The Oxidation of Fuel Radicals

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Kinetics Modules in Databases

Widely used
Problems with rich mixtures

GRIMECH - methane (light hydrocarbon) combustion

Pyrolysis of fuels

Oxidation of larger fuels

Target of most models
Focus of current
NIST work

Recent NIST
experimental and data
evaluation program

Soot formation

Many models, begin
with unsaturates

PREMISE OF WORK

There are simple correlations between structure of fuel molecules and their rate constants for decomposition and isomerization

These correlations can be uncovered from an

examination of the literature

suitable experiments

theoretical treatments

FOR A HOMOLOGOUS SERIES DATA BASE FOR EVERY LARGE FUEL MOLECULE CONTAINS AS A SUBSET THE DATABASE FOR SMALLER FUEL MOLECULES

DETERMINING MECHANISMS AND RATES OF DECOMPOSITION OF FUEL RADICALS

Generate fuel radicals through decomposition of appropriate precursors; alkyl iodide, branched hydrocarbons

Carry out studies in single pulse shock tube

dilute mixtures

short residence times

presence of inhibitors to isolate reaction

obtain direct measure of branching ratios

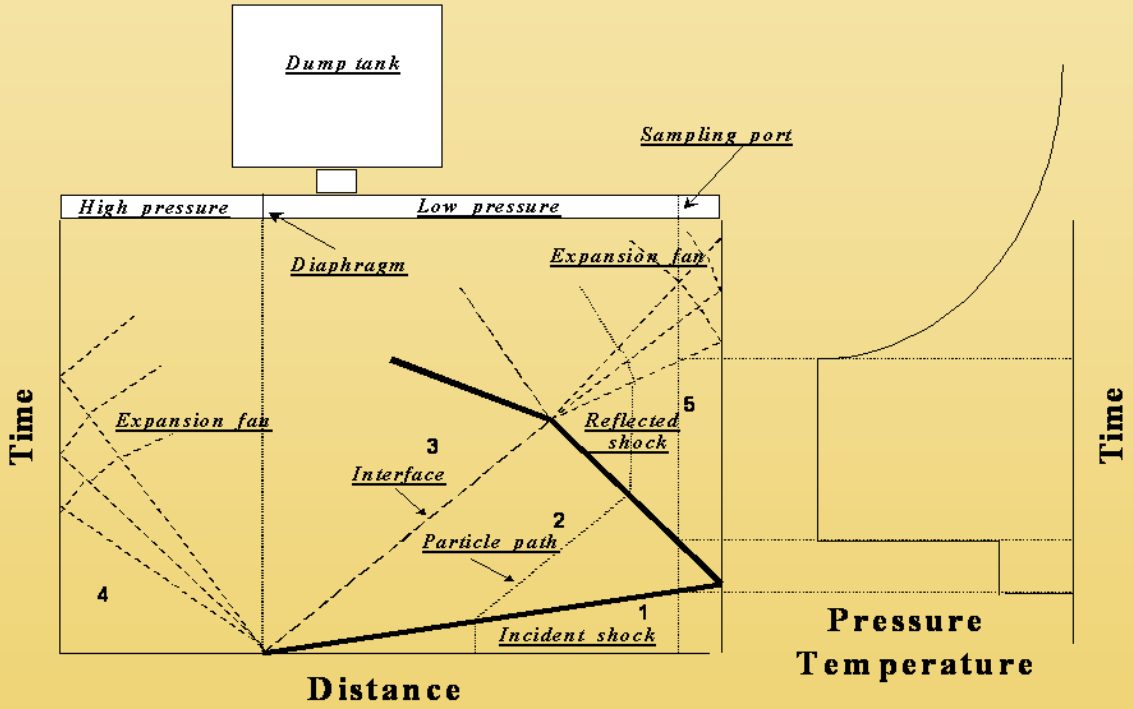
thermal cracking patterns

Convert to high pressure rate expressions

Solution of the master equation to take into account energy transfer effects

Extension to cover all combustion conditions

SINGLE PULSE SHOCK TUBE AND ASSOCIATED WAVE PROCESSES



RADICALS STUDIED

C H3CH2CH2CH2CH2*

CH3CH2CH2CH2CH2CH2*

CH3CH2CH2CH2CH2CH2CH2*

CH3CH2CH2CH2CH2CH2CH2CH2*

CH2=CHCH2CH2CH2*

CH2=CHCHCH2CH2CH2*

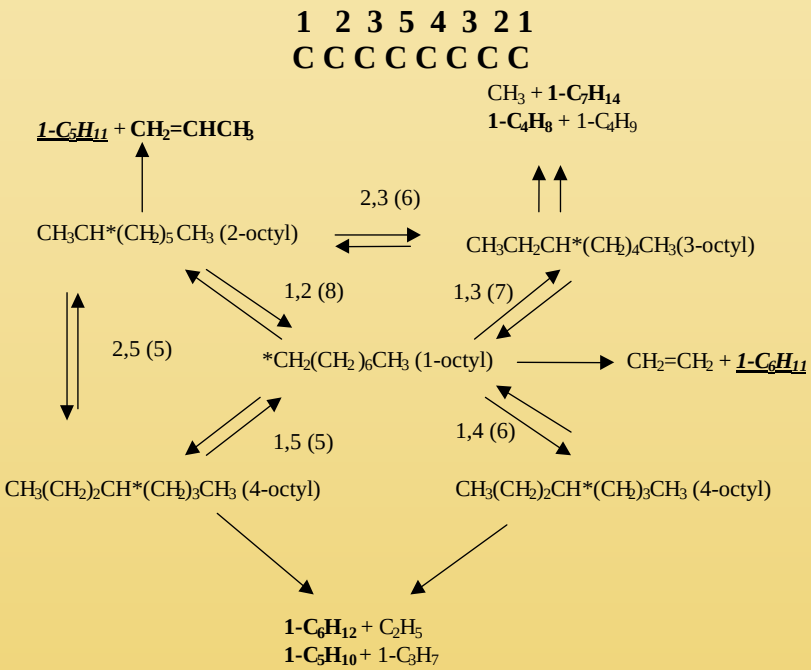
CYCLOHEXYL

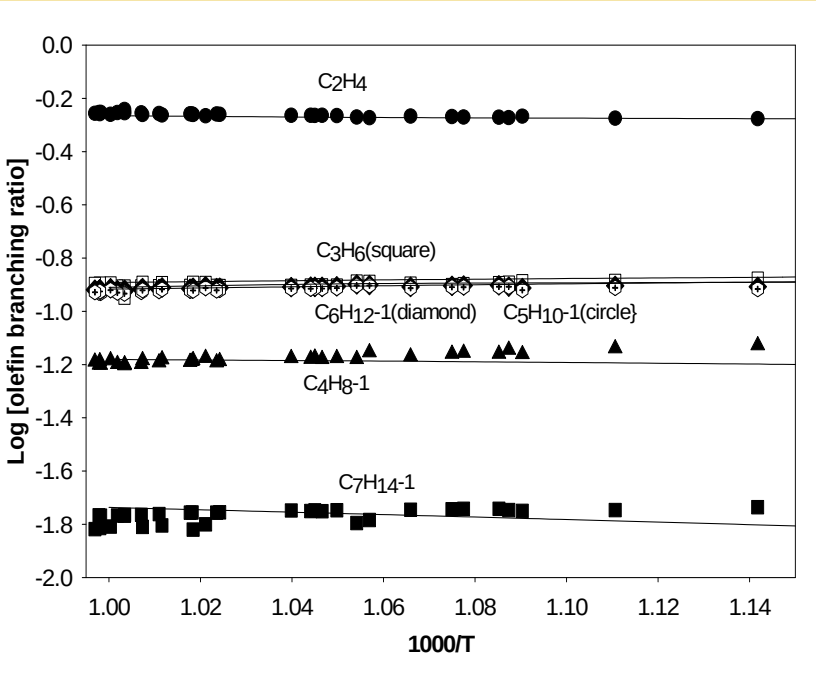
CYCLOPENTYL

CH3CH(CH3)CH2CH2CH2*

CH3CH(CH3)CH2CH2CH2CH2*

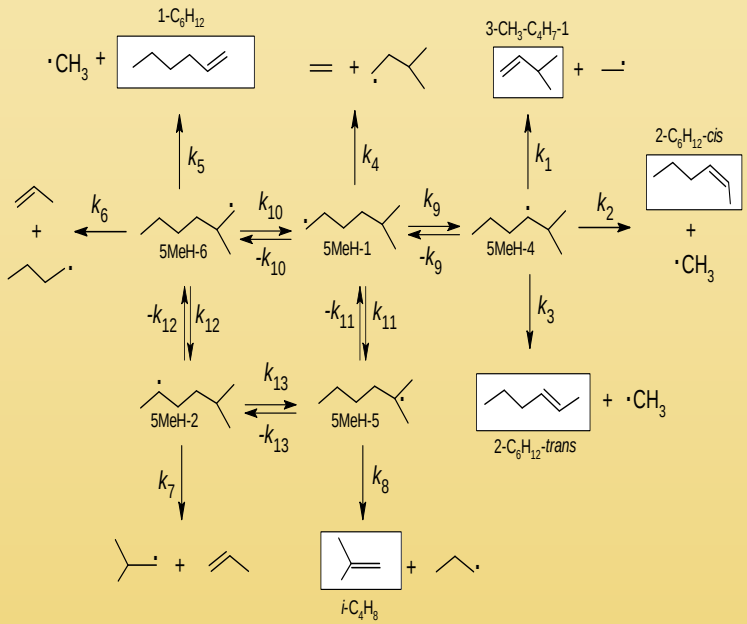
MECHANISM AND BRANCHING RATIOS FOR THE DECOMPOSITION OF OCTYL RADICALS





