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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Fourth MACCCR Fuels Research Review

Argonne, Illinois
20-22 September 2011

Research supported by the Air Force Office of Scientific Research

Program Overview

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**
- **Oxidation at low and intermediate temperatures (500-1000 K) is important in some engine designs; particularly for CI engines**

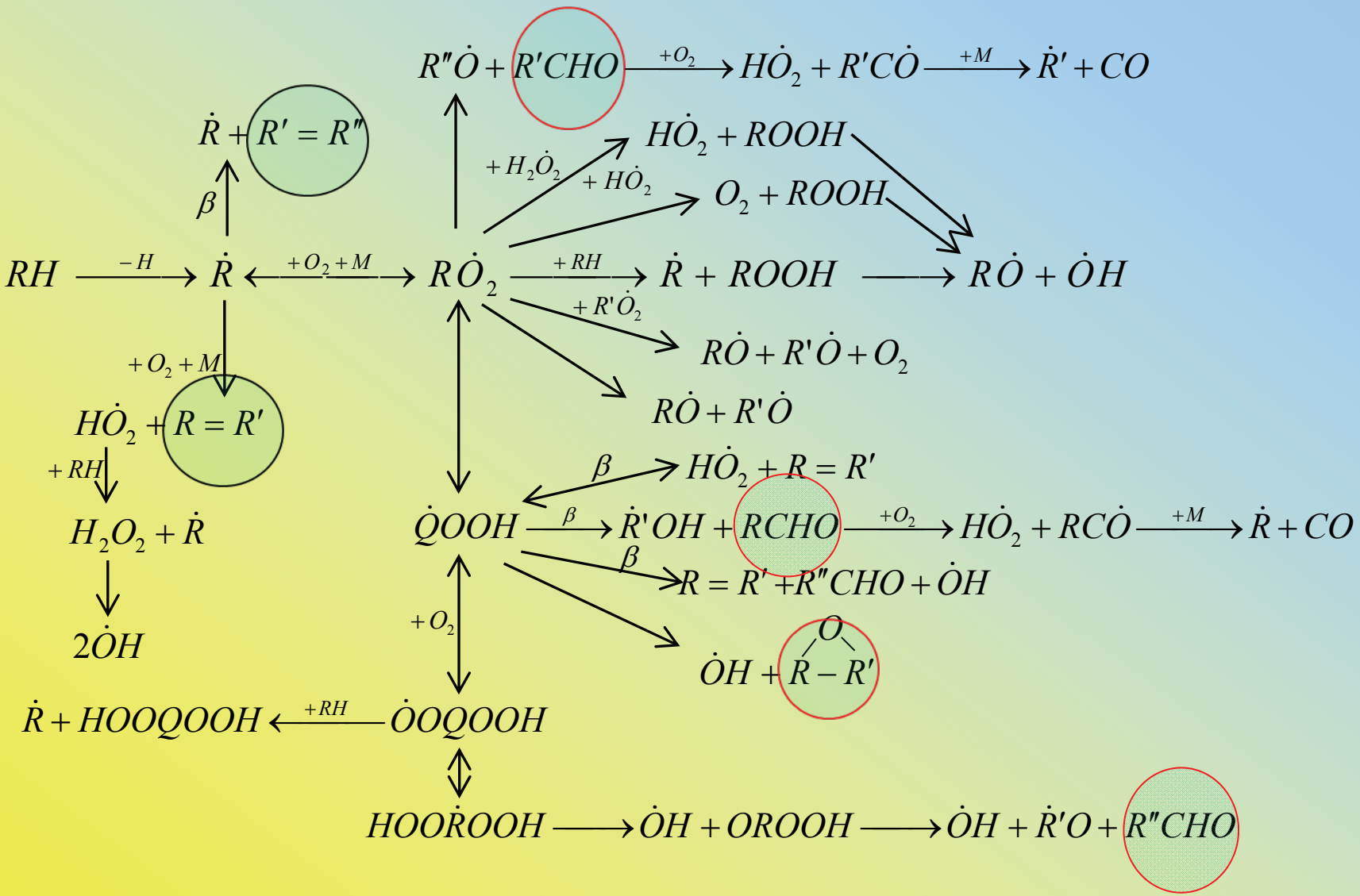
Objectives:

1) **Explore the preignition oxidation behavior of petroleum and alternative jet fuel surrogate components and component mixtures**
2) **Measure the combustion properties of the surrogate components**
3) **Collaborate on mechanistic development**

Approach:

- React the fuel/oxidizer/diluent systems under well-controlled conditions in our Pressurized Flow Reactor (PFR)
  - » Perform bench scale tests on selected hydrocarbon and hydrocarbon mixtures
  - » 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 chemical kinetic model development

