

# Combustion Chemistry

## Part 5

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# Today's Agenda

- Overview of important Combustion Chemistry regimes
  - Diffusion Flames (leading to Soot Formation discussion)
  - Pre-mixed Flames
  - Ignition (leading to Low-T ignition discussion)
- Discussion of Soot Formation (following Hai Wang, Charles McEnally)
- Discussion of Low-T Ignition (following Shamel Merchant)

# Non-Premixed Diffusion Flames: Pyrolysis

- Rate-controlled by diffusion, fluid flows
  - Almost zero chemistry effect: “Mixed is Burnt”
- In flame zone, very high T and radical concentrations: drives most processes to equilibrium (e.g.  $\text{CO}_2 + \text{H}_2\text{O}$ ) very quickly
- Fast Zeldovitch  $\text{NO}_x$  formation ( $\text{O} + \text{N}_2 \rightarrow \text{NO} + \text{N}$ ) in hottest zone
- Relatively little chemistry occurring on air side
- Lots of pyrolysis chemistry occurring on fuel side

# Fuel Pyrolysis Overview

- Radical (e.g. H atom) attacks Fuel RH to make Fuel radical R
- R beta-scissions to smaller radical r
  - $R \rightarrow \text{alkene} + r$
- Process continues until r is so small it can't beta-scission
  - E.g.  $r = \text{H}$  or  $r = \text{CH}_3$
- Large Alkenes can fragment or do similar chemistry to RH
- Pretty quickly all the large molecules are gone, left with mixture of small alkenes, H<sub>2</sub> and CH<sub>4</sub>
  - Takes about 1 second at 1000 K, quite fast by 1400 K

# Ceiling Temperature

- Reactions of the type  $R \rightarrow \text{alkene} + r$  are endothermic
- Both  $\Delta H$  and  $\Delta S > 0$  so  $K_c$  increases with  $T$

$$[r]/[R] = K_c/[C_2H_4]$$

- At low  $T$ , the process runs in reverse, but above Ceiling Temperature the decomposition is favored.

# Different Fuels make different mix of alkenes

- At high T, this is the main difference between fuels: how much ethene and H<sub>2</sub> (reactive with O<sub>2</sub>) vs. how much propene and methane (relatively unreactive)
- One can extend this to understand very complicated fuels e.g. real jet fuels: if you can measure the ratio of alkenes formed from the fuel, you can understand the high T chemistry pretty well.
- Alkene Mix directly important in petrochemical industry: naphtha steam-cracking
  - Biggest part of chemical industry, very heavily studied and well-understood.

# What do the small alkene products do?

- Main alkene is ethene ( $C_2H_4$ ). In absence of  $O_2$  it is gradually converted to acetylene ( $C_2H_2$ ).
- Second most important alkene is propene. It converts to resonance-stabilized radical allyl  $C_3H_5$  (resistant to  $O_2$  reaction), and then gradually to resonance stabilized radical propargyl  $C_3H_3$ .
- Propargyl + Propargyl and various addition reactions of acetylene can lead to aromatics and to soot formation.
- So one idea for clean combustion is to get the ethene and propene into the flame before they have time to form the soot!

Exactly how fast does soot form? What particle-size distribution (matters for filtration, health)

- Many unresolved mysteries, discussed by Hai Wang at Beijing Combustion Symposium...Let's look at Prof. Wang's slides



# Ceiling Temperature for Soot?

- The initial reaction  $\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$  has a  $K_c$  that increases with  $T$
- But the later steps
  - small molecules  $\rightarrow$  single big molecule
- Look like they should have a ceiling temperature
  - This would imply a Temperature Band where soot can form...
- Key question is whether there are reactions which combine small molecules to big ones, but release a second product (increasing  $\Delta S$ )
- How big the molecules get depends sensitively on thermo, which is not known very accurately

# What is the Fate of the Soot after it is Formed?

- In many engines e.g. diesels at high-load, a high fraction of the carbon in the fuel is converted to soot
- But Soot is carbon, it burns. ~99% of the soot formed in a diesel engine burns out
- Why not 100% burn out?
  - Soot particles radiate energy, cause local T to drop
  - Maybe some soot particles get through during a local extinction (from high-strain turbulence)?
  - Soot burn-out kinetics are relatively slow, require high [OH] (a strong flame)
  - Still a lot unknown about soot burn-out