4 isomers undergoing 6 beta bond scissions and 6 reversible isomerizations

MECHANISM AND BRANCHING RATIOS FOR REACTIONS INITIATED WITH 5-METHYL HEXYL RADICALS



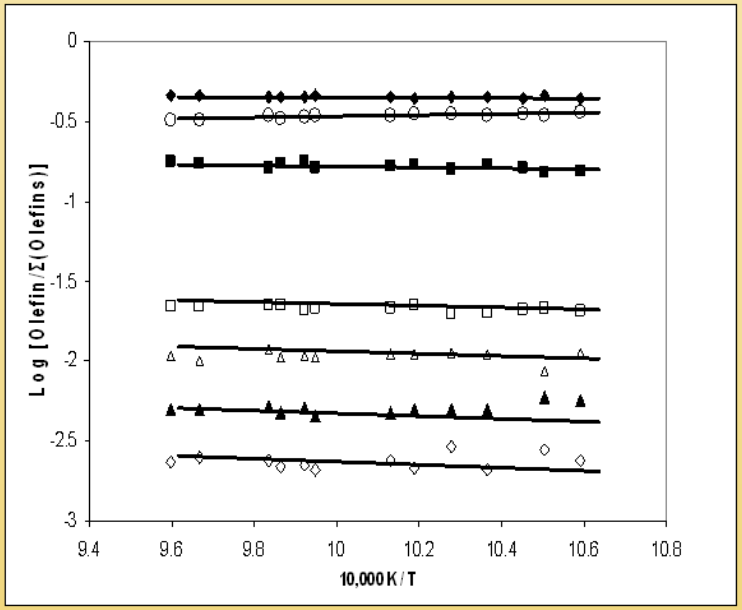


Figure 1. Alkene yields from the decomposition of 5-methylhexyl radicals. Symbols are experimental data: ◆ = ethene; ○ = isobutene; ■ = propene; □ = 3-methylbutene; △ = *cis*-2-hexene; ▲ = *trans*-2-hexene; ◇ = 1-hexene. The values for 1-hexene have been divided by two for clarity. The lines represent fits from the RRKM/Master Equation model described in the text.

MASTER EQUATION SOLVER: PROGRAM TO DETERMINE MOLECULAR DISTRIBUTION FUNCTION

ChemRate - [Workspace]

File Edit View Action Database Compute Tools Window Help

- Workspace
  - Components
    - Active
      - 1-C7H15
      - 2-C7H15
      - 3-C7H15
      - 4-C7H15
    - Transition states
      - 1-2-C7H15TS
      - 1-3-C7H15TS
      - 1-4-C7H15TS
      - 2-3-C7H15TS
      - TS-1-C7H15-B
      - TS-2-C7H15-B
      - TS-3-C7H15-B1
      - TS-3-C7H15-B2
      - TS-4-C7H15-B
    - Inactive
    - Buffer gas
    - Recycle Bin
  - Reactions
    - Input Reactions
      - k10: 1-C7H15 <---> 3-C7H15
      - k11: 3-C7H15 <---> 1-C7H15
      - k12: 1-C7H15 <---> 4-C7H15
      - k13: 4-C7H15 <---> 1-C7H15
      - k14: 2-C7H15 <---> 3-C7H15
      - k15: 3-C7H15 <---> 2-C7H15
      - k3: 1-C7H15 ---> C2H4 + nC5H11
      - k4: 2-C7H15 ---> C3H6 + nC4H9
      - k5: 3-C7H15 ---> 1-C4H8 + nC3H7
      - k6: 3-C7H15 ---> CH3 + 1-C6H12
      - k7: 4-C7H15 ---> 1-C5H10 + C2H5
      - k8: 1-C7H15 <---> 2-C7H15
      - k9: 2-C7H15 <---> 1-C7H15
    - Recycle Bin
  - Activations
  - Parameters

General | Computed Data | Data Fit | Experimental Data

Property	Value
Description	Isomerization reaction backward (dependent) reacti
High pressure rate expression. 1200 K	k = 2.78898e+012·exp(-16.5118/RT)
Activation energy. E kcal	16.5118
log A	12.4454
log k	9.43823