Alkane Oxidation Mechanism



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

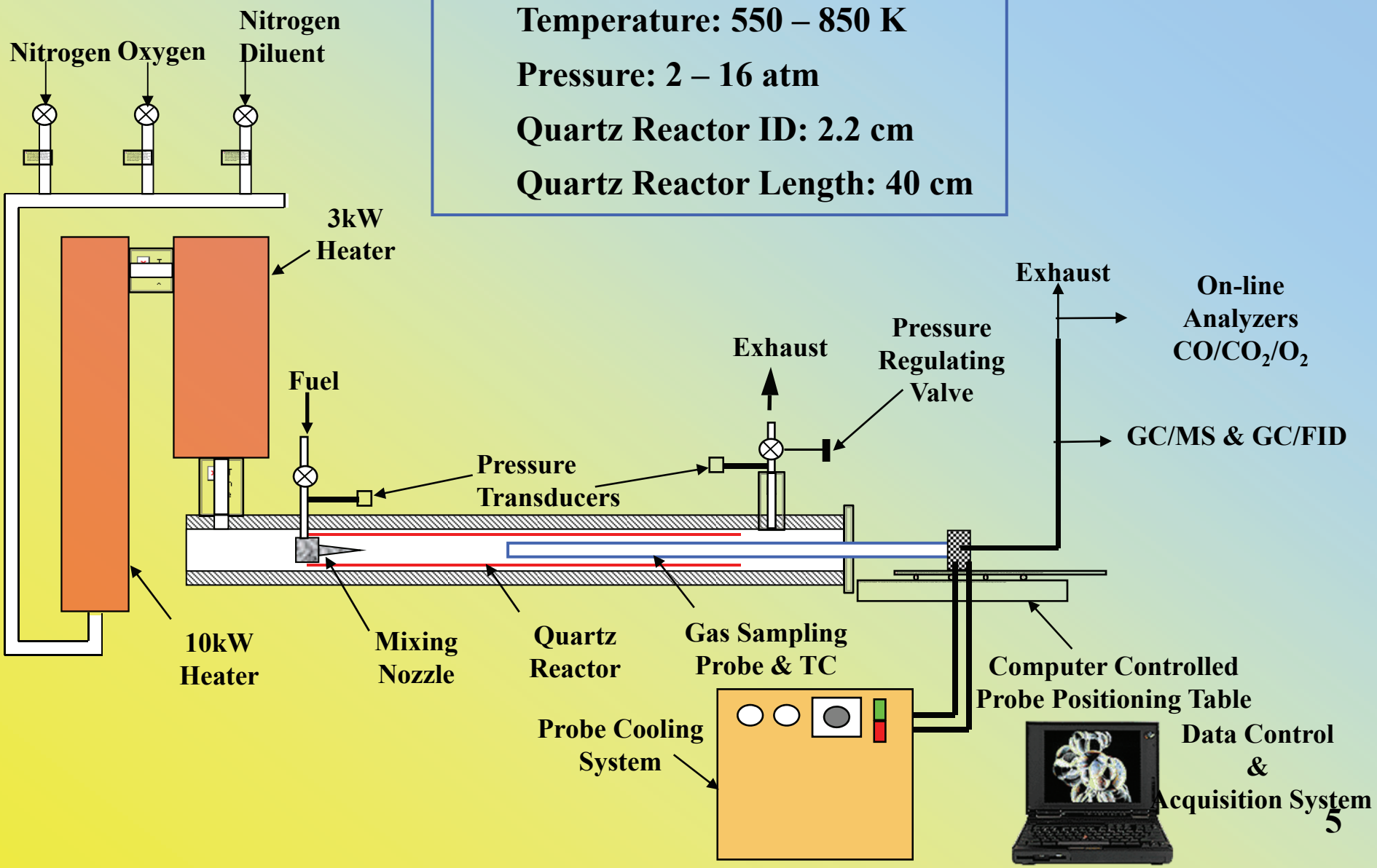
PFR Facility

Temperature: 550 – 850 K

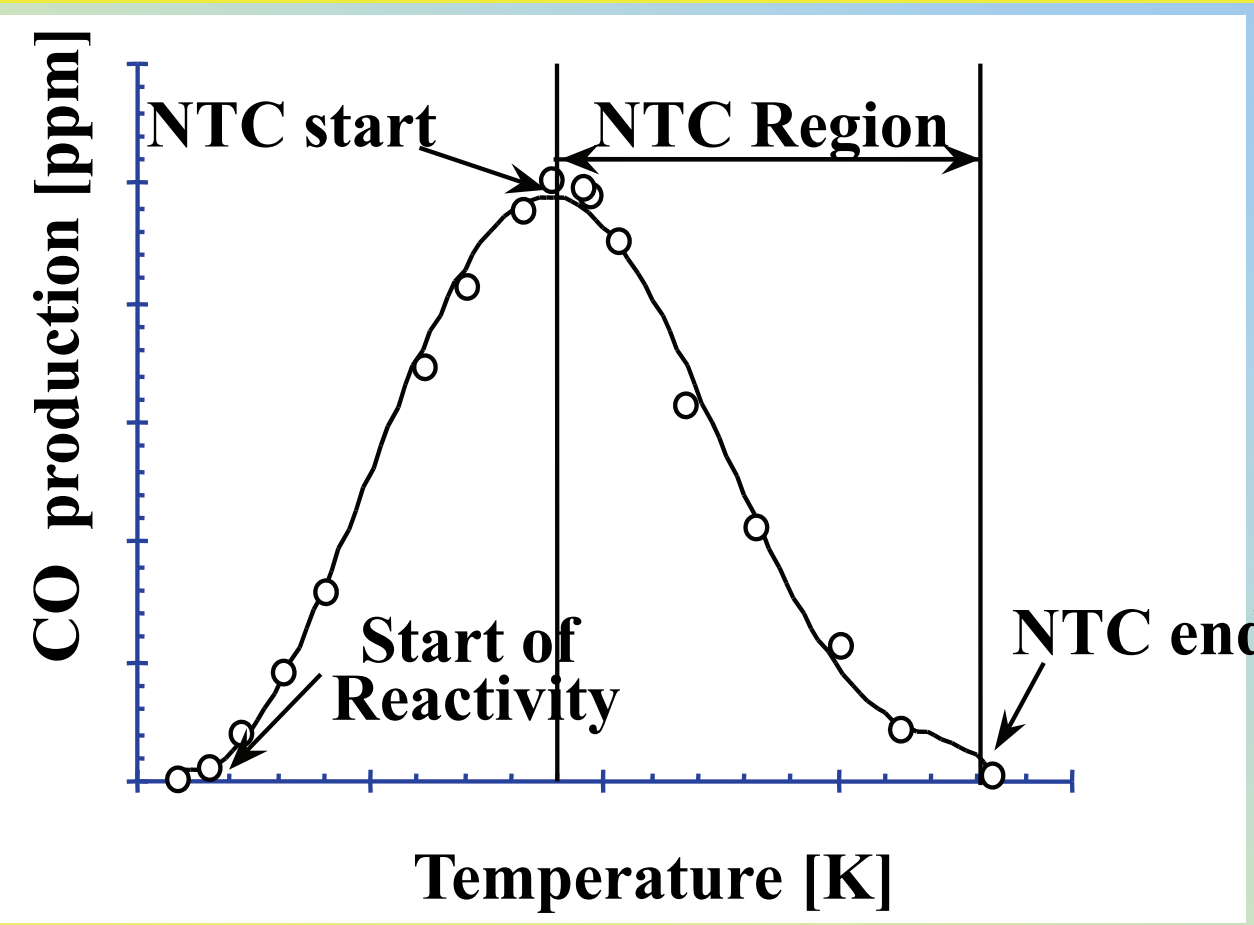
Pressure: 2 – 16 atm

Quartz Reactor ID: 2.2 cm

Quartz Reactor Length: 40 cm



Representative Reactivity Map Profile



- CO is a major indicator of reactivity at low temperatures, we also measure water with the MS which tracks the CO
- Negative Temperature Coefficient (NTC) region is the shift from low to intermediate temperature chemistry

Measurements

- Measure $CO/CO_2/O_2$ with on-line analysis
  - Errors are ±50 ppm for CO and CO_2 from NDIR analyzer, and ±1250 ppm for O_2 from electrochemical oxygen cell
- Measure Fuel/O_2 ratios with GC/MS/FID combined with O_2 Analyzer to calibrate equivalence ratio before each experiment
- FID Calibration of lighter hydrocarbons (n<7) uses 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)

