Fundamental Concepts in Combustion Kinetics

Charles Westbrook

Tsinghua-Princeton
2014 Summer School on Combustion
July 20-25, 2014

Acknowledgments

- Slides provided and consultations with –
  - Henry Curran, National University of Ireland, Galway
  - Mani Sarathy, King Abdullah University of Science and Technology, Jeddah
  - Bill Pitz, LLNL
  - Maarco Mehl, LLNL
  - Pierre-Alexandre Glaude, Universite de Nancy
  - Eliseo Ranzi, Politecnico di Milano
  - Tiziano Faravelli, Politecnico di Milano
  - Ron Hanson, Stanford University
  - Eric Petersen, Texas A&M University

Combustion in human history: from the early steps…

- **500,000 – 100,000 BP**
First use of controlled fire

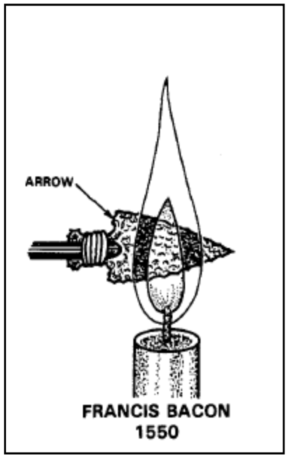
- **100,000 – 50,000 BP**
Routine use of fire

- **500 BC**
Heraclitus - Fire as fundamental substance

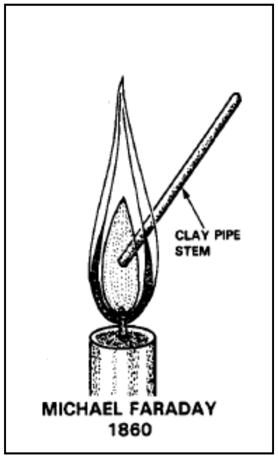
- **500 – 430 BC**
Empedocles – Fire as one of the four elements

Prometheus Brings Fire to Mankind, 1817
Heinrich Friedrich Füger

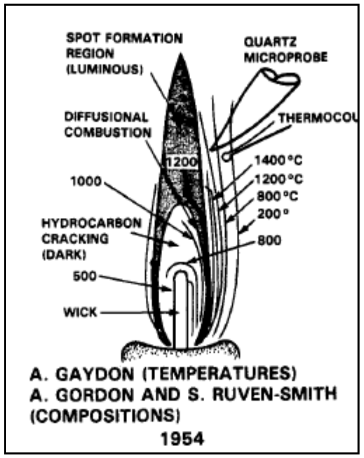
We came a long way…



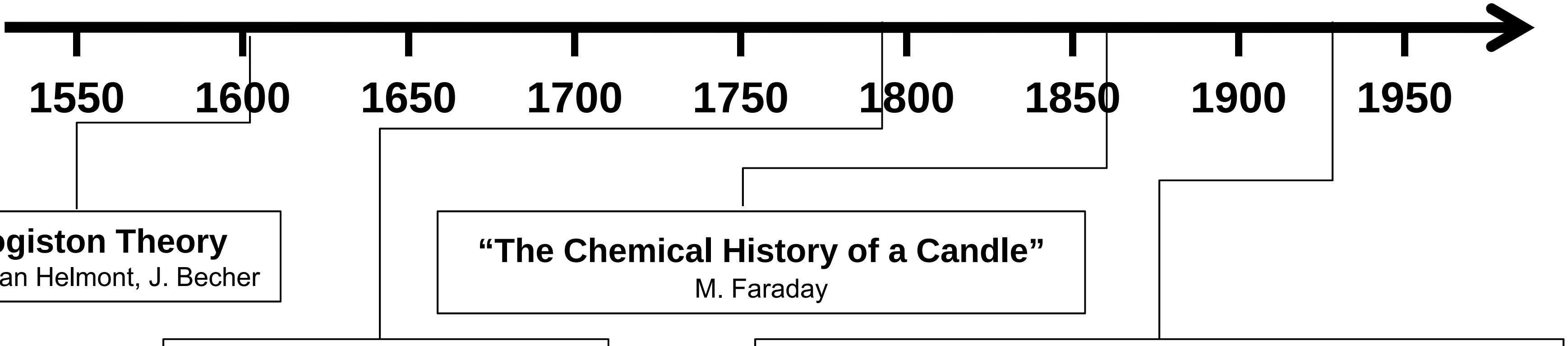
FRANCIS BACON
1550



MICHAEL FARADAY
1860



A. GAYDON (TEMPERATURES)
A. GORDON AND S. RUVEN-SMITH
(COMPOSITIONS)
1954



Phlogiston Theory
J.B. van Helmont, J. Becher

“The Chemical History of a Candle”
M. Faraday

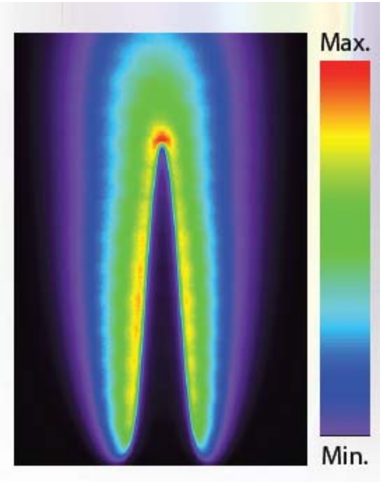
Combustion as Oxidation
A. Lavoisier , P. S. Laplace

Chain reaction and thermal ignition (Nobel 1956)
Semenov, Hinshelwood

→Theory of gas kinetics, free radicals, elementary reactions and reaction mechanisms for combustion applications

Fristrom R. M. (1990)

Combustion Science Today

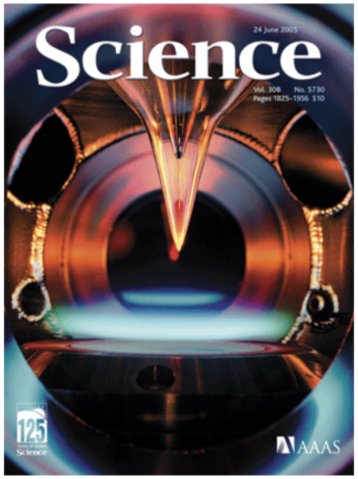


Interference-free composite H-atom LIF image produced with ps excitation in a Φ=1.2 premixed CH4/O2/ N2 flame.

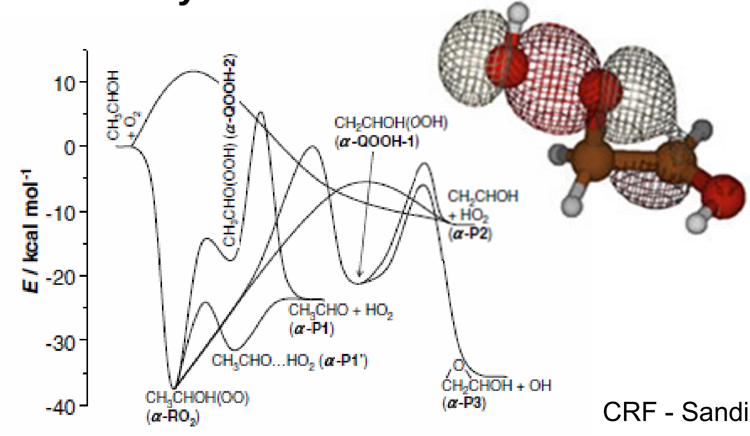
CRF - Sandia

Molecular-beam flame sampling and synchrotron-photoionization mass spectrometry analysis

[Science - 24 June 2005]

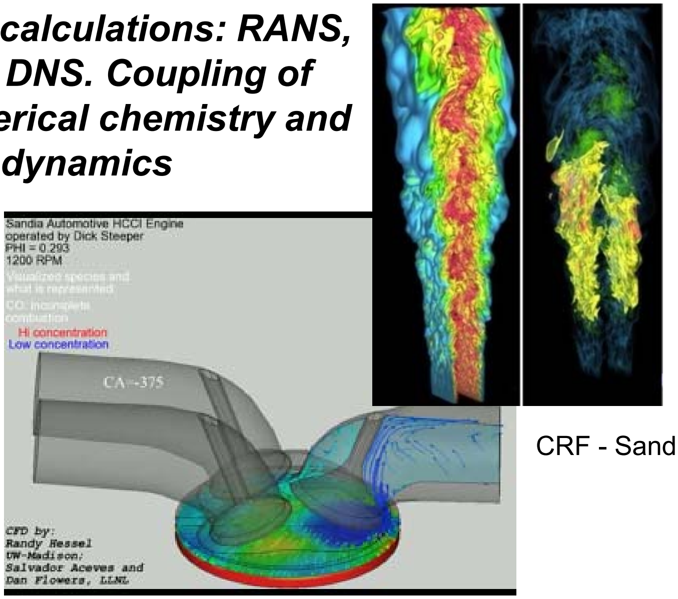


Ab initio **electronic-structure calculations and molecular dynamics simulations**



CRF - Sandia

CFD calculations: RANS, LES, DNS. Coupling of numerical chemistry and fluid dynamics



CRF - Sandia

Combustion chemistry

- Combustion is the sequential disassembly of a (hydrocarbon) fuel molecule, atom by atom, eventually producing stable products (CO_2 and H_2O)
- All possible chemical species are included with coupled differential equations
- Elementary reactions take place between these species, with assigned reaction rates
- Chain carriers are free radicals H, OH, O, HO_2, CH_3, others

Chain reactions exist in many forms

- Populations of bacteria
- Populations of people
- Nuclear reactors
- Chemical reactions

$$dn/dt = \alpha n$$

$$n(t) = n_o \exp^{\alpha t}$$

$\alpha > 0$ growth

$\alpha < 0$ decay

$\alpha = 0$ stable

Reaction mechanisms

- A reaction mechanism is a collection of the reactions that are “important” and their rate expressions as functions of temperature and pressure

Goals for modeling of large hydrocarbon fuels

- Provide validated chemistry models for combustion in:
  - Diesel engines
  - Homogeneous Charge Compression Ignition (HCCI) engines
  - Spark Ignition (SI) engines
  - Turbine engines

- Assist in mechanism reduction for simulations with computational fluid dynamics (CFD)

- Provide combustion insights from kinetic simulations of engine processes

Computational Combustion Chemistry

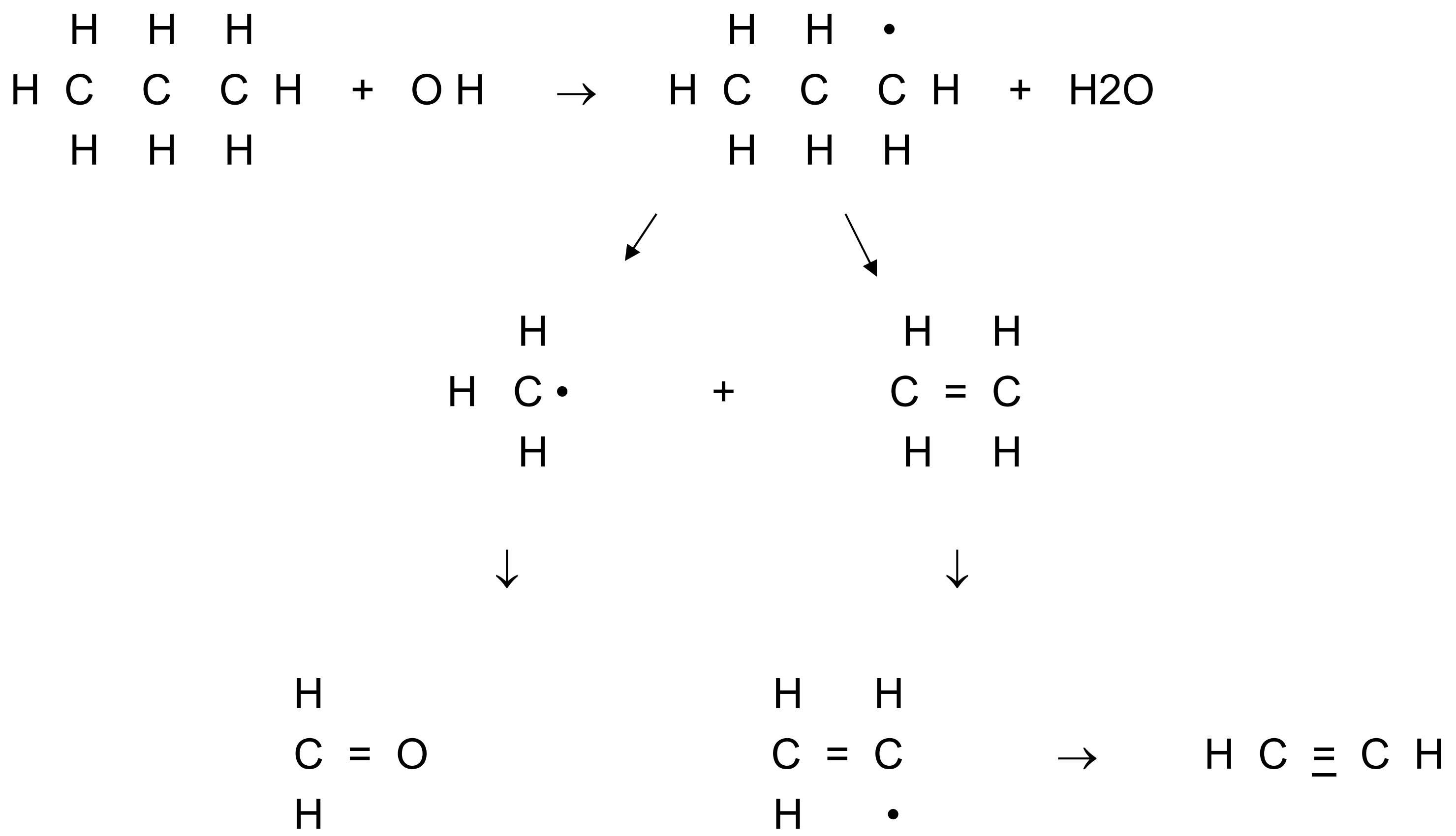
$$\text{Fuel} + (n_1)\,O_2 \longrightarrow (n_2)\,CO_2 + (n_3)\,H_2O$$

$$\text{Rate} = A\,T^{n}\,\exp[-E/RT]\,[\text{Fuel}]^{a}\,[O2]^{b}$$

Single reaction step: Useful simplification in 2D or 3D simulations

However, it misrepresents actual reaction paths

An example: propane oxidation



$$\begin{array}{ccccc} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \\ \mathrm{H} & \mathrm{C} & \mathrm{C} & \mathrm{C} & \mathrm{H} \\ & \mathrm{H} & \mathrm{H} & \mathrm{H} & \end{array} + \mathrm{O\,H} \rightarrow \begin{array}{ccccc} & \mathrm{H} & \mathrm{H} & \bullet & \\ \mathrm{H} & \mathrm{C} & \mathrm{C} & \mathrm{C} & \mathrm{H} \\ & \mathrm{H} & \mathrm{H} & \mathrm{H} & \end{array} + \mathrm{H2O}$$

$$\swarrow \qquad \searrow$$

$$\begin{array}{cc} & \mathrm{H} \\ \mathrm{H} & \mathrm{C}\bullet \\ & \mathrm{H} \end{array} \qquad + \qquad \begin{array}{ccc} \mathrm{H} & & \mathrm{H} \\ \mathrm{C} & = & \mathrm{C} \\ \mathrm{H} & & \mathrm{H} \end{array}$$

$$\downarrow \qquad\qquad \downarrow$$

$$\begin{array}{ccc} \mathrm{H} & & \\ \mathrm{C} & = & \mathrm{O} \\ \mathrm{H} & & \end{array} \qquad\qquad \begin{array}{ccc} \mathrm{H} & & \mathrm{H} \\ \mathrm{C} & = & \mathrm{C} \\ \mathrm{H} & & \bullet \end{array} \rightarrow \mathrm{H\ C} \underline{=} \mathrm{C\ H}$$

Reaction mechanism construction

Reactions $N_2 + O = NO + N$

$N + O_2 = NO + O$

$$\frac{d[NO]}{dt} = k_{1+} [N_2][O]+k_{2+}[N][O_2]-k_{1-}[NO][N]-k_{2-}[NO][O]$$

$$\frac{d[N]}{dt} = k_{1+} [N_2][O]+ k_{2-}[NO][O]- k_{1-}[NO][N]- k_{2+}[N][O_2]$$

$$\frac{d[O_2]}{dt} = k_{2-}[NO][O] - k_{2+}[N][O_2]$$

Chemical Kinetic Model

Contains a large database of:

- Thermodynamic properties of species
- Reaction rate parameters

Size of mechanism grows with molecular size:

Fuel:	H_2	CH_4	C_3H_8 (Propane)	C_6H_{14} (Hexane)	$C_{16}H_{34}$ (Cetane)
Number of species:	7	30	100	450	1200
Number of reactions:	25	200	400	1500	7000

Chemical kinetic modeling for a wide range of fuels and problems

Hydrocarbons

Methane, ethane, paraffins through decane

Natural gas

Alcohols (e.g., methanol, ethanol, propanol

Other oxygenates (e.g., dimethyl ether, MTBE, aldehydes)

Automotive primary reference fuels for octane and cetane ratings

Aromatics (e.g., benzene, toluene, xylenes, naphthalene)

Biodiesel fuels (e.g., alkyl monomethyl esters)

Others

Oxides of nitrogen and sulfur (NOx, SOx)

Metals (Aluminum, Sodium, Potassium, Lead)

Chlorinated, brominated, fluorinated species

Silane

Air toxic species

Chemical warfare nerve agents

Kinetic modeling covers a wide range of systems

Types of systems studied

Flames
Shock tubes
Detonations
Pulse combustion
Flow reactors
Stirred reactors
Supercritical water oxidation
Engine knock and octane sensitivity
Flame extinction
Diesel engine combustion
Combustion of metals
CW agent chemistry
Catalytic combustion
Material synthesis
many others . . . .

Waste incineration
Kerogen evolution
Oxidative coupling
Heat transfer to surfaces
Static reactors
Ignition
Soot formation
Pollutant emissions
Cetane number
Liquid fuel sprays
HE & propellant combustion
Gasoline, diesel, aviation fuels
CVD and coatings
Chemical process control
Rapid compression machine

These studies provide extensive model validation

Hydrogen oxidation mechanism

Overall $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

Actual $H_2 + OH \rightarrow H_2O + H$

$H + O_2 \rightarrow H + OH$

$H + O_2 \rightarrow HO_2$

$H_2 + O_2 \rightarrow HO_2 + H$

………

Rates of elementary reactions

- Reaction $A + B \rightarrow C + D$

Rate $= k_+ = A\ T^n \exp[- E / R T]\ [A]\ [B]$

Usually also a reverse reaction $C + D = A + B$

$k_- = k_+ / K_{eq}$ with equilibrium constant from thermochemistry

Of k_+ k_- and K_{eq}, only two are independent

Some authors use k_+ and k_-, but most use k_+ and K_{eq}

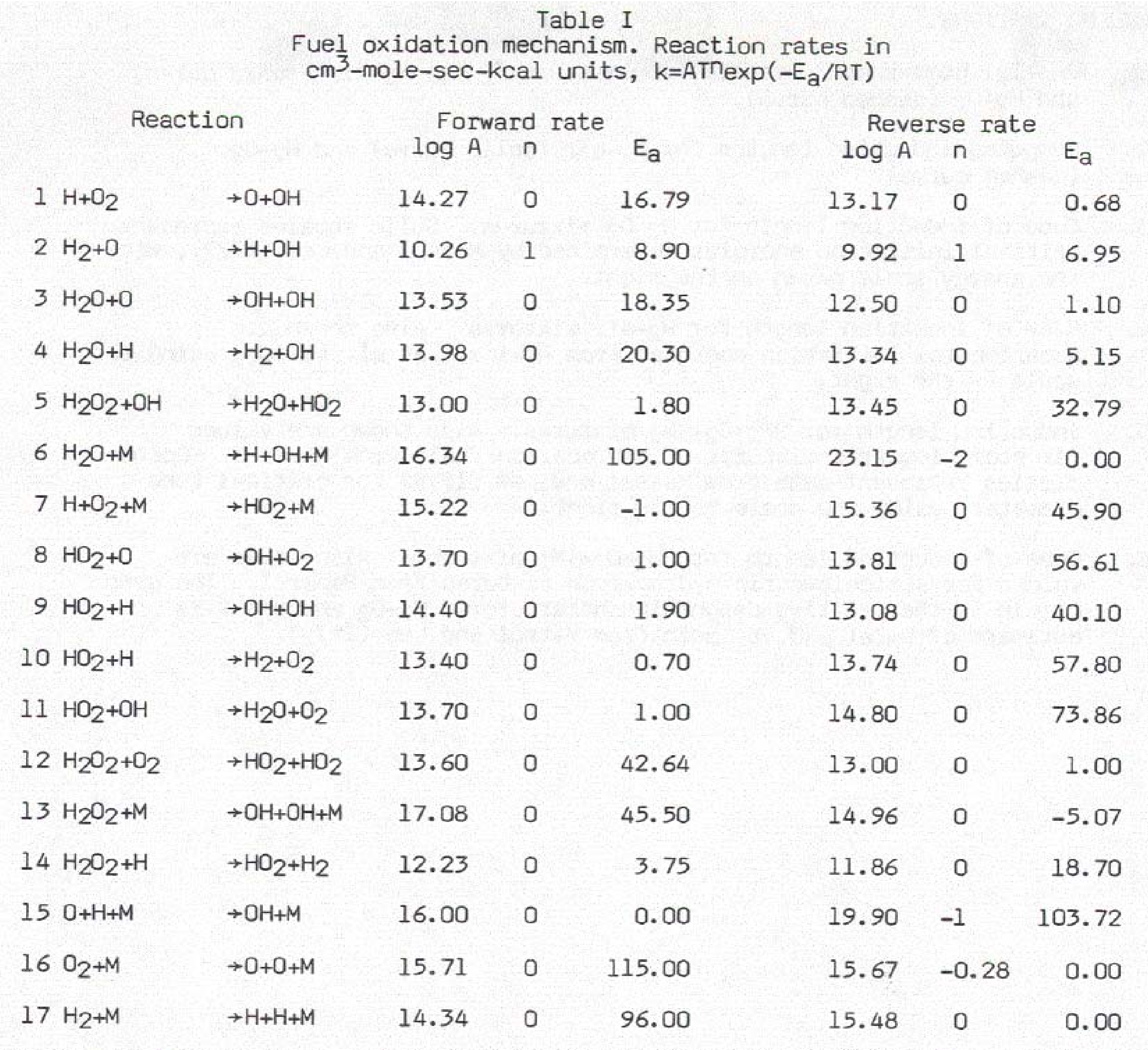


Table I

Fuel oxidation mechanism. Reaction rates in cm^3-mole-sec-kcal units, $k=AT^n\exp(-E_a/RT)$

Reaction		Forward rate log A	n	E_a	Reverse rate log A	n	E_a
1 $H+O_2$	$\rightarrow O+OH$	14.27	0	16.79	13.17	0	0.68
2 H_2+O	$\rightarrow H+OH$	10.26	1	8.90	9.92	1	6.95
3 H_2O+O	$\rightarrow OH+OH$	13.53	0	18.35	12.50	0	1.10
4 H_2O+H	$\rightarrow H_2+OH$	13.98	0	20.30	13.34	0	5.15
5 H_2O_2+OH	$\rightarrow H_2O+HO_2$	13.00	0	1.80	13.45	0	32.79
6 H_2O+M	$\rightarrow H+OH+M$	16.34	0	105.00	23.15	-2	0.00
7 $H+O_2+M$	$\rightarrow HO_2+M$	15.22	0	-1.00	15.36	0	45.90
8 HO_2+O	$\rightarrow OH+O_2$	13.70	0	1.00	13.81	0	56.61
9 HO_2+H	$\rightarrow OH+OH$	14.40	0	1.90	13.08	0	40.10
10 HO_2+H	$\rightarrow H_2+O_2$	13.40	0	0.70	13.74	0	57.80
11 HO_2+OH	$\rightarrow H_2O+O_2$	13.70	0	1.00	14.80	0	73.86
12 $H_2O_2+O_2$	$\rightarrow HO_2+HO_2$	13.60	0	42.64	13.00	0	1.00
13 H_2O_2+M	$\rightarrow OH+OH+M$	17.08	0	45.50	14.96	0	-5.07
14 H_2O_2+H	$\rightarrow HO_2+H_2$	12.23	0	3.75	11.86	0	18.70
15 $O+H+M$	$\rightarrow OH+M$	16.00	0	0.00	19.90	-1	103.72
16 O_2+M	$\rightarrow O+O+M$	15.71	0	115.00	15.67	-0.28	0.00
17 H_2+M	$\rightarrow H+H+M$	14.34	0	96.00	15.48	0	0.00

Basic parameters for combustion

- Temperature
- Pressure
- Fuel structure and other properties
- Ratio of fuel to oxidizer
- Large body of kinetic and thermochemical quantities
- Initial and boundary conditions
- Time, residence time
- Chain branching, propagation, termination reactions

We focus on three distinct chain branching pathways

1) $H + O_2 \rightarrow O + OH$ High T

2) $H + O_2 + M \rightarrow HO_2 + M$ Medium T

$RH + HO_2 \rightarrow R + H_2O_2$

$H_2O_2 + M \rightarrow OH + OH + M$ Degenerate chain branching

3) $R + O_2 \rightarrow RO_2$ Low T

$RO_2 \rightarrow QOOH \rightarrow O_2QOOH \rightarrow$ 3+ radicals

Chain branching at high temperatures

$$H + O_2 \rightarrow O + OH$$

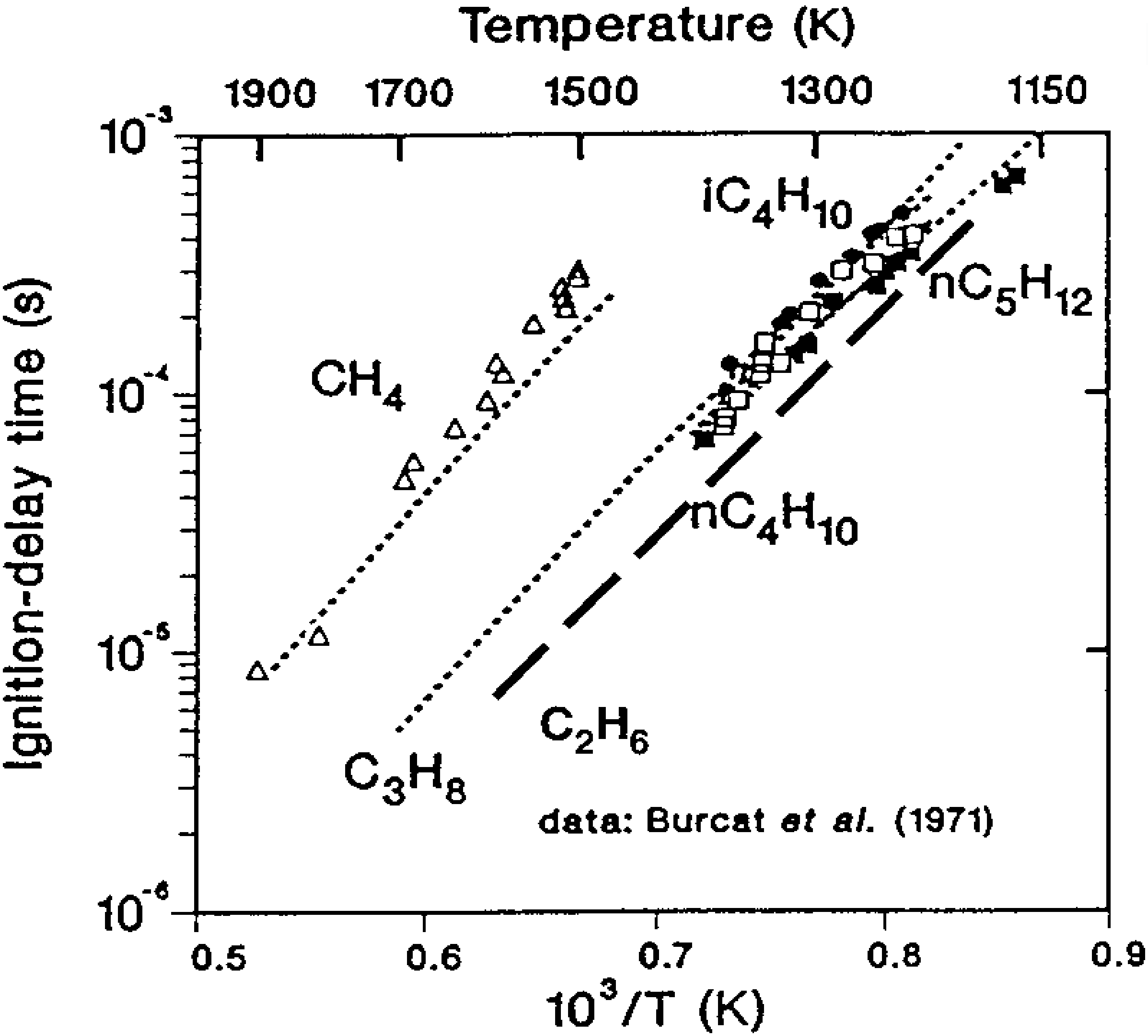
“The most important reaction in combustion”

- Activation energy is relatively high (16.8 kcal/mol)
- H atoms produced by thermal decomposition of radicals
  e.g. C_2H_5 , C_2H_3 , HCO, iC_3H_7 , etc.
  Activation energies relatively high (~ 30 kcal/mol)
- Therefore this sequence requires high temperatures
- Illustrated best by shock tube experiments

Chain branching at high temperatures

$$H + O_2 \rightarrow O + OH$$

- Chain branching for oxidation, not for pyrolysis
- Lean mixtures ignite earlier than rich mixtures
- Different fuels produce H atoms at different rates, and their ignition rates vary correspondingly
- Additives that produce H atoms will accelerate ignition, and additives that remove H atoms slow ignition



Temperature (K)
1900
1700
1500
1300
1150
10^{-3}
10^{-4}
10^{-5}
10^{-6}
Ignition-delay time (s)
iC_4H_{10}
nC_5H_{12}
CH_4
nC_4H_{10}
C_2H_6
C_3H_8
data: Burcat *et al.* (1971)
0.5
0.6
0.7
0.8
0.9
$10^3/T$ (K)

Chain branching often occurs over a series of reactions

Chain branching at intermediate temperatures

$$H + O_2 + M \rightarrow HO_2 + M$$

$$RH + HO_2 \rightarrow R + H_2O_2$$

$$H_2O_2 + M \rightarrow OH + OH + M$$

- At temperatures below about 900K, H_2O_2 decomposition is inhibited, leading to degenerate chain branching (see below)
- At higher temperatures, H_2O_2 decomposes as quickly as it is formed, leading to conventional chain branching
- Other low temperature chain branching paths can be much longer than this sequence (see below)

H_2O_2 decomposes at a fairly distinct temperature

- Reaction consuming H_2O_2 is:

$$H_2O_2 + M \rightarrow OH + OH + M$$

$$k_+ = 1.2 \times 10^{17} \times \exp(-45500/RT)$$

- Resulting differential equation is:

$$\frac{d [H_2O_2]}{d t} = -[H_2O_2] [M] k_+$$

Characteristic time for H_2O_2 decomposition

$$\frac{d\,[\,H_2O_2\,]}{d\,t} = -[\,H_2O_2\,]\ [\,M\,]\ k_+$$

define $\tau = [\,H_2O_2\,] / (d\,[\,H_2O_2\,]/dt)$

$\tau = 1 / (\,k_+\,[M])$

$\tau = 8.3 \times 10^{-18} \times \exp(22750/T) \times [M]^{-1}$

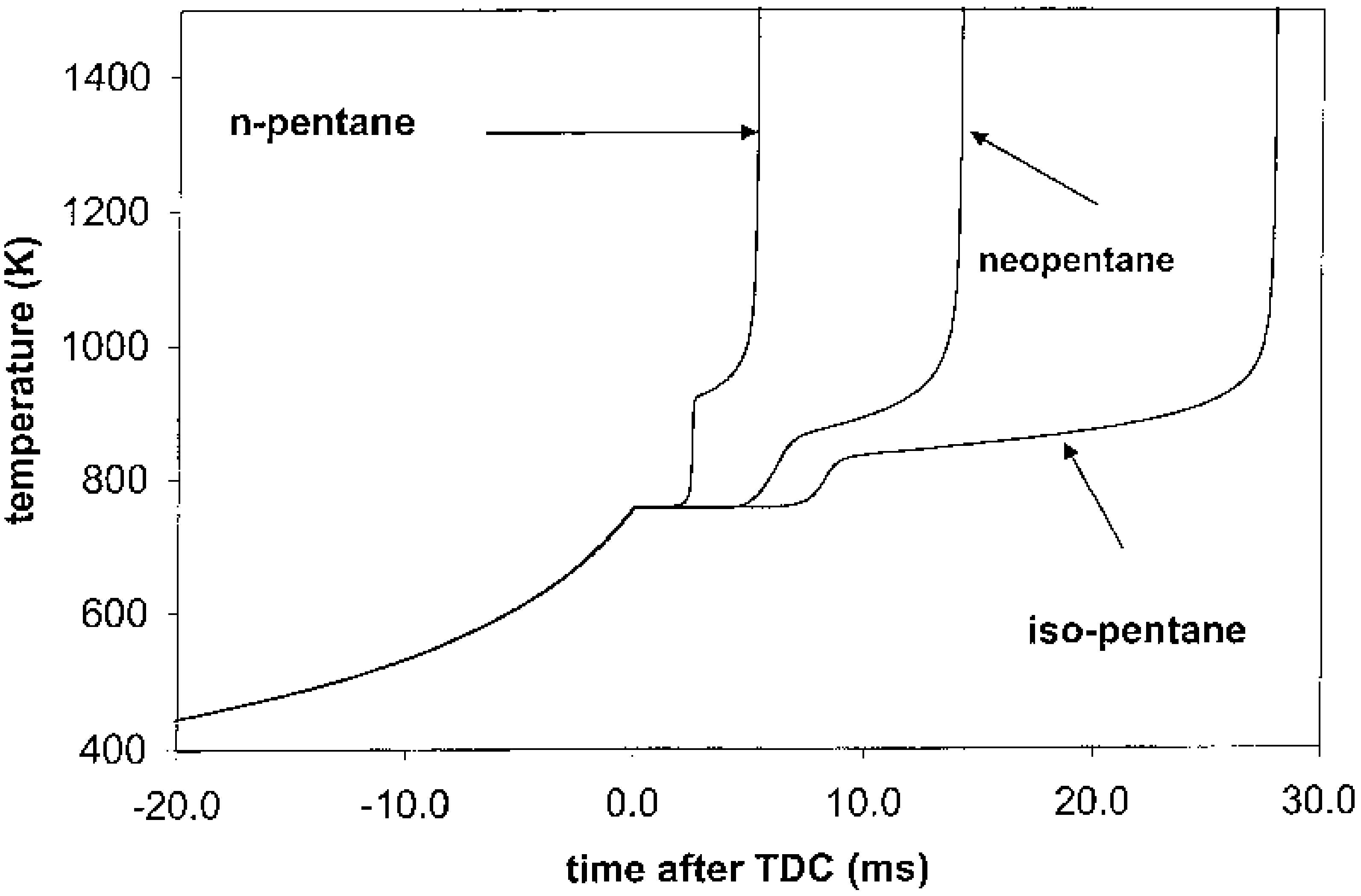
At RCM conditions, with [M] ≈ 1 x 10-4 mol/cc, values of τ are approximately:

7.8 ms at 900K 640 μs at 1000K 80 μs at 1100K

At higher compressions (pressures), values of τ are smaller at comparable temperatures

Rapid compression machine and some turbulent flow reactor experiments are controlled by H_2O_2 decomposition

- Rapid compression machine (RCM) usually operates in a degenerate branching mode
  - H_2O_2 produced at temperatures lower than 900K
  - When system reaches H_2O_2 decomposition temperature, ignition is observed
- Many turbulent flow reactor experiments operate at temperatures between 900 - 1100K where H_2O_2 decomposes as quickly as it is produced



n-pentane
neopentane
iso-pentane
temperature (K)
1400
1200
1000
800
600
400
-20.0
-10.0
0.0
10.0
20.0
30.0
time after TDC (ms)

The central role of the high temperature chain branching reaction

$$H + O_2 = O + OH$$

Ignition

Flame propagation

Flame inhibition

Sensitization of methane for natural gas

Effects of pressure on oxidation rates from competing $H + O_2 + M$ reaction

Laminar flames in quenching problems

- **Mid-volume quenching in direct injection stratified charge (DISC) engine**
- **Bulk quenching due to volume expansion in lean-burn engine mixtures**
- **Flame quenching at lean and rich flammability limits**
- **Flame quenching on cold walls and unburned hydrocarbon emissions from internal combustion engines**

Causes and implication of flammability limits

$$H + O_2 = O + OH$$

$$H + O_2 + M = HO_2 + M$$

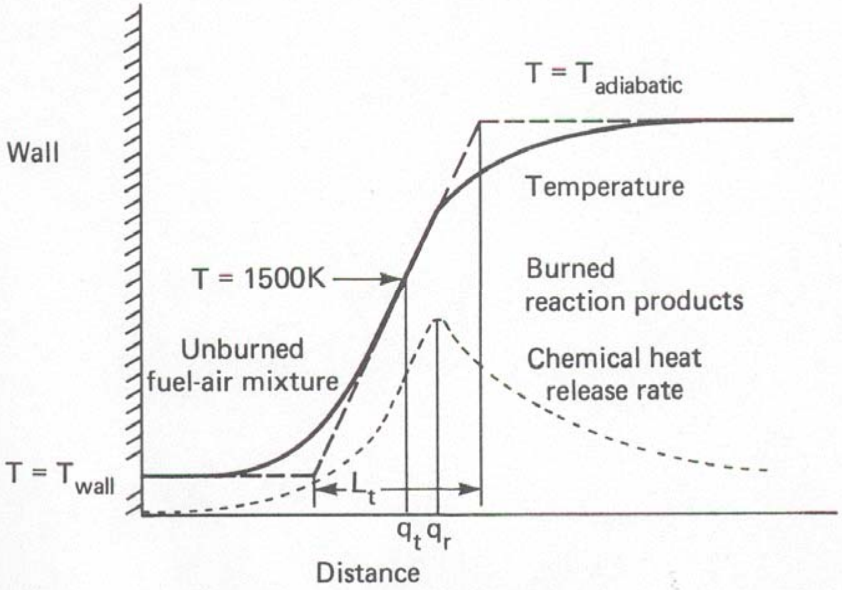
- Law and Egolfopoulos for atmospheric pressure flames
- Flynn et al. extensions to engine pressures

Lean limit moves to richer compositions as pressure increases, and at engine pressures, lean-limit mixtures still produce significant amounts of NO_x

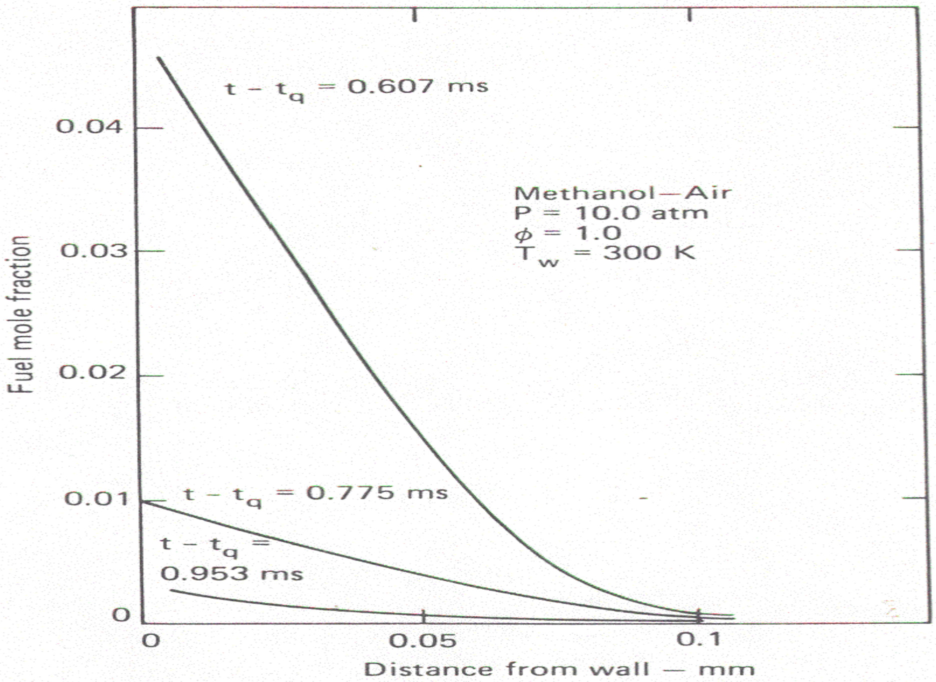
Flame quenching on engine walls

- Previous concept of UHC emissions
- Idea of making wall layers thinner
- Simple flame model results at Ford weren't believed
- Detailed modeling results
- Evidence had been there, Wentworth

Pictures of wall quenching



Flame approaching wall



Fuel diffuses away from wall and is rapidly consumed

Flame inhibition

- Halogens
  - HBr Dixon-Lewis, Lovachev 1970's
  - CF_3Br Biordi et al., Westbrook 1980's

- Organophosphorous compounds (OPC's)
  - Twarowski early studies
  - NIST studies, Linteris, Babushok, Gann, etc.
  - Korobeinichev, Melius, Jayaweera et al.

- Net removal of H atoms from radical pool reduces chain branching from reaction of $H + O_2 = O + OH$

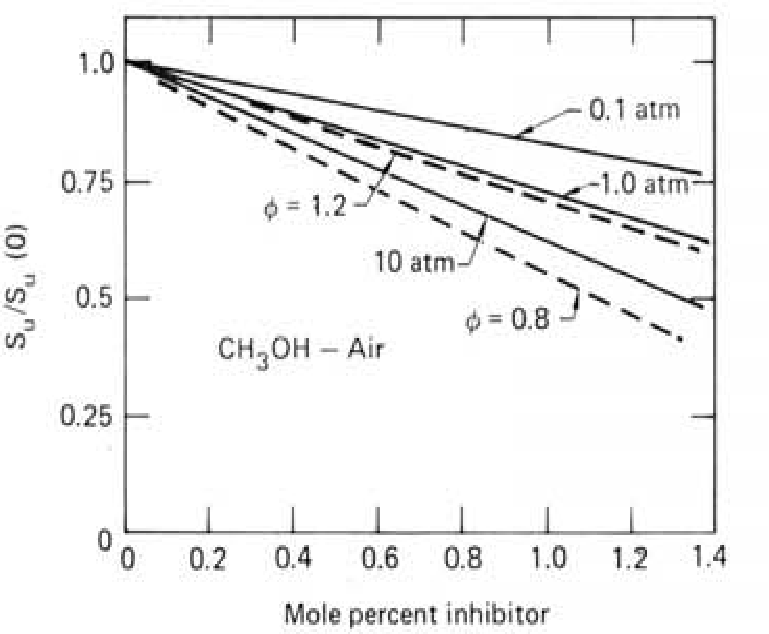
Flame inhibition by halogens

$$H + HBr = H_2 + Br$$

$$H + Br_2 = HBr + Br$$

$$Br + Br = Br_2$$

$$H + H = H_2$$



Other inhibitors

- Organophosphorus compounds
- Iron and other metal compounds

$$H + H = H_2$$

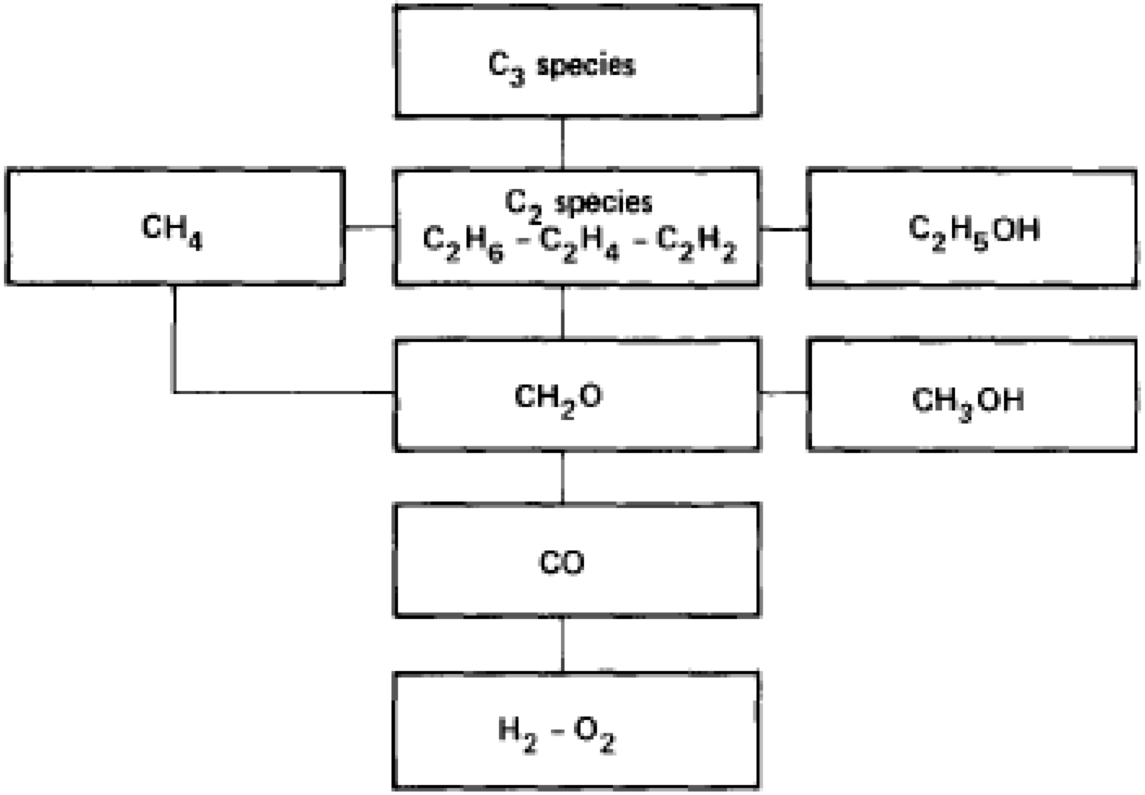
$$H + OH = H_2O$$

others

- All remove radicals and reduce the overall chain branching rates

Hierarchical mechanisms

- H_2/O_2 is the foundation
- CO/CO_2 is the next level
- $CH_4/CH_2O/CH_3OH$ is the next level
- $C_2H_6/C_2H_4/C_2H_2$ is next
- This pattern continues to C10 and C20
- There are many side branches to this tree



C_3 species

CH_4

C_2 species
C_2H_6 - C_2H_4 - C_2H_2

C_2H_5OH

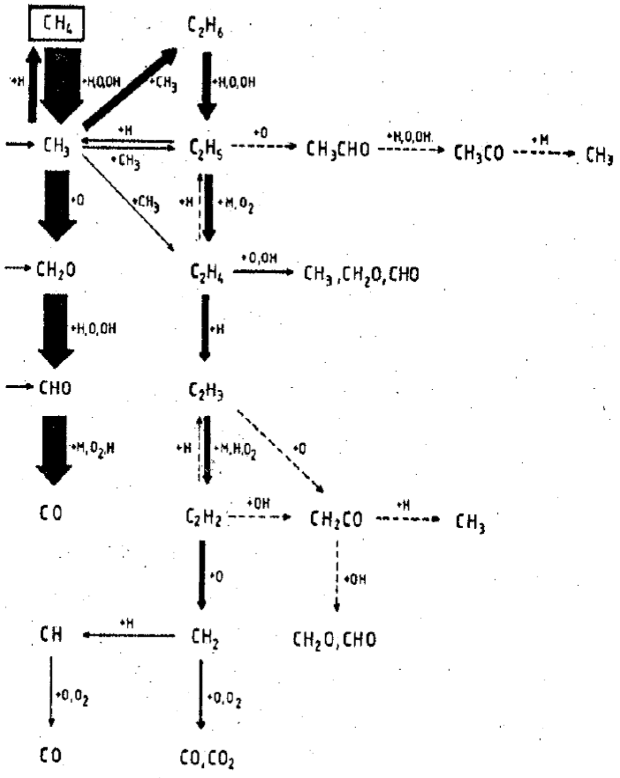
CH_2O

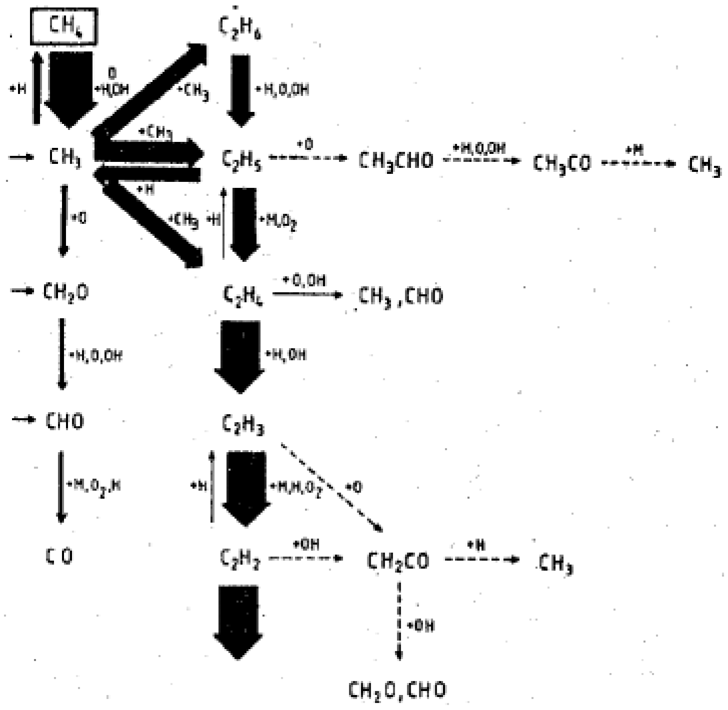
CH_3OH

CO

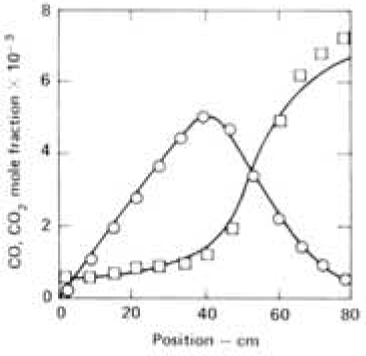
H_2 - O_2

One of the most significant reaction flux diagrams in all of combustion chemistry





Delay of final oxidation by fuel



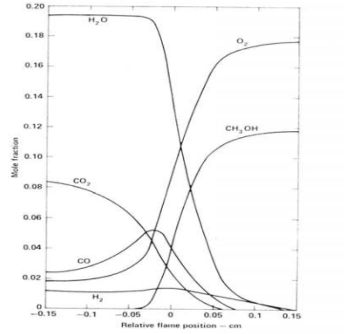
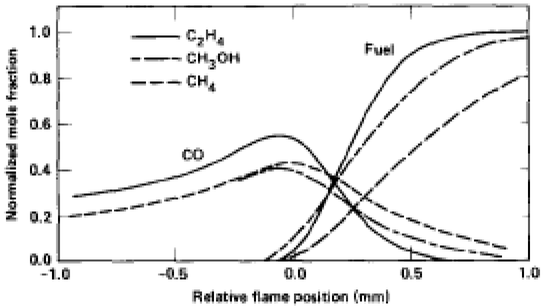
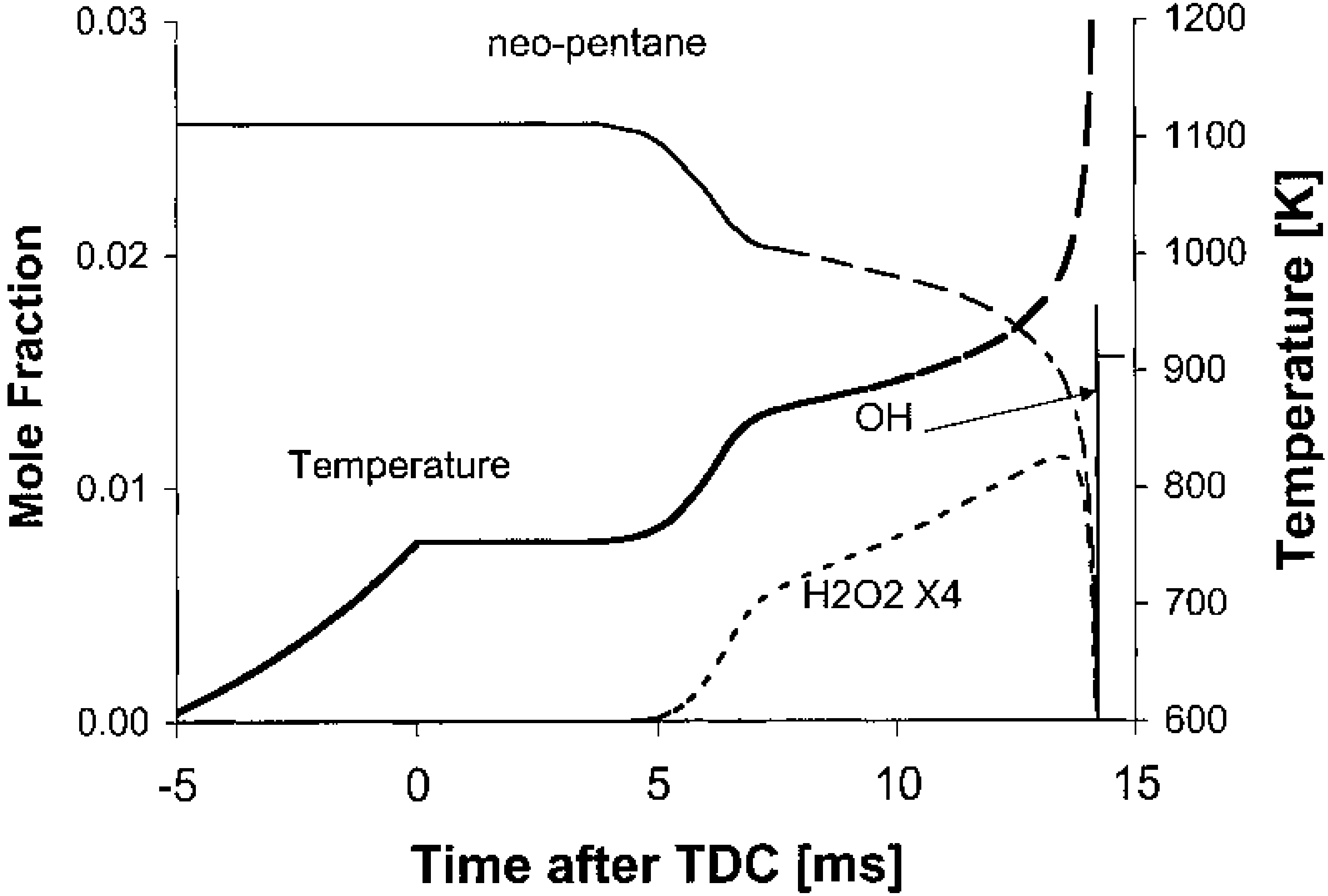
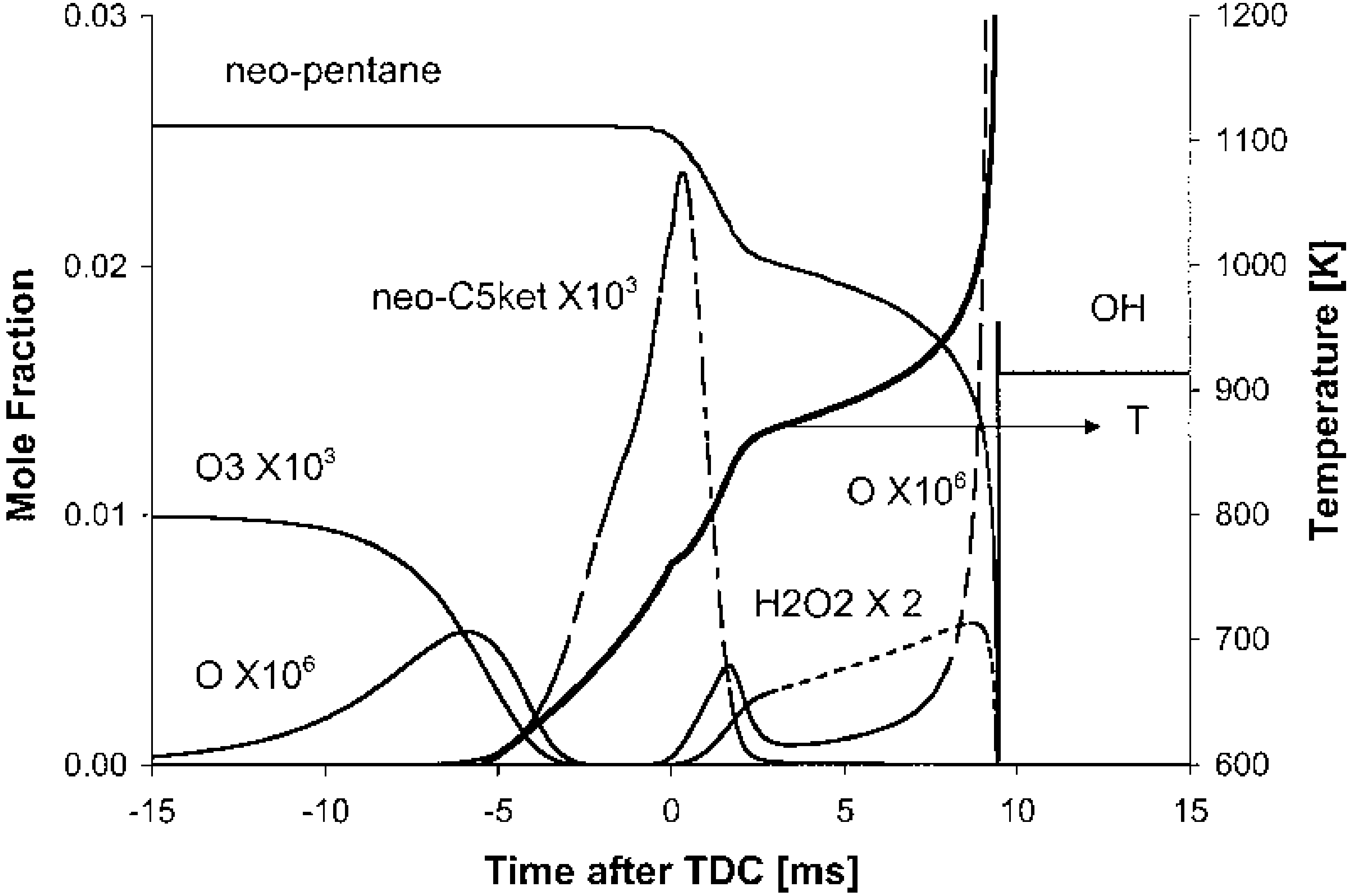


FIGURE 9b Flame profiles of major species in the methanol flame.





0.03
0.02
0.01
0.00
Mole Fraction
1200
1100
1000
900
800
700
600
Temperature [K]
neo-pentane
Temperature
OH
H2O2 X4
-5
0
5
10
15
Time after TDC [ms]



0.03
0.02
0.01
0.00
Mole Fraction
1200
1100
1000
900
800
700
600
Temperature [K]
-15
-10
-5
0
5
10
15
Time after TDC [ms]
neo-pentane
neo-C5ket X10^3
OH
T
O3 X10^3
O X10^6
H2O2 X 2
O X10^6

What is next?

- We want to understand the process of chemical kinetics
- We want to extend our knowledge base to practical hydrocarbon and other fuels
- We want to be able to use kinetic models to understand and improve performance of engines and other practical combustors

Kinetic Reaction Mechanisms for Hydrocarbon Fuels
Part 1 -- Small molecules

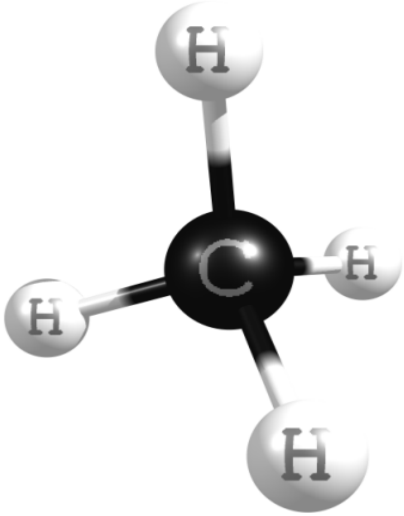
Generation of Detailed Chemical Kinetic Models for C_0–C_4 Hydrocarbon and Oxygenated Fuels

Charles Westbrook

Tsinghua-Princeton
2014 Summer School on Combustion
July 20-25, 2014

Chemical Modeling

- Fuel + O_2 -> CO_2 + H_2O + Energy



- Small hydrocarbon fuel (e.g. methane)
  - 200 reactions
  - 30 chemical intermediates
- Chemical mechanism
  - Kinetics
  - Thermodynamics

Hierarchical structure

H_2-O_2

C.K. Westbrook and F.L. Dryer
Prog. Energy Combust. Sci., 10 (1984) 1–57.

What does a mechanism look like?

Hydrogen

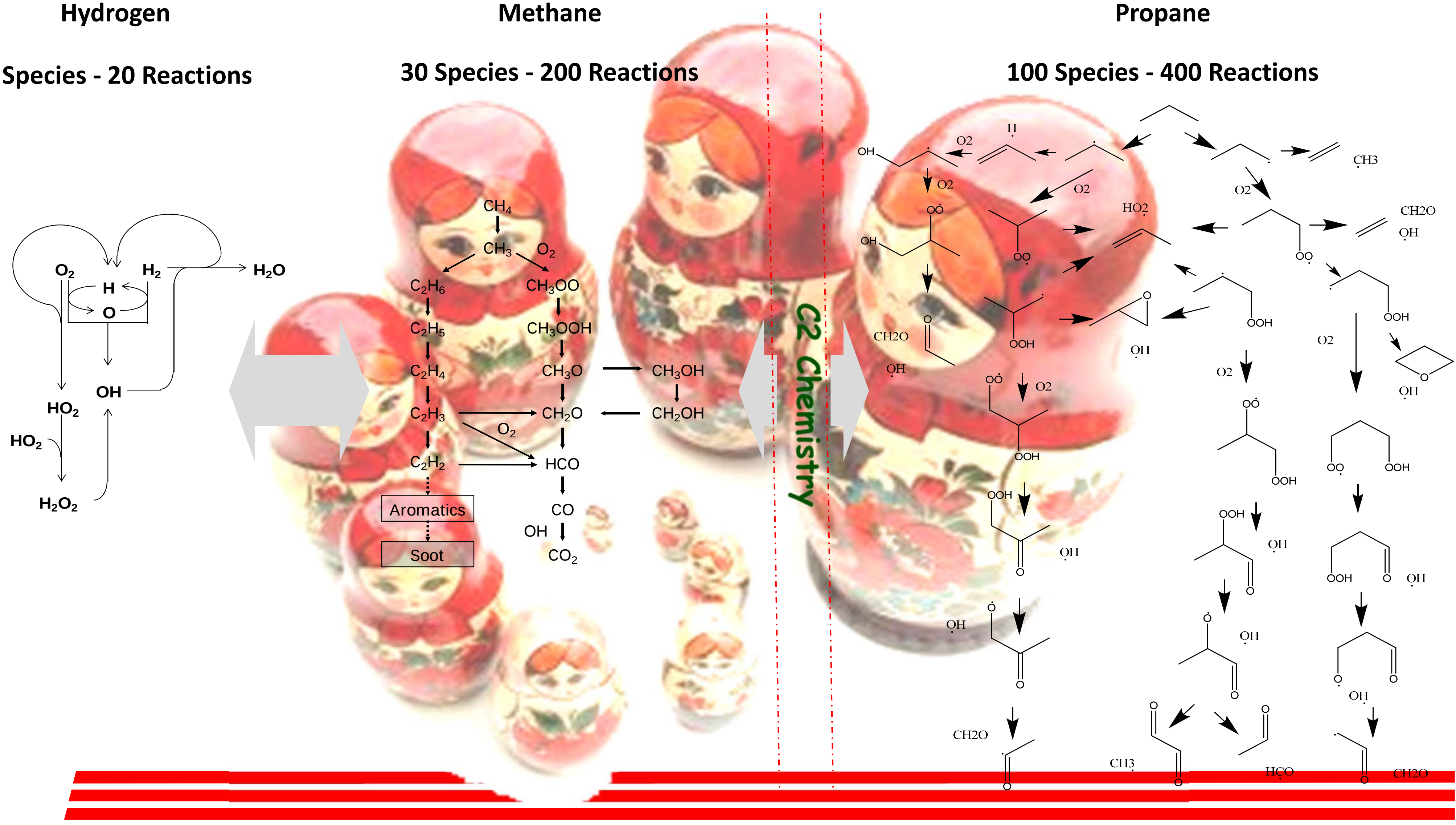
8 Species - 20 Reactions

Methane

30 Species - 200 Reactions

Propane

100 Species - 400 Reactions



Courtesy of William Pitz, Lawrence Livermore National Laboratory

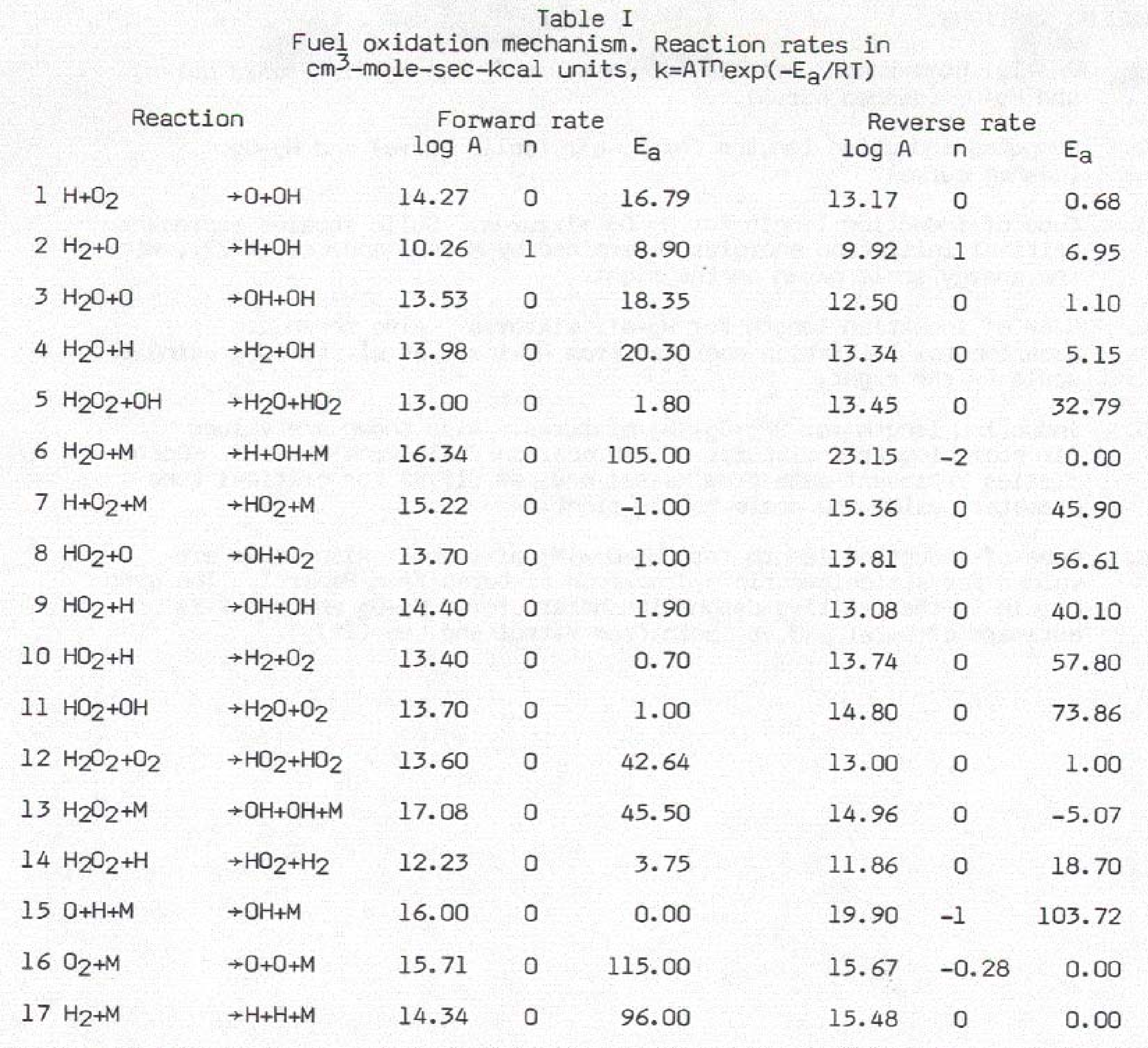


Table I

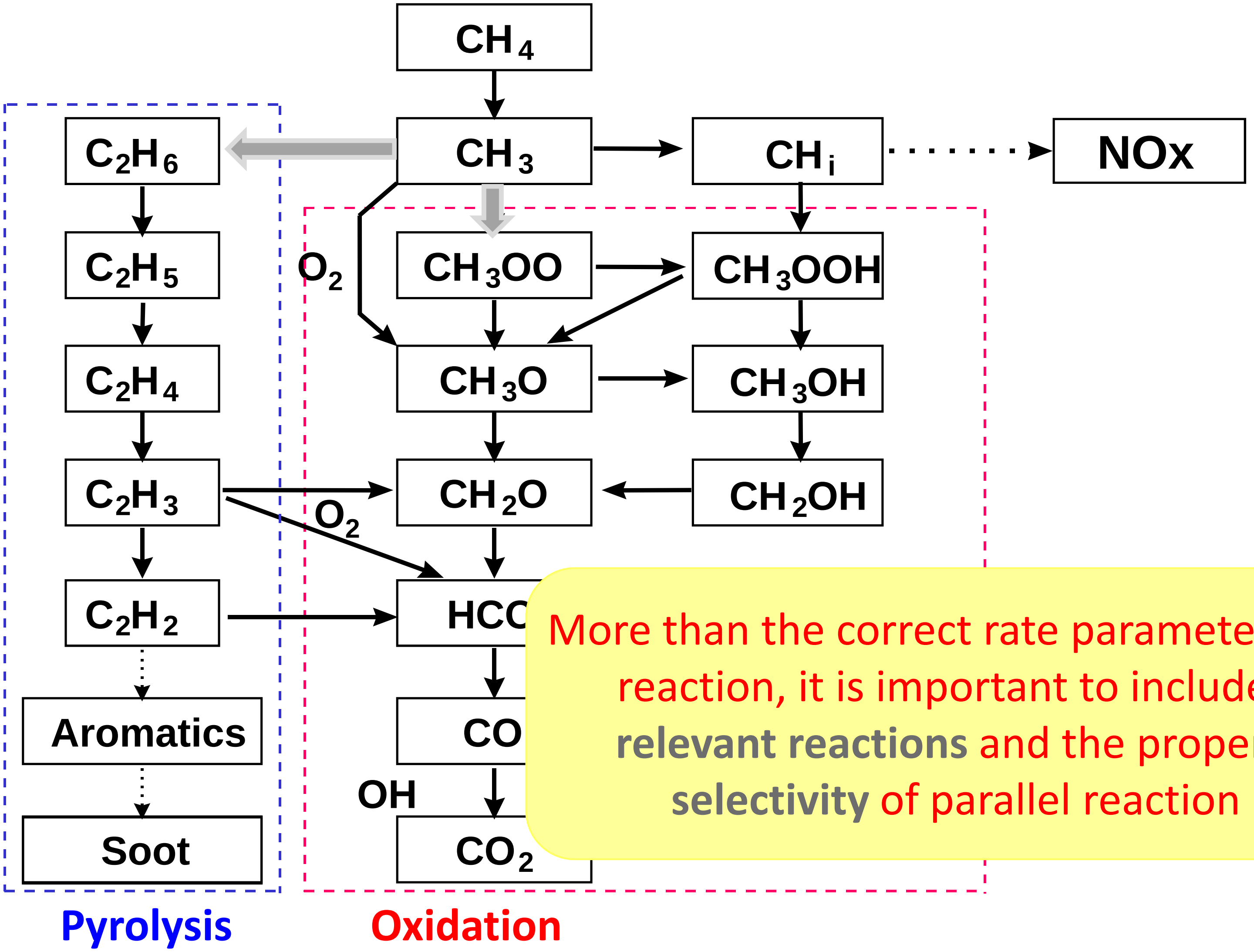
Fuel oxidation mechanism. Reaction rates in cm^3-mole-sec-kcal units, $k=AT^n \exp(-E_a/RT)$

Reaction		Forward rate			Reverse rate		
		log A	n	E_a	log A	n	E_a
1 $H+O_2$	$\rightarrow O+OH$	14.27	0	16.79	13.17	0	0.68
2 H_2+O	$\rightarrow H+OH$	10.26	1	8.90	9.92	1	6.95
3 H_2O+O	$\rightarrow OH+OH$	13.53	0	18.35	12.50	0	1.10
4 H_2O+H	$\rightarrow H_2+OH$	13.98	0	20.30	13.34	0	5.15
5 H_2O_2+OH	$\rightarrow H_2O+HO_2$	13.00	0	1.80	13.45	0	32.79
6 H_2O+M	$\rightarrow H+OH+M$	16.34	0	105.00	23.15	-2	0.00
7 $H+O_2+M$	$\rightarrow HO_2+M$	15.22	0	-1.00	15.36	0	45.90
8 HO_2+O	$\rightarrow OH+O_2$	13.70	0	1.00	13.81	0	56.61
9 HO_2+H	$\rightarrow OH+OH$	14.40	0	1.90	13.08	0	40.10
10 HO_2+H	$\rightarrow H_2+O_2$	13.40	0	0.70	13.74	0	57.80
11 HO_2+OH	$\rightarrow H_2O+O_2$	13.70	0	1.00	14.80	0	73.86
12 $H_2O_2+O_2$	$\rightarrow HO_2+HO_2$	13.60	0	42.64	13.00	0	1.00
13 H_2O_2+M	$\rightarrow OH+OH+M$	17.08	0	45.50	14.96	0	-5.07
14 H_2O_2+H	$\rightarrow HO_2+H_2$	12.23	0	3.75	11.86	0	18.70
15 $O+H+M$	$\rightarrow OH+M$	16.00	0	0.00	19.90	-1	103.72
16 O_2+M	$\rightarrow O+O+M$	15.71	0	115.00	15.67	-0.28	0.00
17 H_2+M	$\rightarrow H+H+M$	14.34	0	96.00	15.48	0	0.00

Dominance of H2/O2 Reactions

For nearly all hydrocarbon oxidation, no matter how large or small the fuel molecule, at high temperatures, the reactions of H2/O2 have the greatest sensitivity controlling the overall rate of reaction. This is true in flames, detonations, shock tubes, and many other practical combustors.

