Development of Detailed and Reduced Kinetic Mechanisms for Surrogates of Petroleum-Derived and Synthetic Jet Fuels:

Drexel Flow Reactor Studies at Low and Intermediate Temperatures

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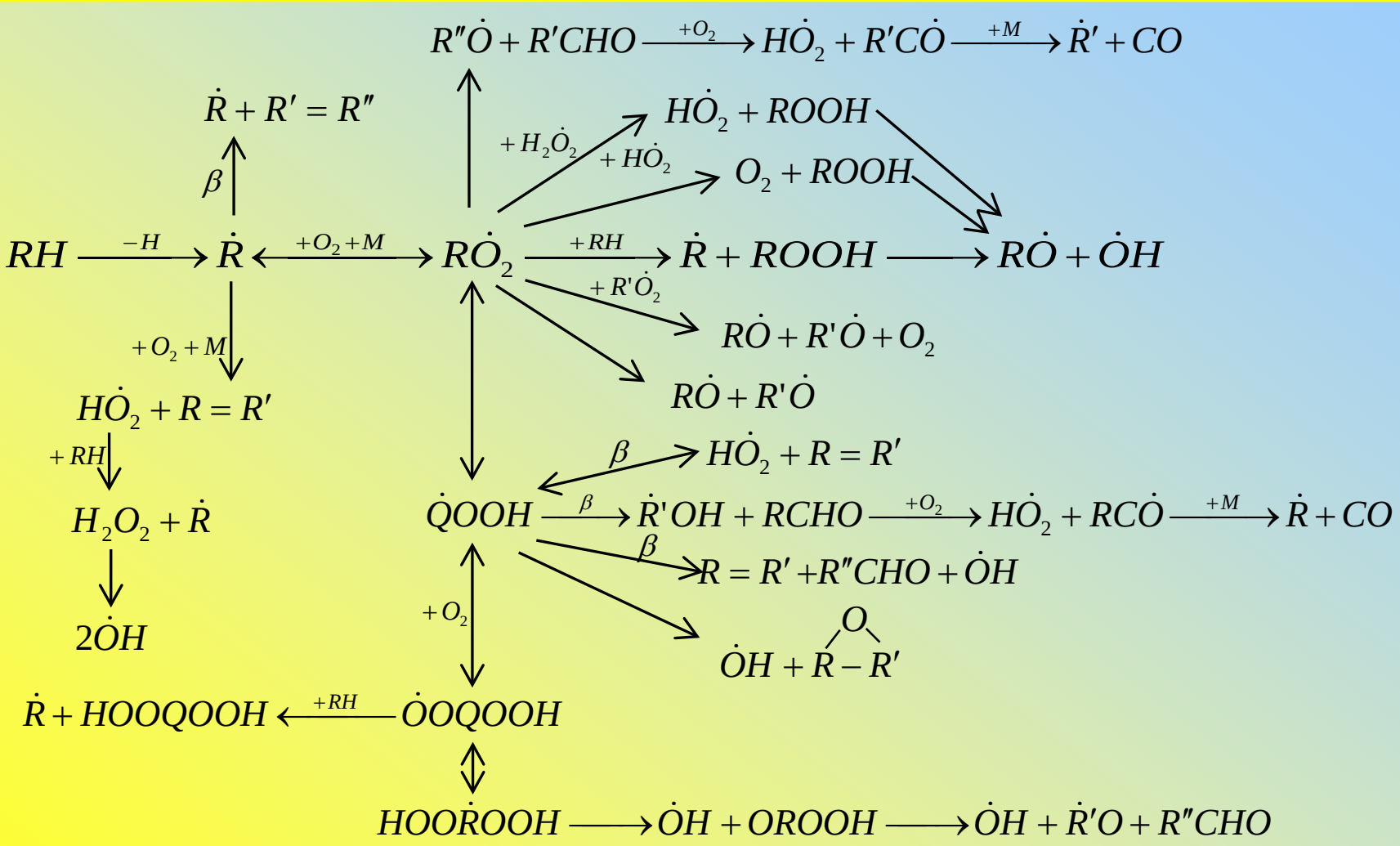
Motivation

- **Detailed kinetic models will aid in the development and optimization of the next series of advanced air-breathing propulsion systems and their use with alternative fuels**
  - **Model development and verification require quantitative characterization of combustion properties**
- **Oxidation at low and intermediate temperatures (600-1100 K) is important in some engine designs**
  - **High-quality, reproducible data quantifying the combustion of jet fuel reference components at these conditions is scarce**

Alkane Oxidation Mechanism



- **CO is the major indicator of reactivity at low temperatures**

Program Overview

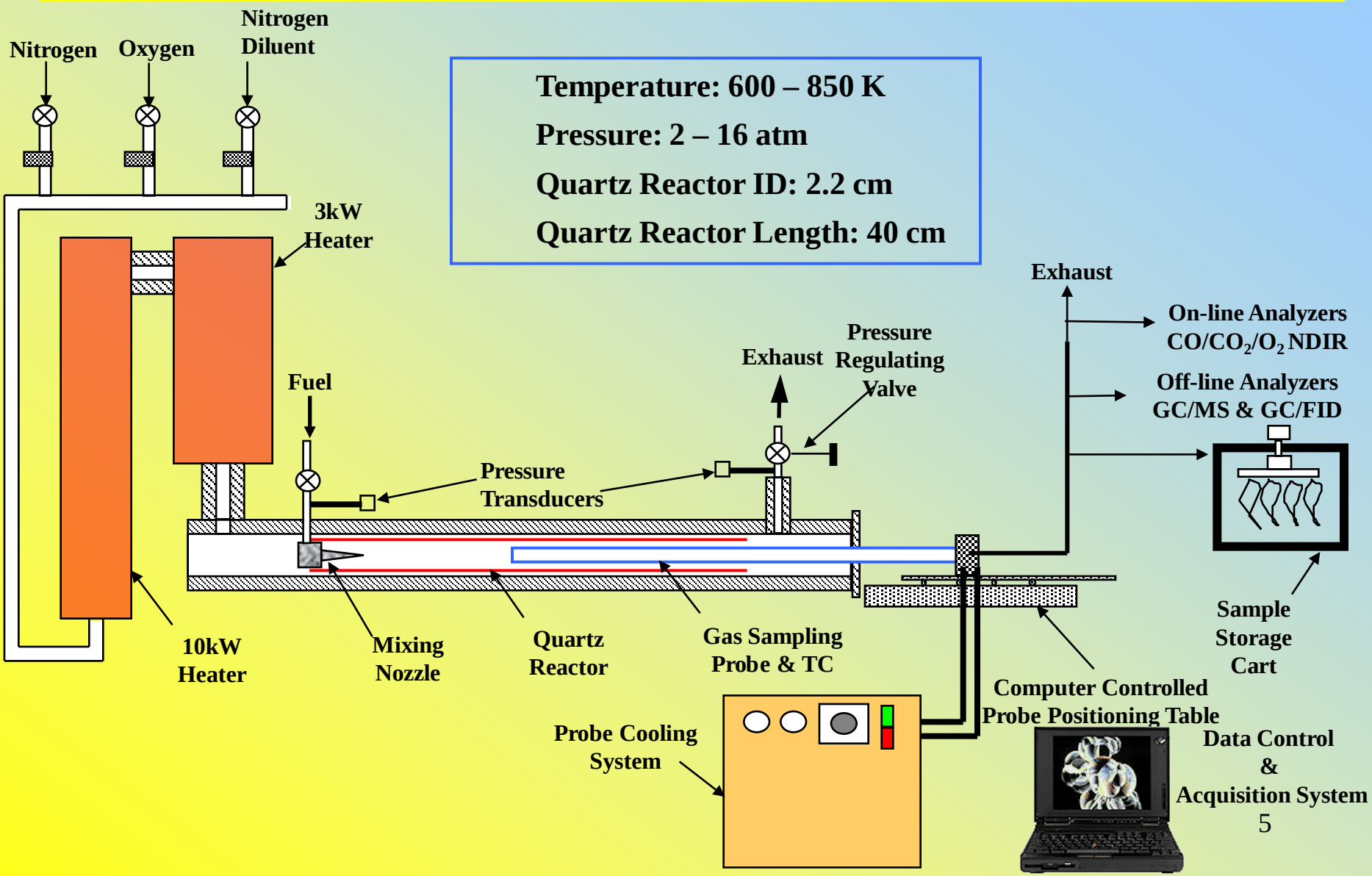
- **Objectives:** **1) Explore the preignition oxidation behavior of petroleum and alternative jet fuel surrogate components**

  2) Quantify the combustion properties of the surrogate components

  3) In Year 1, n-dodecane studies

- **Approach:**
  - **React the fuel/oxidizer/diluent systems under well-controlled conditions in our Pressurized Flow Reactor (PFR)**
    - » **Perform bench scale tests on n-dodecane**
      - **Coordinate with Stanford flow reactor experiments at higher temperatures**
    - » **Monitor reactivity and collect gas samples as a function of experimental and reactant conditions**
    - » **Perform detailed chemical analysis of extracted gas samples**
  - **Mechanistic analysis and development**
  - **Provide data for USC chemical kinetic model development**

PFR Facility



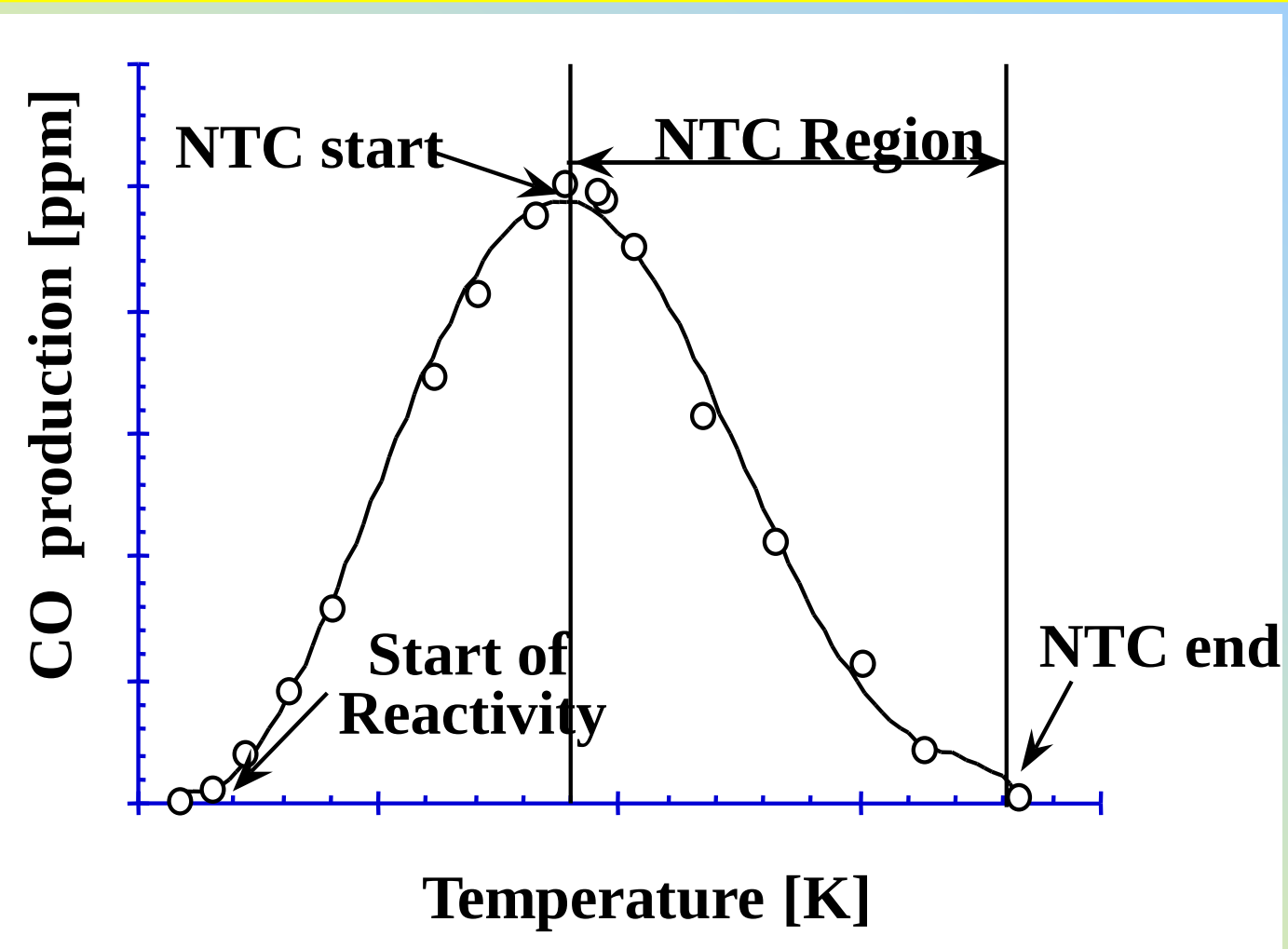
Temperature: 600 – 850 K

Pressure: 2 – 16 atm

Quartz Reactor ID: 2.2 cm

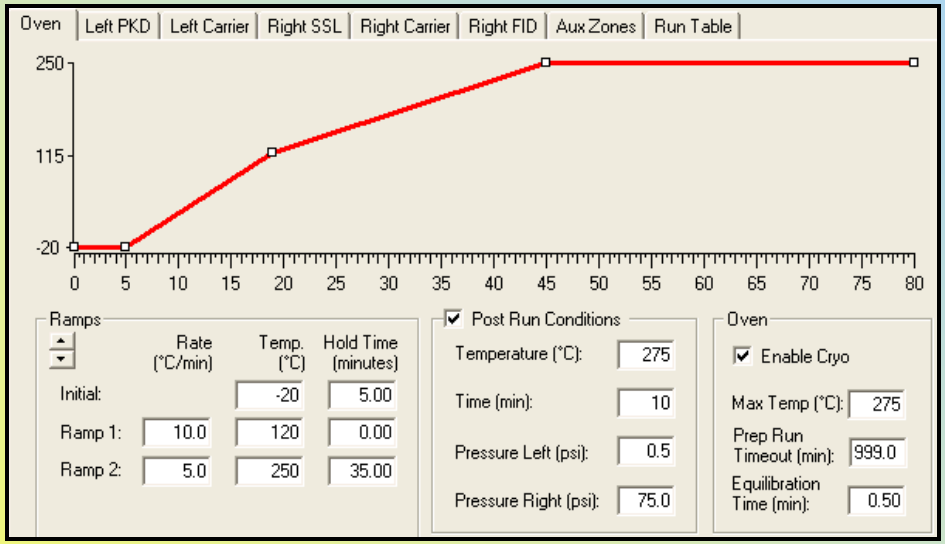
Quartz Reactor Length: 40 cm

Representative Reactivity Map Profile



GC/MS/FID Facility

- Samples from PFR collected in 10-ml loops in sample storage cart heated to 180°C
- Samples injected into GC/MS/FID for analysis
- Separation aided by sub-ambient initial oven temperature
- Identification performed by mass spectra compared to NIST MS Version 2.0
- Supelco Petrocol DH column in GC
  - 100 m, 0.5 μm film thickness
  - 0.25 mm OD, 1250 Phase Ratio (β)
- MS parameters
  - Ion source 200°C
  - Electron ionization -70 eV
  - Multiplier voltage 1456 V
  - Emission current 100 μA



GC temperature ramp

Other Measurements

- **Measure $CO/CO_2/O_2$ with on-line analysis**
  - **Errors are 50 ppm for CO and CO_2, and 1250 ppm for O_2**
- **Measure F/O_2 ratios with Total Hydrocarbon Analyzer combined with O_2 Analyzer to calibrate equivalence ratio before each experiment**
- **Calibration of lighter hydrocarbons is achieved with FID calibration using purchased gas-phase standards at 15, 100, and 1000 ppm**
- **Calibration of heavier species is achieved with correction factors of FID signals that account for differences in carbon, hydrogen, and oxygen numbers between different molecules of similar structures (Schofield, 2008)**
- **In current results, uncertainties are 1 standard deviation of two experiments (Exp 1+2) with similar initial conditions**
  - **Uncertainty calculations will improve with additional experiments**

Schofield, K. (2008). *Prog Energ Combust 34*:330-350.