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

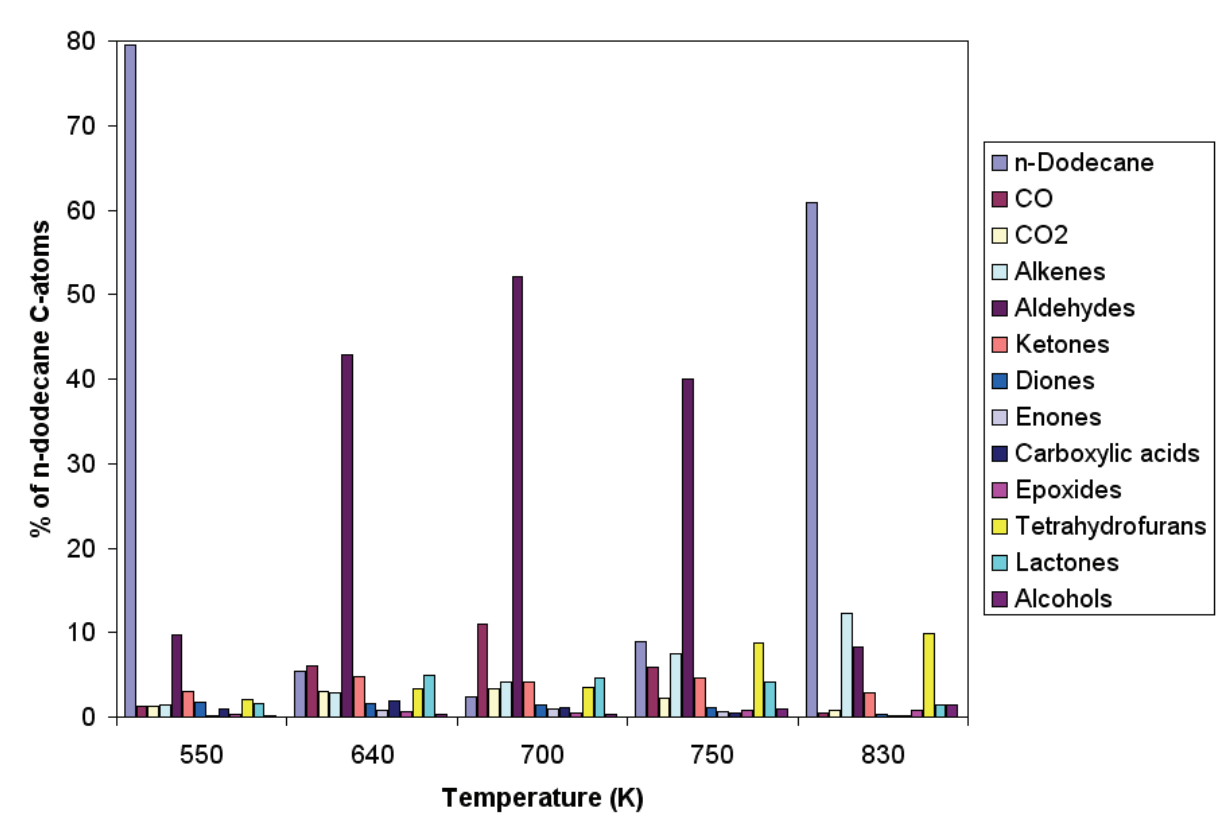
Review of Our Energy-IPT Work

- **Year One: A series of n-dodecane experiments was conducted at low temperatures (550-850 K) at a range of equivalence ratios (0.2-0.9)**
  - **Mapped NTC region for n-dodecane using measurements of CO and CO_2**
  - **Chemical Analysis of samples produced unacceptably low carbon balances - on average 50%, and as low as 20%, depending on the temperature – intermediates produced from this larger fuel require alternative operational and sampling systems**
- **Year Two: Major sampling train modifications were implemented; operational methodology was changed to eliminate sample "aging" questions.**
  - **Prelim n-dodecane: chemical analysis yielded carbon balances greater than 80%; 131 intermediate species compared to 30 in Year 01 work**
  - **Prelim n-butyl cyclohexane: mapped NTC region; carbon balances above 95% for chemical analysis; 65 species identified**

Our Energy-IPT Work (cont)

- Year Three and Beyond: Continued work with n-dodecane, n-butyl cyclohexane and began work with isocetane and n-propyl cyclohexane.
  - n-DODECANE: 531 ± 8 ppm $C_{12}H_{26}$; phi=0.23; t_r=120ms; p=8 atm
    - » NTC begins at 670K
    - » Different hydrocarbon classes were predominant at different reaction conditions:
      - CO, CO_2, and aldehydes all peaked at start of NTC
      - Before NTC: lactones and ketones
      - At NTC: lactones
      - During NTC: alkenes, tetrahydrofurans, and ketones
    - » Measured many species with two O atoms - lactones, carboxylic acids, and diones
    - » Proposed pathways that explained formaldehyde/CO ratio and lactone formation

n-Dodecane: Class Analysis



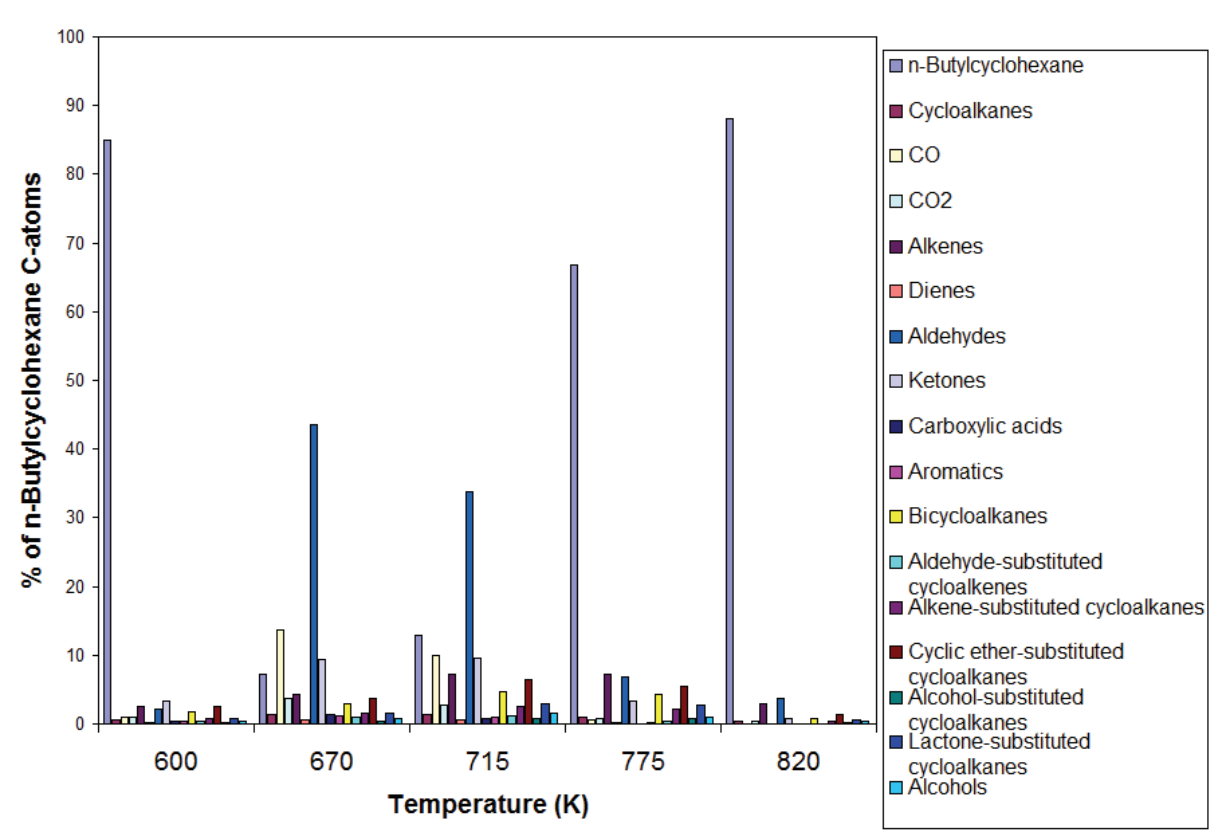
All classes accounting for ≥ 1% of reactant, fractions of reactant and product calculated by C-atoms

Temperature (K)	550	640	700	750	830
Classes accounting for ≥ 5% of reactant, listed in descending order	dodecane, aldehydes	aldehydes, CO, dodecane, lactones, ketones	aldehydes, CO, lactones	aldehydes, dodecane, THF's, alkenes, CO, ketones	dodecane, alkenes, THF's, aldehydes

Our Energy-IPT Work (n-BUTYL CHX)

- n-BUTYL CHX: 1080 ± 20 ppm $C_{10}H_{20}$; phi=0.38; t_r=120 ms; p=8atm
  - » NTC began at 680K
  - » C_{2-4} straight-chain alkenes produced from n-butyl chain
  - » Larger species measured were cycloalkenes, cycloketones, and multi-ring species (cycloalkane / tetrahydrofuran, cycloalkane / lactone, and dicycloalkane)
  - » Different classes of HC's were predominant across the temperature range:
    - Before NTC: aldehydes, cycloketones, and acetic acid
    - During NTC: (cycloalkenes and multi-ring species)

n-butyl CHX: Class Analysis



All classes accounting for ≥ 1% of reactant, fractions of reactant and product calculated by C-atoms