Detailed Kinetics of Methane Combustion



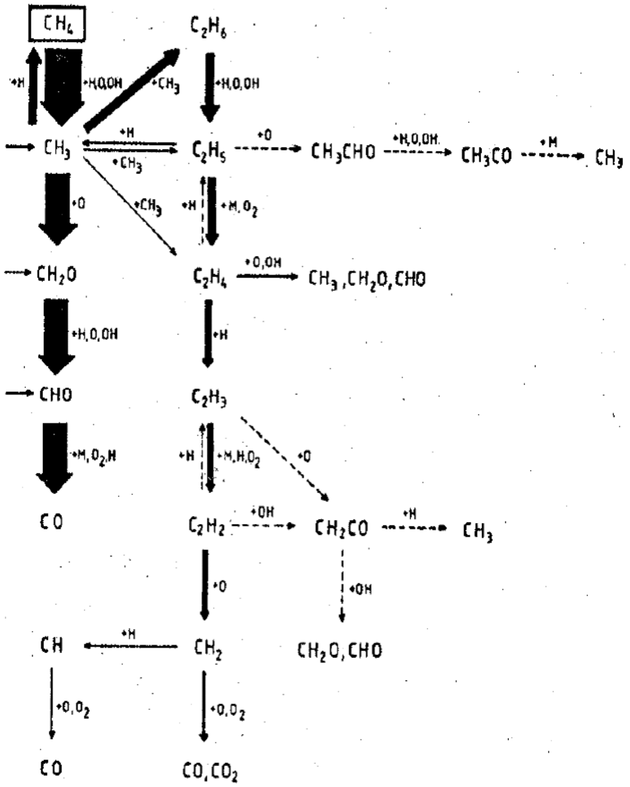
More than the correct rate parameters of specific reaction, it is important to include **all the relevant reactions** and the proper relative **selectivity** of parallel reaction paths.

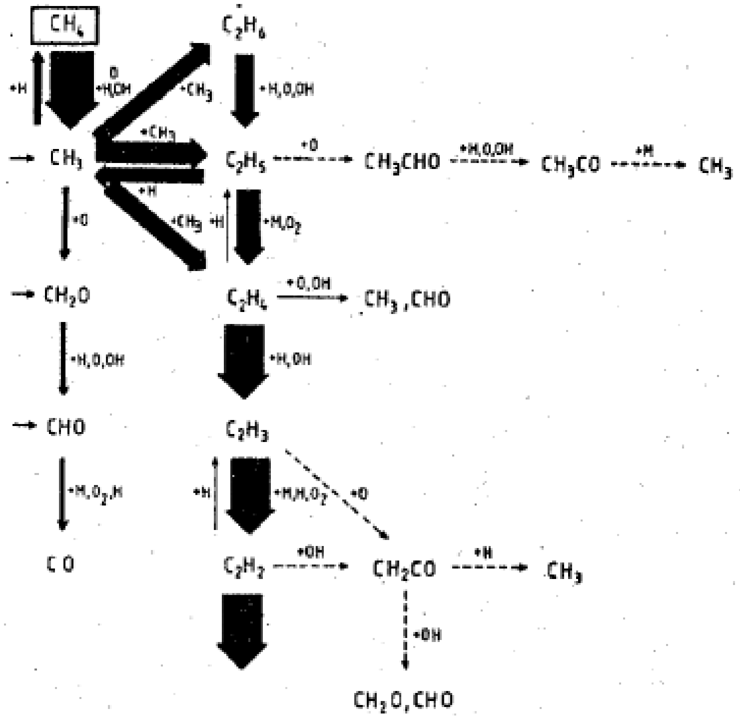
Slide courtesy of Prof. E. Ranzi

Small molecule kinetic mechanisms

- In small molecule kinetics, each elementary reaction is treated individually
- Extensive validation experiments usually exist
- Many of the elementary reactions are rather idiosyncratic or unusual
- Principal reactions are usually
    - $H + O_2 = O + OH$
    - $CO + OH = H + CO_2$

One of the most significant reaction flux diagrams in all of combustion chemistry (J. Warnatz, 18th Symposium)





Reaction mechanism

$k = A\,T^{n} \exp(-E_a/RT)$

Reaction			A_f	n_f	Ea_f	A_r	n_r	Ea_r
c2h5oh	=	c2h4+h2o	1.25E+14	0.1	6.70E+04	1.11E+07	1.77	8.08E+03
c2h5oh	=	ch2oh+ch3	2.00E+23	-1.68	9.64E+04	8.38E+14	-0.22	7.02E+03
c2h5oh	=	c2h5+oh	2.40E+23	-1.62	9.95E+04	9.00E+15	-0.24	4.65E+03
c2h5oh	=	ch3cho+h2	7.24E+11	0.1	9.10E+04	4.91E+07	0.99	7.50E+04
c2h5oh+o2	=	pc2h4oh+ho2	2.00E+13	0	5.28E+04	2.19E+10	0.28	4.43E+02
c2h5oh+o2	=	sc2h4oh+ho2	1.50E+13	0	5.02E+04	1.95E+11	0.09	4.88E+03
c2h5oh+oh	=	pc2h4oh+h2o	1.81E+11	0.4	7.17E+02	4.02E+08	0.92	1.79E+04
c2h5oh+oh	=	sc2h4oh+h2o	6.18E+10	0.5	-3.80E+02	1.63E+09	0.83	2.39E+04
c2h5oh+oh	=	c2h5o+h2o	1.50E+10	0.8	2.53E+03	7.34E+09	0.91	1.72E+04
c2h5oh+h	=	pc2h4oh+h2	1.88E+03	3.2	7.15E+03	3.93E-01	3.83	9.48E+03
c2h5oh+h	=	sc2h4oh+h2	8.95E+04	2.53	3.42E+03	2.21E+02	2.97	1.28E+04
c2h5oh+h	=	c2h5o+h2	5.36E+04	2.53	4.41E+03	2.47E+03	2.74	4.19E+03
c2h5oh+ho2	=	pc2h4oh+h2o2	2.38E+04	2.55	1.65E+04	2.88E+03	2.48	2.83E+03
c2h5oh+ho2	=	sc2h4oh+h2o2	6.00E+12	0	1.60E+04	8.59E+12	-0.26	9.42E+03
c2h5oh+ho2	=	c2h5o+h2o2	2.50E+12	0	2.40E+04	6.66E+13	-0.48	7.78E+03

Rate constant

- Large number of reactions in a combustion mechanism
- Direct experimental determination often difficult for elementary reactions over a wide range of temperature and pressure
- Few experimental data, limited to light species

- Estimation methods:
  - Collision theory (kinetic theory gas) pre-exponential A, radical combination
  - correlations between structure and reactivity
  - LFER (Linear Free Energy Relationships) ex: Evans-Polanyi
  - methods based on the Transition State Theory (estimation of the TS)
  - quantum calculation and TST

Slide courtesy of Dr. Pierre-Alexandre Glaude

Databases

- **On-line databases**

  NIST Chemical Kinetics Database, Standard Reference Database 17
  http://kinetics.nist.gov/kinetics/index.jsp

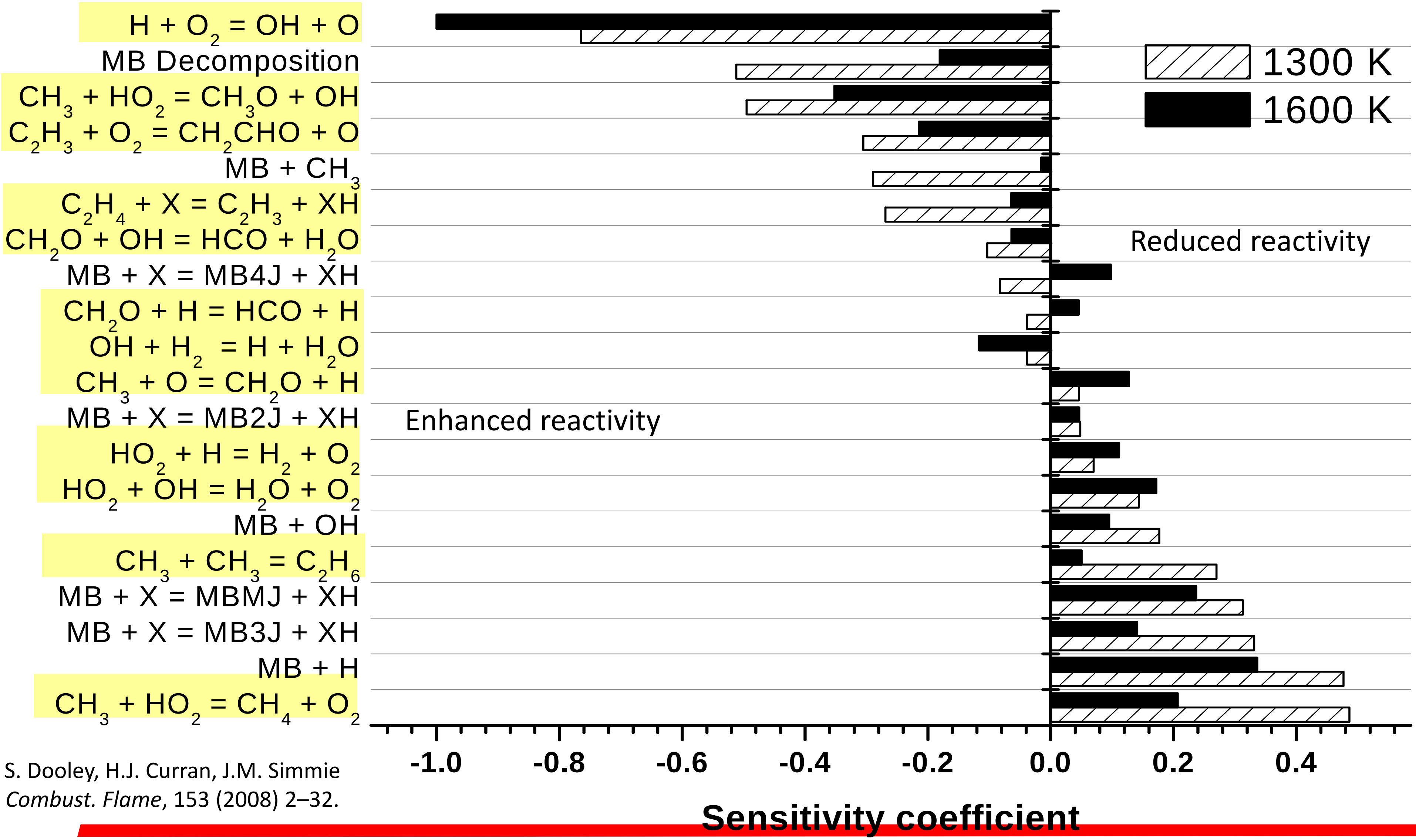
- **Review**
  - **D.L. Baulch, C.T. Bowman, C.J. Cobos, Th. Just, J.A. Kerr, M.J. Pilling, D. Stocker, J. Troe, W. Tsang, R.W. Walker and J. Warnatz, Phys. Chem. Ref. Data, 34, 757 (2006)**
  - **Tsang,W., Hampson, R. F., J. Phys. Chem. Ref. Data 15:3 (1986)**
  - **Tsang,W., J. Phys. Chem. Ref. Data 20:221 (1991)**

- **On-line mechanisms:**
  - **Estimated rate constants for most reactions, to handle and mix carefully**
  - **GRI-mech, LLNL, Leeds, Konnov, NUIG, POLIMI, Jet-Surf, UCSD…**

- **Good website for general links: http://c3.nuigalway.ie/links.html**

Slide courtesy of Dr. Pierre-Alexandre Glaude

Low *p*, High *T*: 1.0% MB, $\phi = 1.0$ in Ar, $P_5 = 1$ atm



S. Dooley, H.J. Curran, J.M. Simmie
Combust. Flame, 153 (2008) 2–32.

Developing a mechanism

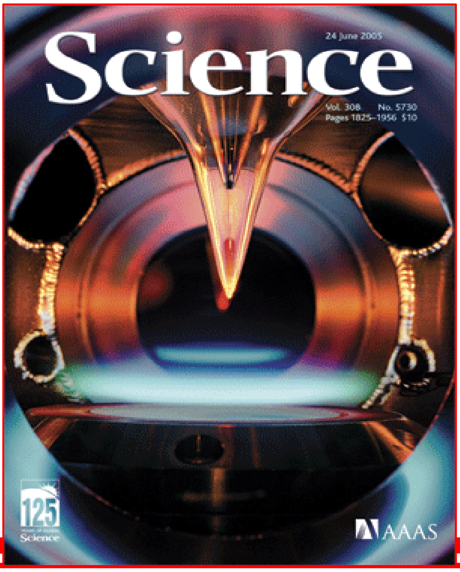
- Detailed chemical kinetic mechanism for C_1—C_2 HC and oxygenated HC species including:
  - CH_4, C_2H_6, C_2H_4, C_2H_2
  - CH_2O, CH_3OH, CH_3CHO, C_2H_5OH
- Measured/ab-initio rate constants if possible
- Validated over a wide range of conditions

Experimental Studies: Engine Relevant

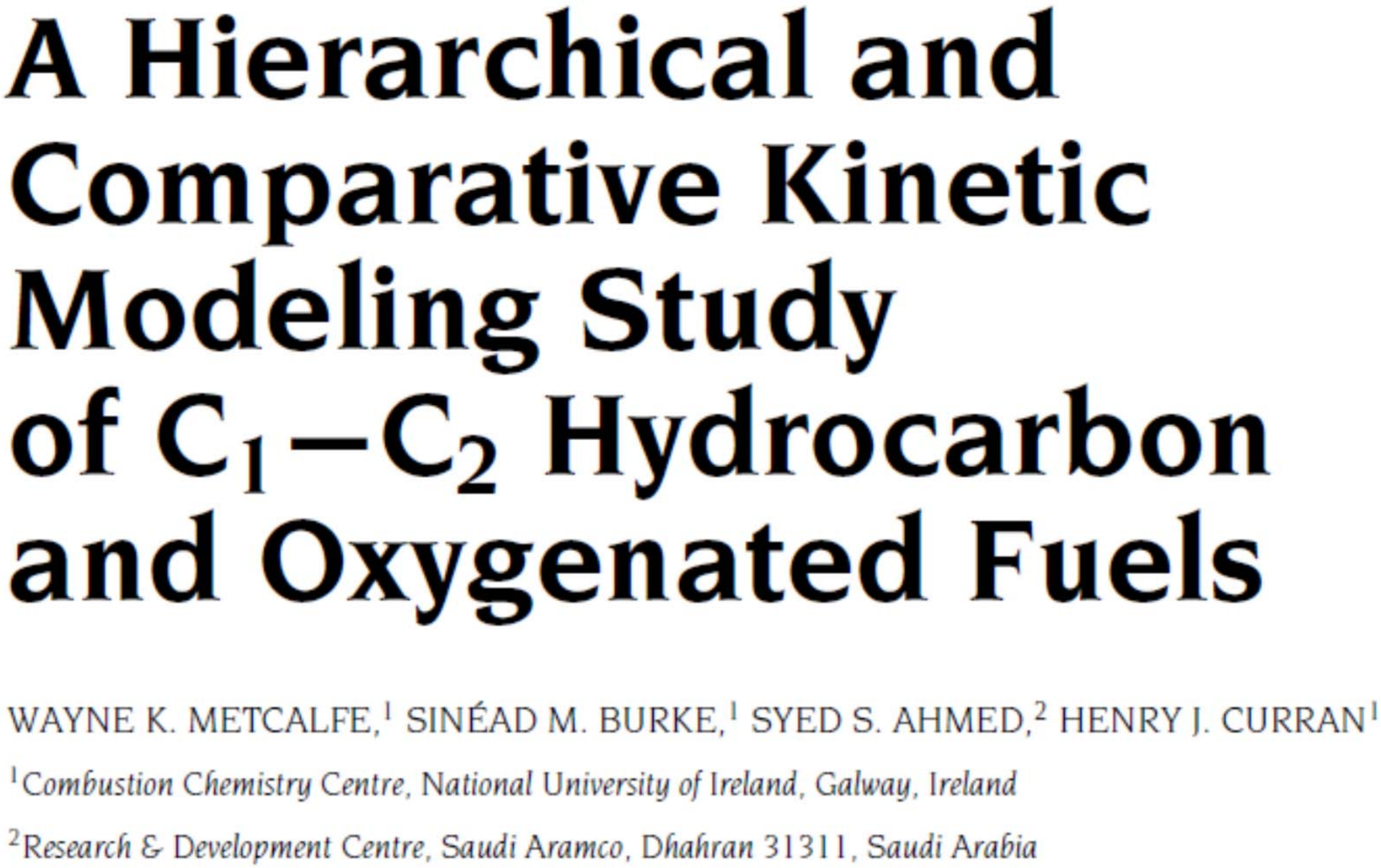

Rapid Compression Machine


Shock Tube


Jet Stirred Reactor



Flat Flame Burner



A Hierarchical and Comparative Kinetic Modeling Study of C_1-C_2 Hydrocarbon and Oxygenated Fuels

WAYNE K. METCALFE,[1] SINÉAD M. BURKE,[1] SYED S. AHMED,[2] HENRY J. CURRAN[1]

[1]*Combustion Chemistry Centre, National University of Ireland, Galway, Ireland*

[2]*Research & Development Centre, Saudi Aramco, Dhahran 31311, Saudi Arabia*

International Journal of Chemical Kinetics 45, 638-675 (2013)

Other “core” small molecule kinetic mechanisms

- Universite de Nancy (F. Battin-LeClerc)
- Polytecnico Milano (T. Faravelli)
- University of Southern California/Stanford (H. Wang
- CNRS (P. Dagaut)
- Chemkin (E. Meeks, C. Naik)
- MIT (W. Green)
- Lund University (A. Konnov)
- Tokyo University (A. Miyoshi)

Important trend

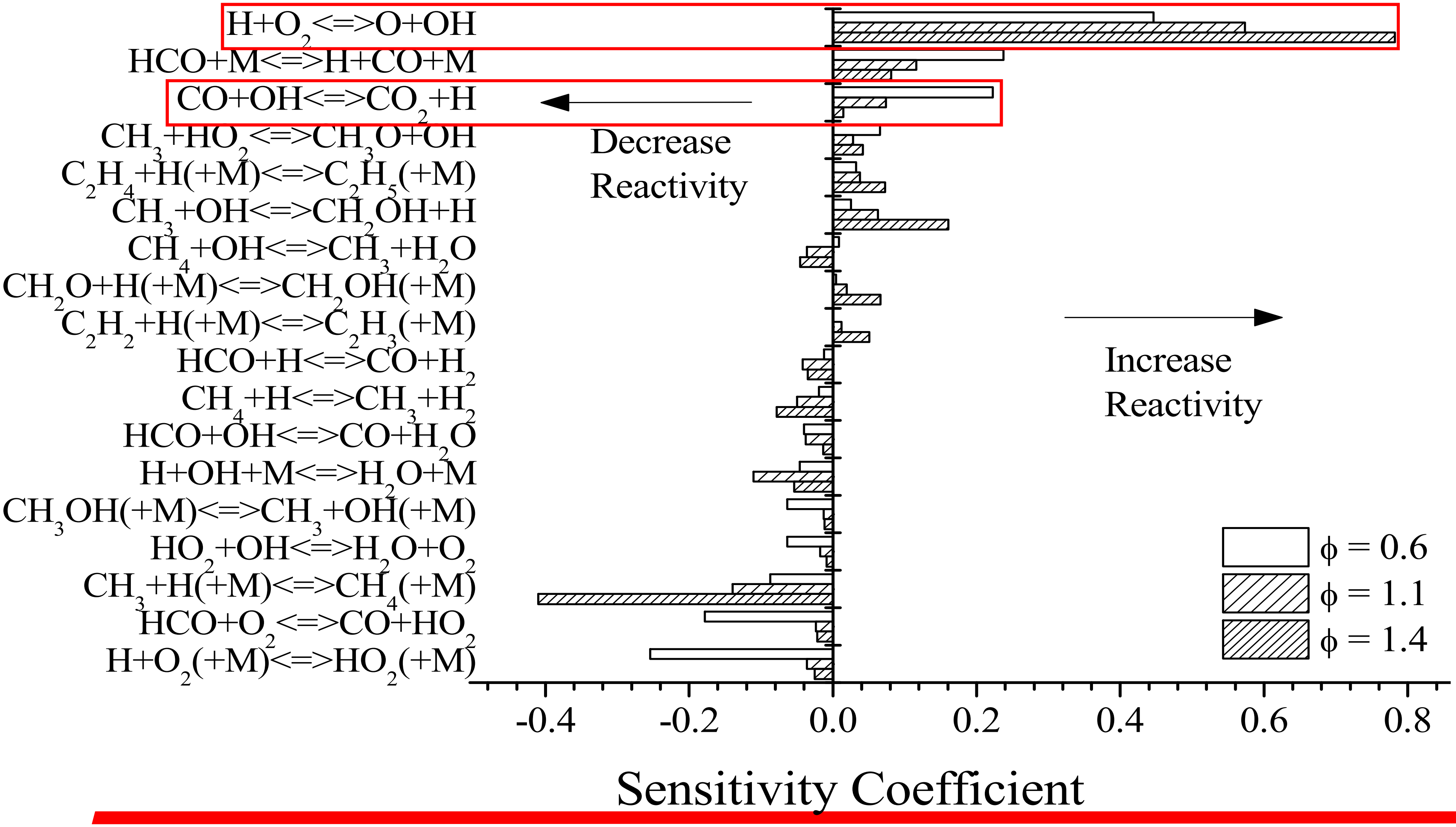
It is very likely that all of these small molecule kinetic mechanisms will steadily converge to a common family of reactions, reaction rates and reaction pathways.

Range of validation

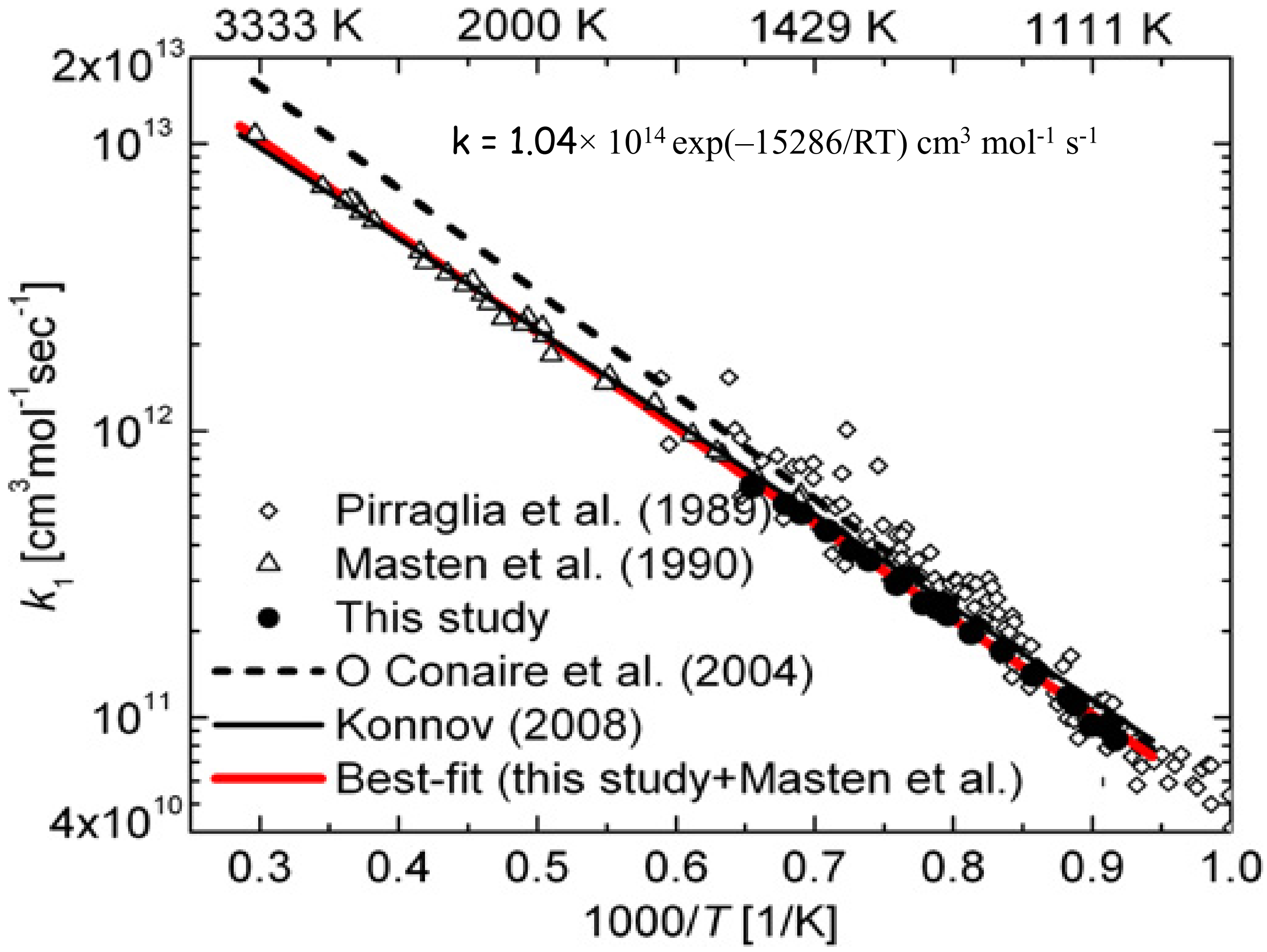
Fuel	Shock Tube	Jet-Stirred Reactor	Flow Reactor	Flame Speed	Flame Speciation
Methane	✓	✓	✓	✓	✓
Ethane	✓	✓		✓	
Ethylene	✓	✓	✓	✓	✓
Acetylene	✓		✓	✓	✓
Formaldehyde			✓		✓
Acetaldehyde	✓		✓		
Methanol	✓		✓	✓	
Ethanol	✓	✓	✓	✓	✓
Temperature / K	833—2500	800—1260	600—1400	295—600	300—2300
Pressure (atm)	0.65—260	1—10	1.0—59.2	1—10	0.03—0.05
Equivalence ratio	0.06—6.0	0.25—5.0	0.05—5.0	0.4—2.2	0.75—2.4

Sensitivity Analysis—CH_4 Flame Speed

p = 1.0 atm, T_i = 298 K



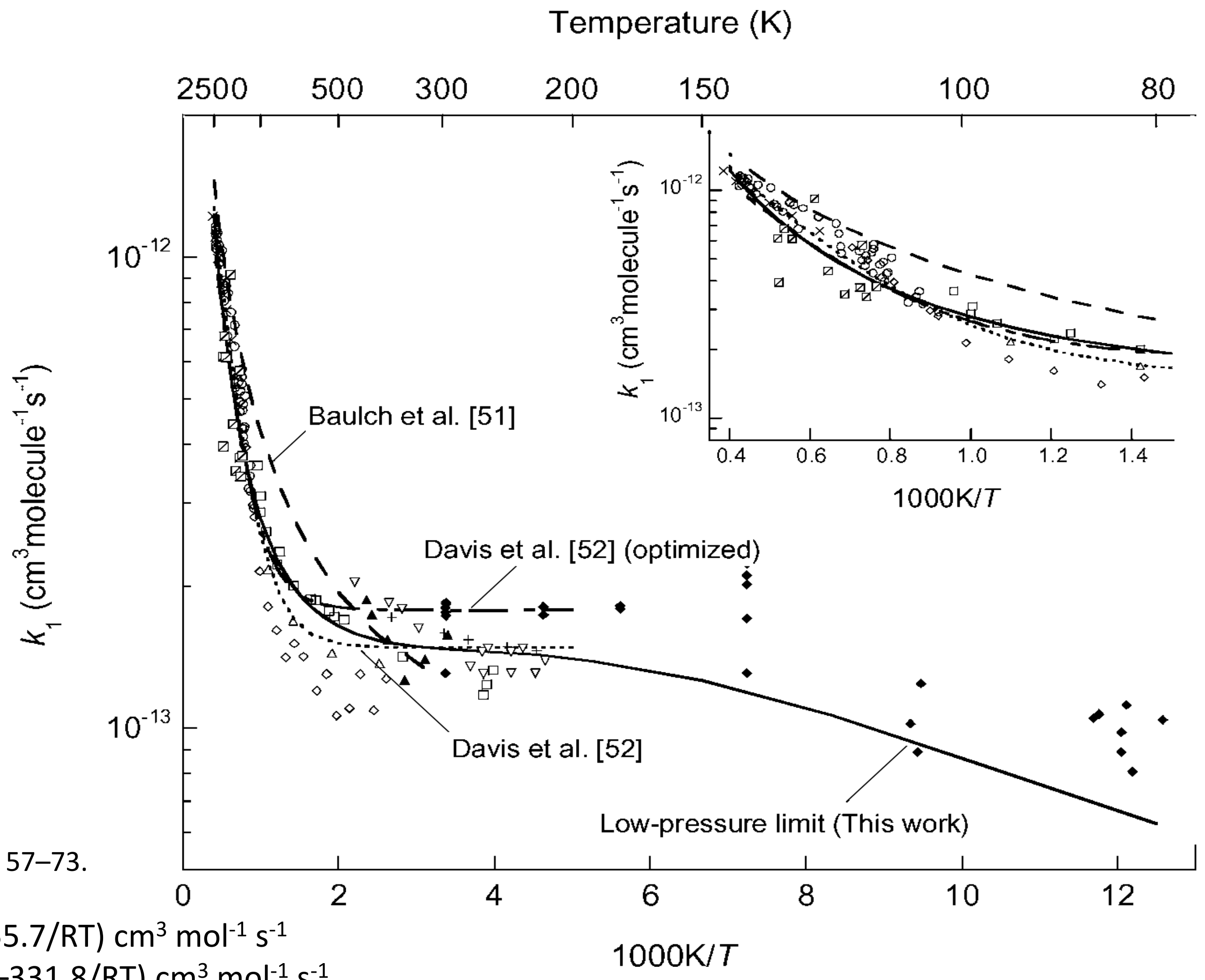
$\dot{H} + O_2 = \ddot{O} + \dot{O}H$



$k = 1.04 \times 10^{14} \exp(-15286/RT)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$

Z. Hong, D.F. Davidson, E.A. Barbour, R.K. Hanson
Proc. Combust. Inst. 33 (2011) 309–316.

$CO + \dot{O}H = CO_2 + \dot{H}$



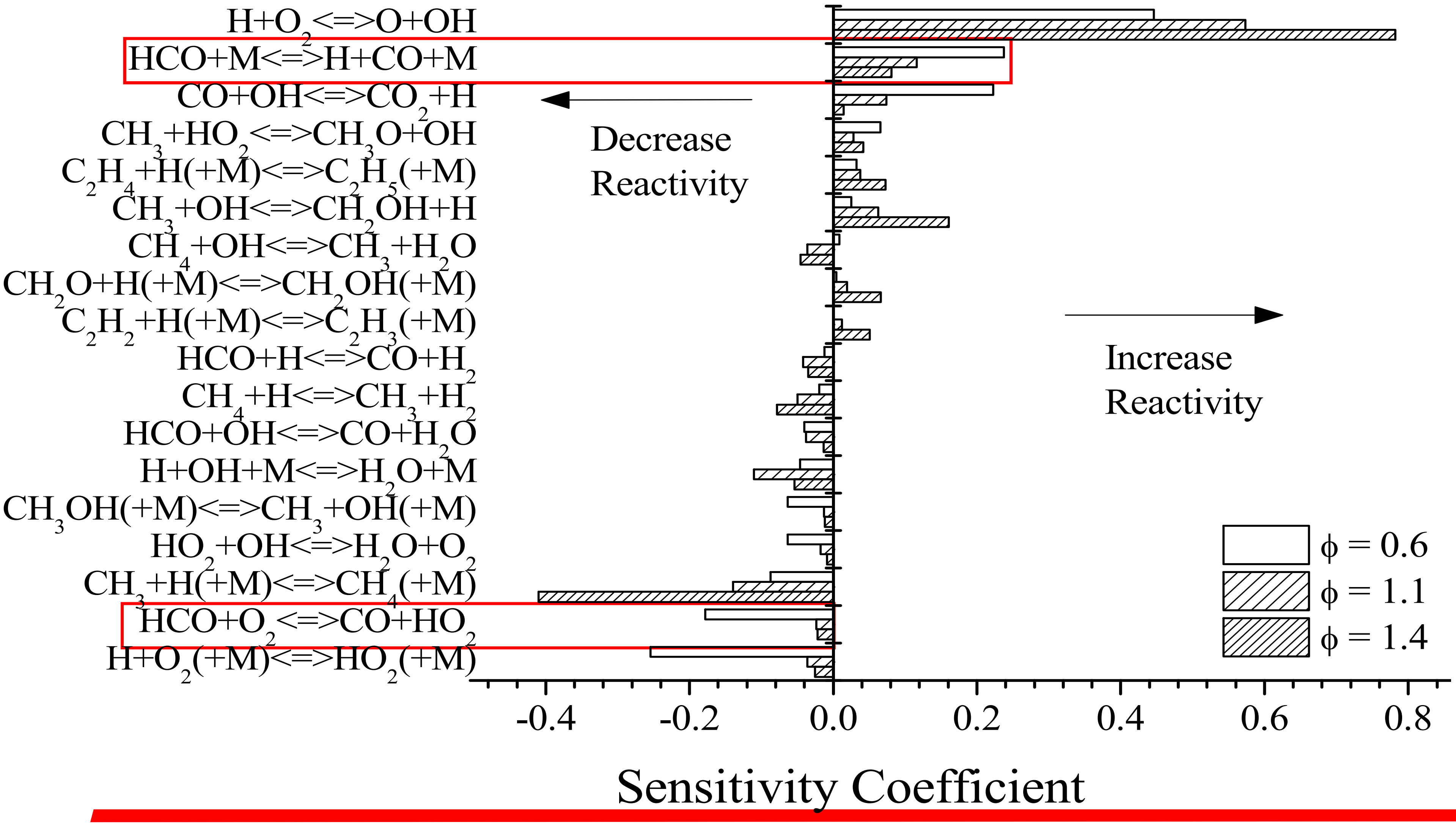
A.V. Joshi, H. Wang

Int. J. Chem. Kinet. 38 (1) (2006) 57–73.

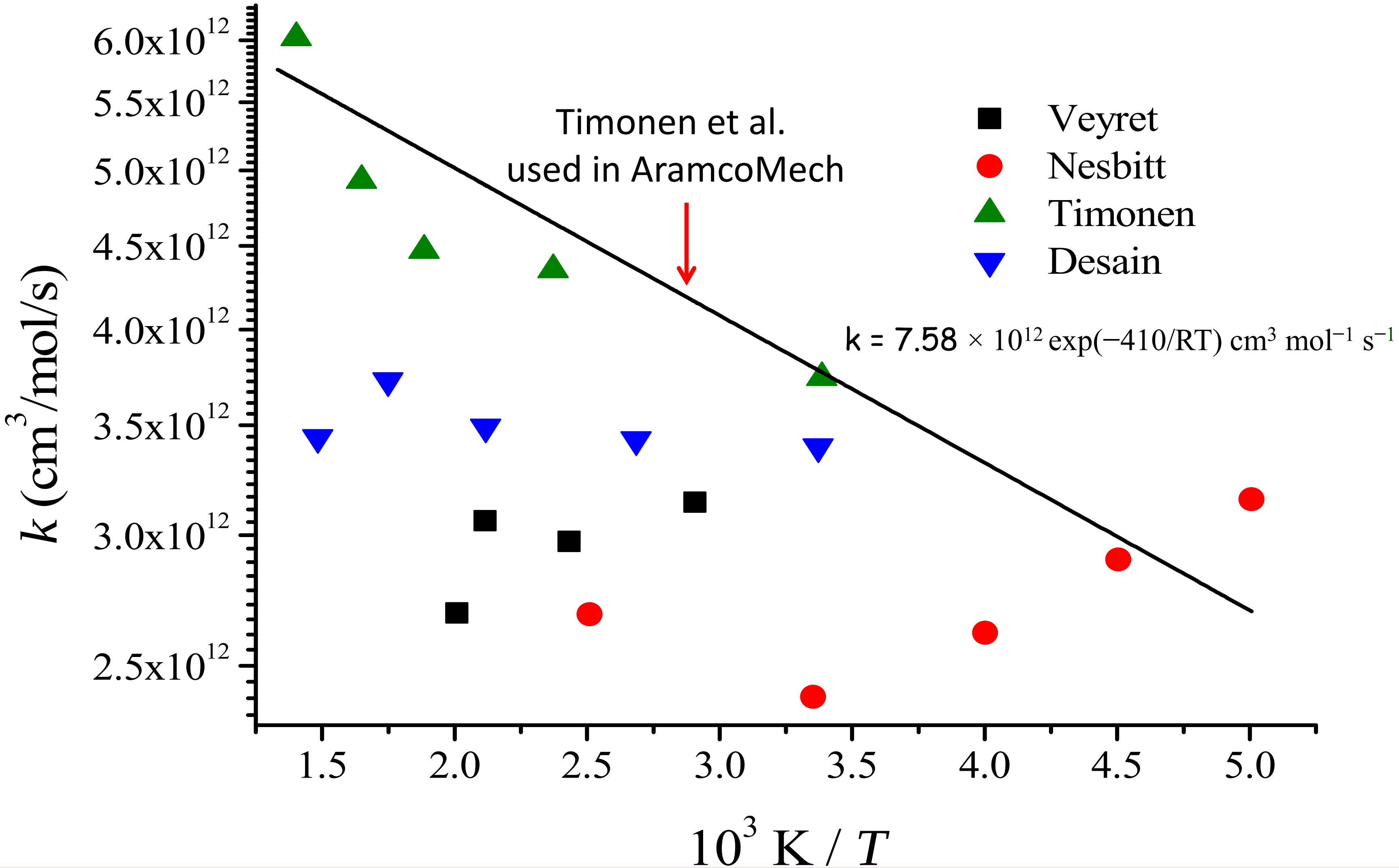
$$k = 7.015\times 10^{14}\, T^{2.053} \exp(355.7/RT)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}} \\ \quad + 5.757\times 10^{12}\, T^{-0.664} \exp(-331.8/RT)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$

Sensitivity Analysis—CH_4 Flame Speed

p = 1.0 atm, T_i = 298 K

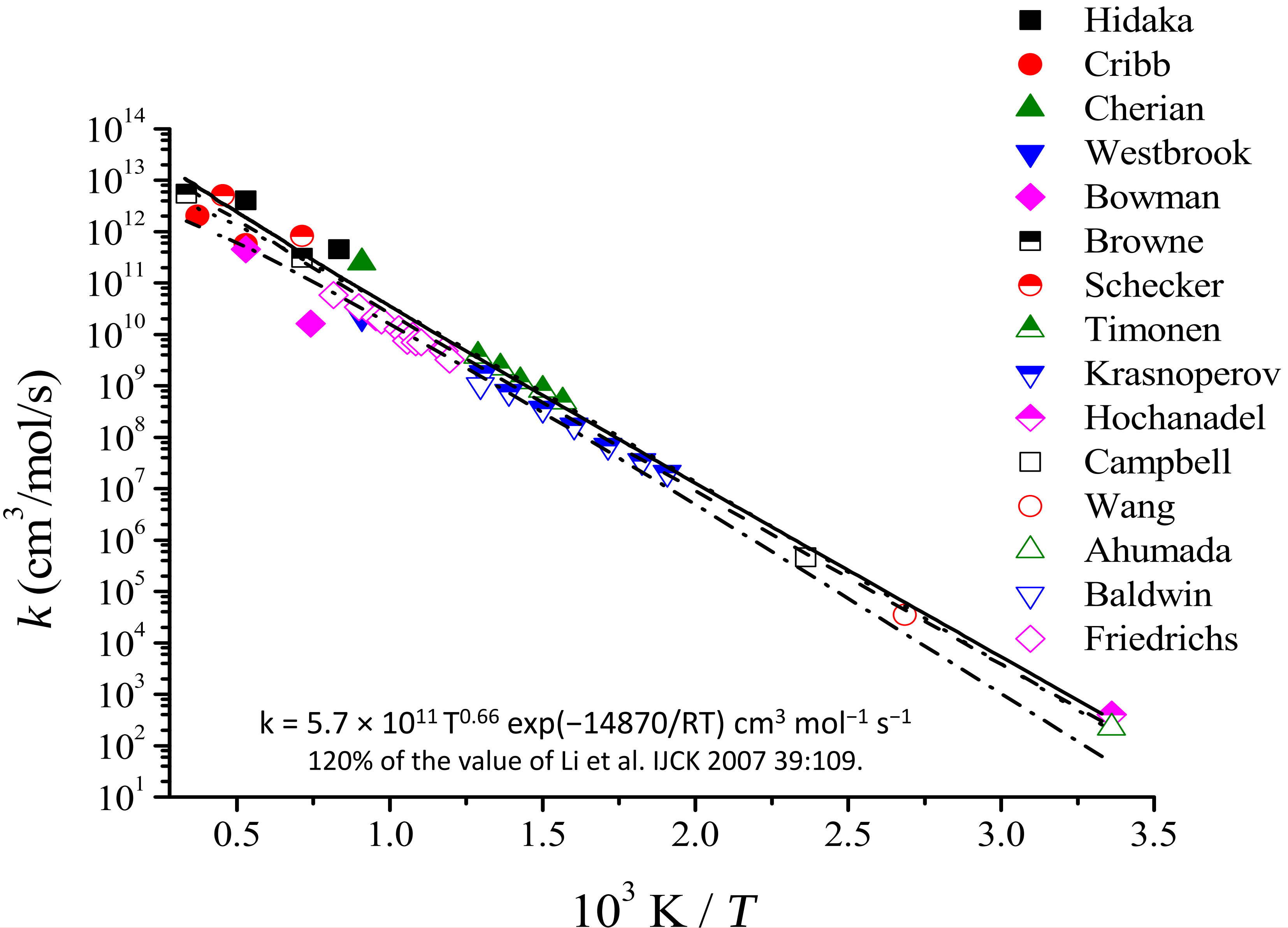


$\mathrm{HC\dot{O}} + \mathrm{O_2} = \mathrm{CO} + \mathrm{H\dot{O}_2}$


Timonen et al.
used in AramcoMech

$k = 7.58 \times 10^{12} \exp(-410/RT)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$

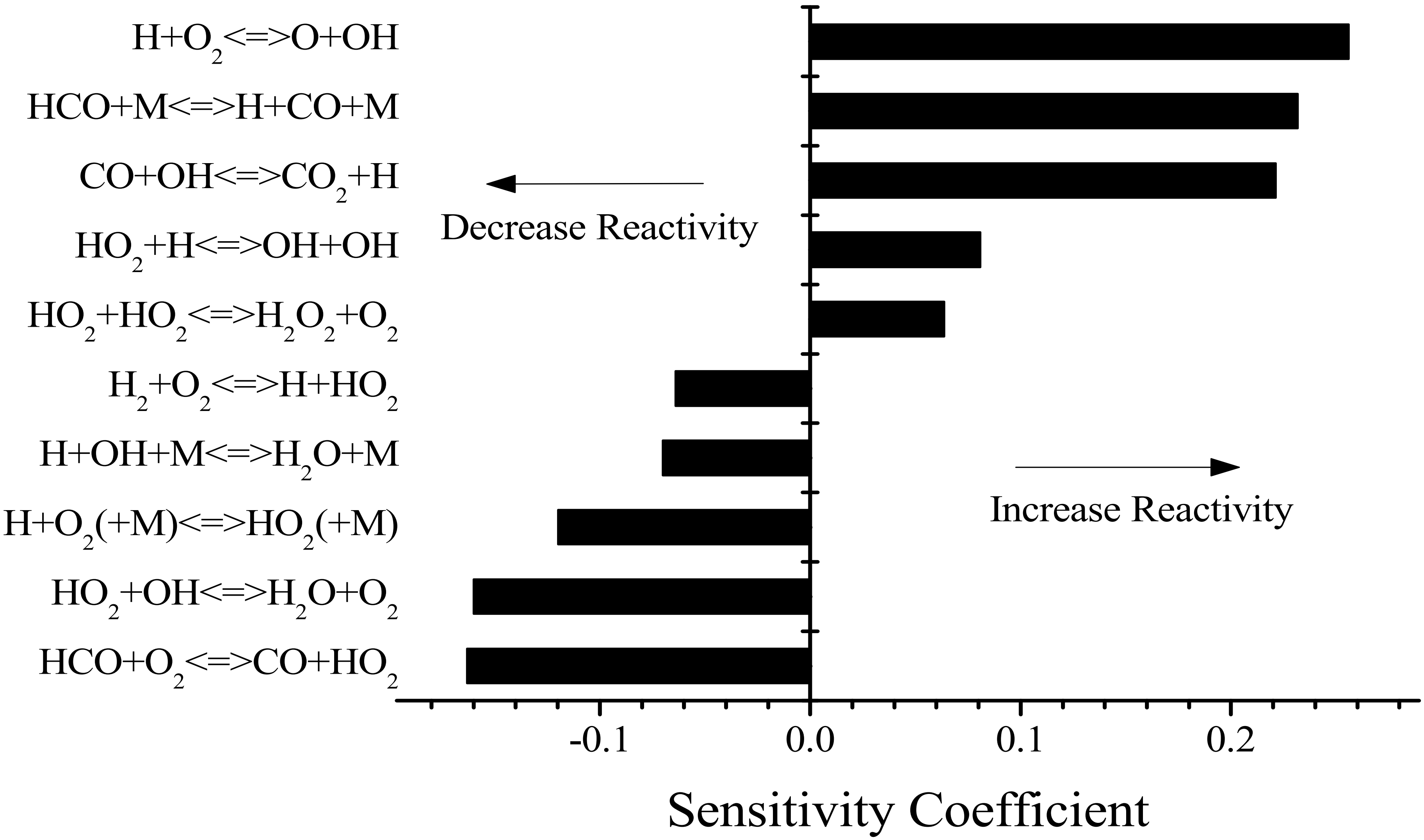
$HC\dot{O} + M = \dot{H} + CO + M$



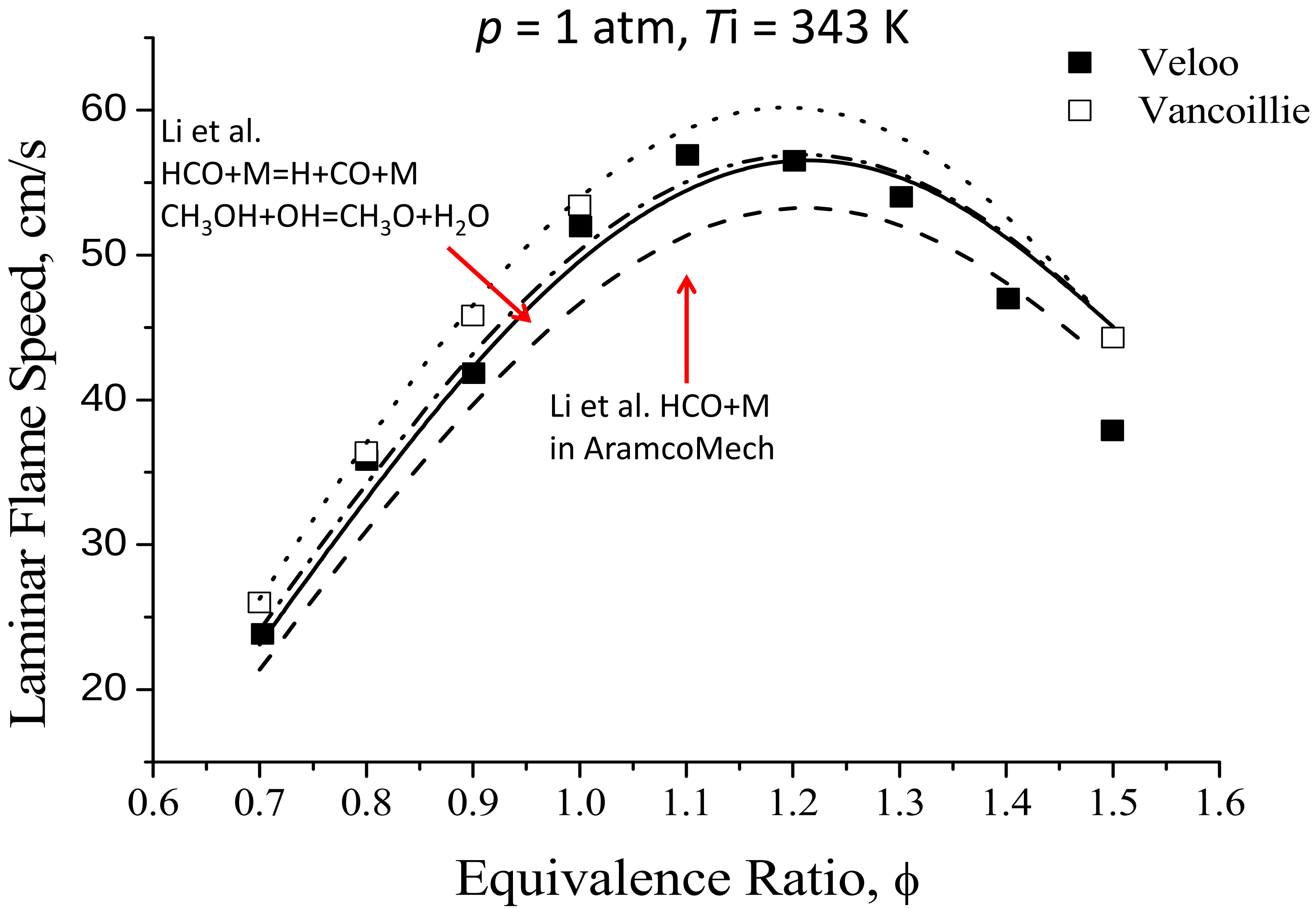
$k = 5.7 \times 10^{11}\, T^{0.66} \exp(-14870/RT)$ cm^3 mol^{-1} s^{-1}

120% of the value of Li et al. IJCK 2007 39:109.

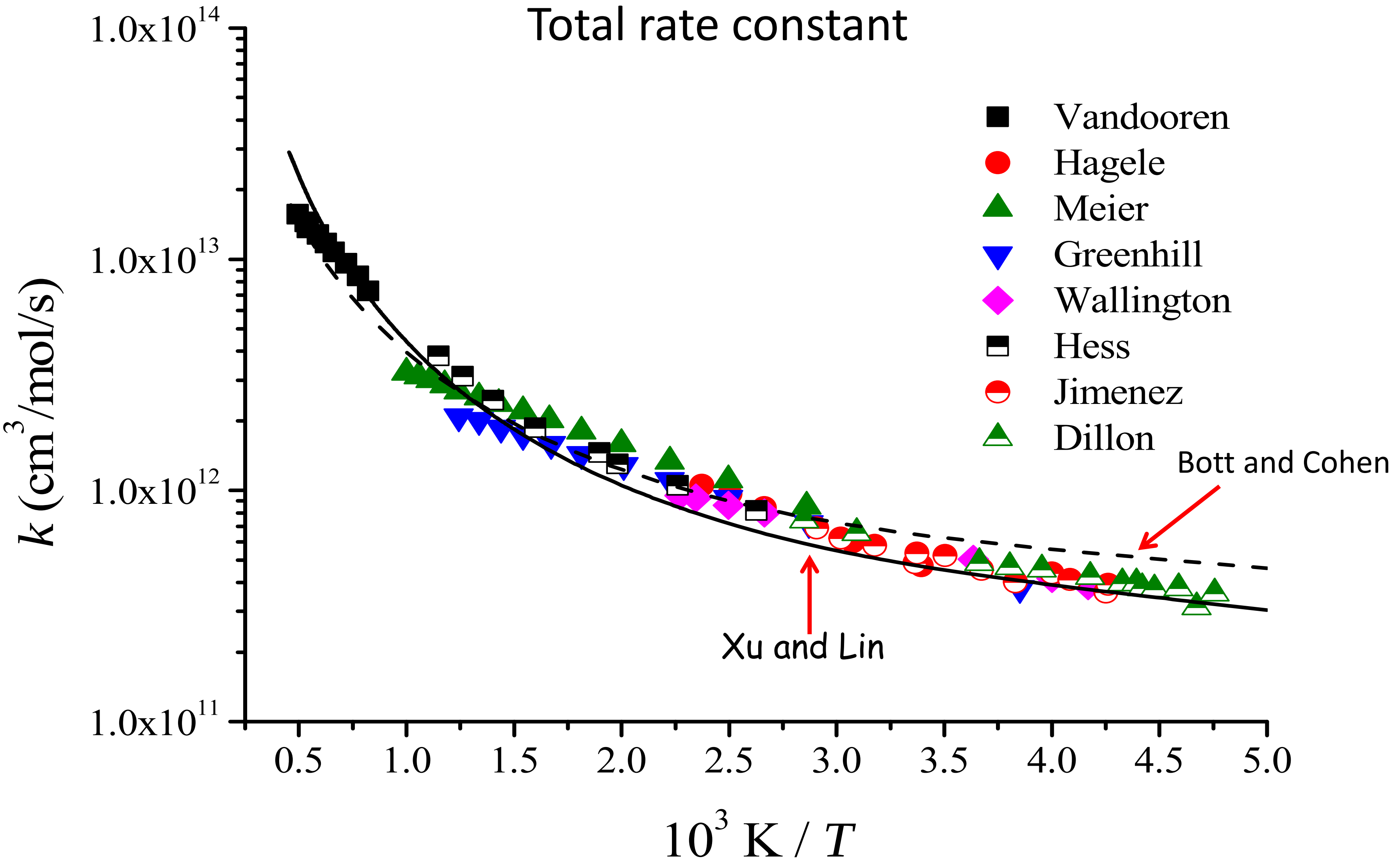
HCȮ + M: large influence on CH_3OH S_L



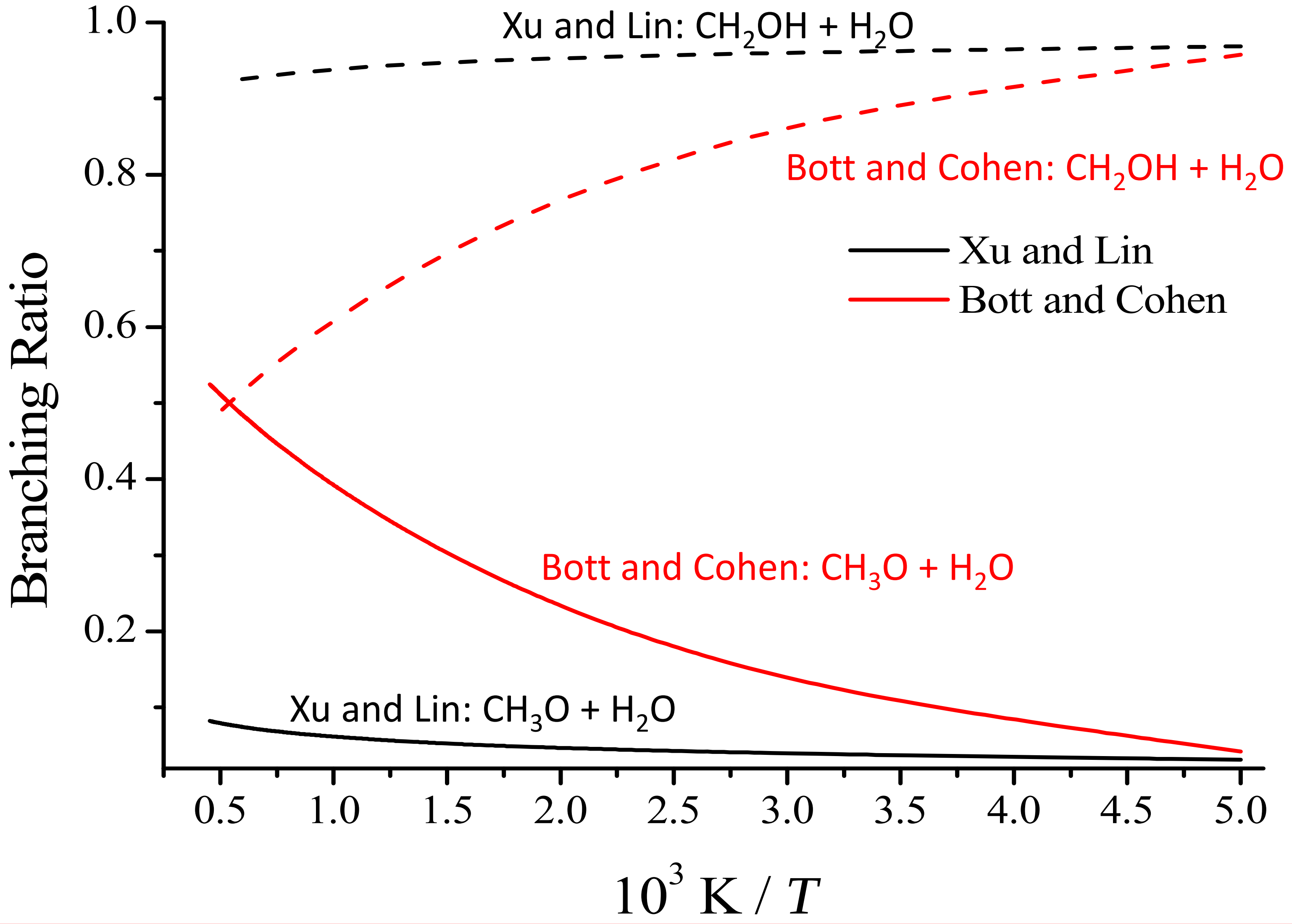
HCȮ + M: large influence on CH_3OH S_L



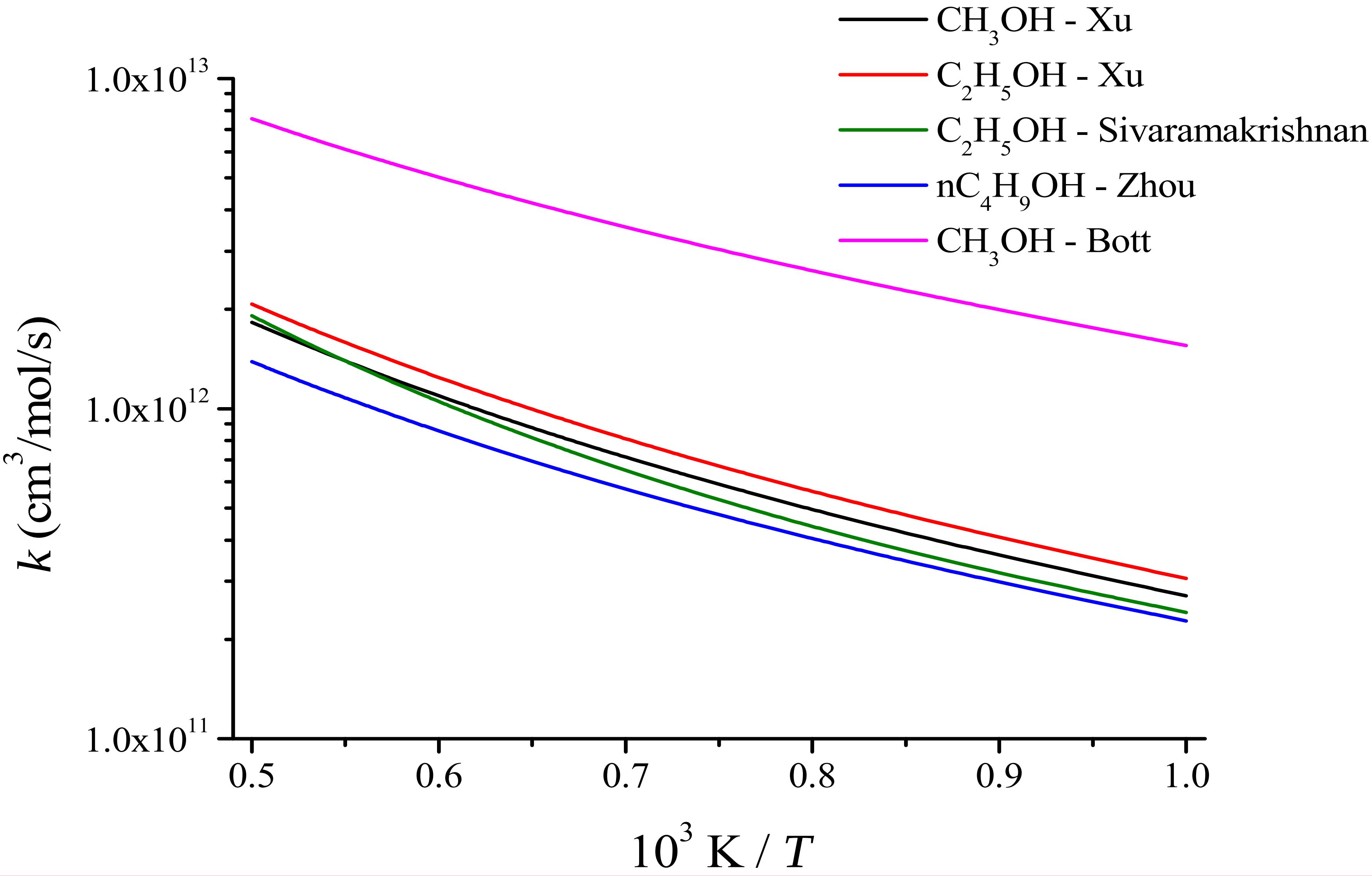
$CH_3OH + \dot{O}H = CH_3\dot{O}/\dot{C}H_2OH + H_2O$



$CH_3OH + \dot{O}H$ = products

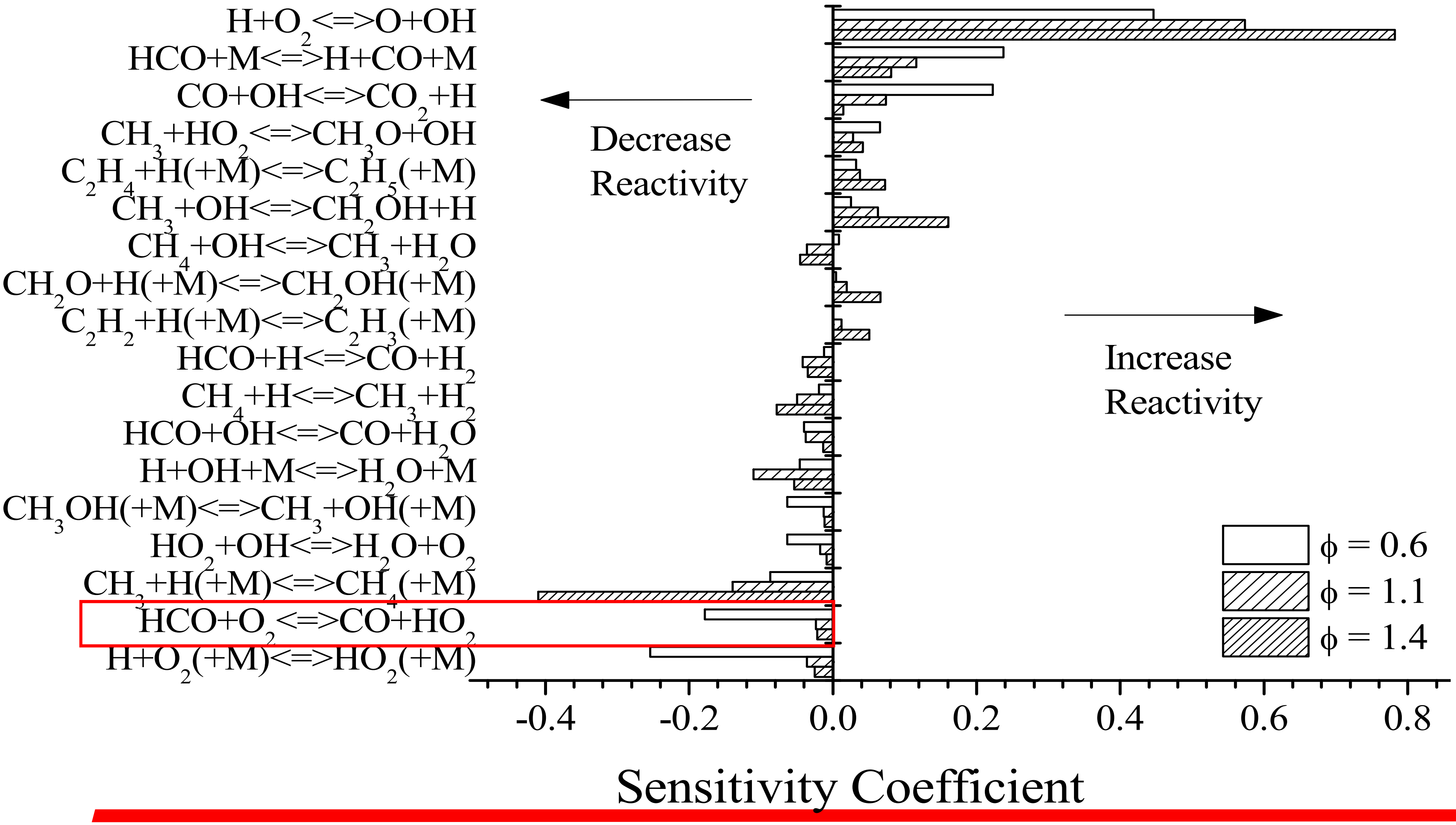


Alcohol + $\dot{O}H = R\dot{O} + H_2O$



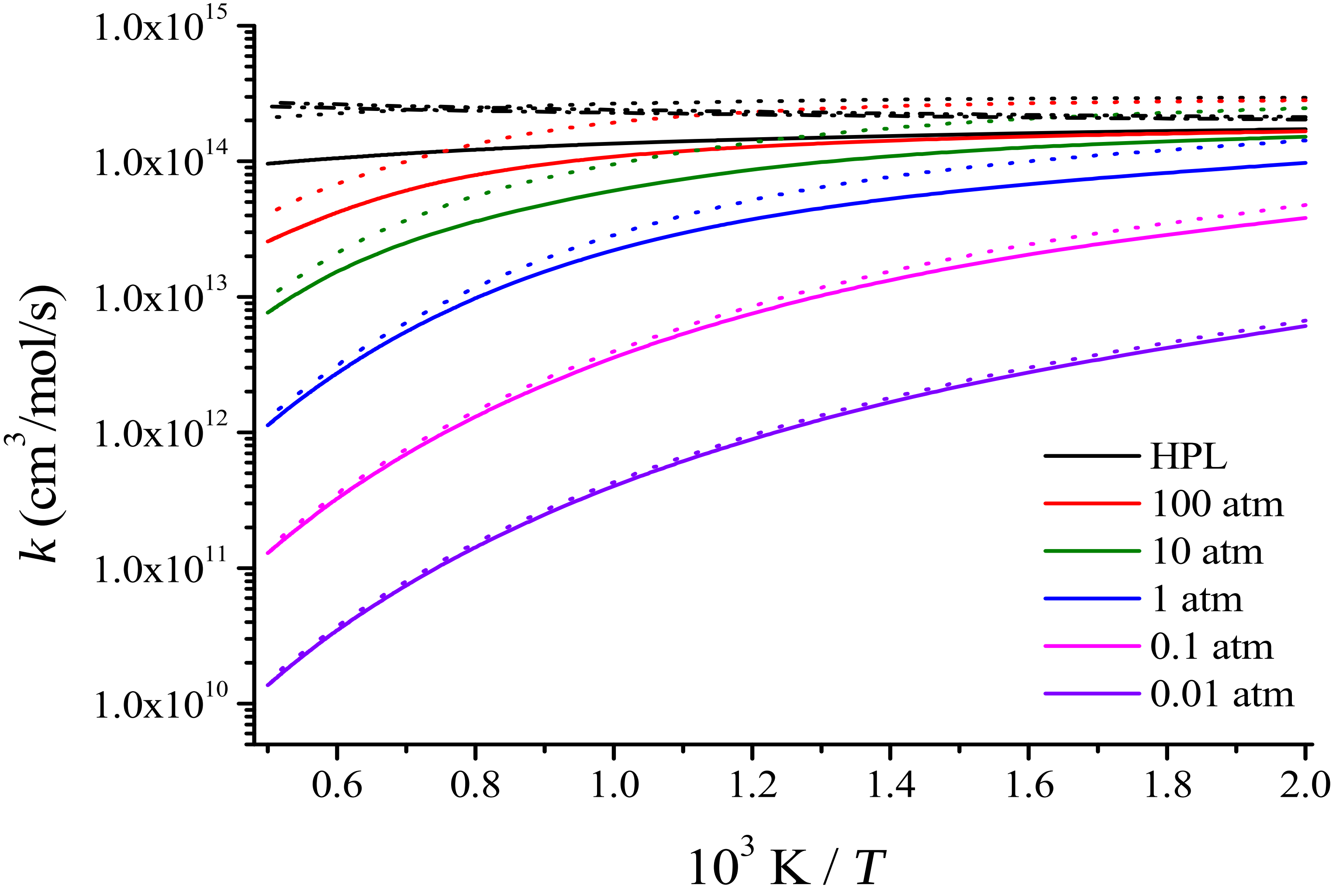
Sensitivity Analysis—CH_4 Flame Speed

$p = 1.0$ atm, $T_i = 298$ K

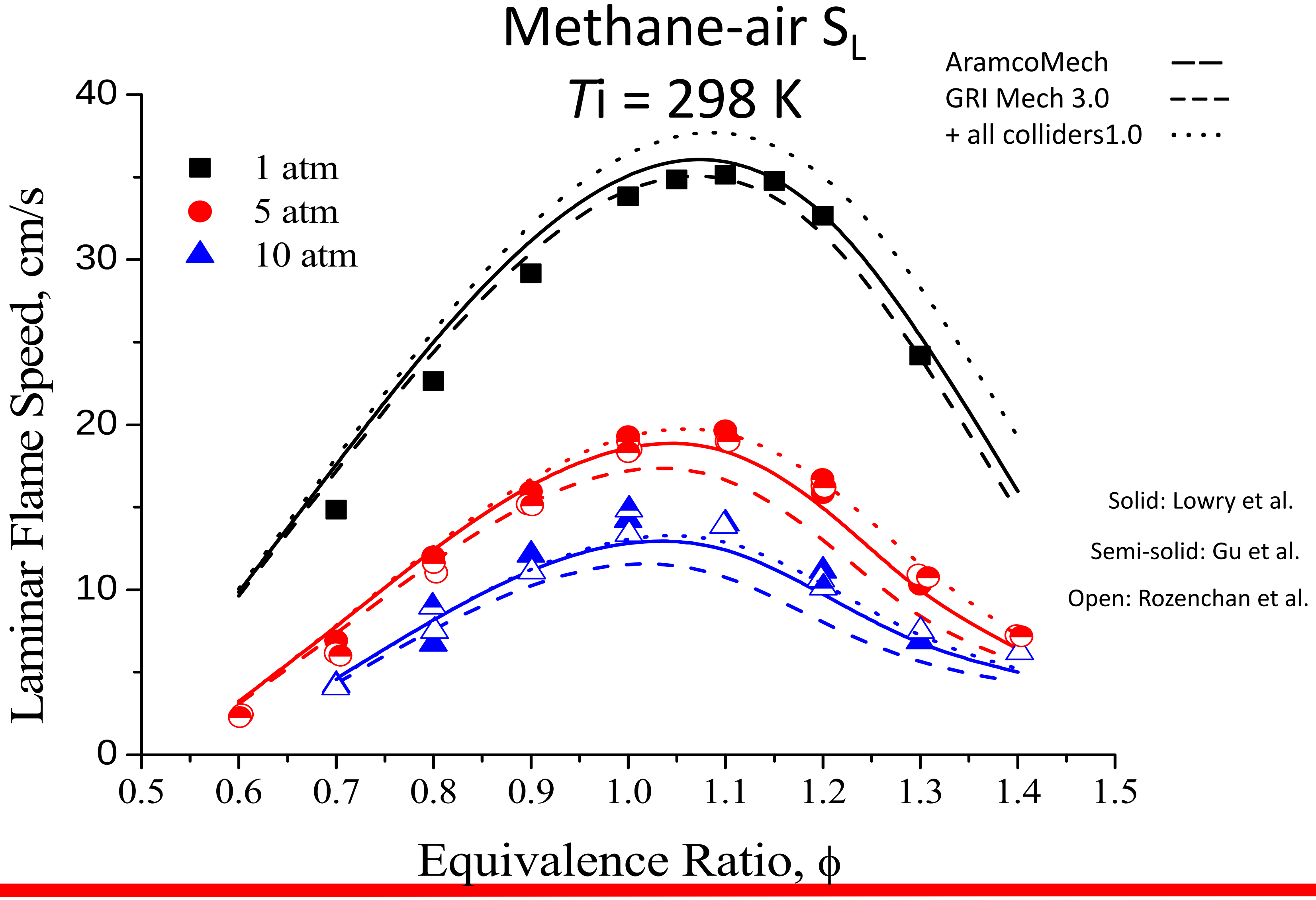


$\dot{C}H_3 + \dot{H}$ (+ M) = CH_4 (+ M)

AramcoMech —
USC Mech II —
San Diego Mech —
GRI Mech 3.0 · · ·
Klippenstein et al. – · –



Effect of $\dot{\mathrm{C}}\mathrm{H}_3 + \dot{\mathrm{H}}\ (+\ \mathrm{M}) = \mathrm{CH}_4\ (+\ \mathrm{M})$



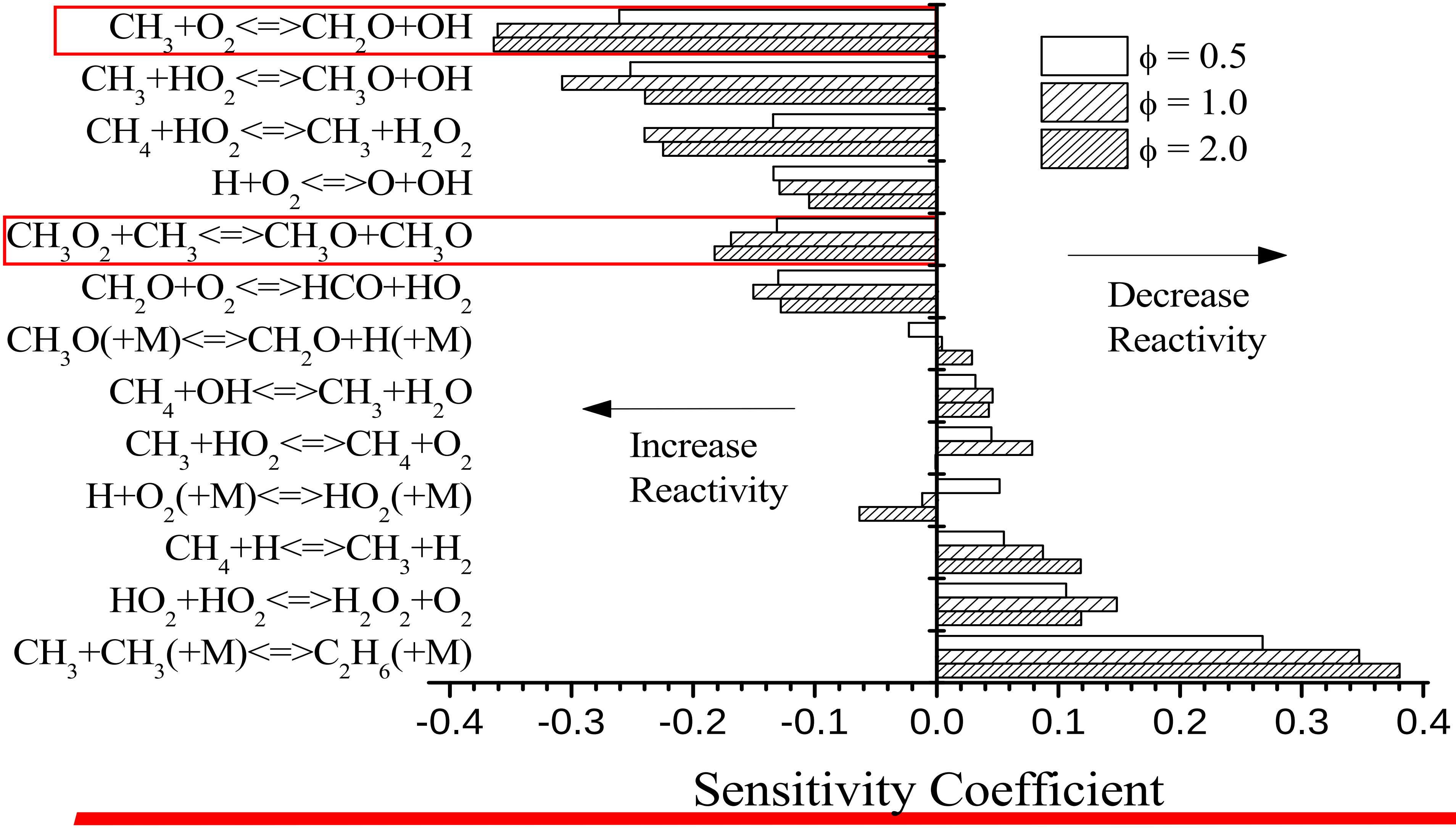
Solid: Lowry et al.