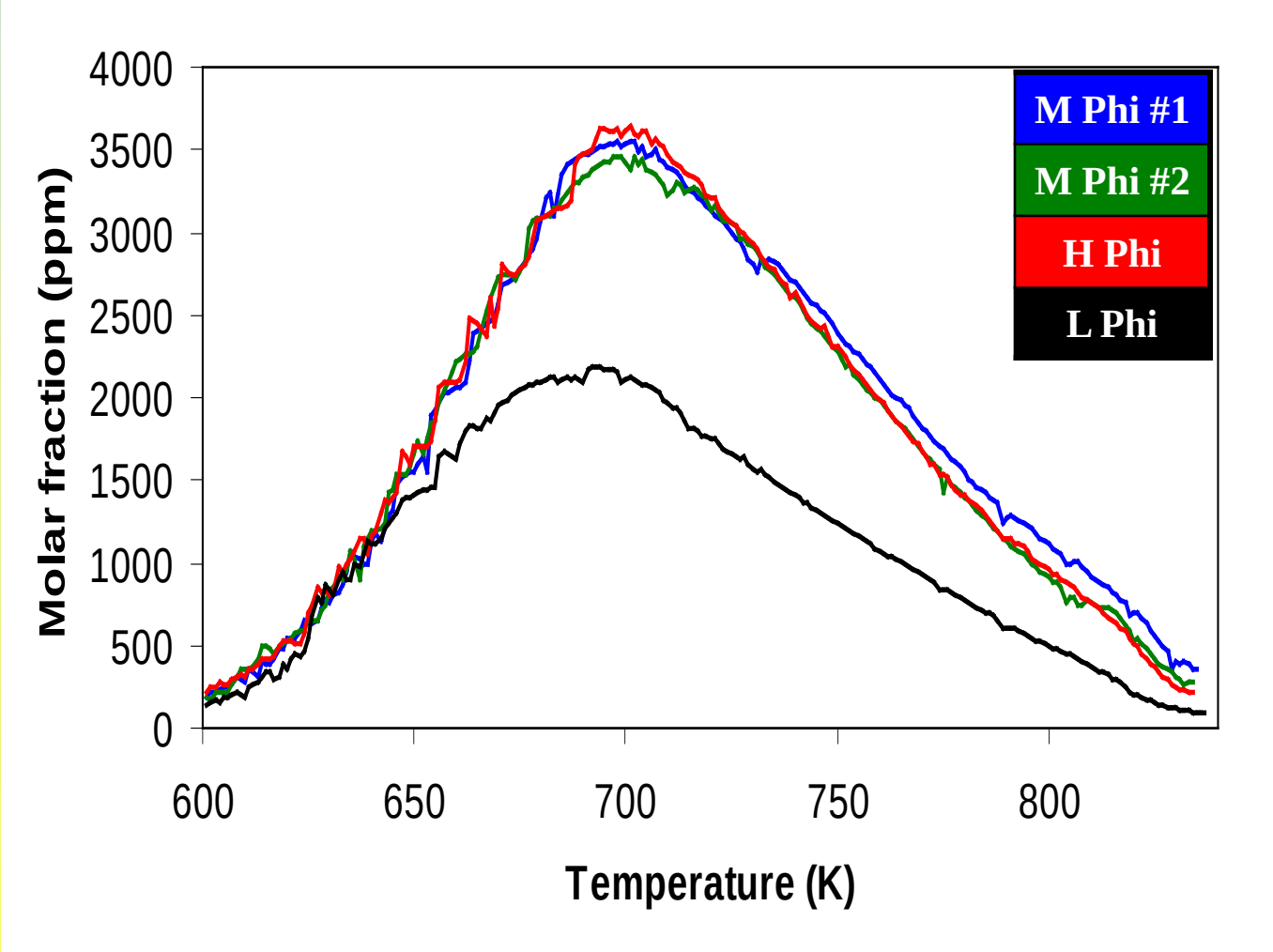
Experimental Conditions

	Exp 1 (5/14/08) "M Phi #1"	Exp 2 (5/28/08) "M Phi #2"	Exp 3 (6/23/08) "H Phi"	Exp 4 (7/28/08) "L Phi"
n-Dodecane (ppm)	1297	1529	1667	519
O_2 (ppm)	37700	37500	35200	42000
ϕ	0.64	0.75	0.88	0.23
N_2 (ppm)	961000	961000	963100	957500

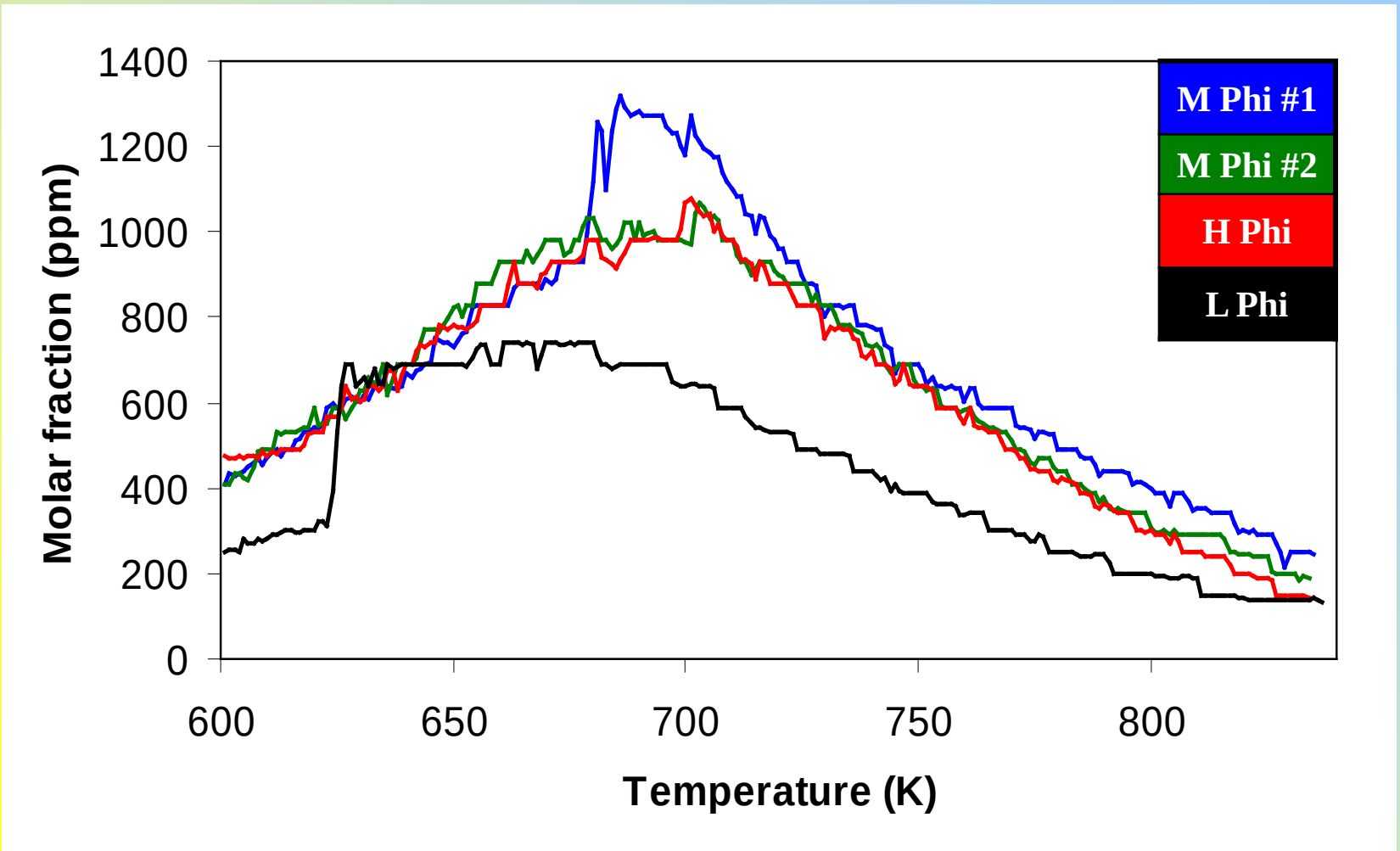
- Equivalence ratios for Exp 1 and Exp 2 are essentially identical, considering uncertainties in O_2 and n-dodecane
- Exp 4 was conducted to reduce hydrocarbon loading on experiment
- For all experiments, pressure maintained at 8.000 0.025 atm and residence time maintained at 120 10 ms

CO

- Peak CO production of Moderate Phi #1 and #2 are within uncertainty
  - 50 ppm uncertainty in CO
- High Phi produced only slightly more CO than Moderate Phi's
- Low Phi had much lower initial n-dodecane molar fraction
  - NTC region started at lower temperature