Temperature (K)	600	670	715	775	820
Classes accounting for ≥ 5% of reactant, listed in descending order	n-BCHX	aldehydes, CO, ketones, n-BCHX	aldehydes, n-BCHX, CO, ketones, alkenes, cyclic ether-substituted cycloalkanes, bicycloalkanes	n-BCHX, alkenes, aldehydes, cyclic ether-substituted cycloalkanes	n-BCHX

Our Energy-IPT Work (ISOCETANE)

- Neat ISOCETANE: 435 ± 20 ppm HC; phi=0.25; t_r=120 ms; p=8 atm
  - » Unreactive
- 50/50 mix with n-decane: 440 ppm HC; phi=0.22; t_r=120 ms; p=8 atm
  - » NTC began at 670K
  - » Different classes of HC's were predominant across the temperature range
    - Before NTC: acetic acid; ketones
    - During NTC: Aldehydes predominate in NTC region

YEAR 3+ Energy-IPT Work (n-PROPYL CHX)

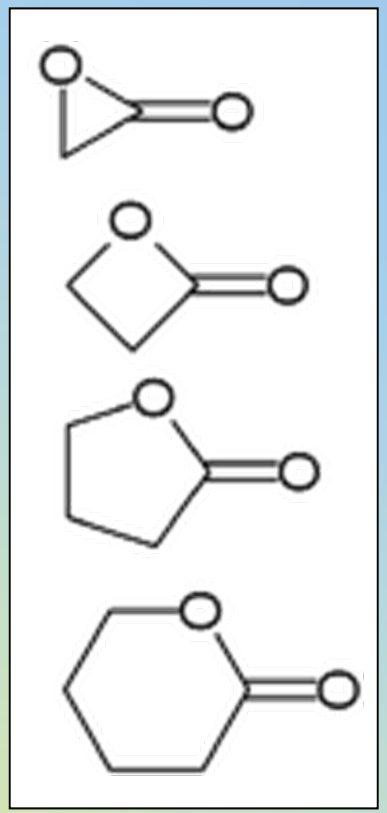
- n-PROPYL CHX: 758 ± 08 ppm HC; phi=0.24; t_r=120 ms; p=8 atm
  - » NTC began at 680 K
  - » 1-butene production with n-propyl CHX is much lower than 1-butene from n-butyl CHX
  - » Similar behavior of cycloalkenes, aldehyds, acetic acid and cycloketones observed as for n-butyl CHX
  - » Different classes of HC's were predominant across the temperature range
    - Before NTC: aldehydes, cycloketones, and acetic acid
    - During NTC: cycloalkenes and multi-ring species

YEAR 3+ Energy-IPT Work - Modeling of Lactone Formation

- Need for a model accounting for measured lactones
- Target Experimental Data
- Proposed Pathways for Lactone Formation
- Development of Model
- Results

Lactones

- Lactones: Cyclic ethers with carbonyl function.
- Reactions involving lactones include degenerate branching steps that may affect auto-ignition.
- Generation of lactones during low temperature combustion reported by Leppard (1991) and Kurman et al. (2010).
- A class of compounds not predicted by any kinetic mechanism today.
- Knowledge of lactone chemistry can be applied to several applications:
  - Dioxin generation and destruction
  - Furan-based cellulosic biofuels
  - Synthesis of lactone based anti-malarial drugs



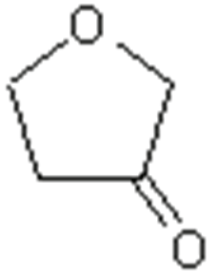
Lactone analogues

Experimental Data

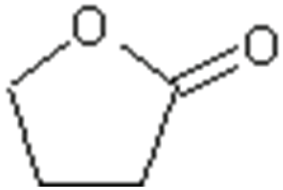
Leppard (1991)

- Motored CFR Engine
- Fuel: Tetrahydrofuran
- Equivalence Ratio:1
- Compression Ratio: 8.7, 600 rpm
- Intake manifold temperature of 400 K, pressure: 80 kPa, water jacket temperature: 373 K
- Reported the formation of several intermediates including two lactones:
  - » dihydro-3(2H)-furanone
  - » dihydro-2(3H)-furanone

tetrahydrofuran



dihydro-3(2H)-furanone



dihydro-2(3H)-furanone

Experimental Data

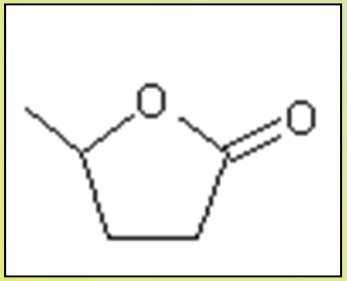
Kurman et al (2010)

- Drexel's Pressurized Flow Reactor
- Fuel: n-Dodecane
- Temperature: 550-830K, Pressure: 8 Atm.
- Dilute and Lean conditions (Equivalence Ratio = 0.23)
- Residence time: 120 ms
- Used a 'direct transfer' analysis technique.
- Intermediates analyzed using a GC with a FID coupled to an MS.
- Continuous monitoring of CO, CO_2, O_2

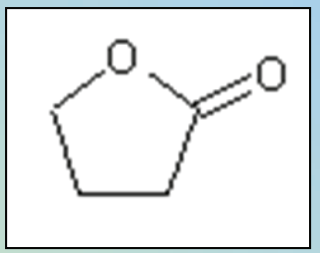
Experimental Data

Kurman et al (2010)

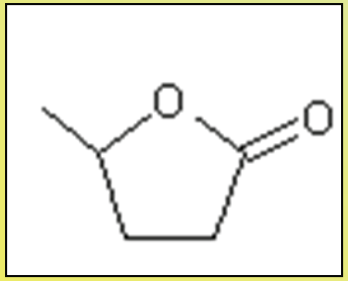
- Reported the presence of <u>alkylated</u> and <u>non-alkylated</u> lactones.



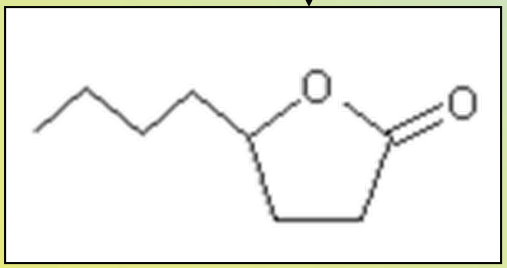
dihydro-5-methyl-2(3H)-furanone



dihydro-2(3H)-furanone



5-methyl-2(3H)-furanone



dihydro-5-butyl-2(3H)-furanone

Model Conditions

- Plug Flow Reactor module in CHEMKIN-PRO
- 2.2 cm diameter, 40 cm length
- Adiabatic approximation
- Inlet composition
  - n-Dodecane: 531 ppm
  - Oxygen: 42,100 ppm
  - Nitrogen: Balance
- Simulations conducted for a range of temperatures (550-830 K at intervals of 10 K)
- Residence Time: 120 ms

Proposed Pathways for Lactone Formation

- **Ring closure followed by addition of the carbonyl adduct**
  - **Leppard's results (1991) suggests that carbonyl can be added to THF without ring opening - '<u>Pathway A</u>'.**
  - **Can also proceed through the hydroperoxybutylperoxy radical. Relevant reactions have been proposed by Battin-Leclerc et al. (2010) - '<u>Pathway B</u>'.**
- **Addition of carbonyl adduct followed by ring closure**
  - **Battin-Leclerc et al. (2010) studied the oxidation of butane and reported the presence of cyclic ethers with a hydroperoxide function, but not tetrahydrofuran or any other C4 cyclic ether - '<u>Pathway C</u>'.**
- **All three pathways can yield both isomers.**

Development of Model

- Model contains 206 new reactions and 35 new species.
  - Pathways A, B and C for lactone formation
  - Consumption pathways for lactones also added
- nC_8-nC_{16} model by Westbrook et al. (2009) used as base
- Rates for the new reactions based on analogous reactions from the LLNL library, and the Nancy group.
- Thermodynamic properties of the new species estimated using THERM

Lactone Mechanisms: Conclusions

- Three pathways to lactone formation
  - Two involving ring closure prior to addition of carbonyl.
    - » Through tetrahydrofuran - ‘Pathway A’
    - » Through hydroperoxybutylperoxy radicals - ‘Pathway B’
  - One involving addition of carbonyl prior to cyclization through C4 carbonyl species.
    - » Through C4 carbonyl species - ‘Pathway C’
- ‘Pathway C’ dominates at all temperatures studied.
- Dihydro-3(2H)-furanone is the dominant isomer.
- Lactone submechanism contains degenerate branching reactions that increases the predicted reactivity at low and intermediate temperatures.

