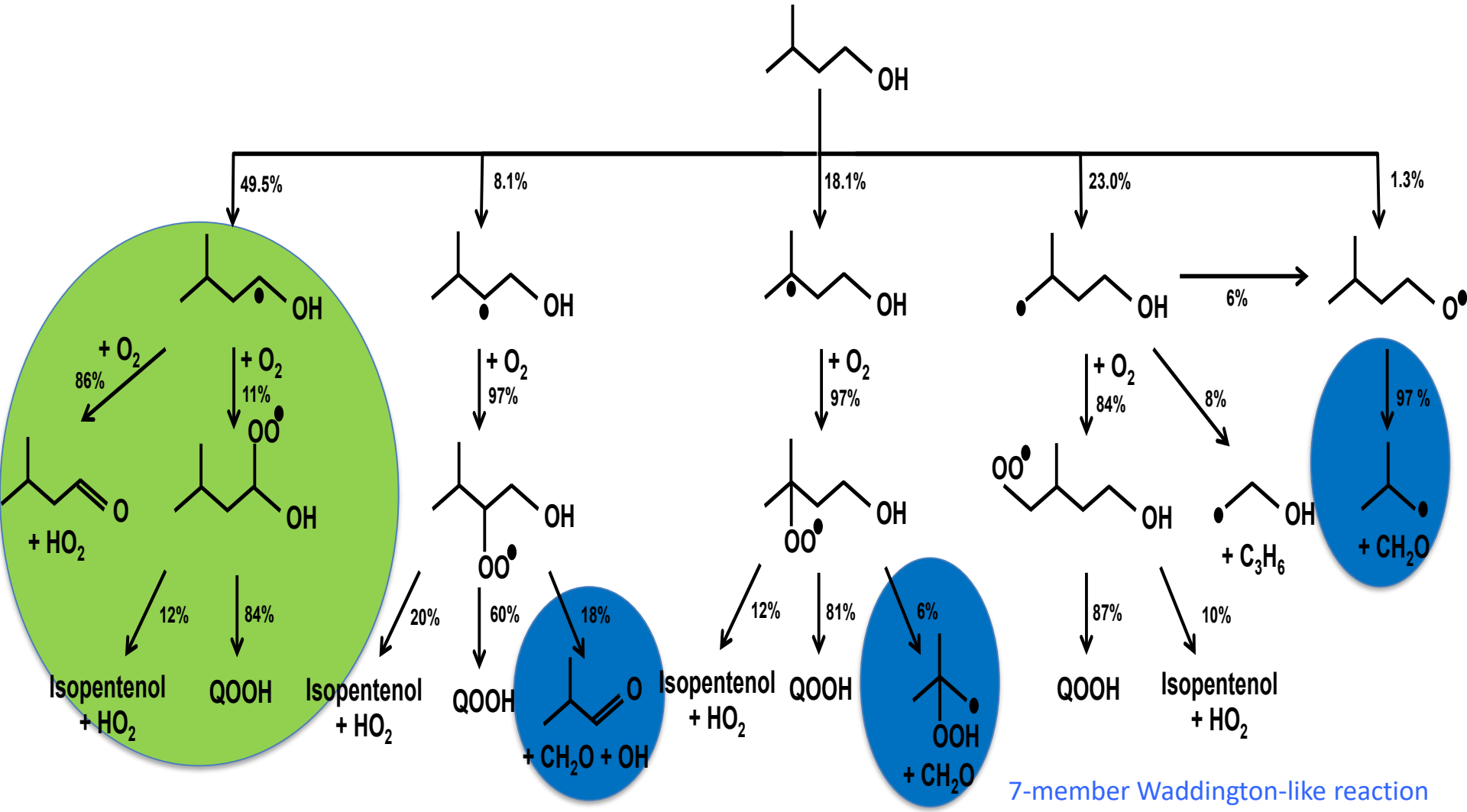
Sensitivity Analysis





Reaction Path Analysis

P=20atm/ T=800K/ Φ=1 – Similar results for other Φ and 40 atm, 689K

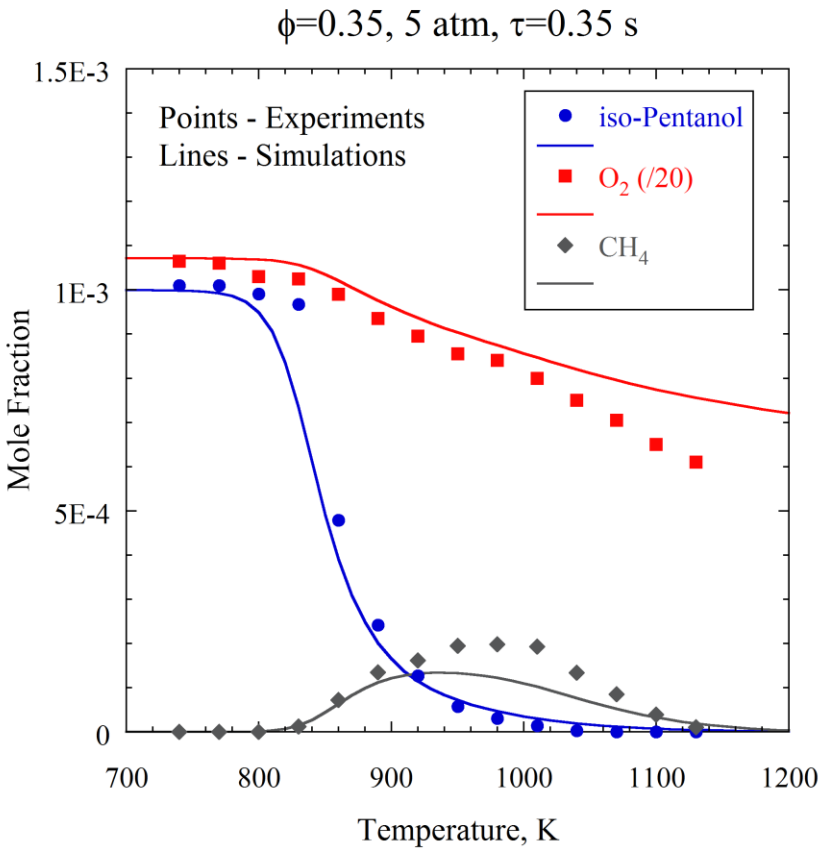


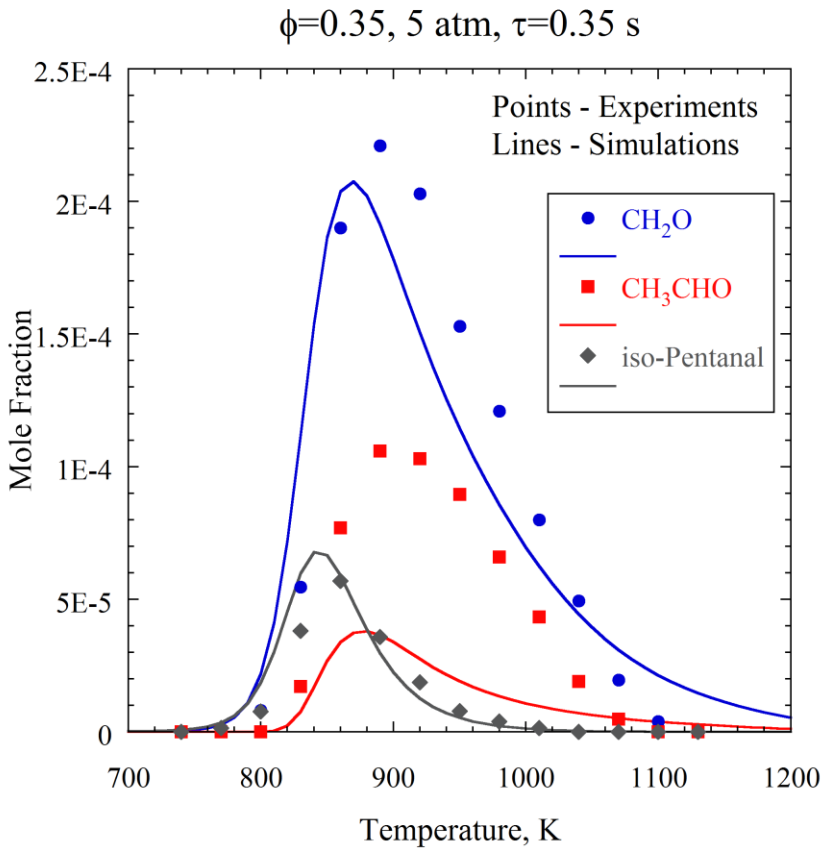
7-member Waddington-like reaction is important. 8-member and water elimination reactions are not

JSR Concentration Profiles

P=5atm/ Φ=0.35/ τ=0.35s

Casimir Togbe, Guillaume Dayma, and Philippe Dagaut (CNRS Orleans)