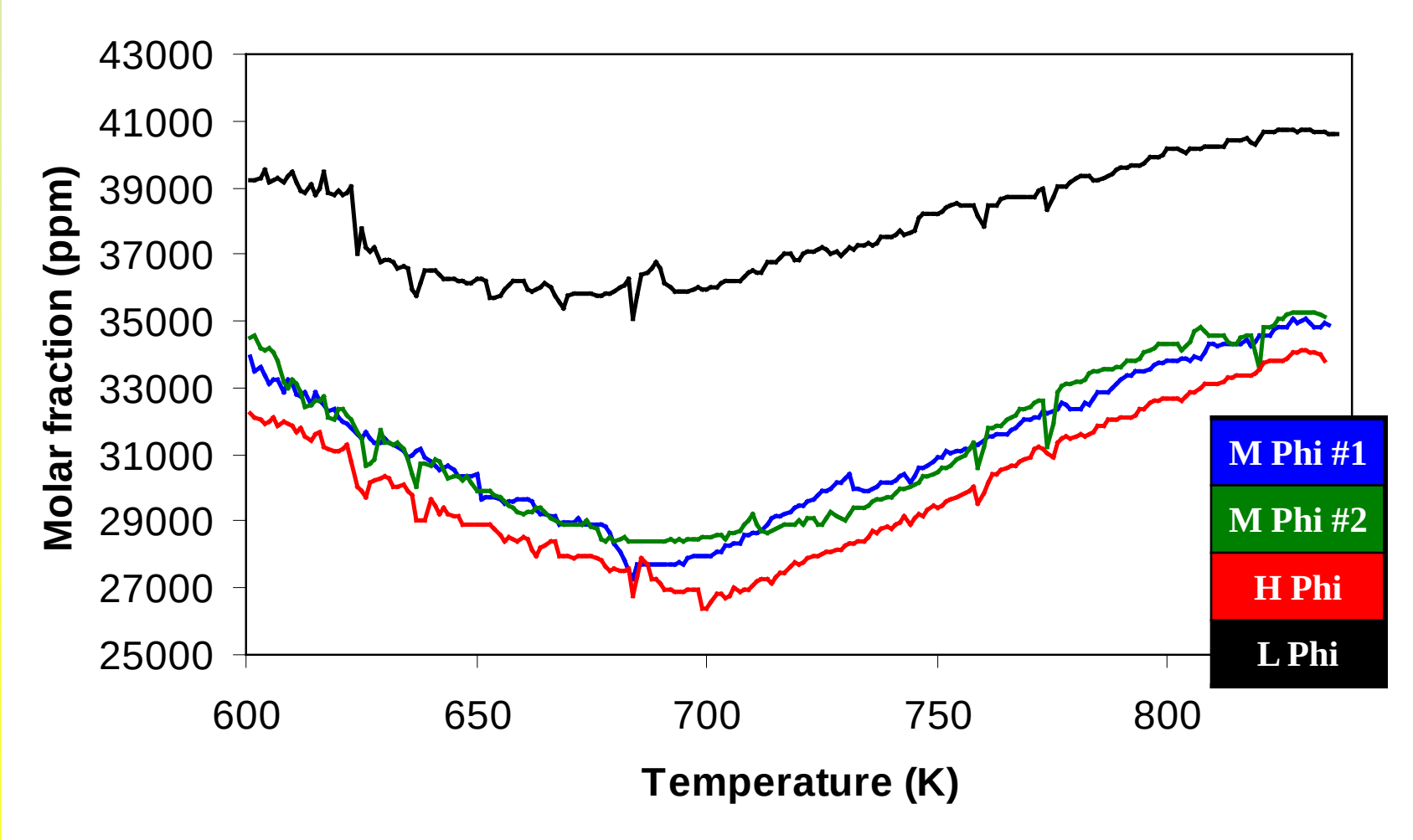


CO_2



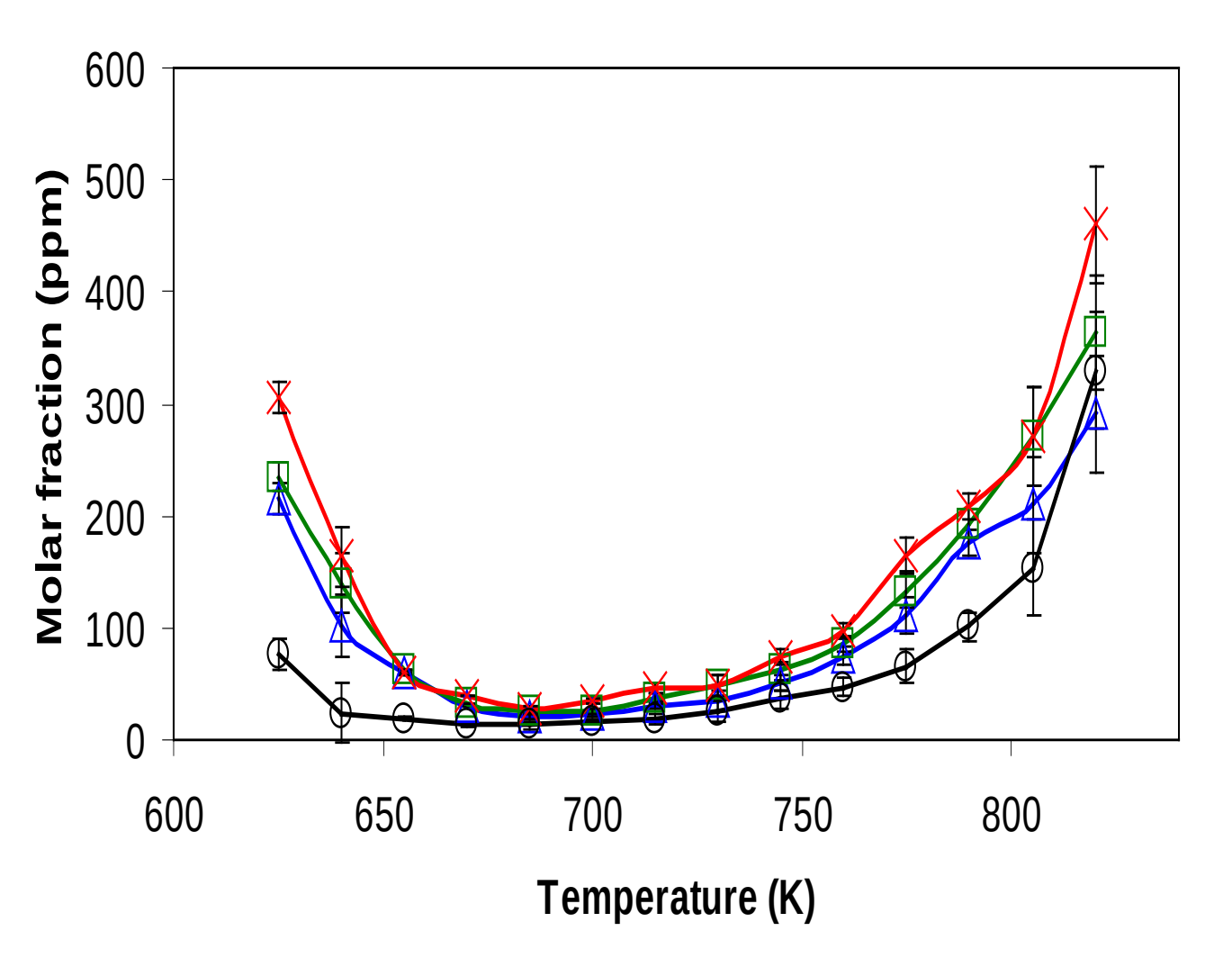
50 ppm uncertainty in CO_2

O_2



1250 ppm uncertainty in O_2

n-Dodecane

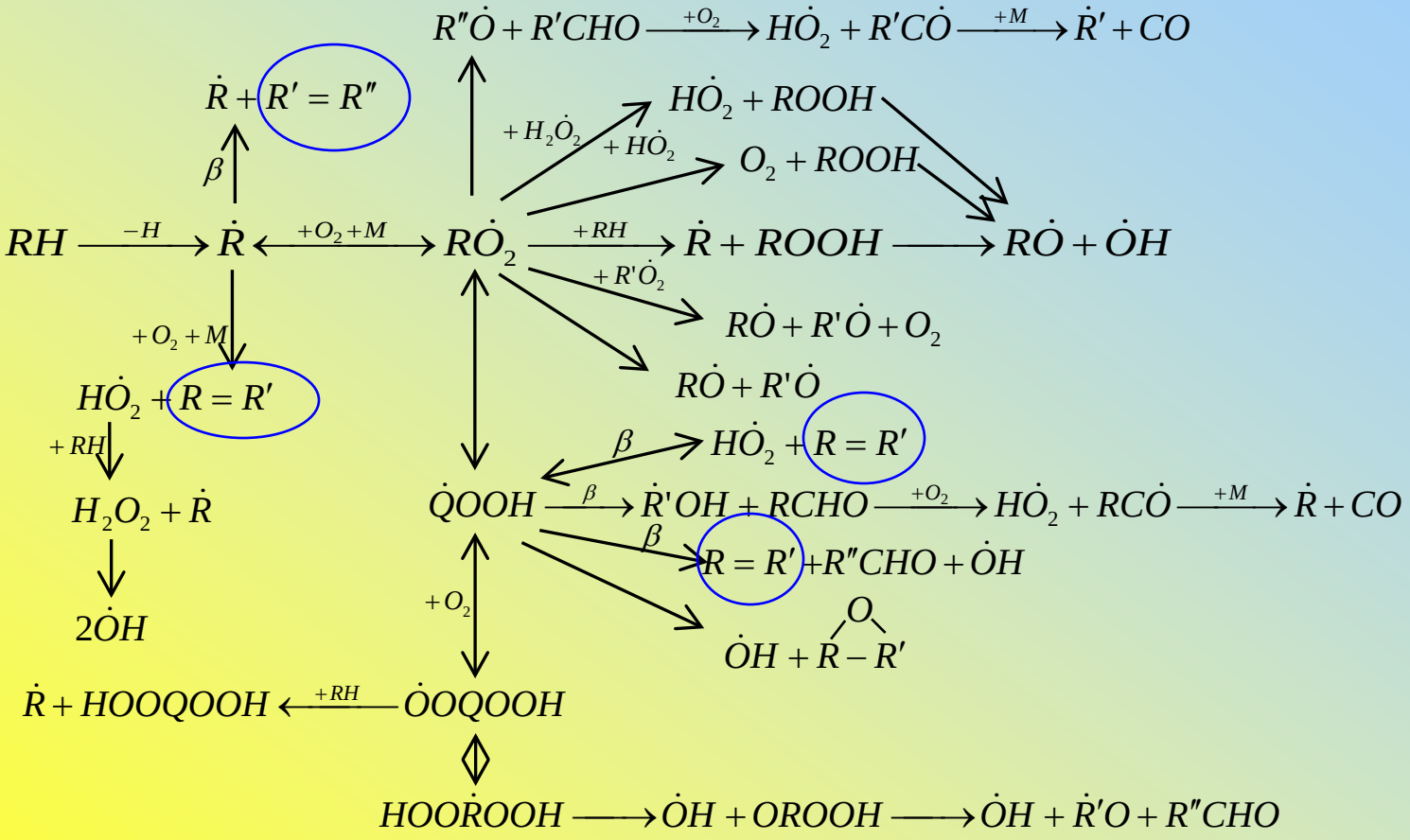


All experiments exhibited similar n-dodecane molar fractions at 670-745 K

Low Phi had significantly lower initial molar fraction

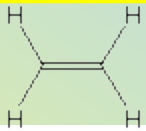
M Phi #1
M Phi #2
H Phi
L Phi

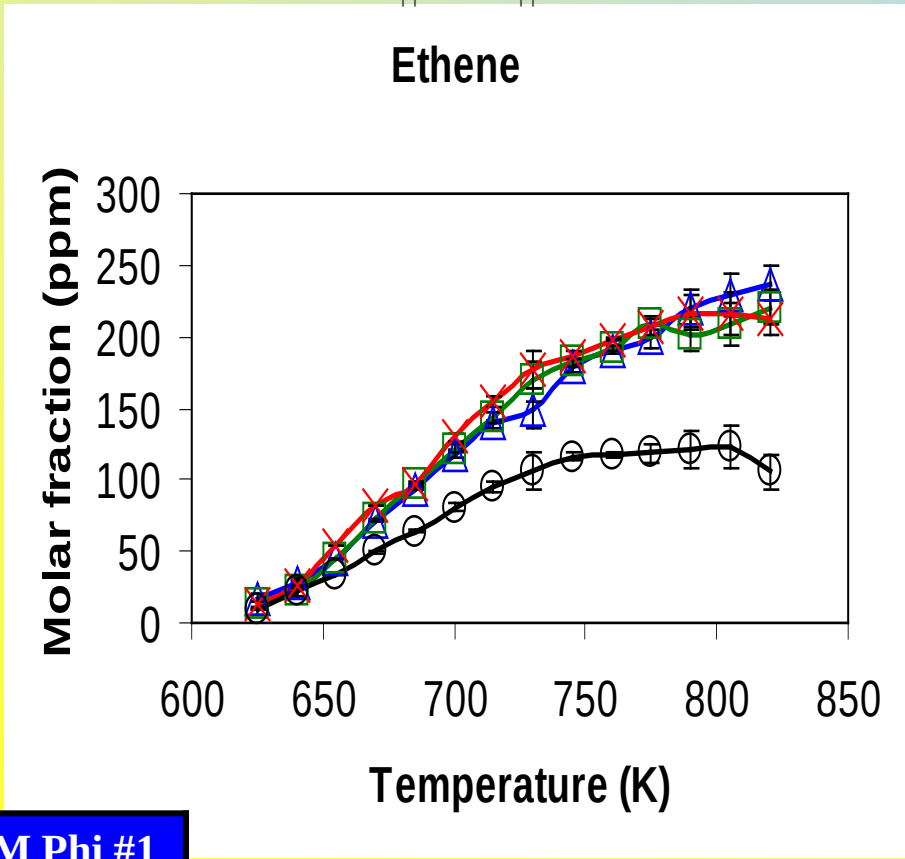
Alkane Oxidation Mechanism – Alkene Formation

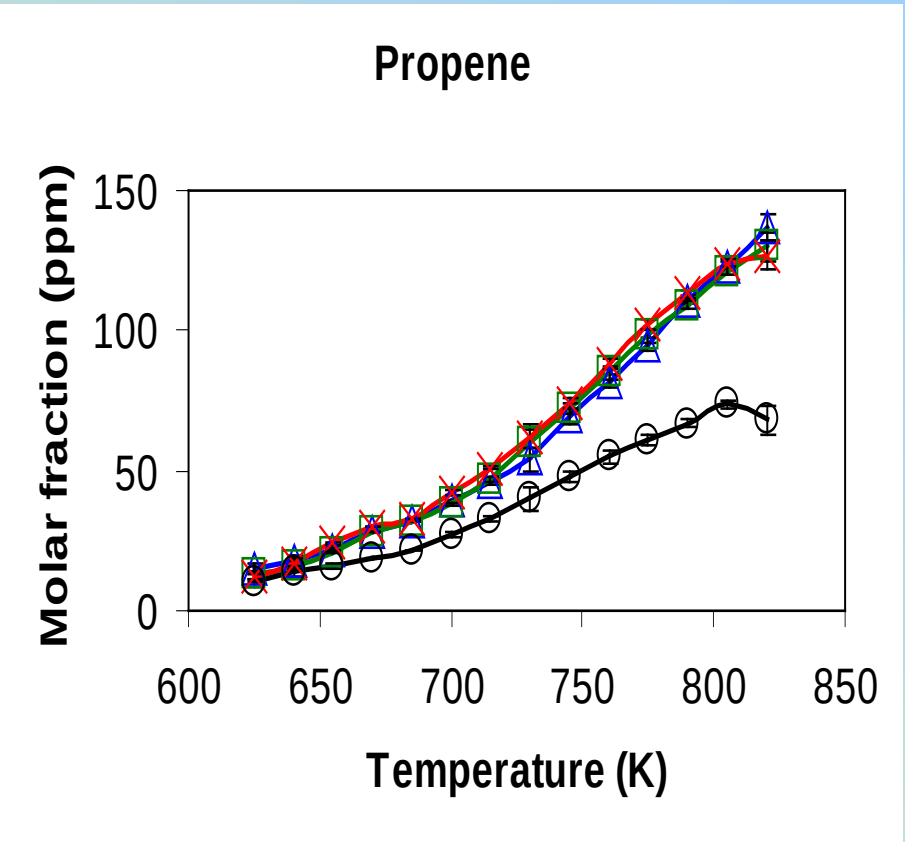


- **In general, alkenes produced from β-scission of alkyl (R·) and alkylhydroperoxy (QOOH·) radicals, and from O_2 addition to alkyl radicals**