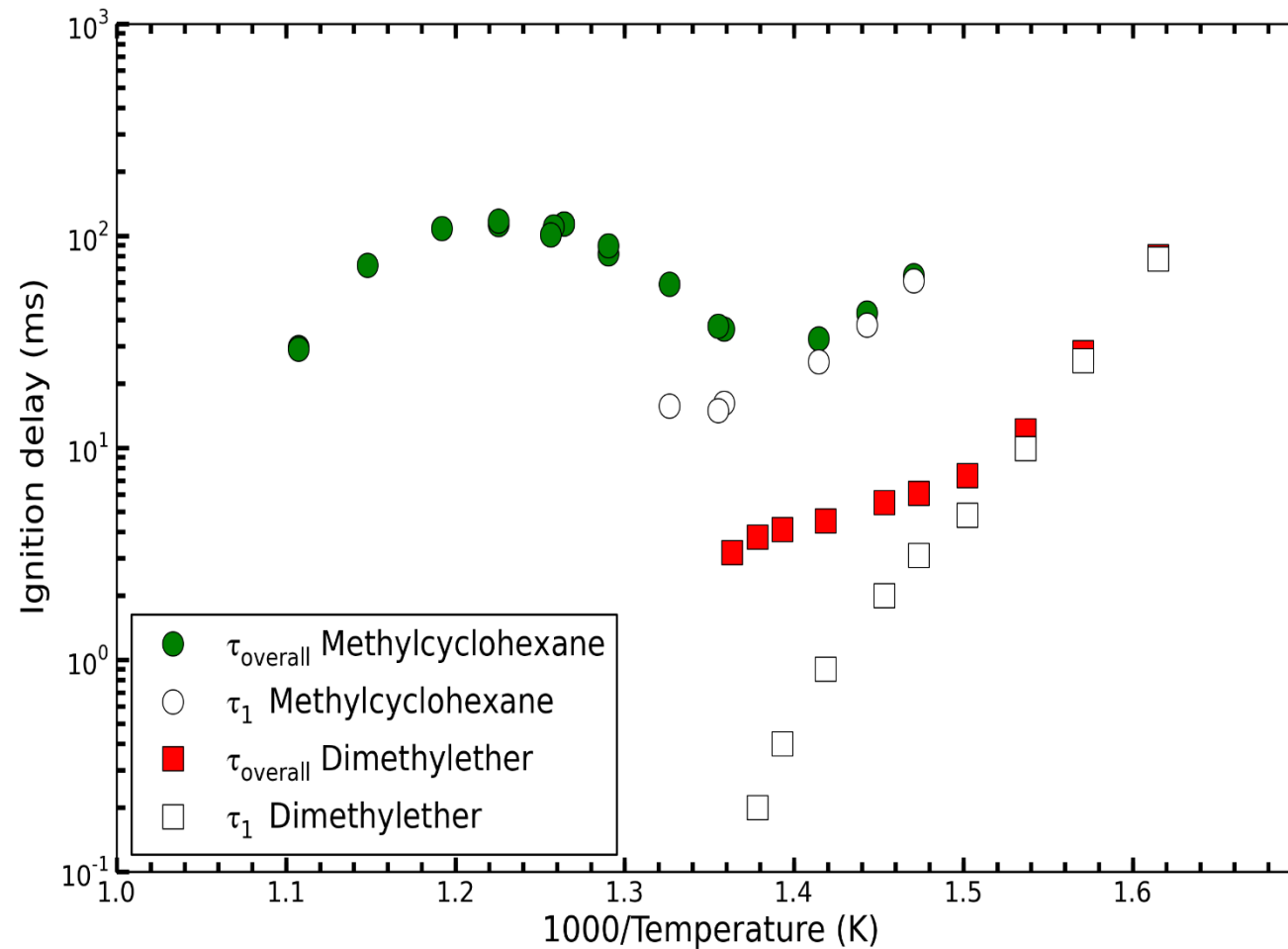
# Combustion Chemistry: Pre-Mixed Flames

- Rate of Combustion is a combination of chemical rates (create large T and [H] gradients), thermal diffusion, and H atom diffusion into unburned fuel+air mixture
  - Simplest analysis says flame speed scales as  $\sqrt{\text{reaction rate}} \cdot \sqrt{\text{Diffusivity}}$
- Most fuels have similar flame speeds (see recent review by C.K. Law)
  - Similar adiabatic flame temperatures and similar thermal diffusivities give similar heat fluxes into fuel+air mixture
  - Some compensation that makes flame speeds similar: e.g. diffusional losses of H, T increase with reaction rate.
  - Note that many times people assume  $Le=1$  for flame speed analysis, but many important cases have different  $Le$ , see papers by Law and by Egolfopoulos
- A few odd cases: H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>
  - H<sub>2</sub> makes much higher [H] than other fuels
  - Also, H<sub>2</sub> diffusion is fast, so it diffuses forward into flame