JSR Concentration Profiles

P=5atm/ Φ=1.0/ τ=0.35s

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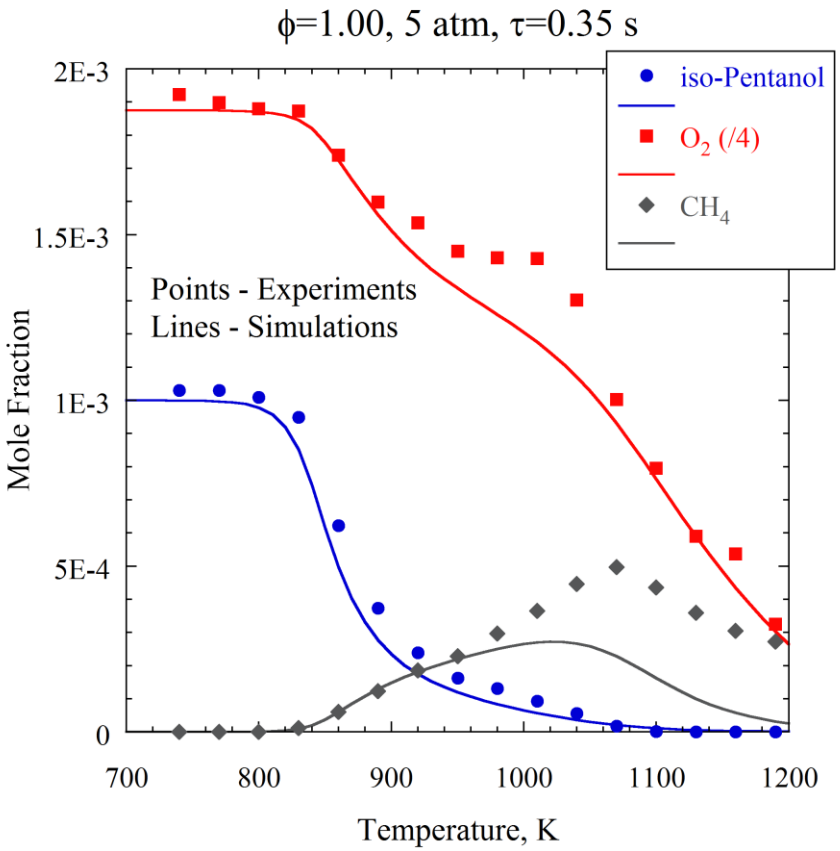
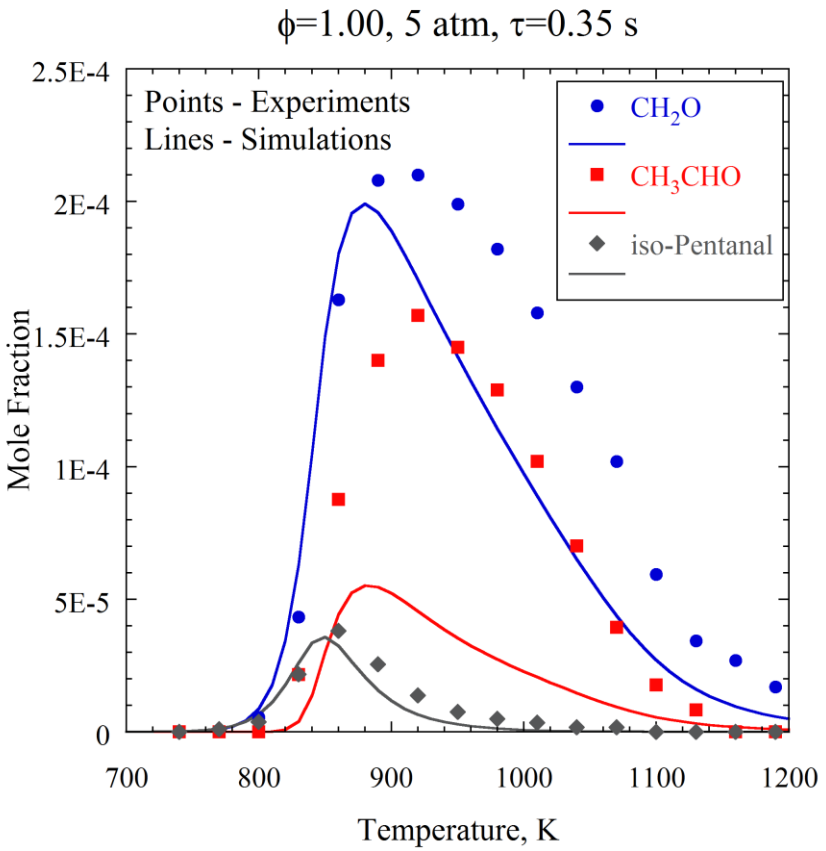
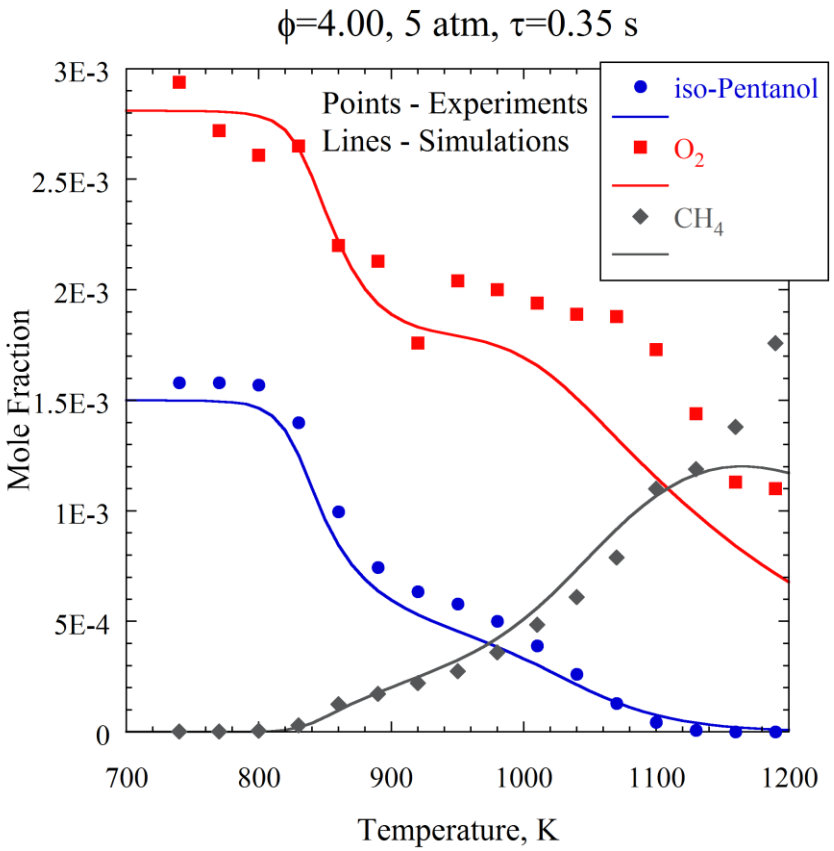