T, K	p, t
1200	760

Workspace Reaction

Reaction | Experimental data | Advanced properties | Comment

3-C7H15 ⇌ 1-C7H15

Transition State: 1-3-C7H15TS

Reaction Properties

- Isomerization
- Decomposition
- Bimolecular

Reversible | Subtract incomes | With Barrier | Without Barrier

Show as rev

Apply

Workspace: 1-3-C7H15TS

General | Frequencies | Rotations | Electronic | Thermo | Geometry | Comment

Name: 1-3-C7H15TS

Atomic Composition: H15C7 example: C10 2H5Cl3

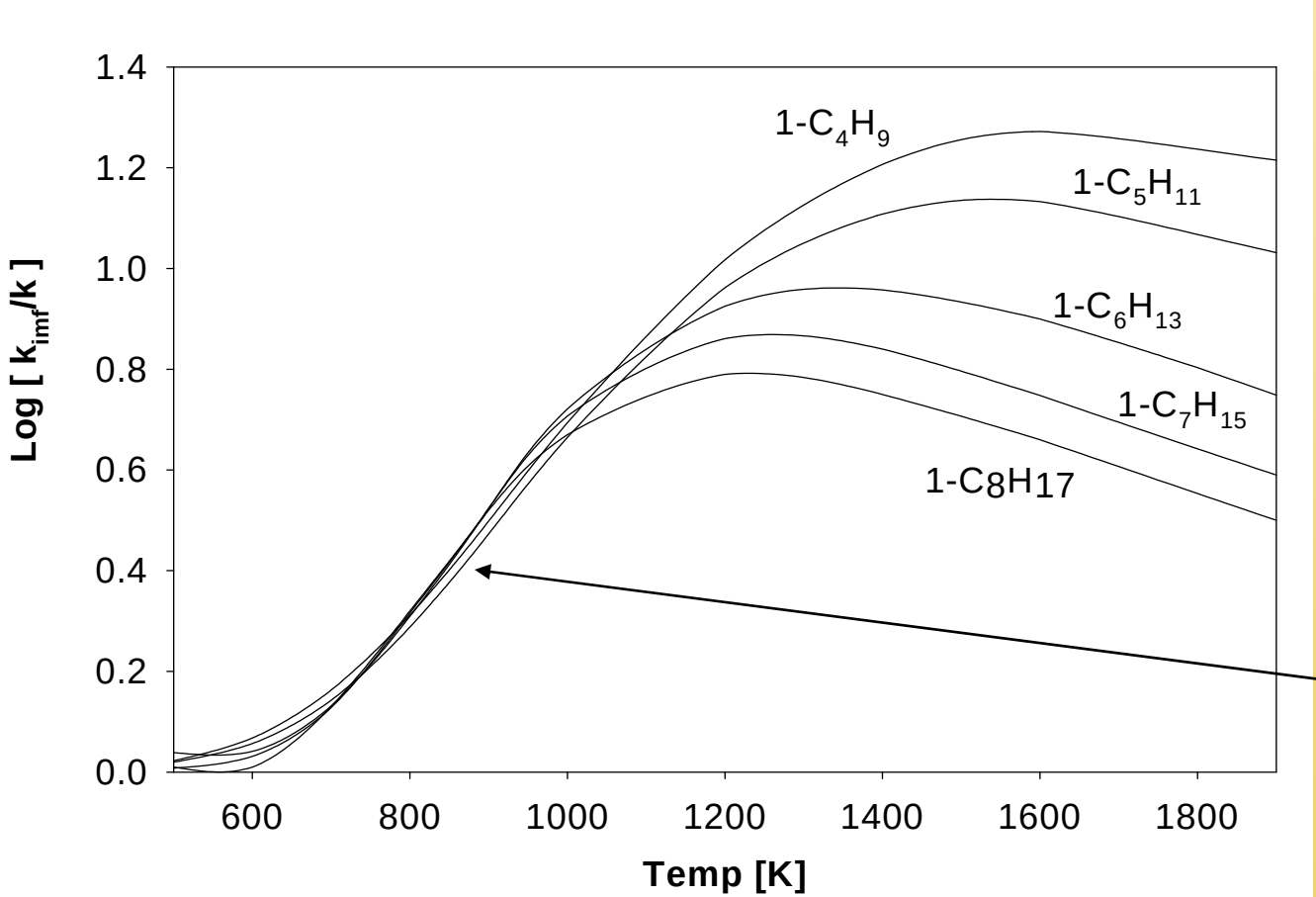
Mass: 99.1961 a.m.u. Compute

Standard Enthalpy of Formation: 16 kcal

CAS Registry Number

Specified as:

FALL-OFF BEHAVIOR FOR THE REACTION N-ALKYL = ETHYLENE + 1-(N-2)OLEFIN FOR N=4 TO 8 AT 1 BAR



Fall-off does not monotonically increase due to low reaction threshold

Fall off effects decreases only slowly with molecular size

Fall off effects are insensitive to molecular size near high pressure limit

HIGH PRESSURE RATE EXPRESSIONS FOR OCTYL RADICAL DECOMPOSITION AND ISOMERIZATION

	A: Reaction	Log A	n	E/R	Log (k [1000])
1	1-octyl = ethene + 1-hexyl	11.96	.31	13708	6.93
2	2-octyl =propene + 1-pentyl	10.78	.84	14001	7.24
3	3-octyl = 1-butene + 1-butyl	13.31	.04	14340	7.21
4	3-octyl = 1-heptene + methyl	9.98	1.08	14790	6.78
5	4-octyl= 1-pentene + 1-propyl	11.74	.55	14134	7.26
6	4-octyl = 1-hexene +ethyl	9.83	1.11	13600	7.25
7	1-octyl = 4-octyl (1-4-H trans)	.71	3.23	8479	6.72
8	1-octyl = 4-octyl (1-5-Htrans)	1.36	2.82	5413	7.46
9	1-octyl = 3-octyl	.47	3.08	5544	7.29
10	4-octyl = 1 octyl 1-4-H trans	-.38	3.57	9532	6.20
11	4-octyl = 1-octyl 1-5-H trans	.27	3.16	6466	6.94
12	3-octyl = 1-octyl	.52	3.11	6579	6.99
13	2-octyl=3-octyl	.27	3.27	6642	7.20
14	2-octyl =4-octyl	.15	3.32	8125	6.60
15	3-octyl = 2-octyl	1.33	2.96	6625	7.34
16	4-octyl = 2-octyl	.071	3.32	8128	6.52

Compound	Equilibrium constant of formation log [k_p]
Octyl-1	$-38.931-1.031\times10^{3}/T+4.904\times10^{6}/T^{2}-2.601\times10^{9}/T^{3}+4.473\times10^{11}/T^{4}$
Octyl-2	$-39.196-1.941\times10^{2}/T+4.736\times10^{6}/T^{2}-2.554\times10^{9}/T^{3}+4.403\times10^{11}/T^{4}$
Octyl-3	$-39.098-5.633\times10^{2}/T+4.912\times10^{6}/T^{2}-2.608\times10^{9}/T^{3}+4.485\times10^{11}/T^{4}$

OXIDATION OF FUEL RADICALS: PAST WORK

No direct studies leading to high pressure unimolecular rate expressions

Products from flame and cool flames sampling

Oxygenated organics

Unsaturated organics

Cyclic ethers

Thermal rate constants used in models; no consideration of chemical activation processes

OH and HO_2 from smaller fuel molecules and modeling

Sandia (Taatjes)

Ab-initio calculations

Green et al

Merle et al

Bozzellie et al

Sandia (Klippenstein)