Alkenes







M Phi #1

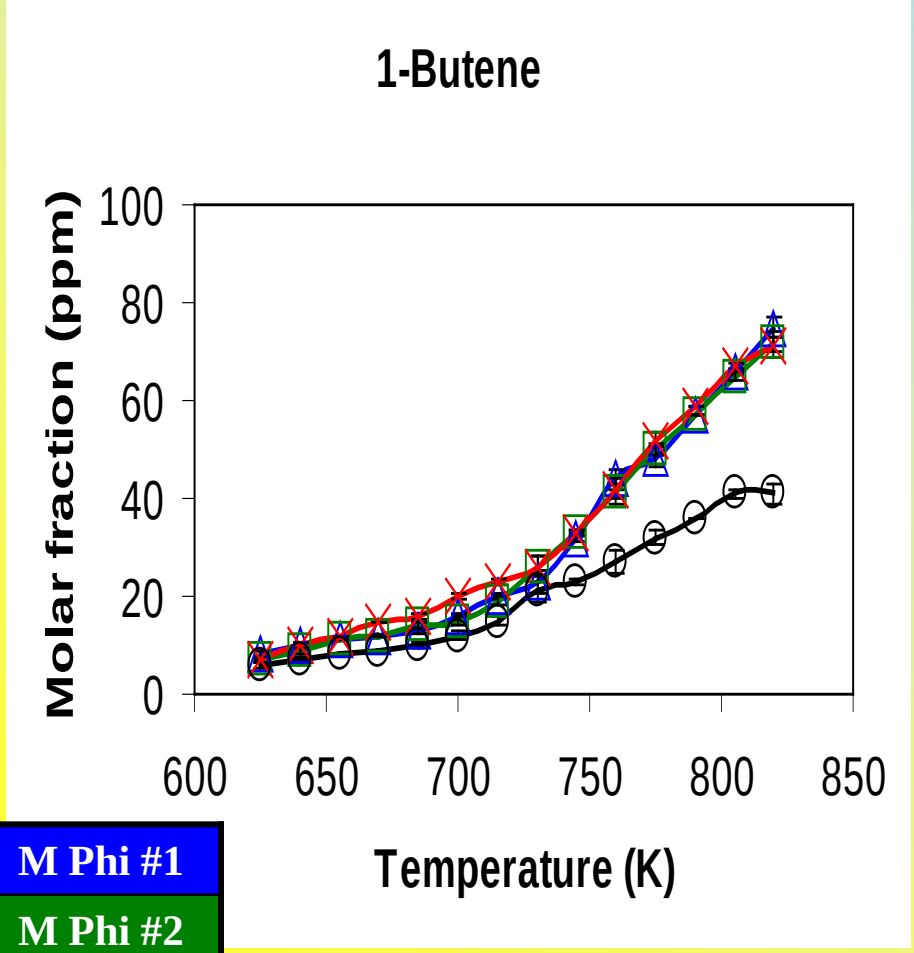
M Phi #2

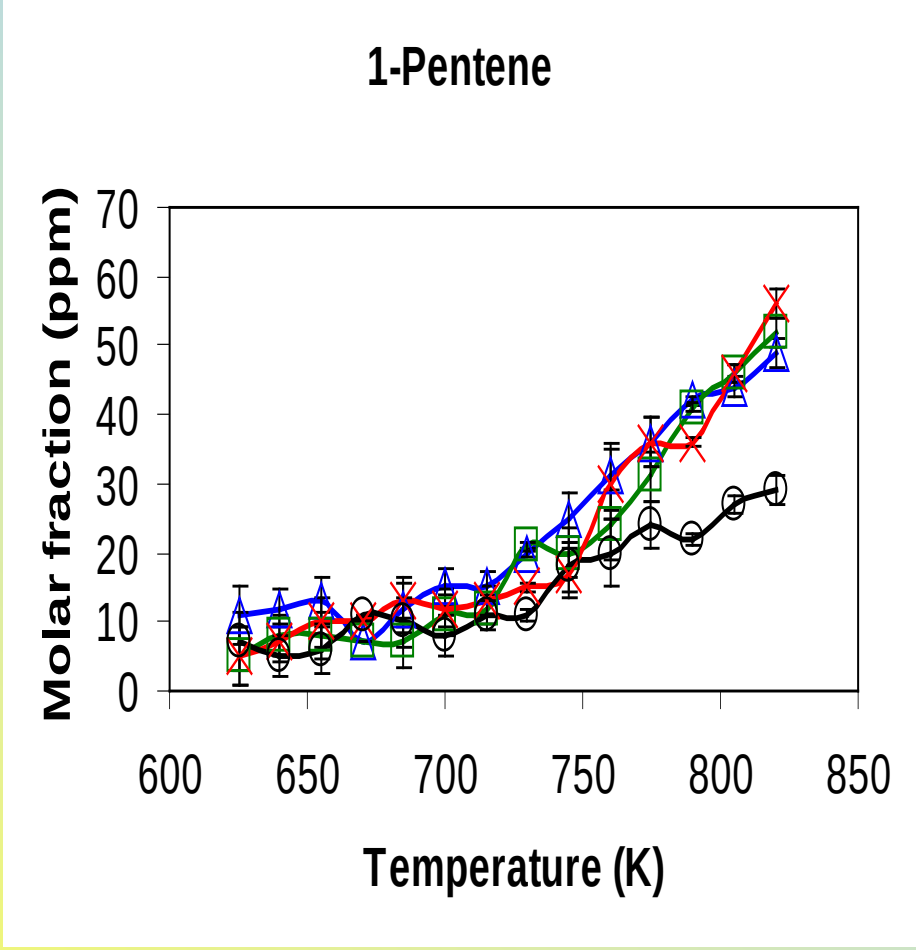
H Phi

L Phi

- **Decrease in light alkenes at 805-820 K temperatures appears in Low Phi experiment**