Semi-solid: Gu et al.

Open: Rozenchan et al.

Sensitivity Analysis—CH_4 ST τ

1250 K, 30 atm

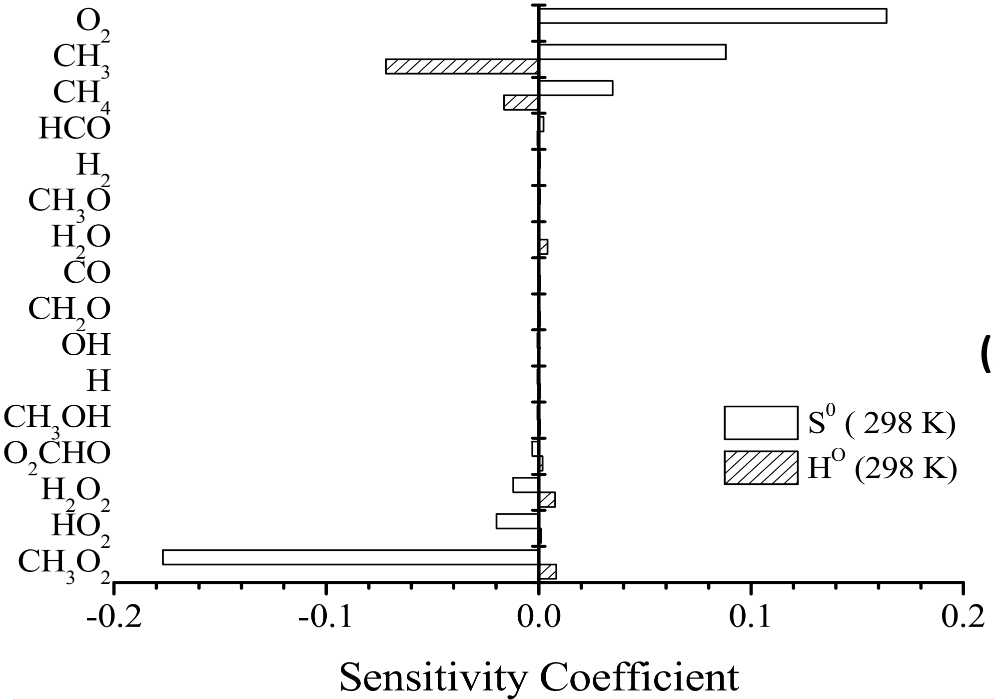


$\dot{C}H_3 + O_2 \rightarrow$ products

- $\dot{C}H_3 + O_2$ (+M) = $CH_3\dot{O}_2$ (+M) (Fernandes et al. JPCA 2006 110:4442)
- $\dot{C}H_3 + O_2 = CH_2O + \dot{O}H$ (S. Klippenstein, private communication)
- $\dot{C}H_3 + O_2 = CH_3\dot{O} + \ddot{O}$ (Srinivasan et al. 2005 JPCA 2005 109:7902)

Sensitivity of τ to thermochemistry

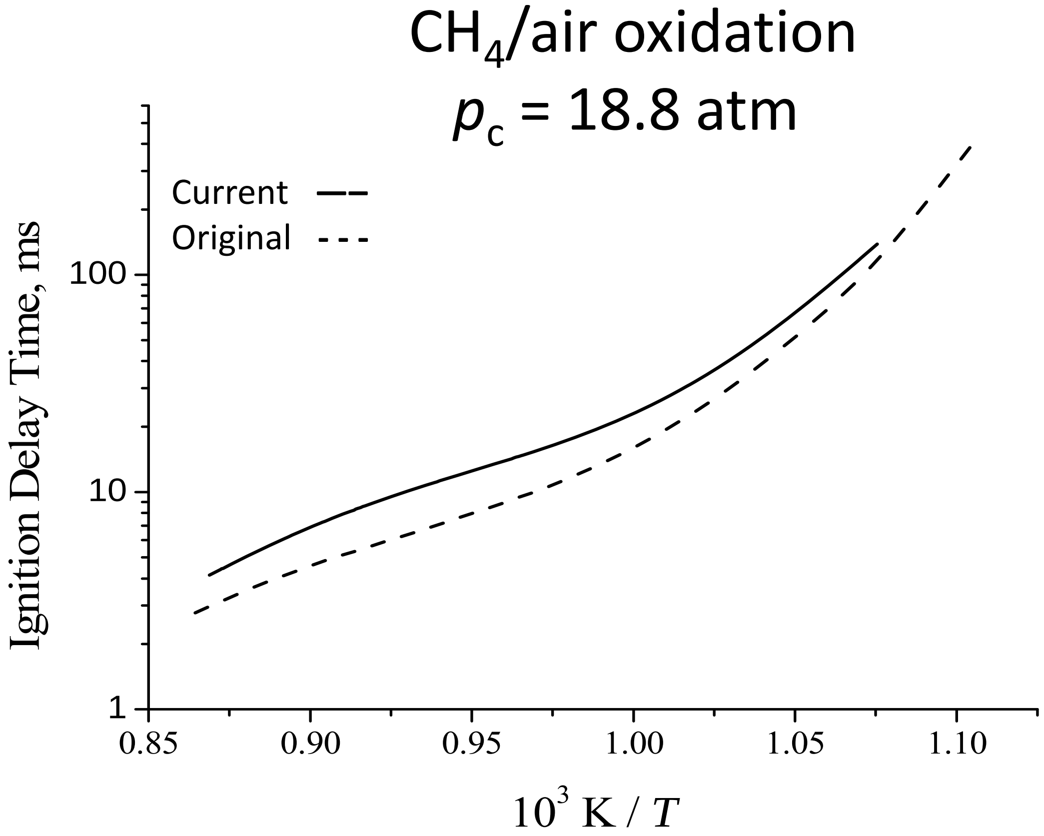
900 K, 20 atm



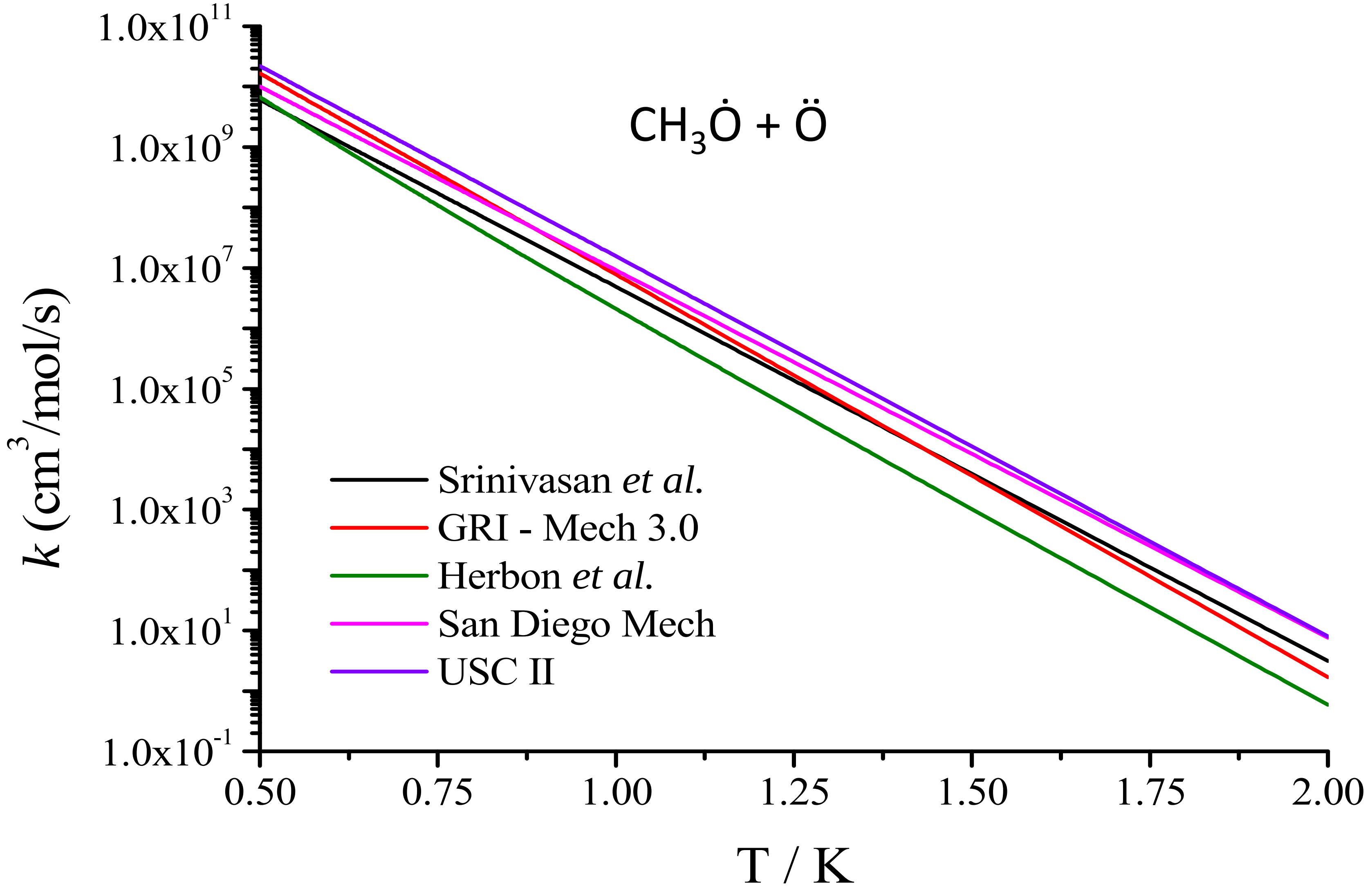
	H_f^0 **@ 298 K (kcal mol⁻¹)**	S_f^0 **@ 298 K (cal K⁻¹ mol⁻¹)**
Original	2.20	64.36
(Simmie et al.)	2.92	64.50

Effect of thermochemistry

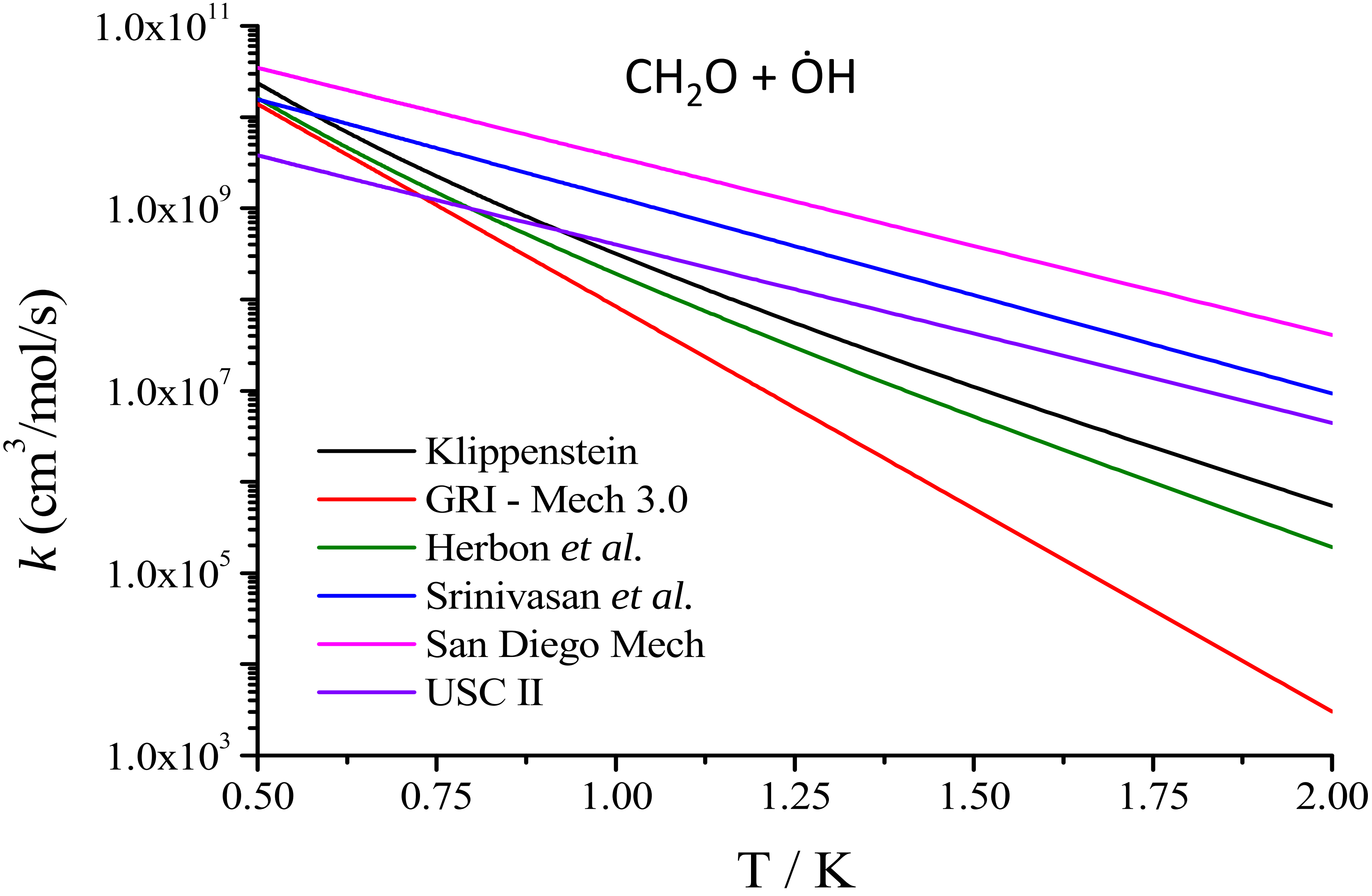
- $\dot{\mathrm{C}}\mathrm{H}_3 + \mathrm{O}_2 \leftarrow\!\!\!\rightleftharpoons \mathrm{CH}_3\dot{\mathrm{O}}_2$
- $\mathrm{CH}_3\dot{\mathrm{O}}_2 + \dot{\mathrm{C}}\mathrm{H}_3 = \mathrm{CH}_3\dot{\mathrm{O}} + \mathrm{CH}_3\dot{\mathrm{O}}\downarrow$



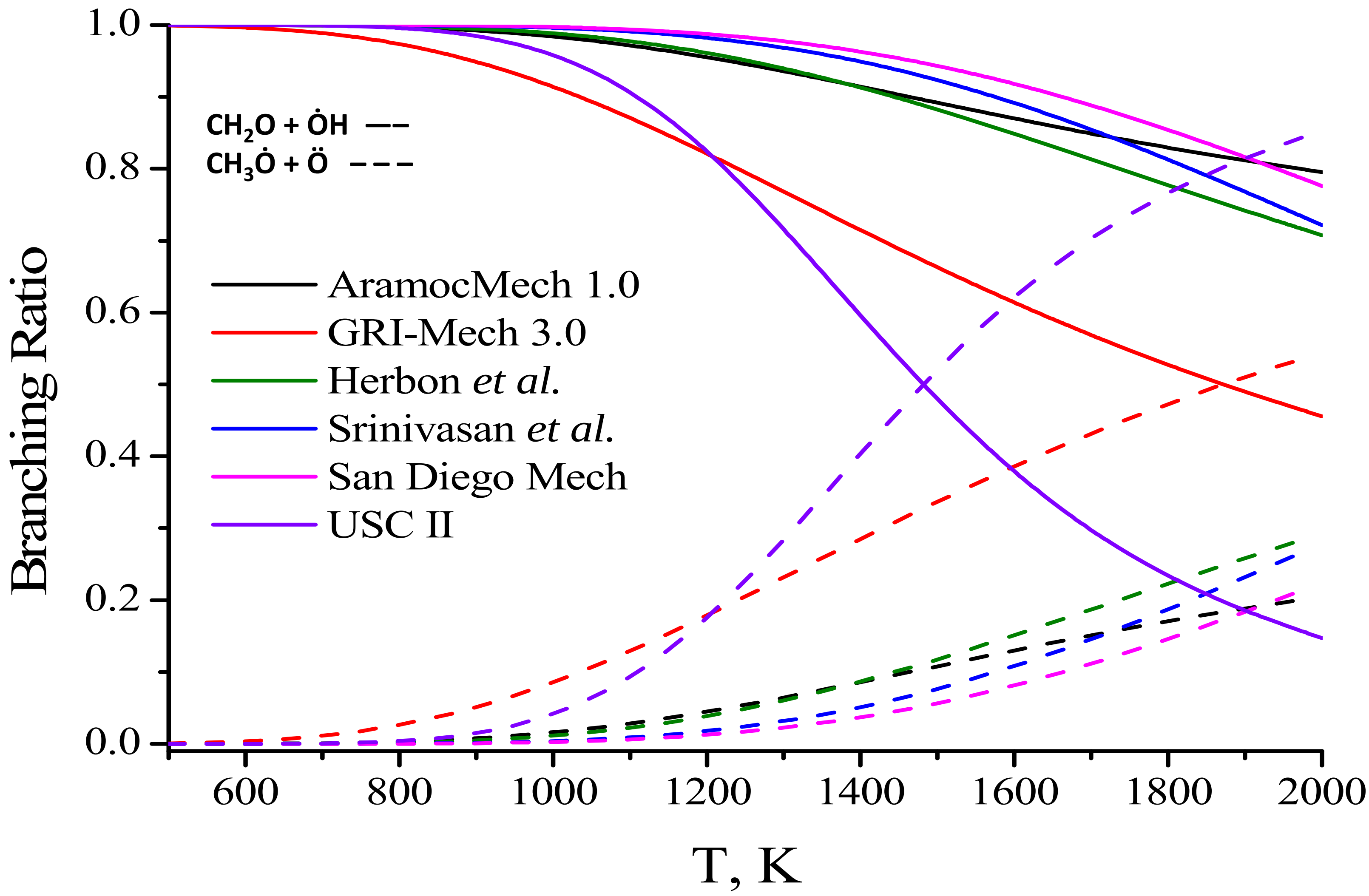
$\dot{C}H_3 + O_2$ reactions



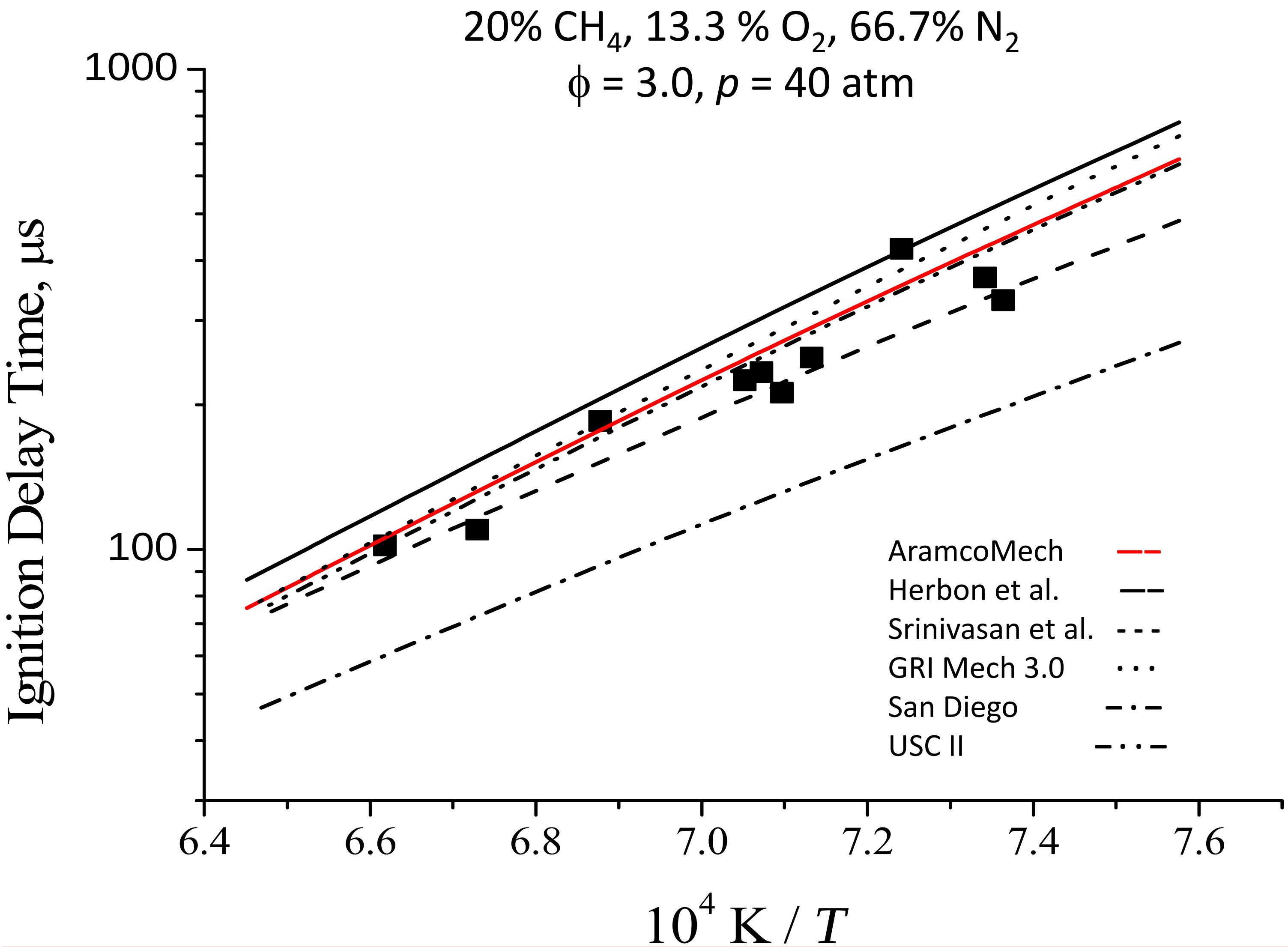
$\dot{C}H_3 + O_2$ reactions



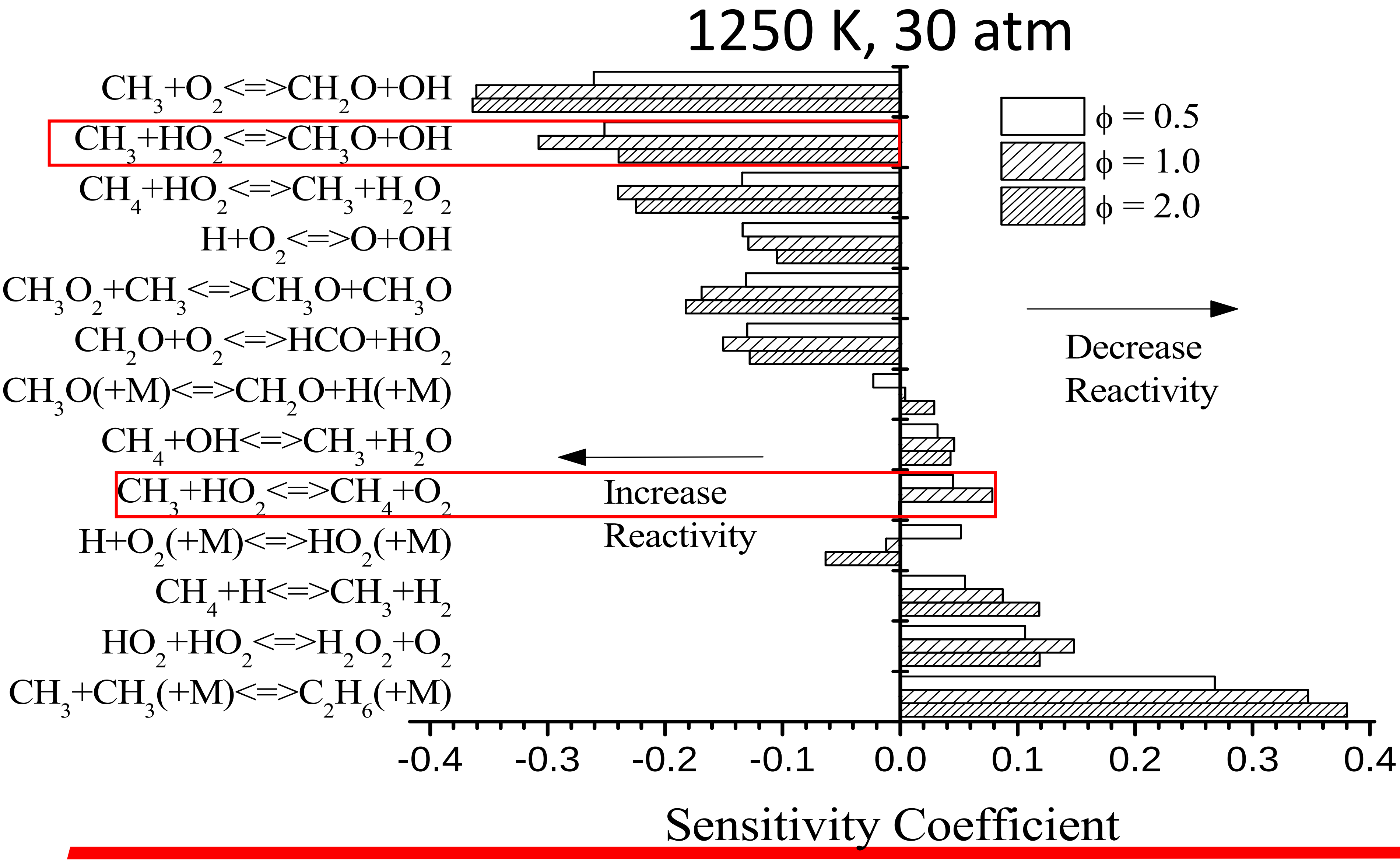
$\dot{C}H_3 + O_2$ reactions



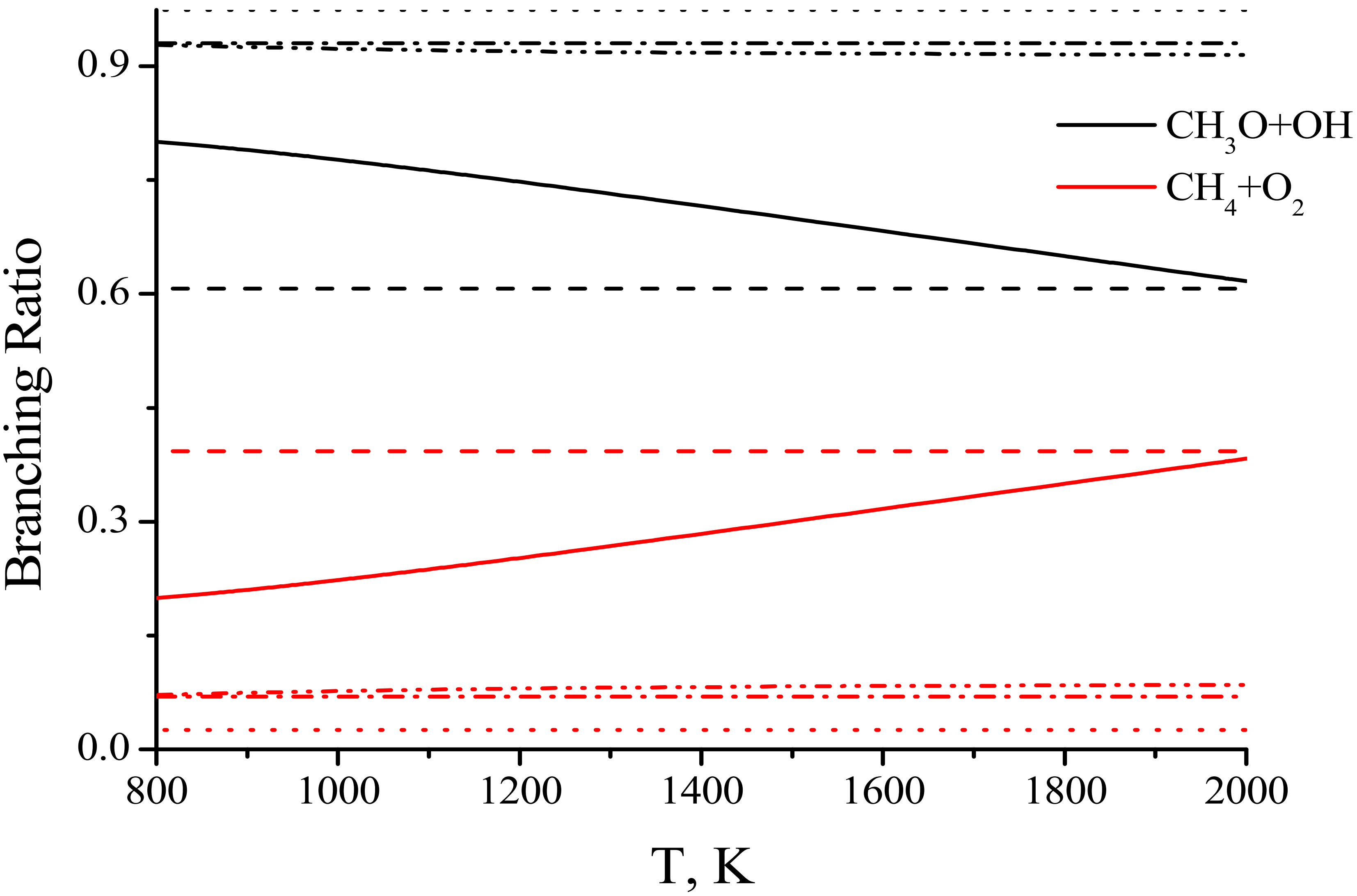
Influence of choice of $\dot{C}H_3 + O_2$ on τ



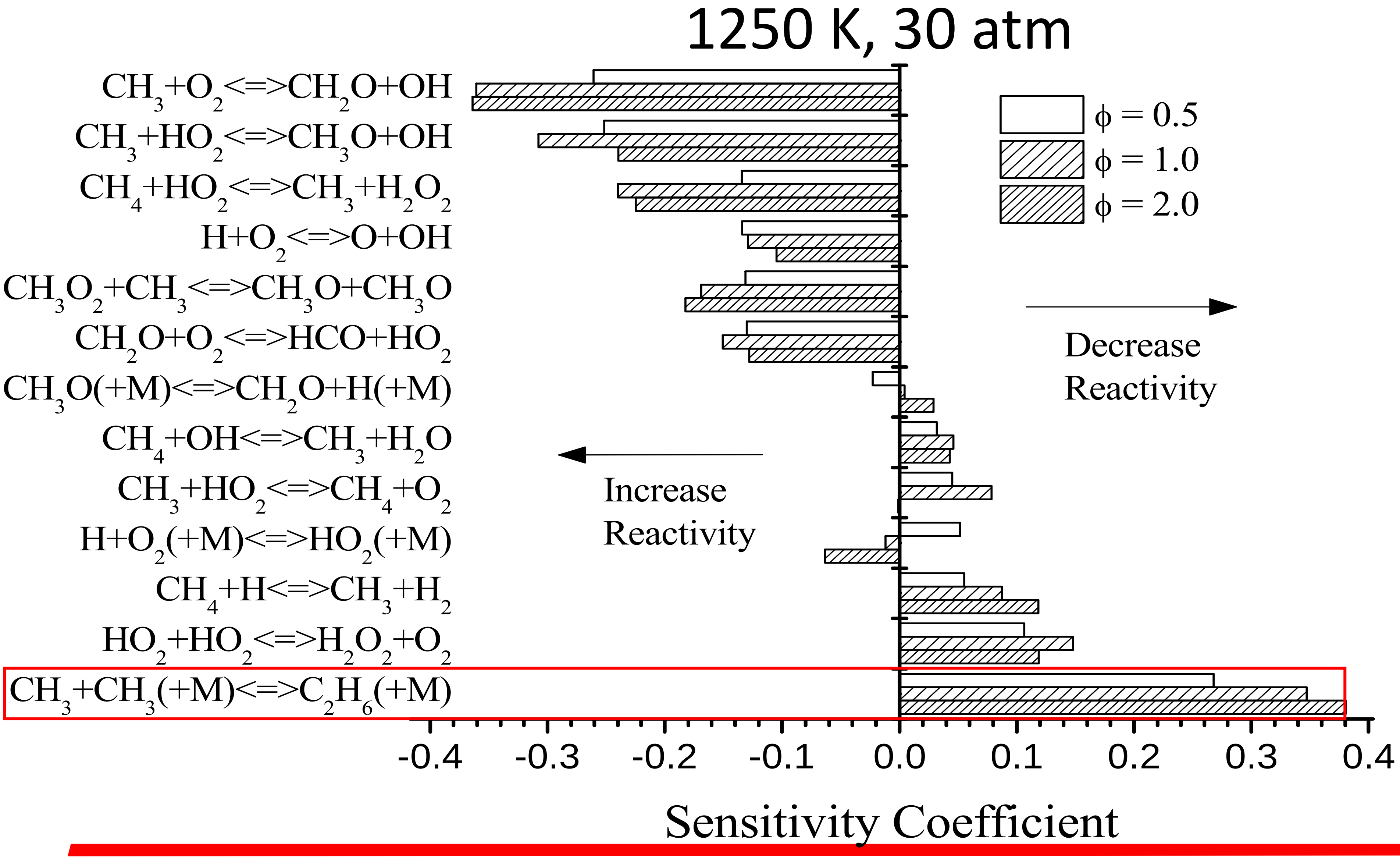
Sensitivity Analysis—CH_4 ST τ



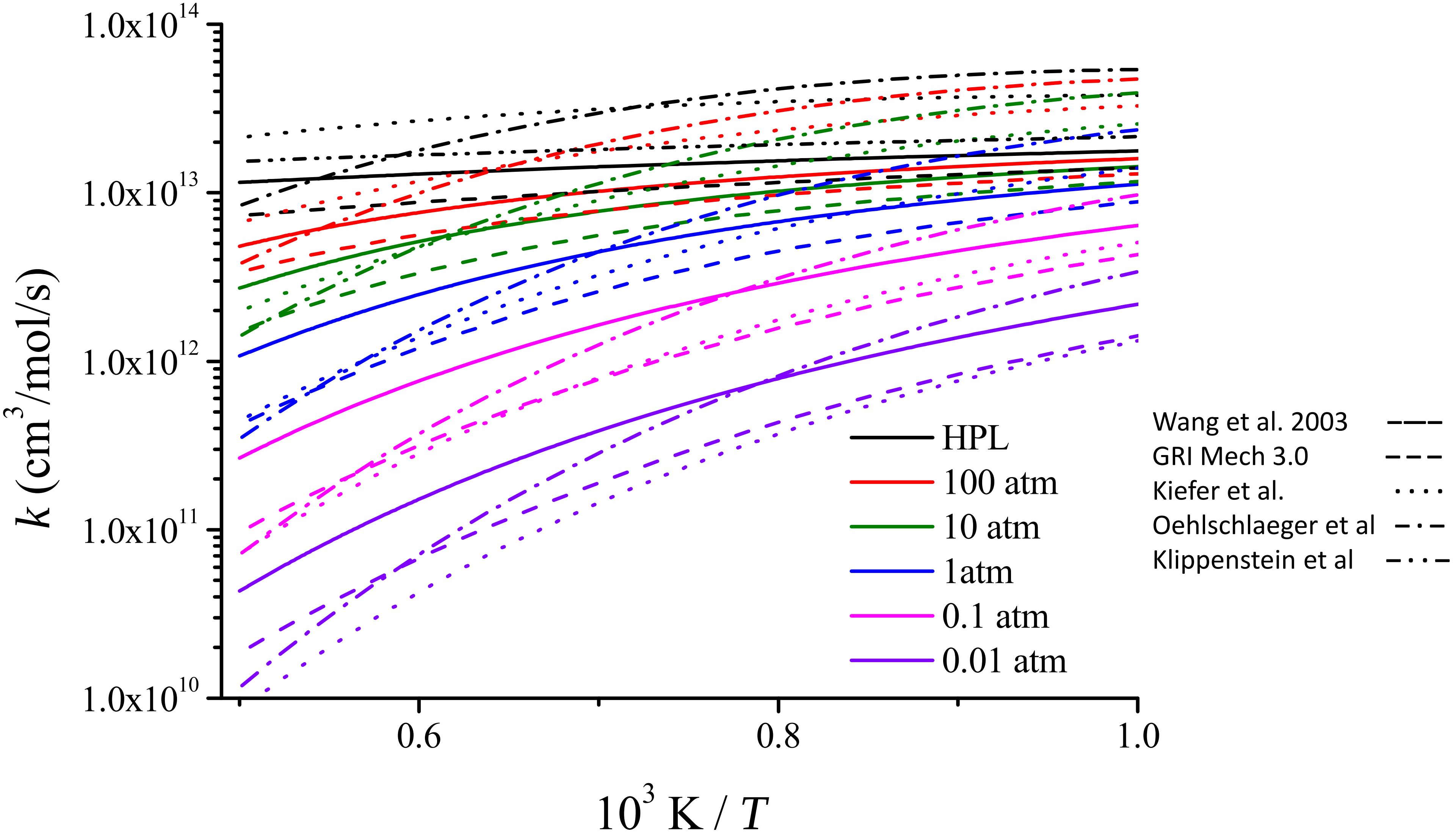
$\dot{C}H_3 + H\dot{O}_2$ branching ratio



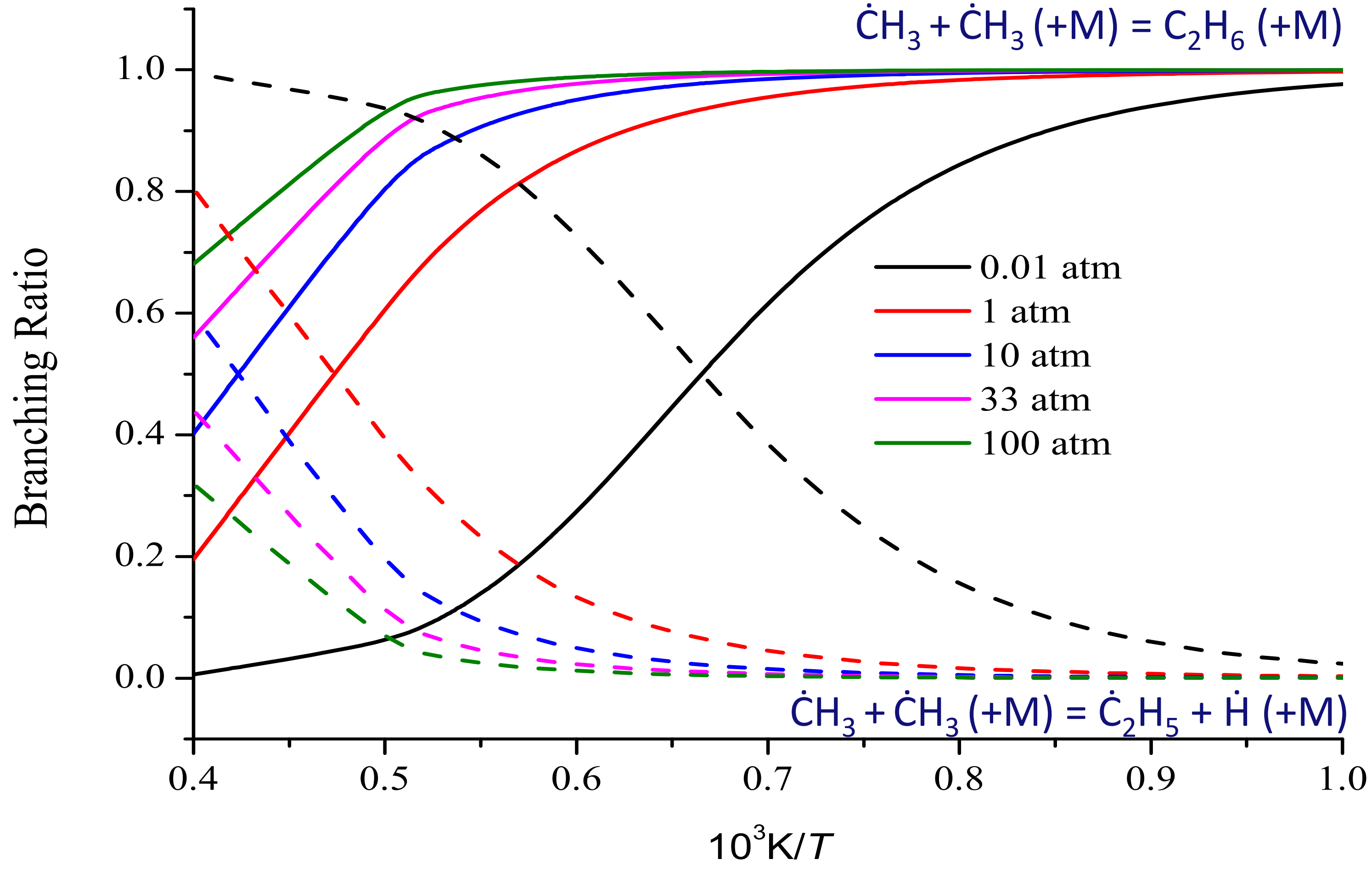
Sensitivity Analysis—ST ignition delay



$\dot{C}H_3 + \dot{C}H_3$ (+M) = C_2H_6 (+M)

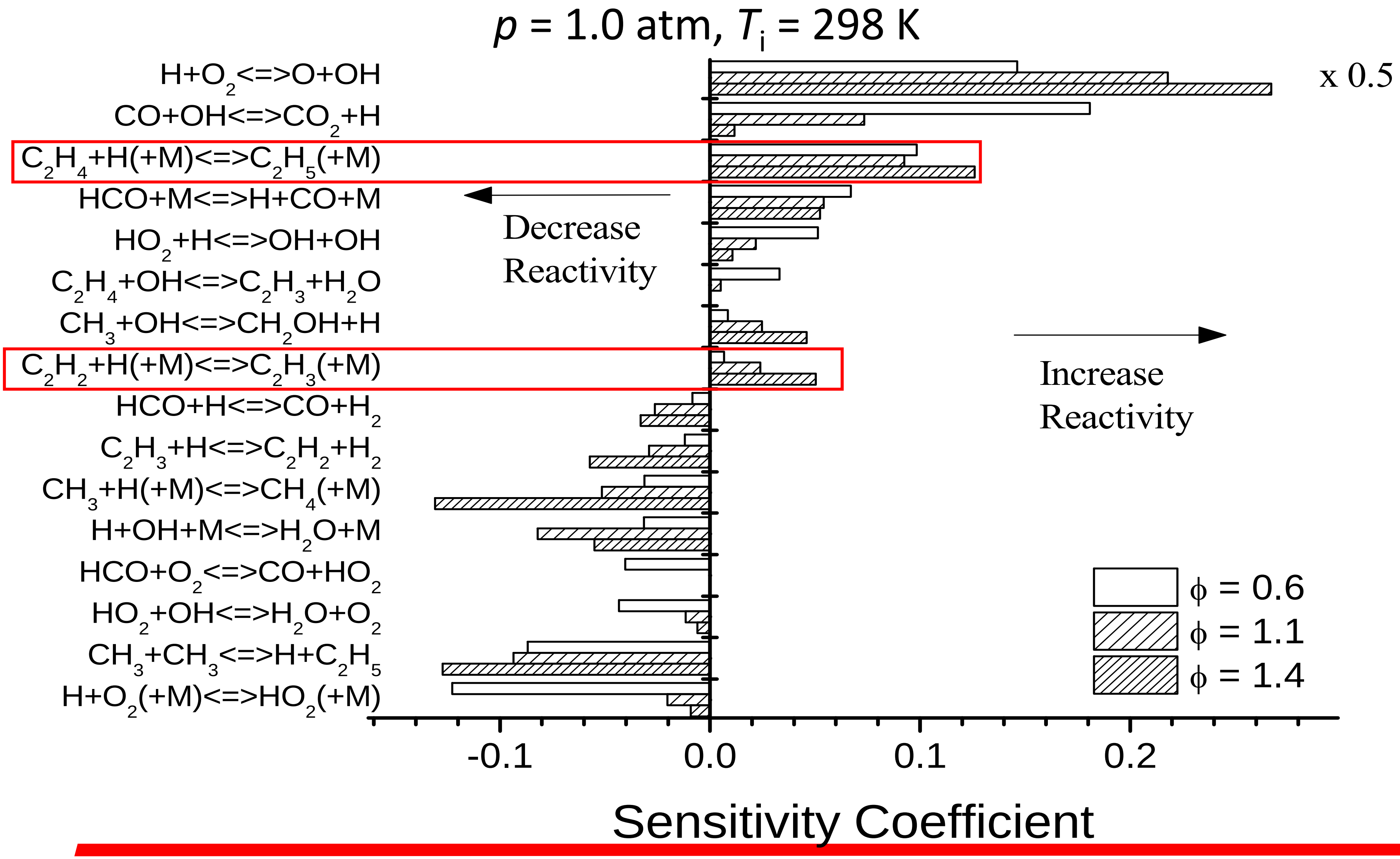


$\dot{C}H_3 + \dot{C}H_3\ (+M) = \dot{C}_2H_5 + \dot{H}\ (+M)$

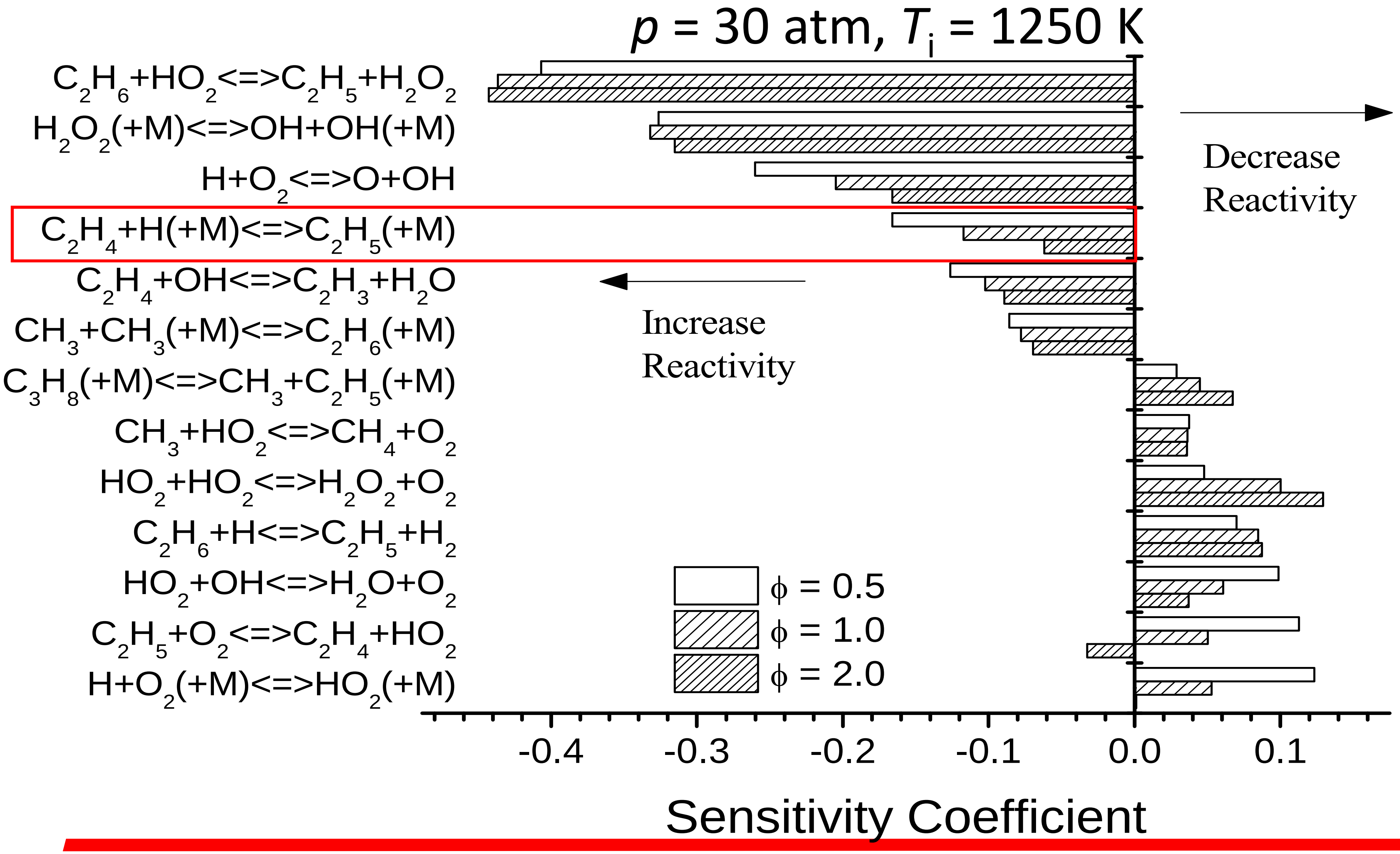


Stewart PH, La
of reacti
$2CH_3$

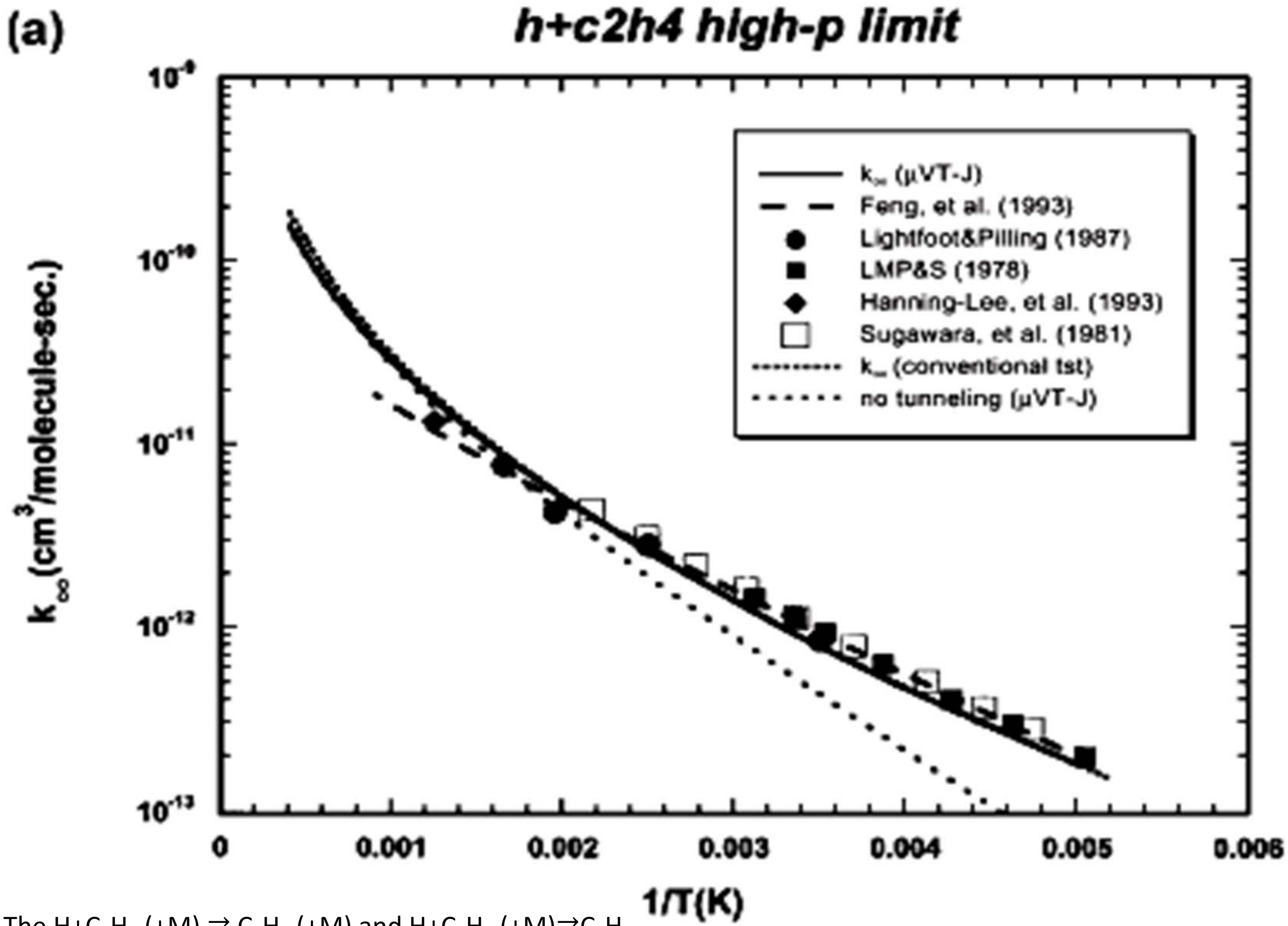
Sensitivity Analysis—C_2H_6 Flame Speed



Sensitivity Analysis—C_2H_6 Ignition delay

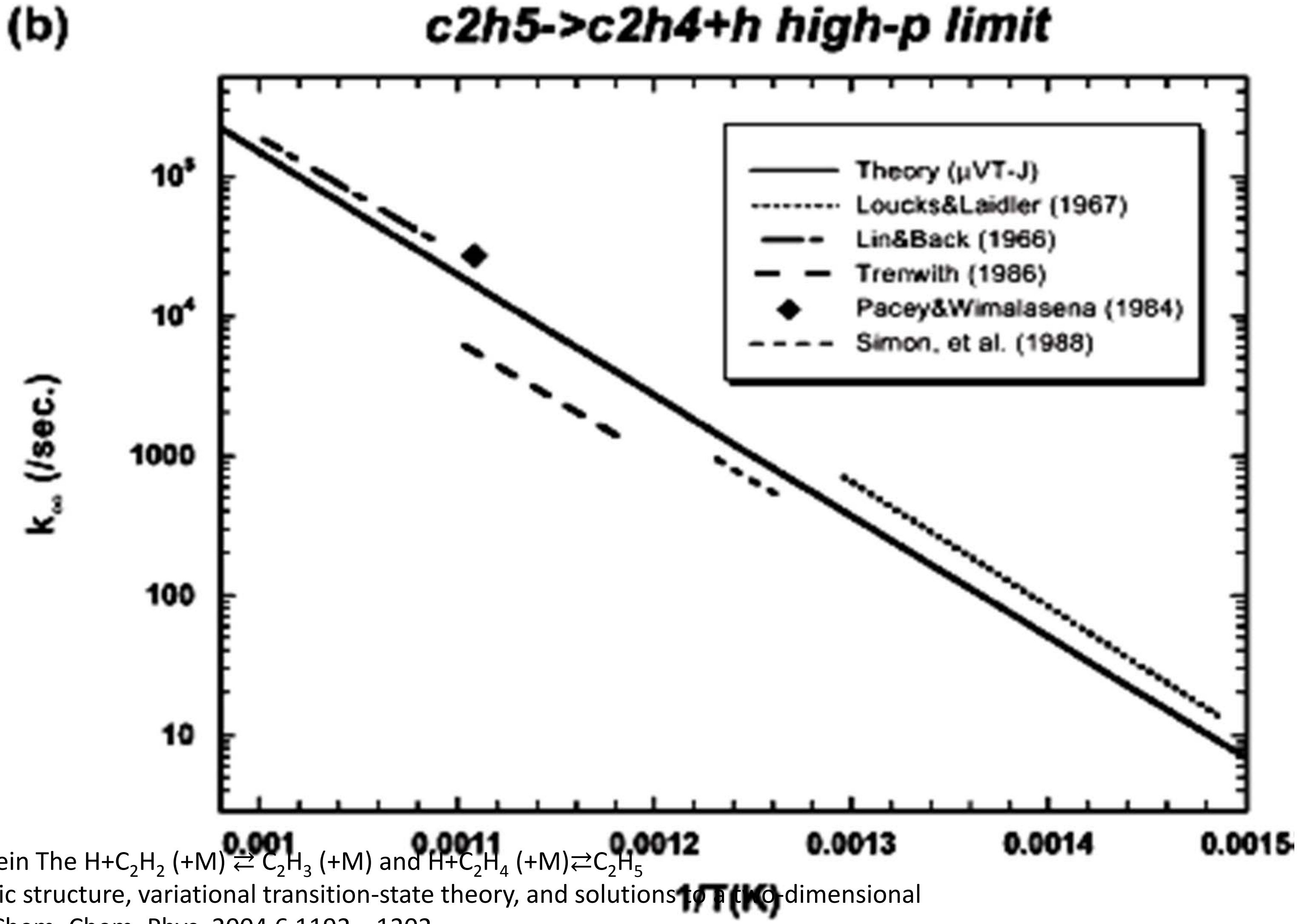


$\dot{H} + C_2H_4$ high-pressure limit



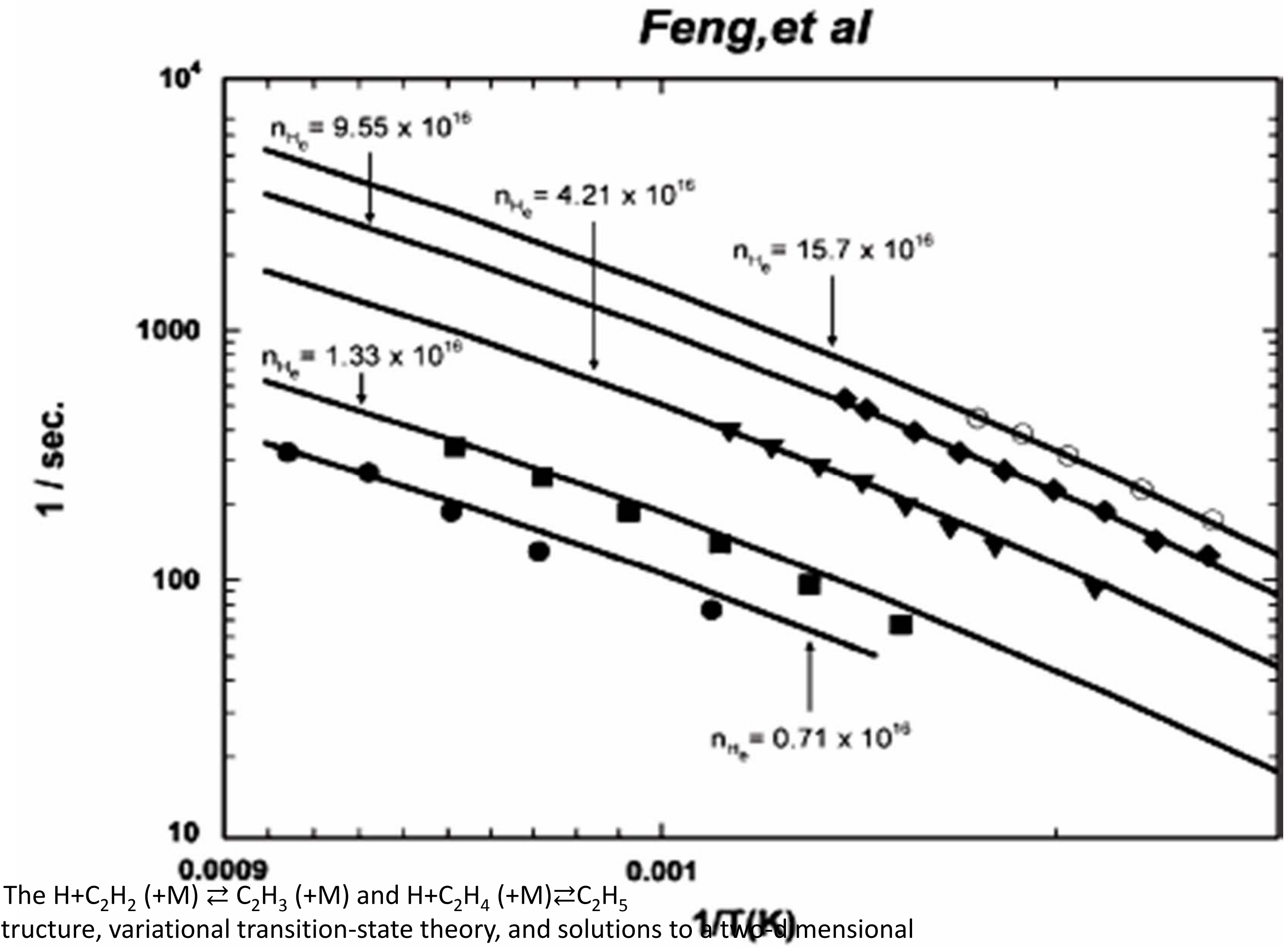
J.A. Miller, S.J. Klippenstein The $H+C_2H_2$ (+M) $\rightleftarrows$ C_2H_3 (+M) and $H+C_2H_4$ (+M)$\rightleftarrows$$C_2H_5$ (+M) reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. Phys. Chem. Chem. Phys. 2004 6 1192—1202.

$\dot{C}_2H_5 = C_2H_4 + \dot{H}$ high-pressure limit



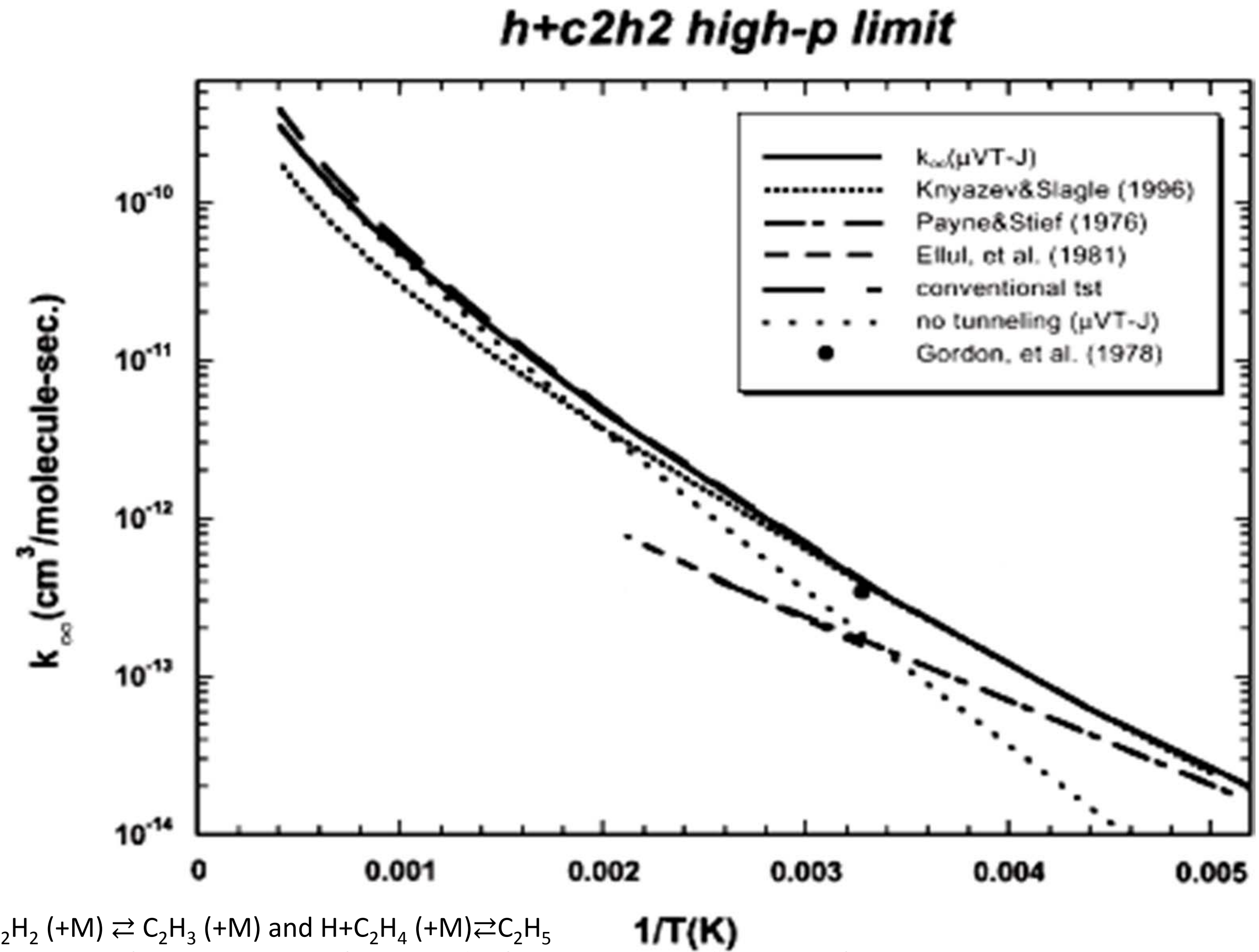
J.A. Miller, S.J. Klippenstein The $H+C_2H_2$ (+M) ⇄ C_2H_3 (+M) and $H+C_2H_4$ (+M)⇄C_2H_5 (+M) reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. Phys. Chem. Chem. Phys. 2004 6 1192—1202.

$\dot{C}_2H_5 = C_2H_4 + \dot{H}$



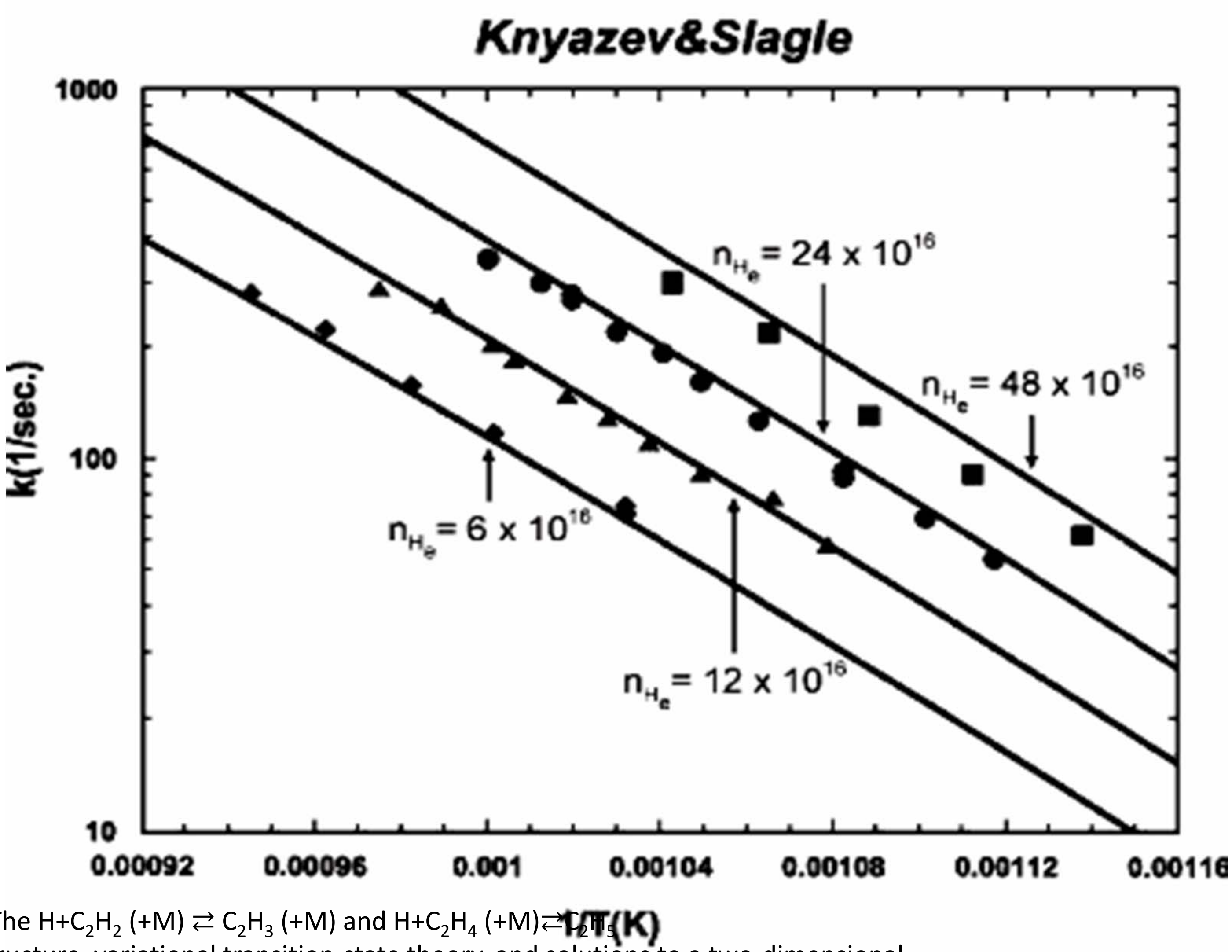
J.A. Miller, S.J. Klippenstein The H+C_2H_2 (+M) $\rightleftarrows$ C_2H_3 (+M) and H+C_2H_4 (+M)$\rightleftarrows$$C_2H_5$ (+M) reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. Phys. Chem. Chem. Phys. 2004 6 1192—1202.

$\dot{H} + C_2H_2 = \dot{C}_2H_3$



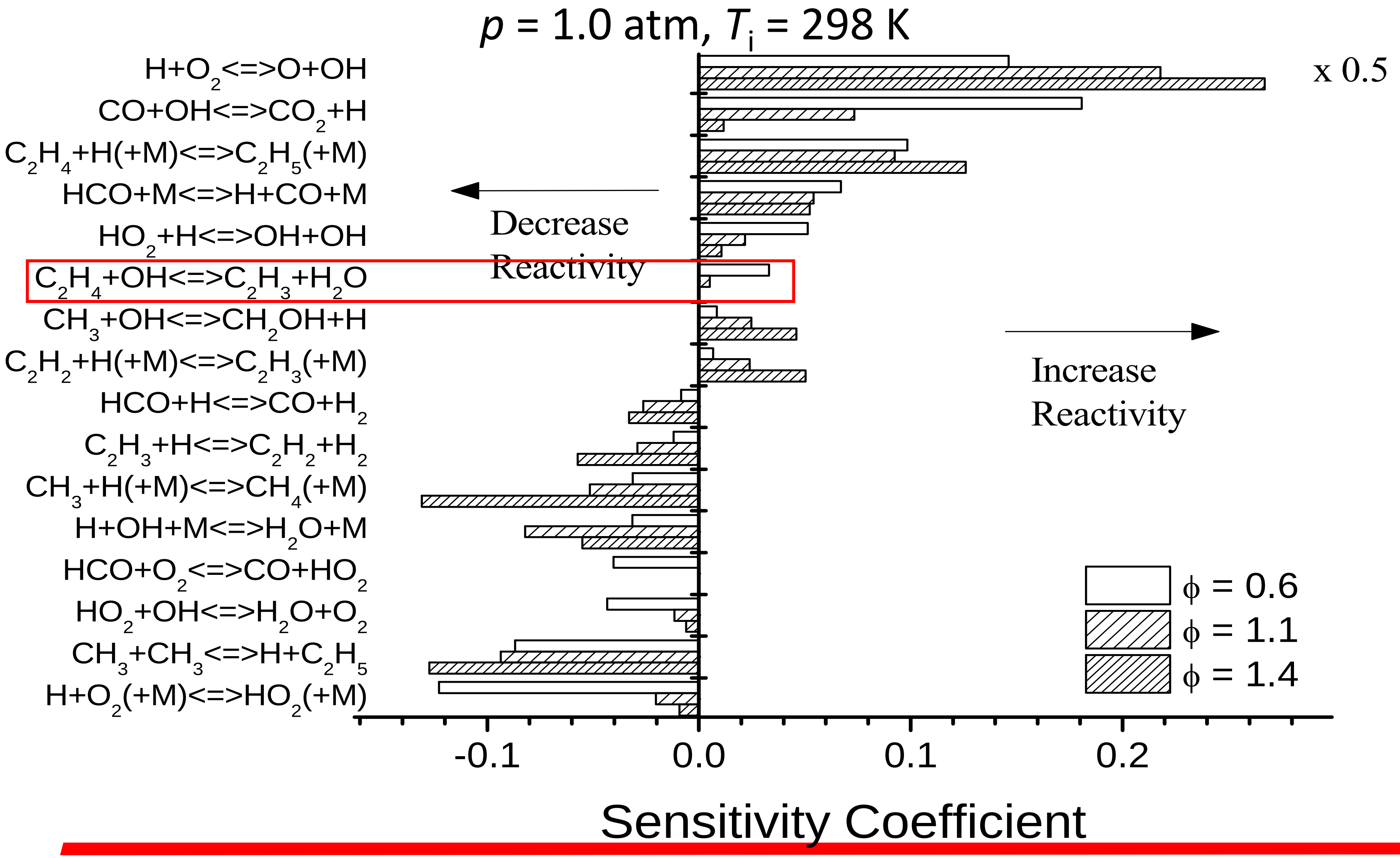
J.A. Miller, S.J. Klippenstein The H+C_2H_2 (+M) ⇄ C_2H_3 (+M) and H+C_2H_4 (+M)⇄C_2H_5 (+M) reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. Phys. Chem. Chem. Phys. 2004 6 1192—1202.