STRATEGY FOR STUDYING RADICAL OXIDATION

Generate radicals as in pyrolysis experiments

Dilute concentrations of radicals

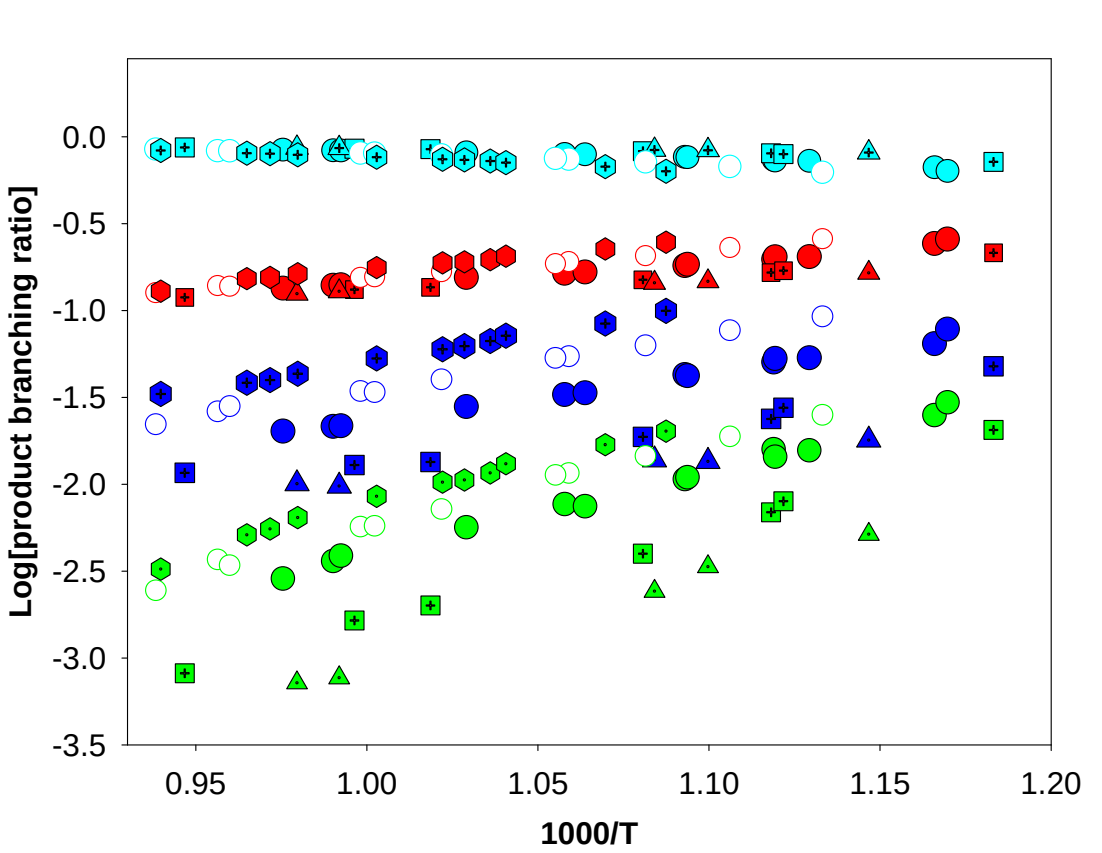
Vast excess of chemical inhibitor

Add sufficient amount of oxygen molecules to change reaction direction from pyrolysis to oxidation

Determine cracking patterns as function of oxygen concentration

Reproduce oxidative cracking pattern through solution of the master equation for <u>chemical activation process</u>

SUMMARY OF EXPERIMENTAL RESULTS



cyan =ethylene

Red = 1-butene

Blue = propene

Green = tetrahydrofuran

Circle =150, 9.15%

Square = 150, 4.04 %

Triangle = 150, 1.51%

White (blue) = 300, 10.35%

Hexagon = 600, 10.15%

n-Butyl Iodide (100 ppm) decomposition with various concentrations of oxygen

Rate Constants from Chemical Activation Processes

Radical + O_2 , <=> RadicalOO* => Variety of products

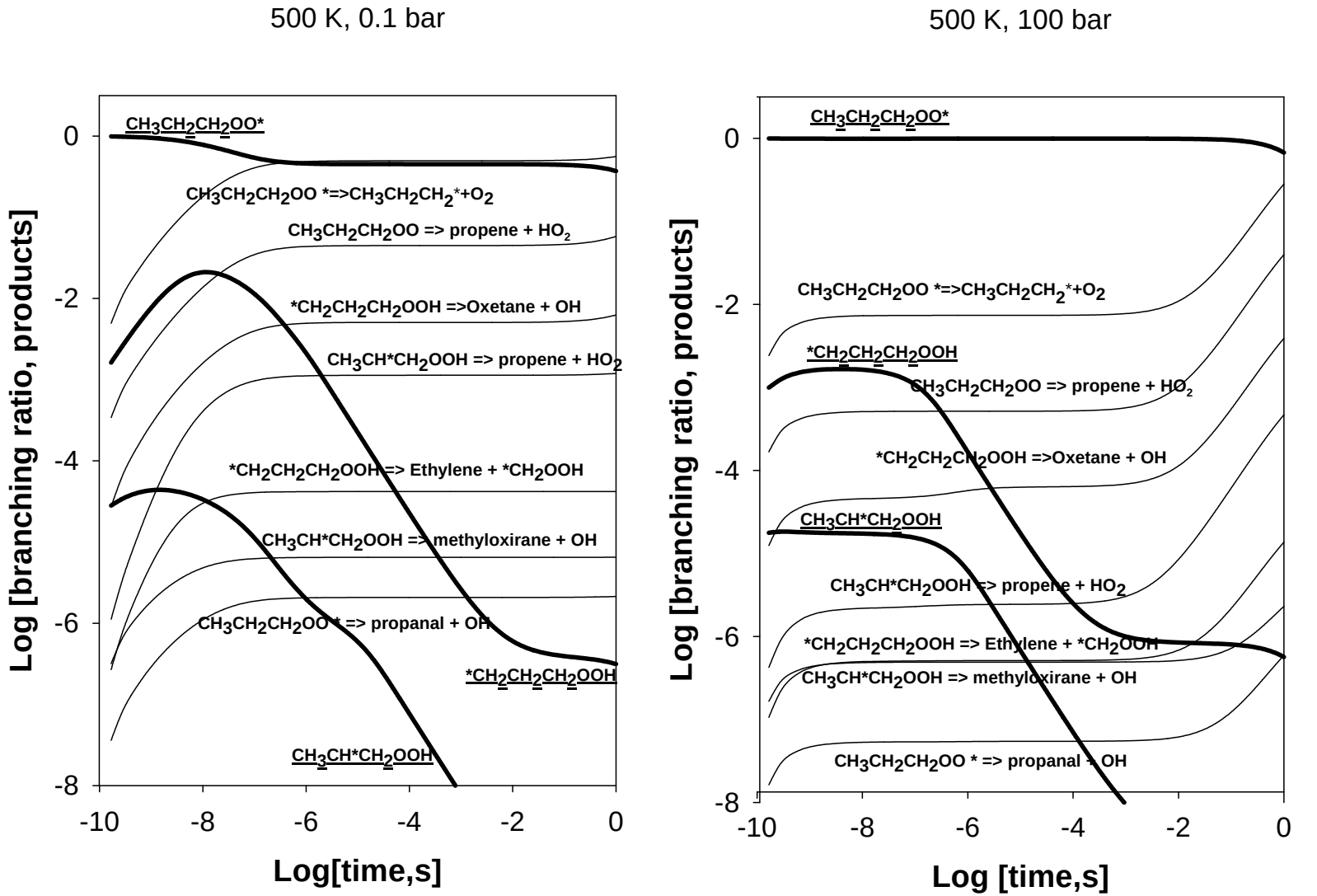
↓ M ↗

RadicalOO

$$k = k_{ca} \text{ x } branching_ratio$$

$$branching_ratio = \frac{(decomposition)_i \text{ or } (stabilization)_i}{\sum all\ channels}$$

Branching Ratios for Products from n-Propyl Peroxy Radical Decomposition



TREATMENT OF DATA

Product (ethylene. Propene, 1-butene) = $k_{uni,BI}$(butyl-I) + $k_{uni,P}$(butyl) + $k_{ox.P}$(butyl) x O_2