Future Work

- Work on some in-house modeling for low temperature data
- Replicate experiments with n-propyl CHX.
- Experiments with 2,7-dimethyl-octane
- Move to lightly branched aromatics
- Compare our measurements with VPFR

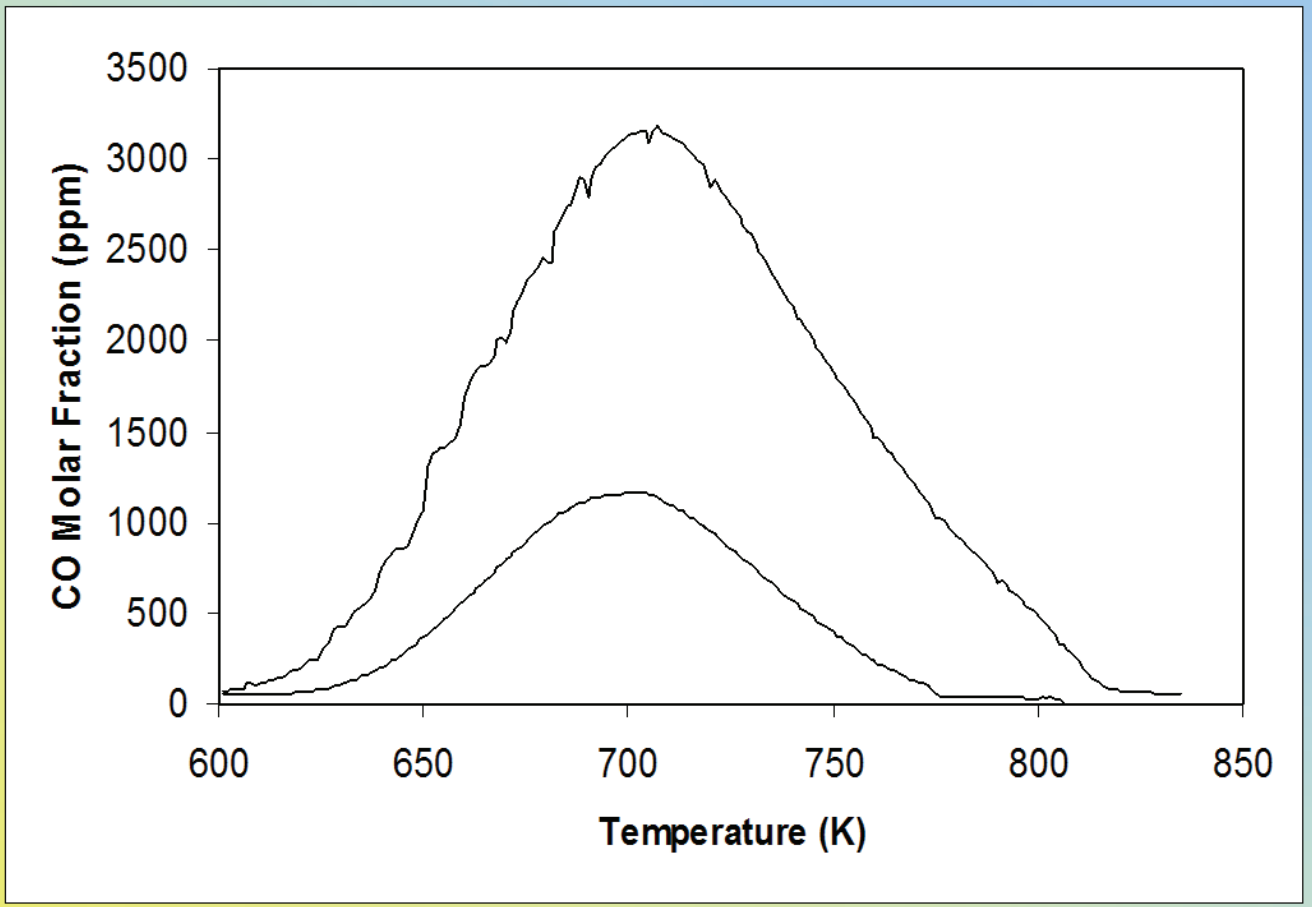
Comparing Flow Reactor Measurements

- **As data on surrogate component oxidation from several flow reactors have becomes available, it only seems natural to compare results**

- **Unfortunately, as each of our reactors were designed slightly differently on first blush there appear to be differences among the measurements**

DU n-decane reactivity

Lower pressure and lower residence time have slight reduction on NTC start temperature, but cause end of NTC reactivity to be at significantly lower temperature



(Kurman et al., 2007)

- Upper line: 8 atm pressure & 120 ms residence time, Lower line: 4 atm pressure & 75 ms residence time
- 810 ppm n-decane, 0.30 phi