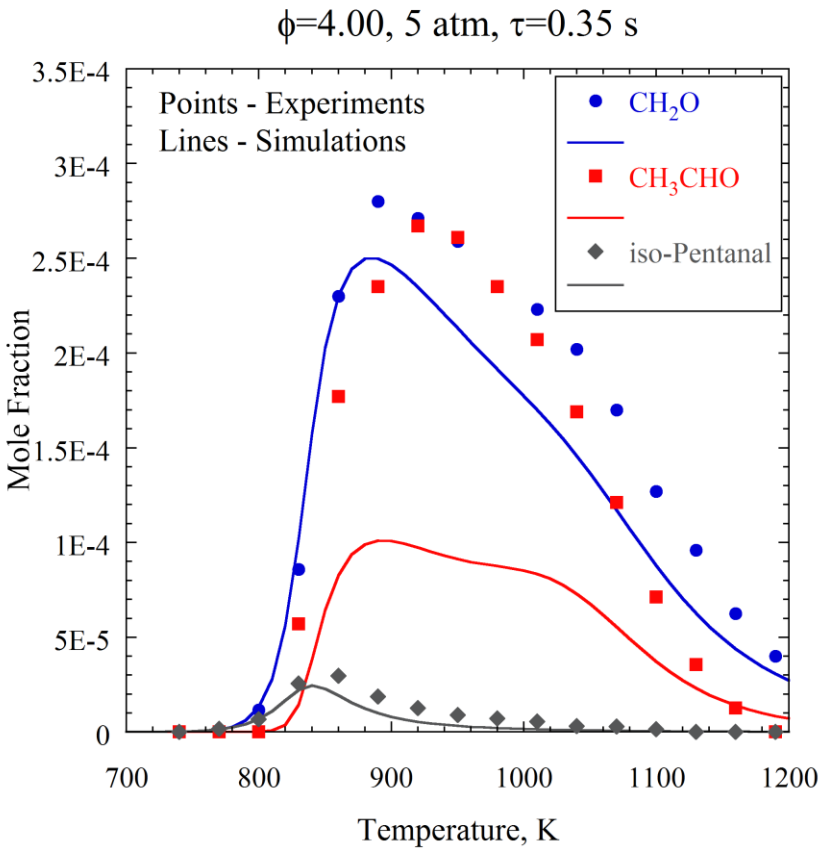


JSR Concentration Profiles

P=5atm/ Φ=4.0/ τ=0.35s

Casimir Togbe, Guillaume Dayma, and Philippe Dagaut (CNRS Orleans)