Alkenes





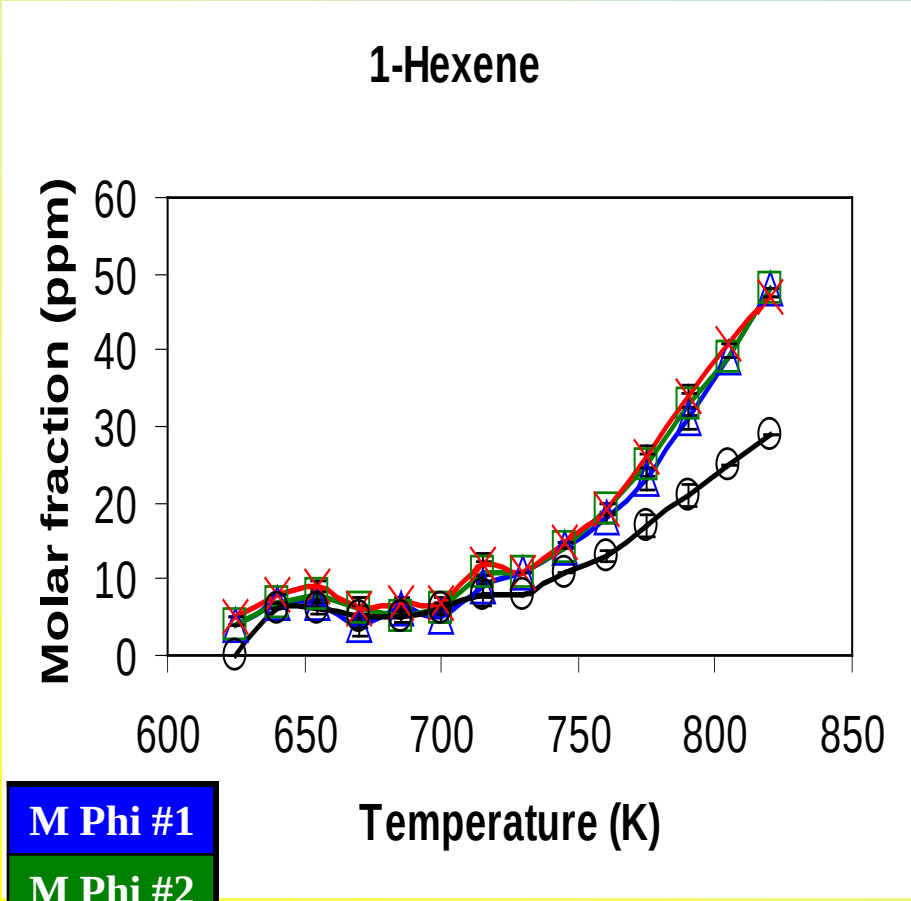
M Phi #1

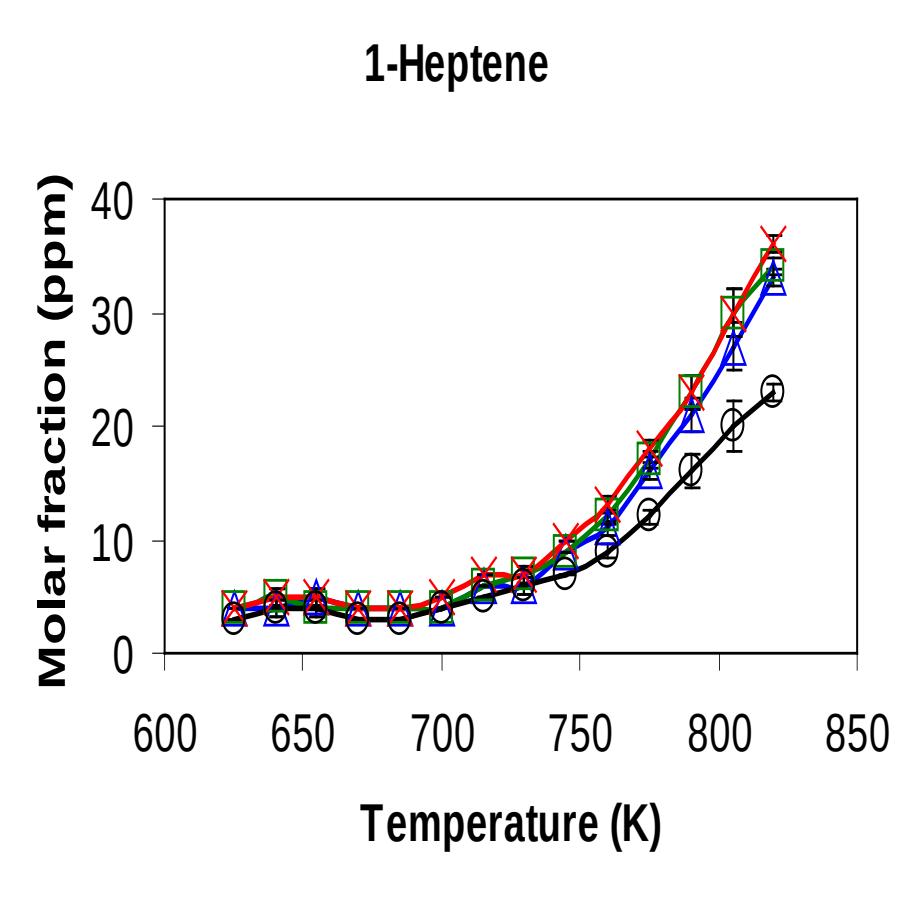
M Phi #2

H Phi

L Phi

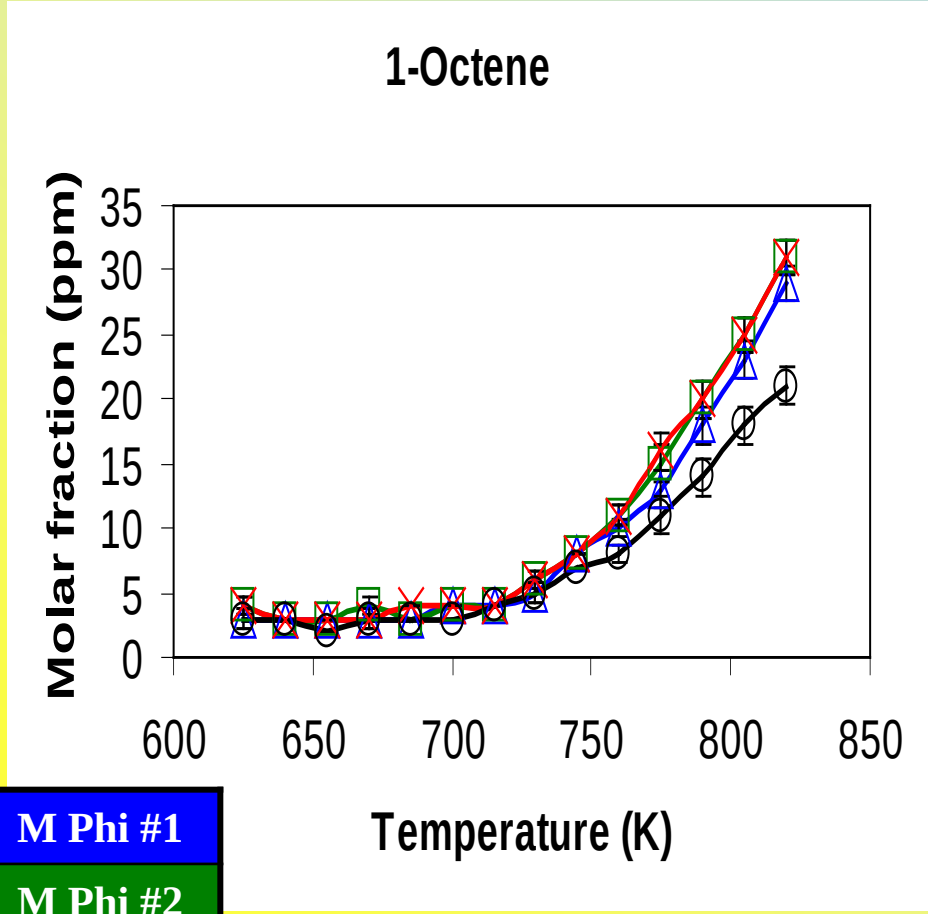
Alkenes

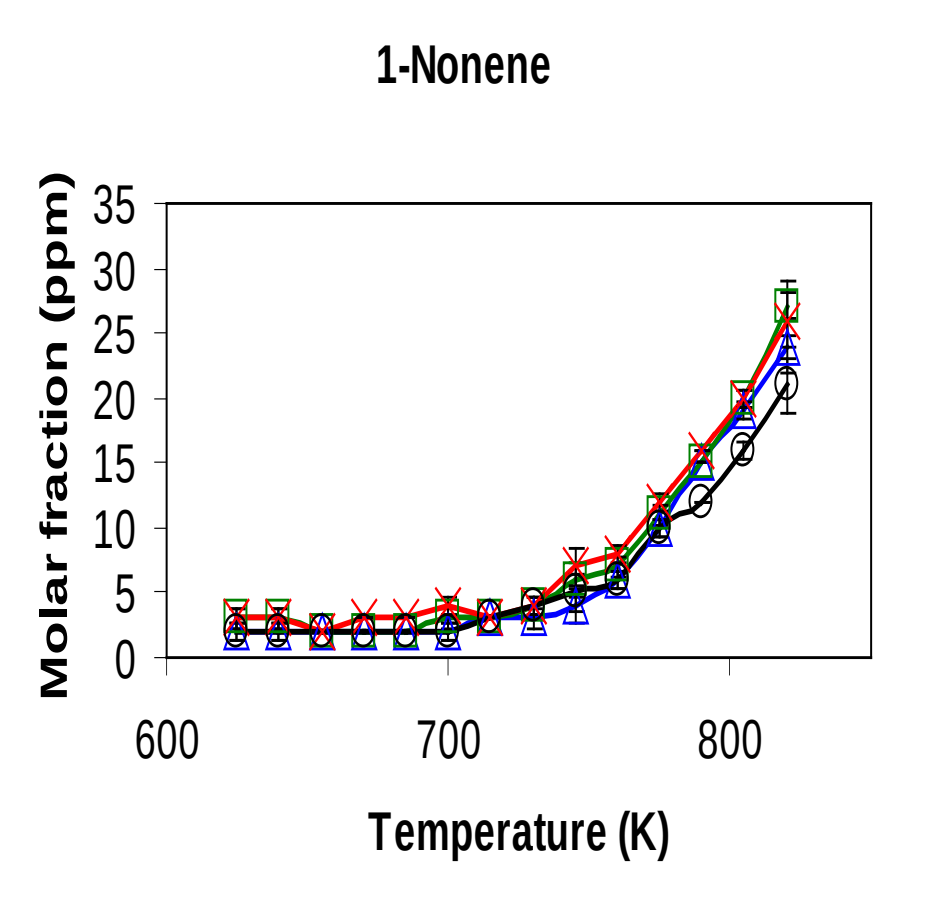




M Phi #1
M Phi #2
H Phi
L Phi

Alkenes





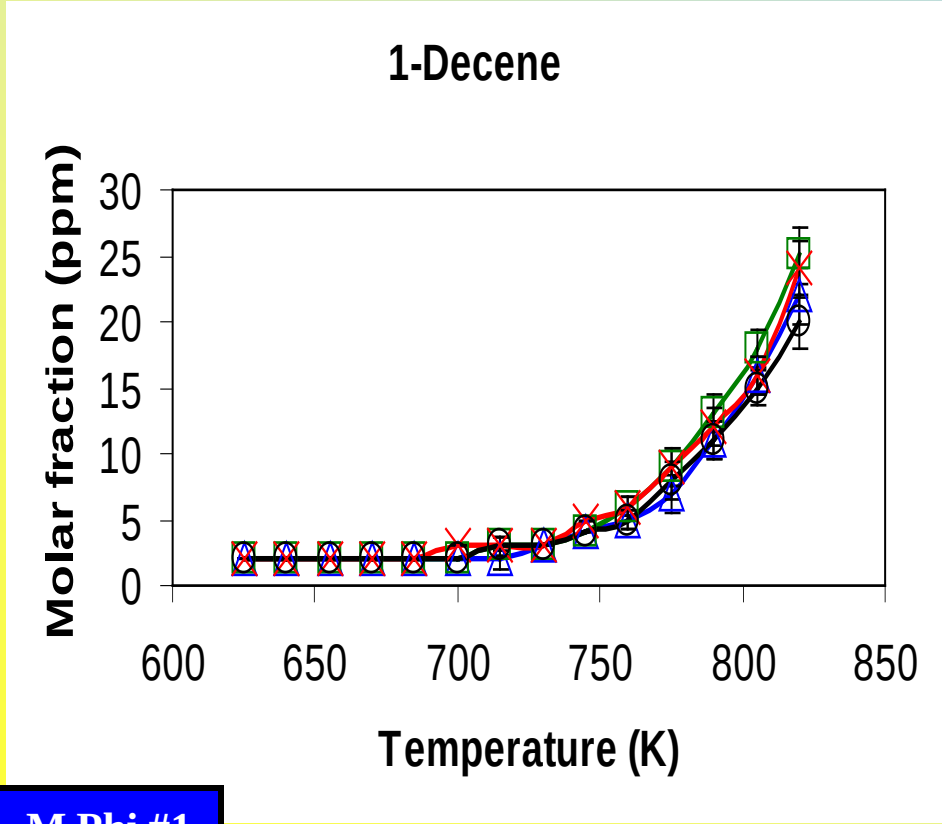
M Phi #1

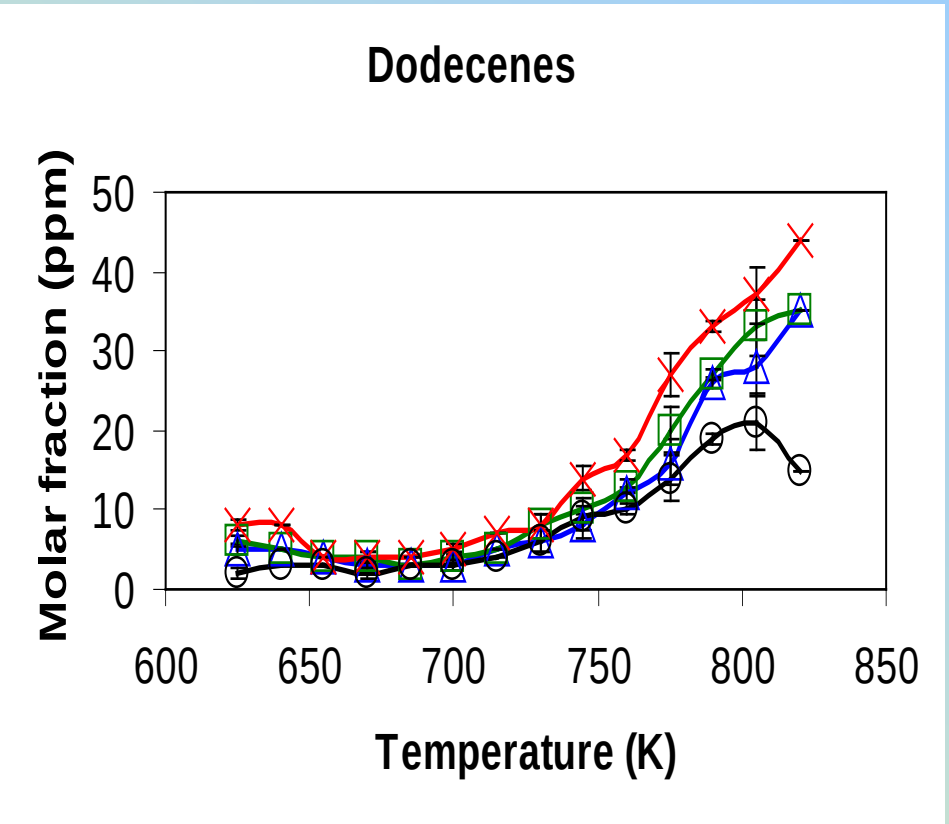
M Phi #2

H Phi

L Phi

Alkenes





M Phi #1

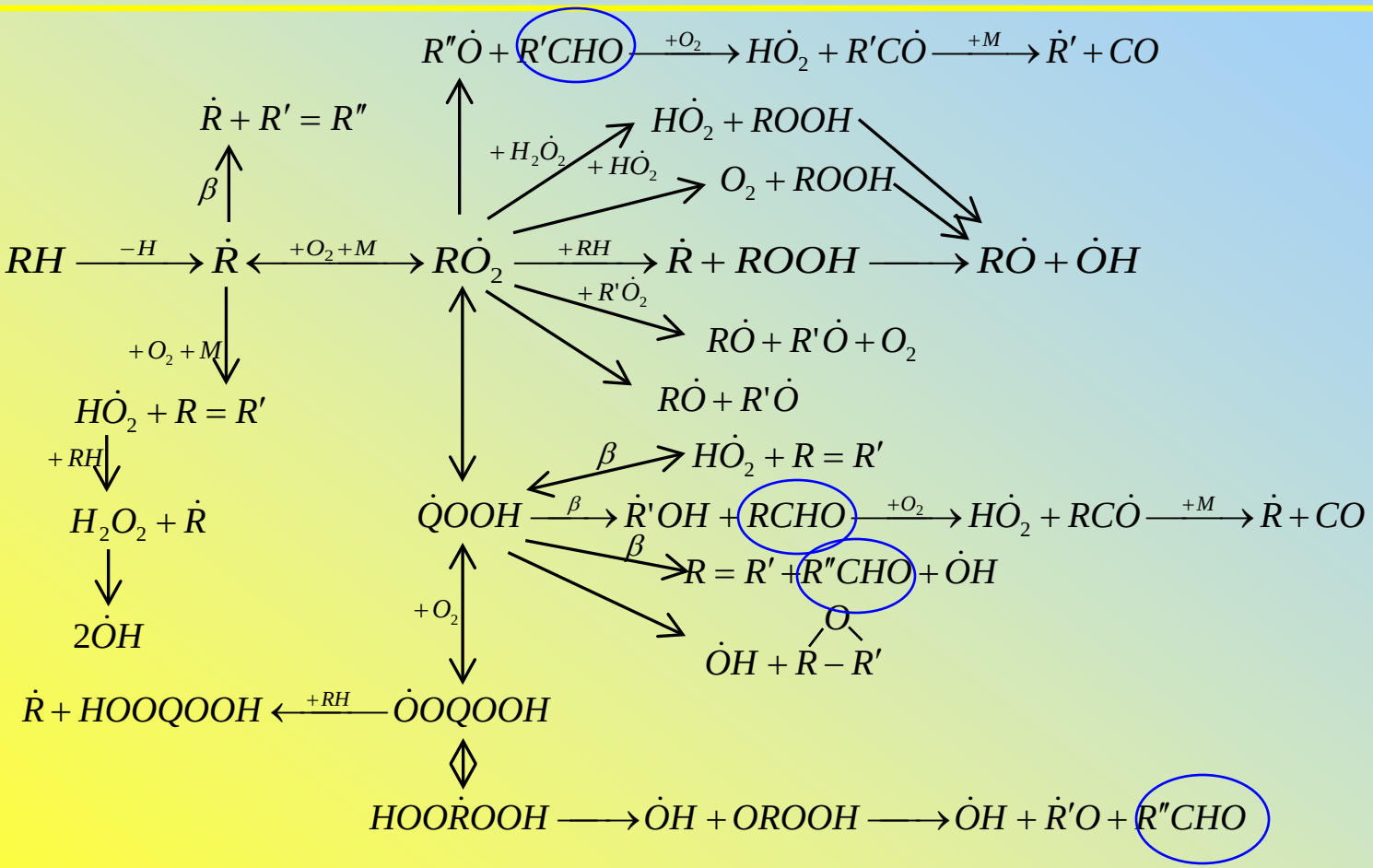
M Phi #2

H Phi

L Phi

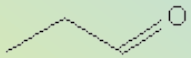
- **Several dodecene isomers are shown lumped as overlapping of GC peaks makes positive identification difficult**

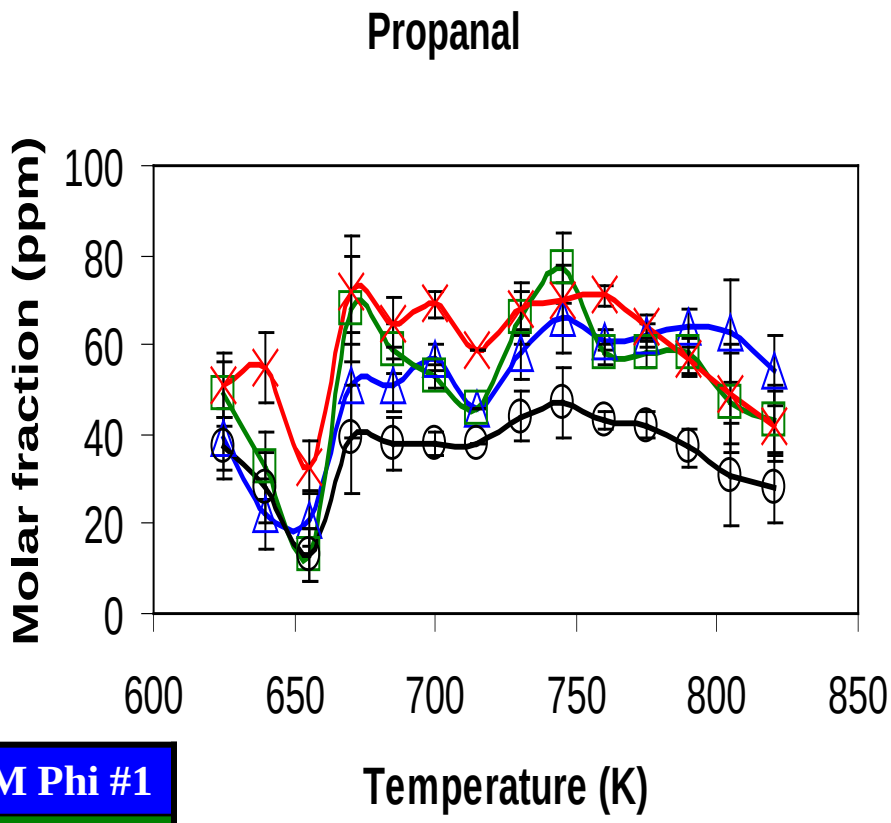
Alkane Oxidation Mechanism – Aldehyde Paths

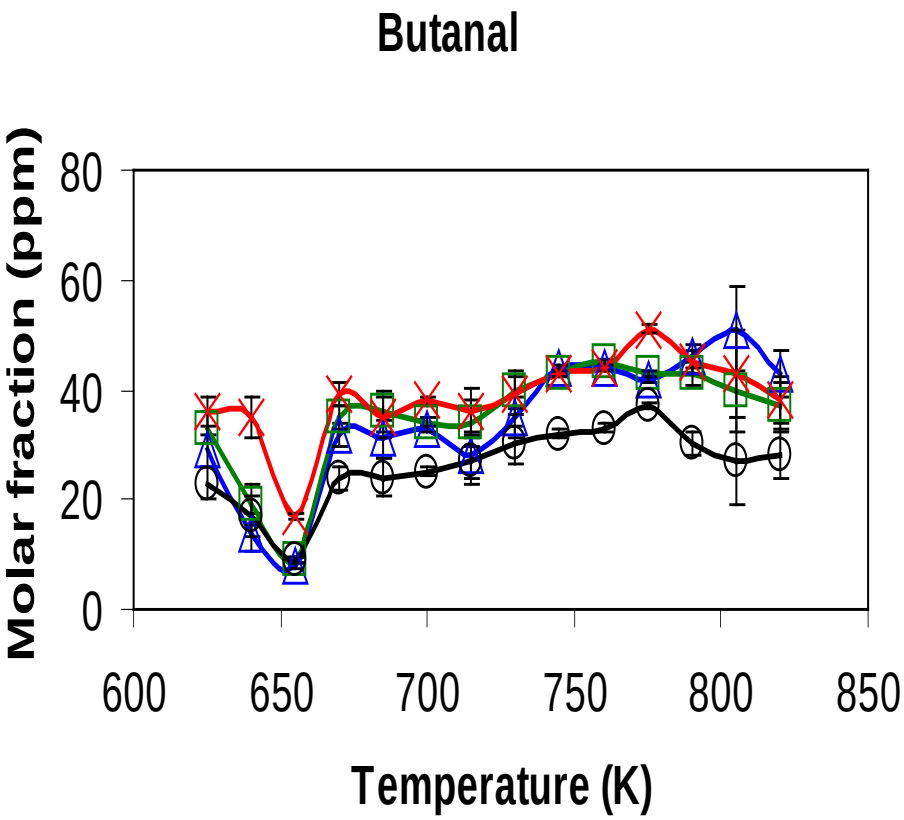


- **In general, aldehydes produced from decomposition of ketohydroperoxides (OROOH) , β-scission of alkylhydroperoxy (QOOH·) radicals, and destruction of alkylperoxy (RO_2·) radicals**