Princeton Data – Comb. & Flame

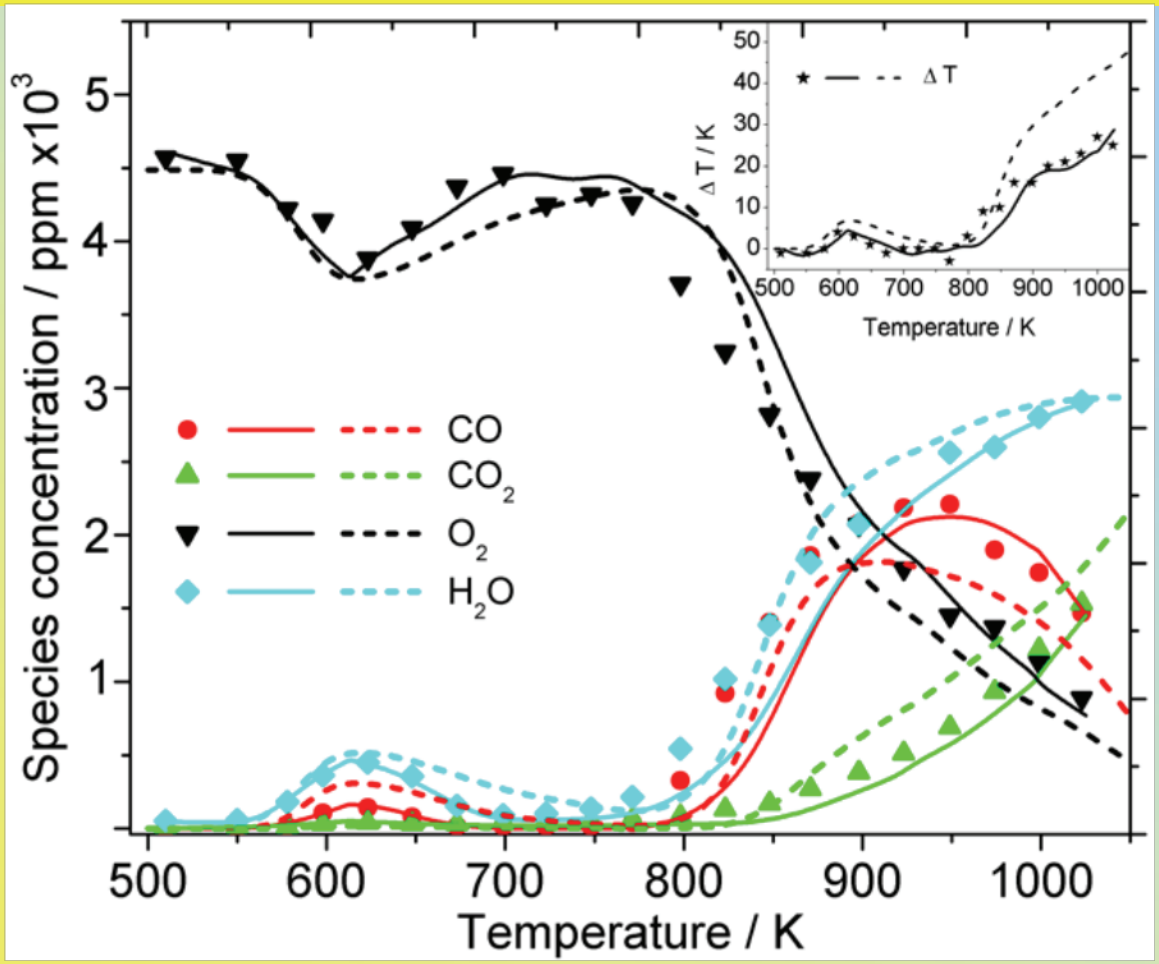
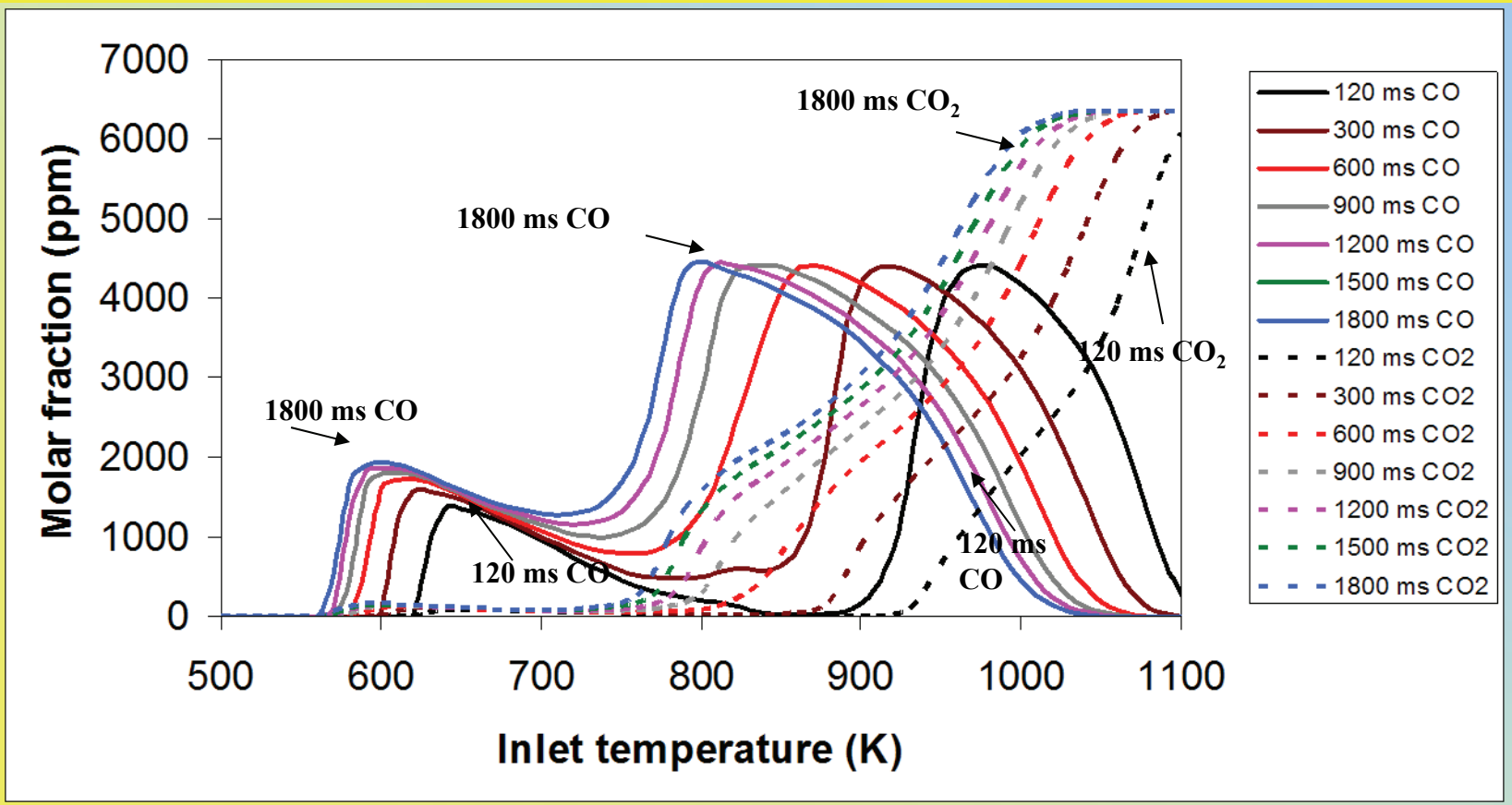


Figure 1 from Dooley et al., 2010: Flow reactor oxidation data for conditions of 12.5 atm, 0.3% carbon, ϕ= 1.0 and τ =1.8s, for POSF-4658 (symbols), POSF-4658 surrogate (solid lines) and model simulation of POSF-4658 surrogate (dashed lines), Inset;ΔT. POSF-4658 surrogate: 42.67/33.02/24.31 mole % n-decane/iso-octane/toluene