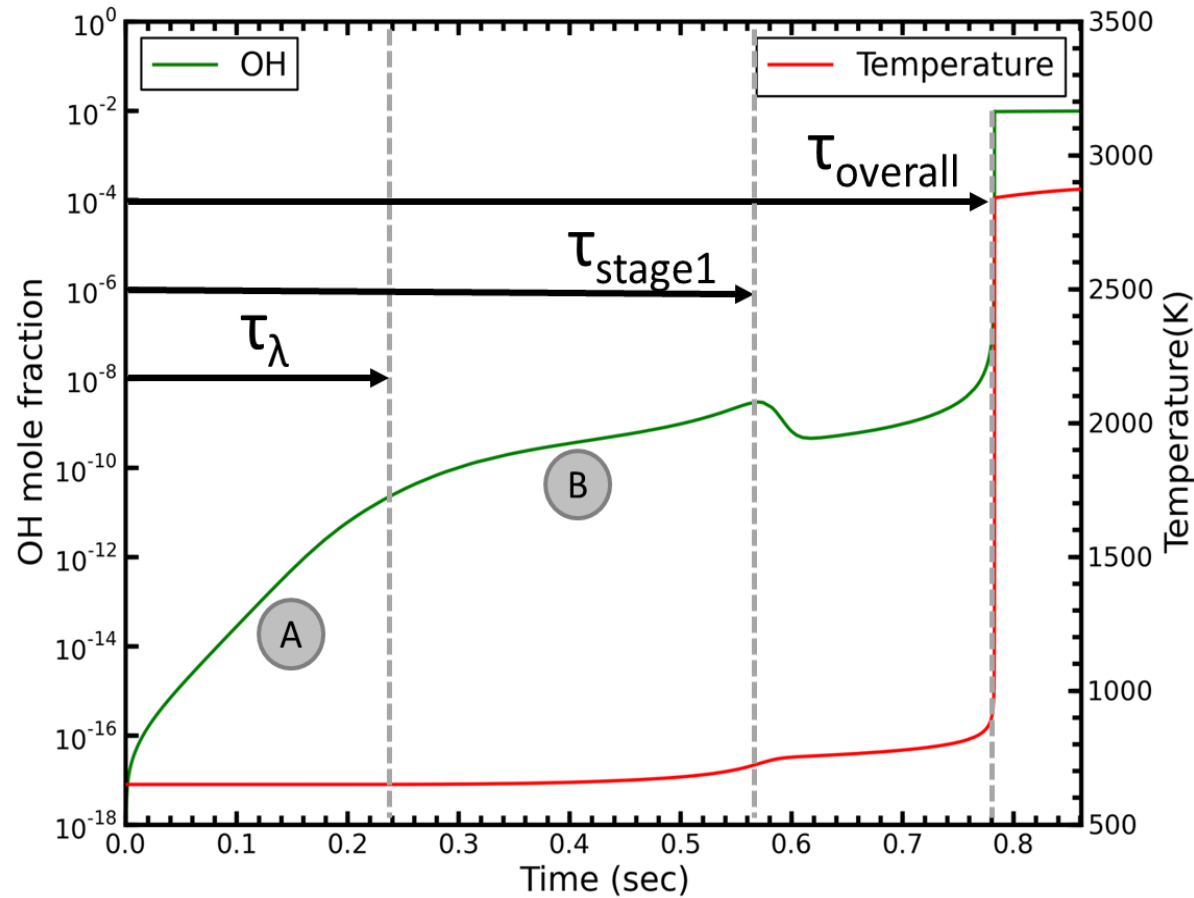
# Ignition

- Ignition chemistry changes drastically with T
- If T is high enough,  $\text{H} + \text{O}_2 = \text{OH} + \text{O}$  is fast, and ignition will be fast
- More complicated things occur starting at lower T....