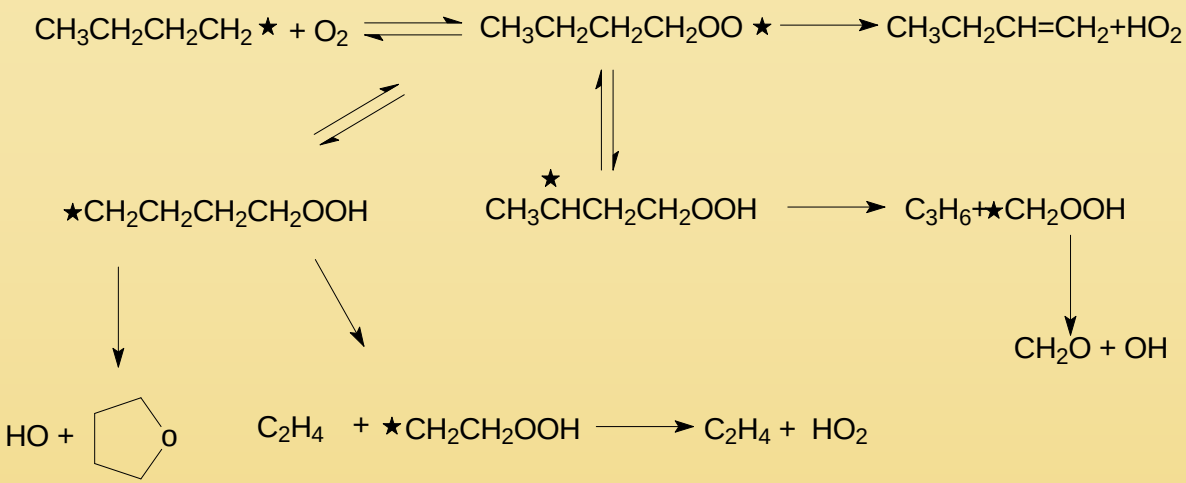
tetrahydrofuran (THF) = $k_{ox,T}$(butyl) x O_2

Product/THF = ($k_{uni,BI}$(butyl-I) + $k_{uni,P}$(butyl))/$k_{ox,T}$(butyl) x O_2

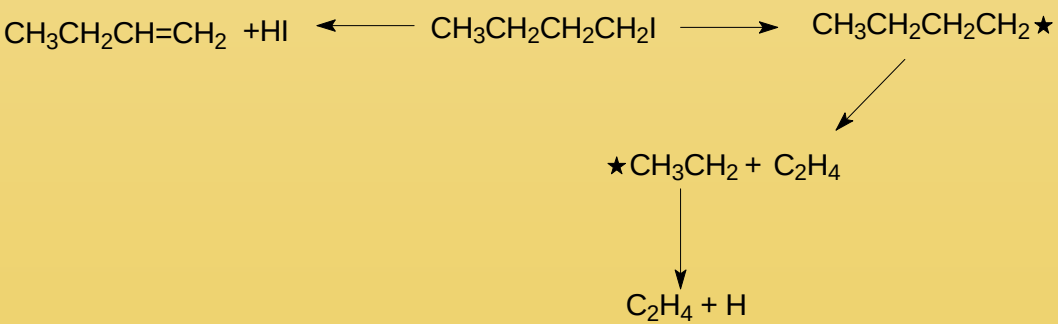
+

$k_{ox.P}$/ $k_{ox,T}$

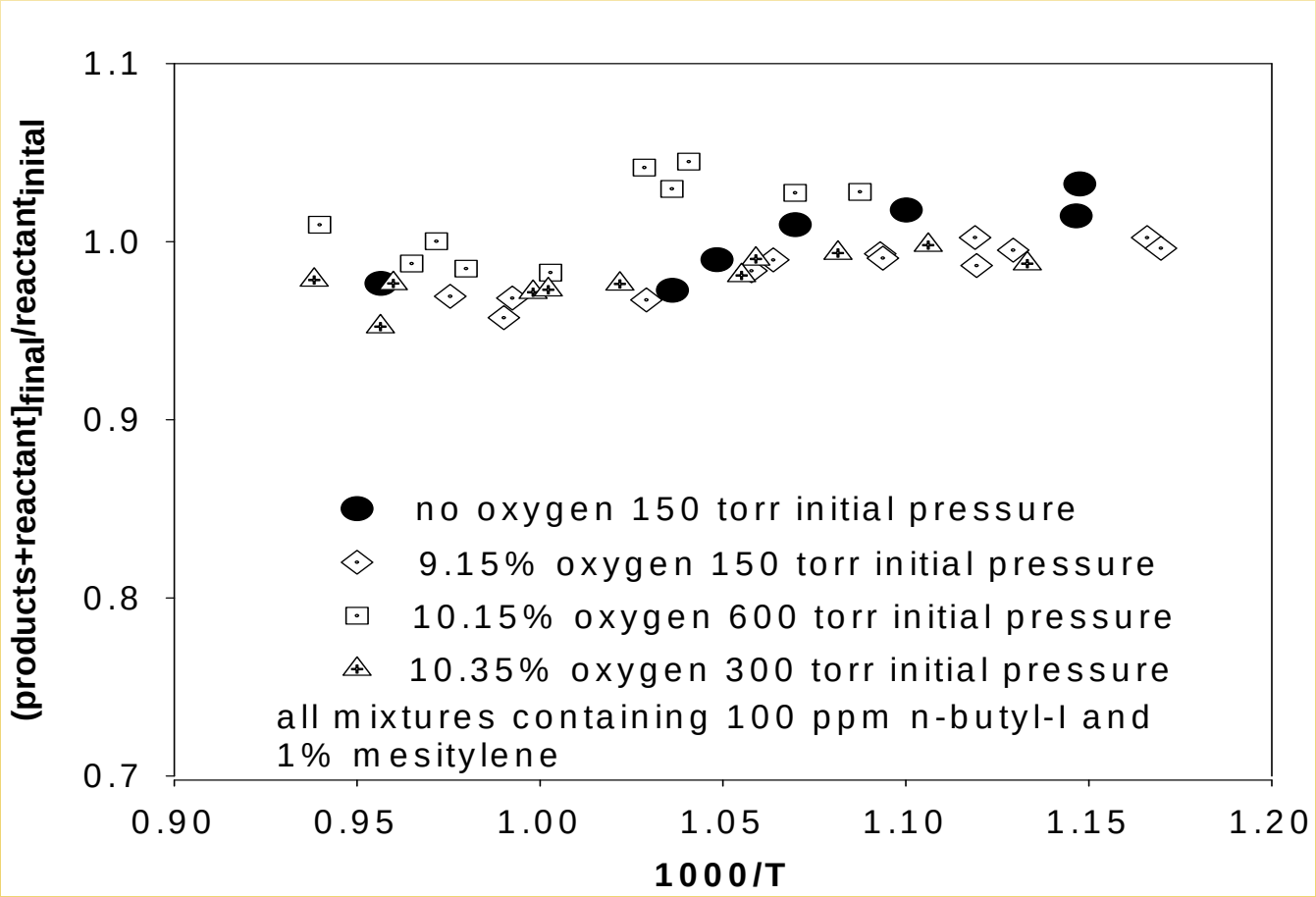
Oxidative Decomposition of n-Butyl Radical