CO & CO_2 Predictions as Residence Time Changes



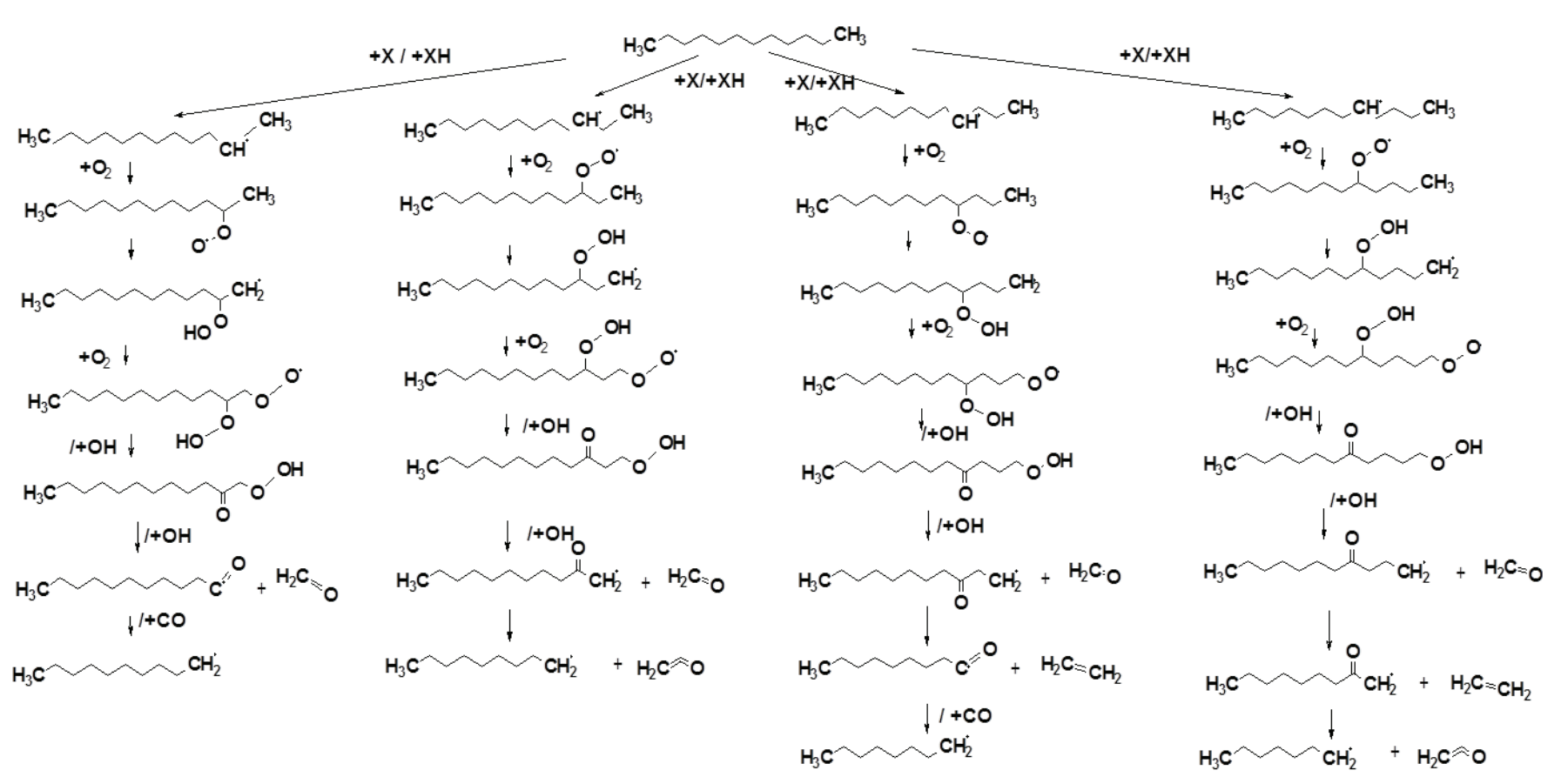
531 ppm n-dodecane / 42,100 ppm O_2 / 957,369 ppm N_2; 0.23 phi; 0.3% carbon by mole; 8 tm; Livermore model (Westbrook et al., 2009) run using plug flow reactor under adiabatic conditions at 10-K intervals. Note: 1500 and 1800 ms CO overlap.

With lower residence time, first-stage and second-stage ignition shift to higher temperatures

- **Thanks**

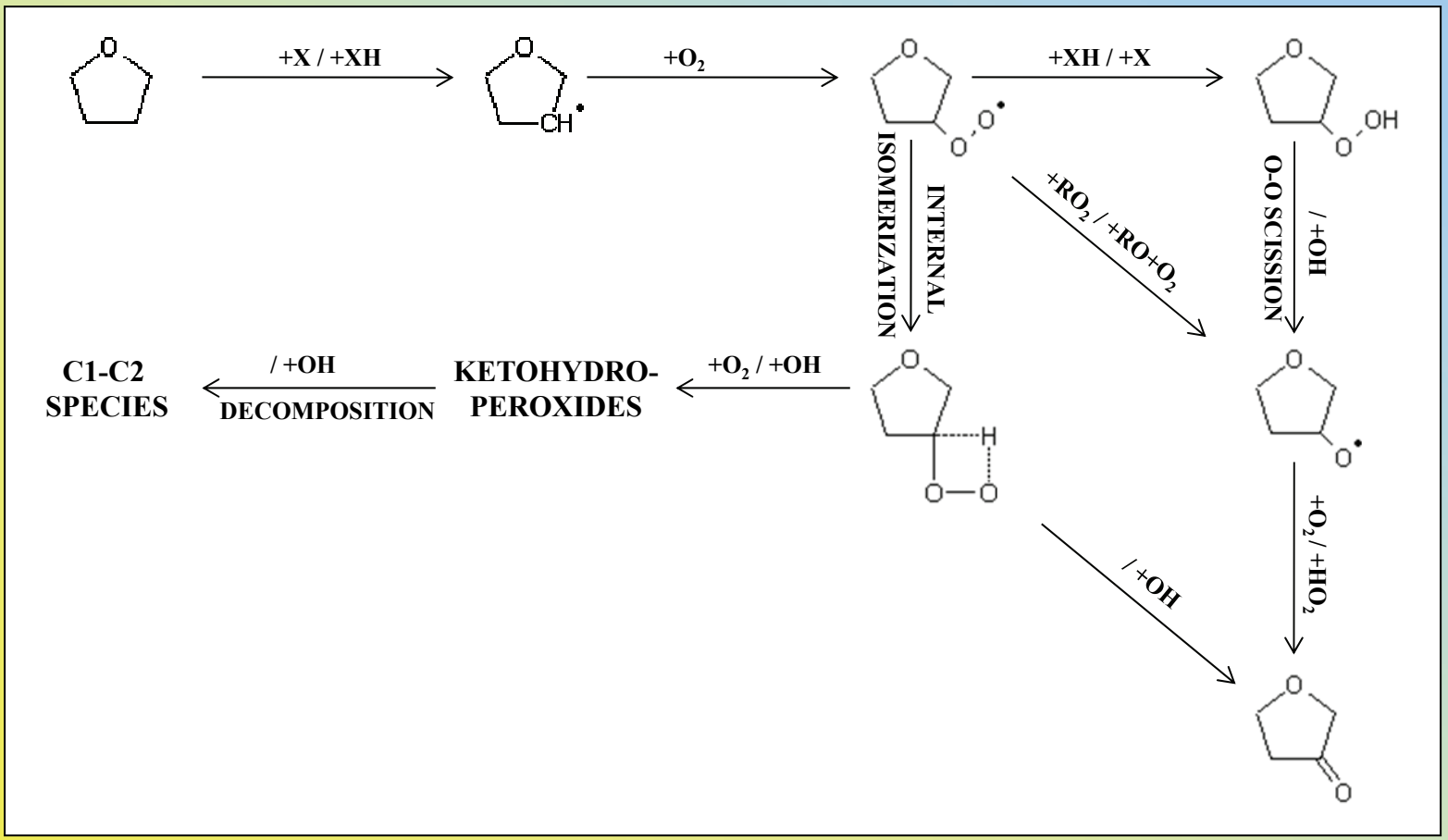
Mechanistic Speculation

- **Measured intermediates suggest that the critical low temperature branching pathway for n-dodecane may be hydrogen abstraction from a secondary carbon followed by molecular oxygen addition and then internal hydrogen shift from the primary carbon**
  - **If this reaction path was more active, Livermore model would predict measured intermediates more appropriately**