# Some fuels show two-stage Ignition

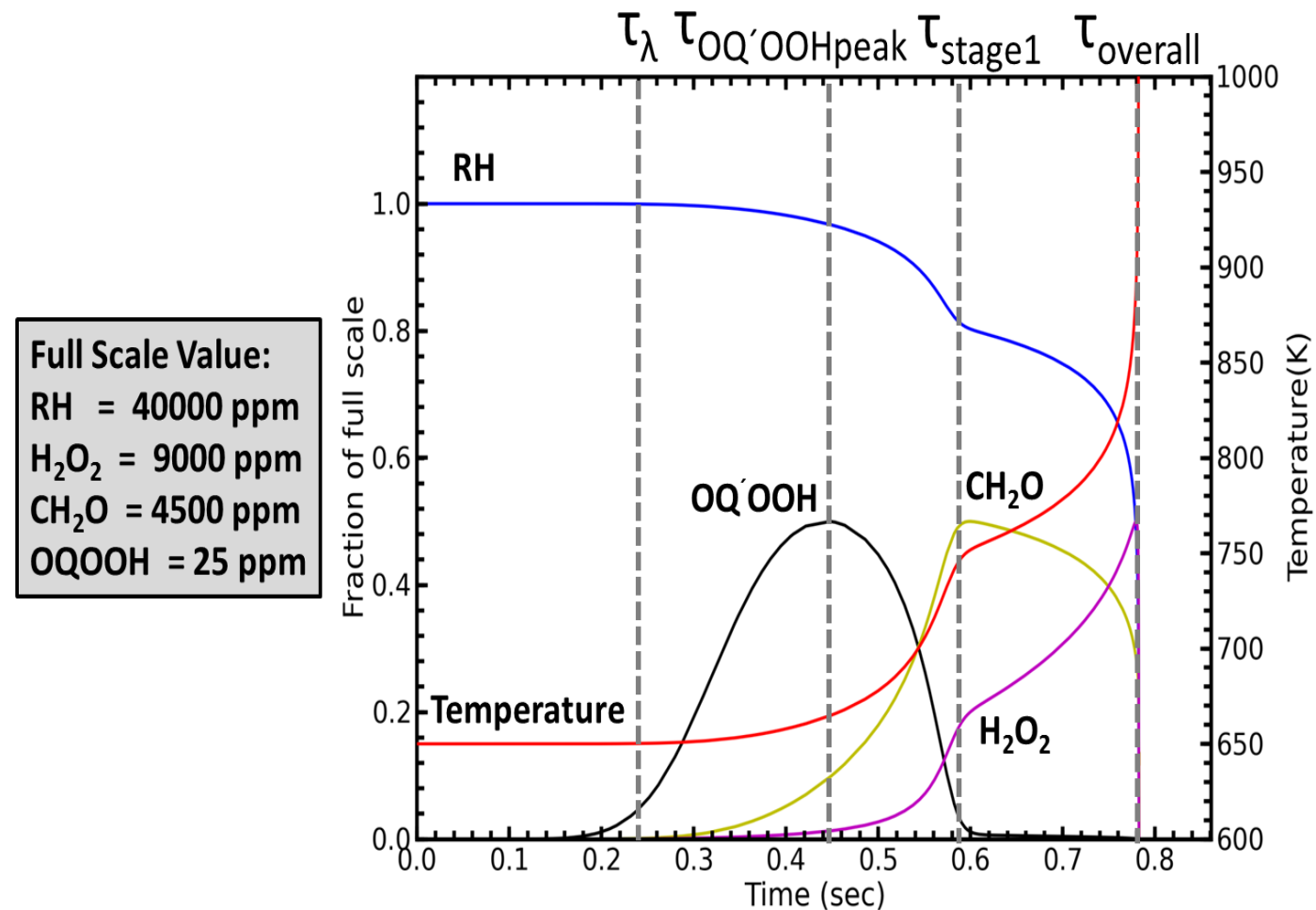


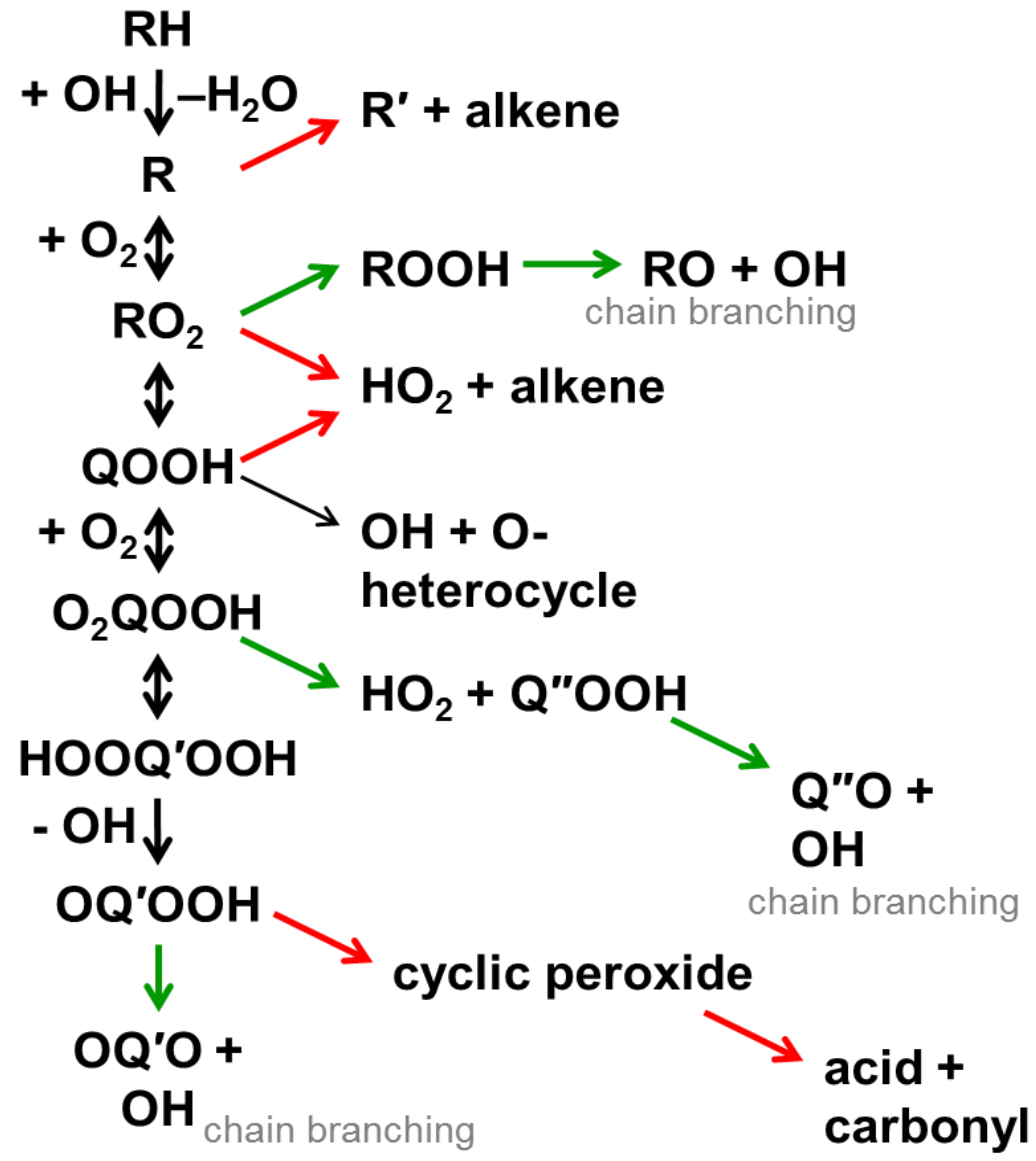
# Computed “Two-stage” ignition of Propane, $T_o=650$ K, $P_o = 10$ bar