$\dot{H} + C_2H_2 = \dot{C}_2H_3$

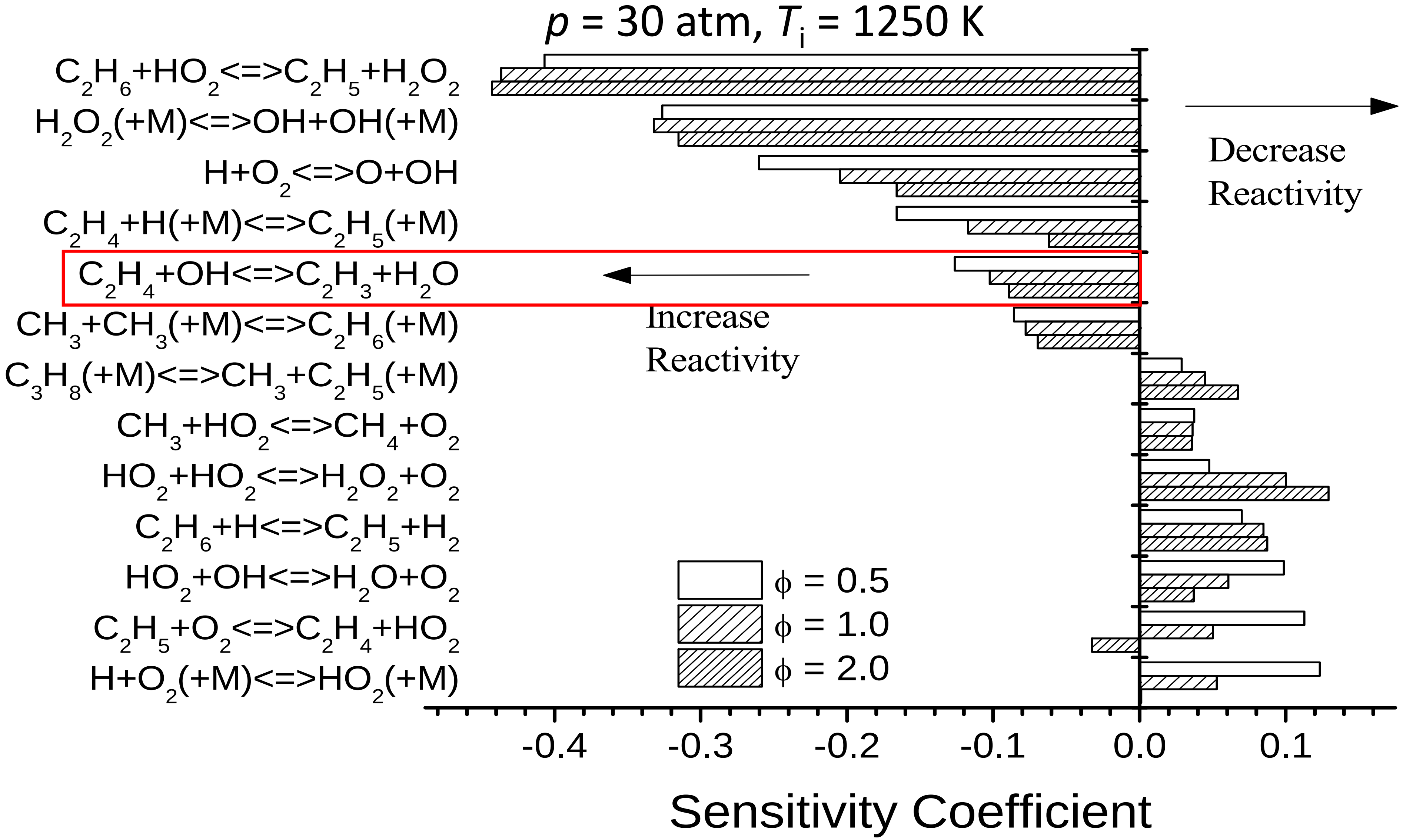


J.A. Miller, S.J. Klippenstein The H+C_2H_2 (+M) ⇄ C_2H_3 (+M) and H+C_2H_4 (+M)⇄C_2H_5 (+M) reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. Phys. Chem. Chem. Phys. 2004 6 1192—1202.

Sensitivity Analysis—C_2H_6 Flame Speed

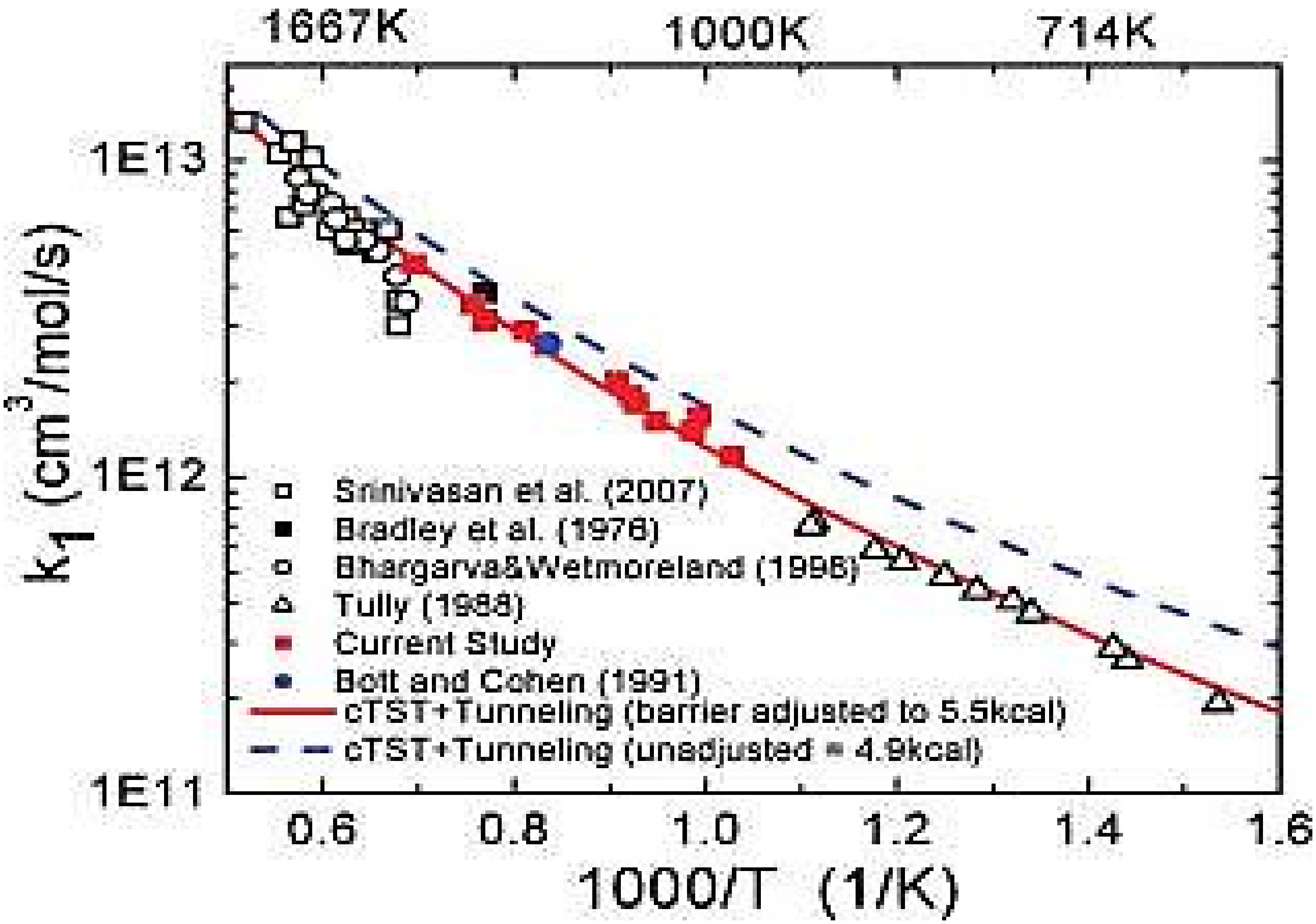


Sensitivity Analysis—C_2H_6 Ignition delay



p = 30 atm, T_i = 1250 K

$C_2H_4 + \dot{O}H = \dot{C}_2H_3 + H_2O$



SS Vasu, Z. Hong, DF Davisdon, RK Hanson, DM Golden, Shock Tube/Laser Absorption Measurements of the Reaction Rates of OH with Ethylene and Propene. Journal of Physical Chemistry A 2010;114:11529–11537.

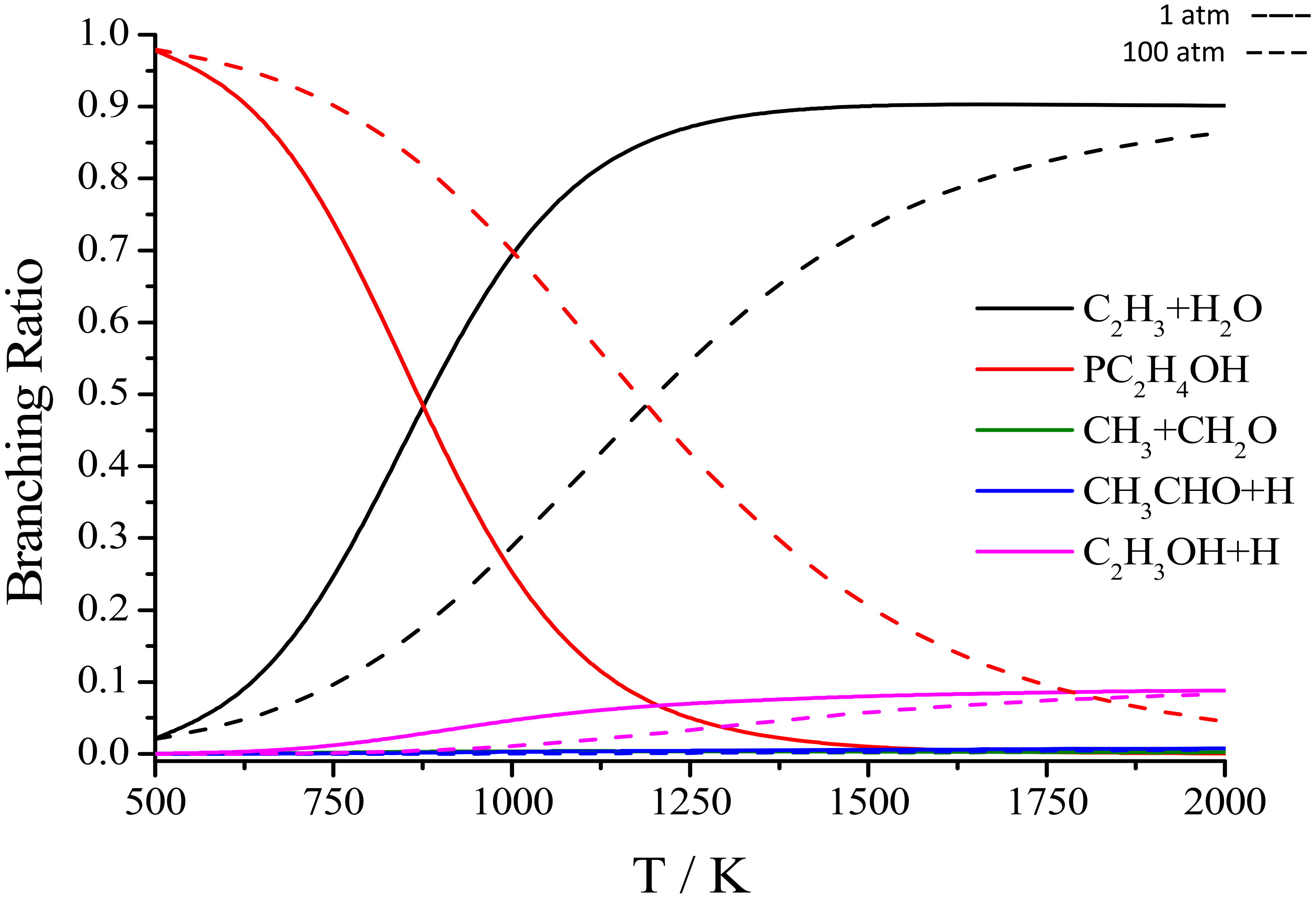
$C_2H_4 + \dot{O}H$

$$
\begin{aligned}
C_2H_4 + \dot{O}H &= \dot{C}_2H_3 + H_2O \\
&= \dot{C}H_3 + CH_2O \\
&= CH_3CHO + \dot{H} \\
&= C_2H_3OH + \dot{H} \\
&= p\dot{C}_2H_4OH
\end{aligned}
$$

JP Senosiain, SJ Klippenstein, JA Miller, Reaction of Ethylene with Hydroxyl Radicals: A Theoretical Study. Journal of Physical Chemistry A 2006;110:6960–6970.

Below 1000 K, addition is also important. Direct abstraction agrees within 35% of the faster Vasu et al. value from 500—2000 K. We use Vasu et al. value for abstraction.

$C_2H_4 + \dot{O}H$


1 atm
100 atm
Branching Ratio
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
500
750
1000
1250
1500
1750
2000
T / K
C2H3+H2O
PC2H4OH
CH3+CH2O
CH3CHO+H
C2H3OH+H

Evans-Polanyi type correlations

Empirical relationships linking the activation energy to the internal energy of the reaction (chemical driving force) and to an intrinsic energy barrier E_0 (chemical inertia)

LFER relationships

$$\Delta^{\ddagger}G = \Delta^{\ddagger}G_0 + a\Delta_rG_0$$

Allow to calculate k (Hammet equation)

Evans-Polanyi relationships

$$E_a = \Delta^{\ddagger}H_0 + a\,\Delta_rH_0$$

Valid for reactions going through the same reaction channel (similar structures of the TSs). Hazardous extrapolations.

Courtesy of Dr. Pierre-Alexandre Glaude

Evans-Polanyi type correlations

Correlation for H-abstractions on a C-atom or a N-atom (Dean and Bozzelli, 1999)

$$RH + {}^{\bullet}X \rightarrow R^{\bullet} + HX$$

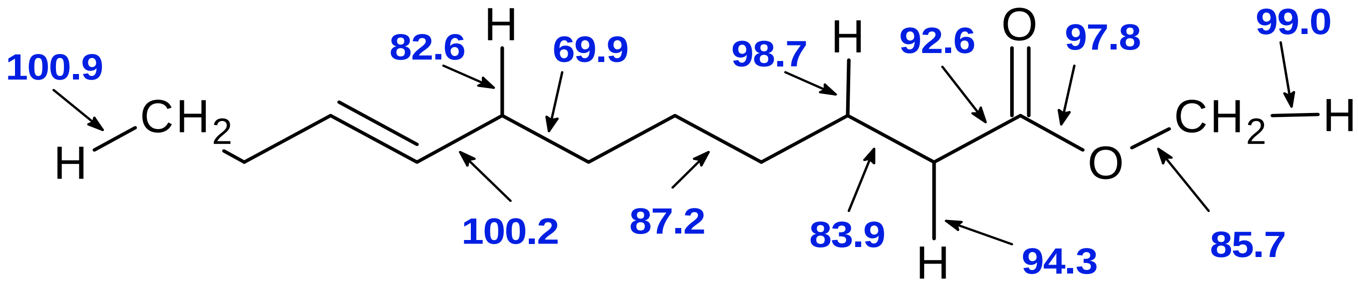
$$k = n_H\, A\, T^n \exp\left(-\{E_0 - f(\Delta H_0 - \Delta H)\}/RT\right)\ \mathrm{cm^3\, mol^{-1}\, s^{-1}}$$

n_H number of equivalent abstractable H-atoms

Formation of a radical center on C-atom, reference: ethane

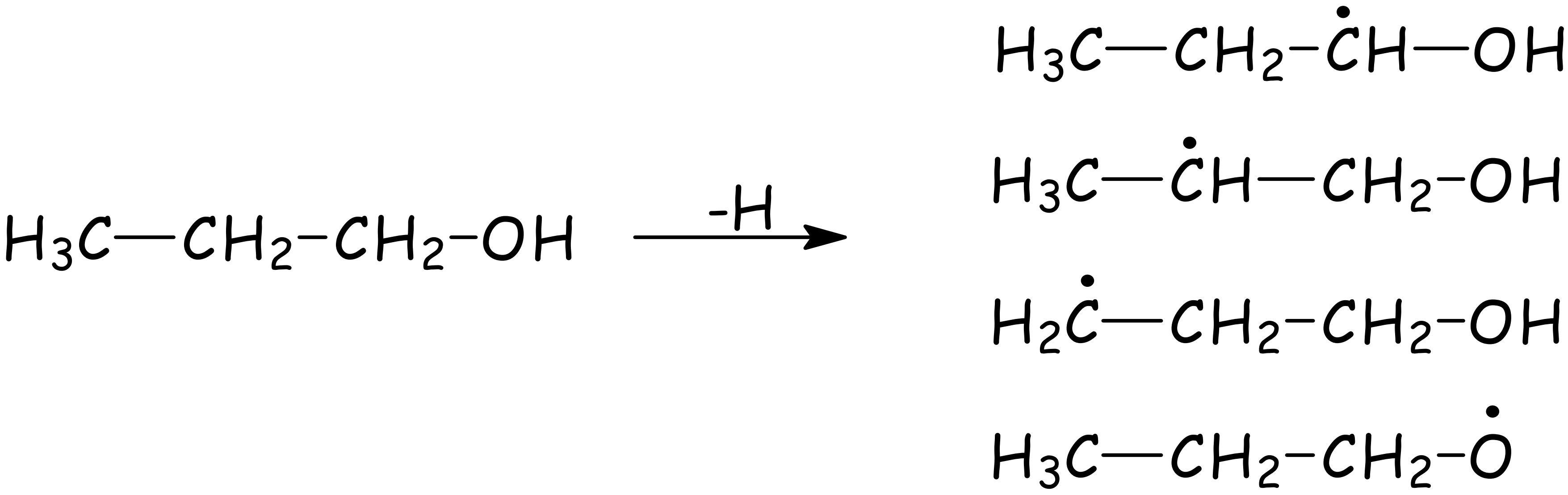
$R^{\bullet}$	A	n	E_0 (kcal)	ΔH_0 (kcal)	f
H	2.4×10^8	1.5	7.4	-3.1	0.65
O	1.7×10^8	1.5	5.8	-1.1	0.75
OH	1.2×10^6	2.0	0.9	-18.3	0.50
NH_2	9.2×10^5	1.94	7.2	-7.5	0.23
CH_3	8.1×10^5	1.87	10.6	-3.7	0.65

Importance of thermo data and BDE



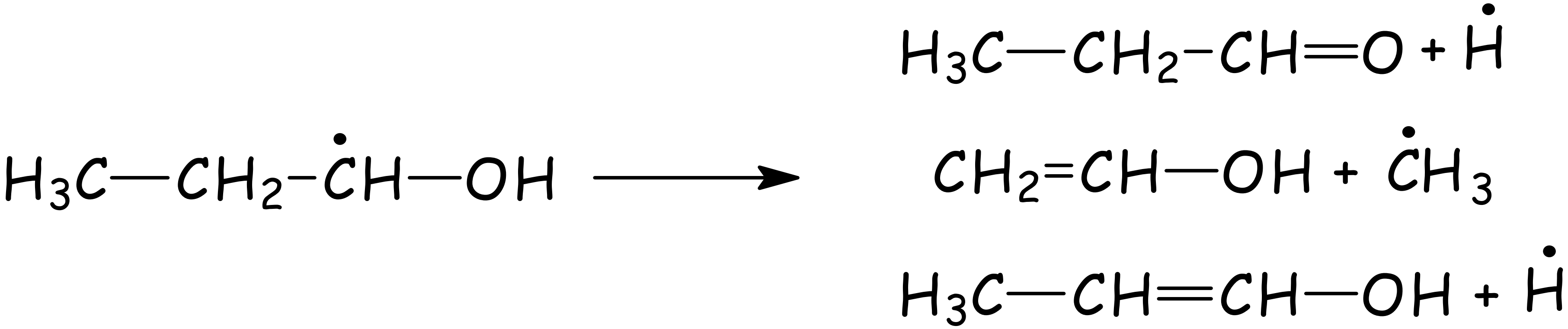
Courtesy of Dr. Pierre-Alexandre Glaude

n-Propanol oxidation



$$H_3C-CH_2-CH_2-OH \xrightarrow{-H} \begin{array}{l} H_3C-CH_2-\dot{C}H-OH \\ H_3C-\dot{C}H-CH_2-OH \\ H_2\dot{C}-CH_2-CH_2-OH \\ H_3C-CH_2-CH_2-\dot{O} \end{array}$$

n-Propanol α-radical decomposition



$$H_3C{-}CH_2{-}\dot{C}H{-}OH \longrightarrow \begin{cases} H_3C{-}CH_2{-}CH{=}O + \dot{H} \\ CH_2{=}CH{-}OH + \dot{C}H_3 \\ H_3C{-}CH{=}CH{-}OH + \dot{H} \end{cases}$$

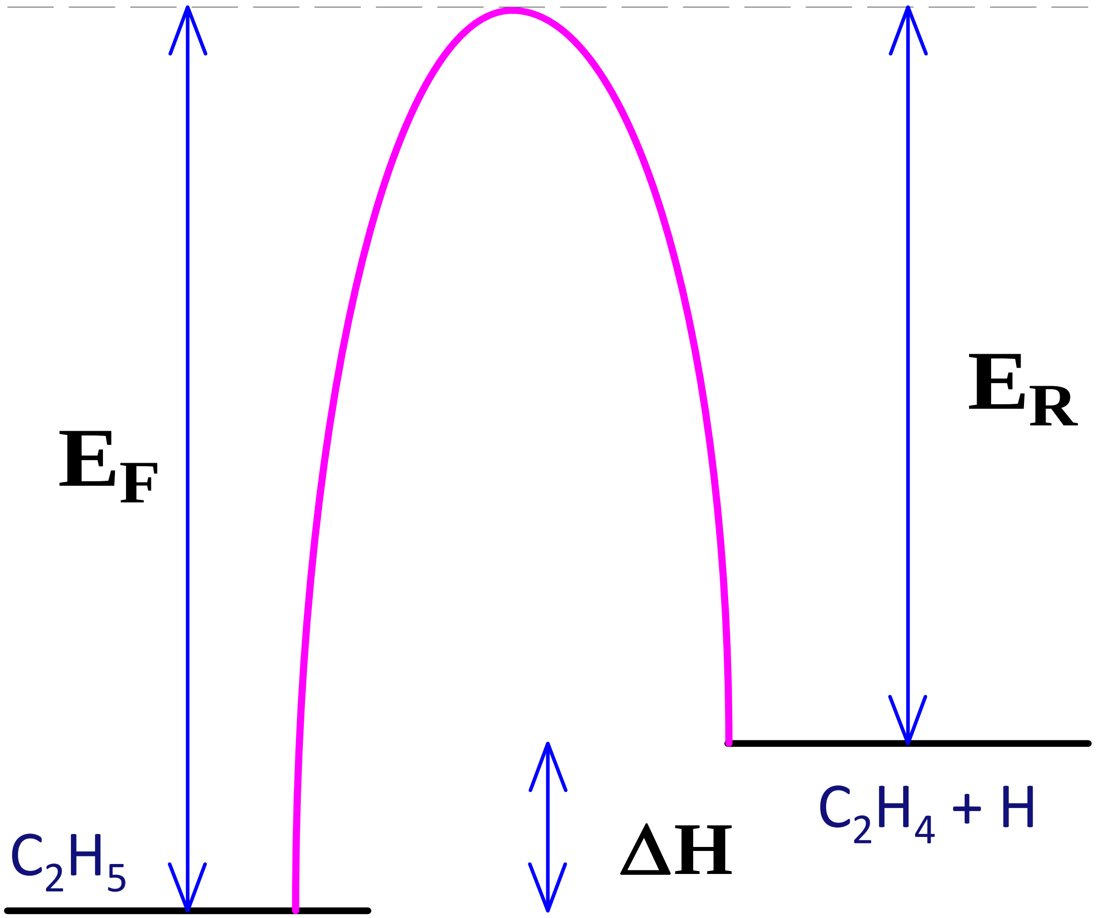
“Enols Are Common Intermediates in Hydrocarbon Oxidation”

Craig A. Taatjes, *et al. Science* **308**, 1887 (2005)

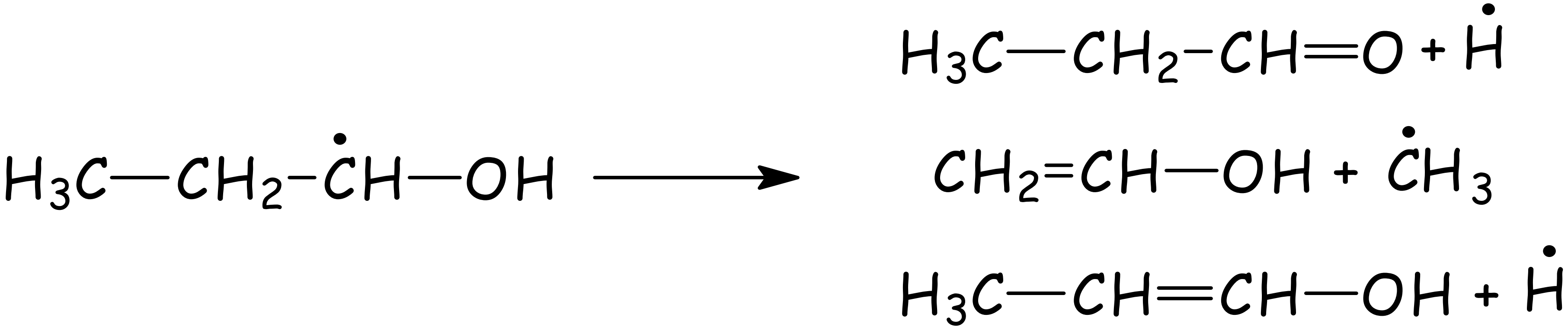
Photoionization mass spectrometry of flames

- Detected substantial quantities of 2, 3, & 4-carbon enols
- Ethenol detected for: allene, propyne, benzene, cyclohexane, 1,3-butadiene, ethanol, propene, cyclopentene, ethene and 1-propanol
- Ethenol below detection for: ethane, methane, propane, and 2-propanol flames

Alkyl radical decomposition



n-Propanol α-radical decomposition



$$H_3C-CH_2-\dot{C}H-OH \longrightarrow \begin{array}{l} H_3C-CH_2-CH{=}O + \dot{H} \\ CH_2{=}CH-OH + \dot{C}H_3 \\ H_3C-CH{=}CH-OH + \dot{H} \end{array}$$

Alkyl radical decomposition

Reaction	A-factor	T^n	Ea (cal/mol)
$C_2H_4 + H = C_2H_5$	1.70×10^{10}	1.07	1450.
$C_3H_6 + H = iC_3H_7$	4.24×10^{11}	0.51	1230.
$C_3H_6 + H = nC_3H_7$	2.50×10^{11}	0.51	2620.
$C_2H_4 + CH_3 = nC_3H_7$	1.76×10^{4}	2.48	6130.
$C_2H_4 + C_2H_5 = nC_4H_9$	1.32×10^{4}	2.48	6130.
$C_3H_6 + CH_3 = sC_4H_9$	1.76×10^{4}	2.48	6130.
$C_3H_6 + CH_3 = iC_4H_9$	1.89×10^{3}	2.67	6850.
$iC_4H_8 + CH_3 = neoC_5H_{11}$	1.30×10^{3}	2.48	8520.

Hydrogen addition

Reaction	$\Delta H^{o,\ddagger}$ / kcal mol^{-1}		Ea / kcal mol^{-1}
	CBS-QB3	CBS-APNO	2006 Study
$CH_2{=}CH_2$	0.65	1.31	1.45
$CH_2{=}CH(CH_3)$	–	0.81	1.23
$CH_2{=}CH(OH)$	–	0.72	–
$CH(CH_3){=}CH_2$	1.96	2.34	2.62
$CH(OH){=}CH_2$	3.51	3.68	–

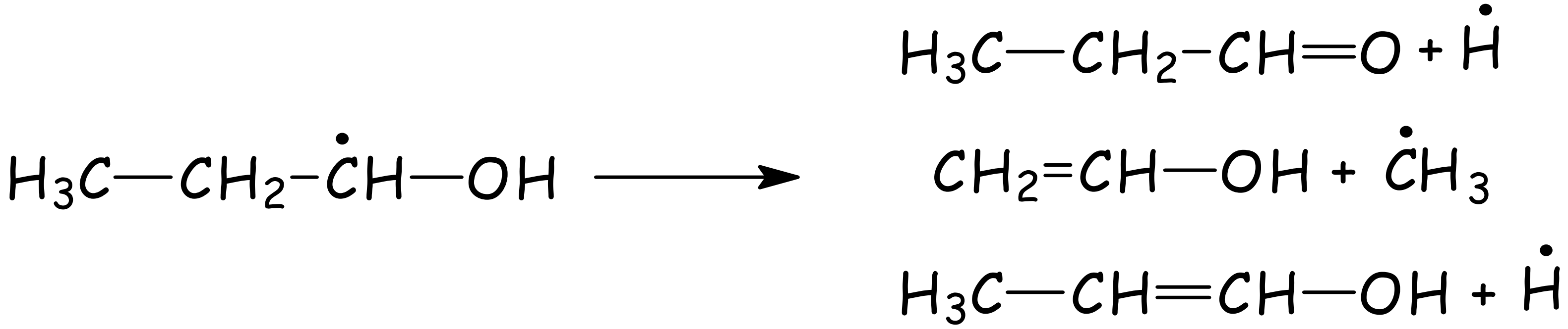
Methyl addition

Reaction	$\Delta H^{o,\ddagger}$ / kcal mol^{-1}		Ea / kcal mol^{-1}
	CBS-QB3	CBS-APNO	2006 Study
CH_2=CH_2	6.14	6.38	6.13
CH_2=CH(CH_3)	5.90	6.24	6.13
CH_2=CH(OH)	6.41	6.62	–
CH(CH_3)=CH_2	7.31	7.53	6.85
CH(OH)=CH_2	8.70	8.91	–

Ethyl addition

Reaction	$\Delta H^{o,\ddagger}$ / kcal mol^{-1}	
	CBS-QB3	CBS-APNO
CH_2=CH(OH)	6.28	6.33
CH(OH)=CH_2	7.74	7.86

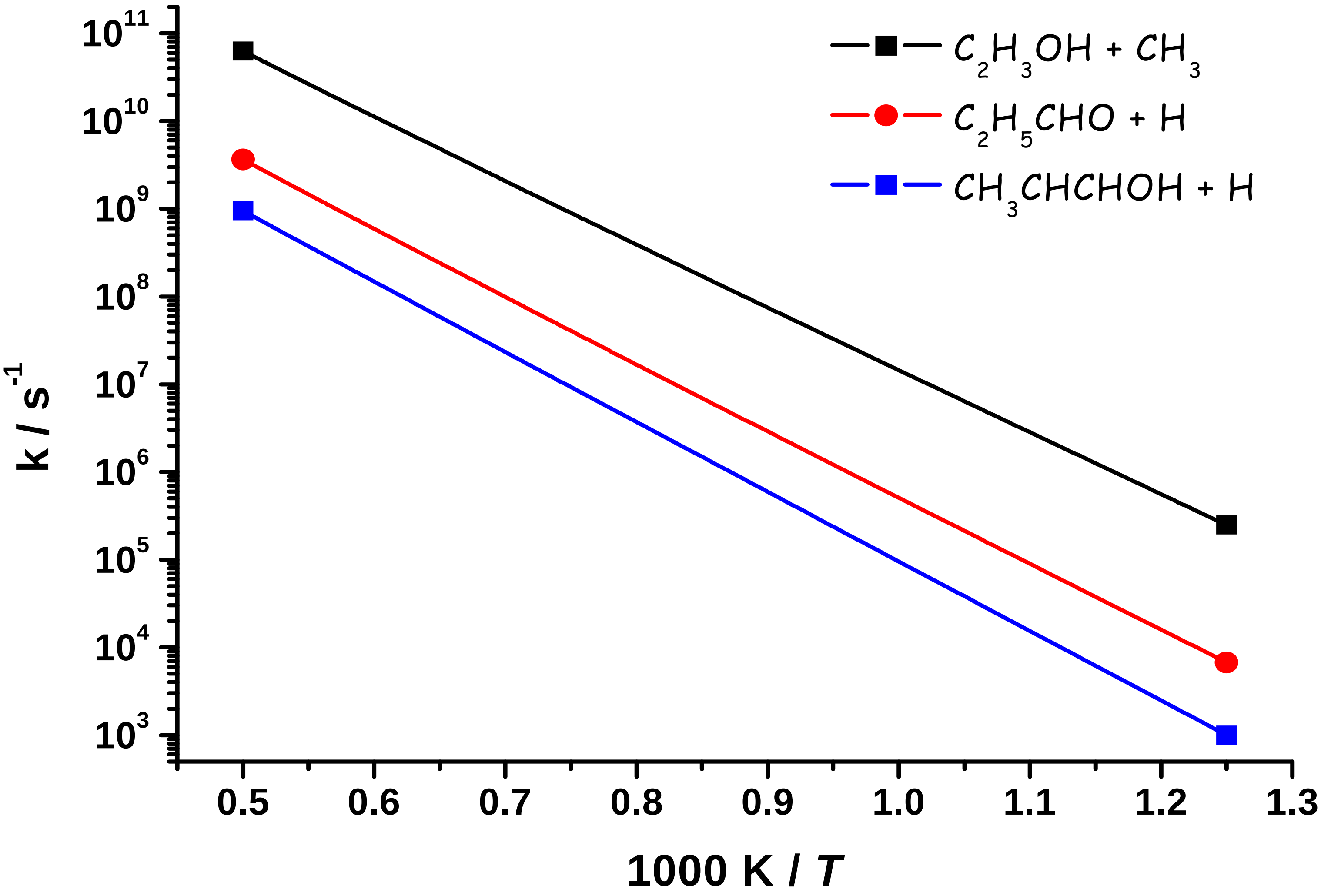
CH_3CH_2CHOH = products?



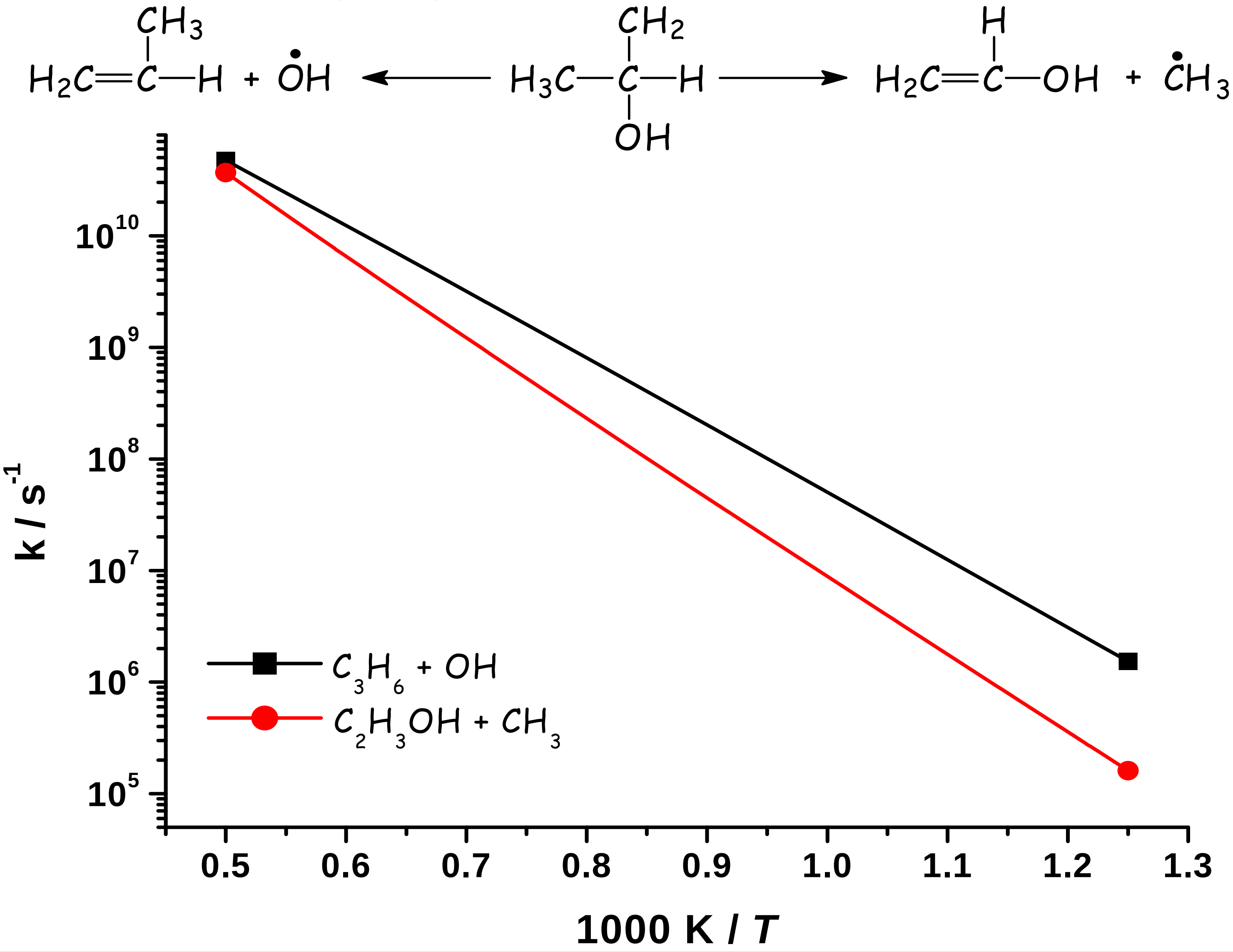
$$H_3C{-}CH_2{-}\dot{C}H{-}OH \longrightarrow \begin{cases} H_3C{-}CH_2{-}CH{=}O + \dot{H} \\ CH_2{=}CH{-}OH + \dot{C}H_3 \\ H_3C{-}CH{=}CH{-}OH + \dot{H} \end{cases}$$

Reaction	A_r	n_r	Ea_r
$CH_3CH_2CH{=}O + H$	8.00×10^{12}	0.00	9500.
$CH_2{=}CHOH + CH_3$	1.76×10^{4}	2.48	6130.
$CH_3CH{=}CHOH + H$	2.50×10^{11}	0.51	2620.
	A_f	n_f	Ea_f
A	7.03×10^{09}	0.99	32590.
B	5.01×10^{10}	1.04	30450.
C	5.46×10^{11}	0.34	35630.

CH_3CH_2CHOH = products?



iC_3H_6OH = products?



$$H_2C{=}C(CH_3){-}H + \dot{O}H \longleftarrow H_3C{-}C(\dot{C}H_2)(OH){-}H \longrightarrow H_2C{=}C(H){-}OH + \dot{C}H_3$$

Now we move on to larger fuels

- Boundary between “small” and “large” fuel molecules is somewhat arbitrary, however ...
- C5 fuels have much more low T kinetics than C4
- C6 fuels have much more low T kinetics than C5
- C6 and larger molecules have lots of low T reaction pathways, “cool flames”, and lower ON values than smaller fuels

Kinetic Reaction Mechanisms for Hydrocarbon Fuels

Part 2 -- Larger molecules

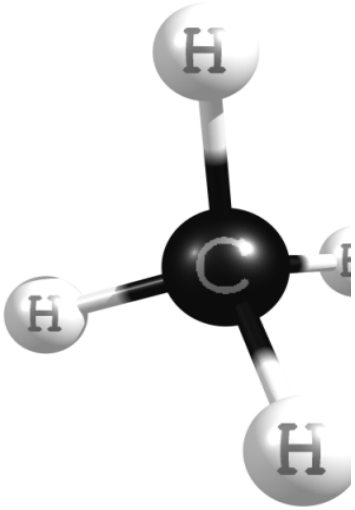
Generation of Detailed Chemical Kinetic Models for Hydrocarbon and Oxygenated Fuels Larger than C_5

Charles Westbrook

Tsinghua-Princeton
2014 Summer School on Combustion
July 20-25, 2014

Chemical Modeling

- Fuel + O_2 -> CO_2 + H_2O + Energy
- Small hydrocarbon fuel (e.g. methane)
  - 200 reactions
  - 30 chemical intermediates
- Chemical mechanism
  - Kinetics
  - Thermodynamics



Chemical Kinetic Model

Contains a large database of:

- Thermodynamic properties of species
- Reaction rate parameters

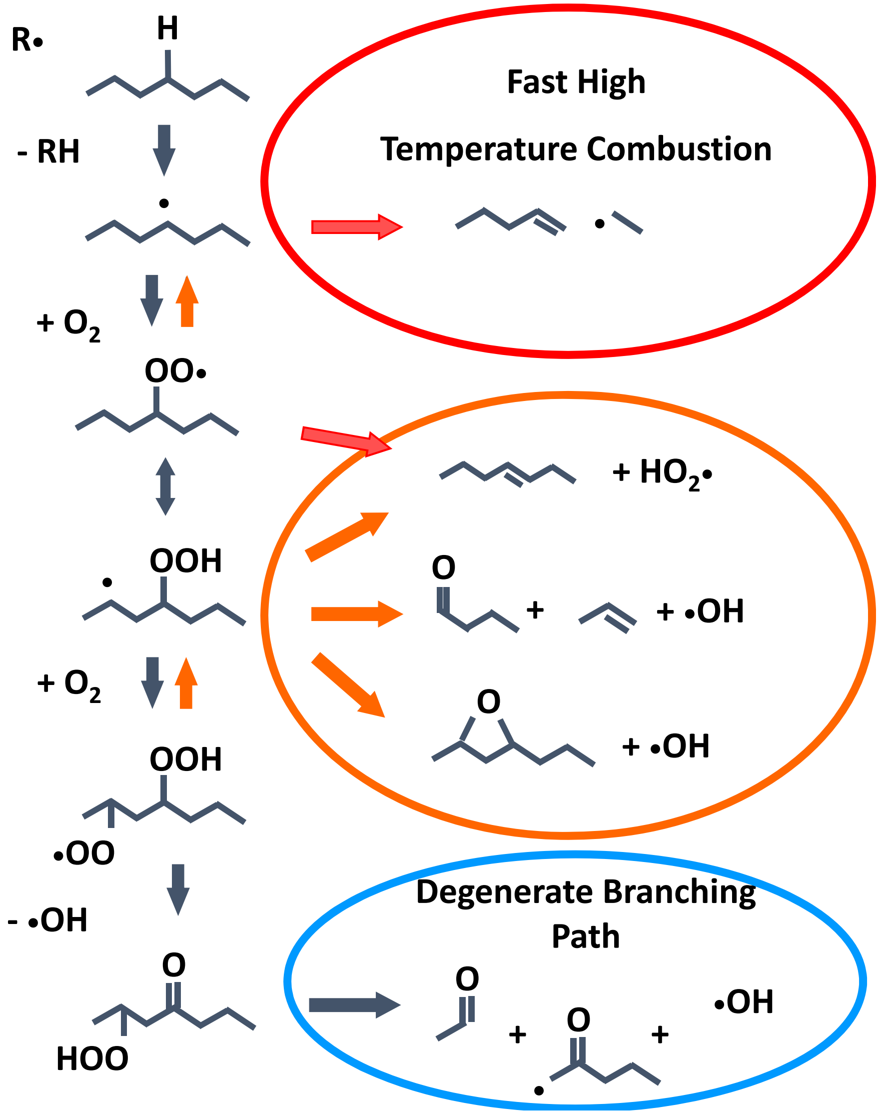
Size of mechanism grows with molecular size:

Fuel:	H_2	CH_4	C_3H_8 (Propane)	C_6H_{14} (Hexane)	$C_{16}H_{34}$ (Cetane)
Number of species:	7	30	100	450	1200
Number of reactions:	25	200	400	1500	7000

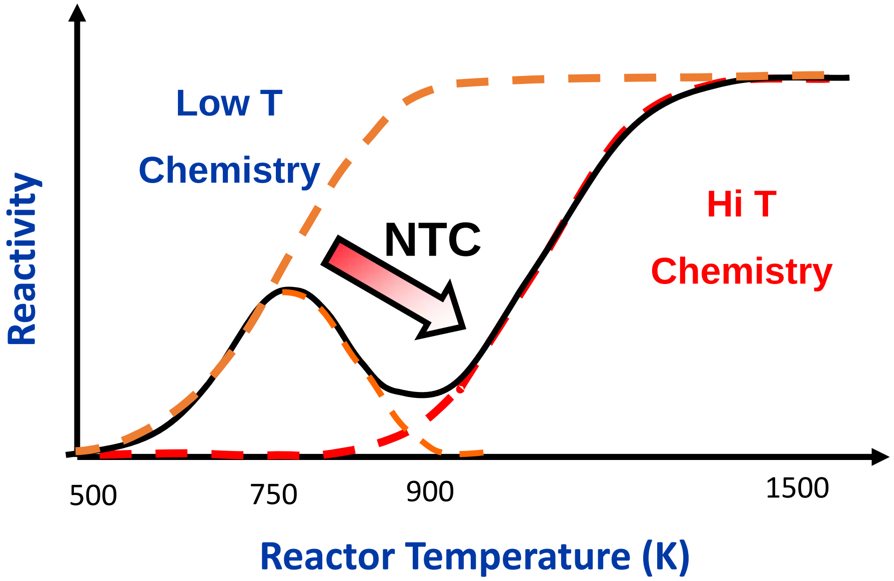
Dominance of H2/O2 Reactions

For nearly all hydrocarbon oxidation, no matter how large or small the fuel molecule, at high temperatures, the reactions of H2/O2 have the greatest sensitivity controlling the overall rate of reaction. This is true in flames, detonations, shock tubes, and many other practical combustors.

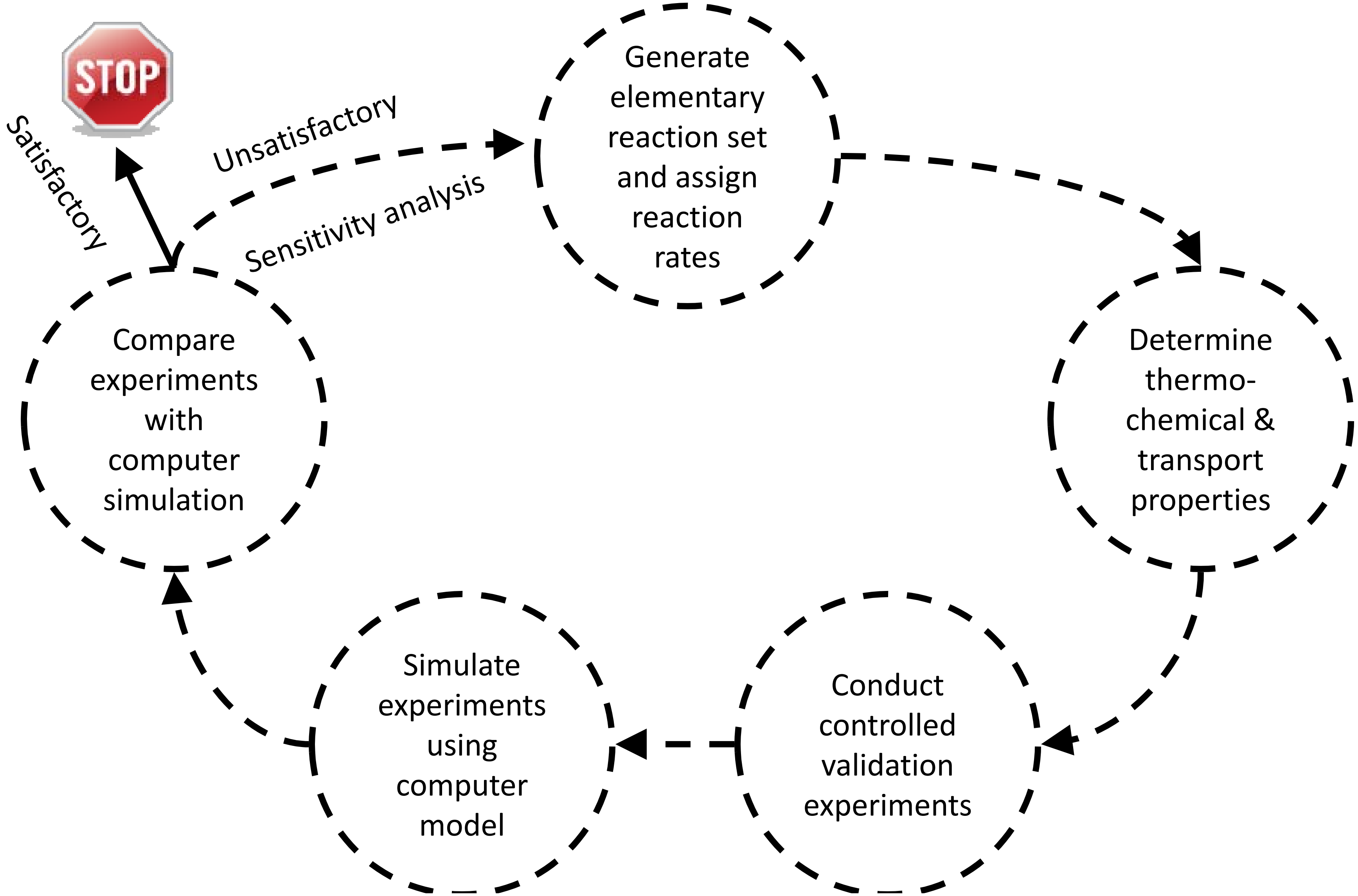
Comprehensive Combustion Chemistry



Long Chain Alkanes



Chemical Kinetic Modeling Process Cycle



Generate elementary reaction set and assign reaction rates

Determine thermo-chemical & transport properties

Conduct controlled validation experiments

Simulate experiments using computer model

Compare experiments with computer simulation

Unsatisfactory

Sensitivity analysis

Satisfactory

STOP

Strategy for generation of large fuel molecule mechanisms

- Number of species and reactions grows rapidly
- Considerable complexity in mechanisms
- Few, if any, elementary reactions have been studied in laboratory conditions, few rates known
- Growing number of heavy atoms discourages many theoretical approaches to study these species and reactions
- Emergence of “bookkeeping” issues
- “Reaction classes” are a useful system to use in mechanism development

Reaction classes for oxidation chemistry

High temperature mechanism

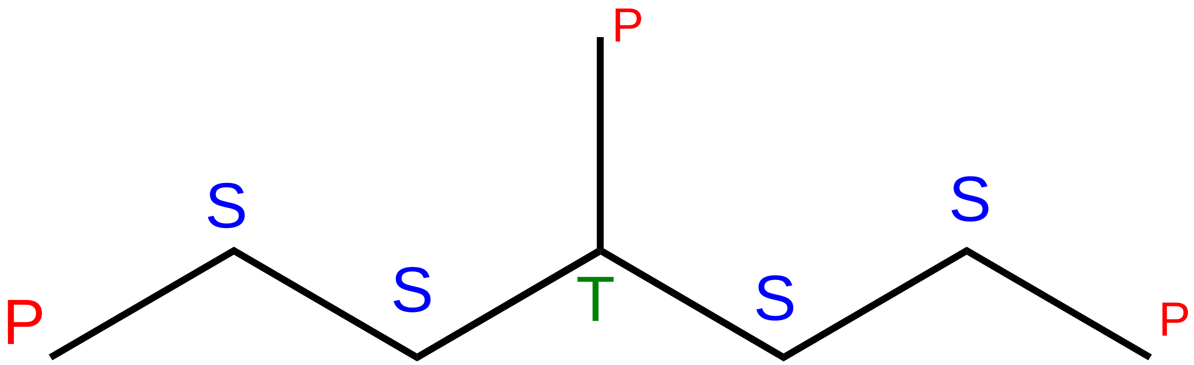
1: Unimolecular fuel decomposition
2: H atom abstractions from fuel
3: Alkyl radical decomposition
4: Alkyl radical isomerization
5: H atom abstraction from alkenes
6: Addition of radical species to alkenes
7: Alkenyl radical decomposition
8: Alkene decomposition
9: Retroene decomposition reactions

Reaction classes for oxidation chemistry

Low temperature mechanism

10: Alkyl radical addition to O_2 ($R + O_2 = RO_2$)
12,13, and 14: $R + R'O_2 = RO + R'O$
15: Alkylperoxy radical isomerization (RO_2=QOOH)
16: Concerted eliminations (RO_2 = alkene + HO_2)
17: $RO_2 + HO_2 = ROOH + O_2$
18: $RO_2 + H_2O_2 = ROOH + HO_2$
19: $RO_2 + CH_3O_2 = RO + CH_3O + O_2$
20: $RO_2 + R'O_2 = RO + R'O + O_2$
21: ROOH = RO + OH
22: RO decomposition
23: QOOH = cyclic ether + OH (cyclic ether formation)
24: QOOH = alkene+ HO_2 (radical beta to OOH)
25: QOOH = alkene + carbonyl + OH (radical gamma to OOH)
26: Addition of QOOH to molecular oxygen O_2 (QOOH+O_2=O_2QOOH)
27: O_2QOOH isomerization to carbonylhydroperoxide + OH
28: Carbonylhydroperoxide decomposition
29: Reactions of cyclic ethers with OH and HO_2

Test molecule



4-methylheptane

Bond dissociation energies

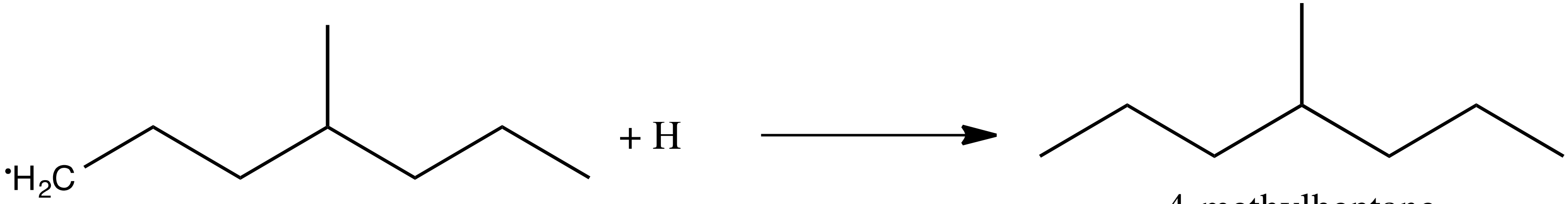
Primary: ~103 kcal/mol

Secondary: ~98 kcal/mol

Tertiary: ~94 kcal/mol

1: Unimolecular fuel decomposition

- Unimolecular fuel decomposition reactions produce either an alkyl radical and an H atom or two alkyl radicals.
- Path leading to H radicals are only important in reverse directions where they can be an important sink for H atoms



4-methyl-1-heptyl

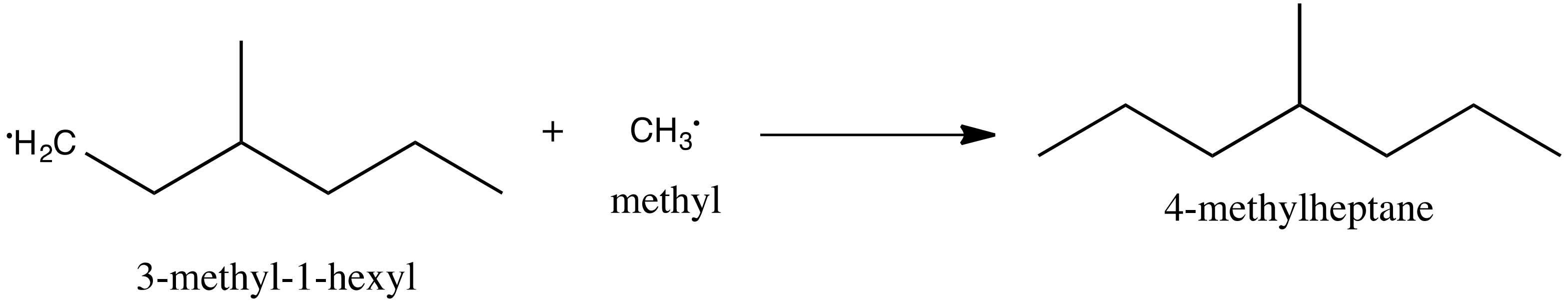
4-methylheptane

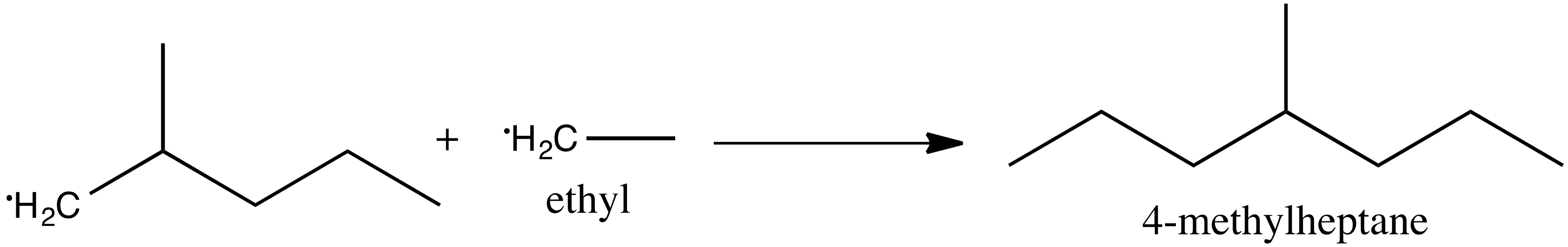
$k = 1\mathrm{x}10^{13}\ \mathrm{cm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$

Recommended by Allara and Shaw,
J. Chem. Phys. Ref. Data 1980

1: Unimolecular fuel decomposition

- Very high activation energies are required (85-95 kcal/mol for C-C bond scission)
- How many unique bond scissions are there in 4-methylheptane?





1: Unimolecular fuel decomposition

$1.57 \times 10^{-9}\ T^{-0.538} \exp(-68.0/T)\ \mathrm{CH_3 + CH_3}$

$2.04 \times 10^{-9}\ T^{-0.562} \exp(-10.3/T)\ \mathrm{CH_3 + C_2H_5}$

$5.33 \times 10^{-10}\ T^{-0.474} \exp(97.7/T)\ \mathrm{CH_3} + i\text{-}\mathrm{C_3H_7}$

$1.16 \times 10^{-9}\ T^{-0.673} \exp(73.8/T)\ \mathrm{CH_3} + t\text{-}\mathrm{C_4H_9}$

$1.45 \times 10^{-9}\ T^{-0.699} \exp(1.6/T)\ \mathrm{C_2H_5 + C_2H_5}$

$5.37 \times 10^{-10}\ T^{-0.596} \exp(161/T)\ \mathrm{C_2H_5 + i\text{-}C_3H_7}$

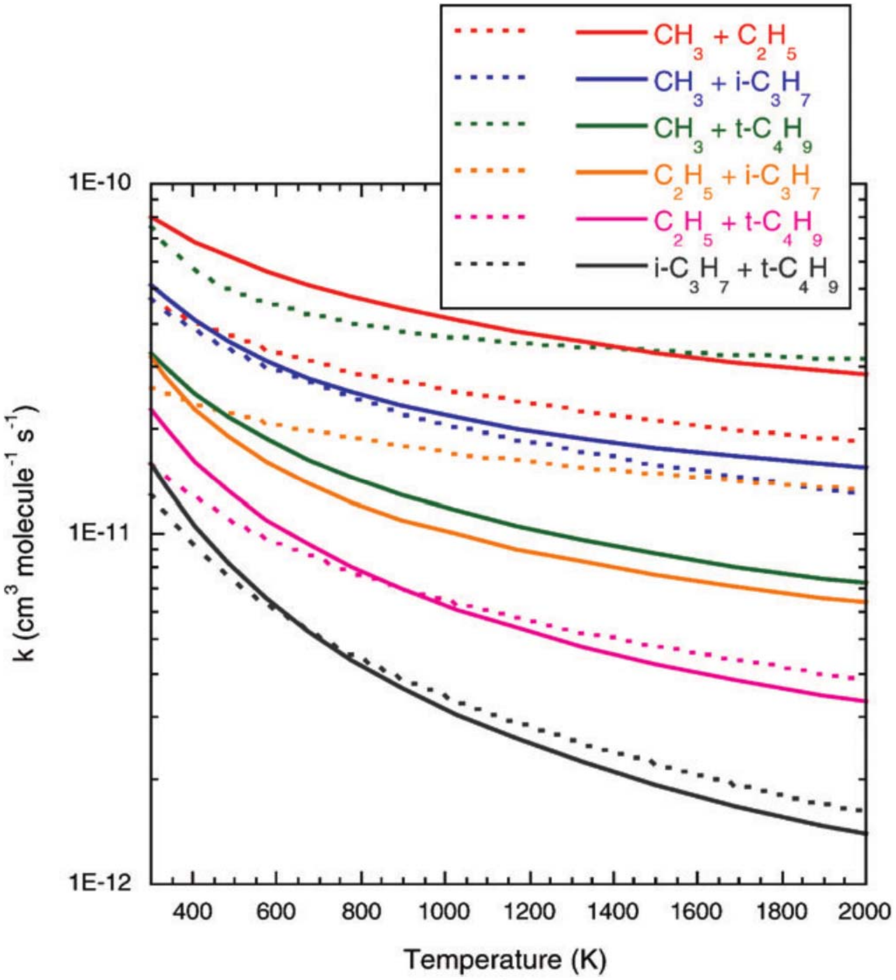
$2.79 \times 10^{-9}\ T^{-0.892} \exp(73.1/T)\ \mathrm{C_2H_5} + t\text{-}\mathrm{C_4H_9}$

$9.79 \times 10^{-10}\ T^{-0.863} \exp(132/T)\ \mathrm{i\text{-}C_3H_7} + i\text{-}\mathrm{C_3H_7}$

$9.66 \times 10^{-9}\ T^{-1.17} \exp(65.0/T)\ \mathrm{i\text{-}C_3H_7} + t\text{-}\mathrm{C_4H_9}$

$2.27 \times 10^{-10}\ T^{-0.918} \exp(350/T)\ t\text{-}\mathrm{C_4H_9} + t\text{-}\mathrm{C_4H_9}$

Klippenstein et al. Phys. Chem. Chem. Phys., 2006,



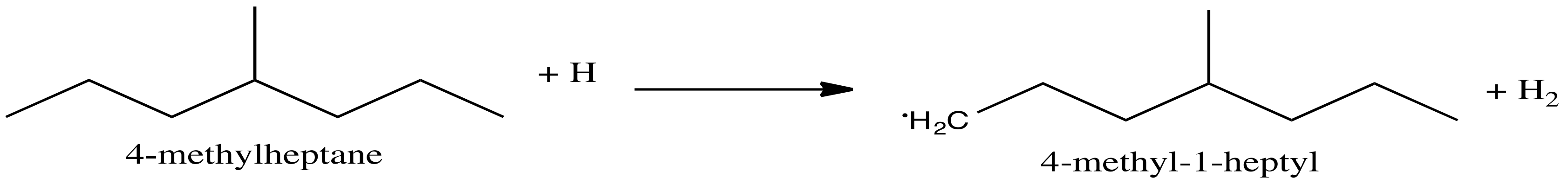
The geometric mean rule, relates the self combination rate coefficients of two radicals and their cross combination rate coefficient

$k_{AB} = 2(k_{AA}k_{BB})^{1/2}$,

where k_{AB} is the rate coefficient for the cross reaction, while k_{AA} and k_{BB} are the rate coefficients for the self reactions.

2: H atom abstractions from fuel

- Abstraction of H atoms from the fuel by radical species (e.g., H, OH, HO_2, CH_3, etc.)
- H atoms can be abstracted from primary (1°), secondary (2°), or tertiary (3°) carbon sites.
- The rate constant depends on the radical species and the type of H atom being abstracted. Primary H atoms have the strongest bond C-H energies are the most difficult to abstract, while tertiary H atoms are the weakest and most easily abstracted.
- How many unique H-atom abstractions are there?

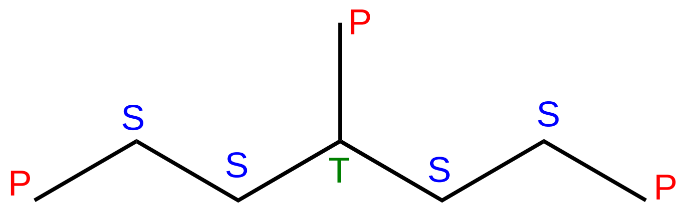


2: H atom abstractions from fuel

- Rate constant rules typically provided on a per H-atom basis

	C-H type	A ($cm^3\ mol^{-1}\ s^{-1}$)	n	E_A (cal)
H	1°	2.22E+05	2.54	6,756
	2°	6.50e+05	2.40	4,471
	3°	6.02E+05	2.40	2,583
OH	1°	1.76E+09	0.97	1,586
	2°	2.34E+07	1.61	-35
	3°	5.73E+10	0.51	63
CH_3	1°	1.51E-01	3.65	7,154
	2°	7.55E-01	3.46	5,481
	3°	6.01E-10	6.36	893
HO_2	1°	6.80E+00	3.59	17,160
	2°	3.16E+01	3.37	13,720
	3°	6.50E+02	3.01	12,090

Orme et al. J. Phys. Chem. A 2006

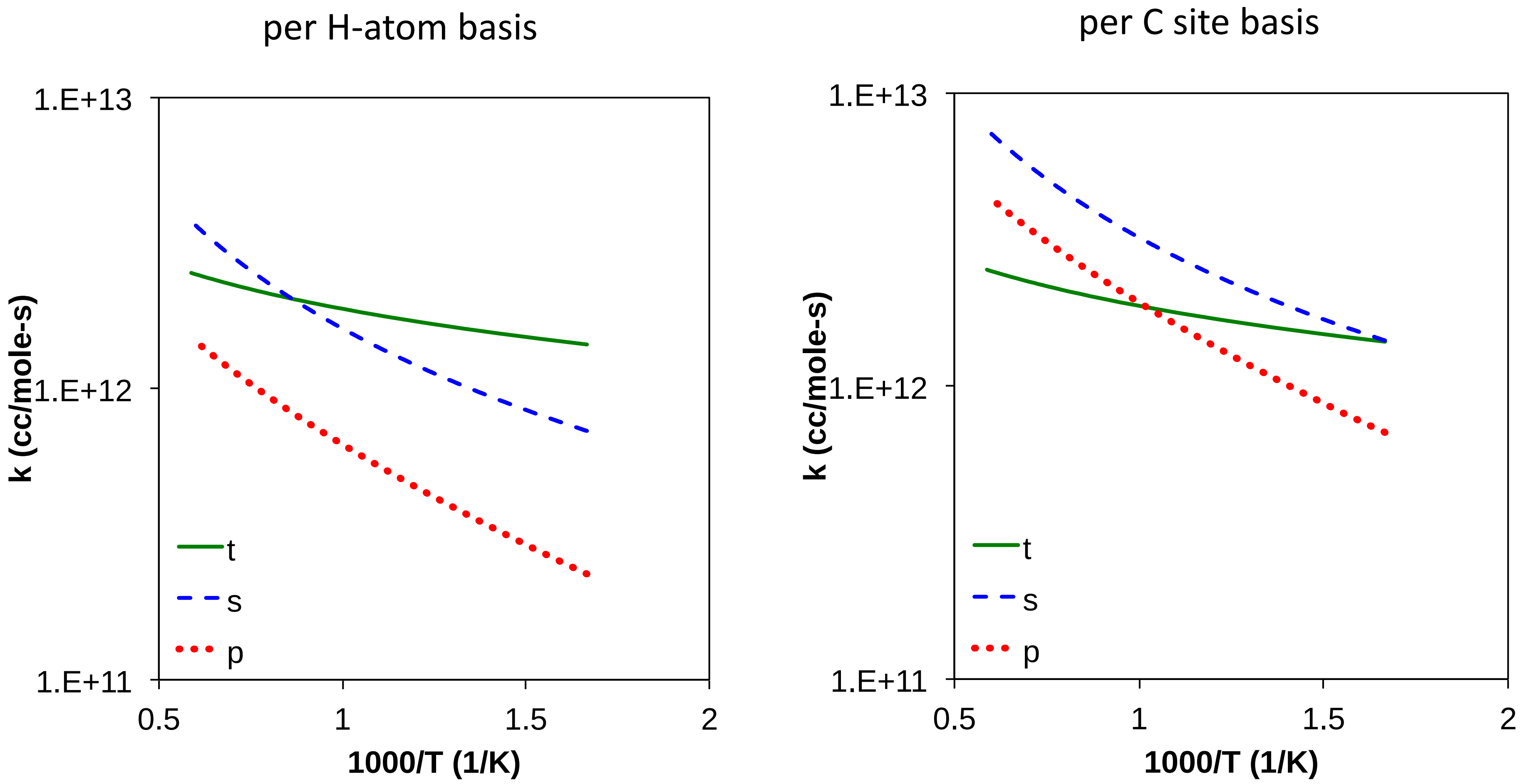


4-methylheptane

- Which abstractors are the most important in fuel oxidation and pyrolysis?

2: H atom abstractions from fuel

- Rate constants for abstraction by OH



2: H atom abstractions from fuel

- Rate constants for abstraction by OH
- Finer considerations take into account next-nearest-neighbor (NNN) configurations and different types of H-atoms (in-plane/out-of-plane).

Sivaramakrishnan et al. J Phys Chem A 2009

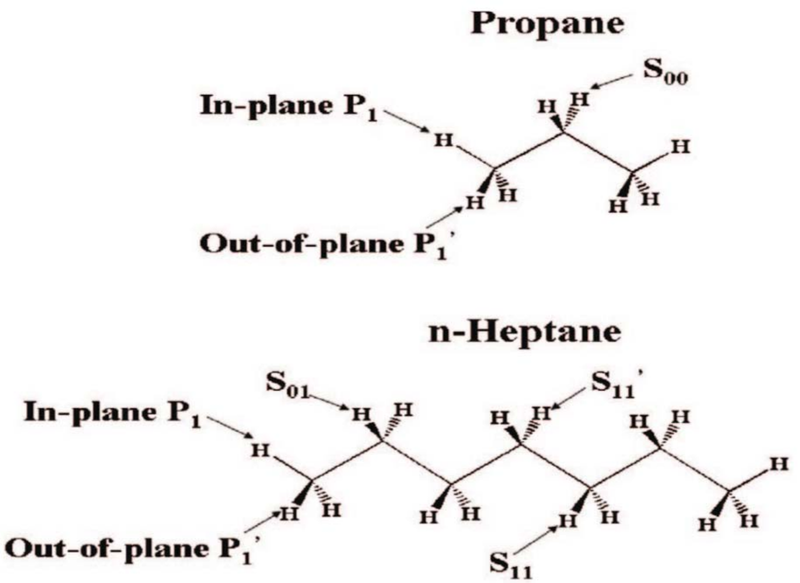


Figure 10. Types of primary and secondary C—H bonds in propane and *n*-heptane.