Aldehydes







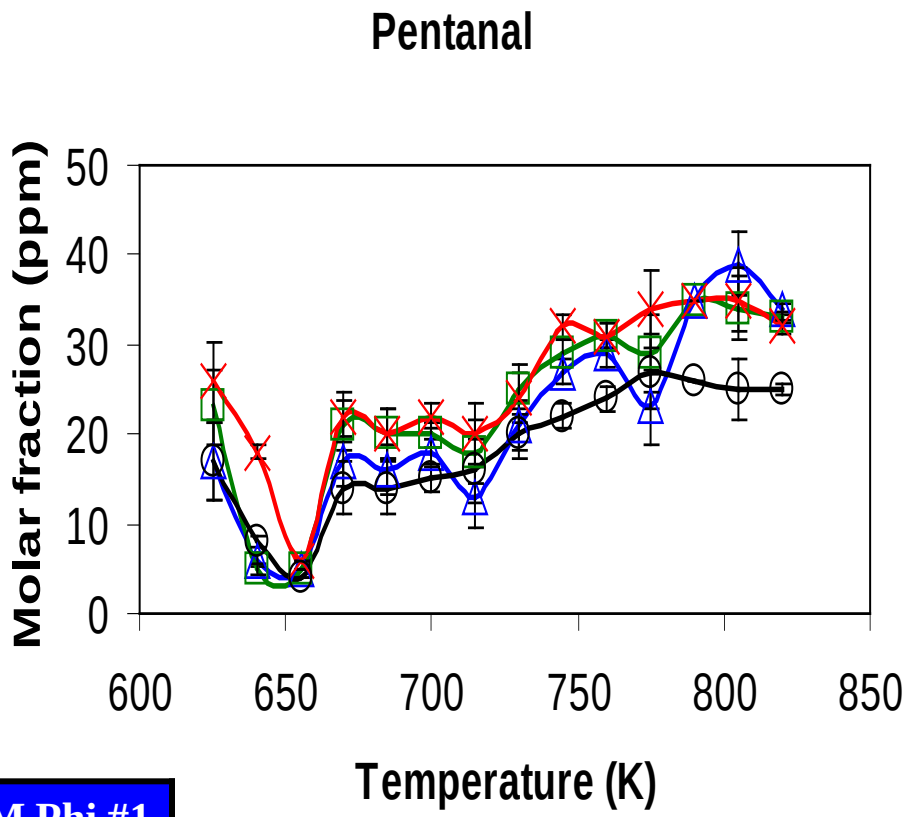
M Phi #1

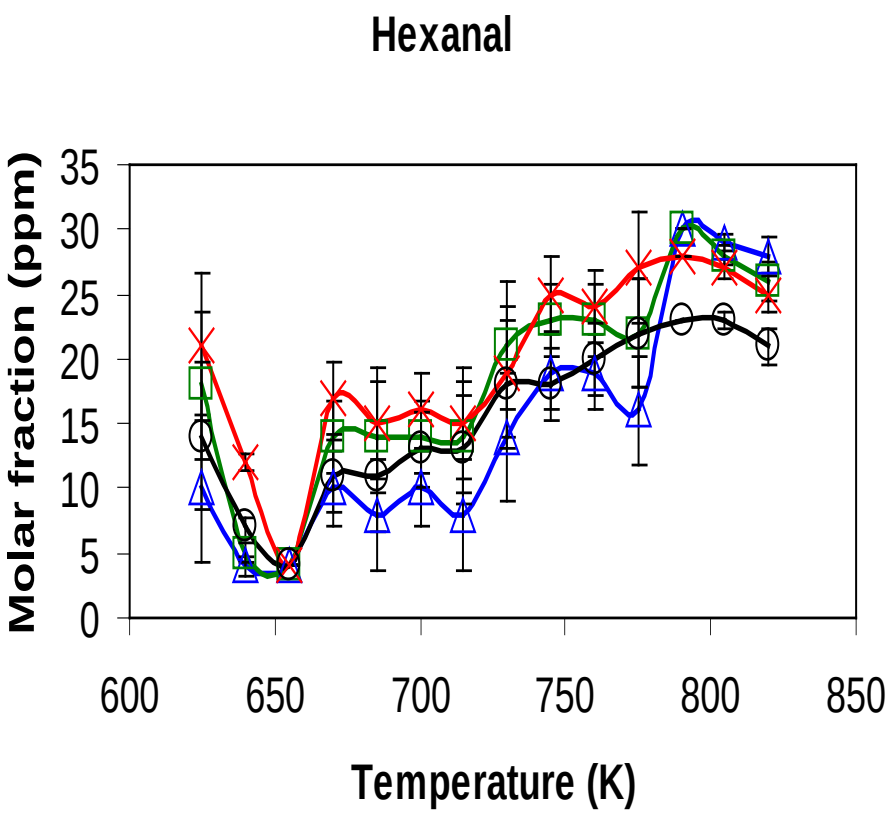
M Phi #2

H Phi

L Phi

Aldehydes





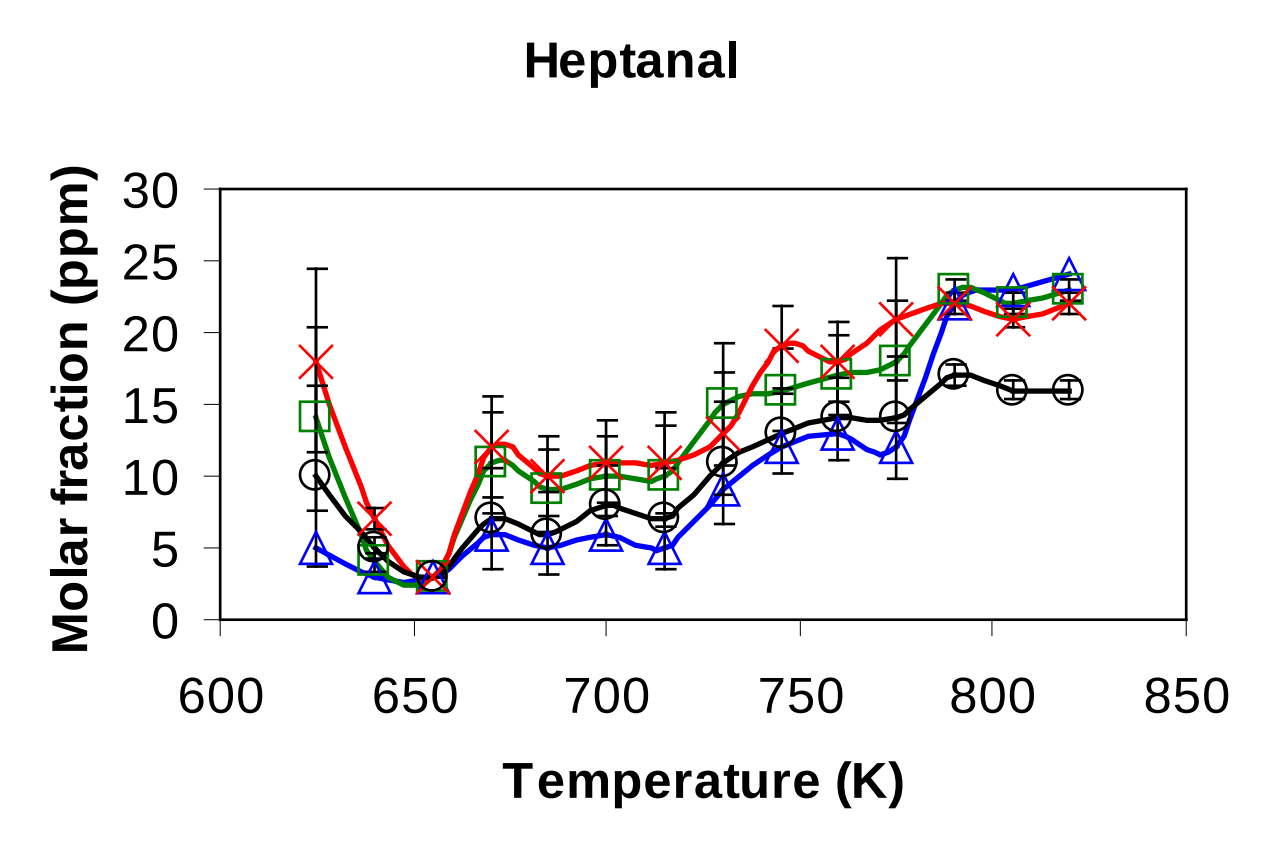
M Phi #1

M Phi #2

H Phi

L Phi

Aldehydes



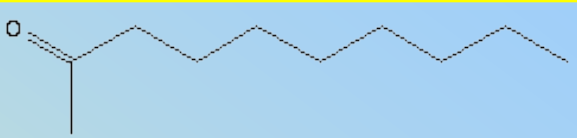
M Phi #1

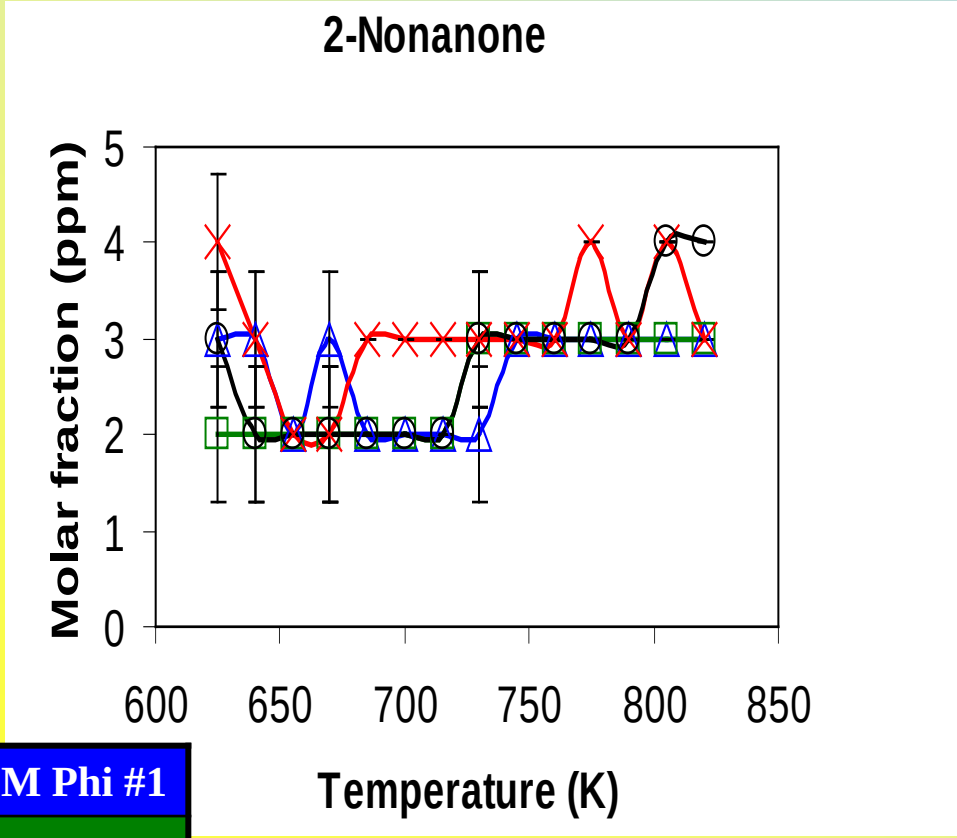
M Phi #2

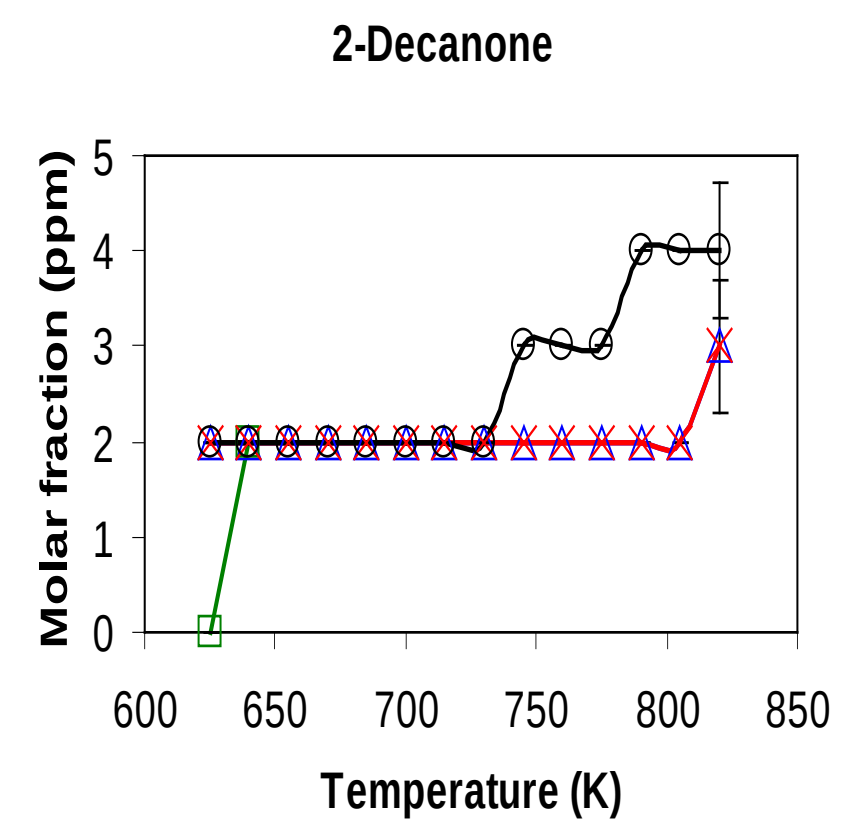
H Phi

L Phi

Ketones







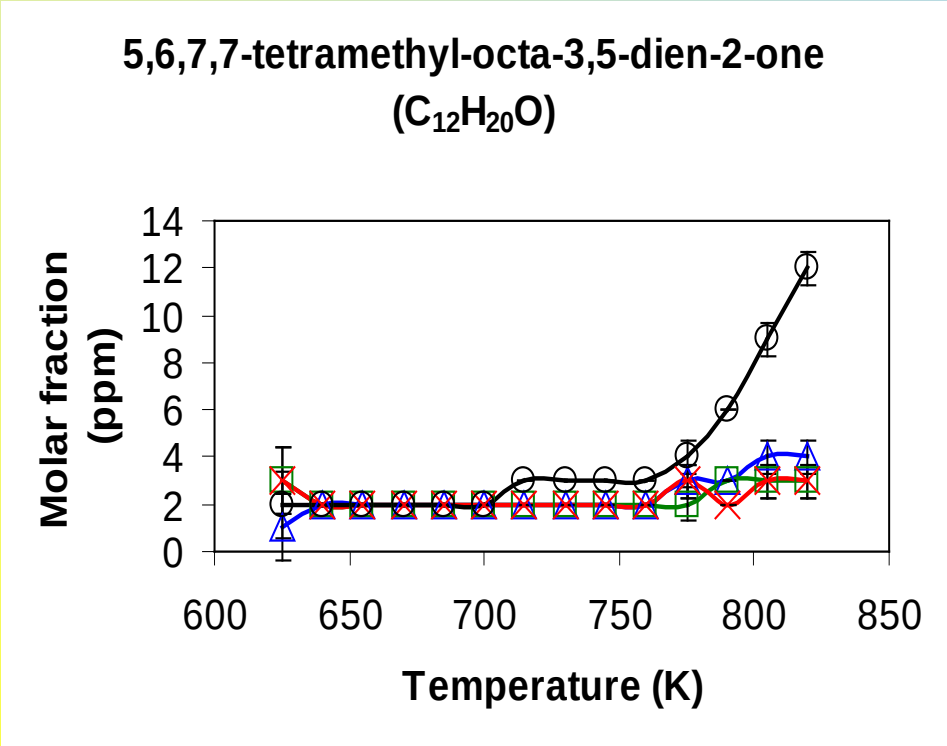
M Phi #1

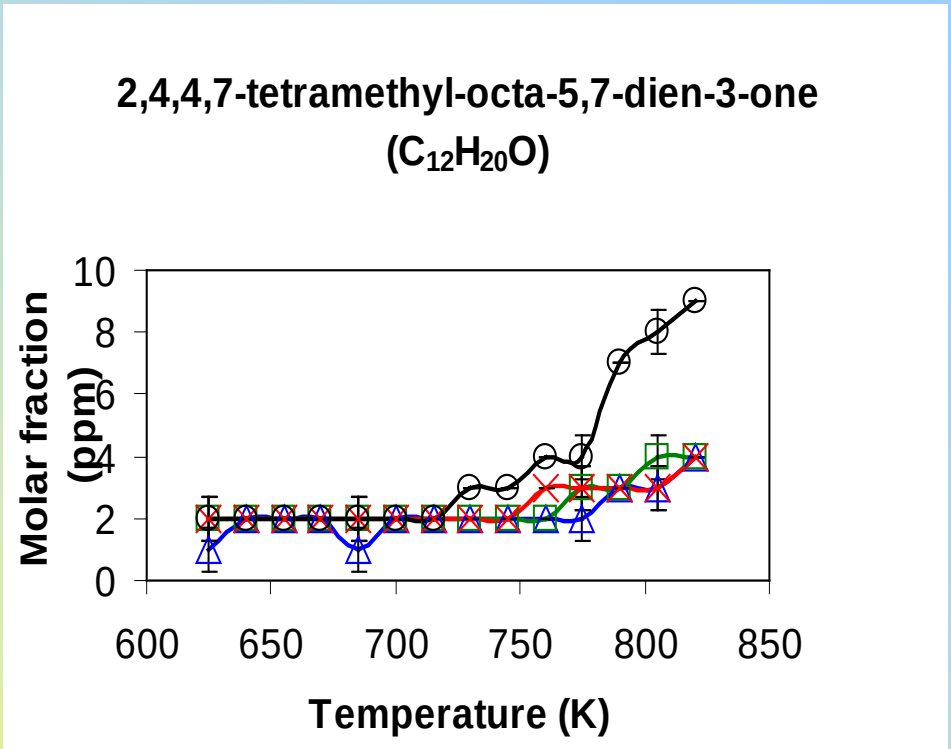
M Phi #2

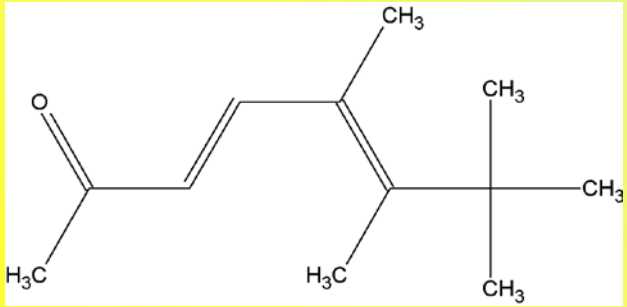
H Phi

L Phi

Ketone-substituted iso-Dienes





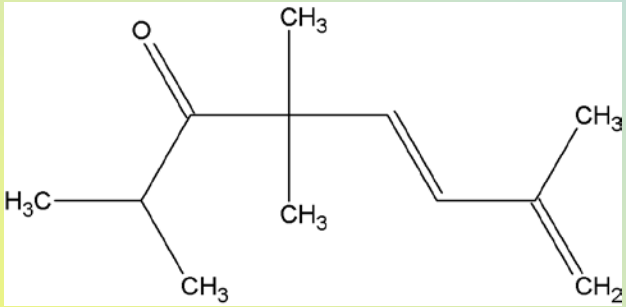


M Phi #1

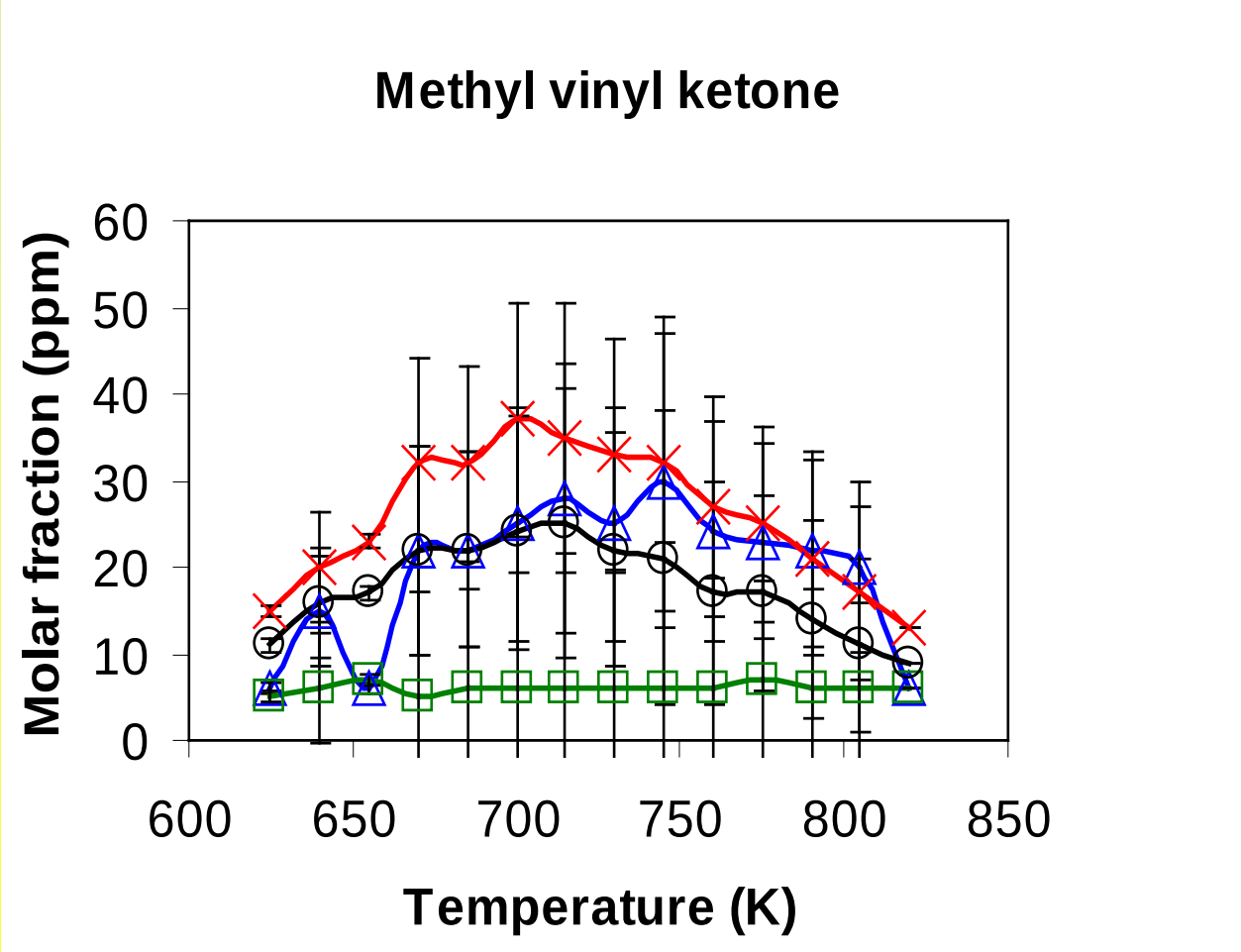
M Phi #2

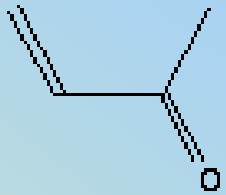
H Phi

L Phi