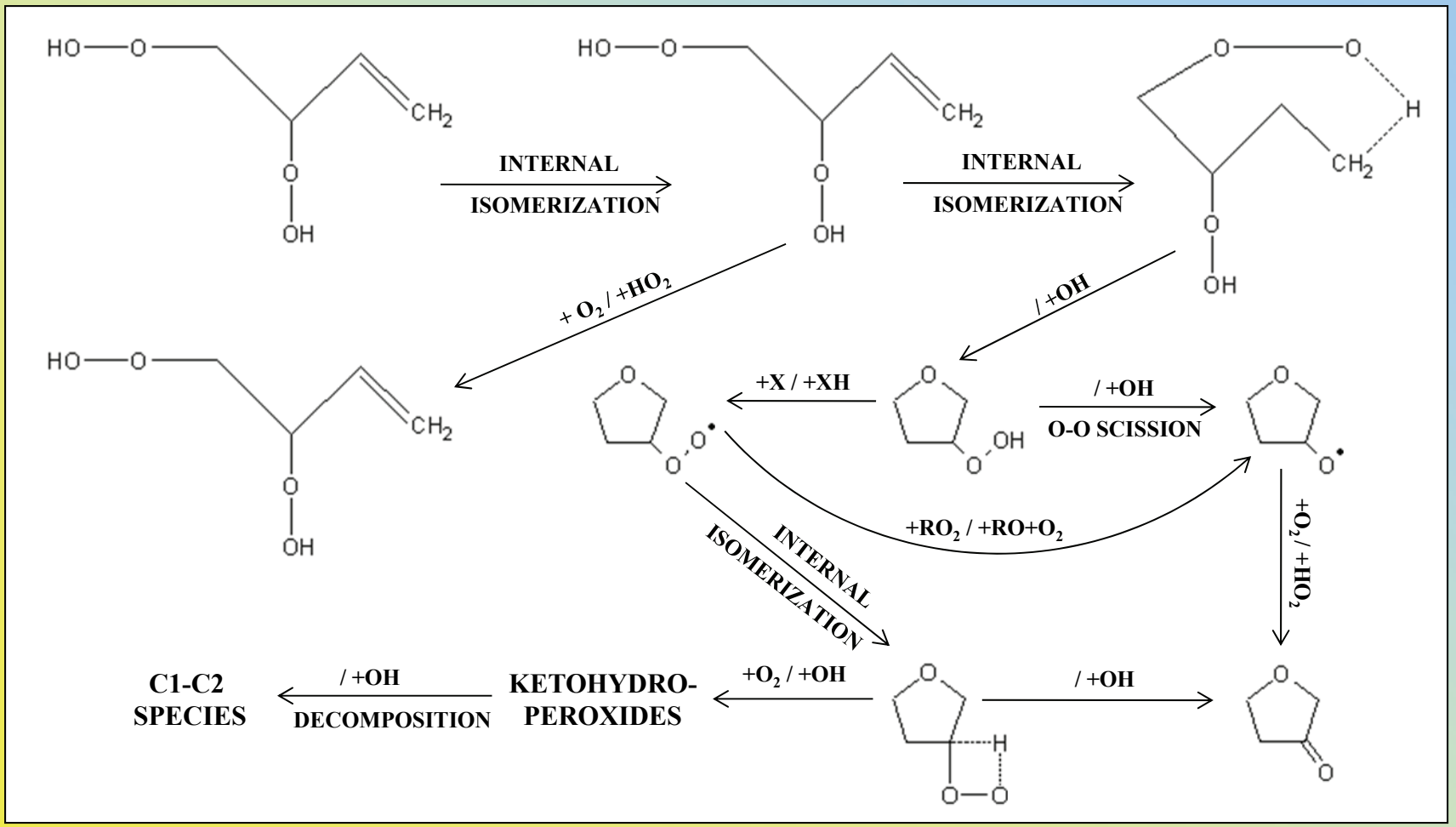
Pathway through Tetrahydrofuran (A)

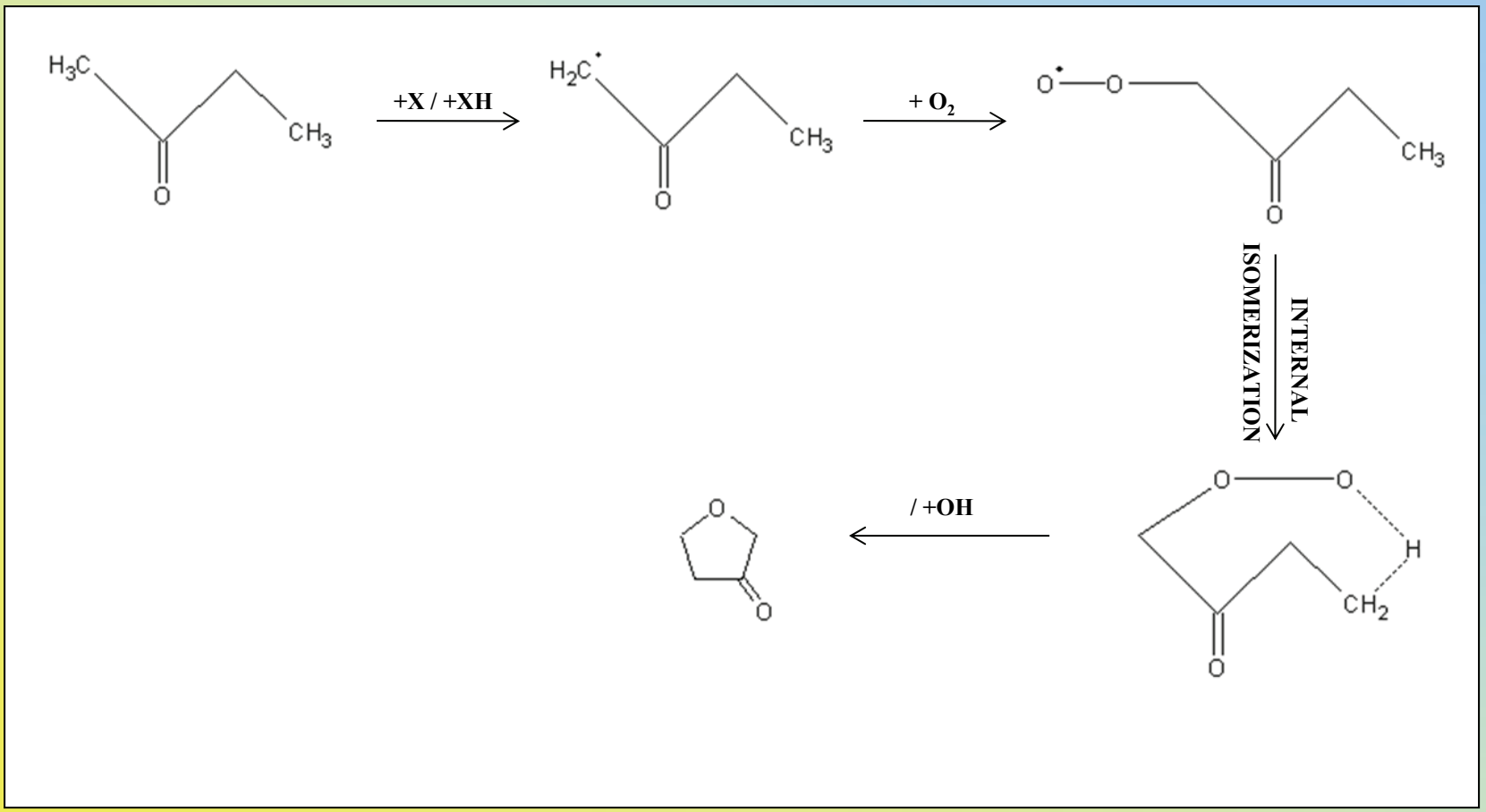
Gupta, Lactone (A)



Pathway through Hydroperoxybutylperoxy radicals (B)

Gupta, Lactone (B)



Pathway through C4 carbonyl species (C)

Gupta, Lactone (C)