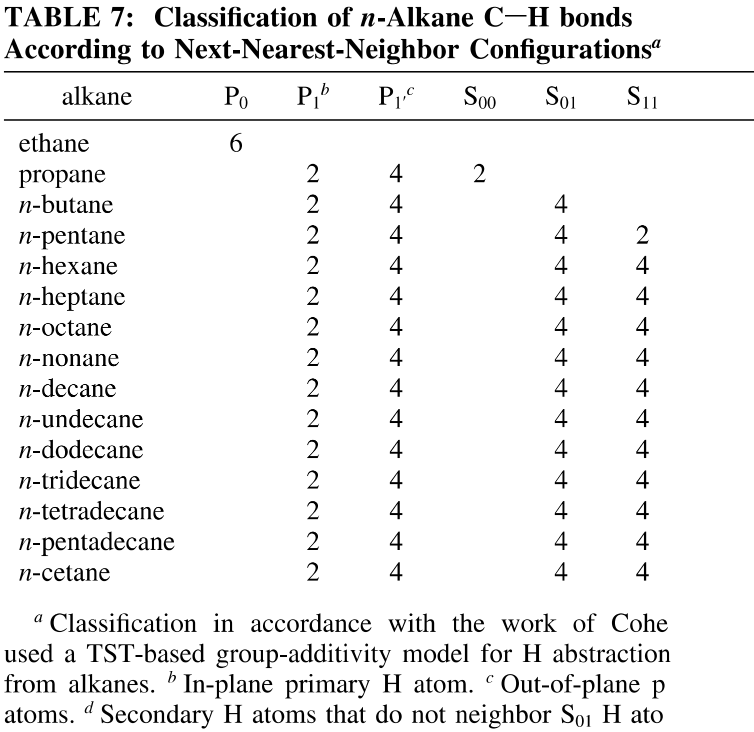


TABLE 7: Classification of *n*-Alkane C—H bonds According to Next-Nearest-Neighbor Configurations[a]

alkane	P_0	P_1[b]	$P_{1'}$[c]	S_{00}	S_{01}	S_{11}
ethane	6					
propane		2	4	2		
n-butane		2	4		4	
n-pentane		2	4		4	2
n-hexane		2	4		4	4
n-heptane		2	4		4	4
n-octane		2	4		4	4
n-nonane		2	4		4	4
n-decane		2	4		4	4
n-undecane		2	4		4	4
n-dodecane		2	4		4	4
n-tridecane		2	4		4	4
n-tetradecane		2	4		4	4
n-pentadecane		2	4		4	4
n-cetane		2	4		4	4

[a] Classification in accordance with the work of Cohe used a TST-based group-additivity model for H abstraction from alkanes. [b] In-plane primary H atom. [c] Out-of-plane p atoms. [d] Secondary H atoms that do not neighbor S_{01} H ato

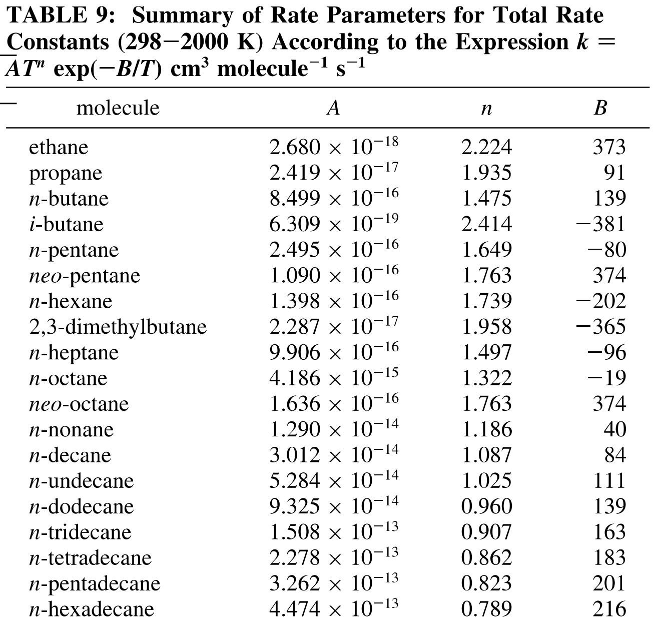
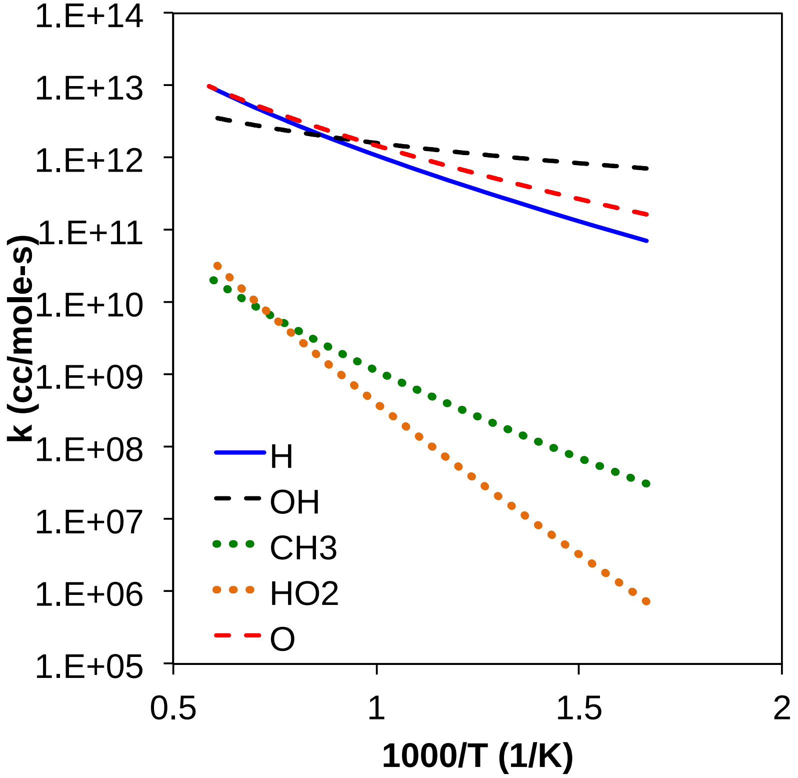


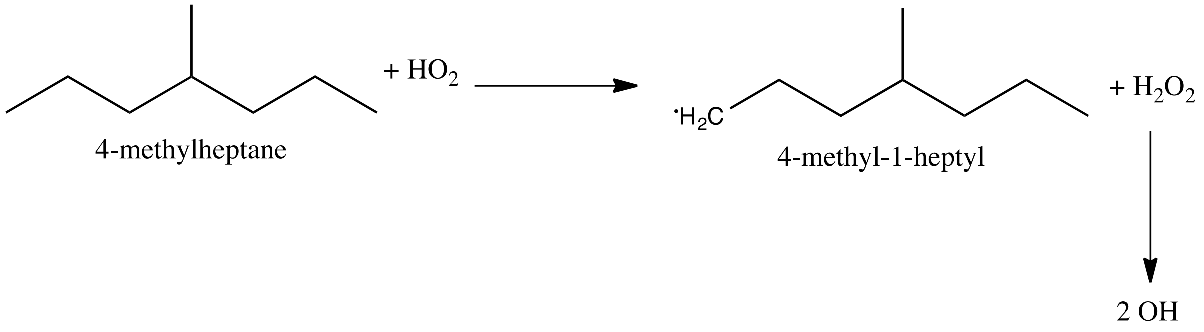
TABLE 9: Summary of Rate Parameters for Total Rate Constants (298−2000 K) According to the Expression $k = AT^n \exp(-B/T)$ cm³ molecule⁻¹ s⁻¹

molecule	*A*	*n*	*B*
ethane	2.680×10^{-18}	2.224	373
propane	2.419×10^{-17}	1.935	91
n-butane	8.499×10^{-16}	1.475	139
i-butane	6.309×10^{-19}	2.414	−381
n-pentane	2.495×10^{-16}	1.649	−80
neo-pentane	1.090×10^{-16}	1.763	374
n-hexane	1.398×10^{-16}	1.739	−202
2,3-dimethylbutane	2.287×10^{-17}	1.958	−365
n-heptane	9.906×10^{-16}	1.497	−96
n-octane	4.186×10^{-15}	1.322	−19
neo-octane	1.636×10^{-16}	1.763	374
n-nonane	1.290×10^{-14}	1.186	40
n-decane	3.012×10^{-14}	1.087	84
n-undecane	5.284×10^{-14}	1.025	111
n-dodecane	9.325×10^{-14}	0.960	139
n-tridecane	1.508×10^{-13}	0.907	163
n-tetradecane	2.278×10^{-13}	0.862	183
n-pentadecane	3.262×10^{-13}	0.823	201
n-hexadecane	4.474×10^{-13}	0.789	216

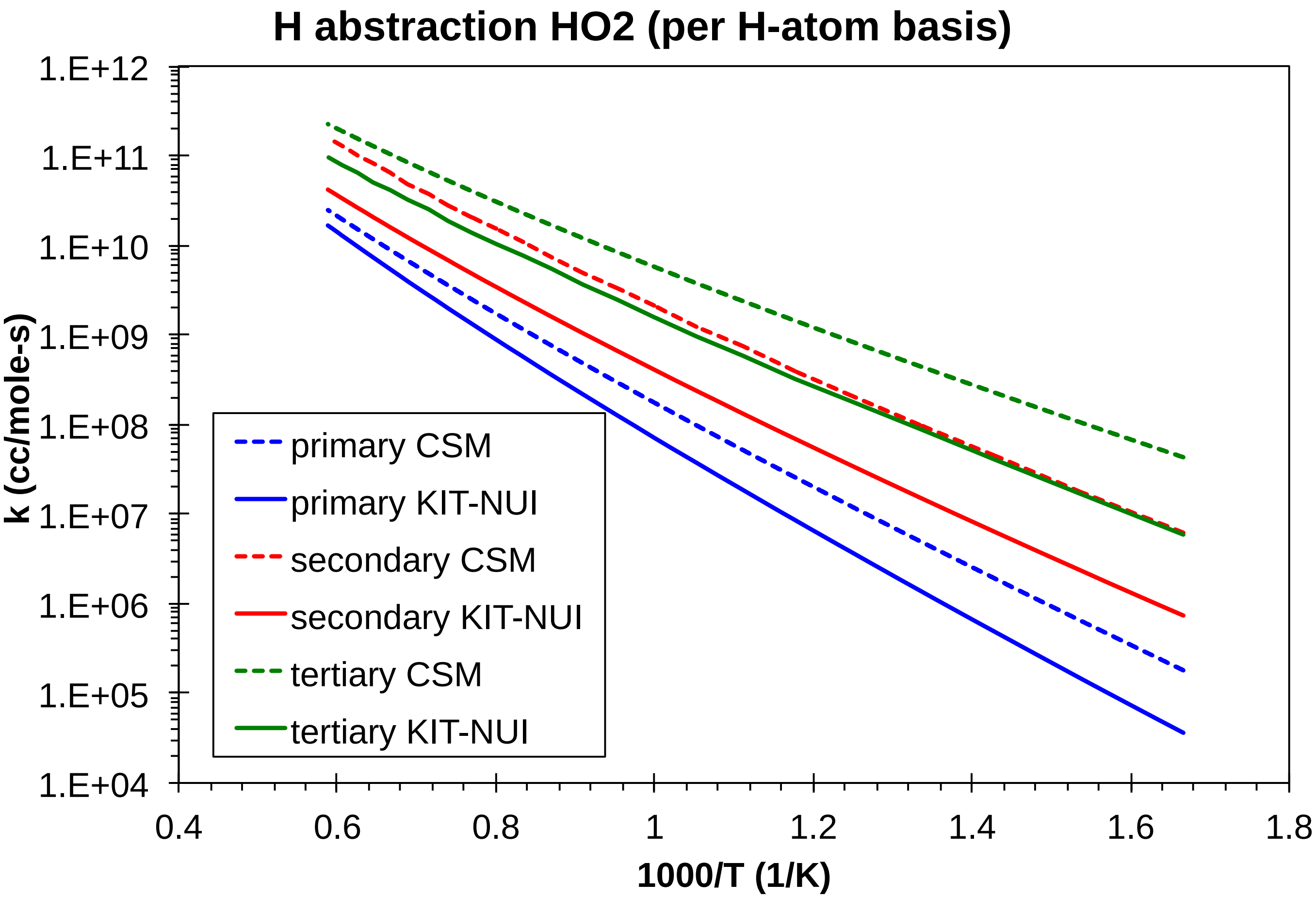
2: H atom abstractions from fuel

- Rate constants for abstraction by various radicals
- OH and H are the most reactive
- O radical is also very reactive, but usually present in small concentrations
- HO_2 is notably less reactive, but it leads to H_2O_2 which decomposes to 2 OH


per H-atom basis from a secondary site



H-atom abstraction from fuel: Uncertainty in HO_2+fuel rate



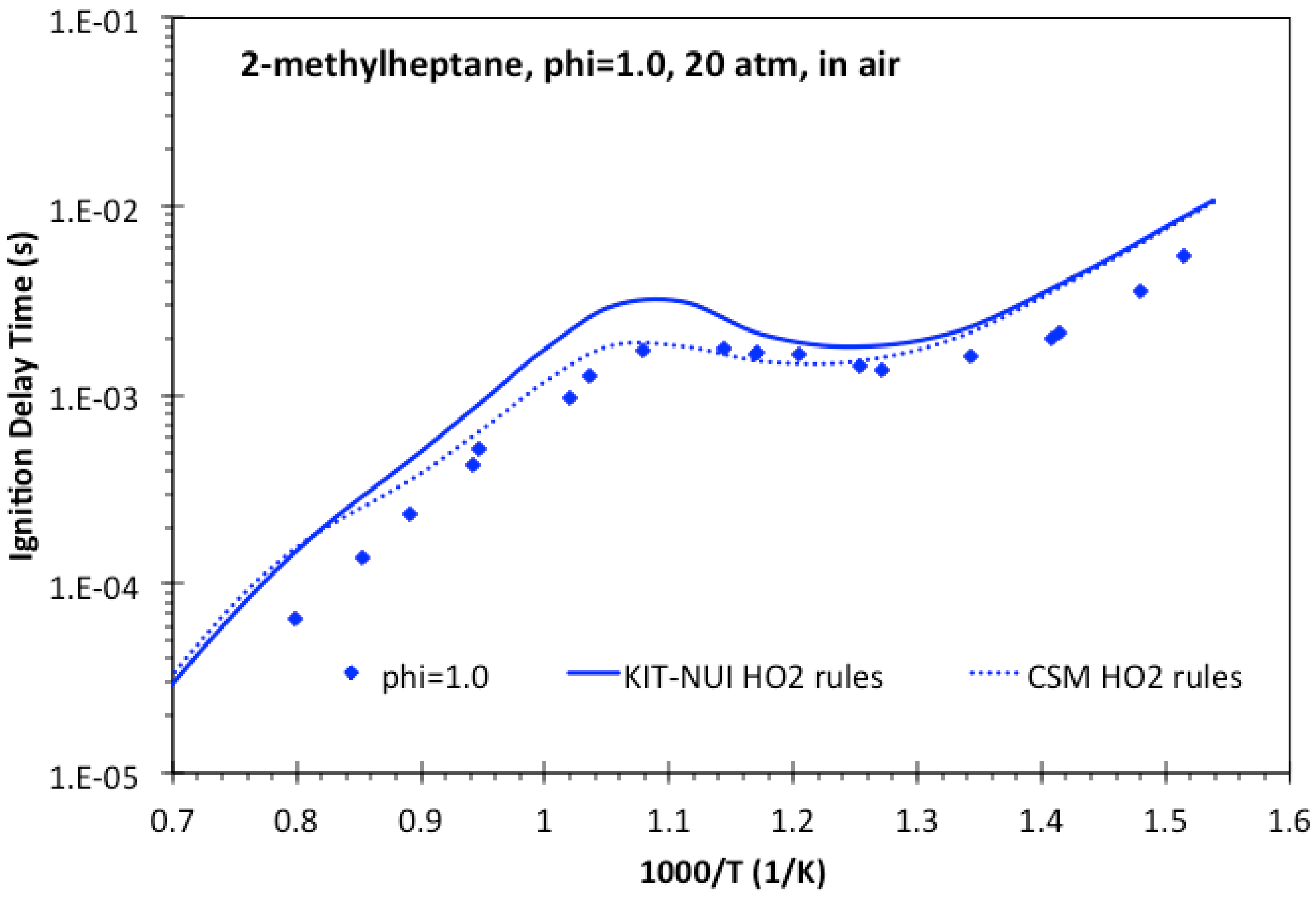
CSM rates are a 2-4x faster than KIT-NUI rate calculations for n-butane/iso-butane systems.

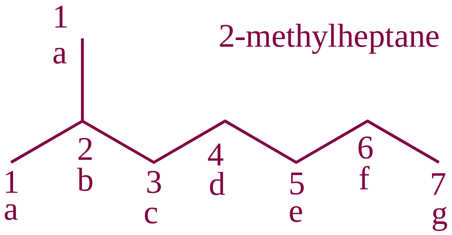
KIT-NUI rate calculations appear to be in better agreement with experimental work.

Aguilera-Iparraguirre et al., J. Phys. Chem. A (2008)

Carstensen et al., Proc. Combust. Inst. (2007)

Uncertainty in HO_2+fuel rate: Effect on shock tube ignition delay time



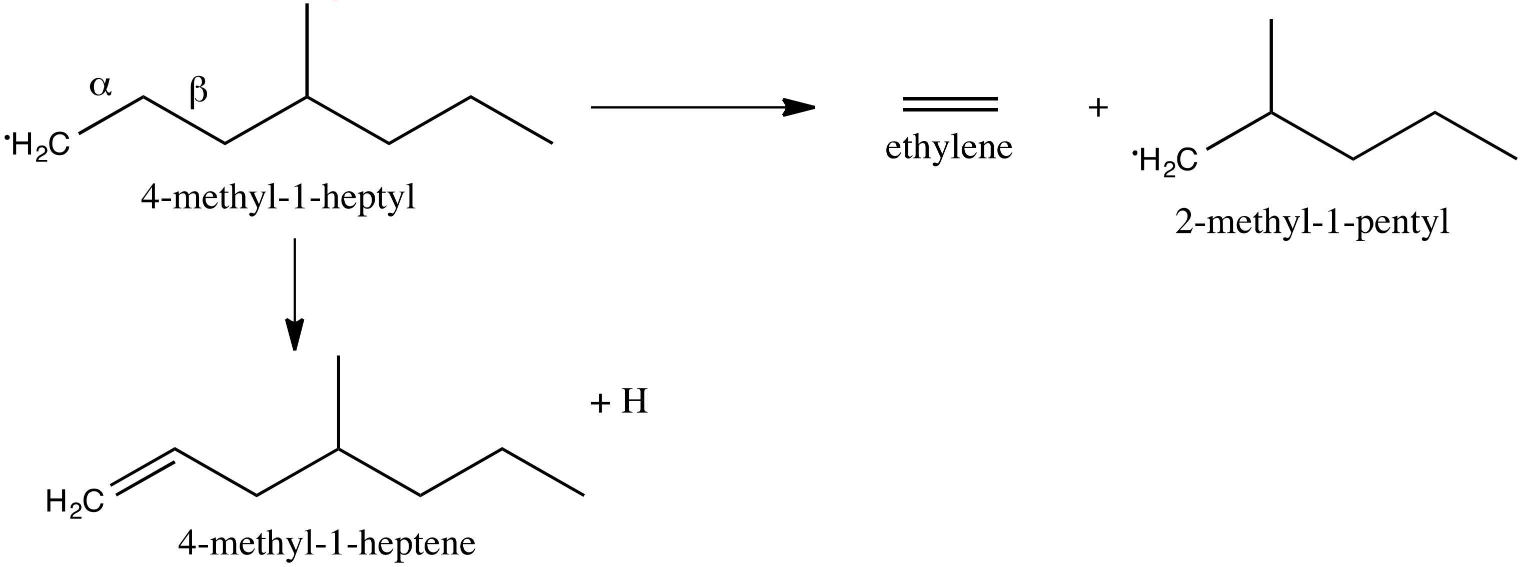


LLNL uses KIT-NUI rate calculations as a rule for large branched alkanes.

Applying CSM estimates would improve intermediate temperature predictions.

3: Alkyl radical decomposition

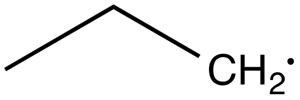
- Alkyl radicals undergo β-scission of C-C and C-H bonds to form a radical and an alkene.
- Bond **<u>once removed</u>** (i.e., β) from the radical site breaks to form a stable molecule an radical.
- β -scissions of C-H are negligible compared to C-C bond scissions in the forward direction.
- How many β-scissions are possible?



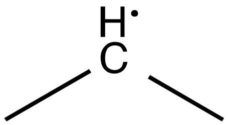
3: Alkyl radical decomposition

- Recombination rates for H-atom addition to an alkene (i.e., reverse of β-scission).

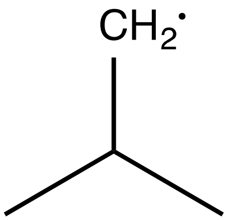
Reaction	A ($cm^3\ mol^{-1}\ s^{-1}$)	n	E_A (kcal)	Analogous reaction from Curran et al. IJCK 2006
$H + C_8H_{16}\text{-1-4} = C_8H_{17}\text{-1-4}$	2.50E+11	0.51	2,620	$H + C_3H_6 = nC_3H_7$
$H + C_8H_{16}\text{-2-4} = C_8H_{17}\text{-2-4}$	4.24E+11	0.51	1,230	$H + C_3H_6 = iC_3H_7$
$H + C_8H_{16}\text{-3-4} = C_8H_{17}\text{-4-4}$	1.06E+12	0.51	1,230	$H + iC_4H_8 = tC_4H_9$



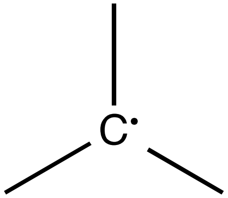
n-propyl



iso-propyl



iso-butyl



tert-butyl

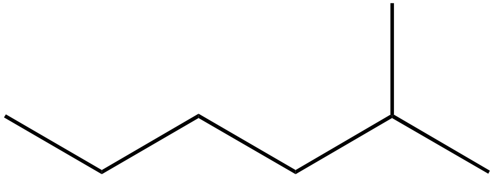
Curran, H.J. Int. J. Chem. Kin. 28 (4) (2006) 250-275

3: Alkyl radical decomposition

- Rates of β -scission reactions involving C-C bonds

Reaction	A ($cm^3\ mol^{-1}\ s^{-1}$)	n	E_A (kcal)	Reference
C7H15-2a = C3H6 + pC4H9	3.68E+15	-0.56	31,359	Awan JPC A 2010
C7H15-2a = CH3 + C6H12-1	9.55E+14	-0.59	30,592	Awan JPC A 2010
C7H15-2b = nC3H7 + iC4H8	1.71E+12	0.31	26,610	Awan JPC A 2010
C7H15-2c = C2H5 + C5H10-1-2	3.08E+13	0.03	28,992	Awan JPC A 2010
C7H15-2c = CH3 + C6H12-2	1.77E+13	0.11	30,542	Awan JPC A 2010
C7H15-2d = CH3 + C6H12-1-2	6.98E+12	0.16	24,963	Awan JPC A 2010
C7H15-2d = iC3H7 + C4H8-1	9.55E+14	-0.59	30,592	Awan JPC A 2010
C7H15-2e = C3H6 + C6H12-1-2	1.06E+13	0.07	27,125	Awan JPC A 2010
C7H15-2f = C2H4 + C5H11-1-2	2.64E+15	-0.55	31,136	Awan JPC A 2010

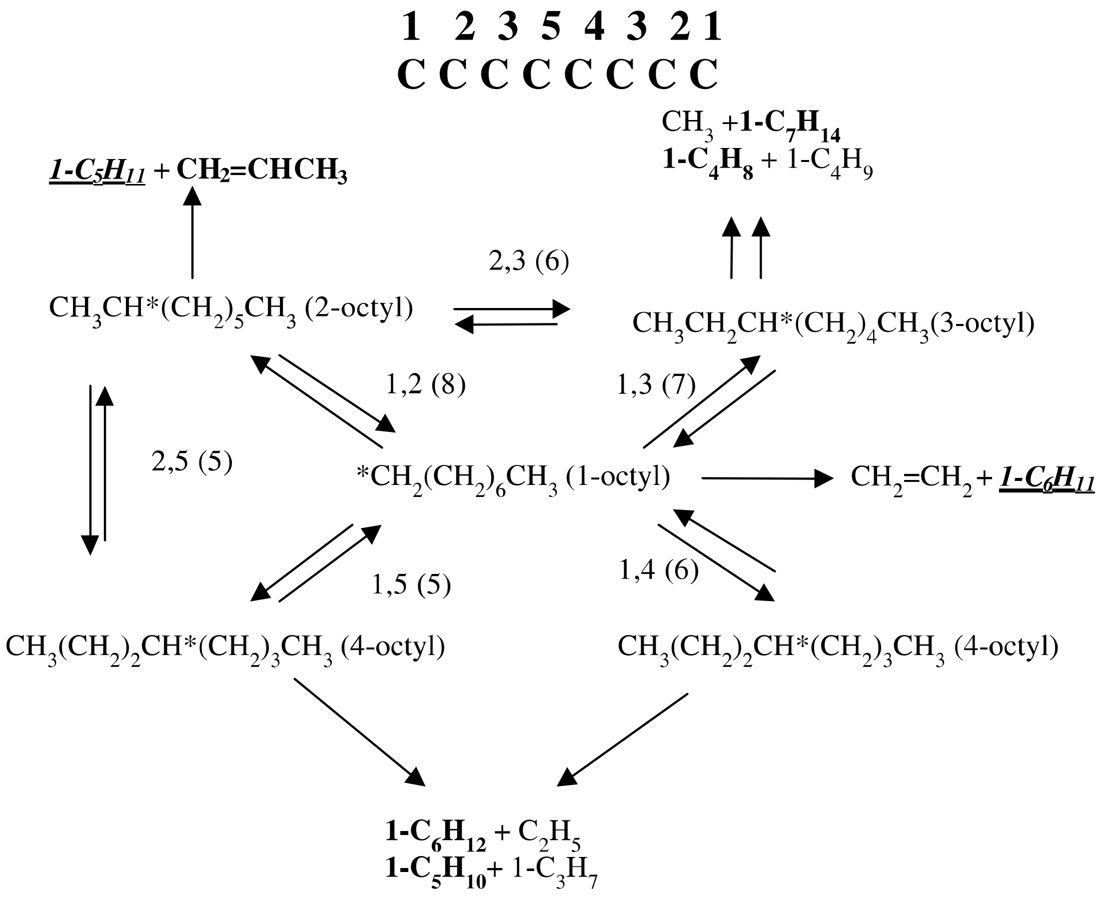
I.A. Awan, W.S. McGivern, W. Tsang, J.A. Manion, J. Phys. Chem. A 114 (2010)



2-methylhexane

4: Alkyl radical isomerization

- Alkyl radical decompositions cannot be separated from radical isomerizations



1 2 3 5 4 3 2 1

C C C C C C C C

CH_3 + **$1\text{-}C_7H_{14}$**

$1\text{-}C_4H_8$ + $1\text{-}C_4H_9$

$1\text{-}C_5H_{11}$ + **$CH_2{=}CHCH_3$**

2,3 (6)

$CH_3CH^*(CH_2)_5CH_3$ (2-octyl)

$CH_3CH_2CH^*(CH_2)_4CH_3$(3-octyl)

1,2 (8)

1,3 (7)

2,5 (5)

$^*CH_2(CH_2)_6CH_3$ (1-octyl)

$CH_2{=}CH_2$ + ***$1\text{-}C_6H_{11}$***

1,5 (5)

1,4 (6)

$CH_3(CH_2)_2CH^*(CH_2)_3CH_3$ (4-octyl)

$CH_3(CH_2)_2CH^*(CH_2)_3CH_3$ (4-octyl)

$1\text{-}C_6H_{12}$ + C_2H_5

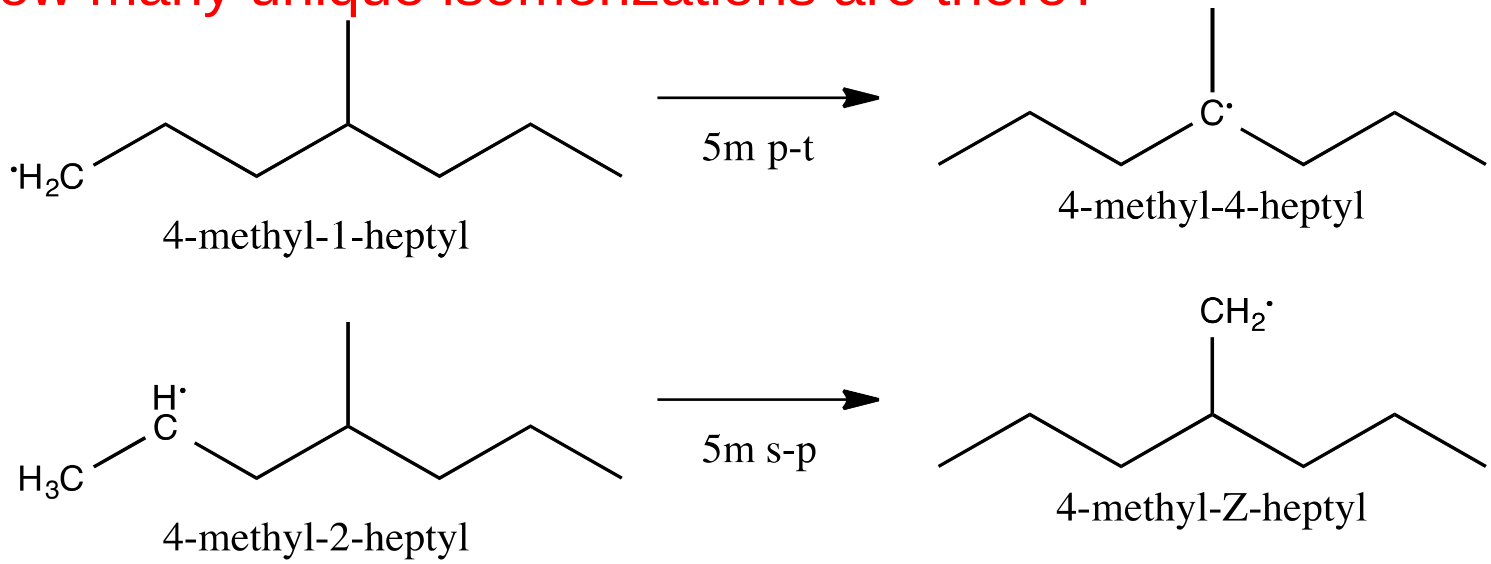
$1\text{-}C_5H_{10}$+ $1\text{-}C_3H_7$

W. Tsang, W.S. McGivern, J.A. Manion, Proc. Combust. Inst. 32 (2009)

- These reactions involved transfer of H-atoms within the molecule
- Typically more important under fuel rich conditions and at temperatures where decomposition are less favored

4: Alkyl radical isomerization

- The rate constant for these reactions depends on the nature of the broken C-H bond (i.e., primary, secondary, or tertiary) and on the ring strain energy barrier.
- Isomerization reactions involving 5-member, 6-member, and 7-member transition state ring are most important
- Radical isomerizations involving fewer than five and greater than seven members are much slower.
- How many unique isomerizations are there?



4: Alkyl radical isomerization

- Evans-Polyani correlations present a general rate rule approach for isomerization rate constants
- E_{rs} is activation energy compensated for ring strain
- DH_{rxn} is the heat of reaction in the exothermic direction

$$E_a^{\infty} \approx E_{rs} + a + b\Delta H_{rxn}^{298}$$

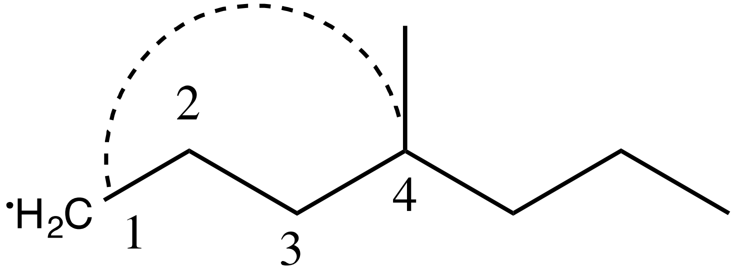
Rotor Loss A and Parameter n^b

number of rotors lost in TS	A^{∞}	n^{∞}
1	3.56×10^{10}	0.88
2	3.80×10^{10}	0.67
3	7.85×10^{11}	−0.12
4	3.67×10^{12}	−0.6
5	2.80×10^{10}	0.0

Ring-Strain Corrections, $E_{rs}{}^c$

ring size	E_a
3	25.6
4	24.1
5	8.8
6	1.0
7	5.0

Evans−Polanyi	a	b
	13.4	0.6

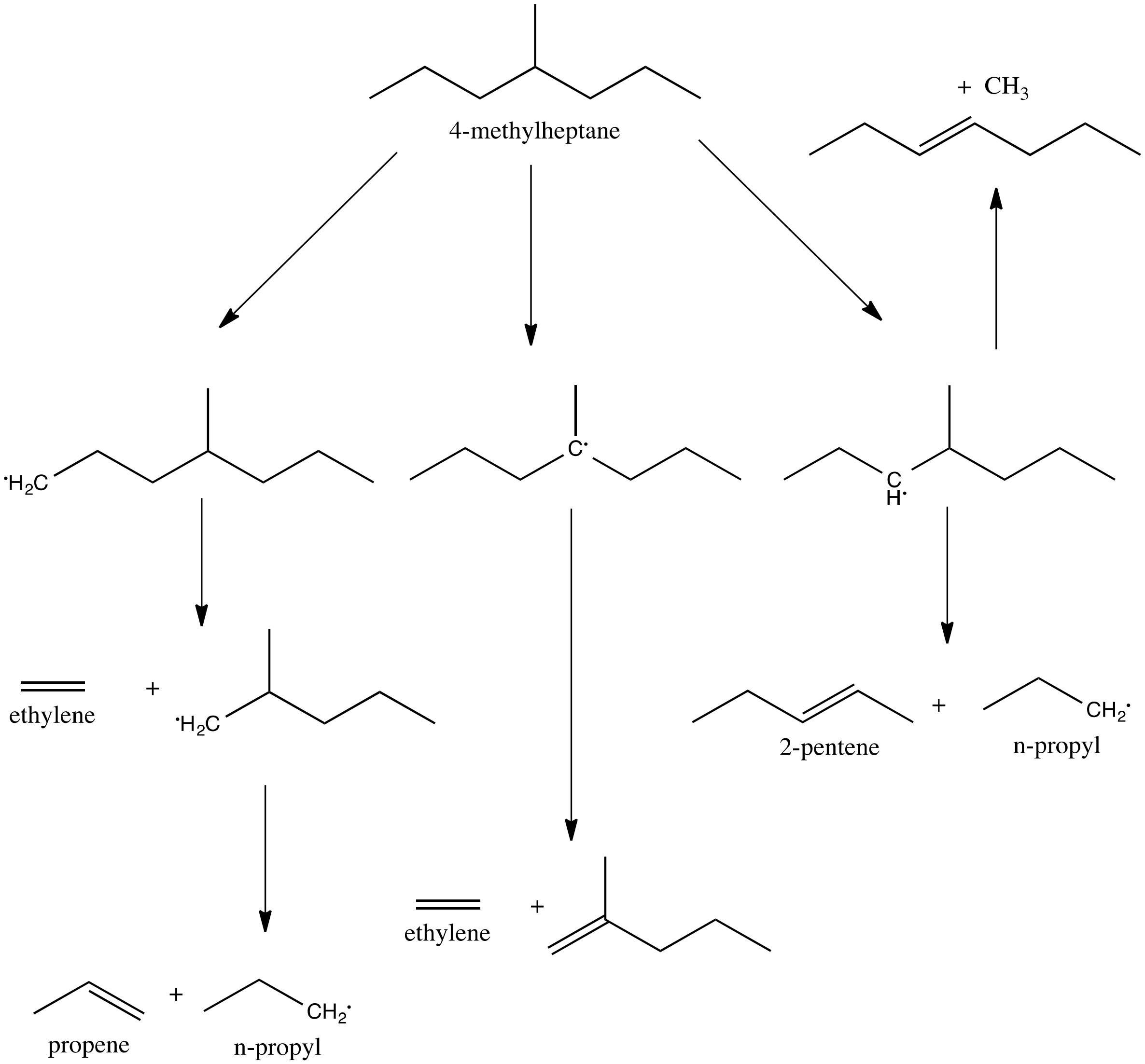


1,4 isomerization ties up 3 rotors

D.M. Matheu, W.H. Green, J.M. Grenda, Int J Chem Kin 2003

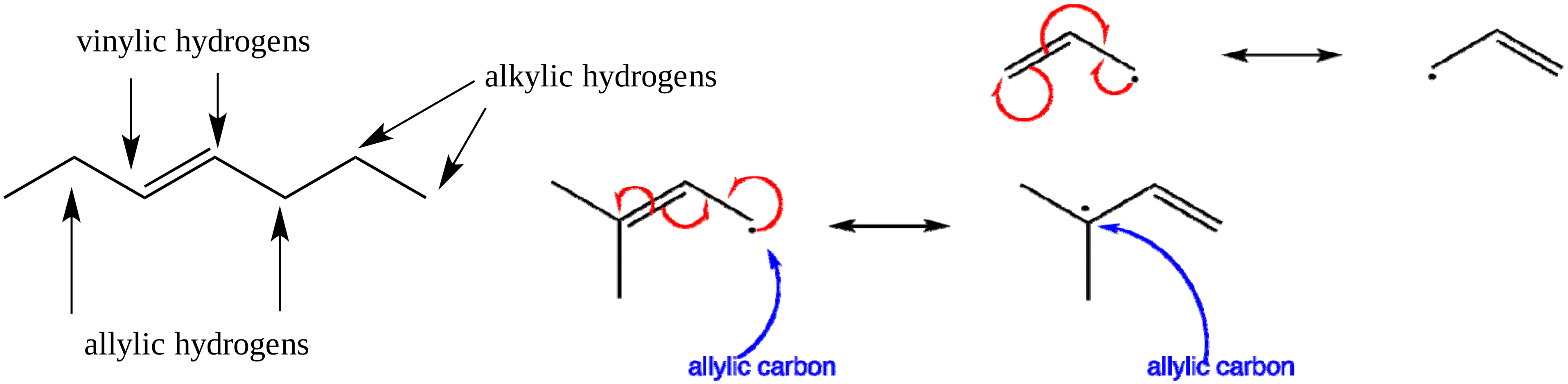
so where are we now?

- Fuel has been decomposed to smaller radicals and alkenes
- Need to oxidize/consume larger intermediates to smaller species



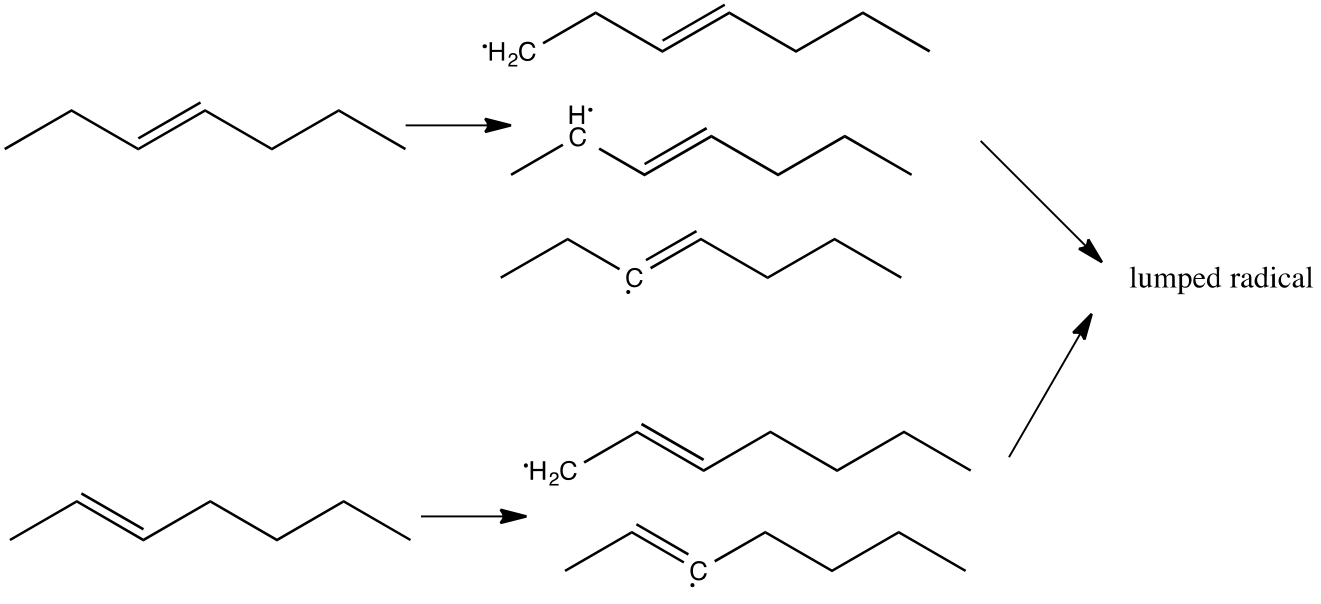
5: H atom abstraction from alkenes

- The addition of a double bond in alkene molecules presents additional complexity in describing/modeling their combustion chemistry.
- H-abstraction from the b-position to the double bond results in electron delocalization in the emerging alkenyl radical.
- The enthalpy of reaction of the initiations with oxygen molecules leading to allylic radicals is about 15 kcal/mol lower than those leading to alkyl radicals.
- A-factors are lower by about a factor of 10 due to the reduction of the entropy of activation caused by the loss of one rotation in the delocalized radical.



5: H atom abstraction from alkenes

- When alkenes are an intermediate (i.e., not the fuel), one can treat abstraction reactions from large alkenes in a simplified manner
- Neglect the presence of primary, secondary, tertiary, allylic, and vinylic C-H sites, so abstraction reactions by radical species (i.e., H, OH, CH_3, HO_2, and O) lead to one “lumped” alkenyl radical.
- The reaction rate constants are assumed to be identical to those of the analogous abstraction reactions from a secondary C-H site in an alkane multiplied by the number of abstractable hydrogens.



C = C double bonds reduce low T reactivity

s s a v v a s s

- C – C – C – C = C – C – C – C

s s a a s s

- Inserting one C=C double bond changes the C-H bond strength for 6 H atoms in the C chain
- Allylic C – H bond sites are weaker than most others
- Therefore they are preferentially abstracted by radicals
- O_2 is also very weakly bound at allylic sites and falls off rapidly, inhibiting low T reactivity

Two double bonds make a huge difference

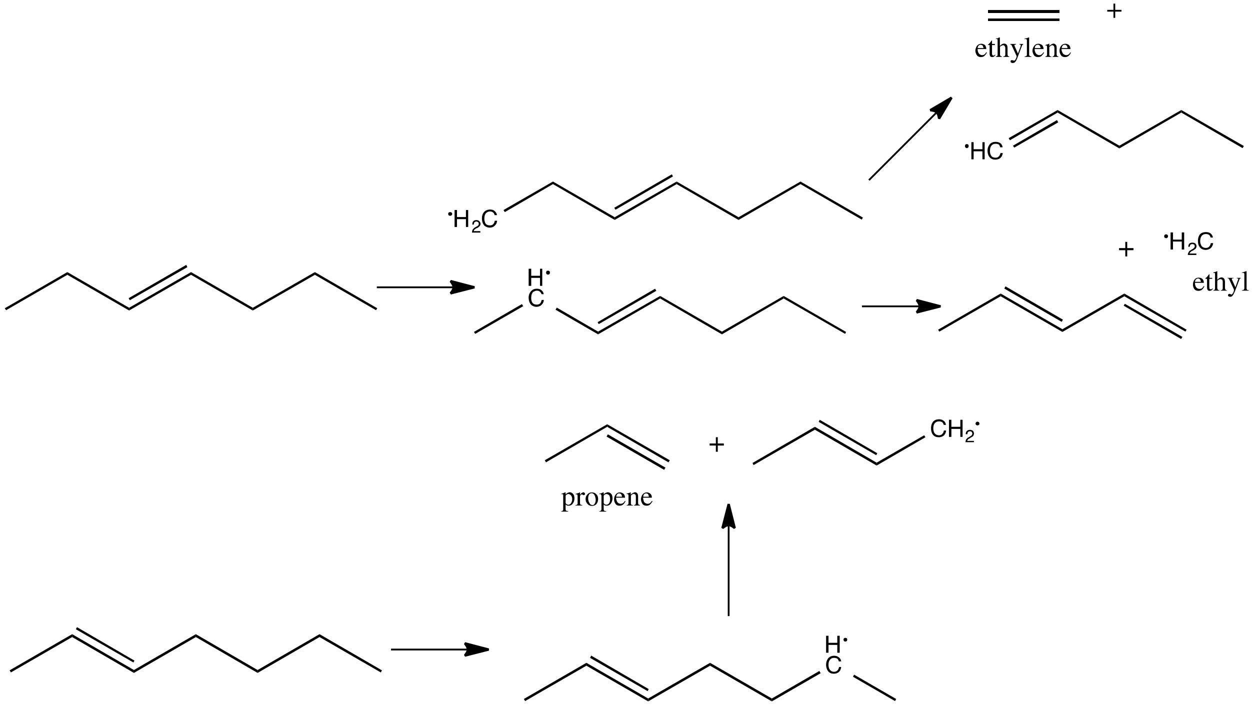
	s		s		a		v		v		a		s		s		s	
-	C	-	C	-	C	-	C	=	C	-	C	-	C	-	C	-	C	-
	s		s		a						a		s		s		s	

	s		s		a		v		v		a'		v		v		a		s	
-	C	-	C	-	C	-	C	=	C	-	C	-	C	=	C	-	C	-	C	-
	s		s		a						a'						a		s	

C – H s site > C – H a site > C – H a’ site

7: Alkenyl radical decomposition

- The decomposition of lumped alkenyl radicals is simplified to produce the “right” distribution of products.
- The activation energy changes depending on the products formed.
- Reactions leading to vinylic (i.e., C_2H_3) and allylic (C_3H_5) radicals have activation energies of 35,000 and 25,000 cal/mol, respectively, while all other reactions have activation energies of 30,000 cal/mol.



Next: low T reactions of large fuels

Kinetic Reaction Mechanisms for Hydrocarbon Fuels

Part 3 -- Larger molecules
Low temperatures

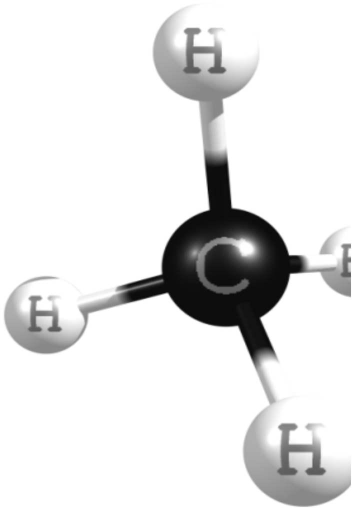
Generation of Detailed Chemical Kinetic Models for Hydrocarbon and Oxygenated Fuels Larger than C_5

Charles Westbrook

Tsinghua-Princeton
2014 Summer School on Combustion
July 20-25, 2014

Chemical Modeling

- Fuel + O_2 -> CO_2 + H_2O + Energy
- Small hydrocarbon fuel (e.g. methane)
  - 200 reactions
  - 30 chemical intermediates
- Chemical mechanism
  - Kinetics
  - Thermodynamics



Chemical Kinetic Model

Contains a large database of:

- Thermodynamic properties of species
- Reaction rate parameters

Size of mechanism grows with molecular size:

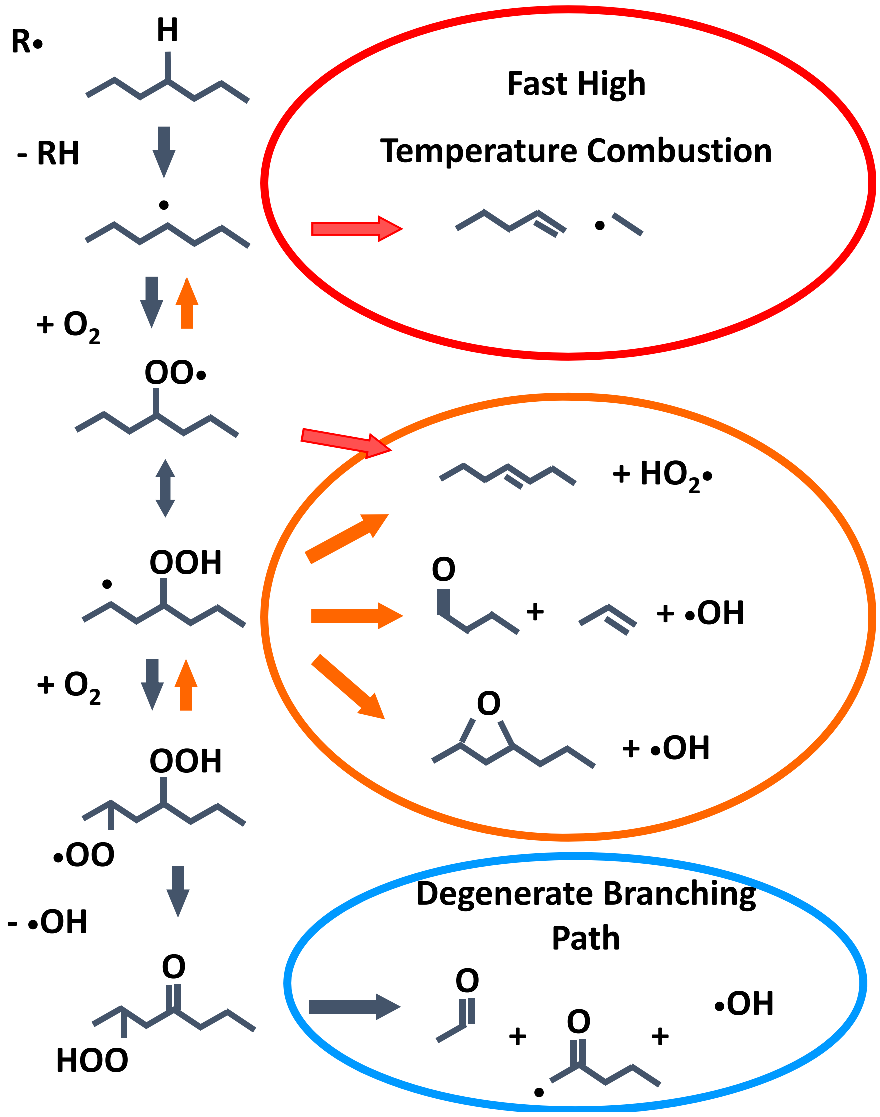
Fuel:	H_2	CH_4	C_3H_8 (Propane)	C_6H_{14} (Hexane)	$C_{16}H_{34}$ (Cetane)
Number of species:	7	30	100	450	1200
Number of reactions:	25	200	400	1500	7000

Dominance of H2/O2 Reactions

For nearly all hydrocarbon oxidation, no matter how large or small the fuel molecule, at high temperatures, the reactions of H2/O2 have the greatest sensitivity controlling the overall rate of reaction. This is true in flames, detonations, shock tubes, and many other practical combustors.

But low temperature reactions can contribute in many interesting and important ways

Comprehensive Combustion Chemistry

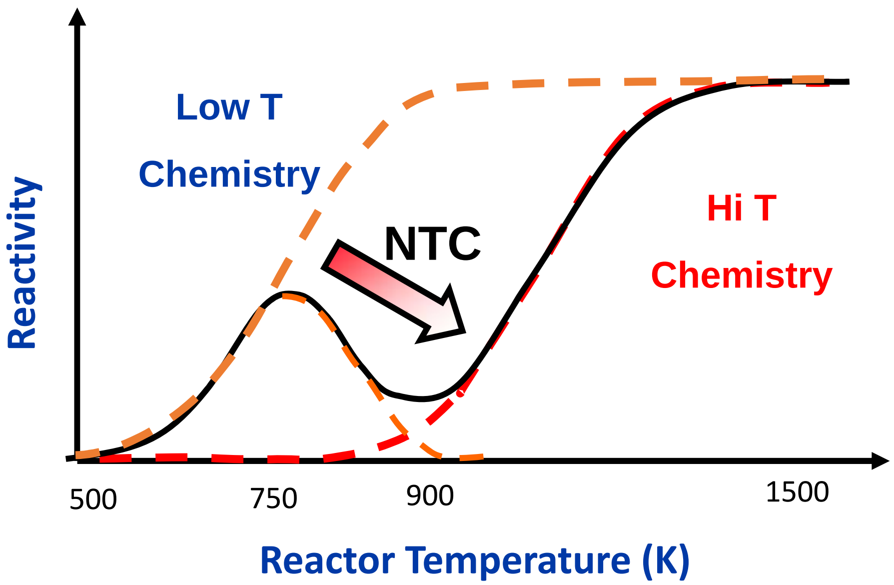


Fast High

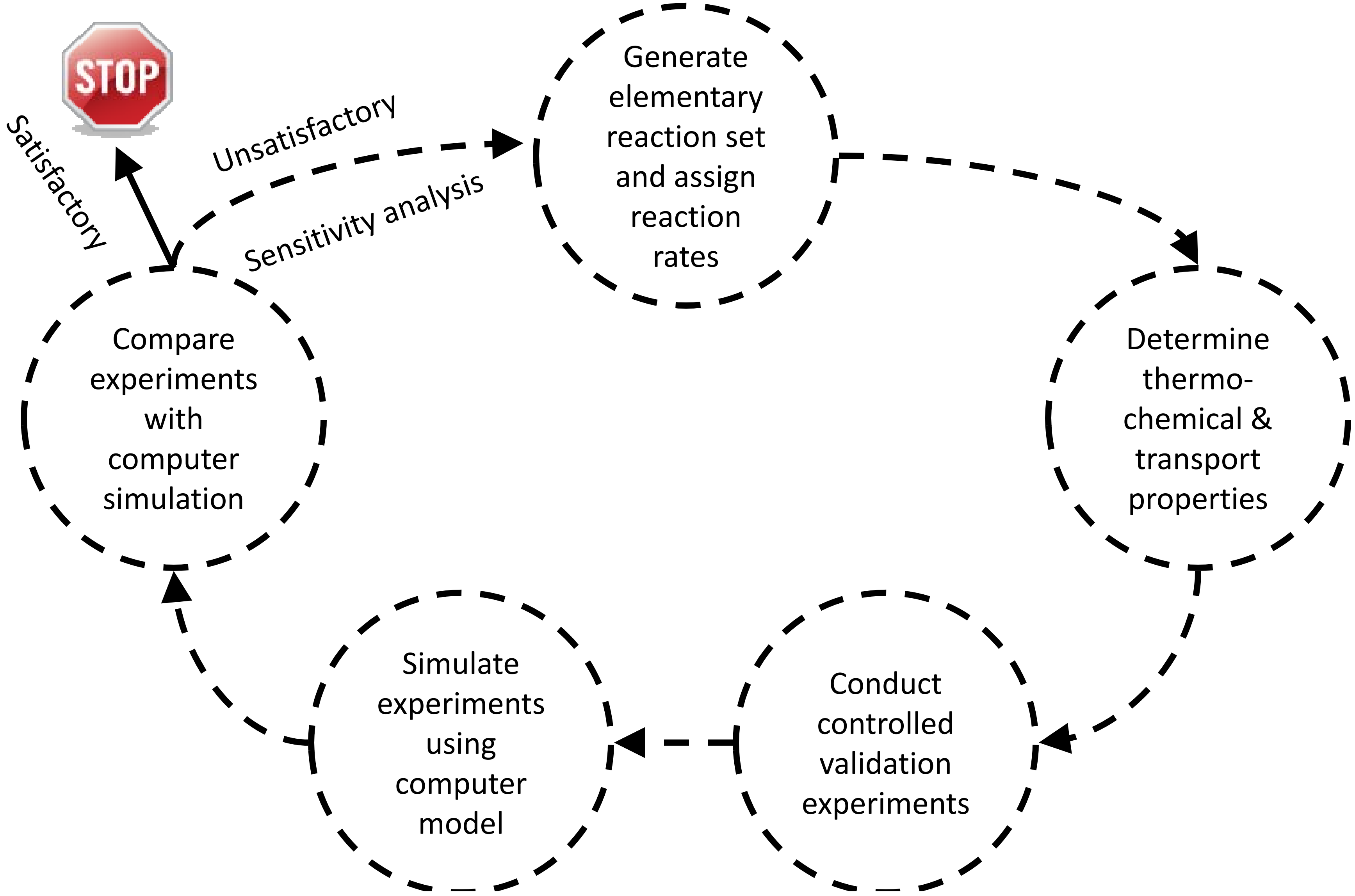
Temperature Combustion

Degenerate Branching Path

Long Chain Alkanes



Chemical Kinetic Modeling Process Cycle



Generate elementary reaction set and assign reaction rates

Determine thermo-chemical & transport properties

Conduct controlled validation experiments

Simulate experiments using computer model

Compare experiments with computer simulation

Unsatisfactory

Sensitivity analysis

Satisfactory

STOP

Reaction classes for oxidation chemistry

High temperature mechanism

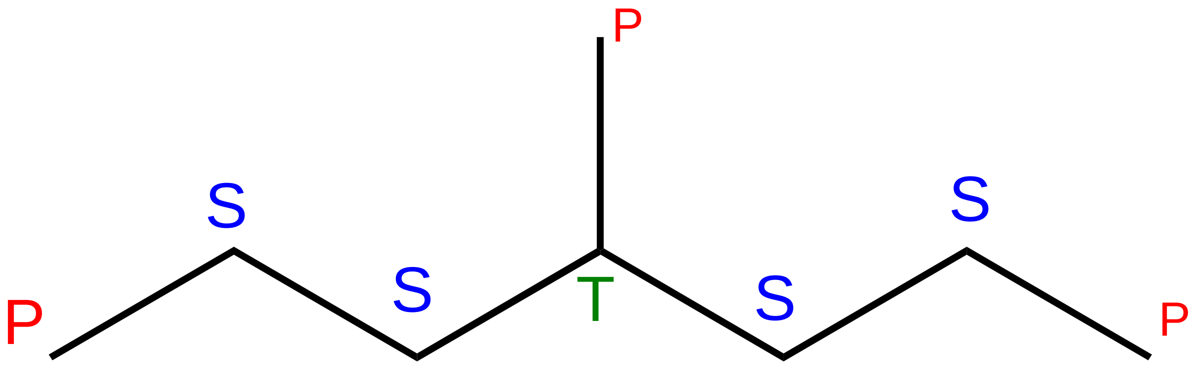
1: Unimolecular fuel decomposition
2: H atom abstractions from fuel
3: Alkyl radical decomposition
4: Alkyl radical isomerization
5: H atom abstraction from alkenes
6: Addition of radical species to alkenes
7: Alkenyl radical decomposition
8: Alkene decomposition
9: Retroene decomposition reactions

Reaction classes for oxidation chemistry

Low temperature mechanism

10: Alkyl radical addition to O_2 ($R + O_2 = RO_2$)
12,13, and 14: $R + R'O_2 = RO + R'O$
15: Alkylperoxy radical isomerization (RO_2=QOOH)
16: Concerted eliminations (RO_2 = alkene + HO_2)
17: $RO_2 + HO_2 = ROOH + O_2$
18: $RO_2 + H_2O_2 = ROOH + HO_2$
19: $RO_2 + CH_3O_2 = RO + CH_3O + O_2$
20: $RO_2 + R'O_2 = RO + R'O + O_2$
21: ROOH = RO + OH
22: RO decomposition
23: QOOH = cyclic ether + OH (cyclic ether formation)
24: QOOH = alkene+ HO_2 (radical beta to OOH)
25: QOOH = alkene + carbonyl + OH (radical gamma to OOH)
26: Addition of QOOH to molecular oxygen O_2 ($QOOH+O_2=O_2QOOH$)
27: O_2QOOH isomerization to carbonylhydroperoxide + OH
28: Carbonylhydroperoxide decomposition
29: Reactions of cyclic ethers with OH and HO_2

Test molecule



4-methylheptane

Bond dissociation energies

Primary: ~103 kcal/mol

Secondary: ~98 kcal/mol

Tertiary: ~94 kcal/mol

Low temperature combustion chemistry

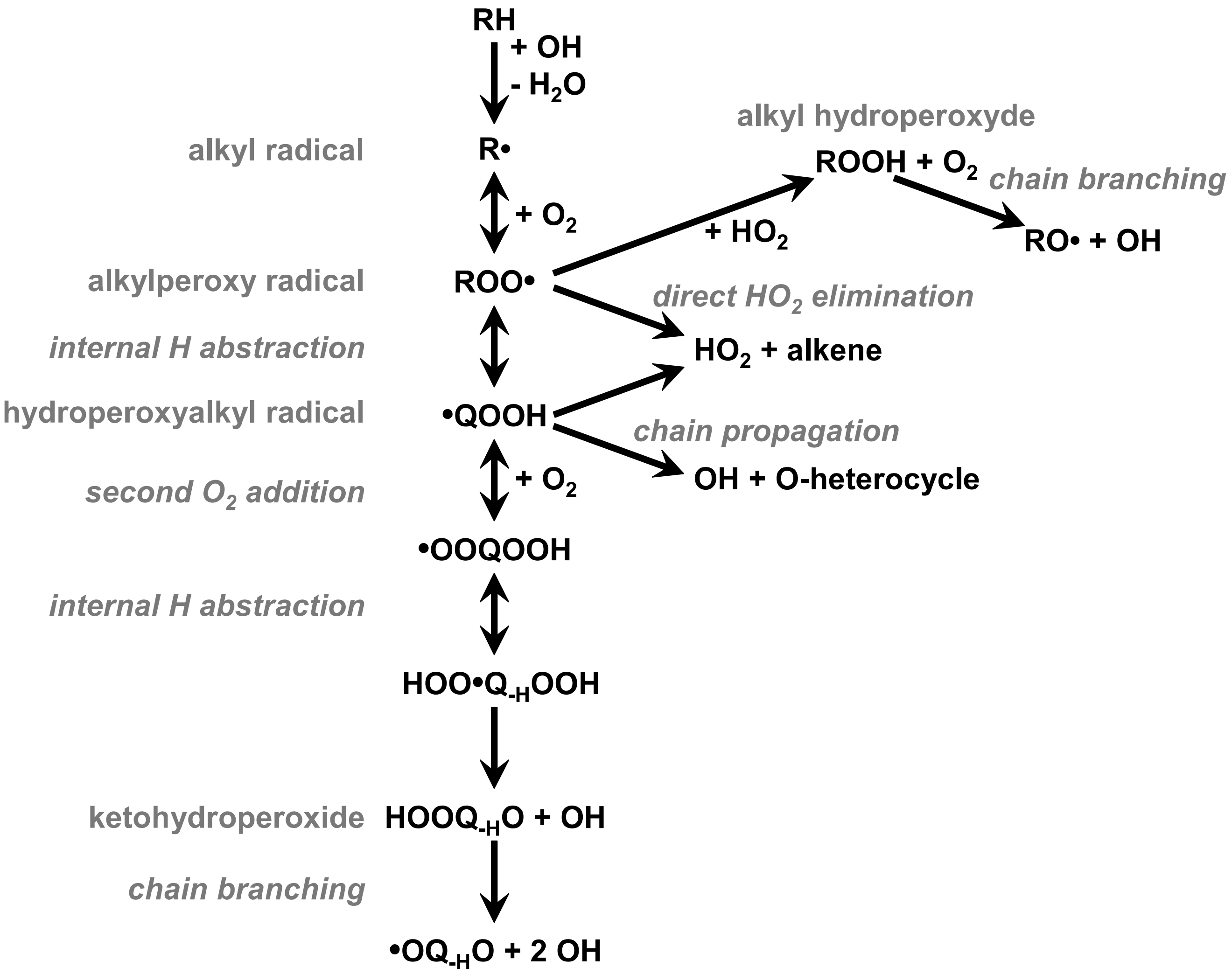
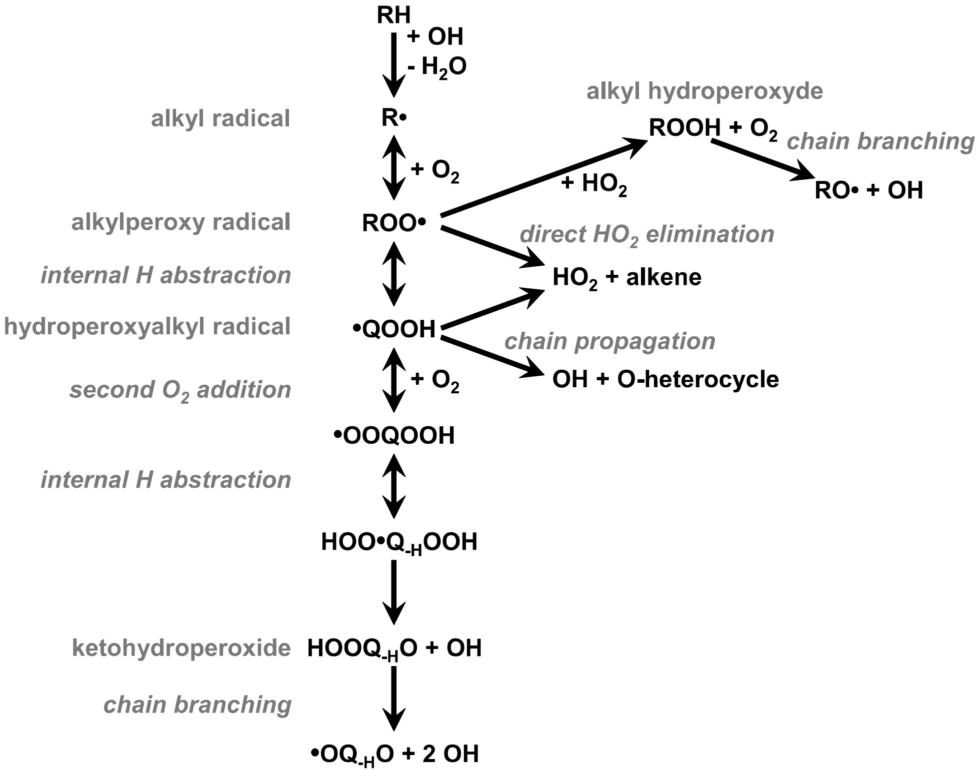


Fig. 1. Schematic mechanism for low-temperature hydrocarbon oxidation and autoignition chemistry.

What is the reason for NTC reactivity?



RH

+ OH

- H_2O

alkyl radical R•

+ O_2

alkylperoxy radical ROO•

internal H abstraction

hydroperoxyalkyl radical •QOOH

second O_2 addition + O_2

•OOQOOH

internal H abstraction

HOO•Q$_{-H}$OOH

ketohydroperoxide HOOQ$_{-H}$O + OH

chain branching

•OQ$_{-H}$O + 2 OH

+ HO_2

alkyl hydroperoxyde

ROOH + O_2

chain branching

RO• + OH

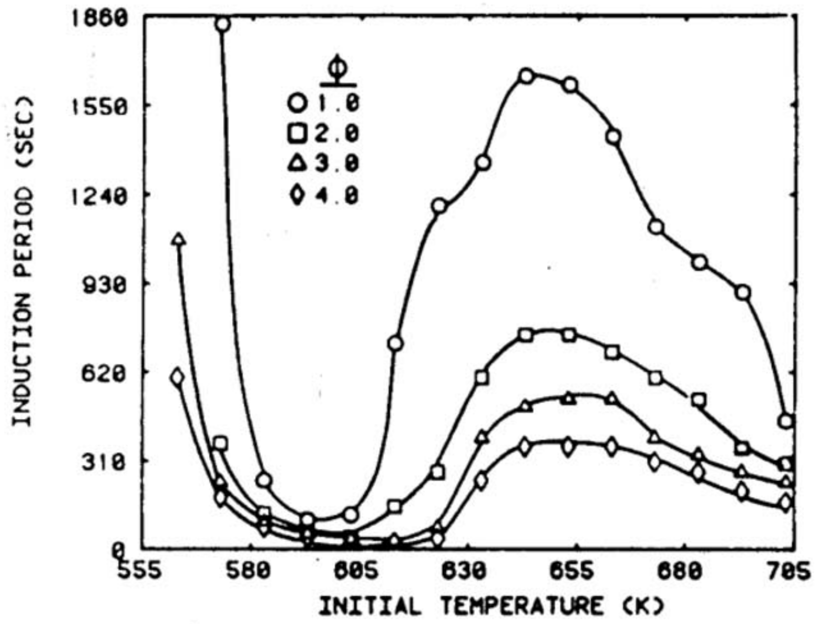
direct HO_2 elimination

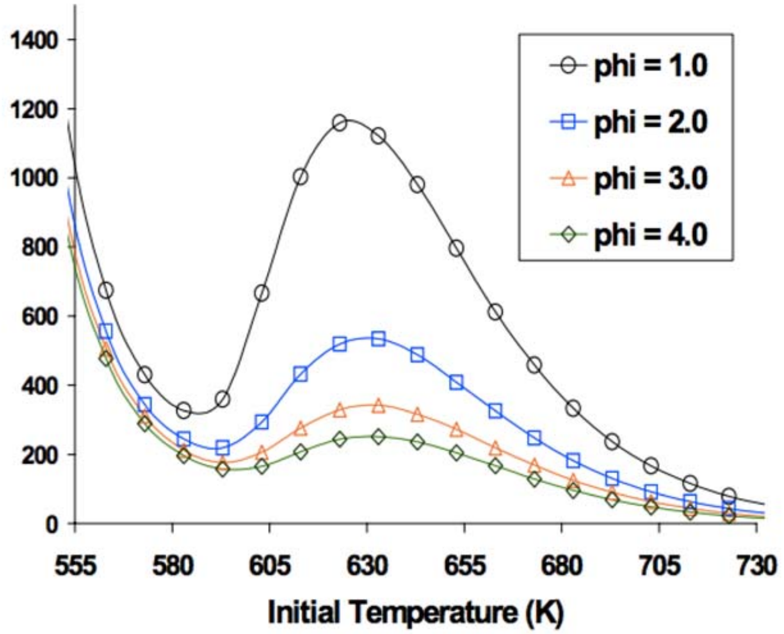
HO_2 + alkene

chain propagation

OH + O-heterocycle

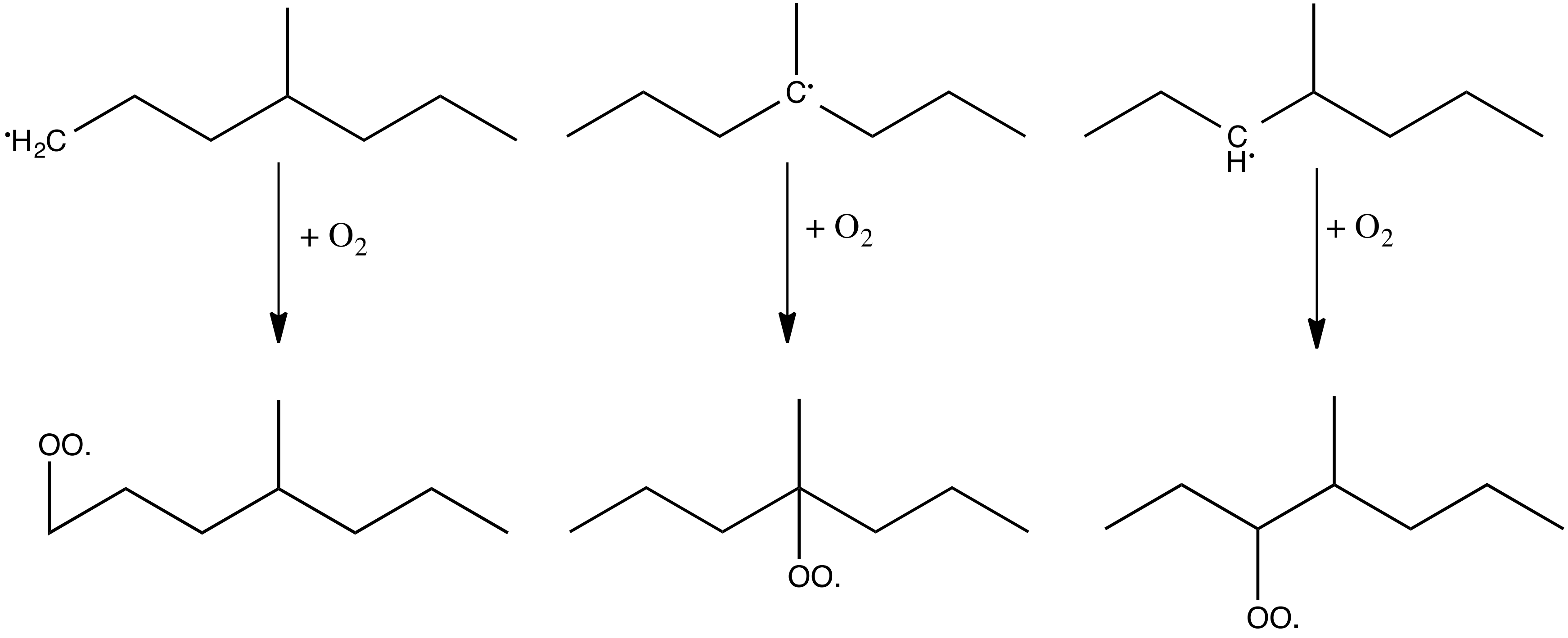
Fig. 1. Schematic mechanism for low-temperature hydrocarbon oxidation and autoignition chemistry.





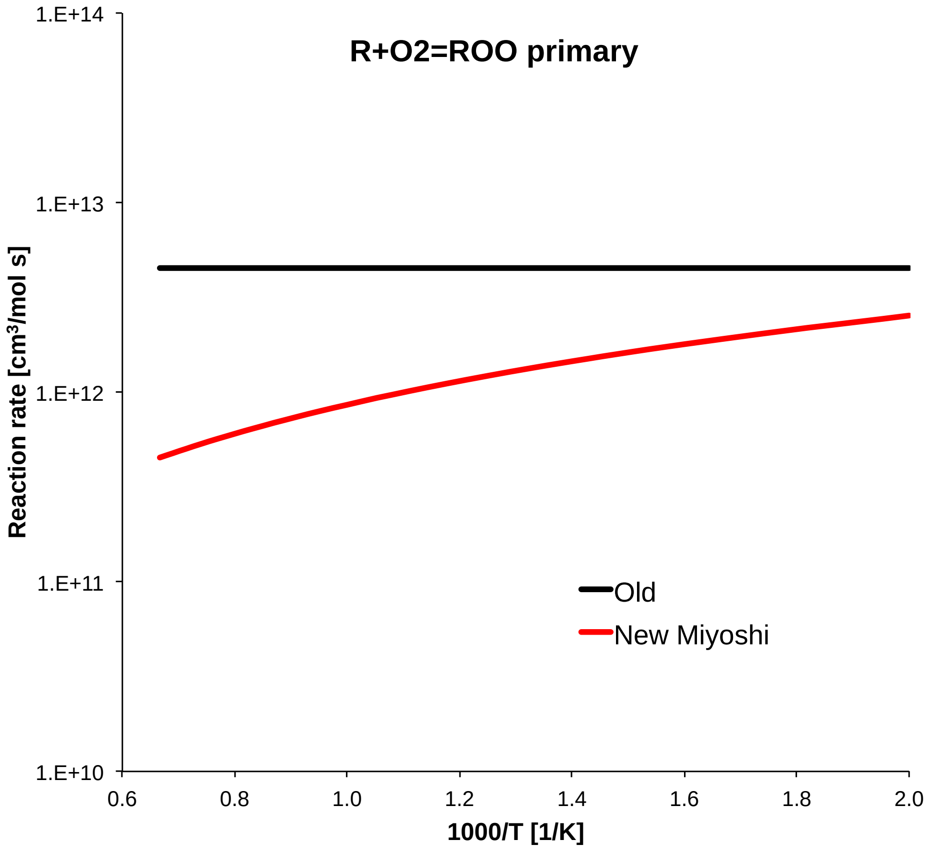
10: Alkyl radical addition to O_2 ($R+O_2=ROO$)

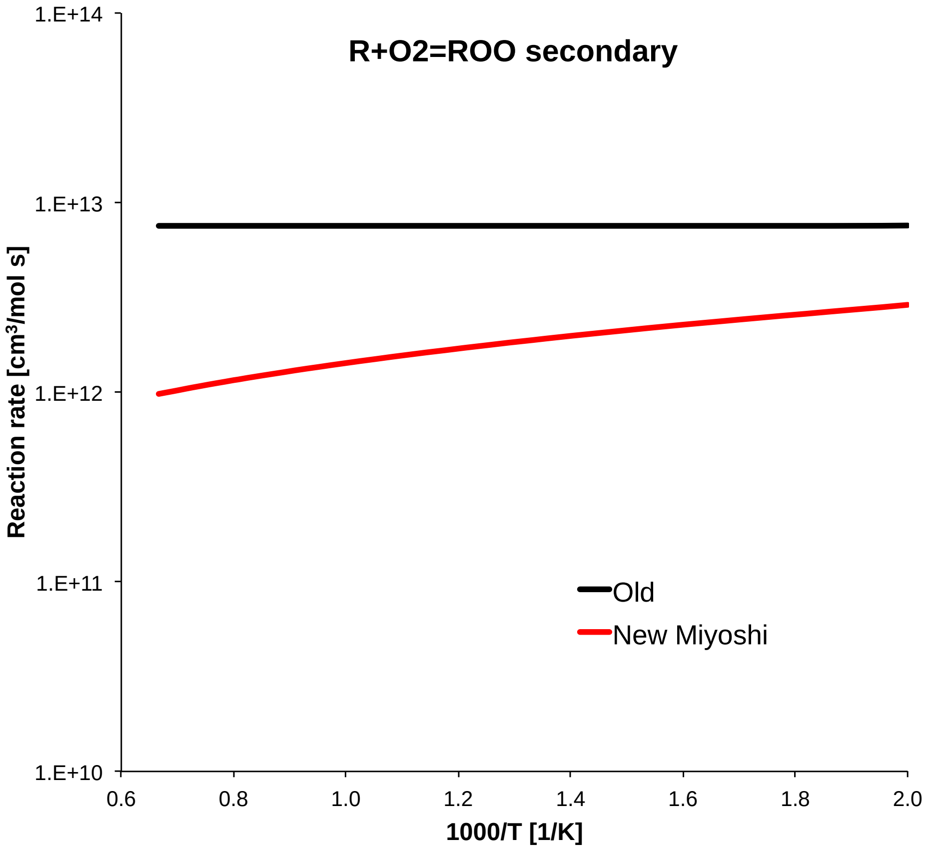
- The addition of molecular oxygen to alkyl radicals is the first step in the low temperature chain branching process.
- Each unique fuel radical leads to an alkylperoxy (ROO.) radical
- The chemistry of alkylperoxy radicals governs tropospheric oxidation of organic species. In combustion chemistry however, the $R+O_2$ reaction displays much more complex behavior.