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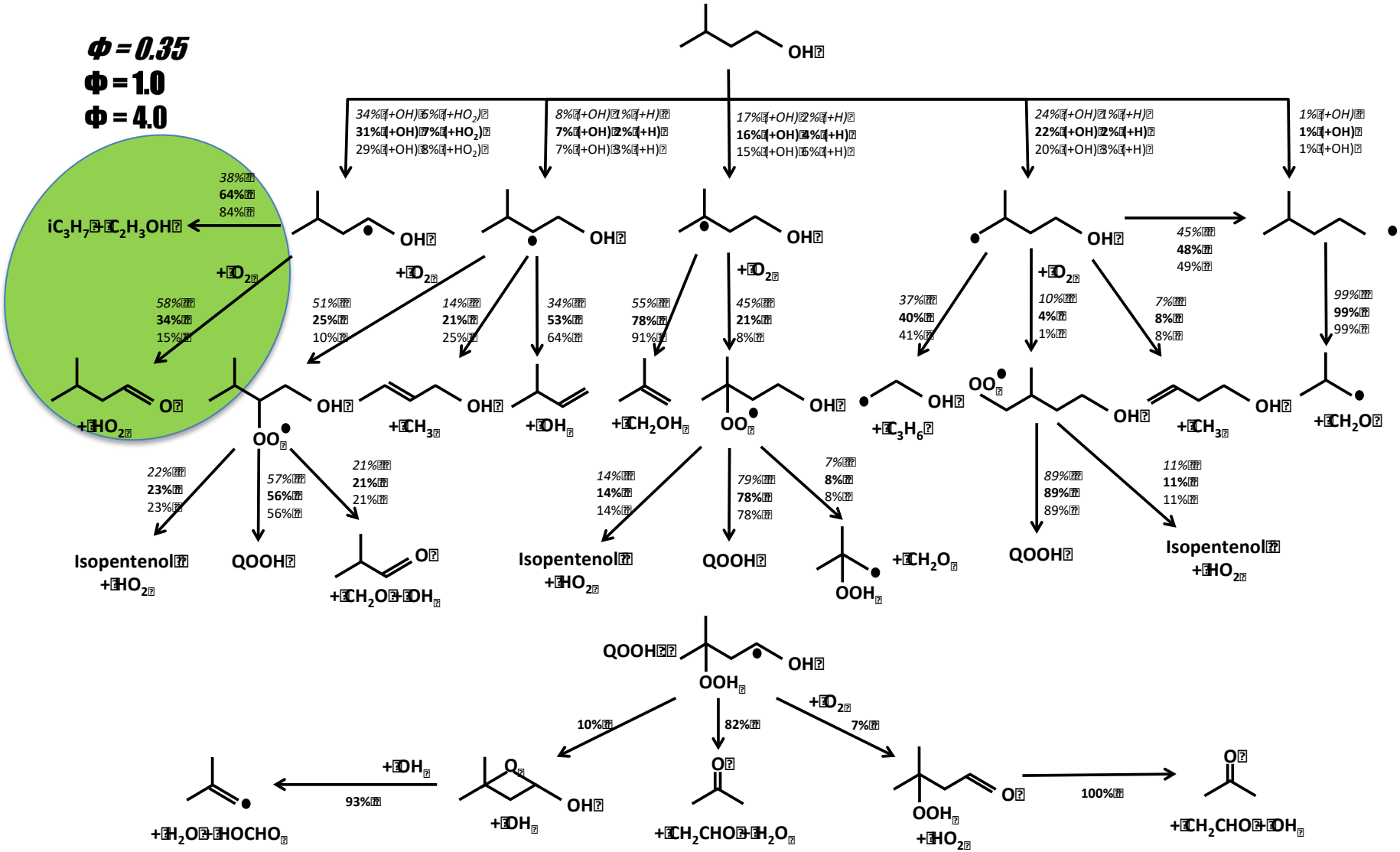
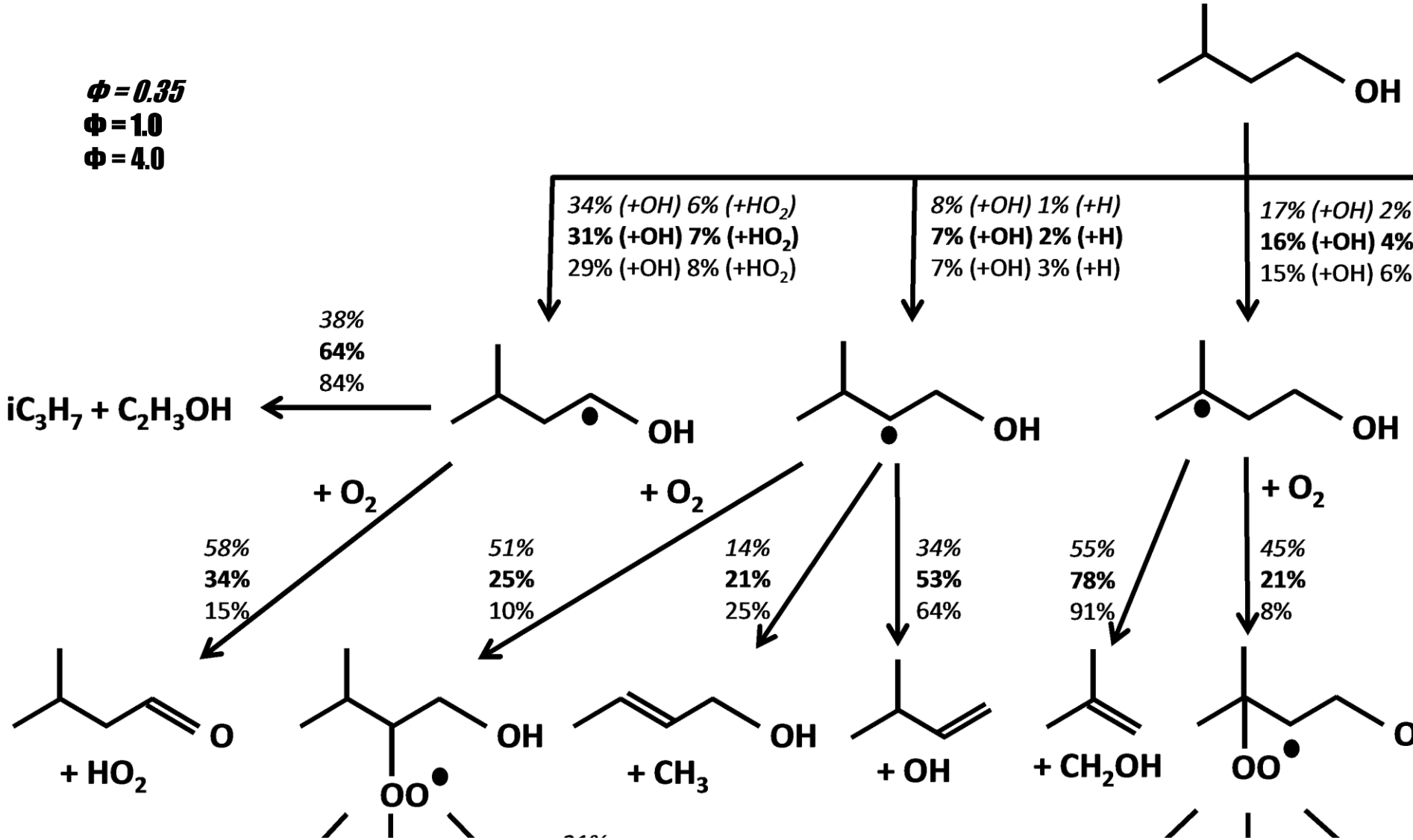
Reaction Path Analysis