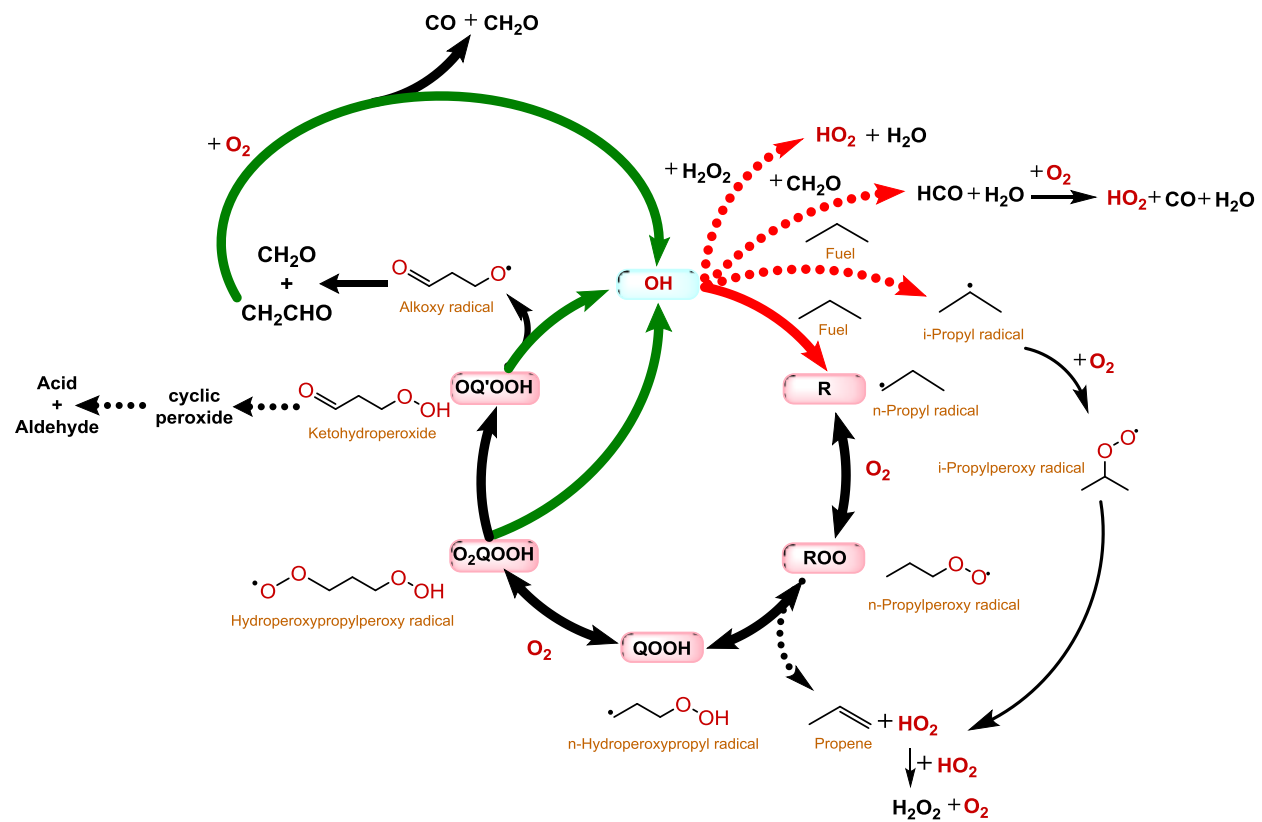
Experimentalists can sometimes  
Discern the point of inflection  
In  $T(t)$  before the “hot” ignition