10: Alkyl radical addition to O_2 ($R+O_2=ROO$)

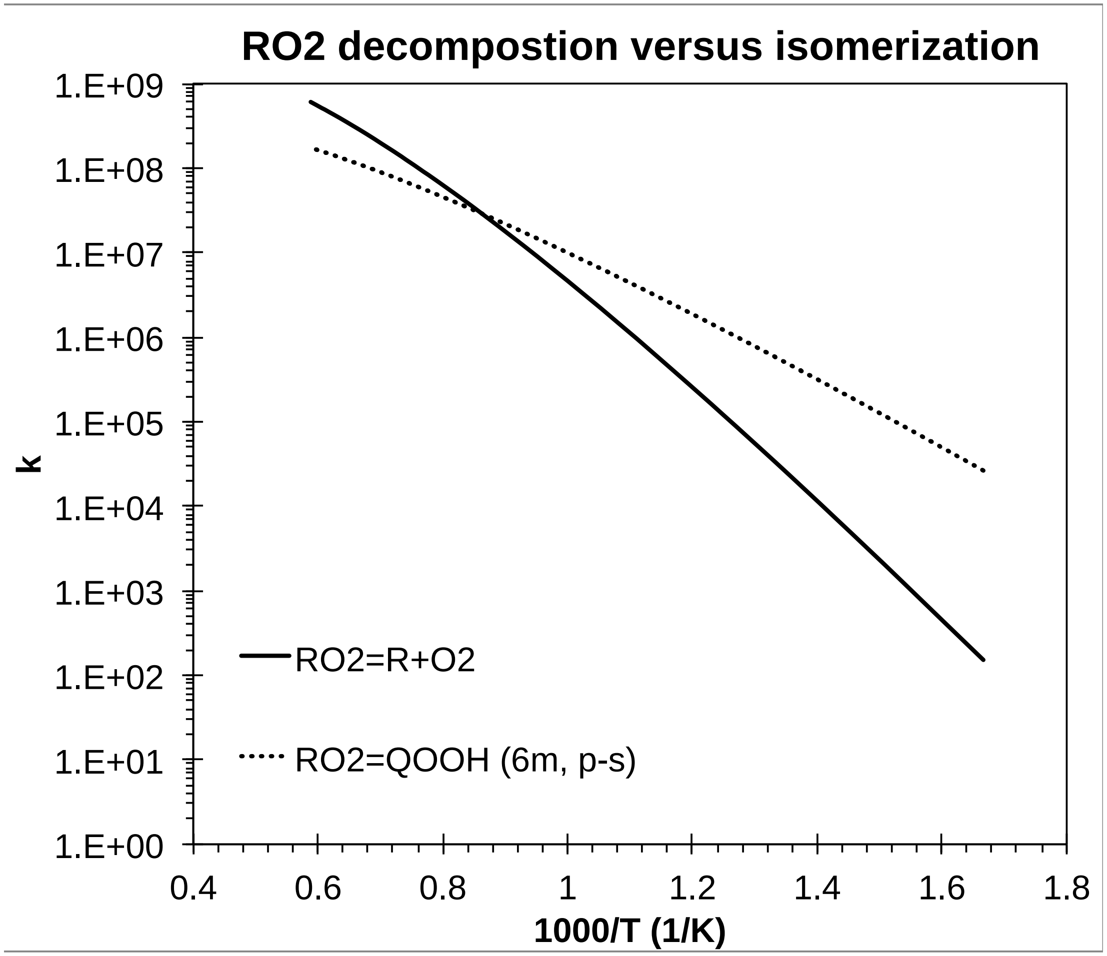
- Usually regarded to be independent of temperature, but ...
- Recent rate calculations from Miyoshi et al. suggest that these rates are temperature dependent.





10: Alkyl radical addition to O_2 ($R+O_2=ROO$)

- Why do we have NTC?



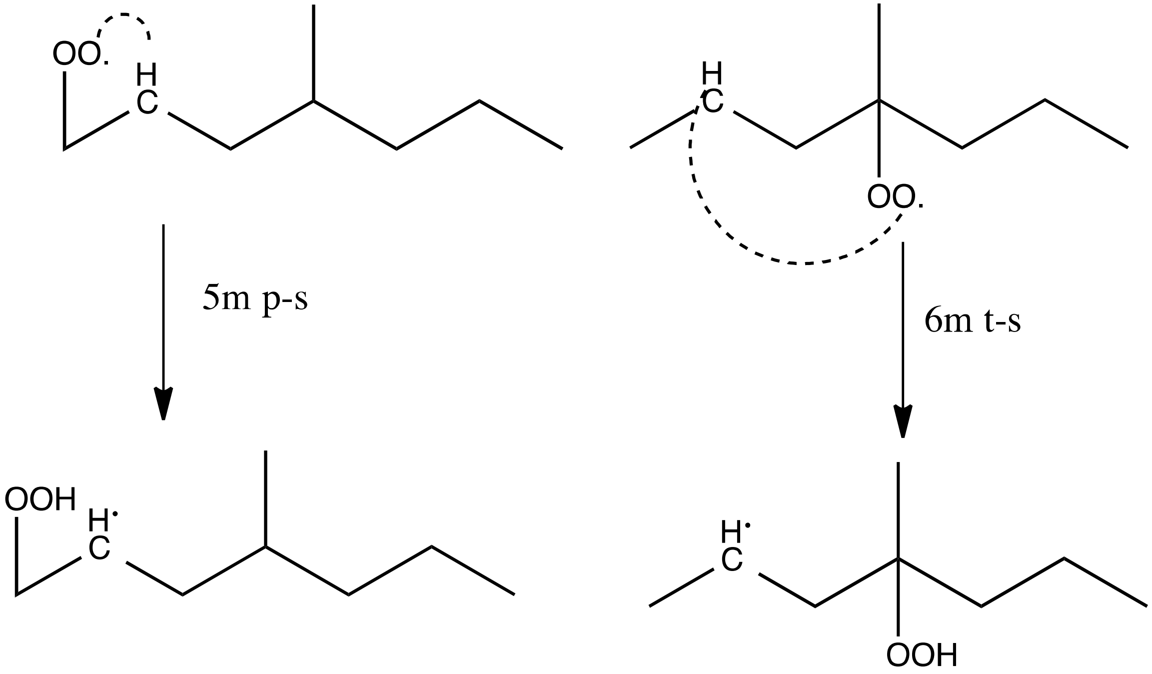
Villano et al., J. Phys. Chem. A 2012, 116, 5068!5089

- RO_2 dissociation becomes competitive with RO_2 isomerization as temperature increases
- This competition leads to a decrease in OH production and thus reduction in overall reactivity.

BDEs of RO2 radicals
P – ~35 kcal/mol
S – ~37 kcal/mol
T – ~39 kcal/mol

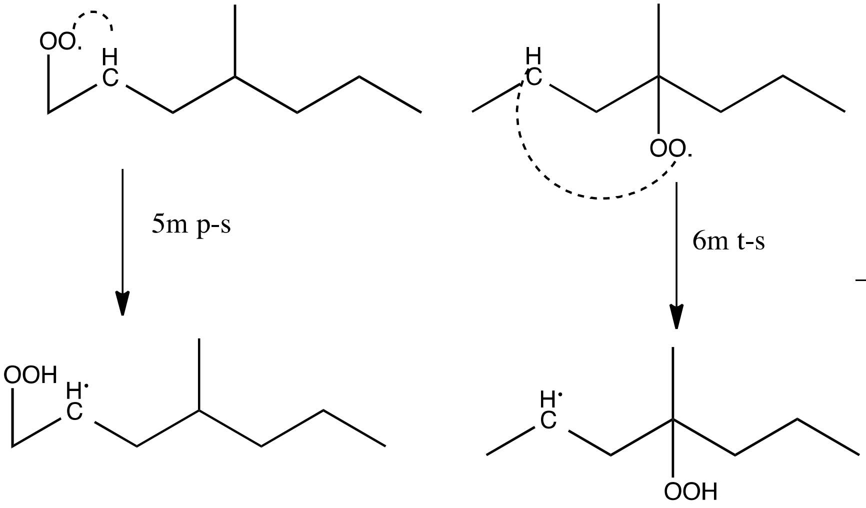
15: Alkylperoxy radical isomerization (RO_2=QOOH)

- The intramolecular H-abstraction of an alkyl peroxy radical (i.e., ROO) to form a hydroperoxyalkyl radical (i.e., QOOH) is the second step in the low temperature chain branching process.
- Include isomerization reactions involving 5-member, 6-member, and 7-member, and 8-member transition state rings.
- Exclude radical isomerizations involving fewer than five and greater than eight members because they are much slower. Also, products of larger isomerizations are not observed experimentally.



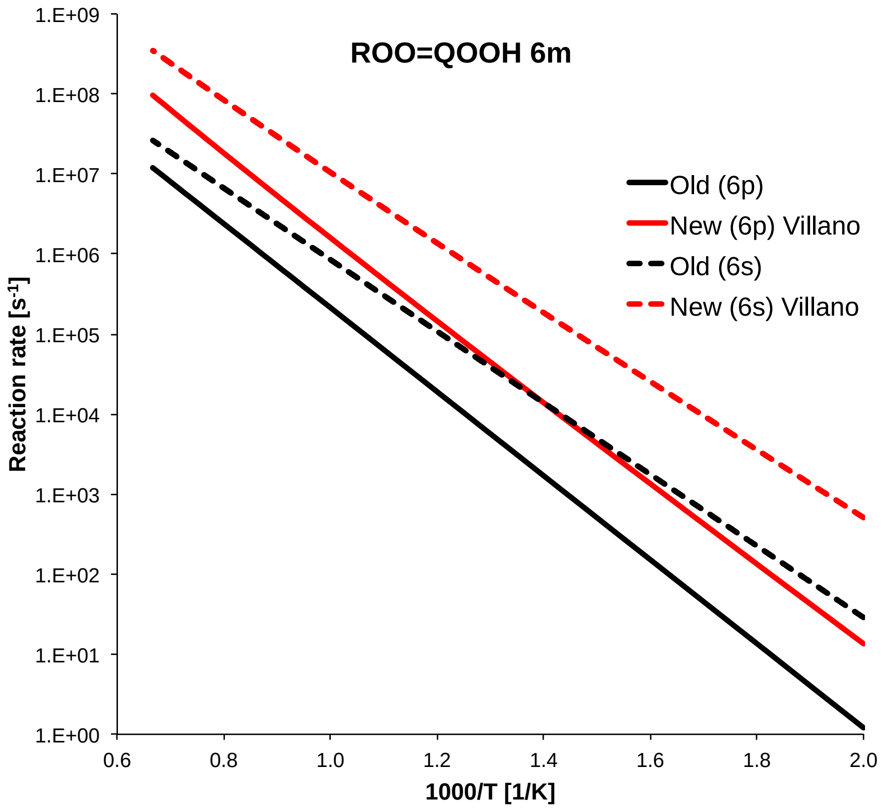
15: Alkylperoxy radical isomerization (RO_2=QOOH)

- The rate constant depends on the nature of the broken C-H bond (i.e., primary, secondary, or tertiary) and on the ring strain energy barrier.

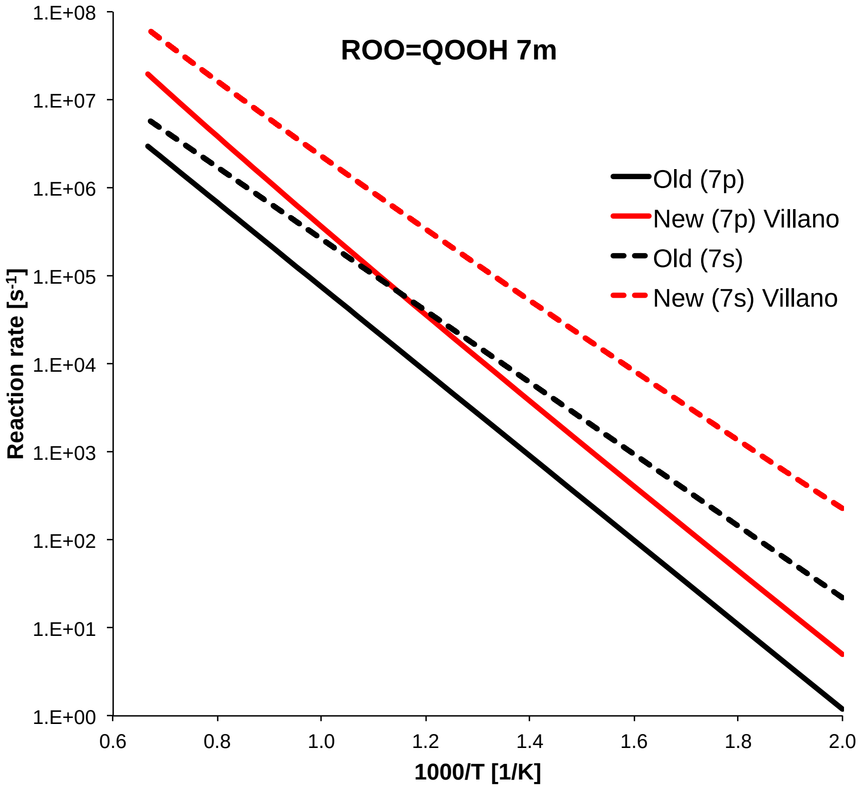


Rize Size	Site	A	n	E_A
5	1°	1.00E+11	0.0	29,000
	2°	1.00E+11	0.0	26,450
	3°	1.00E+11	0.0	23,700
6	1°	1.25E+10	0.0	24,000
	2°	1.25E+10	0.0	20,450
	3°	1.25E+10	0.0	18,700
7	1°	1.56E+09	0.0	21,950
	2°	1.56E+09	0.0	18,650
	3°	1.56E+09	0.0	16,650

Alkylperoxy isomerization (RO_2=QOOH)



Old estimates are based on successful reproduction of ignition delay times for a wide variety of hydrocarbons.

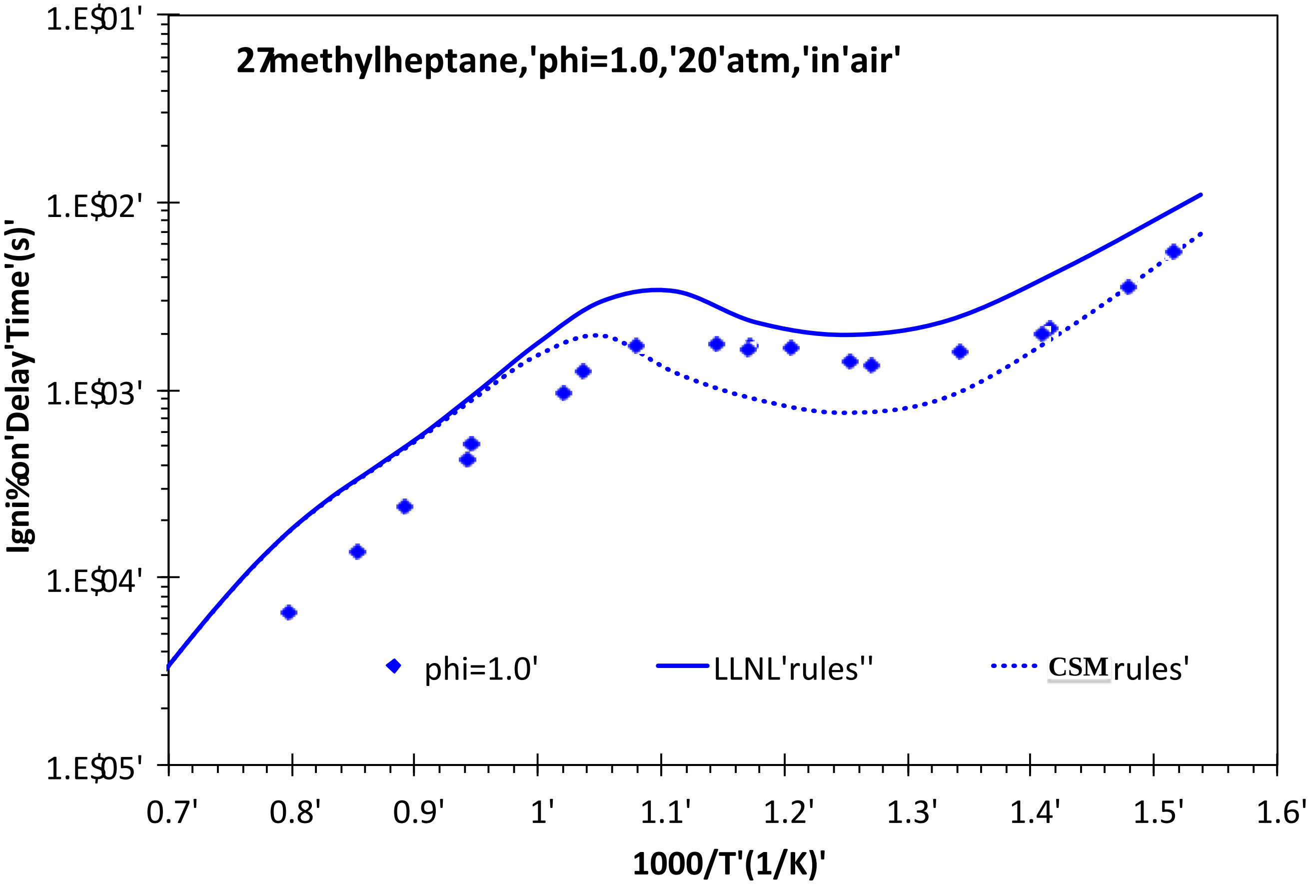


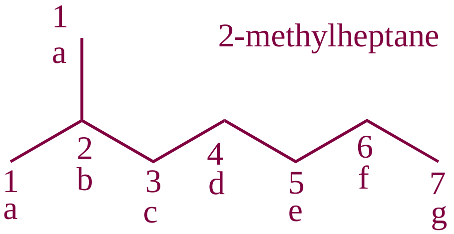
Theoretical calculations are 10-20x faster for 6-membered ring 7-membered ring isomerizations

Villano et al., J. Phys. Chem. A 2012, 116, 5068!5089

How would these new rate rules affect low T ignition delay predictions?

RO$_2$=QOOH isomerization rate effect on shock tube ignition delay time

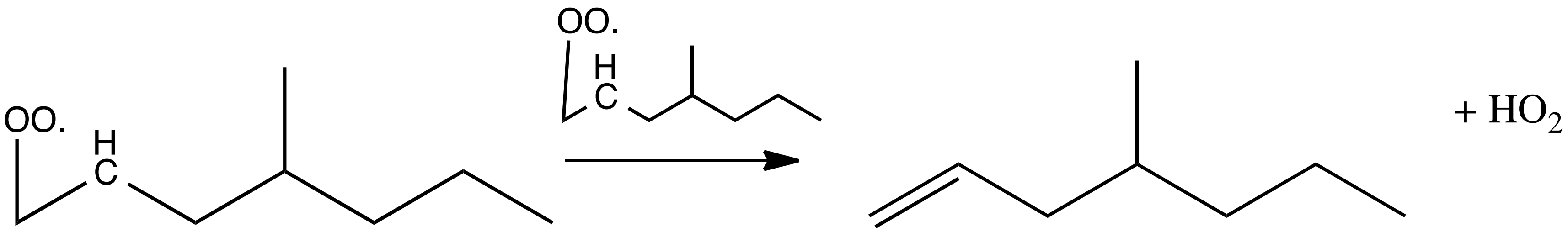




Modifying the rate rules the rate rules does appear to decrease ignition delay times.

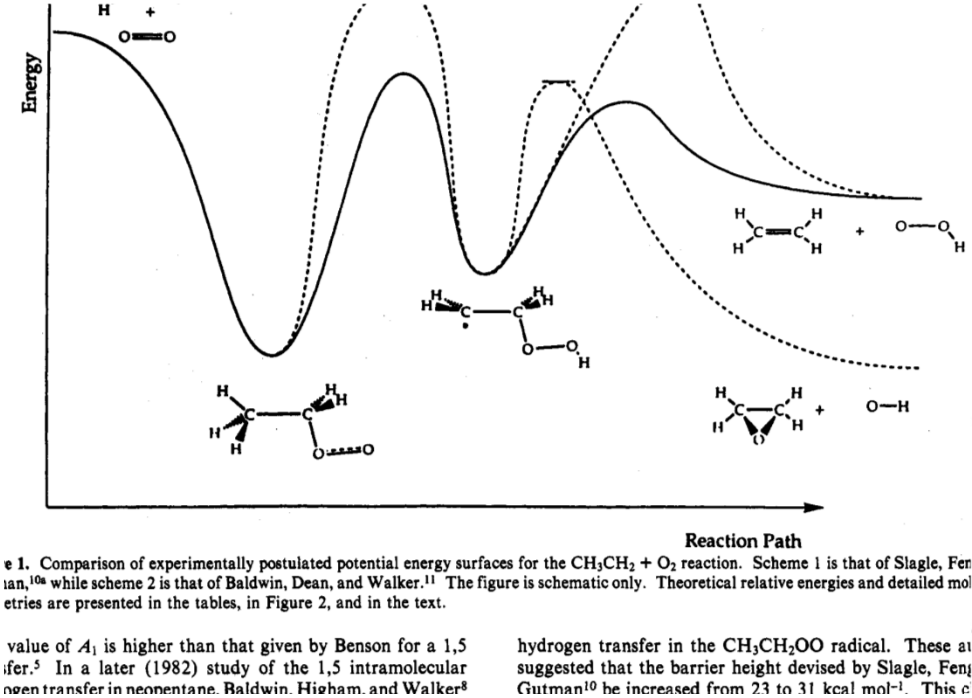
16: Concerted eliminations (RO_2 = alkene + HO_2)

- This concerted (direct) elimination of HO_2 from the alkyl peroxy radical (i.e., ROO) occurs via a 5-membered transition state
- The O-O moiety leaves the ROO molecule, and takes an H atom from the adjacent C atom with it.
- Competes directly with the alkyl peroxy radical isomerization pathway, so it reduces overall low temperature reactivity. It is also responsible for the majority of HO_2 and high molecular weight alkenes formed in the low and intermediate temperature regimes.



16: Concerted eliminations (RO_2 = alkene + HO_2)

- This reaction class was a hot topic of debate for many years
- It was finally put to rest in 2003 with a elegant combination of experiments and theory

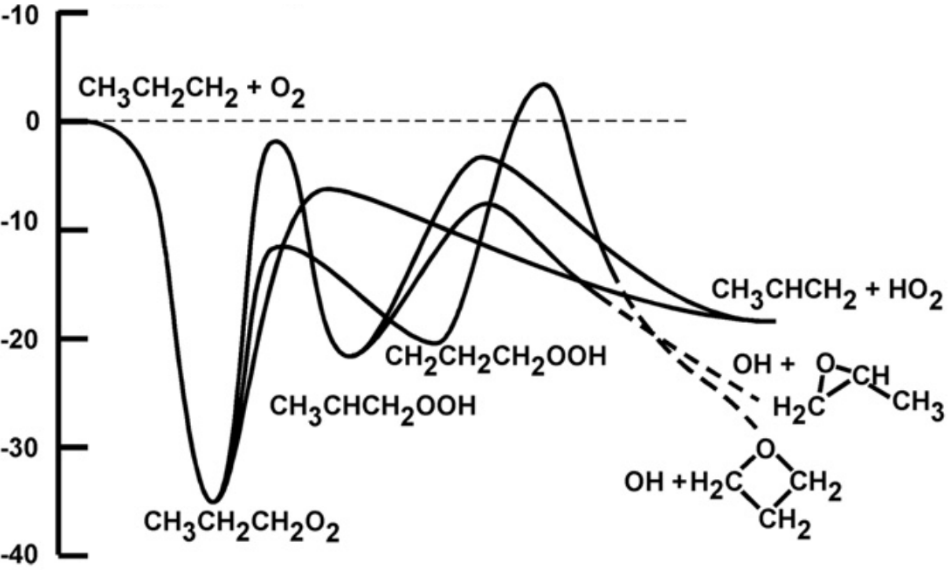


e 1. Comparison of experimentally postulated potential energy surfaces for the $CH_3CH_2 + O_2$ reaction. Scheme 1 is that of Slagle, Fer ıan,[10a] while scheme 2 is that of Baldwin, Dean, and Walker.[11] The figure is schematic only. Theoretical relative energies and detailed mol etries are presented in the tables, in Figure 2, and in the text.

value of A_1 is higher than that given by Benson for a 1,5 ıfer.[5] In a later (1982) study of the 1,5 intramolecular ogen transfer in neopentane. Baldwin. Higham. and Walker[8]

hydrogen transfer in the CH_3CH_2OO radical. These aı suggested that the barrier height devised by Slagle, Fen Gutman[10] be increased from 23 to 31 kcal mol^{-1}. This c

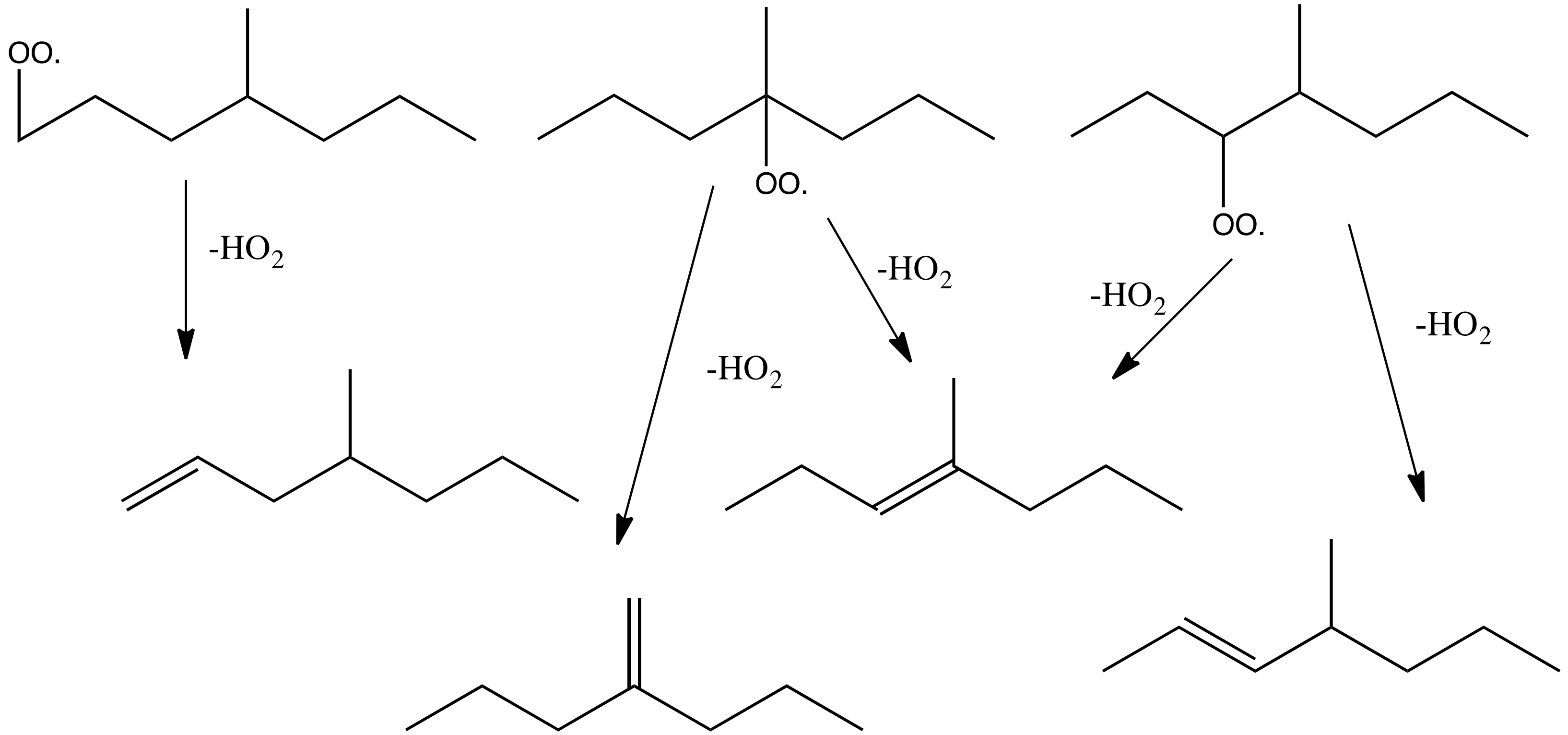
Quelch et al 1994, J. Am. Chem. Soc



De Sain et al, J Phys Chem A 2003

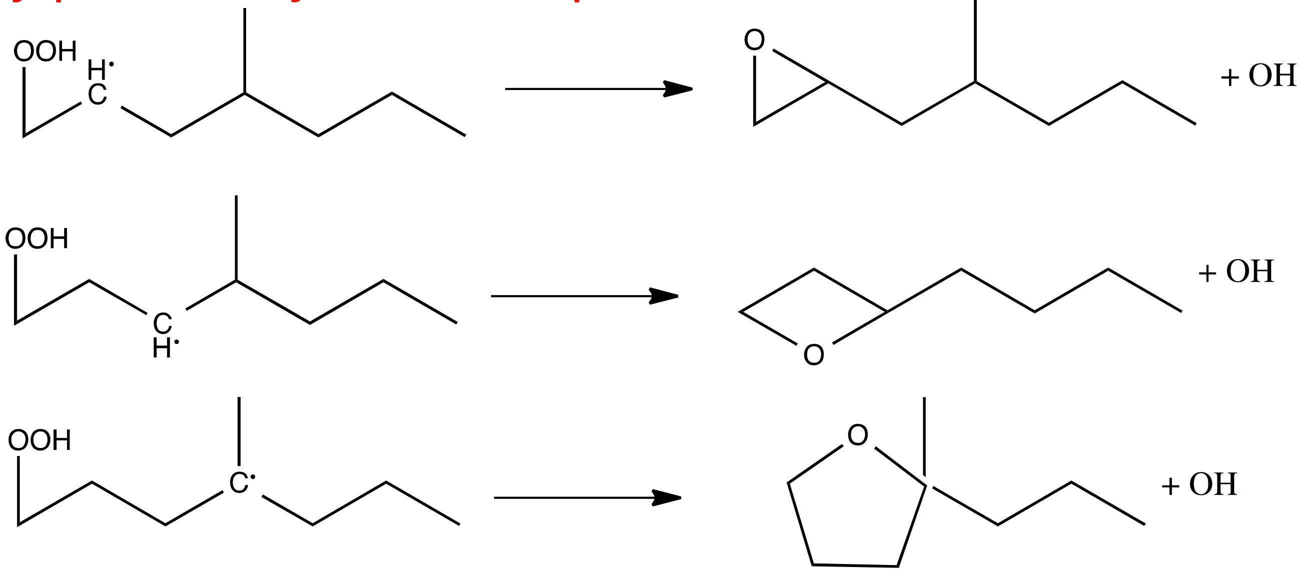
16: Concerted eliminations (RO_2 = alkene + HO_2)

- The rate constant depends on the nature of the C-H bond broken (i.e., primary, secondary, or tertiary) during the direct elimination reaction.
- How many possible concerted eliminations are there?



23: QOOH = cyclic ether + OH (cyclic ether formation)

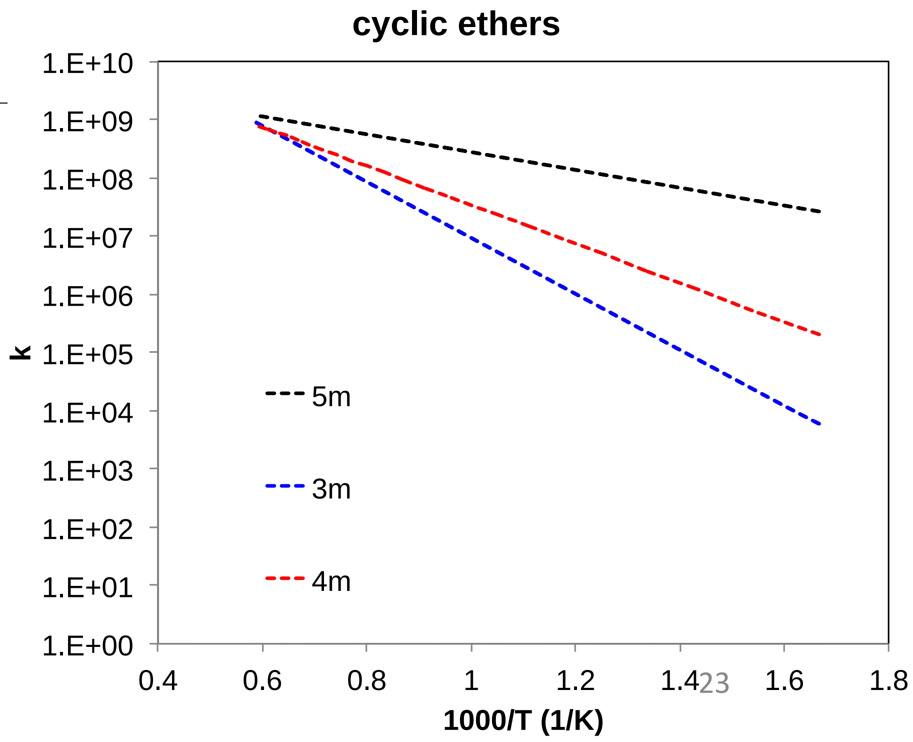
- The cyclization of a hydroperoxyalkyl radical (i.e., QOOH) to form a cyclic ether plus an OH radical is an important pathway that competes with the critical chain branching channel.
- A first approximation assumes that the rate constant only depends on the ring size of the cyclic ether formed.
- 3-member (oxirane), 4-member (oxetane), and 5-member (oxolanes) are important ethers that can be formed.
- How many possible cyclic ether species are there?



23: QOOH = cyclic ether + OH (cyclic ether formation)

- The A factor for oxirane (3m) formation is a factor of ~8-9 higher than that for oxetane (4m), which in turn is a factor of ~8-9 higher than for oxolanes (5m) due to the loss in entropy as one extra rotor is getting frozen with progressive increase of ring size.
- The activation energy decreases with increasing ring size.

Cyclic Ether Ring Size	A	n	E_A
3	6.00E+11	0.0	22,000
4	7.50E+10	0.0	15,250
5	9.38E+09	0.0	7,000
6	1.17E+09	0.0	1,800



These QOOH reactions provide chain propagation, not branching

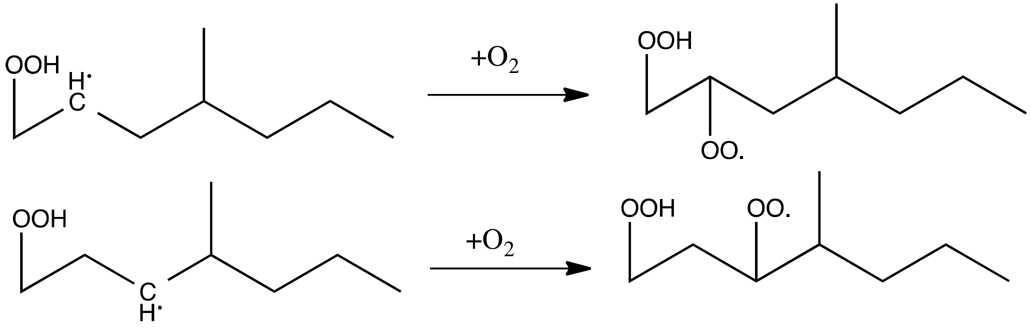
$QOOH = Q + HO_2$

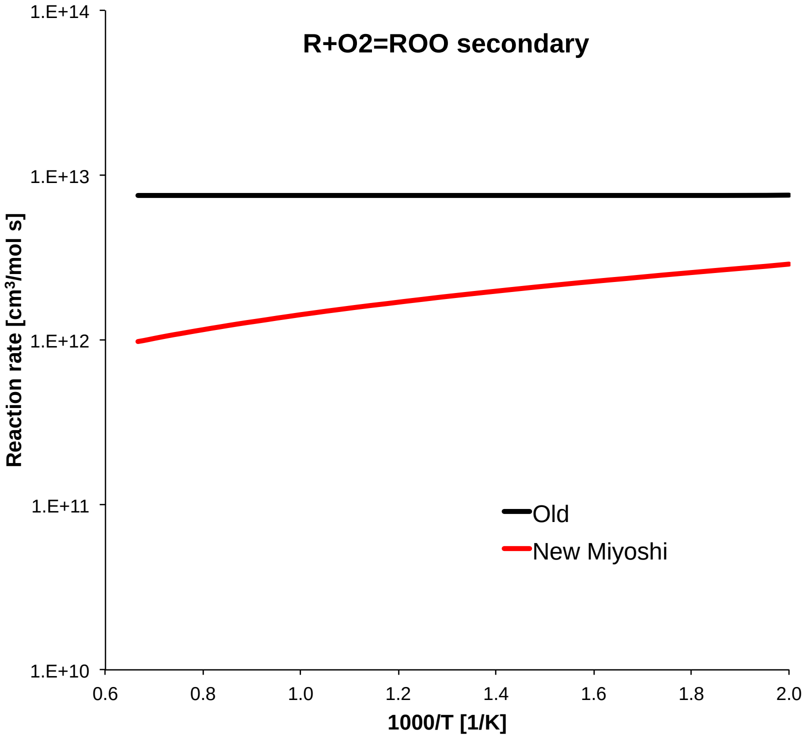
$QOOH =$ Cyclic ether + OH

$QOOH = RO_2$

26: Addition of QOOH to molecular oxygen O_2 ($QOOH+O_2=O_2QOOH$)

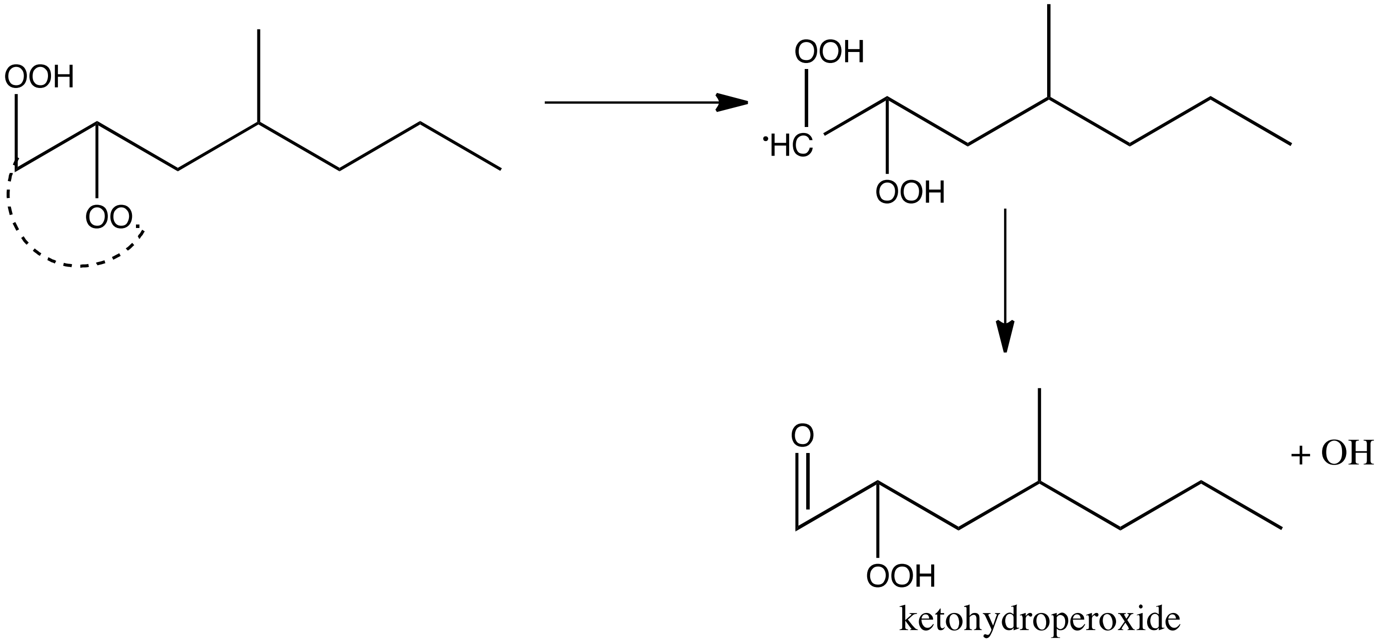
- The addition of molecular oxygen to hydroperoxy alkyl radicals (i.e., QOOH) is the third step in the low temperature chain branching process.
- The rate of O_2 addition to a QOOH radical depends on whether the radical carbon is a primary, secondary, or tertiary site. The prescribed rate constants are the same as the R + O_2 = RO_2 reactions (i.e, class 10).





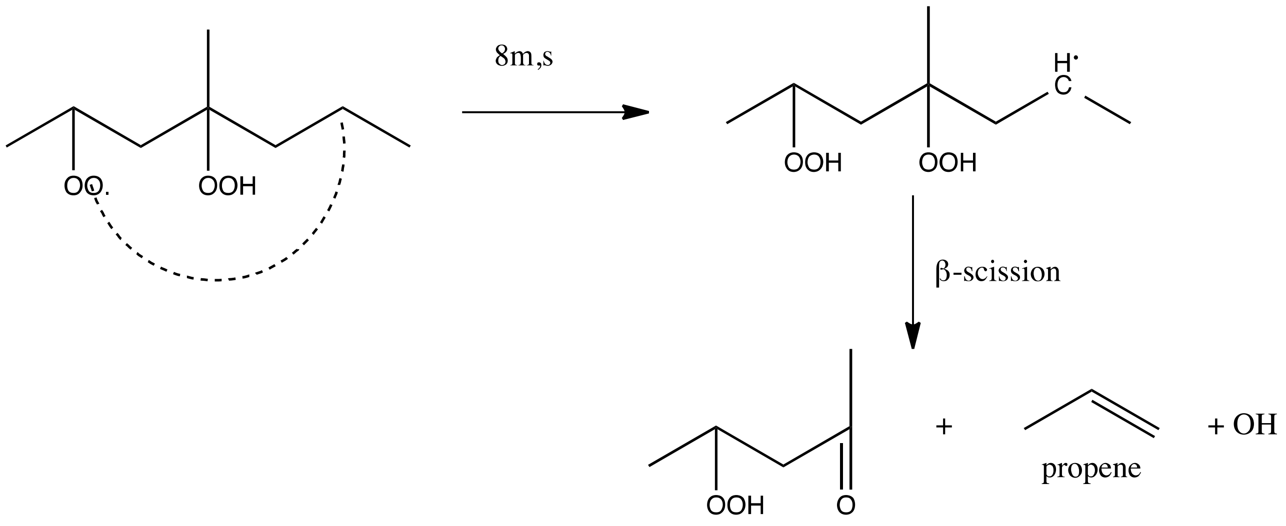
27: O_2QOOH isomerization to carbonylhydroperoxide + OH

- In this reaction class an O_2QOOH radical isomerizes, releases an OH, and then forms a carbonylhydroperoxide (i.e., ketohydroperoxide).
- This is the fourth step in the low temperature chain branching process.



27: O_2QOOH isomerization to carbonylhydroperoxide + OH

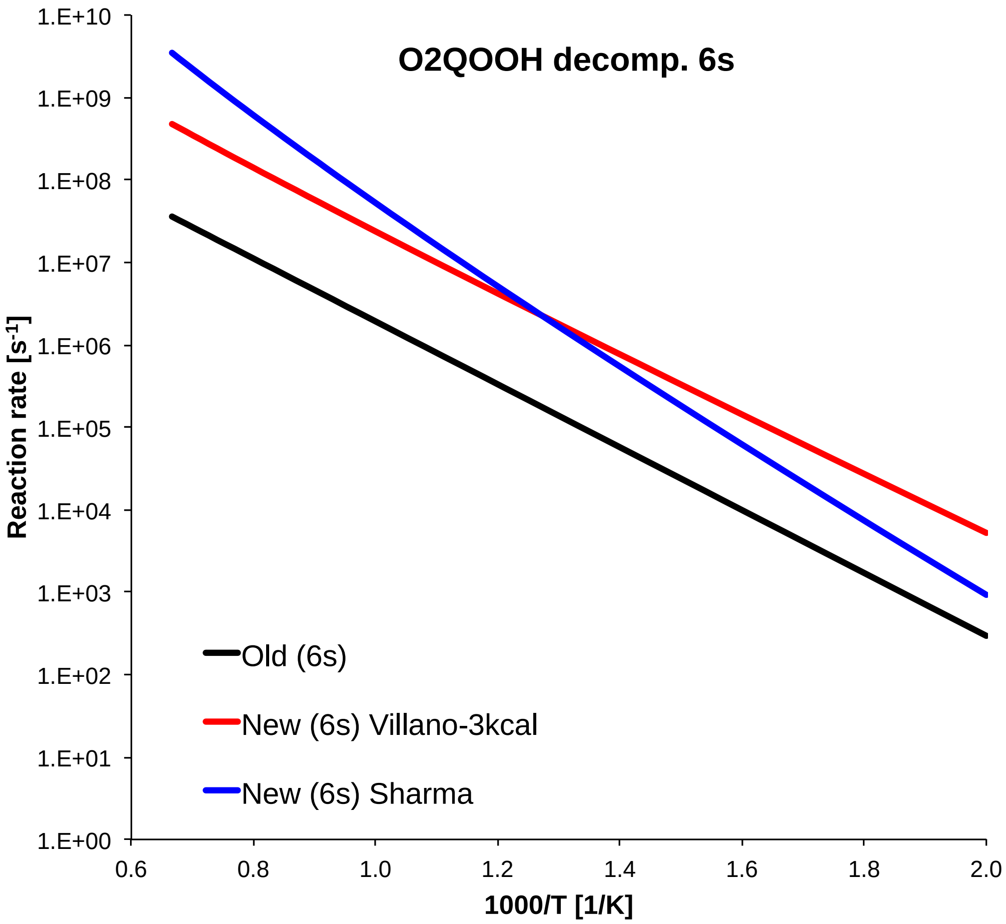
- A basic assumption is that atom being abstracted is bound to the carbon atom bonded to the hydroperoxy (OOH) group, which has a lower C-H bond strength than a normal C-H bond and makes it easier to abstract.
- The reaction rate constant is the same as the RO_2=QOOH isomerizations, except the activation energies have been reduced by 3 kcal/mol to account for the weakened C-H bond.
- Alternate isomerization may also be possible, and should be included for for branched molecules



First OH
from O2QOOH

27: O_2QOOH isomerization to carbonylhydroperoxide + OH

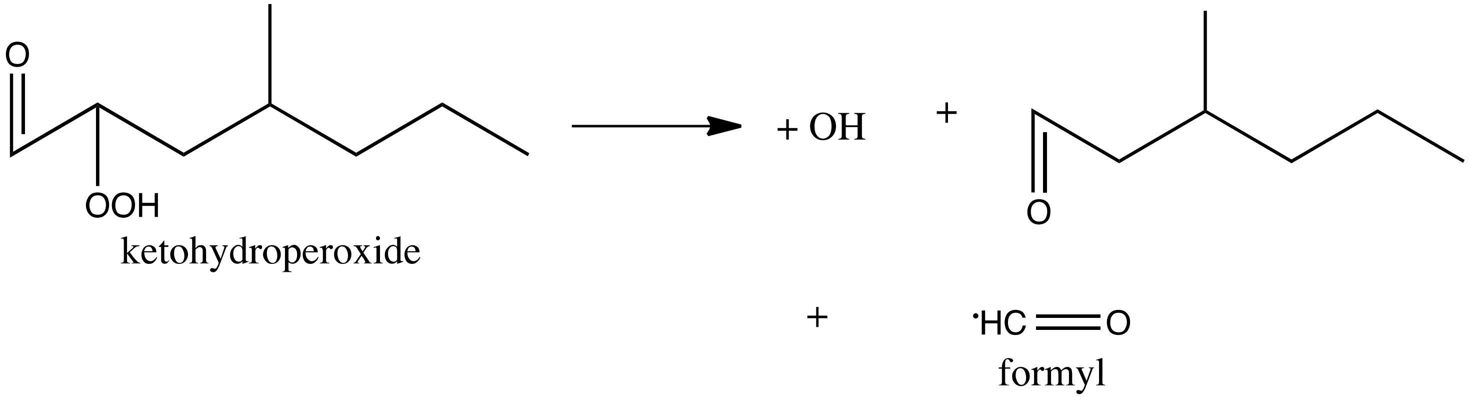
- The reaction rate constant is assumed to be the same as the RO_2=QOOH isomerizations, except the activation energies have been reduced by 3 kcal/mol to account for the weakened C-H bond.
- Some theoretical calculations provide actual rates for these site-specific isomerizations, but their accuracy and testing are yet to be researched.



S. Sharma, S. Raman, W.H. Green, J. Phys. Chem. A 114 (2010)

28: Carbonylhydroperoxide decomposition

- The decomposition of a carbonylhydroperoxide forms an OH radical, a carbonyl radical, and a stable carbonyl (i.e, aldehyde or ketone).
- This reaction pathway is the final step in the low temperature chain branching process because it forms two radical species from one stable reactant. Plus the earlier OH produced from keto-species production.



Prescribe an estimated rate constants of $1.0\mathrm{x}10^{16}$ exp (-39,000/RT) s^{-1}

O_2QOOH leads to chain branching

- Two additions of O2 to R and QOOH are required to produce chain branching and low T ignition
- Decomposition of RO2 and O2QOOH, due to increase in temperature, extinguish low T ignition and result in Negative Temperature Coefficient

Low temperature combustion chemistry

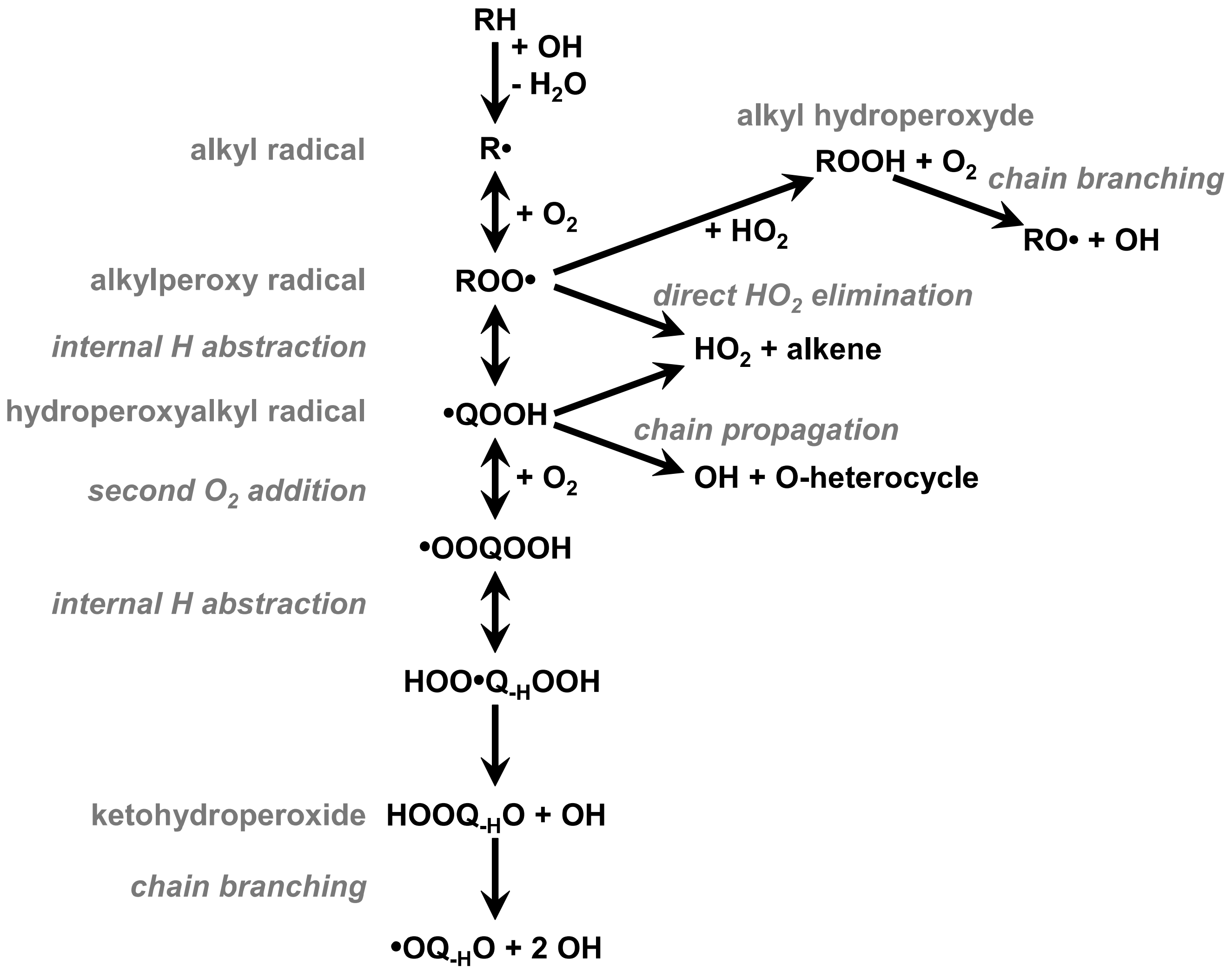


Fig. 1. Schematic mechanism for low-temperature hydrocarbon oxidation and autoignition chemistry.

Shock tube results from Adomeit et al.

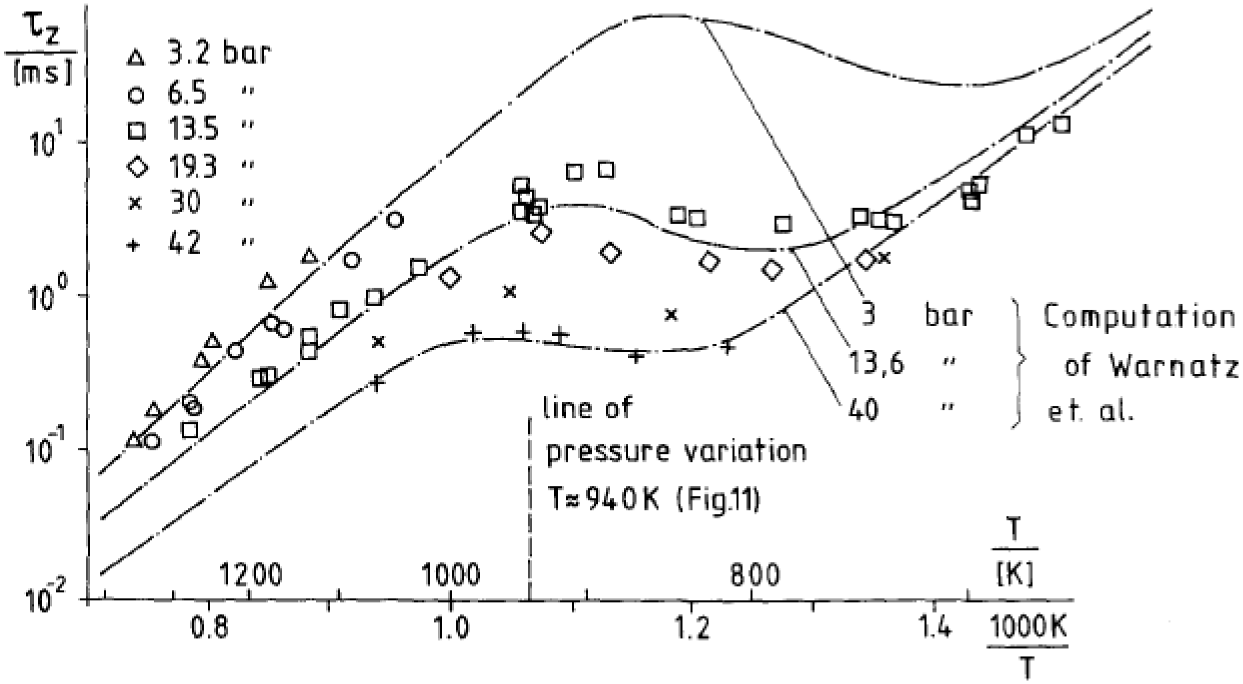
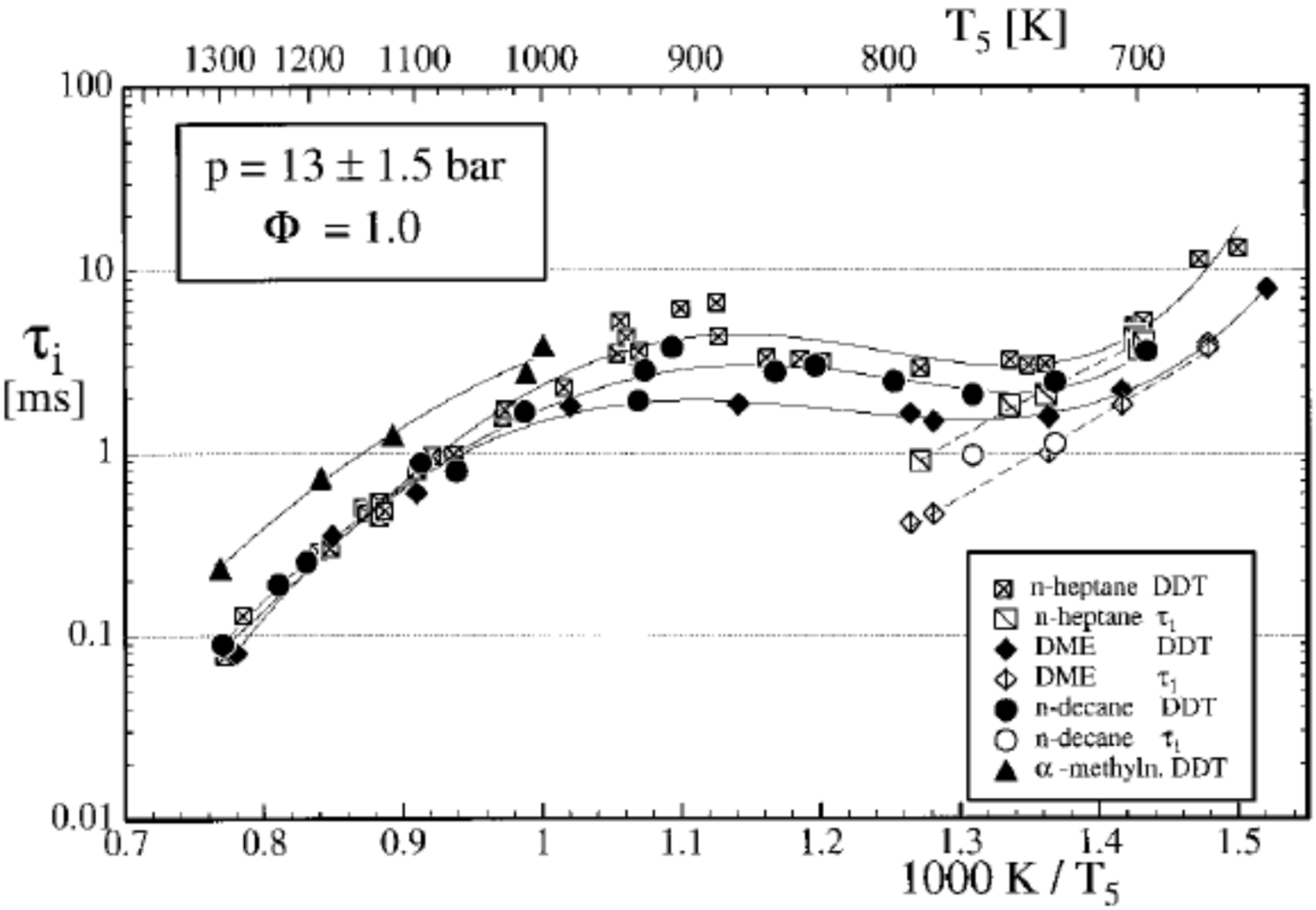


Fig. 3. Ignition delay times.

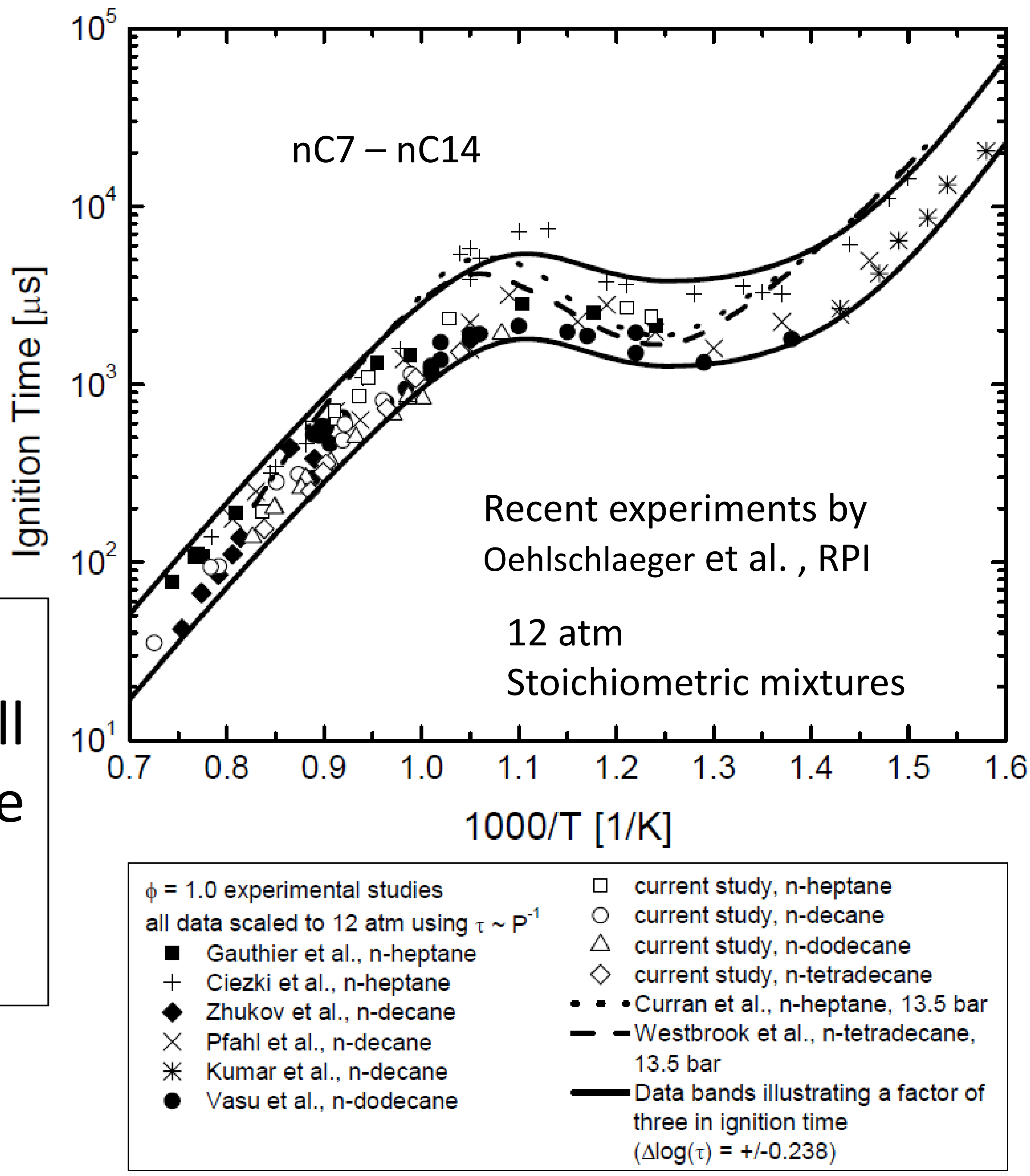
Fuel n-heptane Ciezki et al., 1993

Shock tube results from Adomeit et al.



Fuels n-heptane, n-decane, DME,
a-methyl napthalene   Pfahl et al., 1996

Recent shock tube experiments show all large n-alkanes ignite within a factor of 3

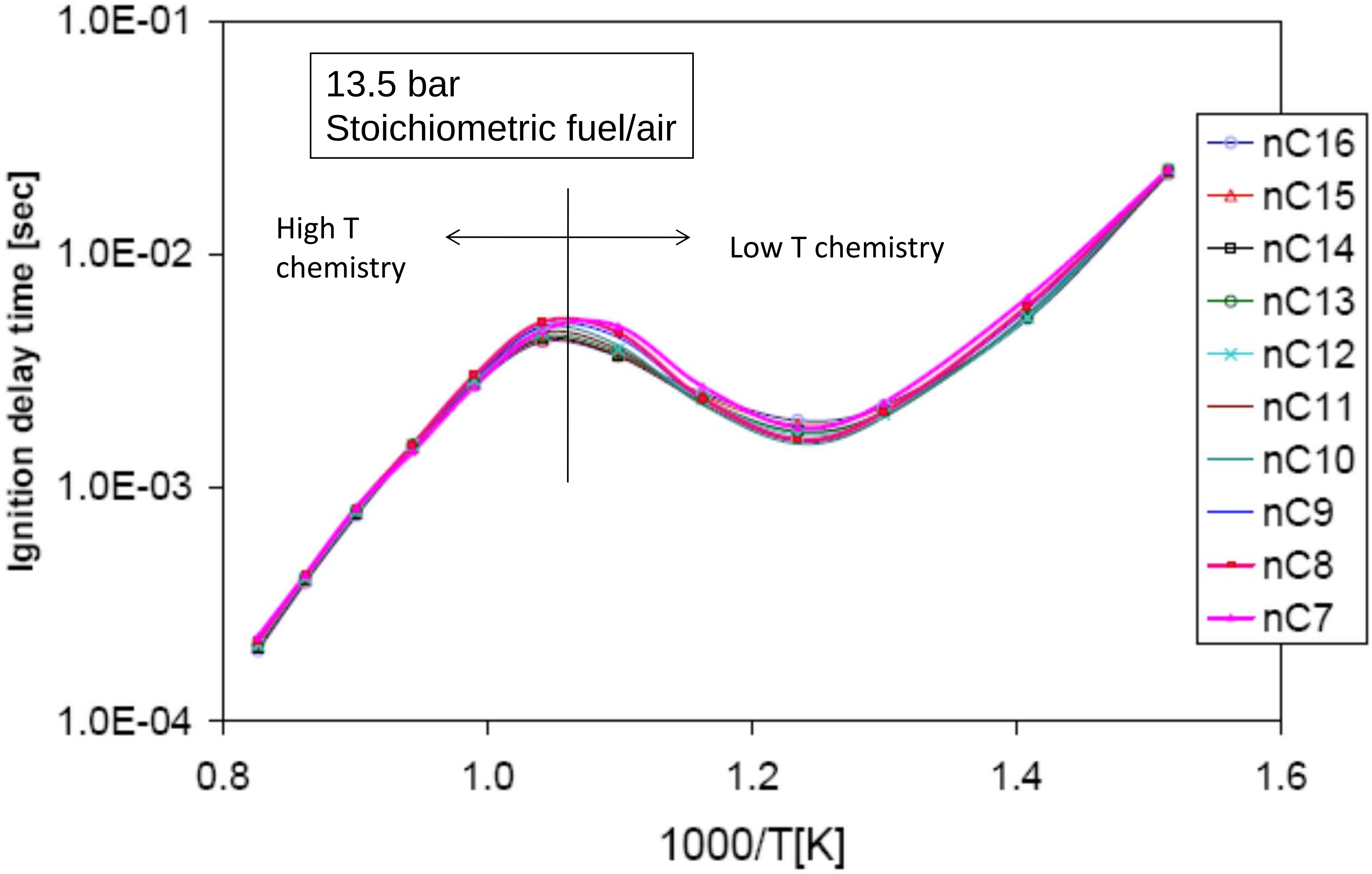


nC7 – nC14

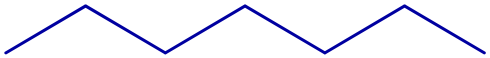
Recent experiments by Oehlschlaeger et al. , RPI

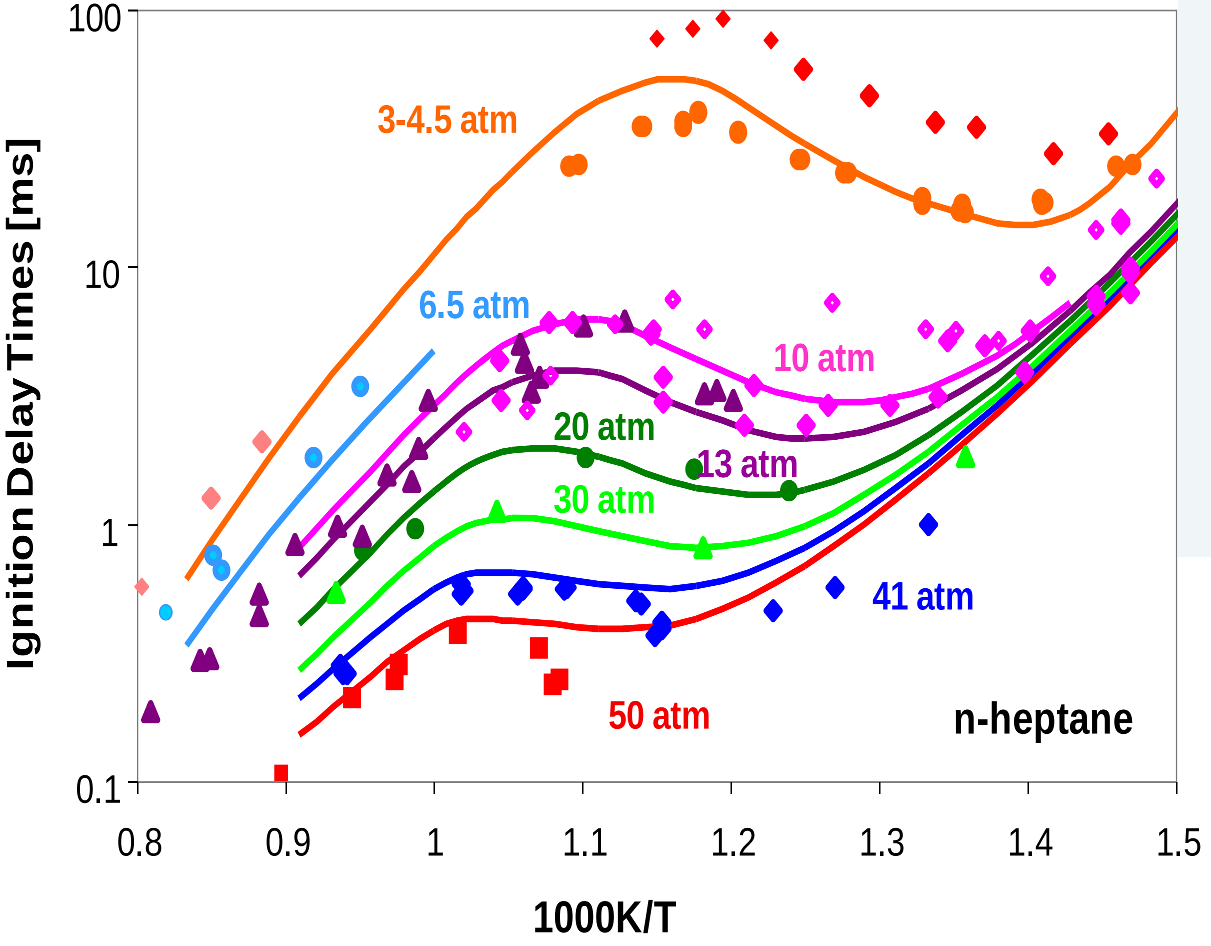
12 atm
Stoichiometric mixtures

Predicted ignition behavior similar for C7-C16 n-alkanes



Improved component model for n-heptane simulates ignition over a wide temperature and pressure range:



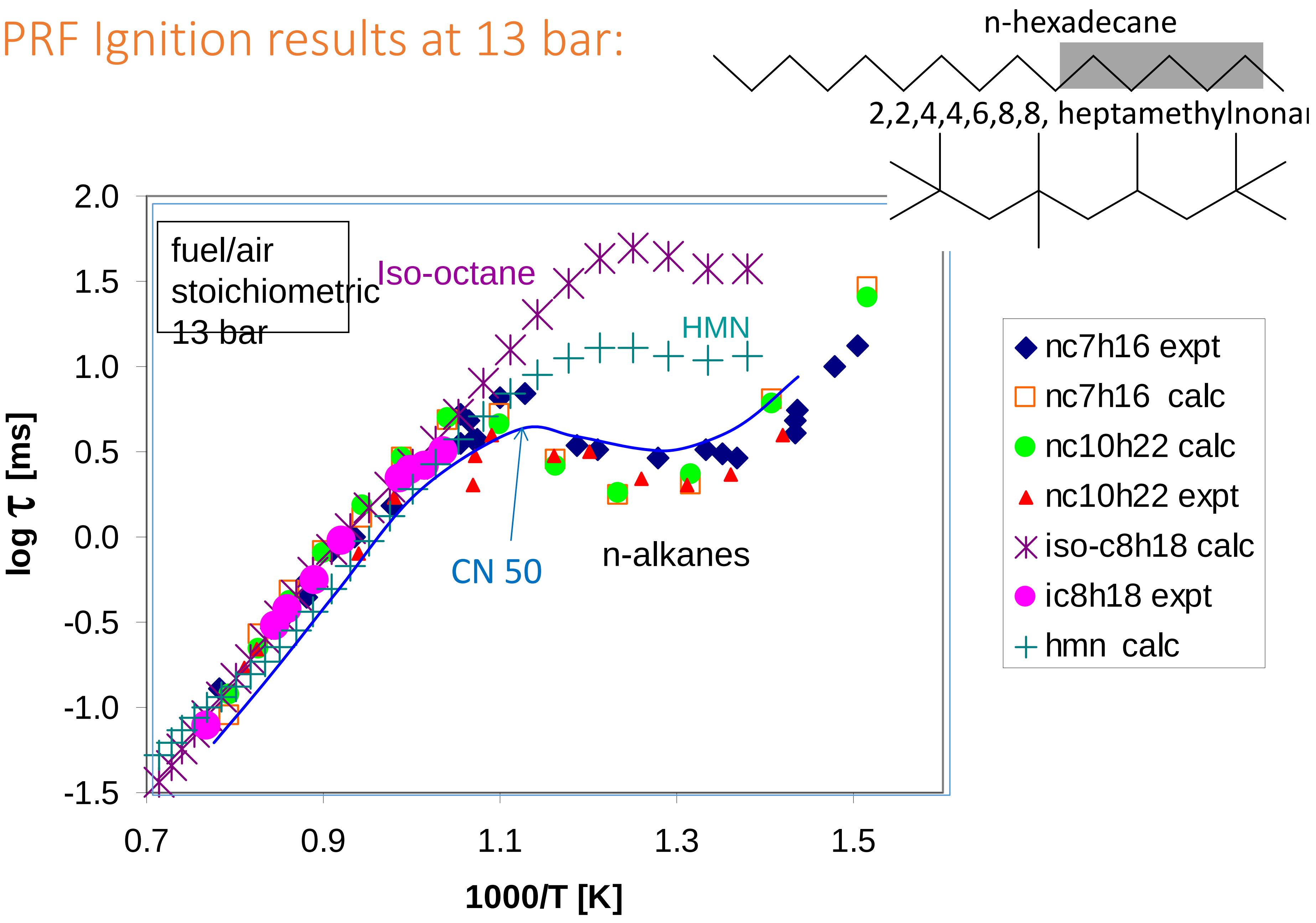


P = 3 - 50 atm
T = 650K - 1200K
Φ = 1

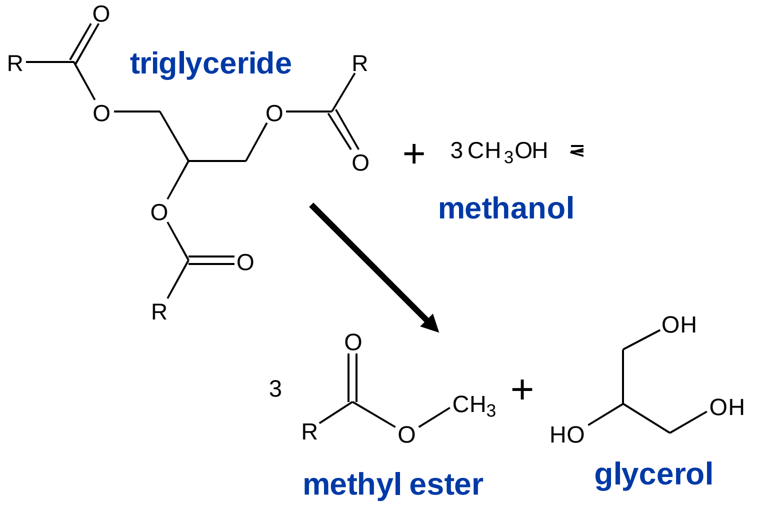
Experimental data from shock tubes and rapid compression machines

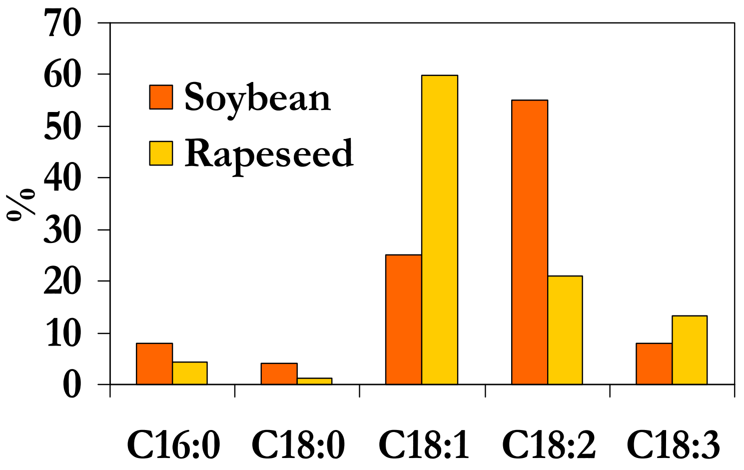
Experimental data: Minetti R., M. Carlier, M. Ribaucour, E. Therssen, L. R. Sochet (1995); H.K.Ciezki, G. Adomeit (1993); Gauthier B.M., D.F. Davidson, R.K. Hanson (2004); Minetti R., M. Carlier, M. Ribaucour, E. Therssen, L.R. Sochet (1996); K. Fieweger, R. Blumenthal, G. Adomeit (1997).