P=5atm/ T=850K



Reaction Path Analysis

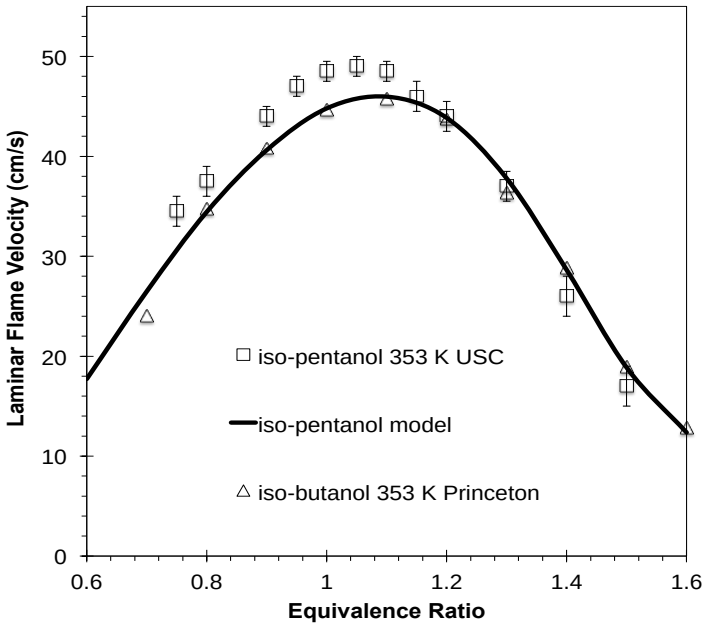
P=5atm/ T=850K



Counterflow Flame Experiments

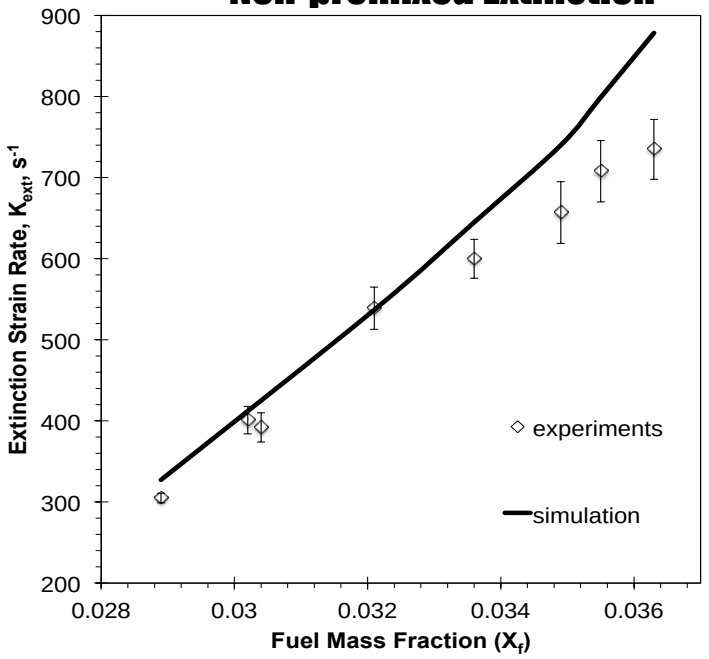
Peter Veloo (Princeton), Okjoo Park and Fokion Egolfopoulos (USC)