# Several stages evident in species-profiles

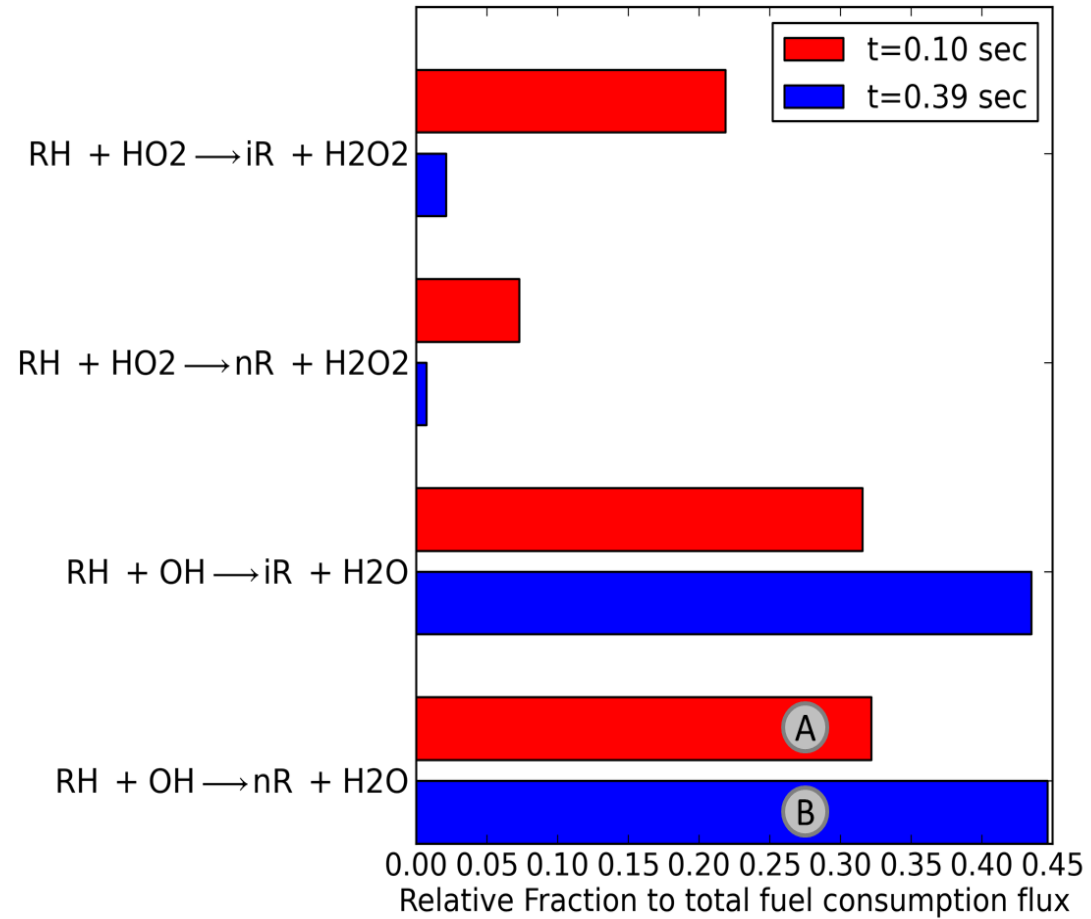