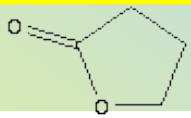
Enones

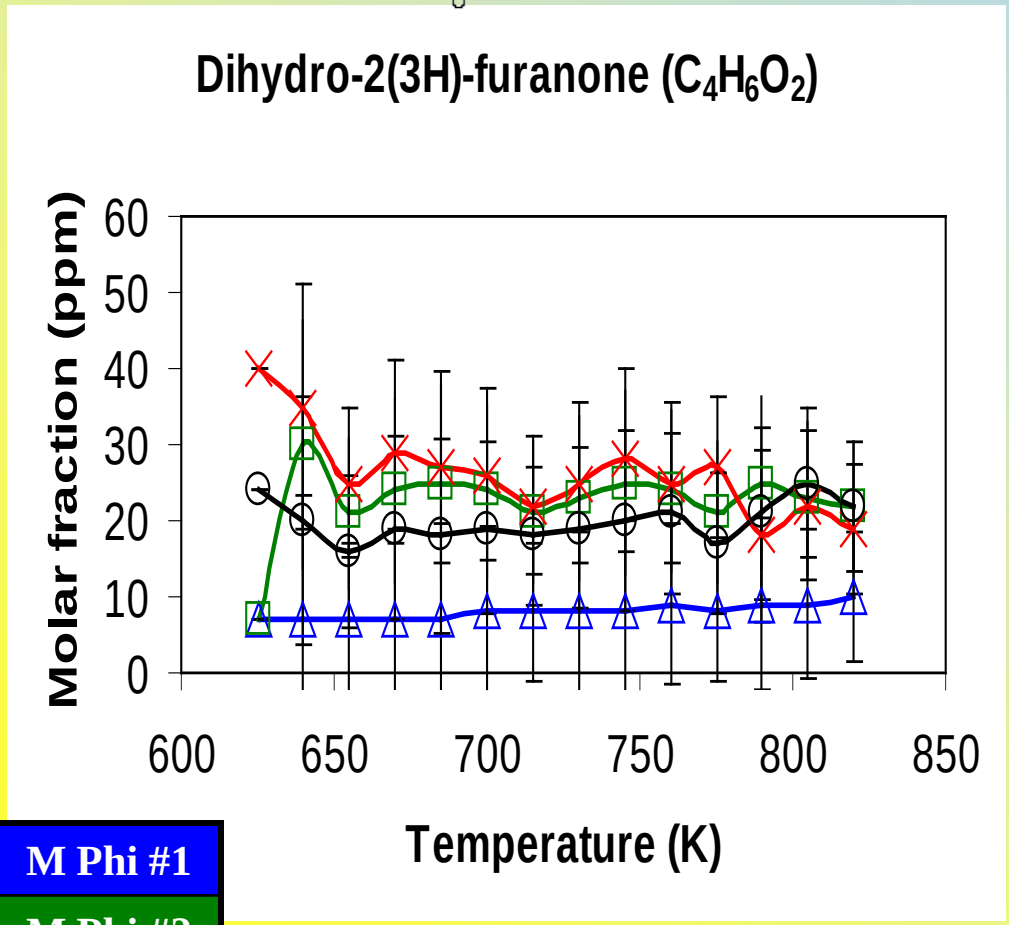




M Phi #1
M Phi #2
H Phi
L Phi

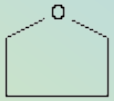
Lactones (Cyclic Esters)





M Phi #1
M Phi #2
H Phi
L Phi

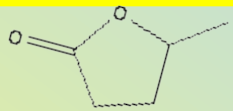
- **Must be cautious about sampling**
  - **dihydro-2(3H)-Furanone (γ-butyrolactone) is easily produced from oxidation of tetrahydrofuran via catalysis**

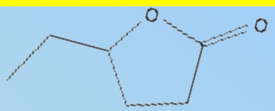


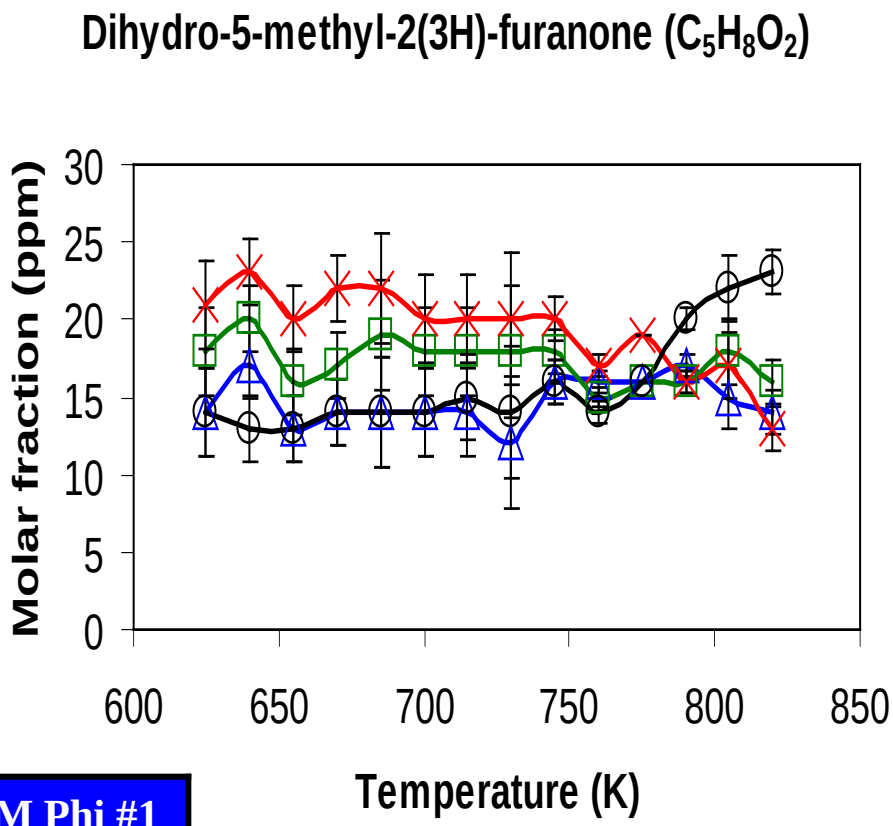
tetrahydrofuran

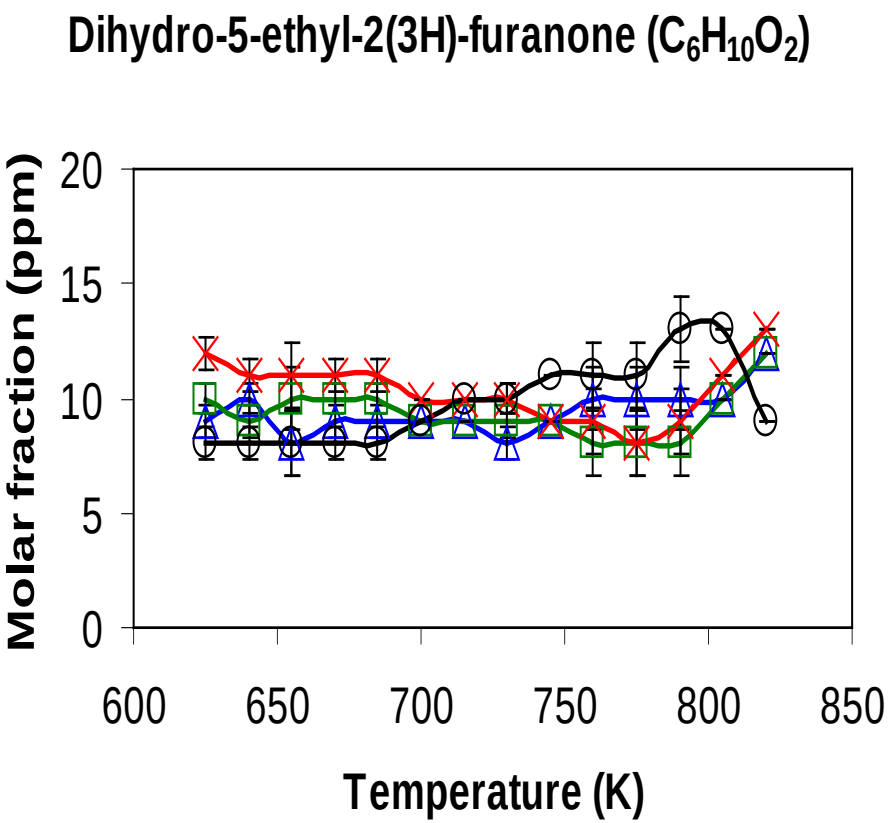
  - **Lactone can be produced from condensation of molecule with alcohol group and carboxylic acid group (such as alkanoic acids with hydroxyl groups)**
  - **Further investigation underway**