PRF Ignition results at 13 bar:

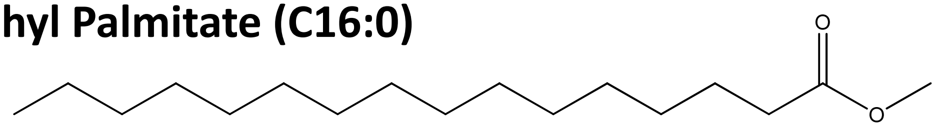


Composition of Biodiesels

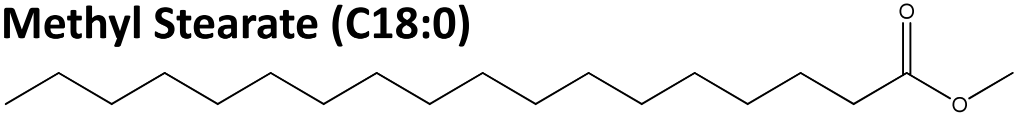




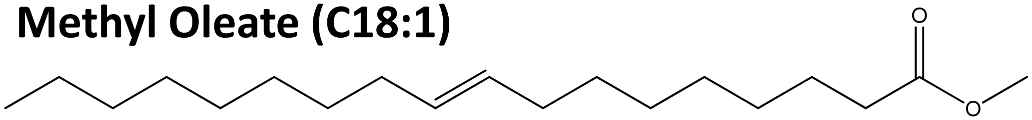
Methyl Palmitate (C16:0)



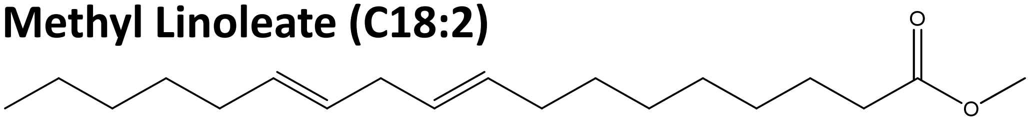
Methyl Stearate (C18:0)



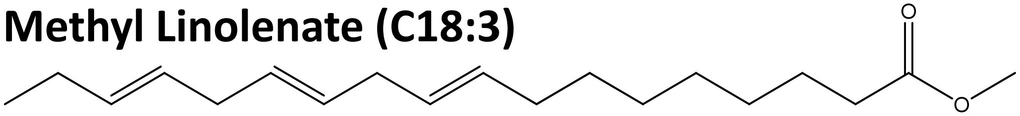
Methyl Oleate (C18:1)



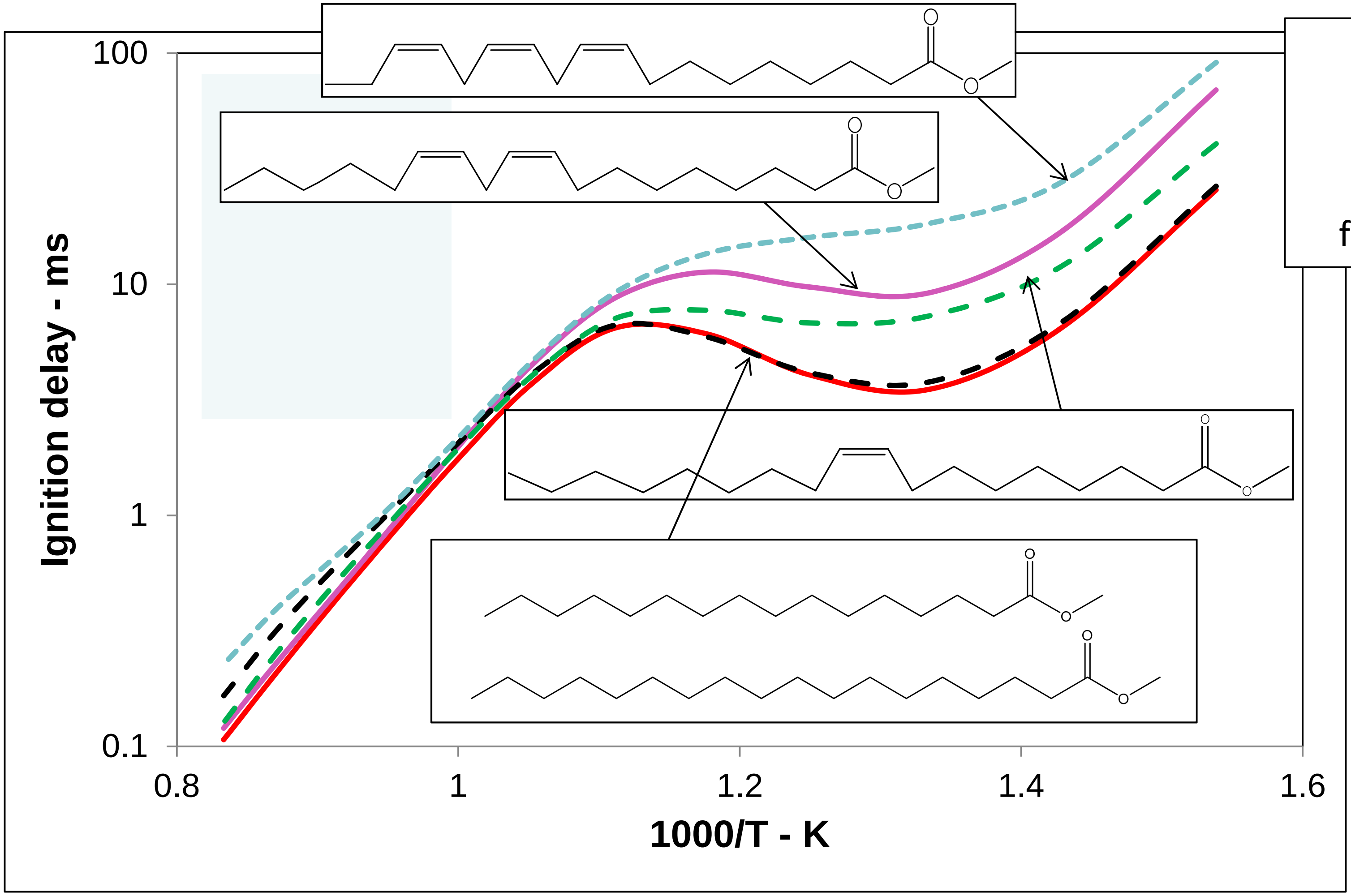
Methyl Linoleate (C18:2)



Methyl Linolenate (C18:3)

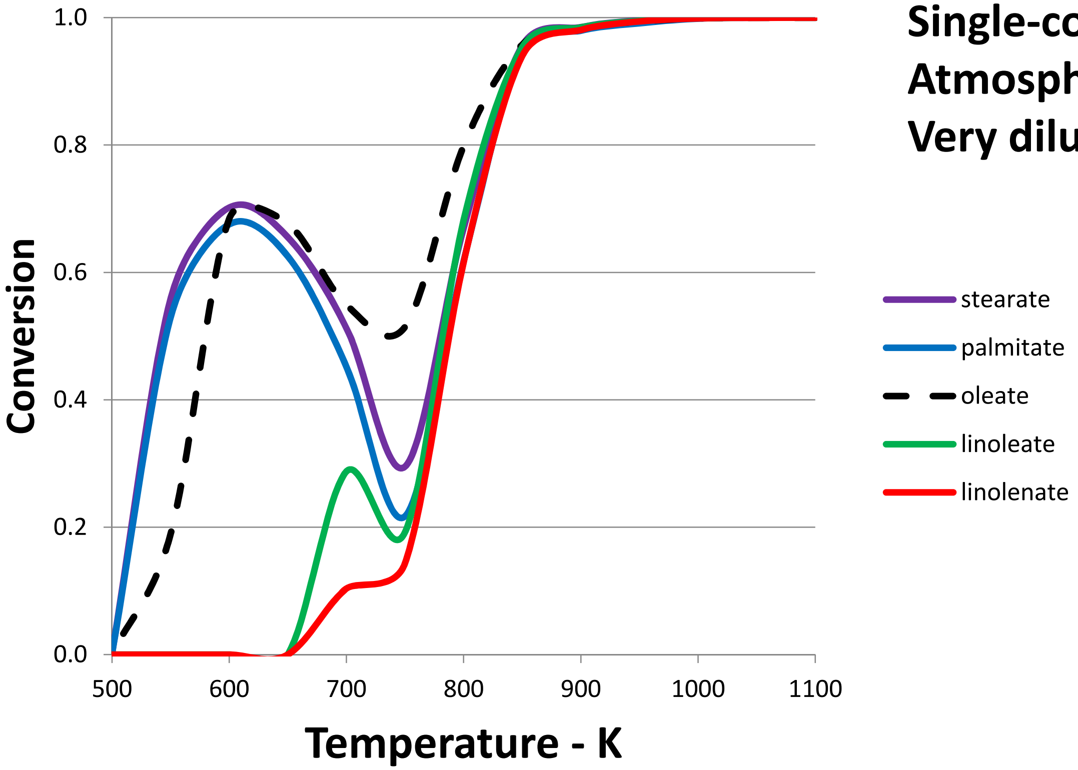


Biodiesel components ignite in order of number of double bonds



Engine-like
conditions:
13.5 bar
Stoichiometric
fuel/air mixtures

Biodiesel component reactivities in JSR



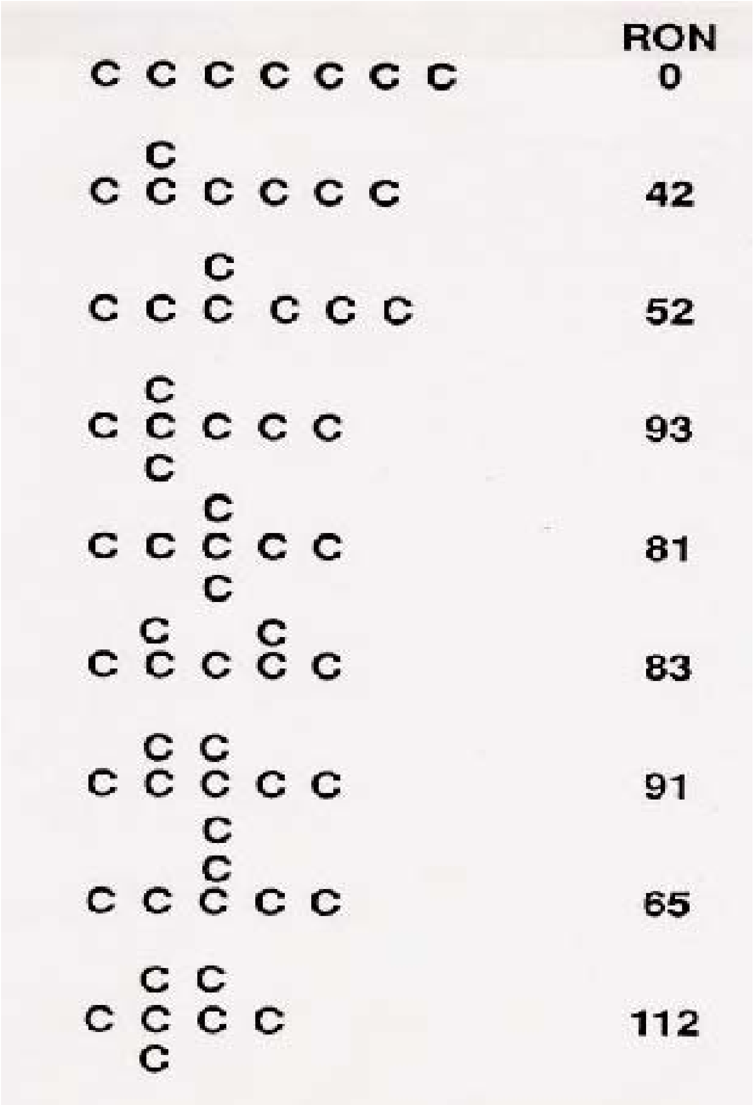
Stoichiometric
Single-component fuels
Atmospheric pressure
Very dilute in He

JSR might be a better CN or ON test than customary shock tubes

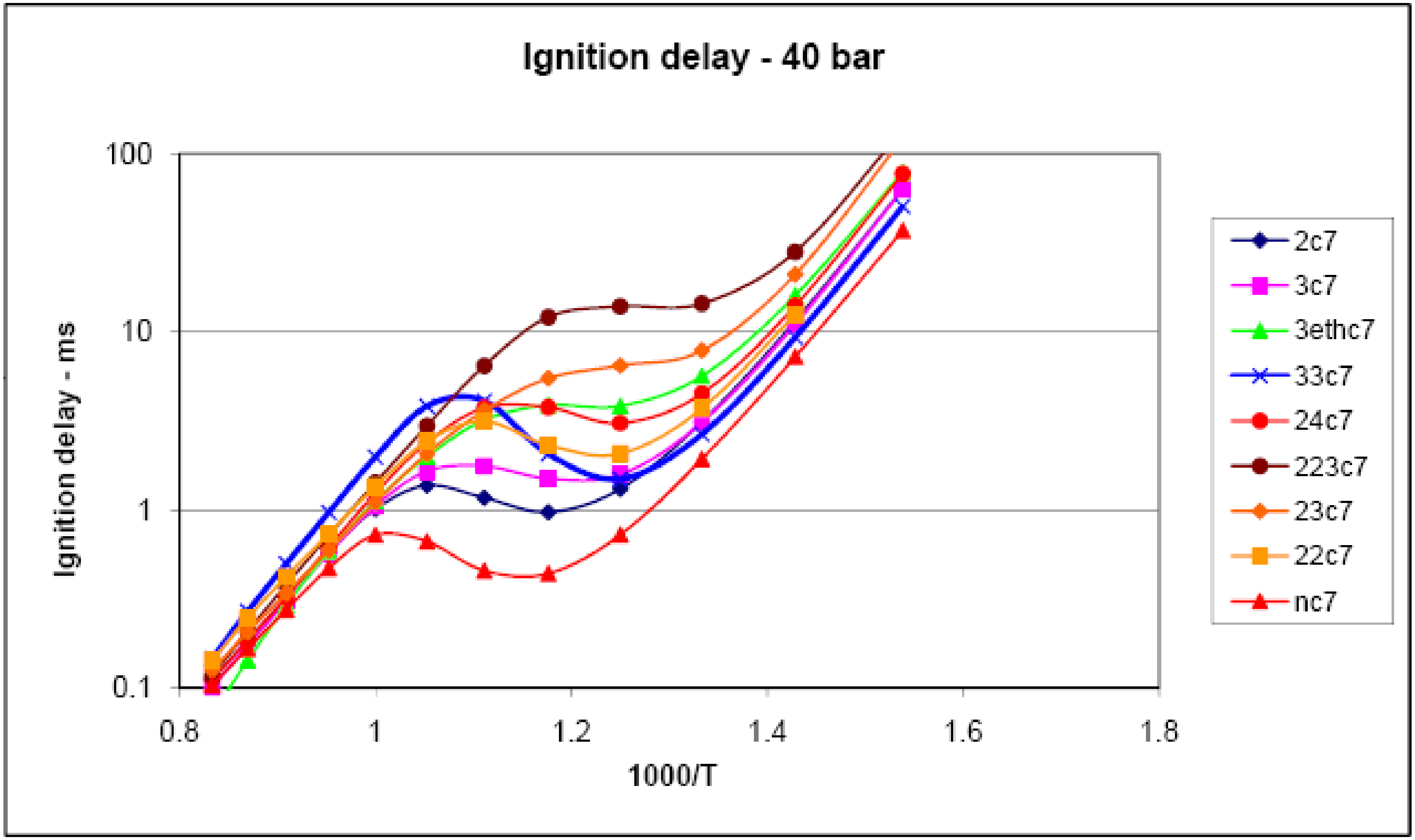
Heptane isomers

Octane numbers of heptanes are due exclusively to their different molecular structures

Low octane fuels have lots of secondary C-H bonds and high octane fuels have lots of primary C-H bonds and lots of tight, 5-membered TS rings



Isomers of heptane – ignition delays



High temperature ignition in shock tubes

Smith et al., IJCK 2005

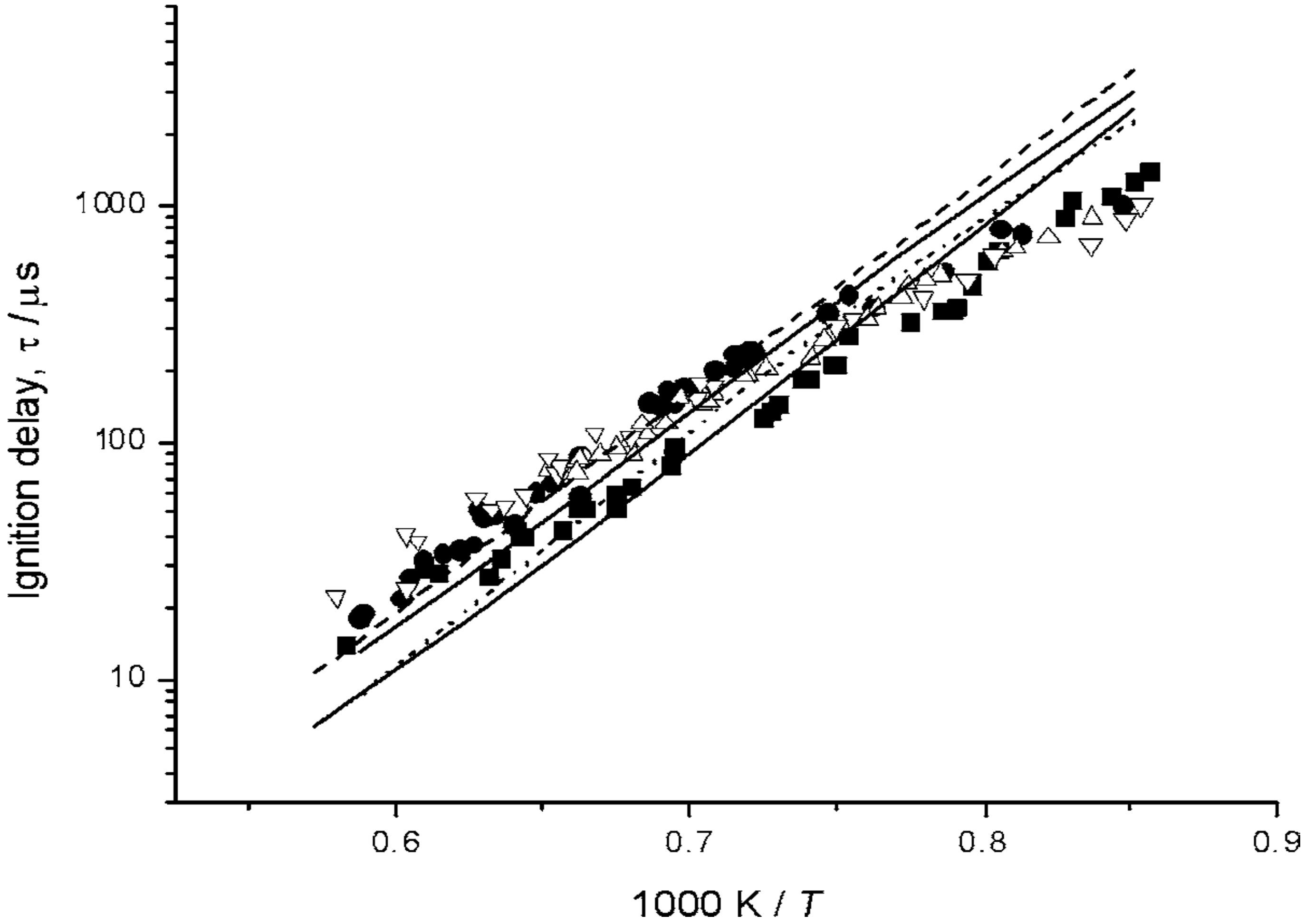


Figure 5 Heptane experimental (points) and model-predicted (lines) ignition delay times at 1.89% fuel, $P_5 = 2.0 \pm 0.2$ atm, and $\phi = 1.0$ in Ar: — ■ *n*-heptane, · · · Δ 2,3-dimethylpentane, — ● 2,2-dimethylpentane, – – – ∇ 2,2,3-trimethylbutane.

ThermoChemistry for Kinetic Modeling

Charles Westbrook

Tsinghua-Princeton
2014 Summer School on Combustion
July 20-25, 2014

Basic kinetic and thermodynamic principles

Thermodynamics

Properties of interest:

- Entropy
- Enthalpy
- Heat capacity (C_p or C_V)
  - Can be used for extrapolation of above
- Gibbs free energy (follows from *S* and *H)*

Why?

- Chemical equilibria ($\ln K = -\Delta G/RT$)
- Chemical insight/will a reaction happen?
  - endo vs. exothermic, spontaneous or not
- Heat release, adiabatic flame temp. etc.

Slide courtesy of Dr. Pierre-Alexandre Glaude

Enthalpy of Formation

Molar standard enthalpy of formation $\Delta_f H°$:

- Is the heat involved when one mole of a substance is produced from its elements in their standard state (1 bar for gases, usually 25°C).

- Standard enthalpy of formation of ammonia

$$1/2\ N_2 + 3/2\ H_2 \rightarrow NH_3$$

- Conventionally, standard enthalpy of elements is fixed to 0 kJ/mol at standard state.
    - H_2 for hydrogen gas, O_2 for oxygen etc.

Slide courtesy of Dr. Pierre-Alexandre Glaude

Enthalpy of Formation

Variation with temperature:

- At constant pressure:

$$\Delta H_{(T2\text{-}T1)} = Q_P = C_P\, \Delta T$$

- C_P is the heat capacity at constant pressure of the compound.
- By integration, the enthalpy of formation of a compound at a temperature T is calculated by:

$$\Delta_f H^{\circ}_{(T)} = \Delta_f H^{\circ}_{298\,K} + \int_{298}^{T} \Delta_r C^{\circ}_P \,\mathrm{d}T = \Delta_f H^{\circ}_{298\,K} + \int_{298}^{T} \left(C^{\circ}_{P_{\text{molecule}}} - C^{\circ}_{P_{elements}} \right) \mathrm{d}T$$

- Permits derivation an analytic expression as a function of T

Slide courtesy of Dr. Pierre-Alexandre Glaude

Entropy

- Linked to the number of states of the particles in the system
- In a reversible transformation $\Delta_r S = Q/T$
- The entropy represents the extensivity of the thermal energy of a system at the temperature T.
- Entropy of elements at 0 K = 0 kJ/mol
- **Free Energy** (Gibbs, G) indicates spontaneity of reaction
  - Dependent on Enthalpy and Entropy
  - Contribution of Entropy becomes important as T increases

$$G = H - TS$$

Slide courtesy of Dr. Pierre-Alexandre Glaude

Thermodynamics

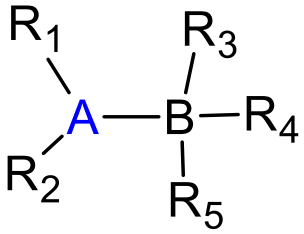
How do we determine C_P, S, H?

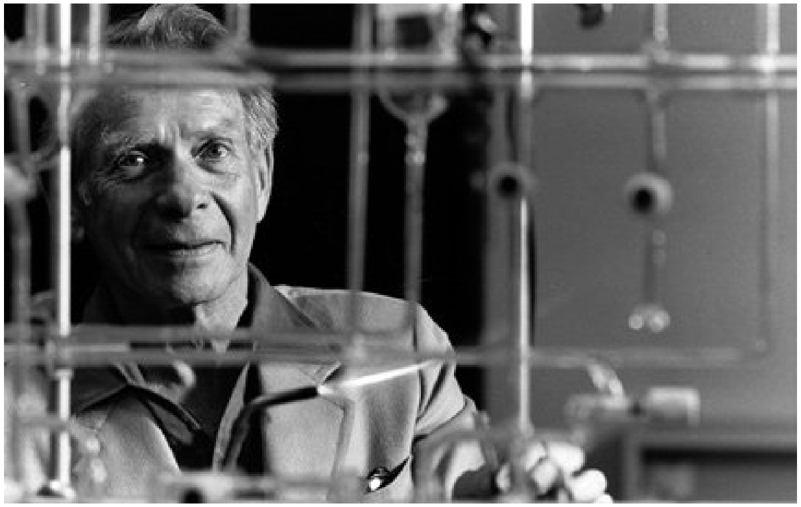
- Experiment?
  - Foundation of thermodynamics BUT….
  - Time consuming
  - Difficult/expensive
  - Fine for stable species, what about radicals?
- Alternatives?
  - Quantum chemistry (accurate and faster than expt.)
    - Not viable for large molecules (e.g. a biodiesel component)
  - Group Additivity (very fast but requires some input from experiment and/or quantum chemistry)

Group Additivity

What is it?

- Empirical method for estimation of thermodynamics
- Pioneered by Prof. Sidney W. Benson
- Thermodynamic functions dependent on:
  - Nature of each atom in a molecule and
  - Nature of each of their bonding partners (short range effects)
  - Long range effects can be important
- Molecule split into groups
- Each group makes a contribution to thermo. functions of molecule





Prof. Sidney W. Benson (1918-2011)

Slide courtesy of Dr. Pierre-Alexandre Glaude

Group Additivity

Consider Ethane:

- Simple molecule with **2 identical groups** ($C/C/H_3$)

$$H_3C—CH_3$$

- Thermodynamics well known
- $\Delta_f H$ = -84. ± 0.4 kJ/mol (NIST)
  - Contribution of each group = -42.0 kJ/mol
- C_P 298.15 K = 52.49 J/mol (NIST)
  - Contribution of each group = 26.25 J/mol
- S 298.15 K = 229.28 J/mol
  - Contribution of each group…..not as simple
  - Corrections for molecular symmetry are applied

Group Additivity

Entropy calculations:

- Sum of the group contributions: intrinsic entropy $S°_i$
- Correction for symmetry:

$$\delta S° = -R \ln \sigma$$

- σ = number of symmetries in the molecule = $\sigma_{ext} \times \sigma_{int}$
  - σ_{ext} number of external symmetries (rotation of molecule)
  - σ_{int} number of internal symmetries (rotations around single bonds)
- Ethane $\sigma_{ext} = 2$, $\sigma_{int} = 9$, total correction $= -R \ln(18)$
- Similar corrections for optical isomers = +R ln(# of OI)

Group Additivity

What about free radicals?

- Estimated through definition of 'Bond Increments' or 'Bond Dissociation' values for H, S and C_P
- $RH \rightarrow R\cdot + H\cdot$ $\Delta_r H$ = Bond Dissociation Energy (BDE)
- $\Delta_f H\ (R\cdot) = BDE + \Delta_f H\ (RH) - \Delta_f H\ (H\cdot)$

Varies based on type of C-H bond broken

Heat of formation of 'parent' species

Well known
$\Delta_f H = 52.1$ kcal/mol

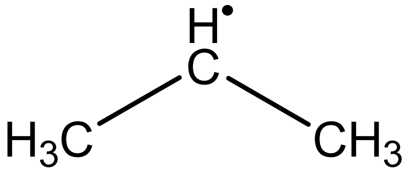
Group Additivity

BDE Groups

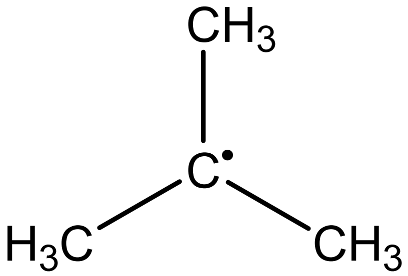
- Strength of C–H bond depends on stability of radical

$H_3C{-}CH_2^{\bullet}$

Type = primary, 101.1 kcal/mol



Type = secondary, 98.45 kcal/mol

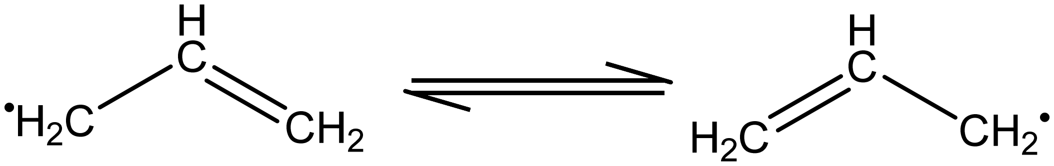


Type = tertiary, 96.50 kcal/mol

Group Additivity

BDE Groups

- Strength of C–H bond depends on stability of radical
- Electron delocalization leads to more stable radicals
  - Reduces BDE



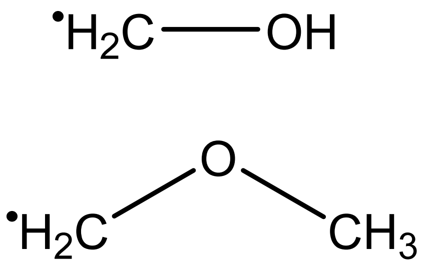
Type = primary allylic, 88.2 kcal/mol

Compare with primary alkane (101.1 kcal/mol)

Group Additivity

BDE Groups

- Locally bonded electronegative atoms reduce BDE



96.2 kcal/mol

Compare with primary alkane (101.1 kcal/mol)

Group Additivity

Can be applied to:

- Alkanes, alkenes, alkynes
- Alcohols, ethers
- Ketones, aldehydes
- Cycloalkanes, aromatics
- Pretty much everything…BUT…
- Parameterization against experiment and/or quantum chemical calculations necessary for best results and widest range of applicability

Groups and super-atoms

Atom differentiation according to the type of liaison

C: sp^3 carbon atom, 4 single bonds

C_d: sp^2 carbon atom, 1 double bond, 2 single, ≡ divalent atom

C_t: sp carbon atom, 1 triple bond, 1 single, ≡ monovalent atom

C_a: allene-like carbon atom, C=C=C, ending atoms are C_d

C_B: carbon-atom in aromatic rings, ≡ trivalent atom

C_{BF}: "fused carbon" carbon-atom belonging to several aromatic rings, ≡ trivalent atom

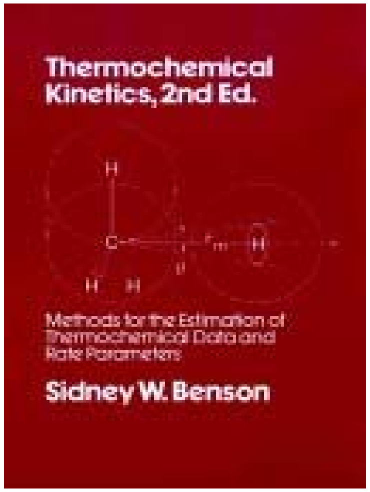
Super-atoms:

C=O, carbonyl group ≡ (CO) divalent

NO, NO_2, SO_2, PO…

Slide courtesy of Dr. Pierre-Alexandre Glaude

Benson’s groups


Thermochemical Kinetics, 2nd Ed.

Methods for the Estimation of Thermochemical Data and Rate Parameters

Sidney W. Benson

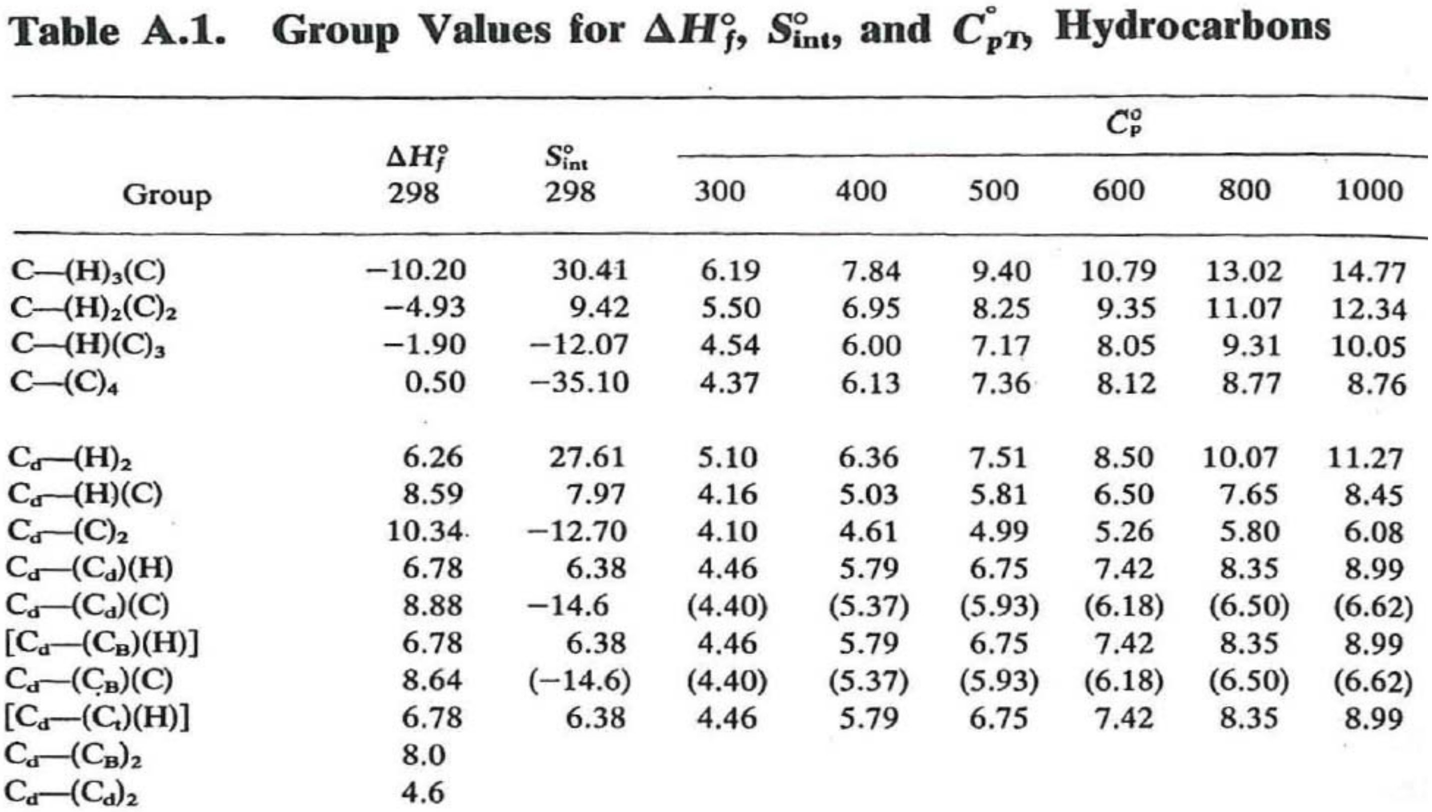


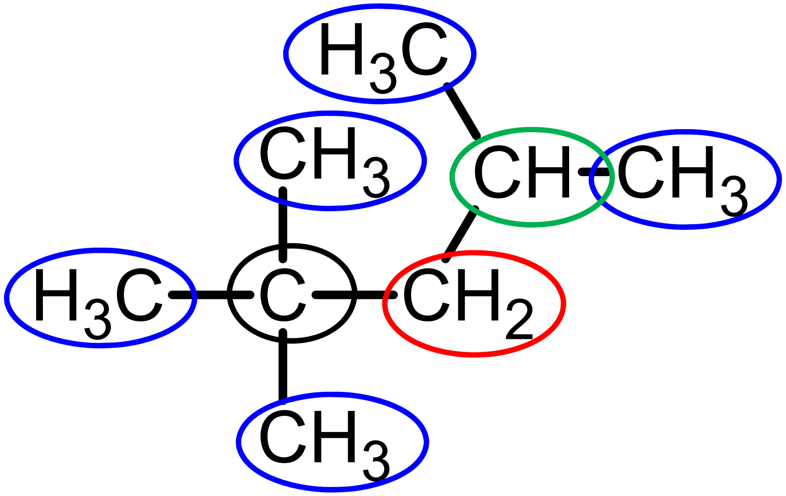
Table A.1. Group Values for ΔH_f°, S°_{int}, and C°_{pT}, Hydrocarbons

	ΔH_f°	S°_{int}	C_p°					
Group	298	298	300	400	500	600	800	1000
$\mathrm{C{—}(H)_3(C)}$	−10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77
$\mathrm{C{—}(H)_2(C)_2}$	−4.93	9.42	5.50	6.95	8.25	9.35	11.07	12.34
$\mathrm{C{—}(H)(C)_3}$	−1.90	−12.07	4.54	6.00	7.17	8.05	9.31	10.05
$\mathrm{C{—}(C)_4}$	0.50	−35.10	4.37	6.13	7.36	8.12	8.77	8.76
$\mathrm{C_d{—}(H)_2}$	6.26	27.61	5.10	6.36	7.51	8.50	10.07	11.27
$\mathrm{C_d{—}(H)(C)}$	8.59	7.97	4.16	5.03	5.81	6.50	7.65	8.45
$\mathrm{C_d{—}(C)_2}$	10.34	−12.70	4.10	4.61	4.99	5.26	5.80	6.08
$\mathrm{C_d{—}(C_d)(H)}$	6.78	6.38	4.46	5.79	6.75	7.42	8.35	8.99
$\mathrm{C_d{—}(C_d)(C)}$	8.88	−14.6	(4.40)	(5.37)	(5.93)	(6.18)	(6.50)	(6.62)
$\mathrm{[C_d{—}(C_B)(H)]}$	6.78	6.38	4.46	5.79	6.75	7.42	8.35	8.99
$\mathrm{C_d{—}(C_B)(C)}$	8.64	(−14.6)	(4.40)	(5.37)	(5.93)	(6.18)	(6.50)	(6.62)
$\mathrm{[C_d{—}(C_t)(H)]}$	6.78	6.38	4.46	5.79	6.75	7.42	8.35	8.99
$\mathrm{C_d{—}(C_B)_2}$	8.0							
$\mathrm{C_d{—}(C_d)_2}$	4.6							

Slide courtesy of Dr. Pierre-Alexandre Glaude

Group Additivity

2,2,4-trimethylpentane (iso-octane):



$C-(H)_3(C)$	5 groups
$C-(H)_2(C)_2$	1 group
$C-(H)(C)_3$	1 group
$C-(C)_4$	1 group

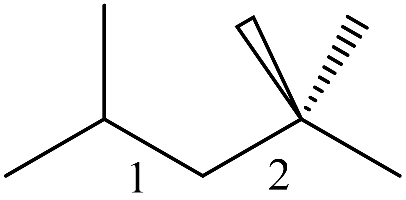
$\sigma_{ext} = 1$, $\sigma_{int} = 729$

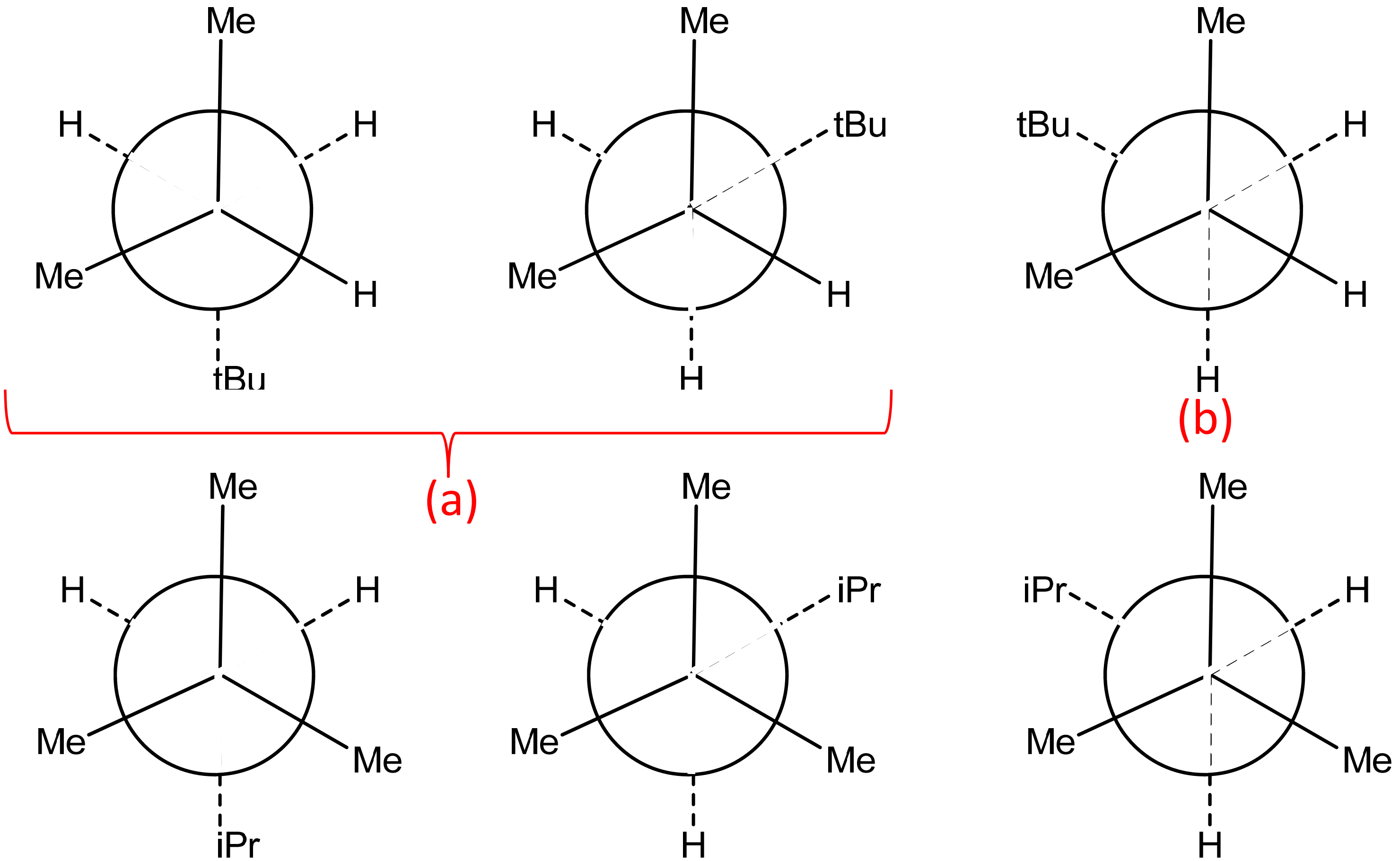
Correction to symmetry

$-R \ln(729) = -13.1$ cal/mol/K

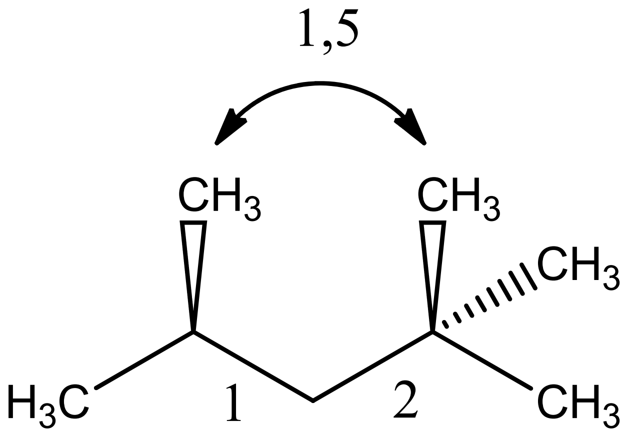
Slide courtesy of Dr. Pierre-Alexandre Glaude

Gauche (C–C) interactions

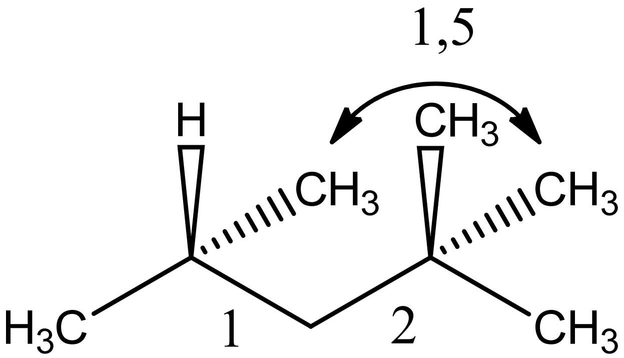




1,5 (H–H) Interaction



or



1.5 kcal/mol

Group additivity in action

2,2,4-trimethylpentane (iso-octane):

group	number	ΔH° (298K) kcal/mol	S° (298K) cal/mol/K	Cp° (300 K) cal/mol/K
$C/C/H_3$	5	–10.03	30.42	6.26
C/C2/H2	1	–4.960	9.42	5.44
C/C3/H	1	–2.130	-12.02	4.39
C/C4	1	0.100	-34.99	4.01
gauche	3	0.7	0	0
H/REPEL/15	1	1.5	0	0
symmetry			–R ln729	
total		–53.54	101.41	45.14

Software

Benson's Additivity Method

THERM Ritter and Bozzelli (1991)

Decomposition into groups and corrections done by the user

NIST database program Stein et al. (1991) Webbook

THERGAS C. Muller, V. Michel, G. Scacchi and G. M. Côme (1995)

CRANIUM : groups of Joback, estimation of other properties

(T_{eb}, T_{fus}, T_c, P_c…)

Quantum Chemistry softwares

- **Semi-empirical approach: MOPAC…**
- **Ab initio : Gaussian, Spartan, Jaguar, Molpro, …**

Slide courtesy of Dr. Pierre-Alexandre Glaude

Thermochemistry in Chemkin

Chemkin uses standard state thermodynamic properties given as polynomial fits to the specific heats at constant *p*

$$\frac{C_p^o k}{R} = \sum_{n=1}^{N} a_{nk} T^{(n-1)}$$

$$H_k^o = \int_0^T C_{p\,k}^o \, dT$$

$$\frac{H_k^o}{RT} = \sum_{n=1}^{N} \frac{a_{nk} T^{(n-1)}}{n} + \frac{a_{N+1,k}}{T}$$

where $a_{N+1,k}R$ is the standard heat of formation at 0 K, but is normally evaluated from the heat of formation at 298 K.

Thermochemistry in Chemkin

$$S_k^o = \int_0^T \frac{C_{p_k}^o}{T} dT$$

$$\frac{S_k^o}{R} = a_{1k} lnT + \sum_{n=2}^{N} \frac{a_{nk} T^{(n-1)}}{(n-1)} + a_{N+2,k}$$

where $a_{N+2,k}R$ is evaluated from knowledge of the standard-state entropy at 298 K.

These are stated for arbitrary-order polynomials, but Chemkin is designed to use NASA polynomials. In this case seven coefficients are needed for each of two temperature ranges. These fits follow the form:

Thermochemistry in Chemkin

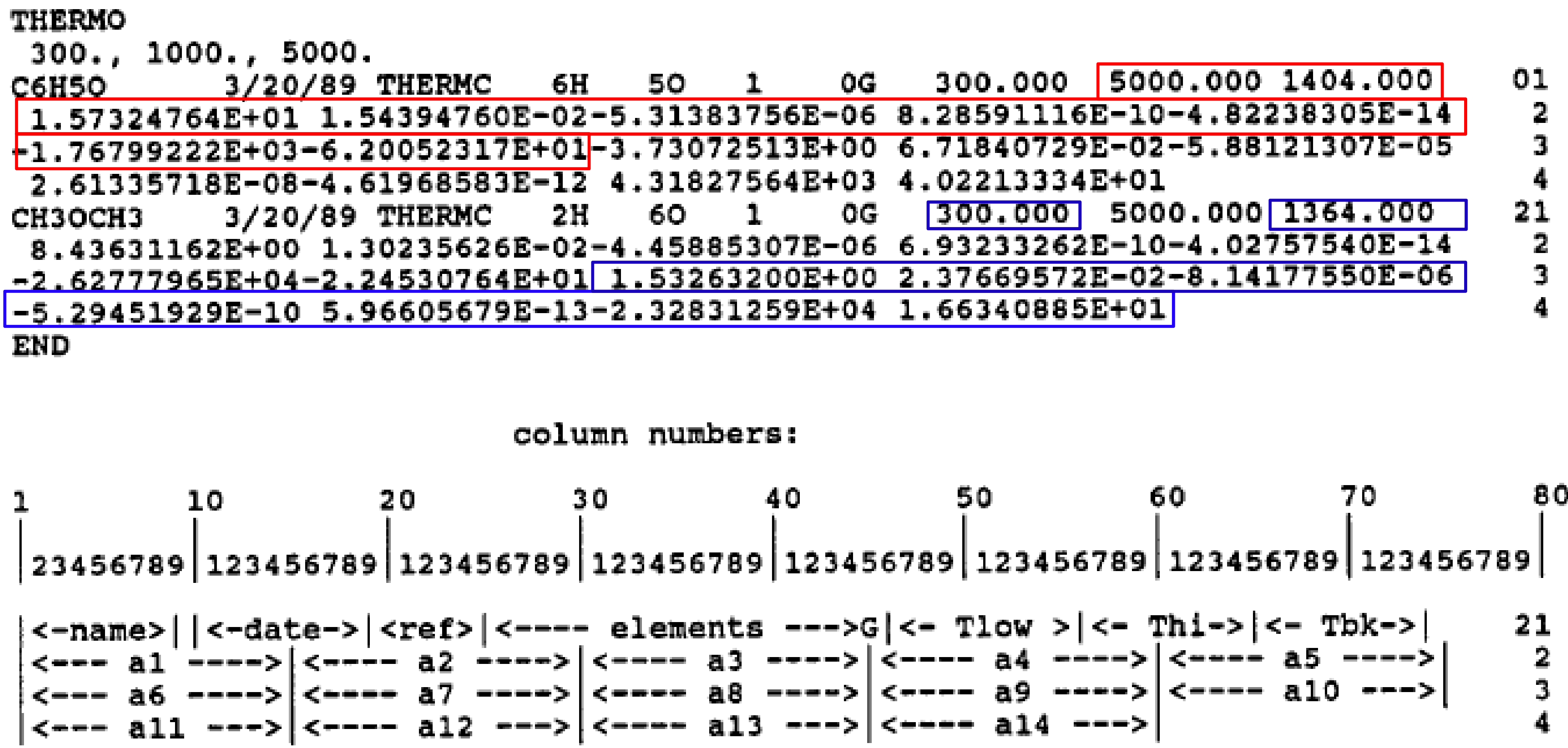
$$\frac{C_p^o k}{R} = a_{1k} + a_{2k}T + a_{3k}T^2 + a_{4k}T^3 + a_{5k}T^4$$

$$\frac{H_k^o}{RT} = a_{1k} + \frac{a_{2k}}{2}T + \frac{a_{3k}}{3}T^2 + \frac{a_{4k}}{4}T^3 + \frac{a_{5k}}{5}T^4 + \frac{a_{6k}}{T}$$

$$\frac{S_k^o}{R} = a_{1k}lnT + a_{2k}T + \frac{a_{3k}}{2}T^2 + \frac{a_{4k}}{3}T^3 + \frac{a_{5k}}{4}T^4 + a_{7k}$$

Other thermodynamics properties are easily given in terms of $C_p^o, H^o, and\ S^o$

NASA polynomials



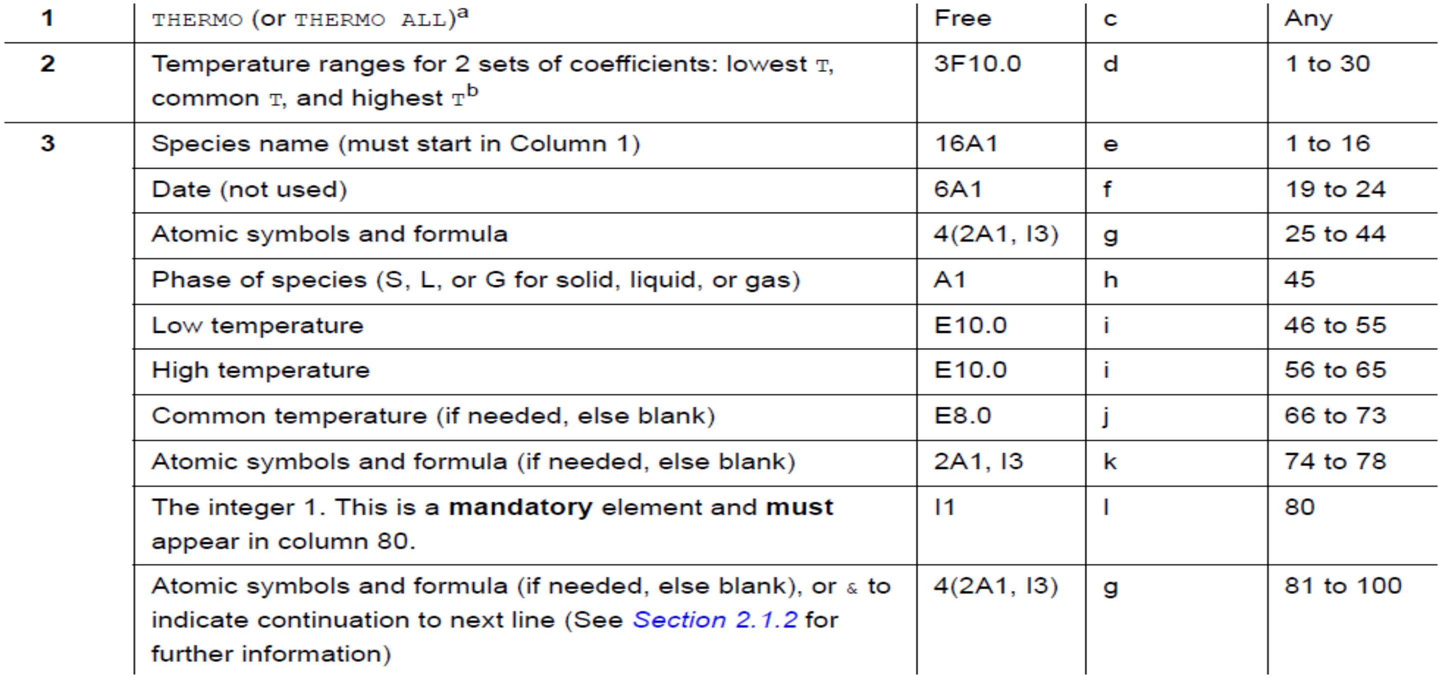
```
THERMO
 300., 1000., 5000.
C6H5O        3/20/89 THERMC   6H   5O   1    0G    300.000  5000.000 1404.000    01
 1.57324764E+01 1.54394760E-02-5.31383756E-06 8.28591116E-10-4.82238305E-14    2
-1.76799222E+03-6.20052317E+01-3.73072513E+00 6.71840729E-02-5.88121307E-05    3
 2.61335718E-08-4.61968583E-12 4.31827564E+03 4.02213334E+01                   4
CH3OCH3      3/20/89 THERMC   2H   6O   1    0G    300.000  5000.000 1364.000    21
 8.43631162E+00 1.30235626E-02-4.45885307E-06 6.93233262E-10-4.02757540E-14    2
-2.62777965E+04-2.24530764E+01 1.53263200E+00 2.37669572E-02-8.14177550E-06    3
-5.29451929E-10 5.96605679E-13-2.32831259E+04 1.66340885E+01                   4
END
```

```
                            column numbers:

1        10        20        30        40        50        60        70        80
|23456789|123456789|123456789|123456789|123456789|123456789|123456789|123456789|

|<-name>||<-date->|<ref>|<---- elements --->G|<- Tlow >|<- Thi->|<- Tbk->|    21
|<--- a1 ---->|<---- a2 ---->|<---- a3 ---->|<---- a4 ---->|<---- a5 ---->|    2
|<--- a6 ---->|<---- a7 ---->|<---- a8 ---->|<---- a9 ---->|<---- a10 --->|    3
|<--- a11 --->|<---- a12 --->|<---- a13 --->|<---- a14 --->|                   4
```

E.R. Ritter J.W. Bozzelli

Intl. J. Chem. Kinet., 23 (1991) 767–778.

```
thermo
   300.000  1000.000  5000.000
h                 120186h   1               g  0300.00   5000.00  1000.00      1
 0.02500000e+02 0.00000000e+00 0.00000000e+00 0.00000000e+00 0.00000000e+00    2
 0.02547163e+06-0.04601176e+01 0.02500000e+02 0.00000000e+00 0.00000000e+00    3
 0.00000000e+00 0.00000000e+00 0.02547163e+06-0.04601176e+01                   4
h2                121286h   2               g  0300.00   5000.00  1000.00      1
 0.02991423e+02 0.07000644e-02-0.05633829e-06-0.09231578e-10 0.01582752e-13    2
-0.08350340e+04-0.01355110e+02 0.03298124e+02 0.08249442e-02-0.08143015e-05    3
-0.09475434e-09 0.04134872e-11-0.01012521e+05-0.03294094e+02                   4
```



1	THERMO (or THERMO ALL)[a]	Free	c	Any
2	Temperature ranges for 2 sets of coefficients: lowest T, common T, and highest T[b]	3F10.0	d	1 to 30
3	Species name (must start in Column 1)	16A1	e	1 to 16
	Date (not used)	6A1	f	19 to 24
	Atomic symbols and formula	4(2A1, I3)	g	25 to 44
	Phase of species (S, L, or G for solid, liquid, or gas)	A1	h	45
	Low temperature	E10.0	i	46 to 55
	High temperature	E10.0	i	56 to 65
	Common temperature (if needed, else blank)	E8.0	j	66 to 73
	Atomic symbols and formula (if needed, else blank)	2A1, I3	k	74 to 78
	The integer 1. This is a **mandatory** element and **must** appear in column 80.	I1	l	80
	Atomic symbols and formula (if needed, else blank), or & to indicate continuation to next line (See *Section 2.1.2* for further information)	4(2A1, I3)	g	81 to 100

```
thermo
   300.000  1000.000  5000.000
h                 120186h   1               g  0300.00   5000.00  1000.00      1
 0.02500000e+02 0.00000000e+00 0.00000000e+00 0.00000000e+00 0.00000000e+00    2
 0.02547163e+06-0.04601176e+01 0.02500000e+02 0.00000000e+00 0.00000000e+00    3
 0.00000000e+00 0.00000000e+00 0.02547163e+06-0.04601176e+01                   4
h2                121286h   2               g  0300.00   5000.00  1000.00      1
 0.02991423e+02 0.07000644e-02-0.05633829e-06-0.09231578e-10 0.01582752e-13    2
-0.08350340e+04-0.01355110e+02 0.03298124e+02 0.08249442e-02-0.08143015e-05    3
-0.09475434e-09 0.04134872e-11-0.01012521e+05-0.03294094e+02                   4
```

4	Coefficients a_1 through a_5 in *Equation 2-17*, *Equation 2-21* and *Equation 2-26* of the *CHEMKIN-MFC Theory Manual*, for **upper temperature interval**	5(E15.8)	m	1 to 75
	The integer 2	I1	I	80

Equation 2-17

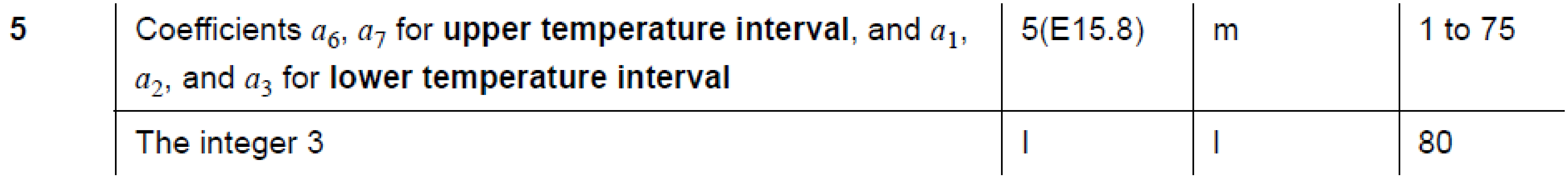
$$\frac{C^o_{pk}}{R} = \sum_{m=1}^{M} a_{mk} T_k^{(m-1)}$$

Equation 2-21

$$\frac{H^o_k}{RT_k} = \sum_{m=1}^{M} \frac{a_{mk} T_k^{(m-1)}}{m} + \frac{a_{M+1,k}}{T_k}$$

$$\frac{S^o_k}{R} = a_{1k} \ln T_k + \sum_{m=2}^{M} \frac{a_{mk} T_k^{(m-1)}}{(m-1)} + a_{M+2,k}$$

```
thermo
   300.000  1000.000  5000.000
h                 120186h   1               g  0300.00   5000.00  1000.00      1
 0.02500000e+02 0.00000000e+00 0.00000000e+00 0.00000000e+00 0.00000000e+00    2
 0.02547163e+06-0.04601176e+01 0.02500000e+02 0.00000000e+00 0.00000000e+00    3
 0.00000000e+00 0.00000000e+00 0.02547163e+06-0.04601176e+01                   4
h2                121286h   2               g  0300.00   5000.00  1000.00      1
 0.02991423e+02 0.07000644e-02-0.05633829e-06-0.09231578e-10 0.01582752e-13    2
-0.08350340e+04-0.01355110e+02 0.03298124e+02 0.08249442e-02-0.08143015e-05    3
-0.09475434e-09 0.04134872e-11-0.01012521e+05-0.03294094e+02                   4
```



5	Coefficients a_6, a_7 for **upper temperature interval**, and a_1, a_2, and a_3 for **lower temperature interval**	5(E15.8)	m	1 to 75
	The integer 3	I	I	80

```
thermo
   300.000  1000.000  5000.000
h                  120186h   1               g  0300.00   5000.00  1000.00      1
 0.02500000e+02 0.00000000e+00 0.00000000e+00 0.00000000e+00 0.00000000e+00    2
 0.02547163e+06-0.04601176e+01 0.02500000e+02 0.00000000e+00 0.00000000e+00    3
 0.00000000e+00 0.00000000e+00 0.02547163e+06-0.04601176e+01                   4
h2                 121286h   2               g  0300.00   5000.00  1000.00      1
 0.02991423e+02 0.07000644e-02-0.05633829e-06-0.09231578e-10 0.01582752e-13    2
-0.08350340e+04-0.01355110e+02 0.03298124e+02 0.08249442e-02-0.08143015e-05    3
-0.09475434e-09 0.04134872e-11-0.01012521e+05-0.03294094e+02                   4
```

6	Coefficients a_4, a_5, a_6, a_7 **for lower temperature interval**	4(E15.8)	n	1 to 60
	The integer 4	I1	I	80

Thermochemical databases

Tables

JANAF Thermochemical Tables 3rd ed., vols. 1-2 , M.W. Chase, American Chemical Society, 1986, SELREF/QD516.D695 1986

Pedley, J. B.; Naylor, R. D.; Kirby, S. P. Thermochemical Data of Organic Compounds: Chapman & Hall, London, 1986.

Tables TRC (Thermodynamics Research Center) Thermodynamic Tables - Hydrocarbons - Department of Chemistry, Texas A&M University

On-line databases

NIST Webbook : http://webbook.nist.gov

Computational Chemistry Comparison and Benchmark Data Base http://srdata.nist.gov/cccbdb/

Active Thermochemical Tables (Branco Ruscic Argonne National Lab.) http://atct.anl.gov/Thermochemical%20Data/version%20Alpha%201.110/index.html

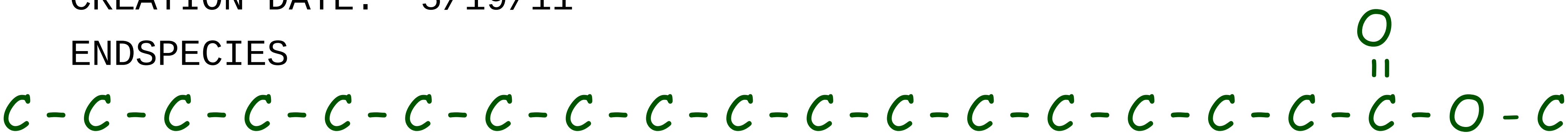
Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion (Burcat) : http://garfield.chem.elte.hu/Burcat/burcat.html

Slide courtesy of Dr. Pierre-Alexandre Glaude

Use of THERM code to apply Benson’s bond additivity rules to compute thermochemical data

- Ritter and Bozzelli code
- Uses tables of bond energies and other data
- Examples of how to use THERM
- Other code families exist to do the same tasks
- Product is a set of JANAF coefficients

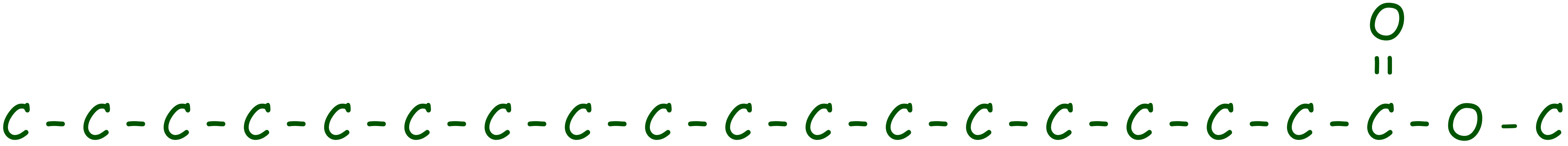
```
         SPECIES
         MOD
Thermo estimation for molecule
 MOD
C19H38O2
 UNITS:KCAL
 GROUPS    6
   Gr # -   GROUP ID   - Quantity  Gr # -   GROUP ID   - Quantity
      1 - C/C/H3           -   1 |      4 - CO/C/O           -   1
      2 - C/C2/H2          -  15 |      5 - O/C/CO           -   1
      3 - C/C/CO/H2        -   1 |      6 - C/H3/O           -   1
  Hf     S    Cp 300    400     500     600     800    1000    1500
-176.74 225.79 111.09 138.64 163.25 184.19 217.39 242.00     .00
            CPINF =  328.85
  NROTORS:19
 SYMMETRY          9
  CREATION DATE:  5/19/11
  ENDSPECIES
```



$$C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-\overset{\overset{\displaystyle O}{\|}}{C}-O-C$$

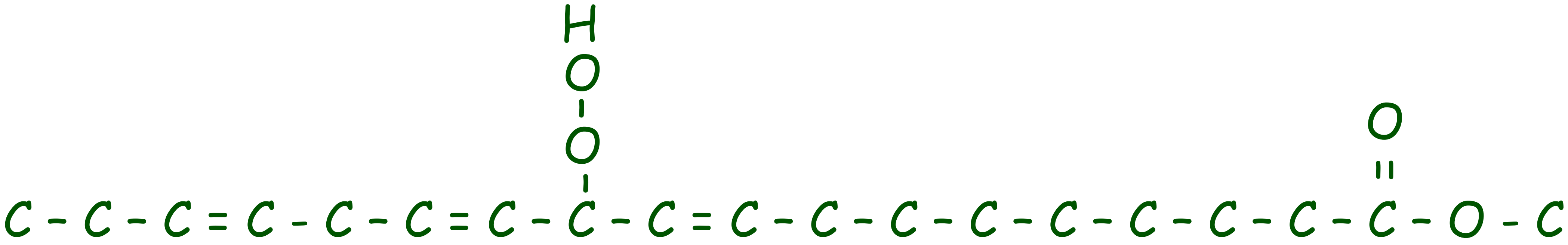
Radicals in this fuel

p	primary	c/c/h3,1
s	secondary	c/c2/h2,15
rcoocj	end methoxy group	c/h3/o,1
ccjcoor	adjacent to C=O	c/c/co/h2,1



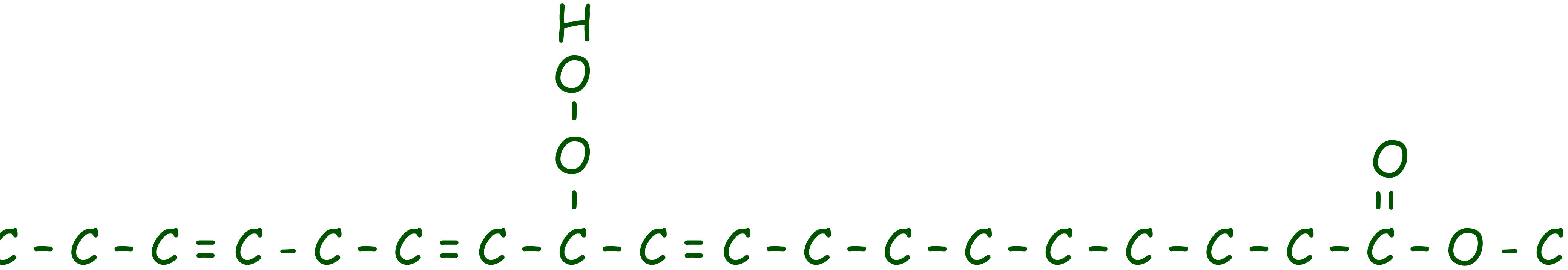
$$C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-\overset{\overset{O}{\parallel}}{C}-O-C$$

```
 SPECIES
 MDO2H11
Thermo estimation for molecule
 MDO2H11                                                    C19H32O4
 UNITS:KCAL
 GROUPS  12
   Gr # -  GROUP ID  - Quantity  Gr # -  GROUP ID  - Quantity
      1 - C/C/H3         -  1 |     7 - C/C2/H2        -  5
      2 - C/C/CD/H2      -  2 |     8 - C/C/CO/H2      -  1
      3 - C/CD2/H2       -  1 |     9 - CO/C/O         -  1
      4 - C/CD2/H/O      -  1 |    10 - O/C/CO         -  1
      5 - OO/C/H         -  1 |    11 - C/H3/O         -  1
      6 - CD/C/H         -  6 |    12 - OI             -  1
  Hf     S   Cp 300    400    500    600    800   1000   1500
-119.88 234.93 109.82 137.00 160.31 179.71 209.69 231.74    .00
           CPINF =  306.00
  NROTORS:18
 SYMMETRY           9
  CREATION DATE:  5/21/11
  ENDSPECIES
```

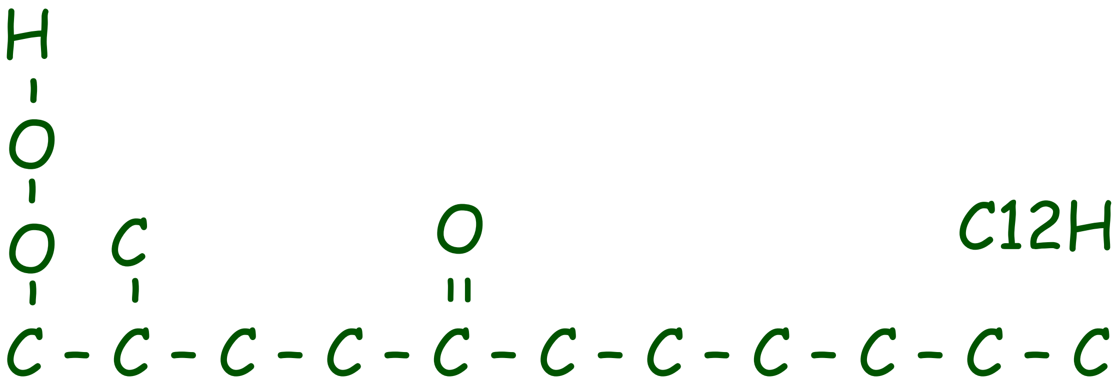


Radicals in this fuel

p	primary	c/c/h3,1
s	secondary	c/c2/h2,5
alperox		oo/c/h,1
vins	vinyl	cd/c/h,6
allyls	allyl	c/c/cd/h2,2
bis-allyl		c*ccjc*c
rcoocj	end methoxy group	c/h3/o,1
ccjcoor	adjacent to C=O	c/c/co/h2,1



```
 SPECIES
 C12KET4-1
Thermo estimation for molecule
 C12KET4-1                                                   C12H24O3
 UNITS:KCAL
 GROUPS   9
   Gr # -   GROUP ID   - Quantity  Gr # -   GROUP ID   - Quantity
      1 - C/C/H3          -  2 |      6 - CO/C2           -  1
      2 - C/C/H2/OO       -  1 |      7 - C/C2/H2         -  5
      3 - OO/C/H          -  1 |      8 - OI              -  2
      4 - C/C3/H          -  1 |      9 - GAUCHE          -  1
      5 - C/C/CO/H2       -  2
  Hf     S    Cp 300    400    500    600    800   1000   1500
-116.59 175.02  75.55  93.40 110.37 125.39 149.41 163.91    .00
           CPINF =  215.59
  NROTORS:13
 SYMMETRY          9
  CREATION DATE:  3/23/14
  ENDSPECIES
```



C12H24ket4-1-2

Radicals in this fuel

p primary c/c/h3,2

s secondary c/c2/h2,5

t tertiary

c/c3/h,1

alperox oo/c/h,1

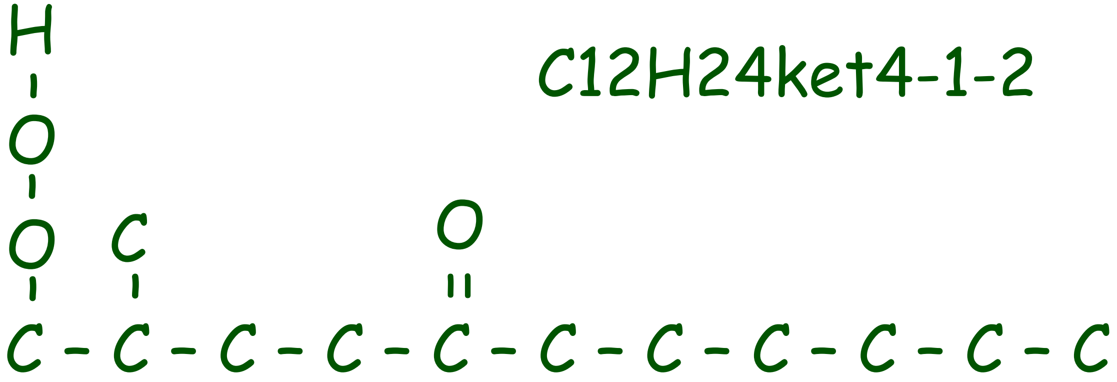
C-H adjacent to C=O

c/c/co/h2,2

C=O between C atoms co/c2,1

OO on primary C

c/c/h2/oo,1



C12H24ket4-1-2

Basic Chemical Kinetic Principles I

Temperature dependence?

$$C_2H_5Cl \rightarrow C_2H_4 + HCl$$

k/s^{-1}	T/K
6.1×10^{-5}	700
30×10^{-5}	727
242×10^{-5}	765

- Conclusion: *very* sensitive to temperature
- Rule of thumb: rate ≈ doubles for a 10K rise

Details of T dependence

Hood

- $k = A \exp\{-B/T\}$

Arrhenius

- $k = A \exp\{-E / RT\}$

A pre-exponential factor

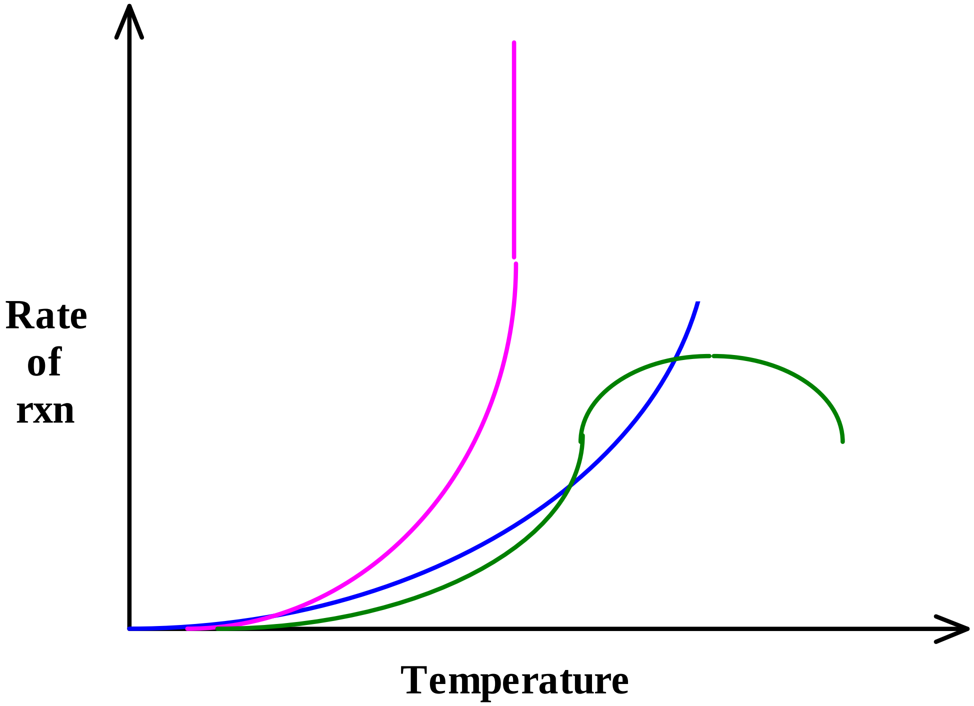
orA-factor

$\equiv k$ at $T \rightarrow \infty$

E activation energy

(*energy barrier*) J mol $^{-1}$ or kJ mol^{-1}

R gas constant.