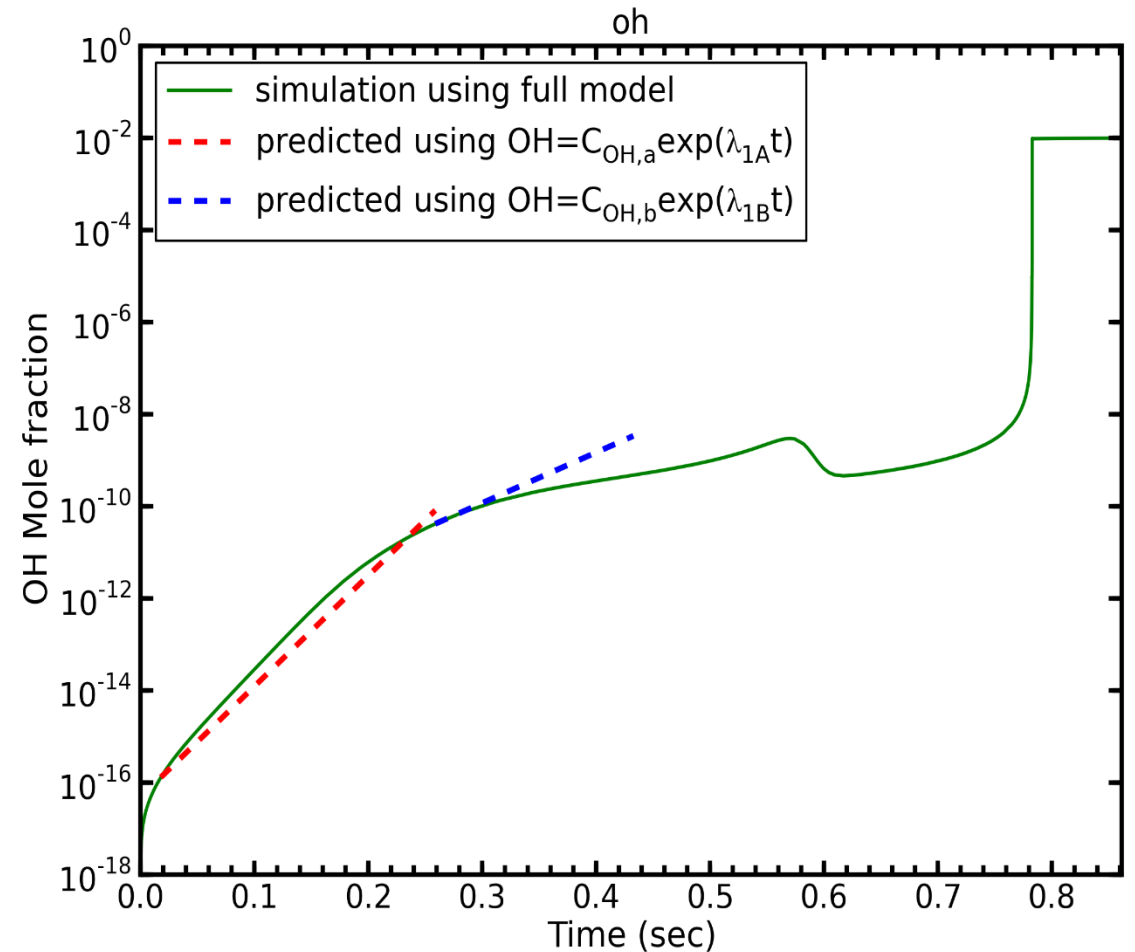
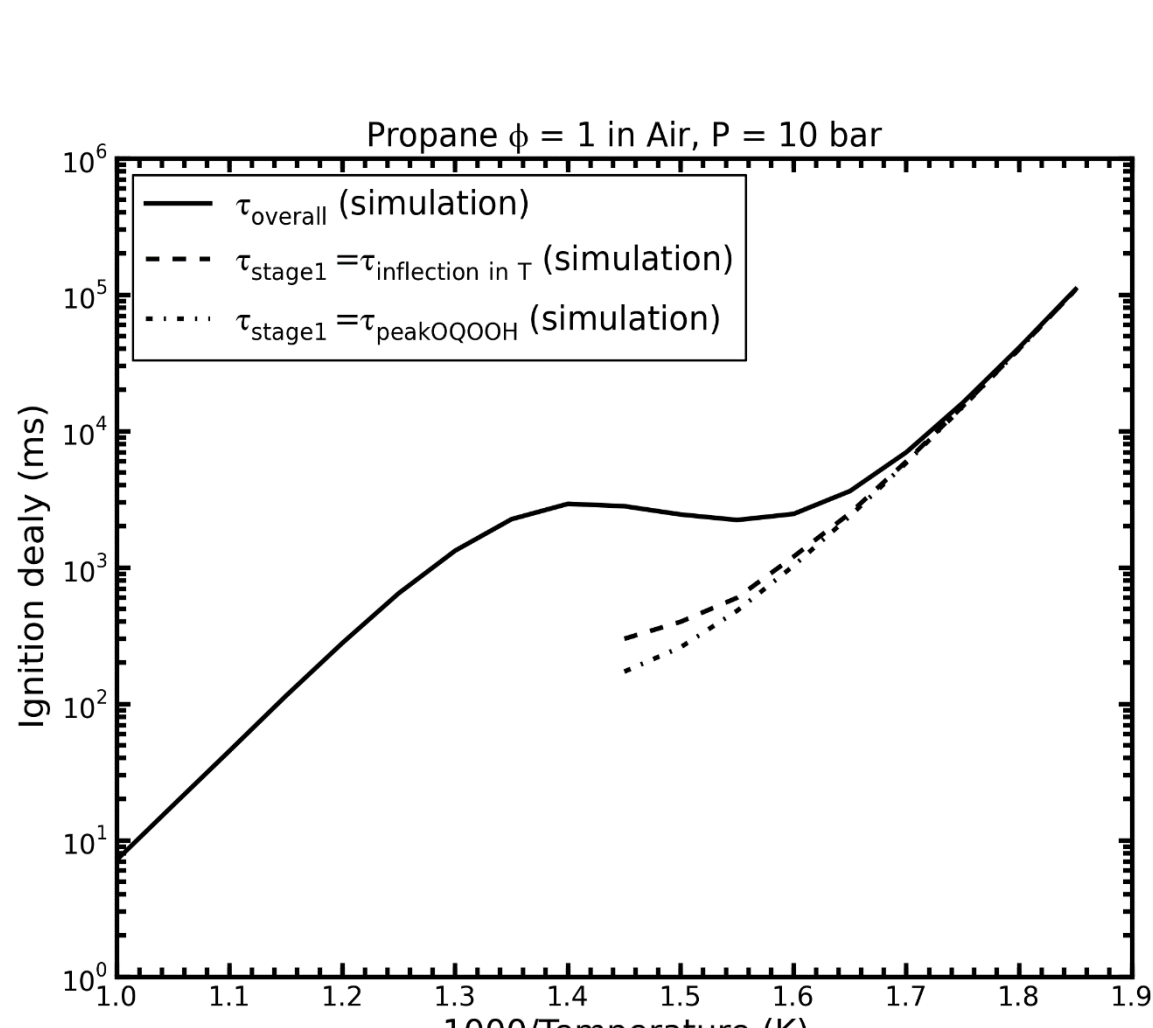