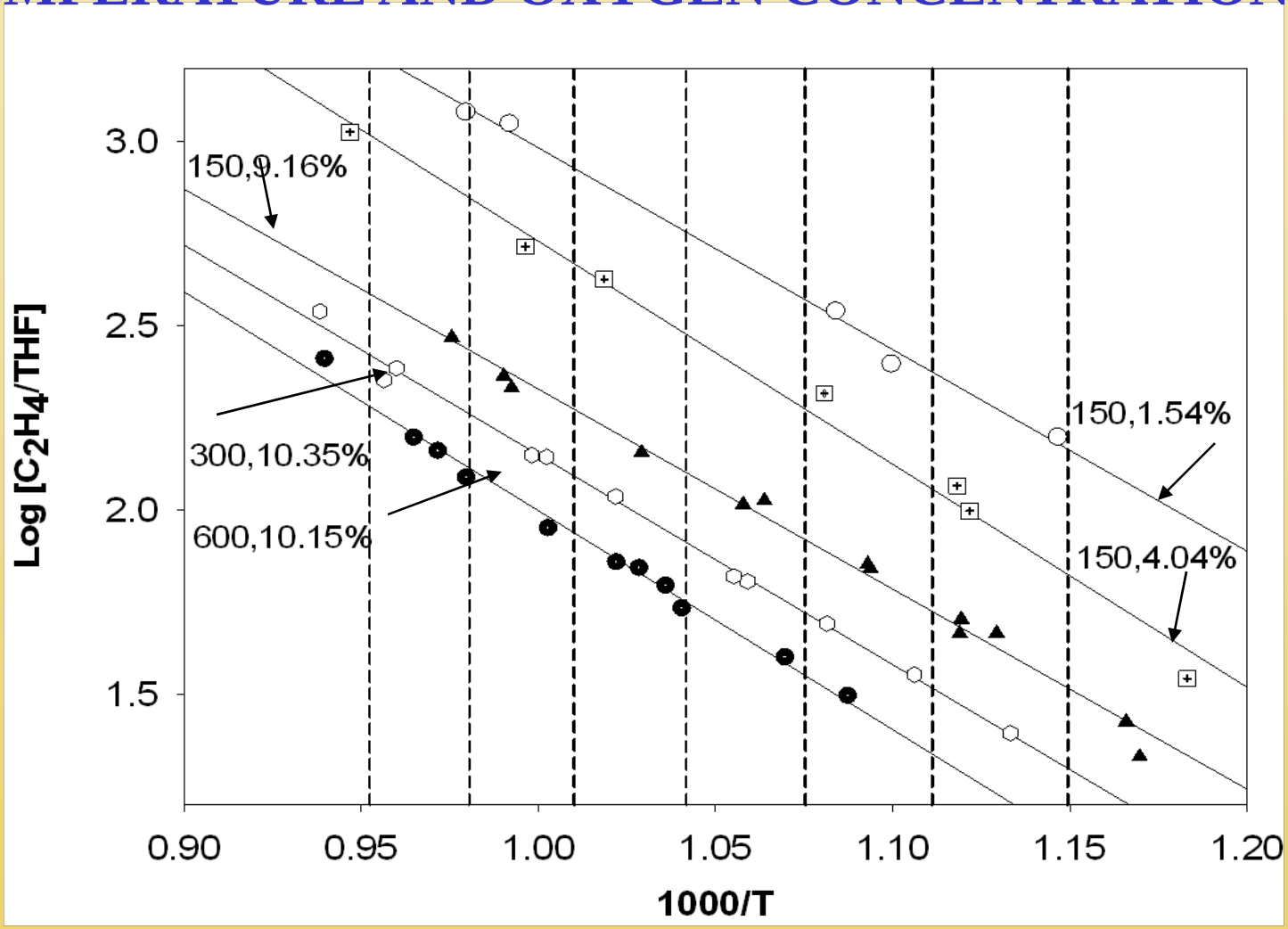
Pyrolytic Decomposition of n-Butyl Radical (through n-Butyl Iodide)