Arrhenius eqn. $k=A \exp\{-E/RT\}$

Useful *linear* form: $\ln k = -(E/R)(1/T) + \ln A$

- Plot $\ln k$ along Y-axis *vs* $(1/T)$ along X-axis

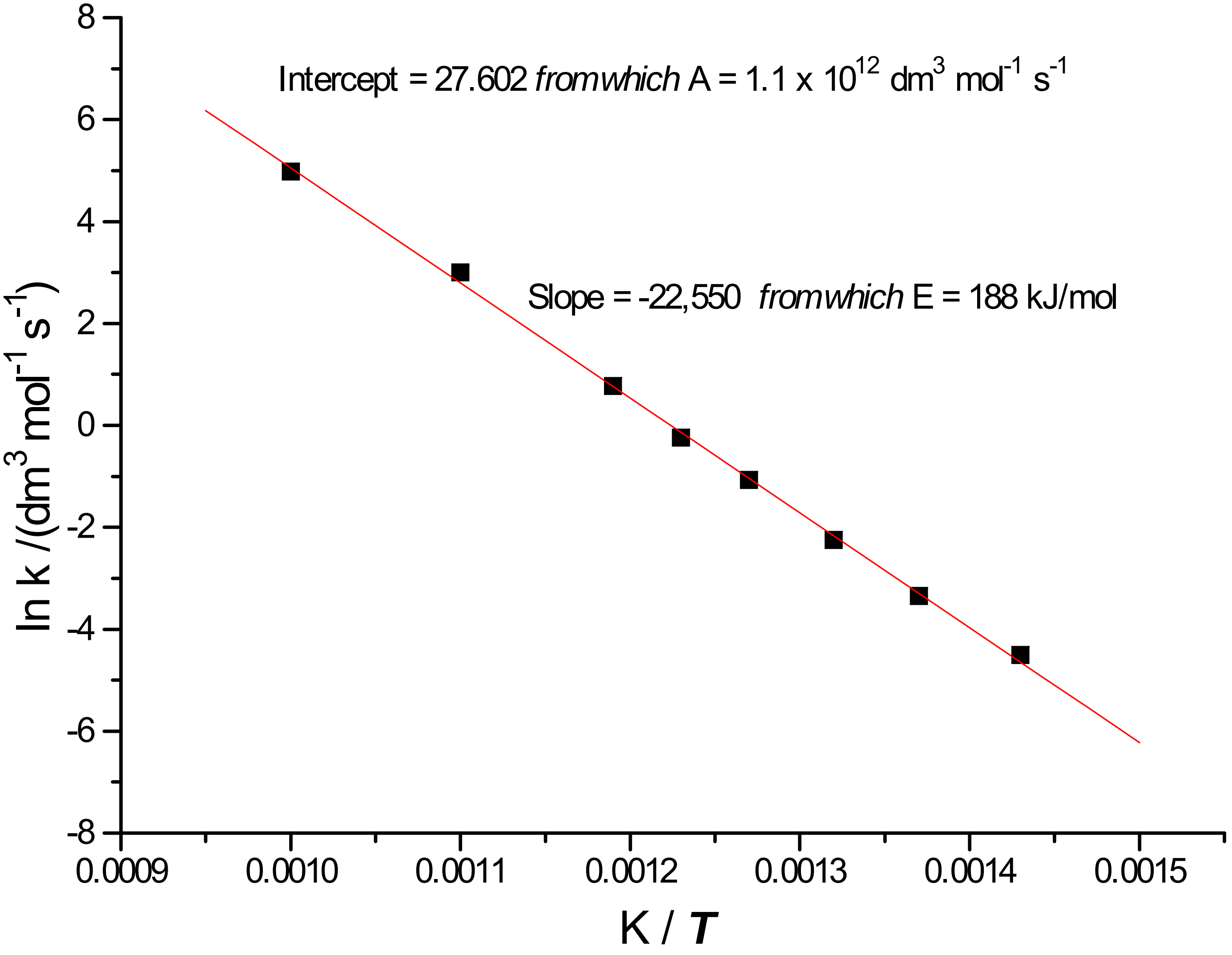
Slope is *negative* $-(E/R)$; intercept $= \ln A$

- Experimental Es range from 0 to +400 kJ mol^{-1}

Examples:

$H^{\cdot} + HCl \rightarrow H_2 + Cl\cdot$	19 kJ mol^{-1}
$H\cdot + HF \rightarrow H_2 + F\cdot$	139 kJ mol^{-1}
$C_2H_5I \rightarrow C_2H_4 + HI$	209 kJ mol^{-1}
$C_2H_6 \rightarrow 2CH_3$	368 kJ mol^{-1}

Practical Arrhenius plot, origin not included



Common mathematical functions

Kinetics, Arrhenius

- **$k = A \exp\{-E/RT\}$**

Vapour pressure, Clausius-Clayperon

- **$p = p_{\infty} \exp\{-\Delta H_V/RT\}$**

Viscosity, Andrade

- $\eta = A \exp\{+E/RT\}$
- But re-define as inverse: $F = F_{\infty} \exp\{-E/RT\}$

Examples of results of faulty thermochemical data

- High temperature ignition of natural gas
- Natural gas is a mixture of methane (~90%), ethane (5-10%), and higher hydrocarbons
- Methane is often used as a surrogate for natural gas
- Ignition and detonations are particular concerns

Alkane ignitions

- Methane ignites very slowly
    - Influence of methyl radical
- Ethane is unusually ignitable
    - Unusual in production of ethyl radicals and H atoms
- Larger n-alkanes ignite at intermediate rates
- Natural gas ignition is a good example of ignition sensitizing

A common problem in kinetic models

- If rates of addition reactions are specified, bad thermo can produce unreasonably large activation energies for dissociation reactions
- Must test new mechanisms to look for this

Transport in combustion simulations

- Characterizing the molecular transport of species, momentum, and energy in a multicomponent gaseous mixture requires the evaluation of diffusion coefficients, viscosities, thermal conductivities, and thermal diffusion coefficients.

$$\mathcal{D}_{kj} = \frac{3}{16}\frac{\sqrt{2\pi k_B^3 T^3 / m_{jk}}}{P\pi\sigma_{jk}^2 \Omega^{(1,1)*}}$$

$$\frac{\varepsilon_{jk}}{k_B} = \sqrt{\left(\frac{\varepsilon_j}{k_B}\right)\left(\frac{\varepsilon_k}{k_B}\right)}$$

where m_{jk} is the reduced molecular mass for the $(j\,,\,k)$ species pair and σ_{jk} is the reduced collision diameter. The collision integral $\Omega^{(1,1)*}$ (based on Stockmayer potentials) depends on the reduced temperature, T_{jk}^* which in turn may depend on the species dipole moments μ_k, and polarizabilities α_k. In computing the reduced quantities, we consider two cases, depending on whether the collision partners are polar or nonpolar. For the case that the partners are either both polar or both nonpolar the following expressions apply:

$$\sigma_{jk} = \frac{1}{2}(\sigma_j + \sigma_k)$$

$$\mu_{jk}^2 = \mu_j\mu_k$$

Important transport parameters

- An index indicating whether the molecule has a monatomic, linear or nonlinear geometrical configuration. If the index is 0, the molecule is a single atom. If the index is 1 the molecule is linear, and if it is 2, the molecule is nonlinear.
- The Lennard-Jones potential well depth ε∕kB in Kelvins.
- The Lennard-Jones collision diameter σ in angstroms.
- The dipole moment μ in Debye.
- The polarizability α in cubic angstroms.
- The rotational relaxation collision number Zrot. at 298 K.

Determining L J Parameters

$$\sigma\left(\frac{P_c}{T_c}\right)^{1/3} = a_\sigma - b_\sigma\omega$$

$$\frac{\varepsilon}{k_B T_c} = a_\varepsilon + b_\varepsilon\omega.$$

σ = L-J collision diameter

ε = L-J potential well depth

$$a_\sigma = 2.3511, \quad b_\sigma = 0.3955,$$
$$a_\varepsilon = 0.8063 \quad \text{and} \quad b_\varepsilon = 0.6802.$$

P_c – critical pressure
T_c – critical temperature
T_b – boiling points

$$\omega = \frac{-\ln(P_c) - 5.93 + 6.10\theta^{-1} + 1.29\ln\theta - 0.17\theta^6}{15.25 - 15.69\theta^{-1} - 13.47\ln\theta + 0.44\theta^6},$$

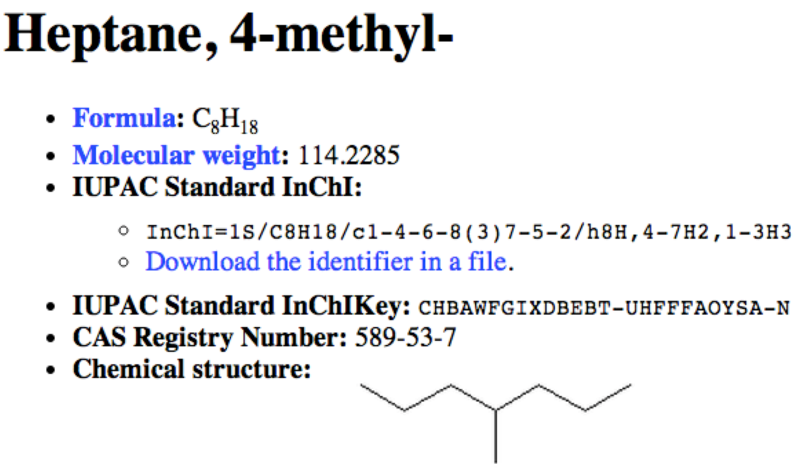
The acentric factor w isevaluated using the Lee–Kesler vapor–pressure relations

$$\theta = T_b/T_c$$

A.T. Holley et al. / Proceedings of the Combustion Institute 32 (2009) 1157-1163

L.S. Tee, S. Gotoh, W.E. Stewart, I&EC Fundam. 5 (1966) 356-363

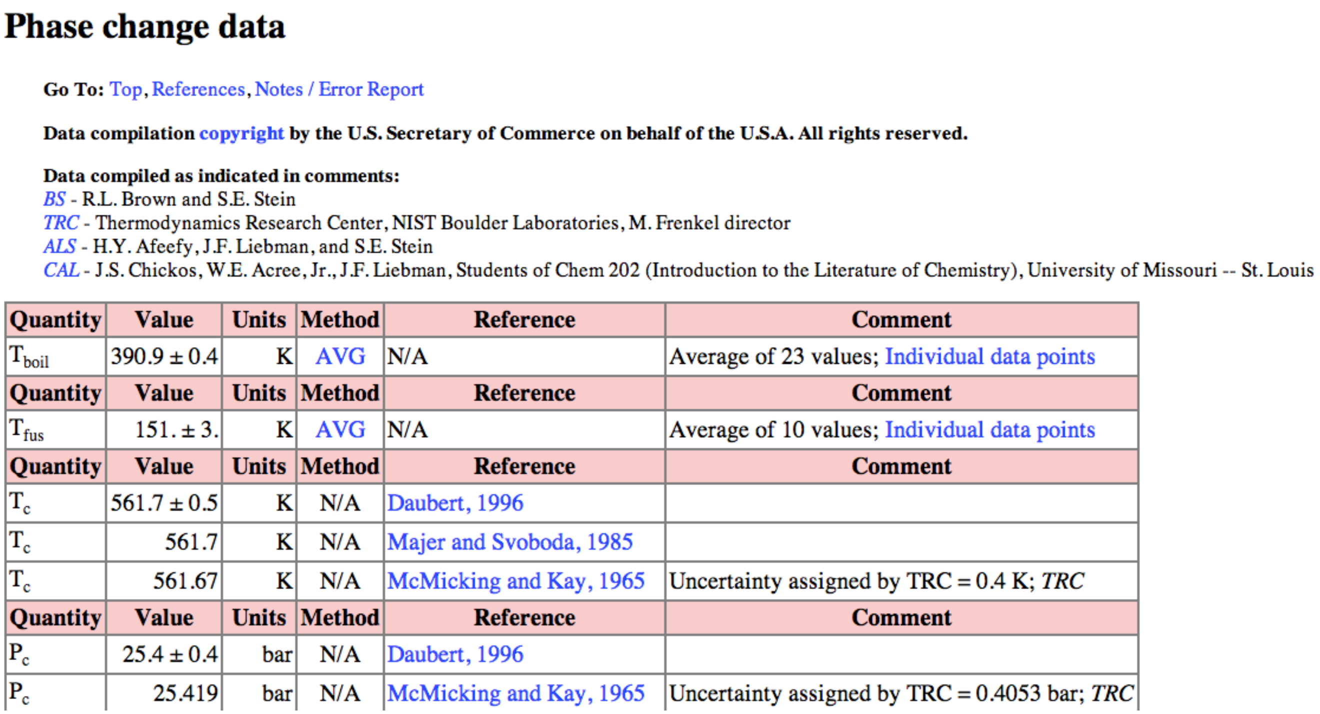
Obtaining T_b, T_c, and P_c



Heptane, 4-methyl-

- **Formula:** C_8H_{18}
- **Molecular weight:** 114.2285
- **IUPAC Standard InChI:**
  - `InChI=1S/C8H18/c1-4-6-8(3)7-5-2/h8H,4-7H2,1-3H3`
  - Download the identifier in a file.
- **IUPAC Standard InChIKey:** `CHBAWFGIXDBEBT-UHFFFAOYSA-N`
- **CAS Registry Number:** 589-53-7
- **Chemical structure:**

- For many stable species, these values are available on the NIST chemistry WebBook (webbook.nist.gov)



Phase change data

Go To: Top, References, Notes / Error Report

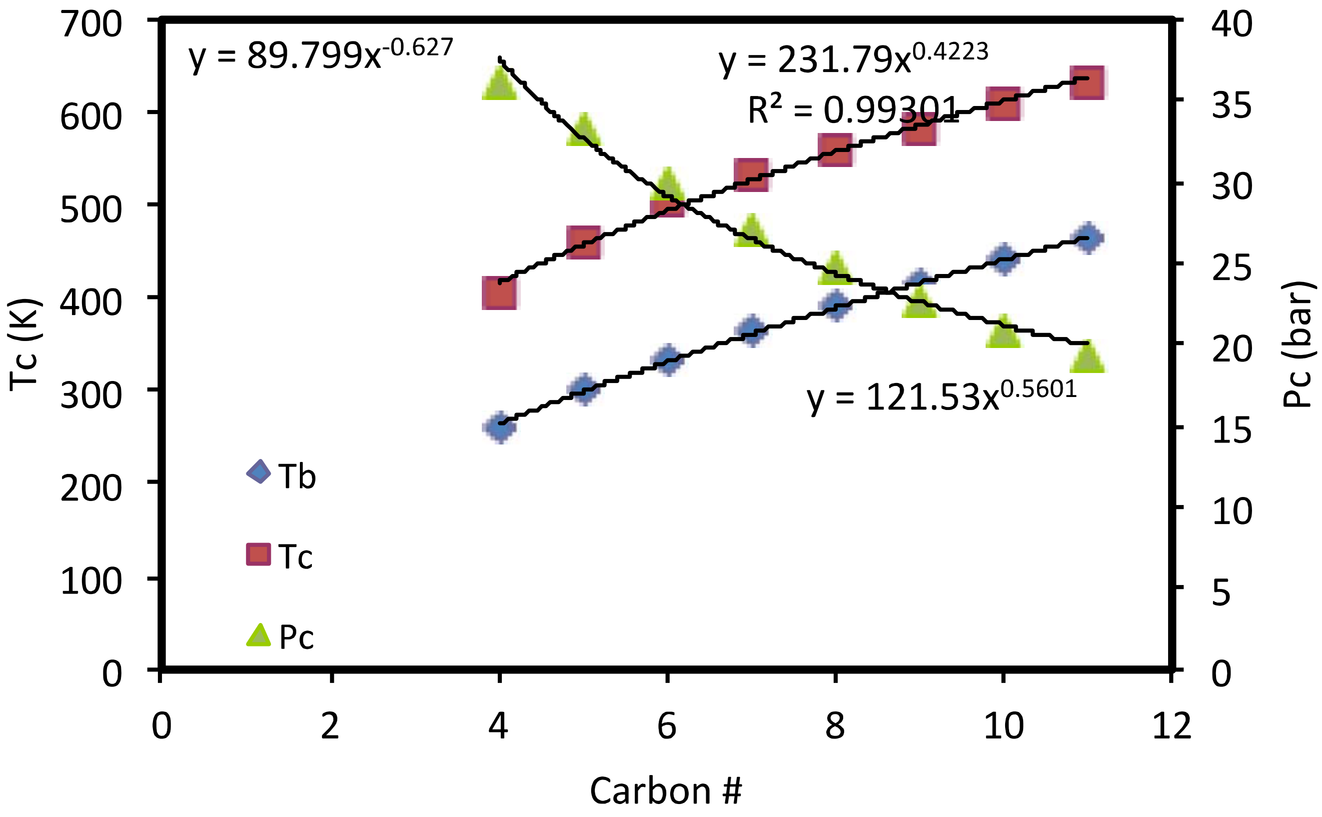
Data compilation copyright by the U.S. Secretary of Commerce on behalf of the U.S.A. All rights reserved.

Data compiled as indicated in comments:
BS - R.L. Brown and S.E. Stein
TRC - Thermodynamics Research Center, NIST Boulder Laboratories, M. Frenkel director
ALS - H.Y. Afeefy, J.F. Liebman, and S.E. Stein
CAL - J.S. Chickos, W.E. Acree, Jr., J.F. Liebman, Students of Chem 202 (Introduction to the Literature of Chemistry), University of Missouri -- St. Louis

Quantity	Value	Units	Method	Reference	Comment
T_{boil}	390.9 ± 0.4	K	AVG	N/A	Average of 23 values; Individual data points
Quantity	**Value**	**Units**	**Method**	**Reference**	**Comment**
T_{fus}	151. ± 3.	K	AVG	N/A	Average of 10 values; Individual data points
Quantity	**Value**	**Units**	**Method**	**Reference**	**Comment**
T_c	561.7 ± 0.5	K	N/A	Daubert, 1996	
T_c	561.7	K	N/A	Majer and Svoboda, 1985	
T_c	561.67	K	N/A	McMicking and Kay, 1965	Uncertainty assigned by TRC = 0.4 K; *TRC*
Quantity	**Value**	**Units**	**Method**	**Reference**	**Comment**
P_c	25.4 ± 0.4	bar	N/A	Daubert, 1996	
P_c	25.419	bar	N/A	McMicking and Kay, 1965	Uncertainty assigned by TRC = 0.4053 bar; *TRC*

Determining Tc and Pc

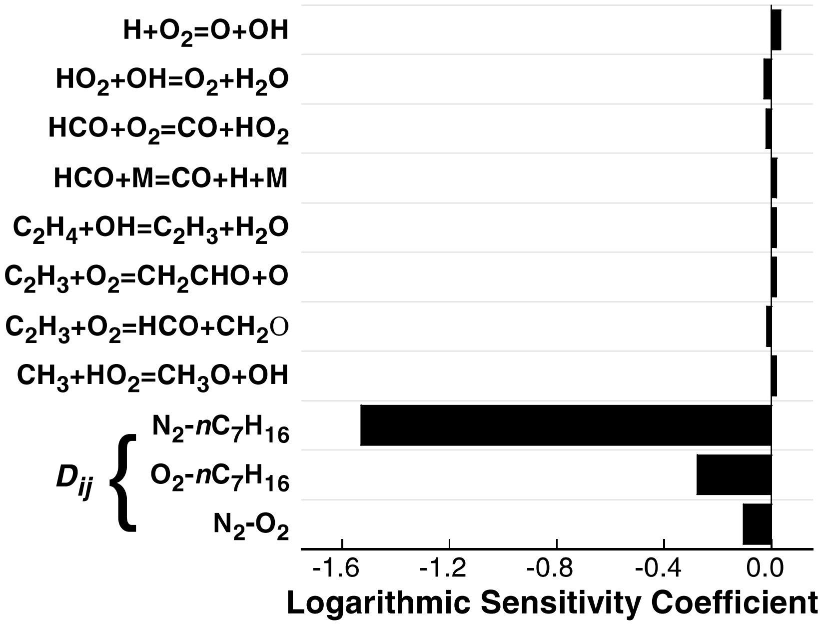
- Regression analysis and interpolation/
- extrapolation can be used to determine these values for high molecular weight fuels.

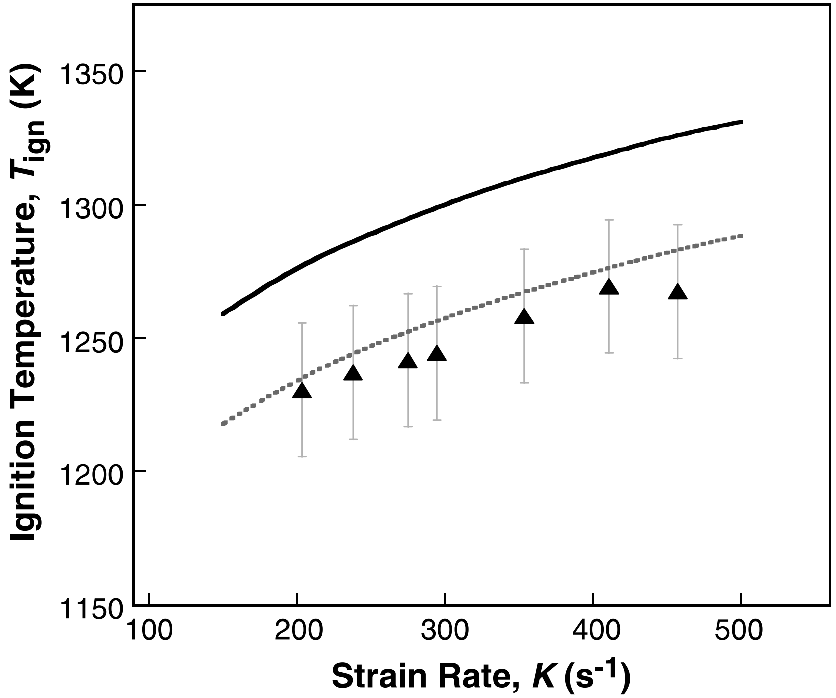


Effects of LJ parameters of combustion

- LJ parameters affect the binary diffusion coefficient
- Changing the collision diameter can impact combustion

$$\mathcal{D}_{kj} = \frac{3}{16}\frac{\sqrt{2\pi k_B^3 T^3 / m_{jk}}}{P\pi\sigma_{jk}^2\Omega^{(1,1)*}}$$





A.J. Smallbone et al. / Proceedings of the Combustion Institute 32 (2009) 1245–1252

Dashed line 25% reduction in collision diameter

Dipole moments

- The dipole moment (μ) is a measure of the extent of polarity in covalent molecules.
- It is dependent on the difference electronegativity of the bonding atoms, and is precisely defined as the product of the magnitude of the charge and the distance between the charges.
- Nonpolar compounds, such as fully saturated hydrocarbons have zero dipole moments while oxygenated compounds display higher dipole moments.

A. McClellan, Tables of Experimental Dipole Moments. San Francisco: Freeman, 1963.

Polarizability

- The polarizability (α) of a molecule quantifies the tendency of a molecules charge distribution (i.e., electron cloud) to be distorted from its normal shape by an external electric field (e.g., a nearby dipole or ion).
- Experimentally measured polarizability values in cubic Angstroms can be obtained from the "CRC Handbook of Chemistry and Physics" [24].
- Bosque and Sales have presented an empirical additive formula that allows the estimation of polarizability from the molecular formula (i.e., # of C, H, and O atoms)

$$\alpha = 0.32 + 1.51 * \#C + 0.17 * \#H + 0.51 * \#O$$

R. Bosque and J. Sales, "Polarizabilities of solvents from the chemical composition," Journal of Chemical Information and Computer Sciences, vol. 42, no. 5, pp. 1154– 1163, September-October 2002.

Sources of Reaction Rates

Charles Westbrook

Tsinghua-Princeton
2014 Summer School on Combustion
July 20-25, 2014

Some sources of kinetic rate data

- Experimental studies of individual reactions
- Chemical theory
- Estimates, based on “similar” reactions of other species
- Previously published studies
- Optimization of computed results vs. expeimental data
- Literature databases

SINGLE-PULSE SHOCK-TUBE STUDY ON THE DECOMPOSITION OF 1-PENTYL RADICALS

WING TSANG, JAMES A. WALKER AND JEFFREY A. MANION
National Institute of Standards and Technology
Gaithersburg, MD 20899, USA

1-Pentyl radicals have been decomposed in single-pulse shock-tube experiments. The precursor is *n*-pentyl iodide, and the reaction conditions are 850–1000 K and 1.5–5 bar pressure. With 1-pentyl radicals being released with the rate expression

$$k(n\text{-}C_5H_{11}I = 1\text{-}C_5H_{11} + I) = 4 \times 10^{14} \exp(-25{,}820/T)\text{s}^{-1}$$

we find the branching ratios for the decomposition to form olefin products to be

$$k(1\text{-}C_5H_{11} = 2C_2H_4 + CH_3)/k(1\text{-}C_5H_{11}) = 2.3 \exp(-2018/T)$$

$$k(1\text{-}C_5H_{11} = C_3H_6 + C_2H_5)/k(1\text{-}C_5H_{11}) = 0.27 \exp(803/T)$$

$$k(1\text{-}C_5H_{11} = 1\text{-}C_4H_8 + CH_3)/k(1\text{-}C_5H_{11}) = 0.068 \exp(310/T)$$

where $k(1\text{-}C_5H_{11})$ is the total rate constant for 1-pentyl radical decomposition. The results from the last two channels are interpreted in terms of radical isomerization through 1,4- and 1,3-hydrogen migration to form 2-pentyl and 3-pentyl radicals. From kinetic modeling, we find

$$k(1\text{-}C_5H_{11} \rightarrow 2\text{-}C_5H_{11}) = 1 \times 10^{12} \exp(-11{,}330/T)\text{s}^{-1}$$

$$k(1\text{-}C_5H_{11} \rightarrow 3\text{-}C_5H_{11}) = 3 \times 10^{11} \exp(-12{,}100/T)\text{s}^{-1}$$

Under the present conditions, pentyl radicals are not being equilibrated. Some of the problems in the interpretation and extrapolation of experimental results on the decomposition of complex radicals are considered. It appears that the isomerization of secondary pentyl radicals will not be competitive with β C–C bond fission. The molecular elimination of HI from *n*-pentyl iodide is characterized by the rate expression

$$(n\text{-}C_5H_{11}I = 1\text{-}C_5H_{10} + HI) = 1.05 \times 10^{13} \exp(-25{,}730/T)\text{s}^{-1}$$

and is relatively unimportant in the present context.

Rates determined from production of different olefins from different reaction pathways

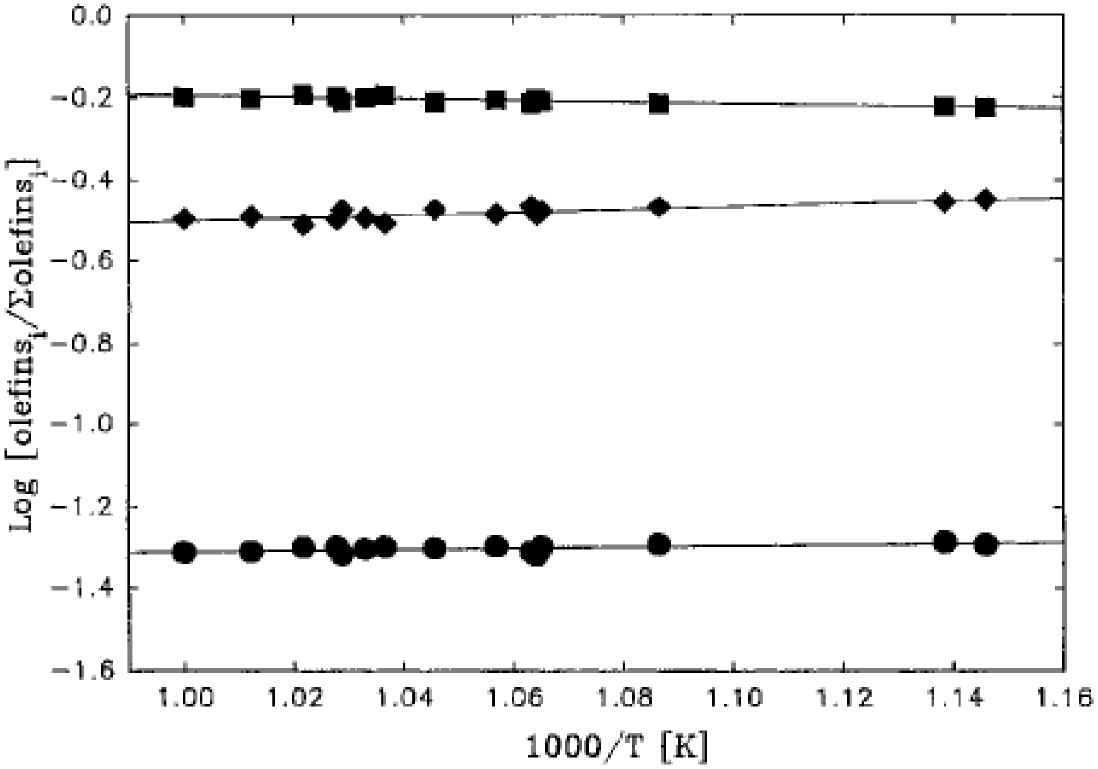
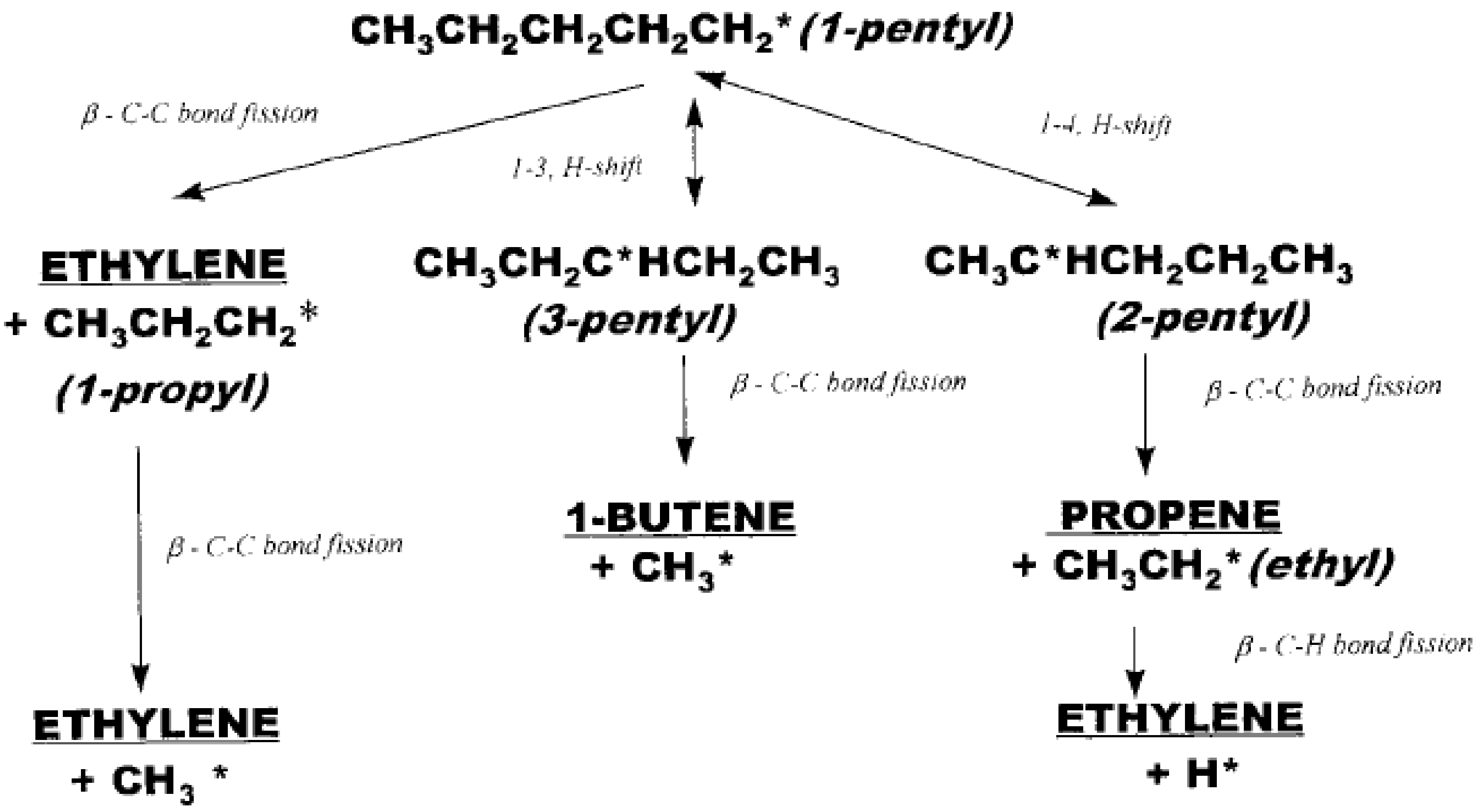


FIG. 1. Olefin products from the decomposition of the 1-pentyl radical. Squares are for ethylene, diamonds for propene, and circles for 1-butene.


CH3CH2CH2CH2CH2* (1-pentyl)
β - C-C bond fission
1-3, H-shift
1-4, H-shift
ETHYLENE
+ CH3CH2CH2*
(1-propyl)
CH3CH2C*HCH2CH3
(3-pentyl)
CH3C*HCH2CH2CH3
(2-pentyl)
β - C-C bond fission
β - C-C bond fission
β - C-C bond fission
1-BUTENE
+ CH3*
PROPENE
+ CH3CH2* (ethyl)
β - C-H bond fission
ETHYLENE
+ CH3 *
ETHYLENE
+ H*

The decomposition of normal hexyl radicals ☆

Wing Tsang *, James A. Walker, Jeffrey A. Manion

National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Abstract

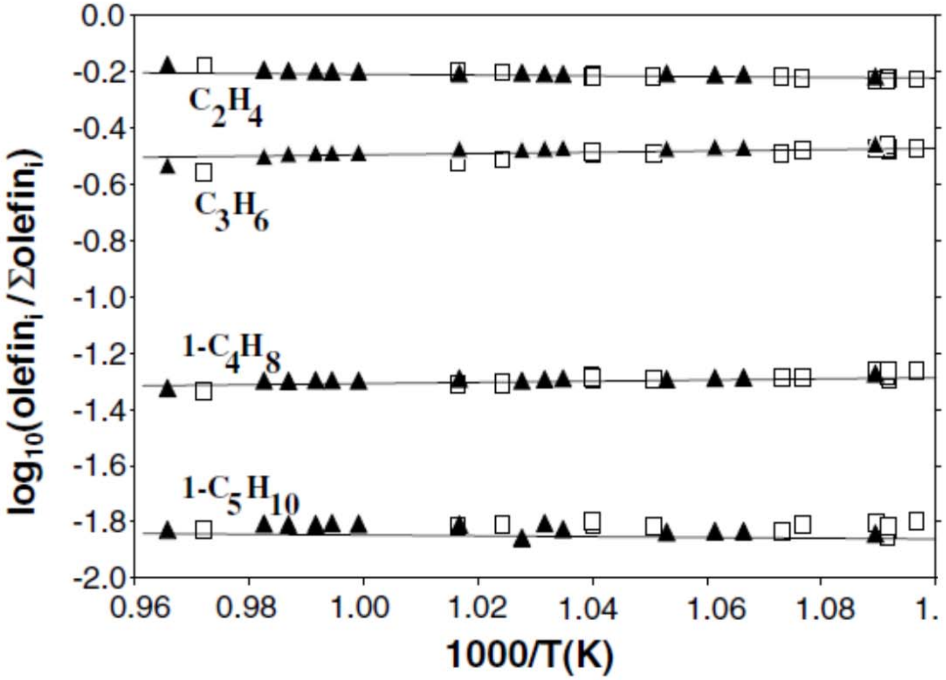
Normal hexyl radicals generated from the decomposition of *n*-hexyl iodide have been decomposed in single pulse shock tube experiments. All the products arising from the decomposition of 1-hexyl (the initial reactant) and 2-hexyl and 3-hexyl (isomerization products) have been detected in the temperature range 890–1020 K and 1.5–5 bar pressures. We find that

$$k(C_6H_{13}\text{-}3 => C_2H_5 + 1\text{-}C_4H_8)/k(C_6H_{13}\text{-}3 => CH_3 + 1\text{-}C_5H_{10}) = 3.4 \pm 0.1$$

when this is combined with literature values of the beta bond scission reactions of hexyl radicals we find the following high pressure rate expressions for the isomerization processes;

$$k(C_6H_{13}\text{-}1 <=> C_6H_{13}\text{-}2) = 1.83 \times 10^2 T^{2.55} \exp(-5516/T)\text{s}^{-1}$$

$$k(C_6H_{13}\text{-}1 <=> C_6H_{13}\text{-}3) = 6.98 \times T^{3.2} \exp(-8333/T)\text{s}^{-1}$$



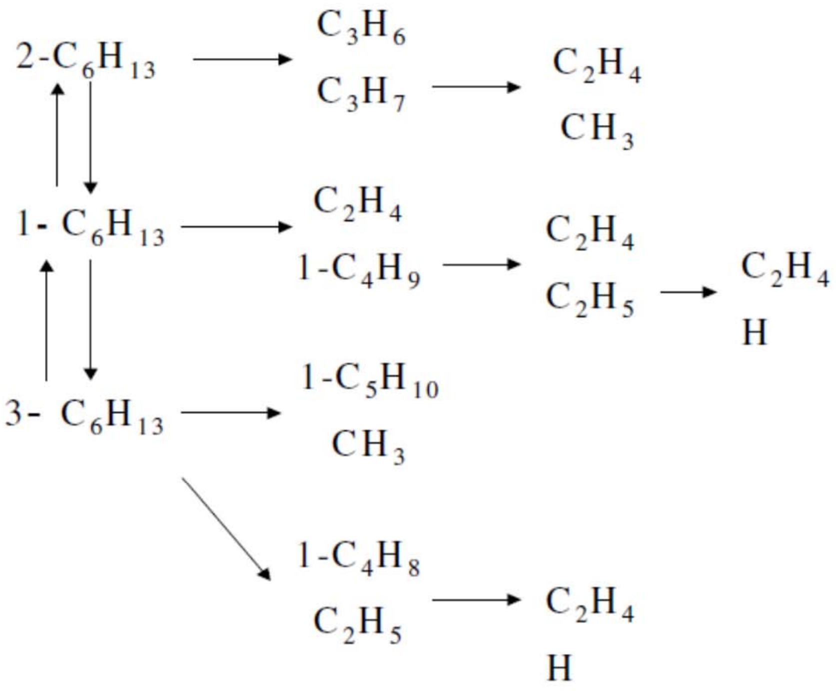


Fig. 2. Mechanism for the decomposition and isomerization of hexyl radicals.

KINETIC INVESTIGATIONS OF THE REACTIONS OF TOLUENE AND OF *p*-XYLENE WITH MOLECULAR OXYGEN BETWEEN 1050 AND 1400 K

R. A. ENG.,[1] C. FITTSCHEN,[2] A. GEBERT,[1] P. HIBOMVSCHI,[1] H. HIPPLER[1] AND A.-N. UNTERREINER[1]

[1]*Lehrstuhl für Molekulare Physikalische Chemie*
Institut für Physikalische Chemie und Elektrochemie
Universität Karlsruhe
Kaiserstr. 12, D-76128 Karlsruhe, Germany
[2]*Université des Sciences et Technologies de Lille*
Laboratoire de Cinétique et Chimie de la Combustion
59665 Villeneuve d'Ascq, Cedex France

The reaction of toluene with molecular oxygen was studied behind reflected shock waves. Mixtures of 0.5–1 mol % toluene and 5–10 mol % oxygen in argon were investigated in the temperature range between 1050 and 1400 K at total pressures between 2 and 4 bar. We followed the rate of formation of the benzyl radicals by time-resolved UV absorption at 257 nm. The measured concentration-time profiles of the benzyl radicals were numerically reproduced using a simple reaction mechanism. For the initial reaction

$$C_6H_5CH_3 + O_2 \rightarrow C_6H_5CH_2 + HO_2 \qquad \text{(R1)}$$

a rate coefficient k_1 of

$$k_1 = 3 \times 10^{14} \exp\left[\frac{-180 \text{ kJ/mol}}{RT}\right] \frac{\text{cm}^3}{\text{mol s}} \quad (1050 \text{ K} < T < 1400 \text{ K})$$

was determined with an accuracy of 30%. The rate constant k_2 of the subsequent reaction

$$C_6H_5CH_3 + HO_2 \rightarrow C_6H_5CH_2 + H_2O_2 \qquad \text{(R2)}$$

was determined to be

$$k_2 = 3 \times 10^{14} \exp\left[\frac{-92 \text{ kJ/mol}}{RT}\right] \frac{\text{cm}^3}{\text{mol s}} \quad (1150 \text{ K} < T < 1250 \text{ K})$$

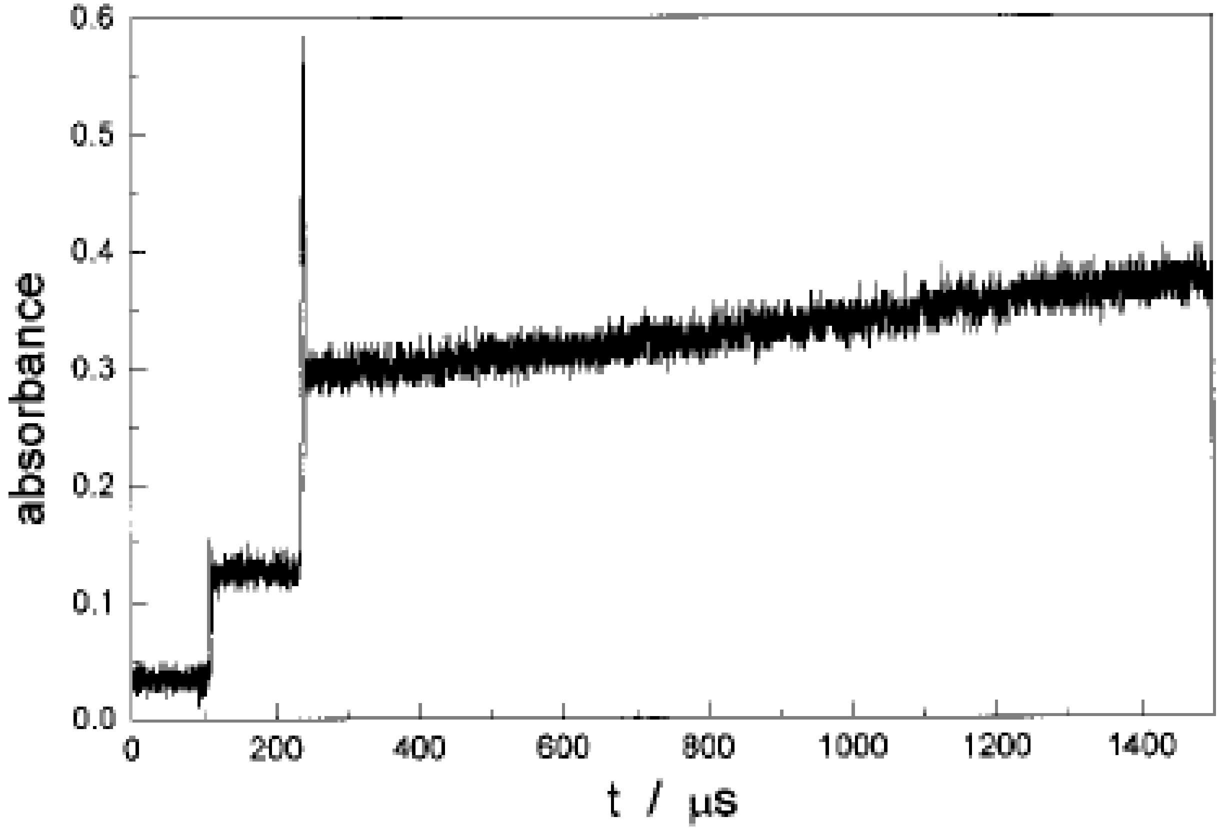


FIG. 1. Absorption-time profile at $\lambda = 257$ nm of a mixture of 1 mol % toluene and 10 mol % oxygen in argon at $T_5 = 1140$ K and $p_5 = 1.86$ bar.

$$C_6H_5CH_3 + O_2 \rightarrow C_6H_5CH_2 + HO_2 \tag{R1}$$

$$C_6H_5CH_3 + HO_2 \rightarrow C_6H_5CH_2 + H_2O_2 \tag{R2}$$

$$H_2O_2 + M \rightarrow 2\ HO + M \tag{R5}$$

$$C_6H_5CH_3 + HO \rightarrow C_6H_5CH_2 + H_2O \tag{R6}$$

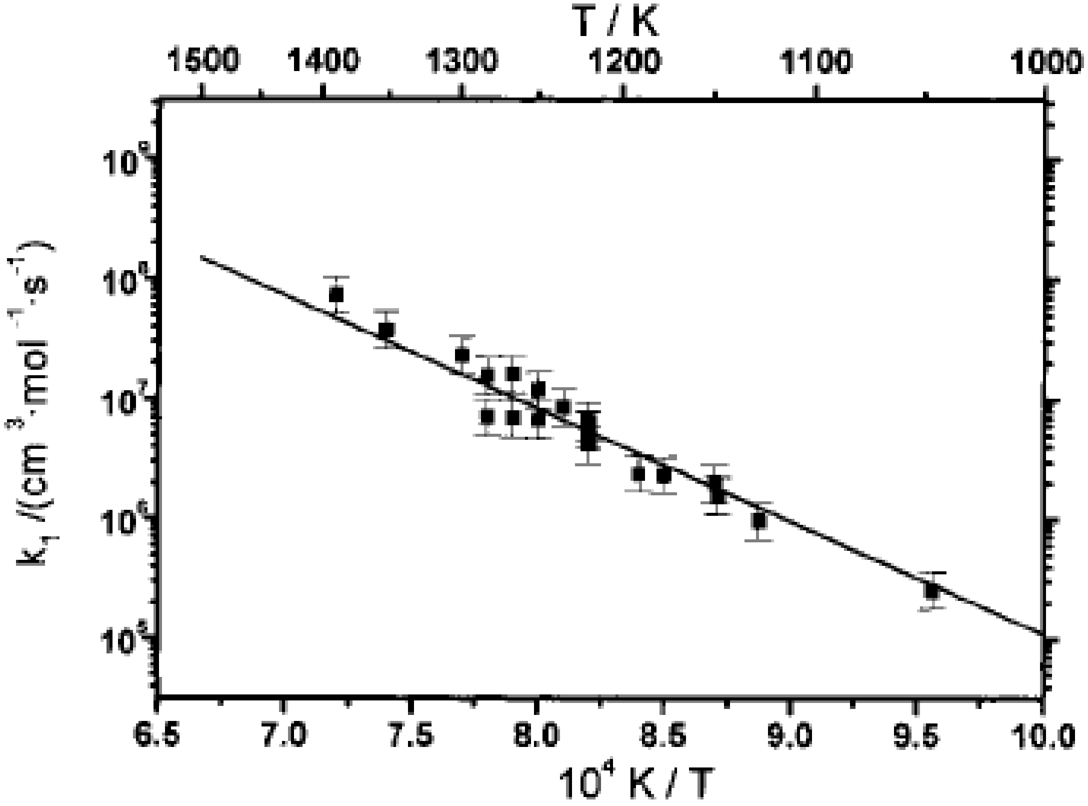


FIG. 2. Arrhenius representation of the second-order rate constant k_1 of reaction R1.

A THEORETICAL ANALYSIS OF THE REACTION OF H WITH C_2H_5

LAWRENCE B. HARDING[1] AND STEPHEN J. KLIPPENSTEIN[2]
[1]Chemistry Division
Argonne National Laboratory
Argonne, IL 60439, USA
[2]Chemistry Department
Case Western Reserve University
Cleveland, OH 44106-7078, USA

The interaction of H with C_2H_5 is analyzed at the CAS+1+2 level using a correlation-consistent polarized valence double zeta basis set. These *ab initio* calculations show three barrierless pathways, two leading to association and one for abstraction. The association channels are substantially more attractive than the abstraction one and thus dominate the kinetics. An analytic representation of the *ab initio* data is implemented in a variable reaction coordinate transition state theory study of the temperature dependence of the association kinetics. These theoretical estimates for the high pressure association rate constant are directly compared with related experimental measurements in an effort to resolve the discrepancy between recent and earlier results.

$$\mathrm{H} + \mathrm{C_2H_5} \rightarrow \mathrm{H_2} + \mathrm{C_2H_4} \qquad (1)$$

$$\begin{tikzcd}
\mathrm{H} + \mathrm{C_2H_5} \arrow[r] & (\mathrm{C_2H_6})^* \arrow[r] \arrow[d] & \mathrm{C_2H_6} & (2) \\
& \mathrm{CH_3} + \mathrm{CH_3} & & (3)
\end{tikzcd}$$

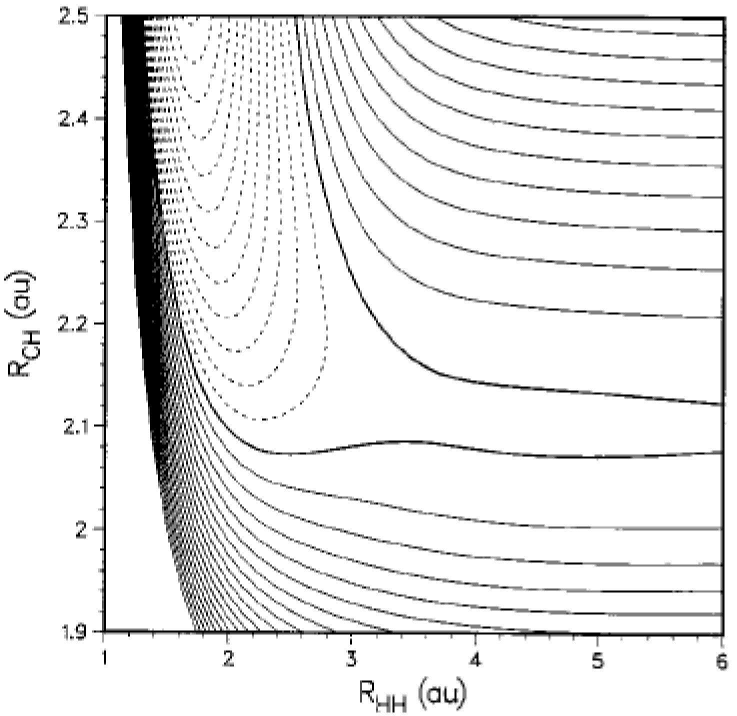
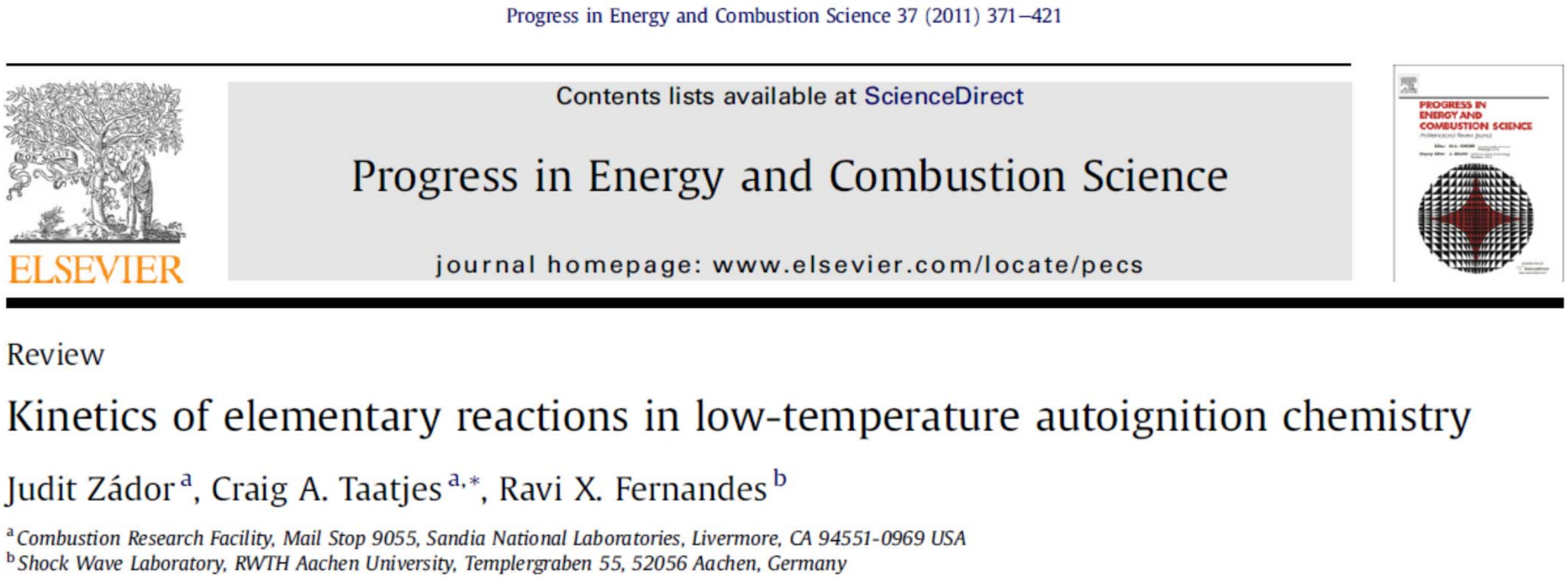


FIG. 1. Two-dimensional potential surface for the H + $C_2H_5 \rightarrow H_2 + C_2H_4$ abstraction reaction. Solid contours are positive, dashed contours are negative, and the zero energy contour (defined to be the energy of the reactant aymptote) is shown with a heavy solid line. The contour increment in 1.0 kcal/mole, and all distances are in atomic units (one atomic unit equals 0.52918 Å).

Recent theory studies provide new rates for reactions

- Usually based of Electronic Structure techniques



Progress in Energy and Combustion Science 37 (2011) 371–421

Contents lists available at ScienceDirect

Progress in Energy and Combustion Science

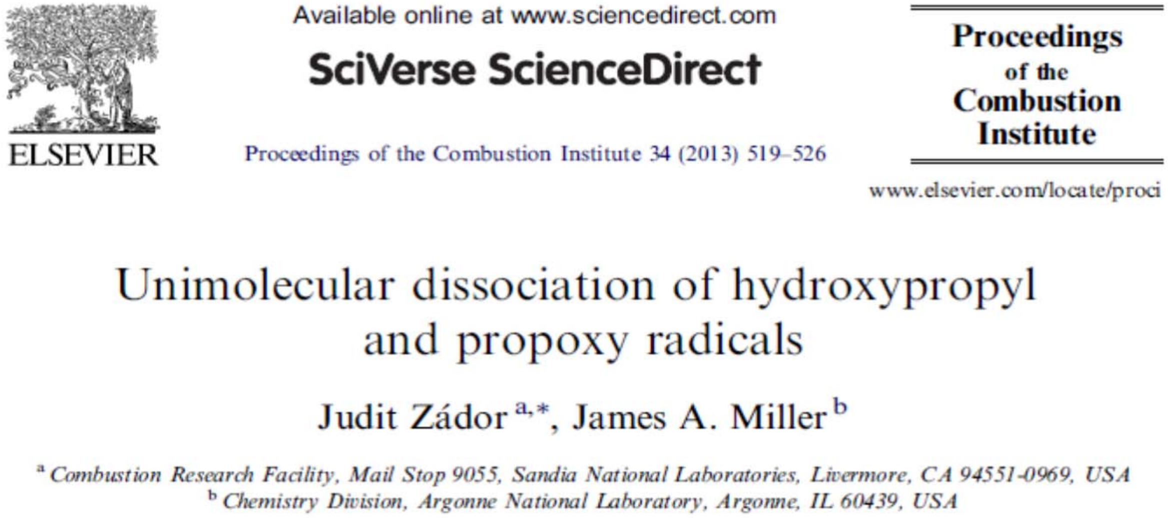
journal homepage: www.elsevier.com/locate/pecs

Review

Kinetics of elementary reactions in low-temperature autoignition chemistry

Judit Zádor [a], Craig A. Taatjes [a,*], Ravi X. Fernandes [b]

[a] *Combustion Research Facility, Mail Stop 9055, Sandia National Laboratories, Livermore, CA 94551-0969 USA*
[b] *Shock Wave Laboratory, RWTH Aachen University, Templergraben 55, 52056 Aachen, Germany*



Available online at www.sciencedirect.com

SciVerse ScienceDirect

Proceedings of the Combustion Institute 34 (2013) 519–526

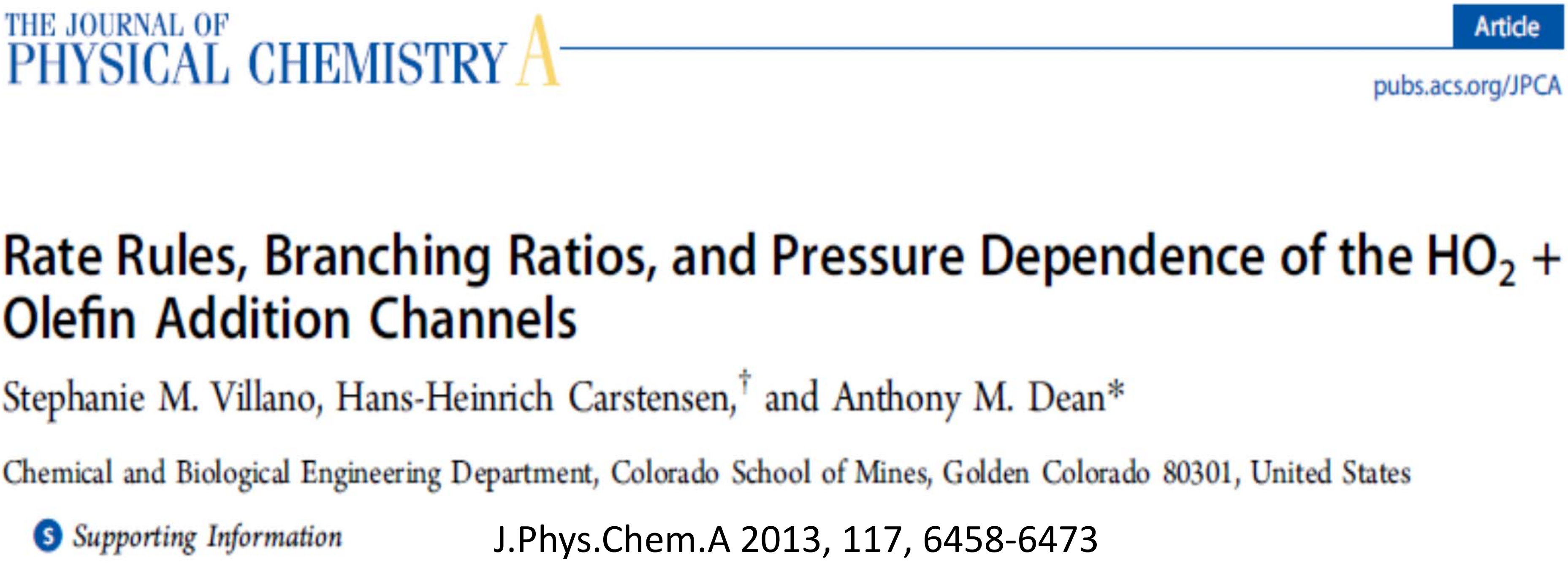
Proceedings of the Combustion Institute

www.elsevier.com/locate/proci

Unimolecular dissociation of hydroxypropyl and propoxy radicals

Judit Zádor [a,*], James A. Miller [b]

[a] *Combustion Research Facility, Mail Stop 9055, Sandia National Laboratories, Livermore, CA 94551-0969, USA*
[b] *Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA*



THE JOURNAL OF
PHYSICAL CHEMISTRY A
Article
pubs.acs.org/JPCA

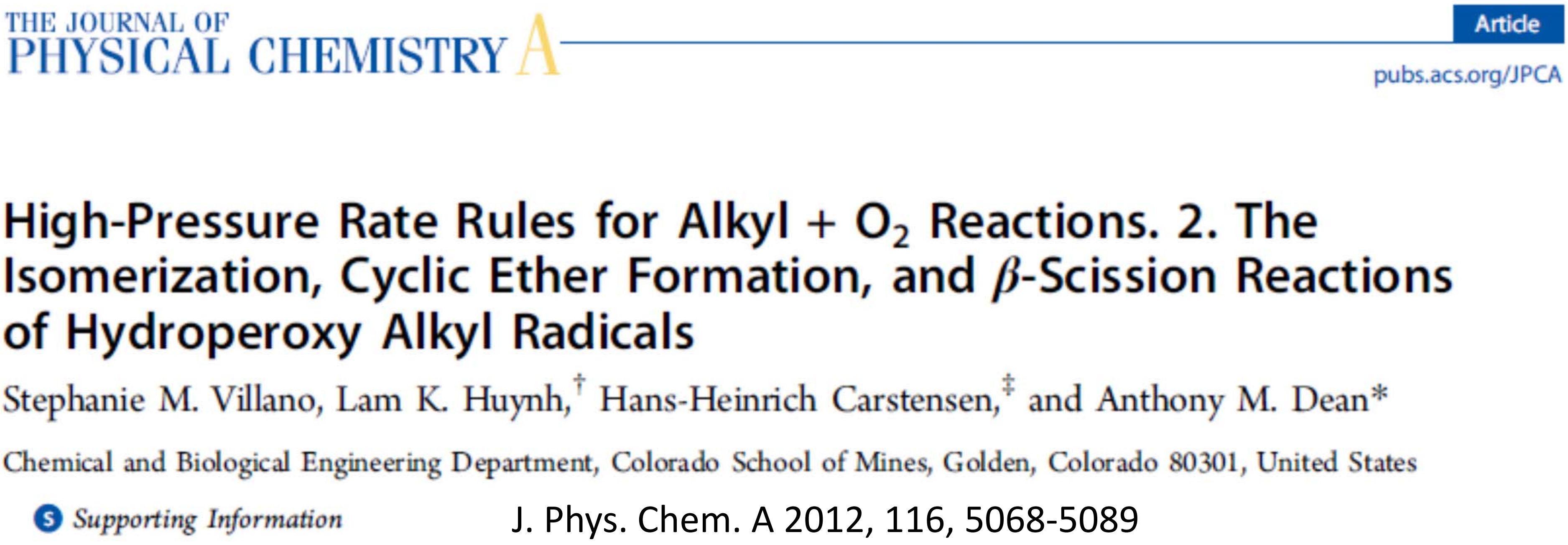
Rate Rules, Branching Ratios, and Pressure Dependence of the HO_2 + Olefin Addition Channels

Stephanie M. Villano, Hans-Heinrich Carstensen,[†] and Anthony M. Dean*

Chemical and Biological Engineering Department, Colorado School of Mines, Golden Colorado 80301, United States

Supporting Information

J.Phys.Chem.A 2013, 117, 6458-6473



THE JOURNAL OF
PHYSICAL CHEMISTRY A
Article
pubs.acs.org/JPCA

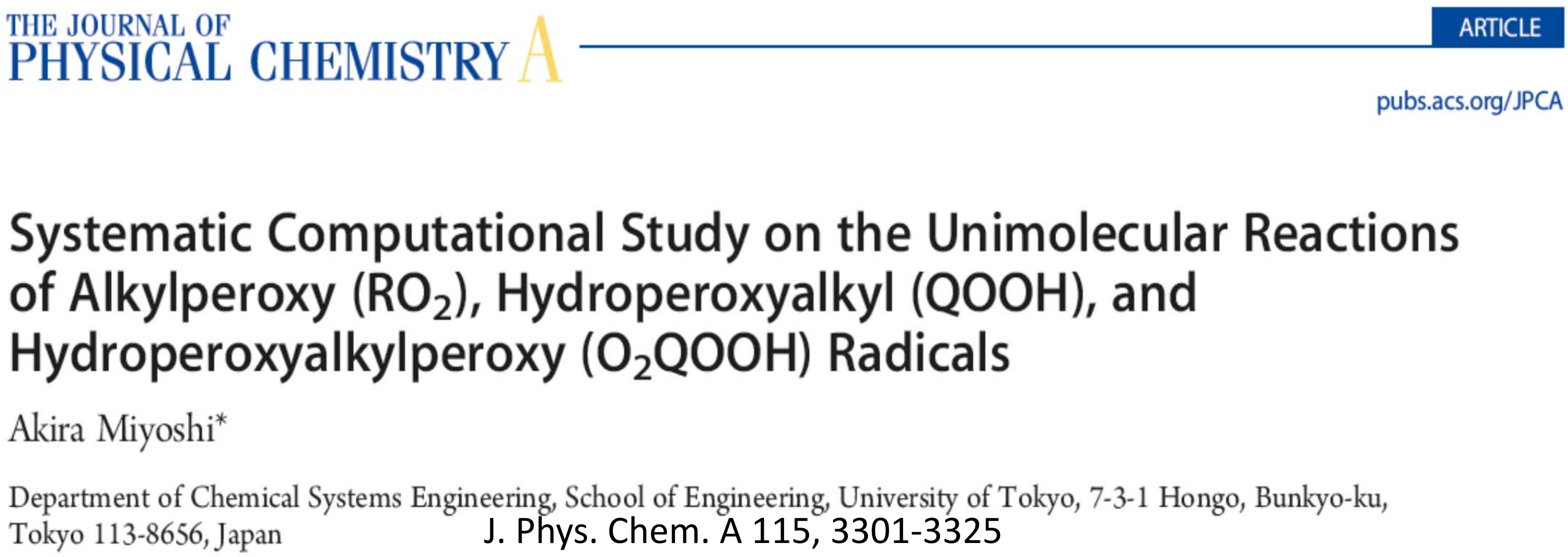
High-Pressure Rate Rules for Alkyl + O_2 Reactions. 2. The Isomerization, Cyclic Ether Formation, and β-Scission Reactions of Hydroperoxy Alkyl Radicals

Stephanie M. Villano, Lam K. Huynh,[†] Hans-Heinrich Carstensen,[‡] and Anthony M. Dean*

Chemical and Biological Engineering Department, Colorado School of Mines, Golden, Colorado 80301, United States

Supporting Information

J. Phys. Chem. A 2012, 116, 5068-5089



THE JOURNAL OF PHYSICAL CHEMISTRY A

ARTICLE

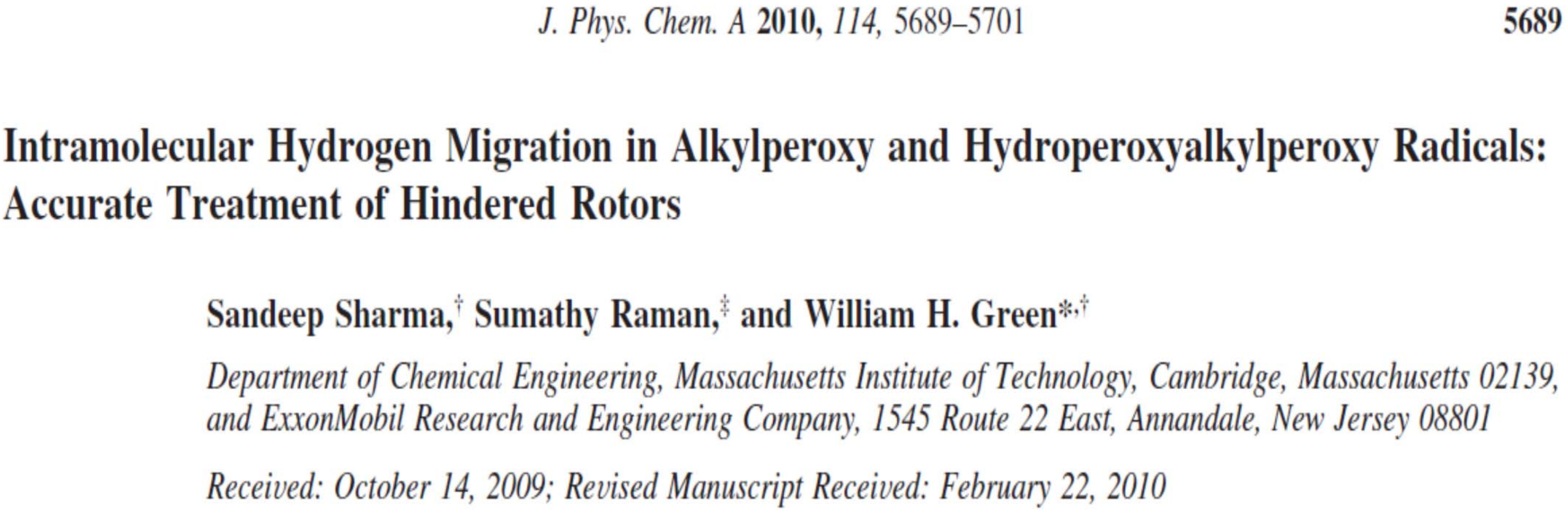
pubs.acs.org/JPCA

Systematic Computational Study on the Unimolecular Reactions of Alkylperoxy (RO_2), Hydroperoxyalkyl (QOOH), and Hydroperoxyalkylperoxy (O_2QOOH) Radicals

Akira Miyoshi*

Department of Chemical Systems Engineering, School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku,
Tokyo 113-8656, Japan

J. Phys. Chem. A 115, 3301-3325



J. Phys. Chem. A **2010,** *114,* 5689–5701 **5689**

Intramolecular Hydrogen Migration in Alkylperoxy and Hydroperoxyalkylperoxy Radicals: Accurate Treatment of Hindered Rotors

Sandeep Sharma,[†] Sumathy Raman,[‡] and William H. Green*[,†]

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and ExxonMobil Research and Engineering Company, 1545 Route 22 East, Annandale, New Jersey 08801

Received: October 14, 2009; Revised Manuscript Received: February 22, 2010

Optimization of computed results

Methanol modeling example

CH3OH → CH2OH

$CH_2OH + M = CH_2O + H + M$

$CH_2OH + O_2 = CH_2O + HO_2$

$HCO + M = H + CO + M$

$HCO + O_2 = HO_2 + CO$

Websites for mechanisms and individual reaction rates

- https://www-pls.llnl.gov/?url=science_and_technology-chemistry-combustion
- http://c3.nuigalway.ie/mechanisms.html
- http://kinetics.nist.gov/kinetics/index.jsp