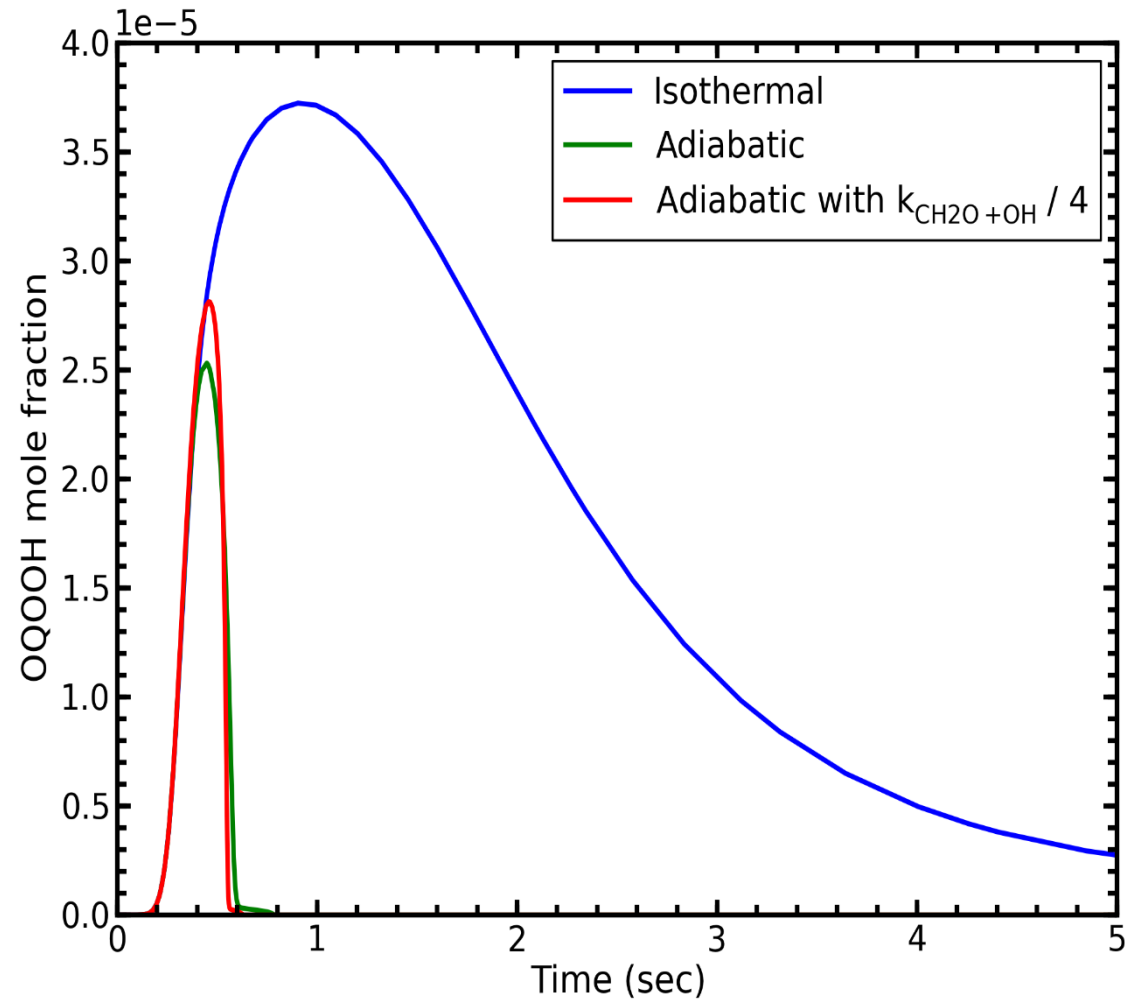
# HO2 much less important in Stage 1B



From Eigenvalue analysis, can derive simple formulas for  $\tau_1$



# Small T rise matters a lot!



# Formulae derived from Propane work for other alkanes