Alkyl-substituted Lactones









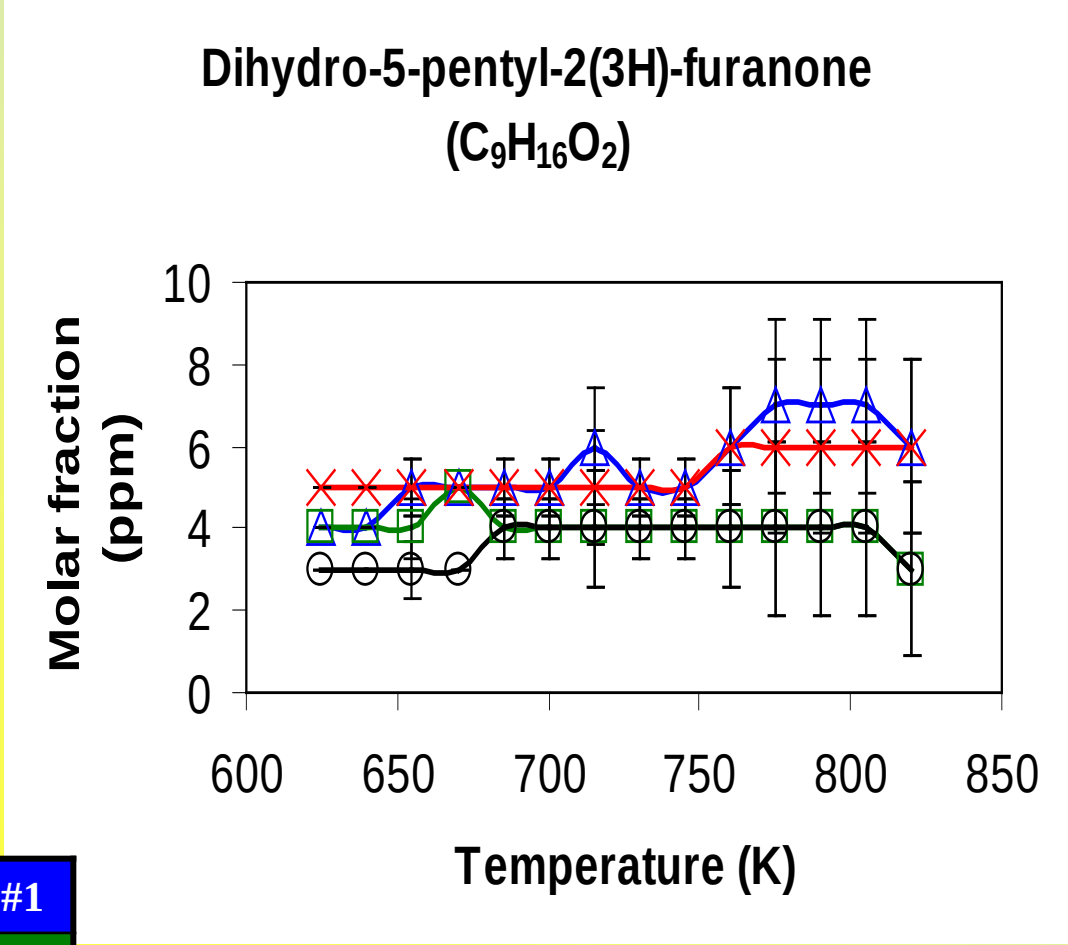
M Phi #1

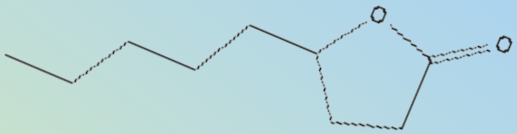
M Phi #2

H Phi

L Phi

Alkyl-substituted Lactones





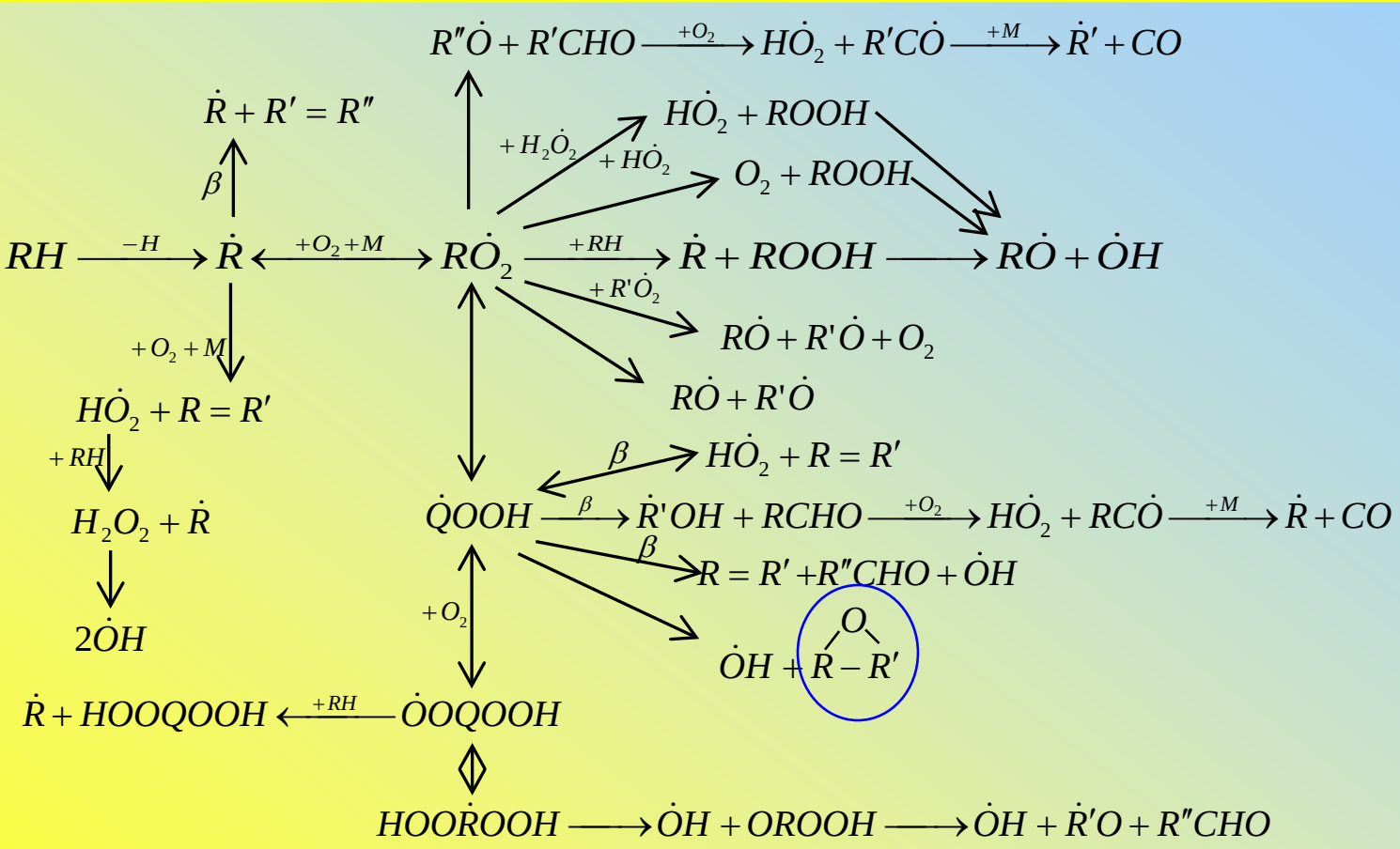
M Phi #1

M Phi #2

H Phi

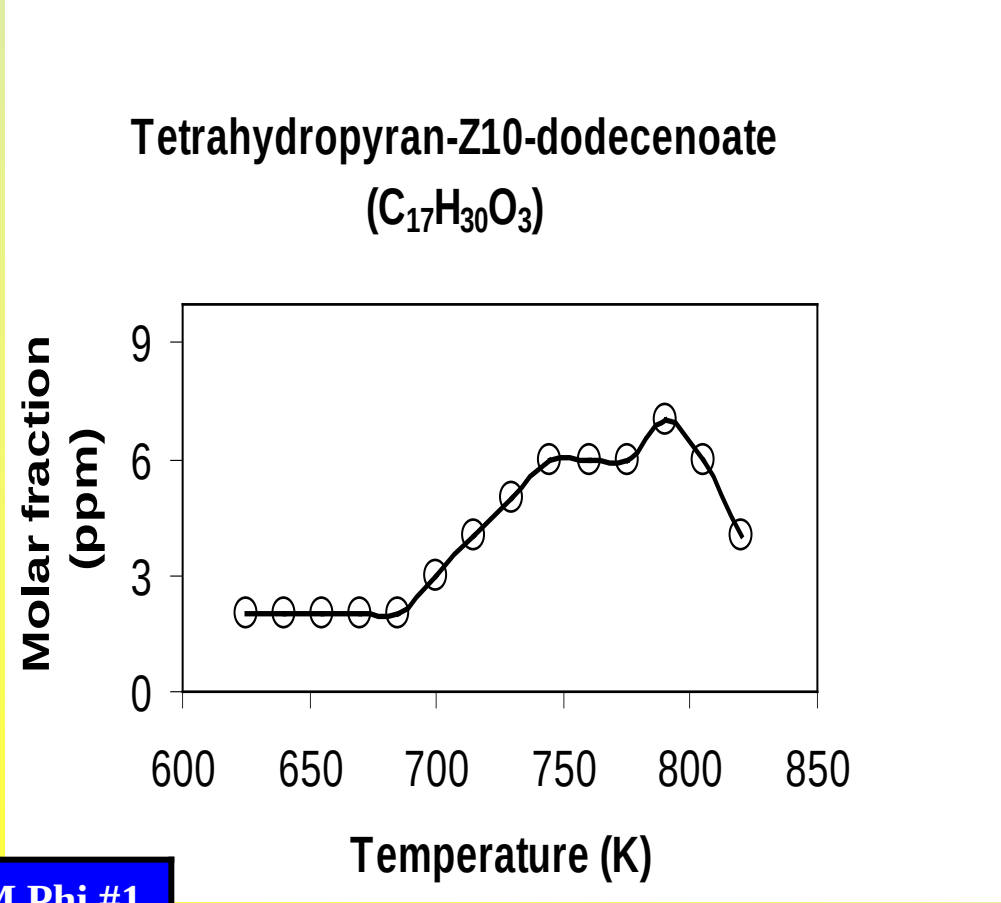
L Phi

Alkane Oxidation Mechanism – Cyclic Ether Paths

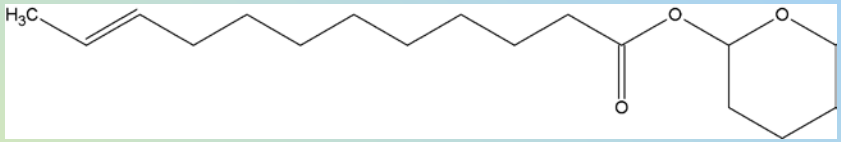


- **In general, cyclic ethers produced from decomposition of alkylhydroperoxy (QOOH·) radicals**

Ester-substituted Cyclic Ethers



- **Low GC peak made identification questionable**
  - **Experiments at higher fuel loadings may increase identification capabilities**



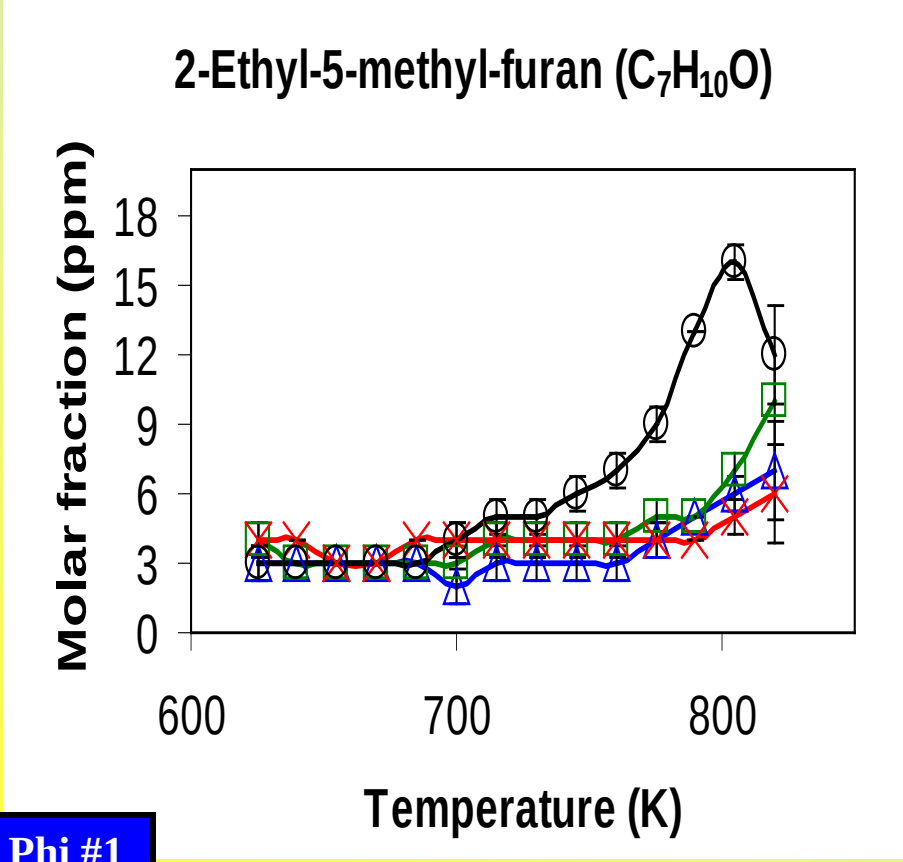
M Phi #1

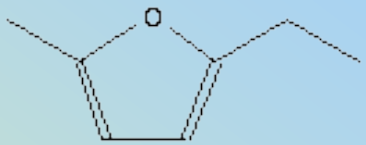
M Phi #2

H Phi

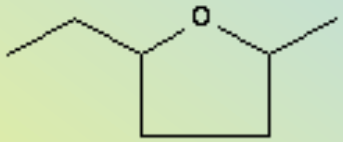
L Phi

Alkyl-substituted Furans





- **Possible dehydrogenation of 2-ethyl-5-methyl-tetrahydrofuran (a cyclic ether)**



2-ethyl-5-methyl-tetrahydrofuran

M Phi #1
M Phi #2
H Phi
L Phi

Highlights and Ongoing / Future Work

- **Four detailed experiments on the oxidation of n-dodecane in our PFR with NDIR and GC/MS/FID analysis have been conducted**
- **Over 30 species have been identified and quantified in the oxidation of n-dodecane at low and intermediate temperatures**
- **Further studies at similar initial conditions will be conducted to test for reproducibility so that experimental uncertainties can be characterized with high accuracy**
- **Collaboration with Hai Wang is underway so that our data are used in the development of the USC chemical kinetic model**
- **Coordination with Tom Bowman is underway so that our low and intermediate temperature flow reactor experiments mesh with the Stanford intermediate and high temperature flow reactor experiments**
- **Next hydrocarbon will be selected in collaboration with the consortium**