Premixed Flame Propagation



- Utilized detailed reaction mechanism
- Flame speeds are under predicted at lean and stoichiometric conditions
- Model prediction similar to iso-butanol data from Princeton (Liu et al PROCI 2011)
- Previous iso-butanol model gave similar predictions of the iso-butanol flame speed
- This suggests flame speed predictions are not dependent on chain length

Non-premixed Extinction



- Utilized skeletal mechanism consisting of 187 species and 1235 reactions using DRG-X from Luo and Lu (UCONN)
- Model well predicts extinction strain rate at low fuel mass fractions
- Extinction strain rate over predicted at higher fuel mass fractions
- Sensitivity to fuel diffusive transport at higher fuel mass fraction

Conclusion

- ✓ A detailed chemical kinetic model for iso-pentanol including high- and low-temperature chemistry was developed using a consistent set of reaction classes and rate rules
- ✓ The proposed model for iso-pentanol was validated against experimental data in shock tubes, rapid compression machines, jet stirred reactors, and counterflow flames
- ✓ The present mechanism shows good overall agreement with the data obtained from a wide variety of experimental conditions.
- ✓ Reaction path and ignition delay sensitivity analyses were conducted for identifying key reactions pathways in the oxidation of iso-pentanol at various conditions.
- ✓ Further comprehensive experimental and modeling studies on alcohol specific reaction mechanisms and rate constant estimates at LTC-relevant conditions are warranted.

Thank you!

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JSR Concentration Profiles

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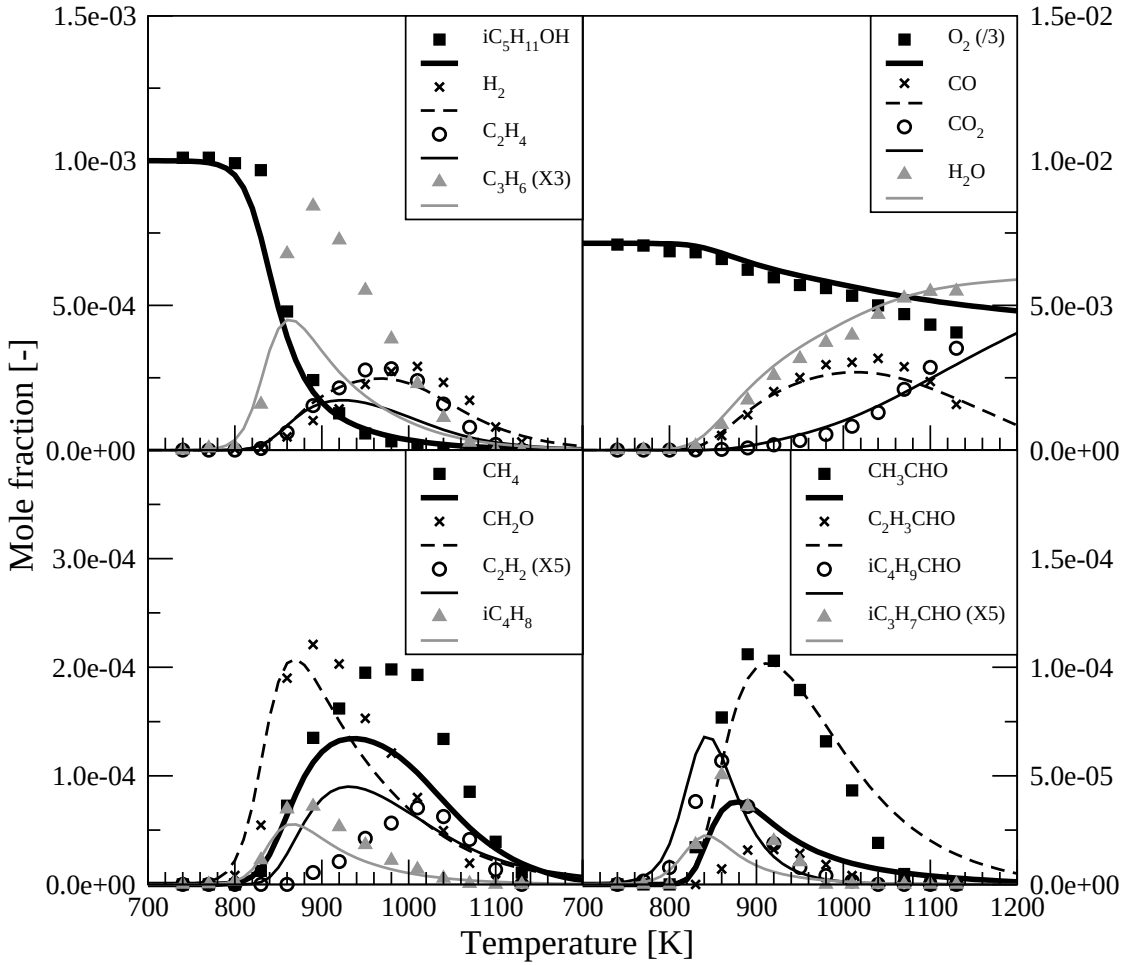