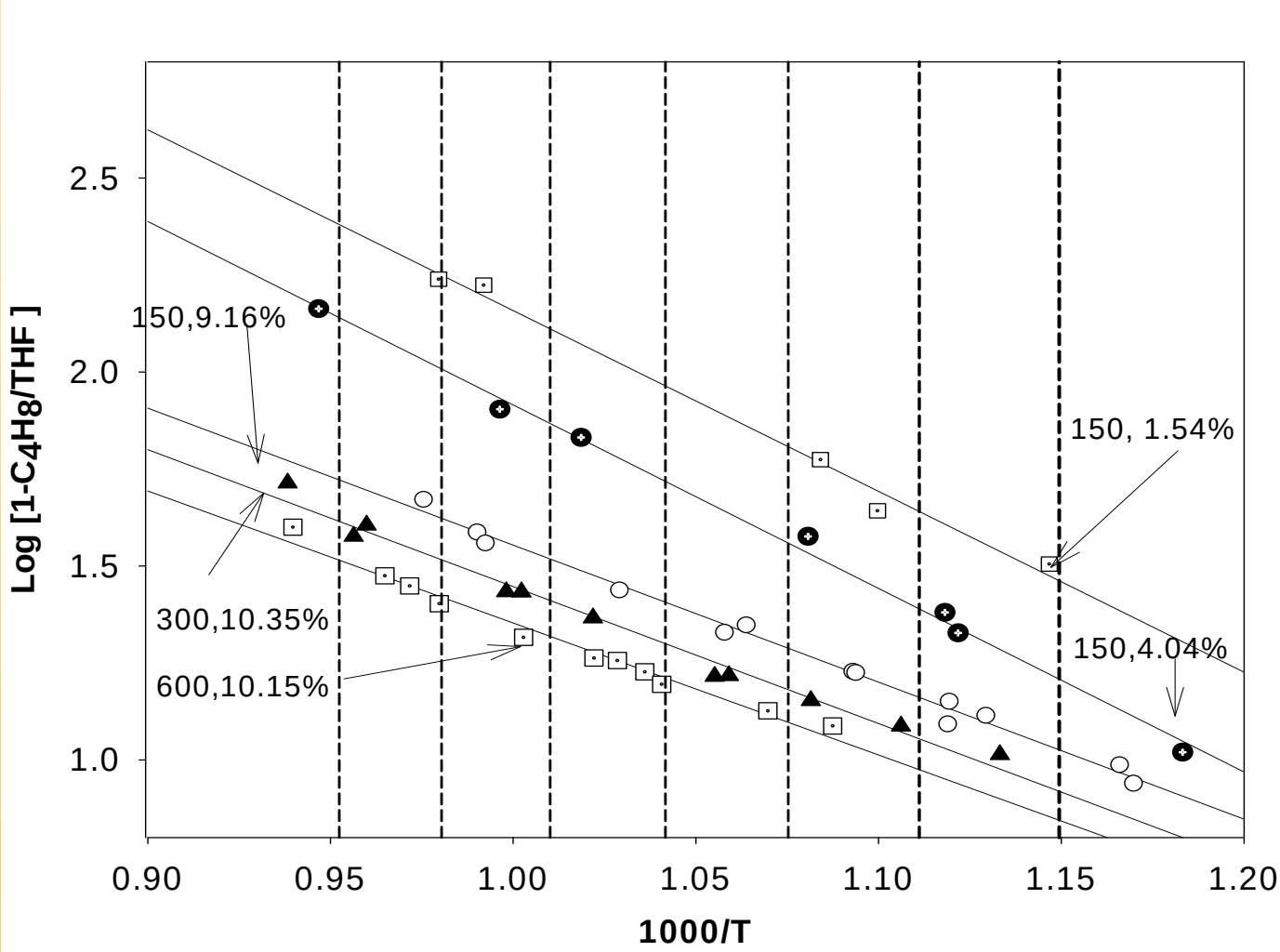
MASS BALANCE



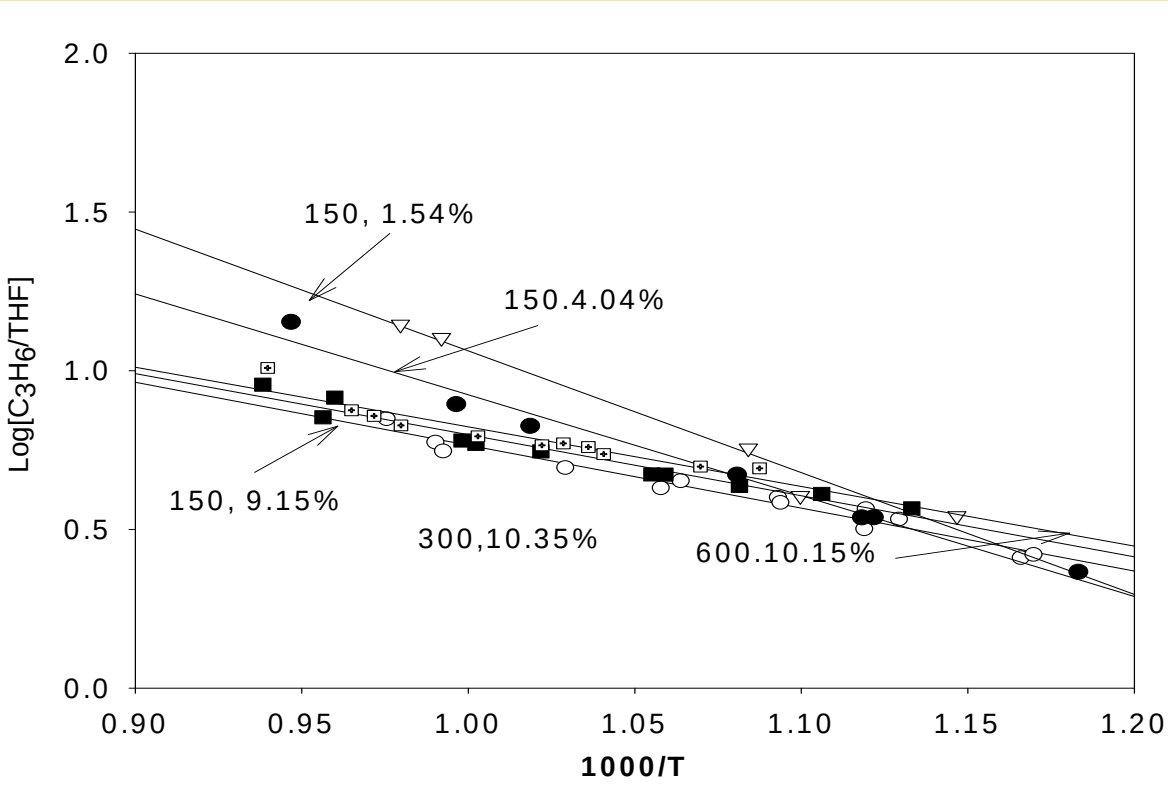
ETHYLENE/THF RATIOS AS A FUNCTION OF TEMPERATURE AND OXYGEN CONCENTRATION



1-BUTENE/THF RATIOS AS A FUNCTION OF TEMPERATURE AND OXYGEN CONCENTRATION

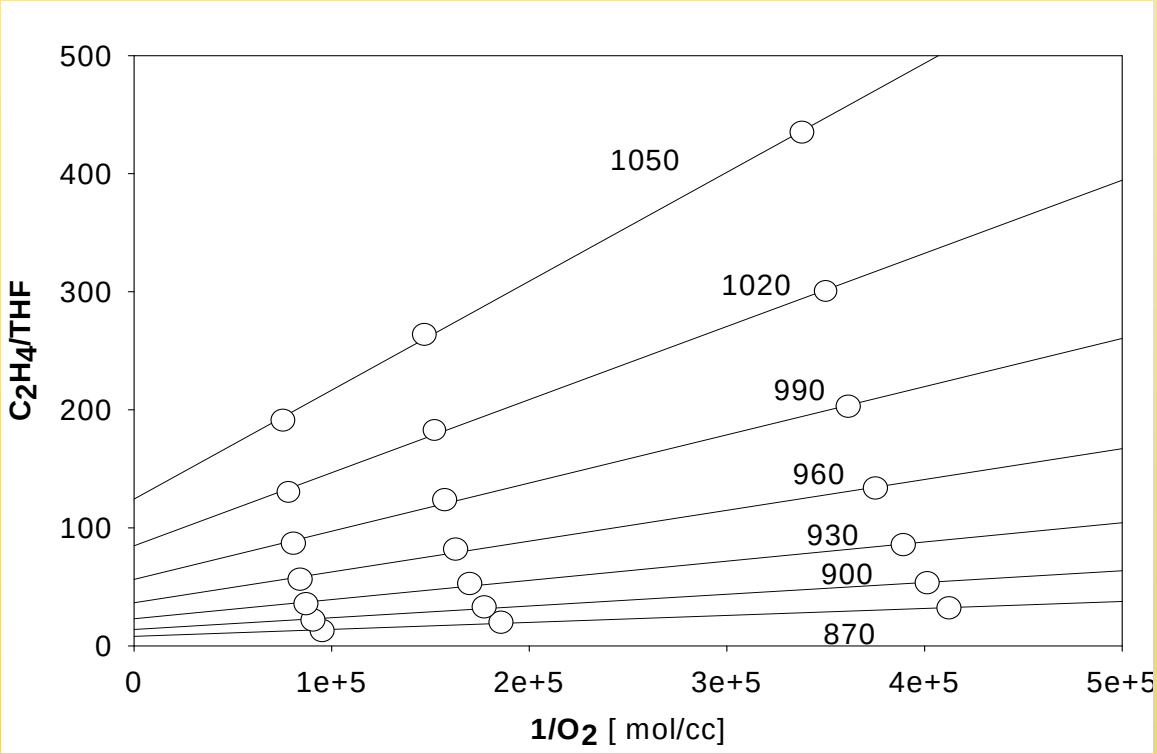


PROPENE/THF RATIOS AS A FUNCTION OF TEMPERATURE AND OXYGEN CONCENTRATION



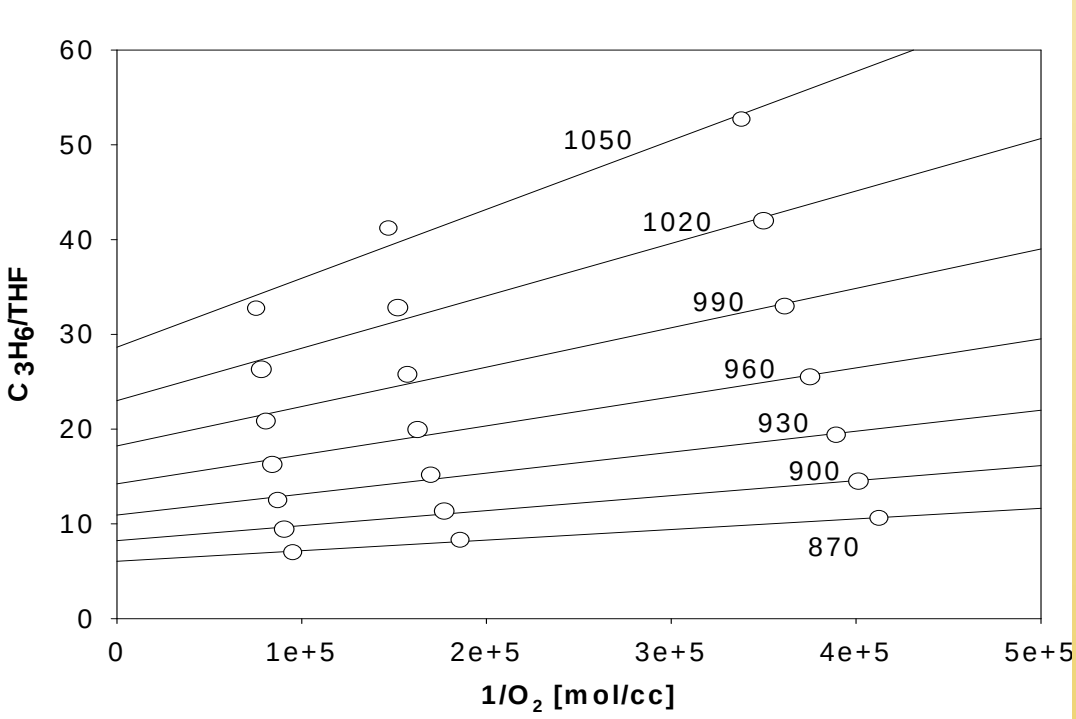
Log $[C_3H_6/THF] = 2.92 - 2120/T = .64$ (930K)

Ethylene/THF Yields as a Function of $1/O_2$: Extrapolation to Infinite Oxygen Concentration



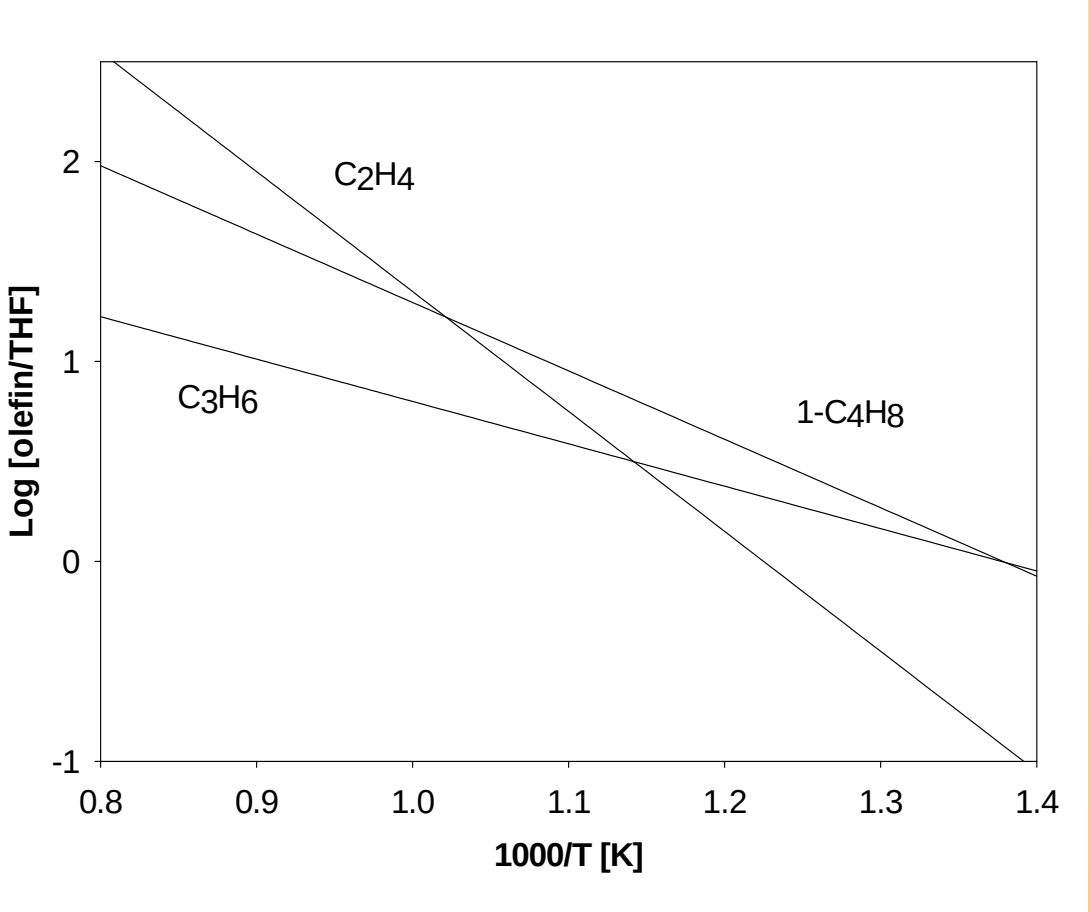
Log $[C_2H_4/(2xTHF)] = 7.35 - 6000/T$ =1.1 at 930 K

1-BUTENE/THF Yields as a Function of $1/O_2$: Extrapolation to Infinite Oxygen Concentration



$$\text{Log}\,[1\text{-}C_4H_8/THF] = 4.717 - 3422/T$$

OLEFIN VS TETRAHYDROFRAN YIELDS



MECHANISTIC INFERENCES

Ethylene and propene are formed from beta bond scissions after H-transfer isomerization

1-Butene is formed prior to isomerization

No formation of larger aldehydes

Contribution from oxirane (3) and oxetane (4) channels are neglible

NEXT STEPS

Derive high pressure rate expressions

Reactions	Basis for deriving rate expressions
CH3CH2CH2CH2* + O2 => CH3CH2CH2CH2OO*	Merle et al and data on R+O2
CH3CH2CH2CH2OO* => CH3CH2CH=CH2 + HO2	From 1-butene/THF
CH3CH2CH2CH2OO* => *CH2CH2CH2CH2OOH	From branching of ethyleneZ:1-butene:propene