JSR Concentration Profiles

P=5atm/ Φ=1.0/ τ=0.35s

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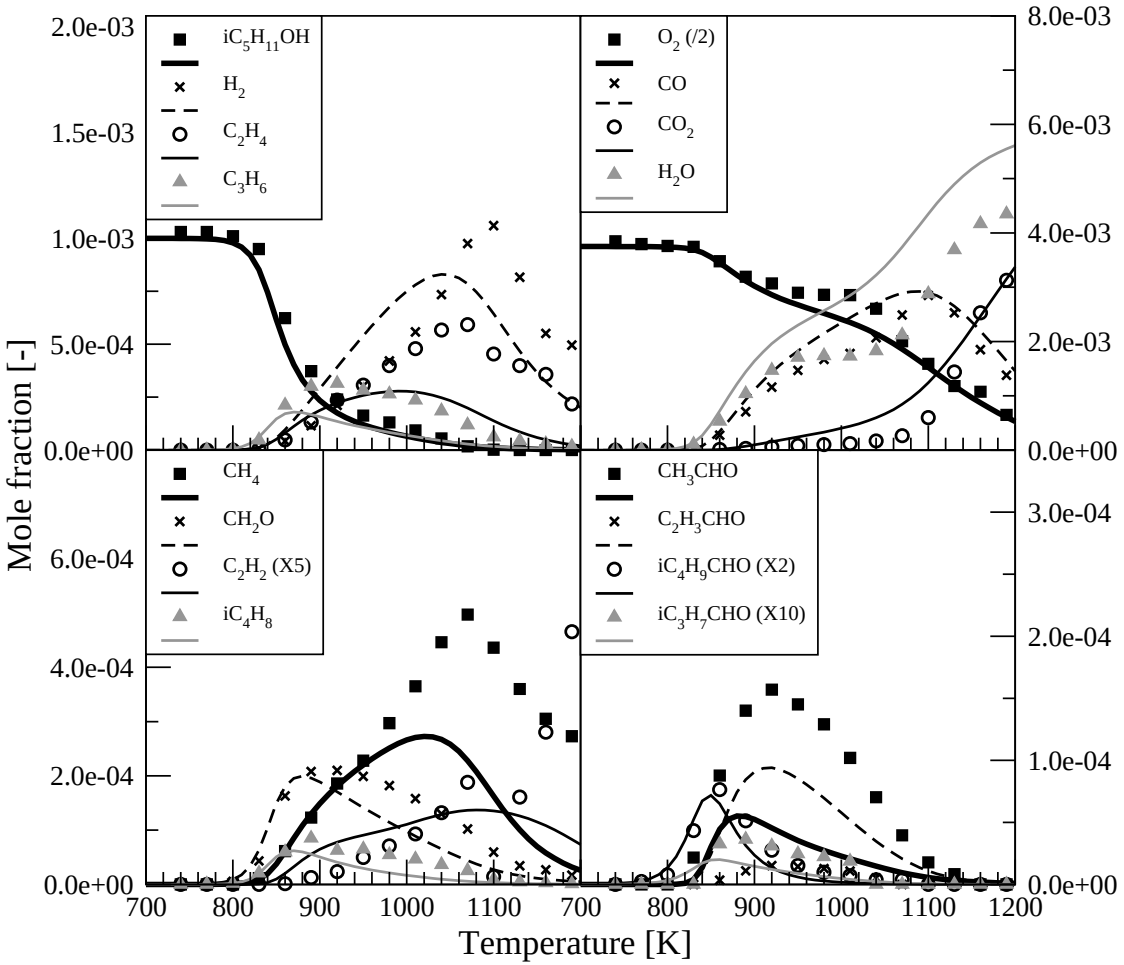

JSR Concentration Profiles

P=5atm/ Φ=4.0/ τ=0.35s

Casimir Togbe, Guillaume Dayma, and Philippe Dagaut (CNRS Orleans)