CH2CH2CH2CH2OOH=> CH3CH2CH2CH2OO	Detailed balance
*CH2CH2CH2CH2OOH => CH2=CH2 + *CH2CH2OOH	From beta bond scission
CH3CH2CH2CH2OO* => CH3CH*CH2CH2OOH	From branching of ethyleneZ:1-butene:propene
CH3CH*CH2CH2OOH => CH3CH2CH2CH2OO*	Detailed balance
CH3CH*CH2CH2OOH => CH3CH=CH2 + *CH2OOH	From propene/THF
*CH2CH2OOH => CH2=CH2 + HO2	Fast
*CH2COOH = CH2O + OH	Fast
*CH2CH2CH2CH2OOH => Tetrahydrofuran + OH	From ethylene/THF, check with calculation of Wijaya et al

TASKS AND PROBLEMS

Molecular properties of oxygenates: hydroperoxides and peroxy radicals
depend on ab initio calculations

Fit results through solution of master equation using CHEMRATE

Expand data to cover all relevant combustion conditions
differentiate between chemical activation and thermal processing

Larger radicals: n-pentyl

Lower temperatures: smaller oxygen loading

Use nitrites

SUMMARY

A new method for determining the mechanisms and rate constants for the oxidation of alkyl radicals has been developed

Results have been demonstrated for n-butyl radicals generated from n-butyl-iodide pyrolysis in varying concentrations of oxygen and excesses of a chemical inhibitor

Ethylene is the main product, smaller amounts of 1-butene, propene and THF are also detected

Results for limiting oxygen concentrations have been determined

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